

Design, Synthesis and Reactivity of Novel
Carbazole-*bis*(azole) Ligands for use in
Lanthanide and Transition Metal Complexes

by

Leah Gajecki
B.Sc., University of Victoria, 2015

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Abstract

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An array of carbazole-*bis*(azole) (CzT^{R} and CzTr^{R} , Cz = carbazole, T = tetrazole, Tr = triazole, R = Me, iPr, Bz and CH_2Mes) pincer ligands were synthesized and fully characterized by NMR, X-ray crystallography and high resolution mass spectrometry. The physical properties of these ligands, as well as their applications in metal coordination compounds, were extensively studied. Mono, bis- and tris-ligand lanthanide (Y, Yb, Er, Sm, and Ce) complexes were synthesized and the solid state crystal structures of these complexes revealed the unusual binding modes of these ligands. The capability of these ligands to distort from planarity and bind in a *fac* type fashion, as well as bidentate, rather than tridentate modes was unexpected. The reactivity of the mono-ligand lanthanide complexes was explored and showed modest activity in ring-opening polymerization of lactones, as well as some unusual one electron redox chemistry.

Bis-ligand complexes of some first row transition metals (Fe, Co, Ni and Zn) were also explored. These air-stable complexes proved invaluable in studying the physical properties of the ligands themselves, as well as the metal complexes. The bis-ligand zinc complexes $(\text{CzT}^{\text{iPr}})_2\text{Zn}$ and $(\text{CzTr}^{\text{iPr}})_2\text{Zn}$ showed reversible oxidation of the CzT and CzTr ligands at modest potentials, as well as ligand-based fluorescence. Two bis-ligand iron complexes were synthesised using sterically diverse ligands $(\text{CzT}^{\text{iPr}})_2\text{Fe}$ and

$(\text{CzT}^{\text{CH}_2\text{Mes}})_2\text{Fe}$ and while $(\text{CzT}^{\text{CH}_2\text{Mes}})_2\text{Fe}$ showed temperature-independent paramagnetism, the similar $(\text{CzT}^{\text{iPr}})_2\text{Fe}$ complex showed a two-step thermally induced spin crossover phenomenon near room temperature in the solid state. The oxidation of $(\text{CzT}^{\text{iPr}})_2\text{Fe}$ yielded $[(\text{CzT}^{\text{iPr}})_2\text{Fe}]^+ \text{BF}_4^-$; we have speculated that this complex is initially oxidized at the ligand and then undergoes an electron transfer from the metal to the ligand to result in an Fe(III) complex.

Mono-ligand iron complexes using the CzT^{iPr} ligand were also synthesized. While ligand redistribution hindered initial progress, the use of a bulky phenoxide ancillary ligand arrested the redistribution pathway and allowed the synthesis of $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})(\text{THF})$. This iron complex proved to be the most successful in terms of isolating stable and reactive complexes with our ligands, and several adducts (THF, tBuNC, TPPO) were synthesized. Synthetic and DFT studies of these complexes demonstrated the tendency for the Fe to bind σ -donor ligands, but not π -acceptor ligands. This led to the isolation of a thermally sensitive four-coordinate iron complex $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})$. The catalytic activity of these Fe phenoxide complexes in the hydrosilylation of styrene with phenylsilane was explored. These catalysts were able to selectively produce the Markovnikov hydrosilylation product with good activity. The apparent preservation of the Fe(II) oxidation state throughout the catalytic transformation suggests a possible ligand-assisted mechanism where the CzT ligand acts as a proton reservoir.

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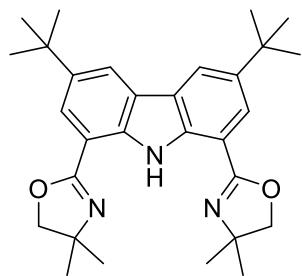
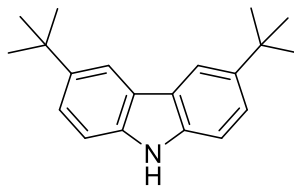
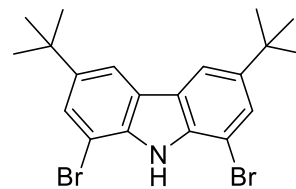
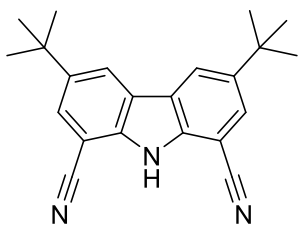
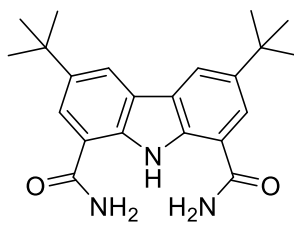
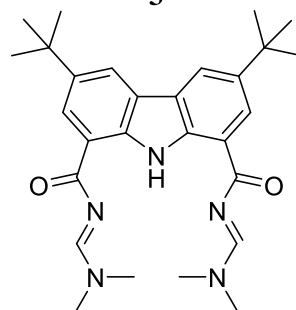
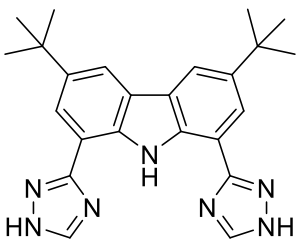
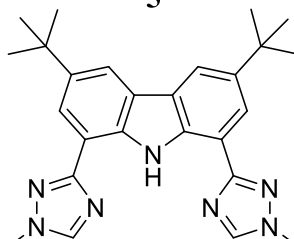
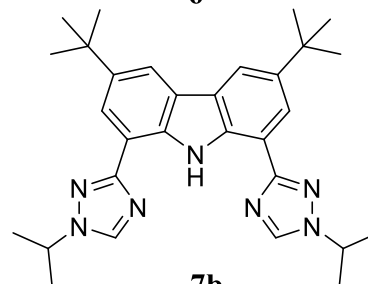
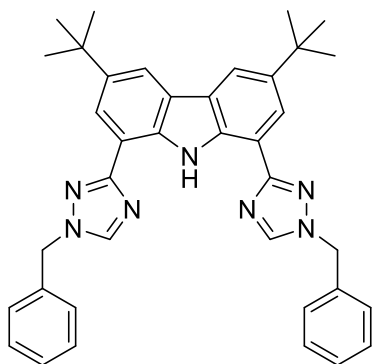
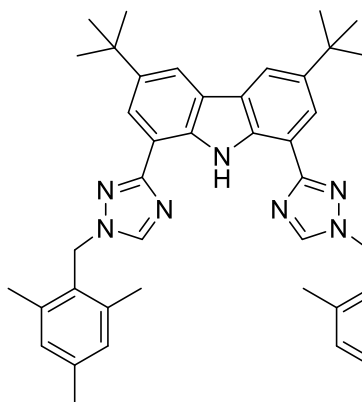
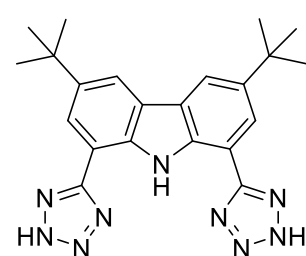
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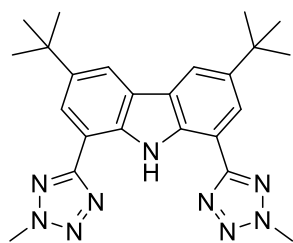
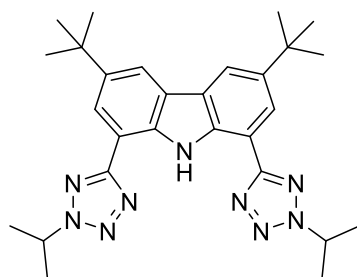
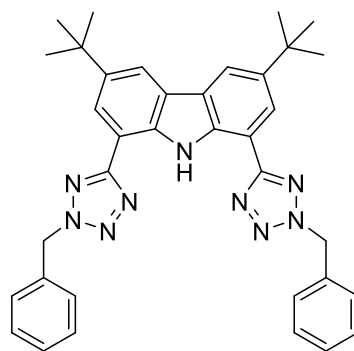
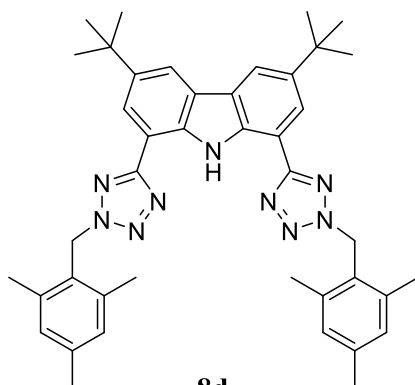
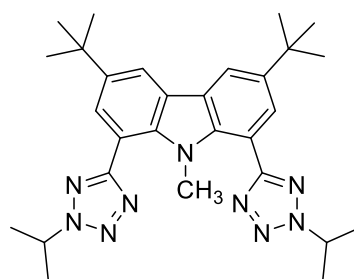
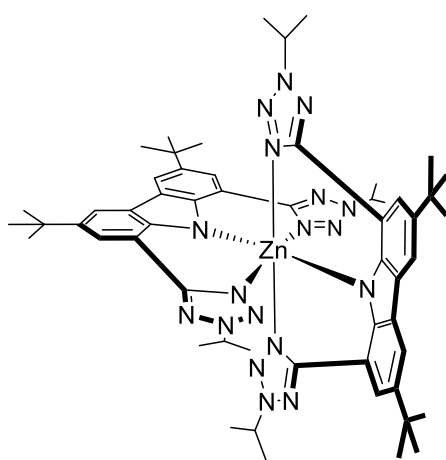
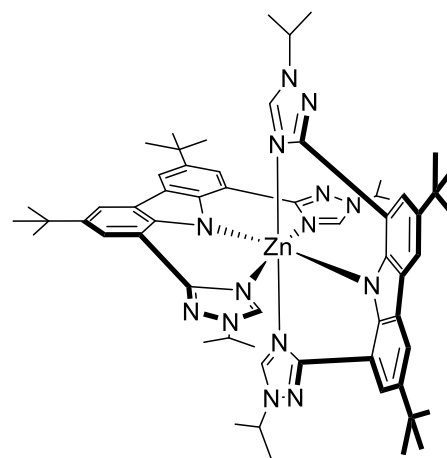
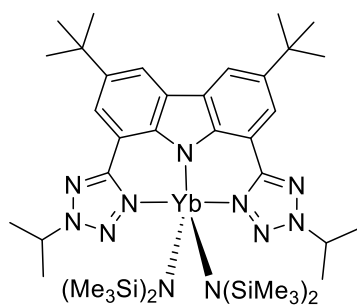
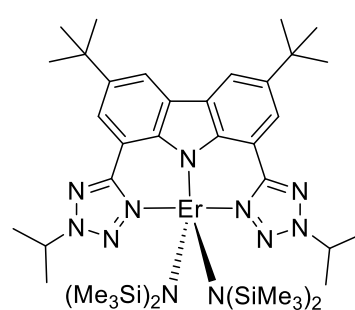
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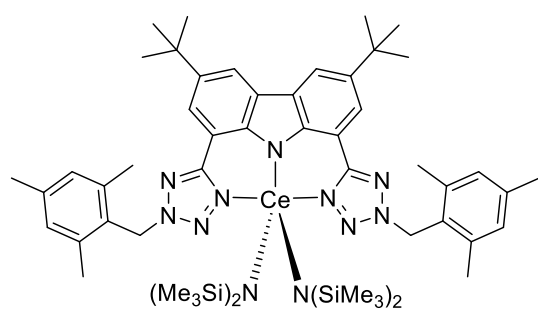
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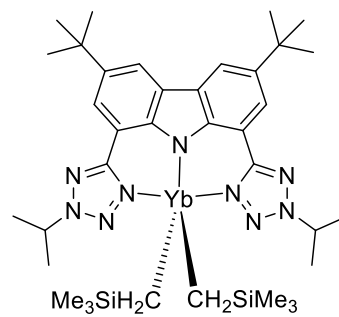
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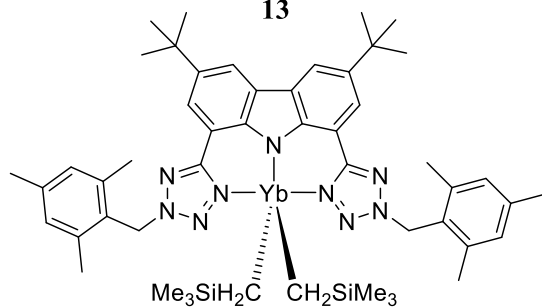
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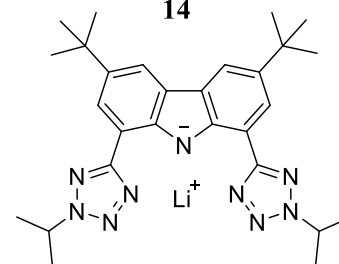
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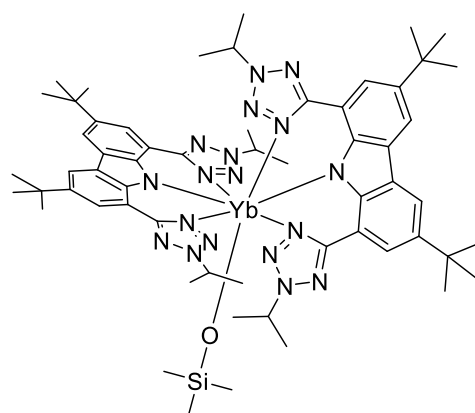
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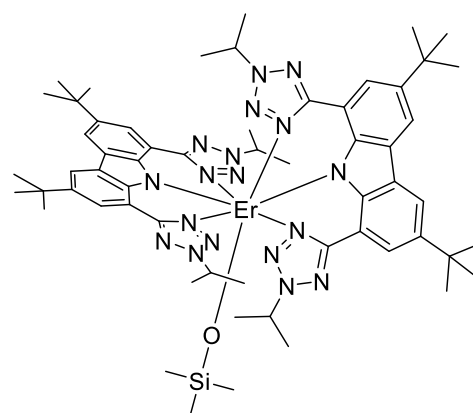
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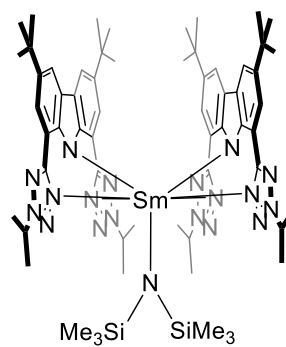
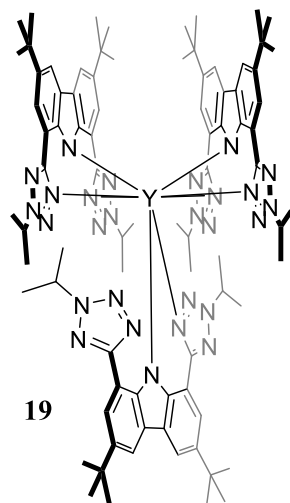
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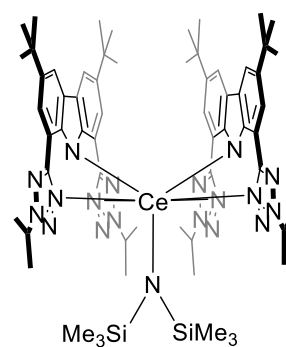
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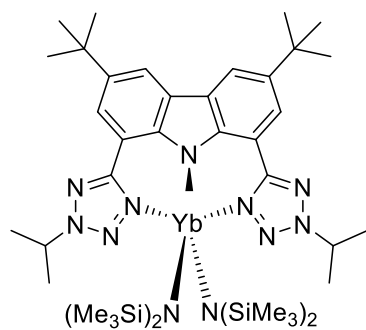
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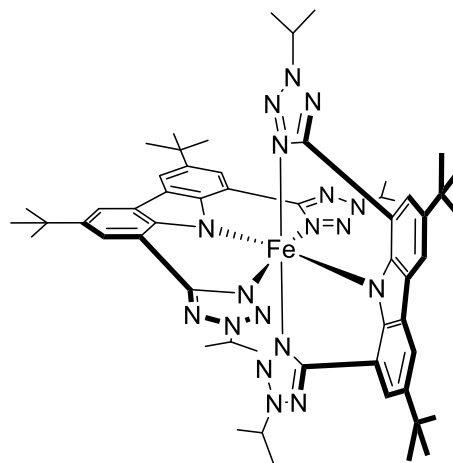
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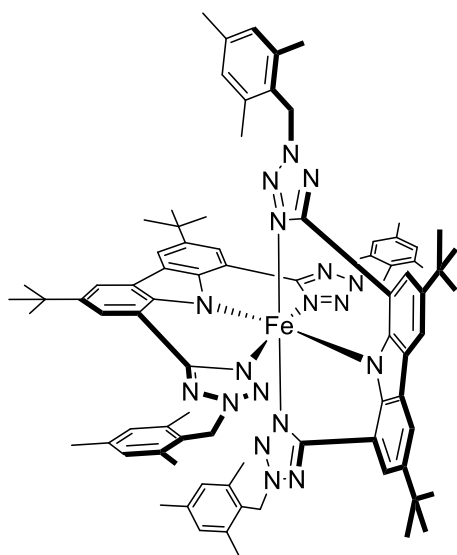
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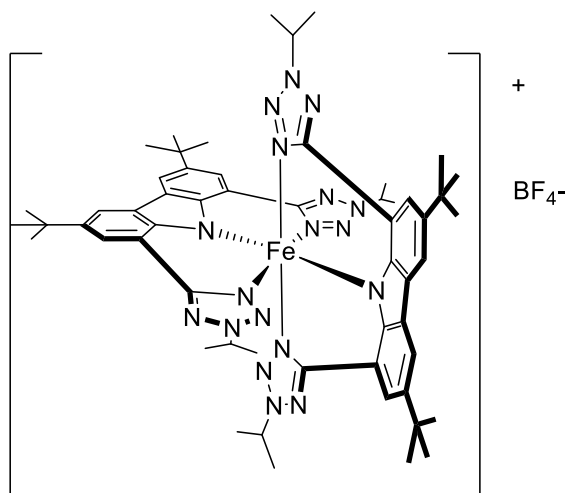
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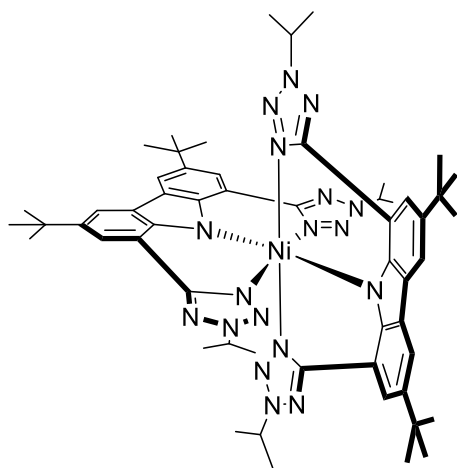
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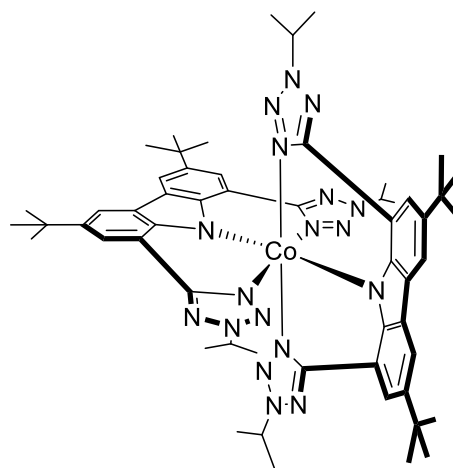
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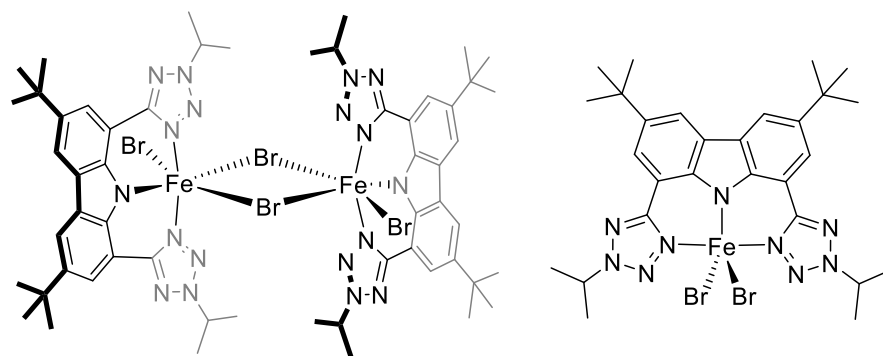
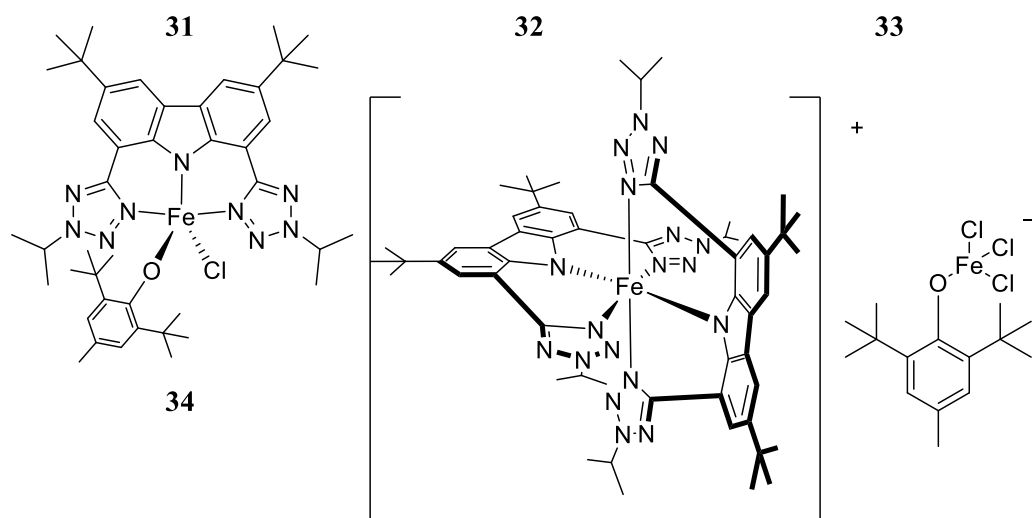
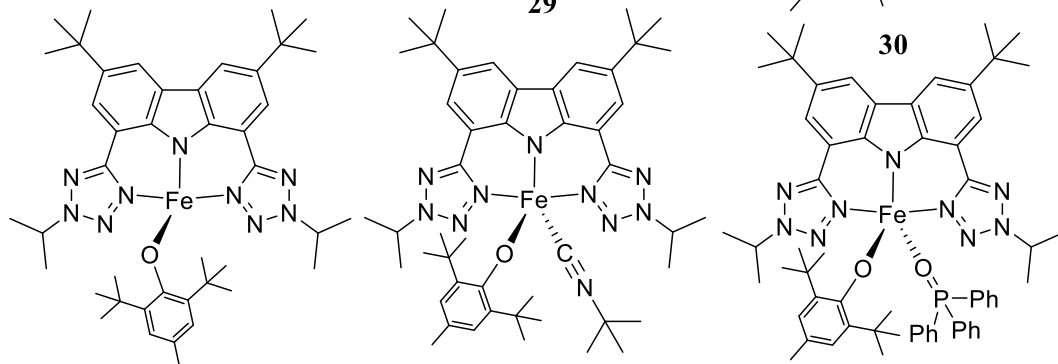
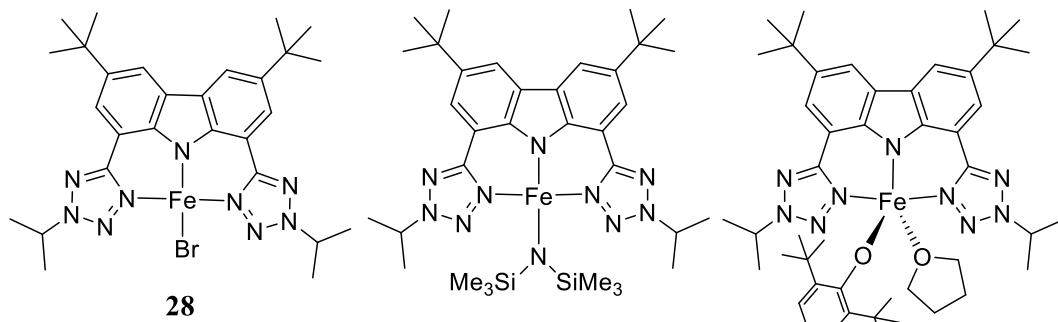
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List of Abbreviations

Å	angstrom
ACN	acetonitrile
Al ⁱ Bu ₃	triisobutylaluminum
aM	anti-Markovnikov
Ar	aryl
br	broad
Bz	benzyl
CAN	cerium ammonium nitrate
Cz	carbazole
CFT	crystal field theory
CN	coordination number
COSY	correlation spectroscopy
Cp	cyclopentadienyl
Cp [*]	1,2,3,4,5-pentamethylcyclopentadienyl
CSD	crystal structure database
CV	cyclic voltammetry
Cy	cyclohexyl
d	doublet
<i>d</i>	deuterium
dd	doublet of doublets
DCM	dichloromethane
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
dec	decomposed
DFT	density functional theory
DMF	dimethylformamide
DMF-DMA	dimethylformamide dimethyl acetal
DMSO	dimethylsulfoxide
dppf	bis(1,1'-diphenylphosphino)ferrocene
EPR	electron paramagnetic resonance
ESI	electrospray ionization
Et	ethyl
EtOAc	ethyl acetate
Fc	ferrocene
Fc ⁺	ferrocenium
HCzTr	carbazole- <i>bis</i> (1,2,4-triazole)
HCzT	carbazole- <i>bis</i> (1,2,3,4-tetrazole)
HCzx	carbazole- <i>bis</i> (oxazoline)
HMBC	heteronuclear multiple bond correlation
HOMO	highest occupied molecular orbital
HS	high spin
HSAB	hard-soft-acid-base
HSQC	heteronuclear single quantum coherence
Hz	Hertz

IPA	isopropanol
iPr	isopropyl
IR	infrared spectroscopy
<i>J</i>	coupling constant (in Hertz)
K	Kelvin
Ln	lanthanide or lanthanoid
LS	low spin
LUMO	lowest unoccupied molecular orbital
M	Markovnikov
M	molar
m	multiplet
Me	methyl
m/z	mass per charge unit
MAO	methylaluminumoxane
MB	Mössbauer spectroscopy
MeOH	methanol
Mes	2,4,6-trimethylphenyl
MHz	megahertz
MO	molecular orbital
MOF	metal-organic framework
mol	mole
MP	melting point
MS	mass spectrometry
NMP	N-methyl-2-pyrrolidone
NMR	nuclear magnetic resonance
NOESY	nuclear overhauser enhancement spectroscopy
OAr	4-methyl-2,6-di-tBu-phenoxy
Oh	octahedral
PDI	pyridine diimine
Ph	phenyl
ppm	parts per million
ROP	ring opening polymerization
s	singlet
SCO	spin crossover
SET	single electron transfer
SHE	standard hydrogen electrode
SOMO	singly occupied molecular orbital
SQUID	superconducting quantum interference device
T	temperature
tBu	tert-butyl
tBuNC	tert-butyl isocyanide
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TIP	temperature independent paramagnetism
TM	transition metal
TOF	turnover frequency

TPPO	triphenylphosphine oxide
Tr	triazole
Tz	tetrazole
UV	ultraviolet
V	volt
VT	variable temperature
Δ	heating
Δ_o	crystal field splitting
ΔE_Q	quadrupole splitting
δ	chemical shift (ppm)
$\delta(\text{Fe})$	isomer shift
μ_B	Bohr magnetons
μ_{eff}	effective magnetic moment
ϵ	molar extinction coefficient or molar absorptivity

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Dedication

To my family, thank you for your never-ending love and support.

To the glovebox,

thank you for holding out long enough for me to graduate,

may the antechamber vacuum pump rest in peace

Chapter 1 Introduction

The physical properties and reactivity of d and f block elements have proven to be powerful tools used in several everyday applications. The range of oxidation states encountered in the d block allows for many different catalytic applications, such as the use of Pd in the Wacker oxidation¹ process to produce ethanol from ethane, the production of ammonia in the Haber process² using Fe or Mo and the Ziegler-Natta³⁻⁴ polymerization of polyethylene with the use of Al and Ti to name a few of the most well known. Along with chemical reactivity, d and f block elements have magnetic capabilities for use in things such as batteries⁵⁻⁶, memory storage devices⁷⁻⁸ and MRI contrast agents⁹⁻¹⁰. The chemical industry is worth hundreds of billions of US dollars per year¹¹ and the search for new, more efficient, environmentally friendly and cost efficient catalysts is a major driving force behind organometallic and inorganic research. While the range of reactivity possible with these metals make them extremely valuable, harnessing the specific reactivity is not always straightforward. The use of organic ligands has long been used to manipulate these properties by adjusting both the steric and electronic profile of these inorganic complexes in order to better adapt and optimize each metal for a specific end goal¹². The full scope of ligands used in d and f block complexes is too wide to fully cover in this introduction, but a brief description of the properties, reactivity and suitable ligands for use in both lanthanide and transition metal complexes will be discussed.

1.1 Lanthanides

The development of ligands for use in lanthanide complexes is fairly recent¹³ considering the first lanthanide was discovered in the 1750s. This is mainly due to the high air and moisture sensitivity of organometallic lanthanide complexes and their paramagnetic nature which makes them difficult to study by NMR spectroscopy. The bonding and chemical reactivity of lanthanides is quite unique compared to the d block metals and it is important to have a complete understanding of these properties before being able to properly design an appropriate ligand system.

1.1.1 Properties of Lanthanides

The lanthanides consist of the 15 unique elements ranging from atomic number 57 (La) to 71 (Lu); Y and Sc are commonly studied with the lanthanides because while technically group 3 metals, they share many physical and chemical properties with the lanthanides. Taken together these 17 elements make up the lanthanoids (Ln). The lanthanoids have also been referred to as “rare earth metals” due to their similarity to the group 2 alkaline earths and because they were originally thought to be scarce. Moving across the series from La to Lu involves the gradual filling of the 4f subshell $[\text{Xe}]4f^n6s^2$ ($n = 1-14$), but due to the small radial extension of the 4f valence orbitals (**Figure 1.1**) they are buried within the core and are shielded from the outside environment by the filled 5s and 5p orbitals. This phenomenon causes a larger than expected decrease in atomic radius going across the series (**Table 1.1**) known as the lanthanide contraction¹⁴⁻¹⁵.

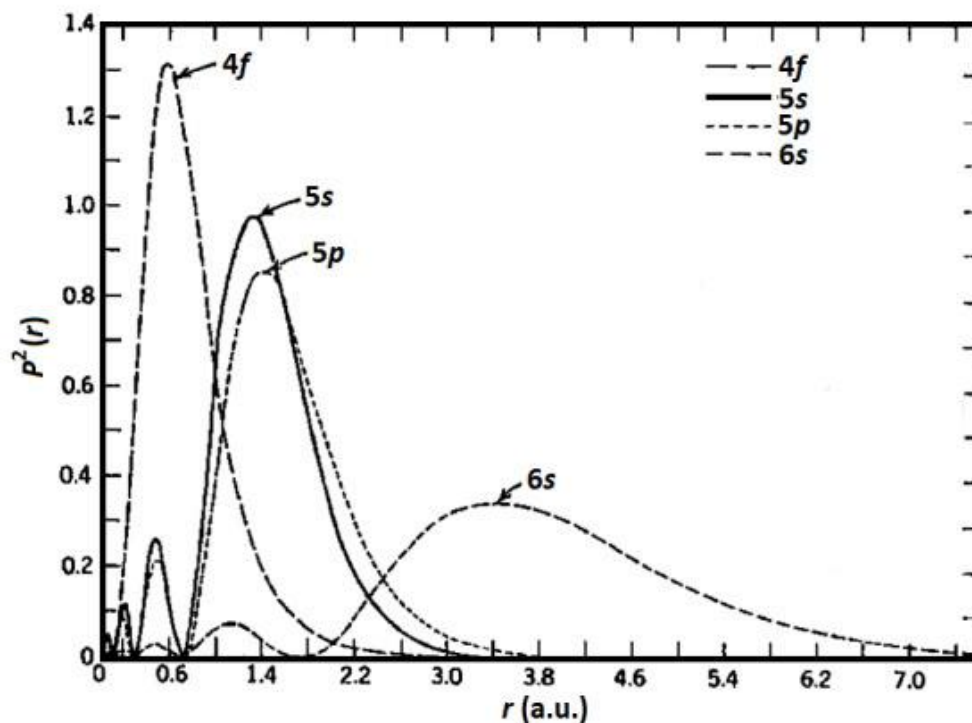


Figure 1.1 Radial distribution of the 4f orbitals (reprinted with permission from ¹⁶⁻¹⁷)

All lanthanoids are most stable in the (III) oxidation state, although some also possess a relatively stable (II) (e.g. Sm, Eu, Yb) or (IV) (e.g. Ce) state¹⁴. However, none of the lanthanides have two oxidation states separated by two units which prevents lanthanides from participating in classical oxidative-addition and reductive-elimination catalytic cycles. Lanthanides can however undergo sigma (σ) bond metathesis type catalytic cycles, as observed in alkene polymerization¹⁸⁻¹⁹, hydrosilylation²⁰⁻²¹, hydroboration²²⁻²³, hydroamination²⁴ and hydrogenation²⁵ reactions (see **Scheme 1.1**). Most of the Ln(III) are paramagnetic due to unpaired 4f electrons, the exceptions to this are f^0 elements [Sc(III), Y(III), La(III) and Ce(IV)] and f^{14} elements [Lu(III) and Yb(II)].

All lanthanide metals are strong reducing agents and readily react with oxygen when exposed to air.

Table 1.1 Properties of lanthanides

Ln	Electronic Configuration		Ionic Radii (Ln³⁺, CN 6) (pm)
	Ln⁰	Ln³⁺	
Sc	3d ¹ 4s ²	[Ar]	74.5
Y	4d ¹ 5s ²	[Kr]	90.0
La	5d ¹ 6s ²	[Xe]4f ⁰	103.2
Ce	4f ¹ 5d ¹ 6s ²	[Xe]4f ¹	101.0
Pr	4f ³ 6s ²	[Xe]4f ²	99.0
Nd	4f ⁴ 6s ²	[Xe]4f ³	98.3
Pm	4f ⁵ 6s ²	[Xe]4f ⁴	97.0
Sm	4f ⁶ 6s ²	[Xe]4f ⁵	95.8
Eu	4f ⁷ 6s ²	[Xe]4f ⁶	94.7
Gd	4f ⁷ 5d ¹ 6s ²	[Xe]4f ⁷	93.8
Tb	4f ⁹ 6s ²	[Xe]4f ⁸	92.3
Dy	4f ¹⁰ 6s ²	[Xe]4f ⁹	91.2
Ho	4f ¹¹ 6s ²	[Xe]4f ¹⁰	90.1
Er	4f ¹² 6s ²	[Xe]4f ¹¹	89.0
Tm	4f ¹³ 6s ²	[Xe]4f ¹²	88.0
Yb	4f ¹⁴ 6s ²	[Xe]4f ¹³	86.8
Lu	4f ¹⁴ 5d ¹ 6s ²	[Xe]4f ¹⁴	86.1

Since most lanthanides have relatively high charge/radius ratios they act as “hard” Lewis acids preferring to bind “hard” highly electronegative donors such as F⁻ or O⁻¹⁴ and their large ionic radius allows for high coordination numbers (commonly 7-9)¹⁵. Coordination geometries of lanthanide complexes are governed by ligand steric factors rather than crystal field effects¹⁴ as is seen in transition metals. Hard donor solvents such as THF or H₂O usually bind to the lanthanide centre to assist in stabilizing the complex²⁶. The unavailability of the 4f orbitals to overlap in covalent bonding causes mainly ionic bonding in lanthanide complexes²⁷ and the highly ionic nature of the bonding in these complexes results in labile complexes that easily undergo ligand exchange¹⁴. The lack of

orbital overlap also prevents pi (π) back-bonding interactions that are commonly seen in d-block metals and this is the reason why carbonyl complexes of the lanthanides are not isolable²⁶. The 4f electrons are almost unaffected by the ligand environment resulting in the spectroscopic and magnetic properties of lanthanide complexes being characteristic of the metal ion and not the ligand environment^{14, 27}. As a result, the main function of the ligand is for stabilization and steric saturation rather than for electronic effects. Due to the large ionic radius, multidentate or sterically bulky ligands are needed to form kinetically stable lanthanide complexes.

While lanthanides possess a variety of interesting magnetic, fluorescent and physical properties, the main focus of this work is the synthesis of lanthanide complexes for use in catalysis and chemical reactivity. Due to this, the main focus of the lanthanide complexes reviewed will be based around catalytically active lanthanide complexes and the use of ligands specific to this reactivity. Ligands used in lanthanide complexes designed for different applications, such as NMR shift reagents or MRI contrast agents, will not be discussed as the end application and therefore the ligand design, would be different.

1.1.2 Ligands used in Lanthanide Complexes

Due to the unique properties of the lanthanides mentioned above, there is a preference for specific properties of ligands used in lanthanide chemistry in order to allow for stabilization of the complex. Generally, monoanionic ligands consisting of hard donor atoms are desirable in order to decrease lability and prevent redistribution. It is also important to employ sterically crowding or multidentate ligands to ensure stability of the complex²⁶ without allowing bridging interactions between metal centres that tend to

decrease both solubility and reactivity. However, since the geometries of the resulting lanthanide complexes are not governed or restricted by covalent orbital overlap, the coordination number is large compared to the smaller d block metals and several different modes of ligand bonding and hapticity are possible with the lanthanides.

Historically, Cp ligands were used in the development of organolanthanide complexes²⁸⁻³¹ due to their large size, negative charge and the fact they do not rely on π -back-bonding. This led to the successful synthesis of the first organolanthanide complexes in 1954 by Wilkinson and Birmingham³⁰ in the form of $\text{Ln}(\text{C}_5\text{H}_5)_3$ ($\text{Ln} = \text{Sc}, \text{Y}, \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}$ and Gd). The X-ray crystal structures of these complexes³² showed polymeric structures proving that even three Cp ligands surrounding the lanthanide centre were not sterically crowding enough to prevent bridging. These bridging interactions also prevented the study of the reactivity of these complexes due to low solubility. Modification of the Cp ligand by the addition of methyl groups to form Cp^* (C_5Me_5^-) allowed for synthesis of lanthanide complexes with increased solubility. The first structurally characterized LnCp^*_3 complex was that of Sm synthesized by the Evans group³³, even though it was initially thought that complexes of the type LnCp^*_3 would not exist due to excessive steric bulk. However, this extreme bulk led to new reactivity as “sterically induced reduction” chemistry, suggested by Evans, allowed SmCp^*_3 to function as a surprisingly active catalyst for ring-opening and polymerization reactions³¹. These Sm(III) complexes react and behave more similarly to that of Sm(II) where the ligand itself is involved in the reducing process.

Bis-Cp and Cp^* complexes of the lanthanides are less sterically crowded than the tris ligand versions and show relatively high stability, but low reactivity^{32, 34}. Bis-Cp

complexes of the transition metals are also known but in that case they show a sandwich structure with the metal sitting directly between the two Cp rings (a metallocene), whereas the lanthanides form bent sandwich structures (**Figure 1.2**). Dimerization of these complexes is a common feature which is a disadvantage in catalyst design as the metal centre is less available for substrates to bind. While bis-Cp* lanthanide alkyl complexes have been shown to be catalytic in polymerization³⁵, hydrosilylation²⁰ and hydroamination²⁴, it has also been shown that a more sterically open catalyst, such as the linked-Cp *ansa* type lanthanide complexes (**Figure 1.2**), reveal higher reactivity²⁸ due to the metal centre being more available and less sterically crowded. These results demonstrate how important the balance between steric bulk needed to stabilize the complex and substrate access is in the reactivity of these metals. While Cp and Cp* complexes of lanthanides have been extensively studied and prove the potential reactivity of organolanthanide complexes, there is increasing attention on non-Cp type ligands³⁶ where the steric bulk can be more finely tuned.

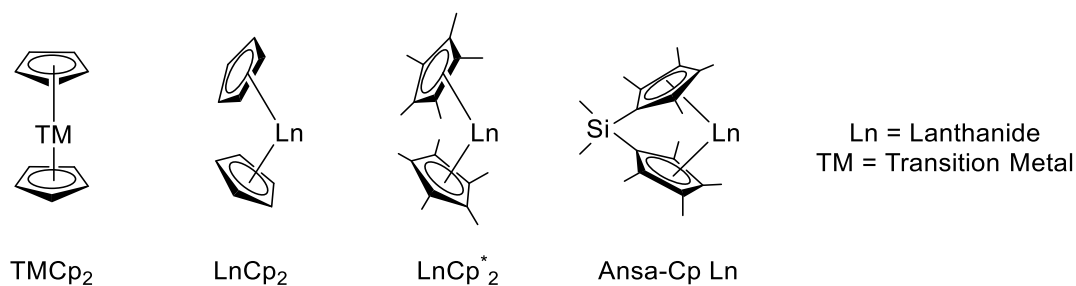


Figure 1.2 Bis-Cp, bis-Cp* and ansa ligand metal complexes (other ligands may be present on the Ln centre)

Recent advances in non-Cp-based ligands for use in lanthanide chemistry consist of mainly N and O donors in a multidentate scaffold in attempts to avoid ligand

redistribution and formation of unwanted LnX_4^- complexes (also known as “ate” complexes)³⁷. Tripodal neutral and monoanionic type ligands have also been used to successfully isolate dialkyl³⁸ and trialkyl³⁹ lanthanide complexes to give capped trigonal prismatic structures. More commonly, bidentate and tridentate *mer* type monoanionic ligands have been used to isolate lanthanide dihalide and dialkyl complexes with the majority of these ligands being nitrogen-based. β -diketiminato ligands (**Figure 1.3**) are widely used as bidentate ligands in lanthanide complexes due to their ease of steric tunability through simple synthetic adjustments to the ligand scaffold. Bis-diketiminato ligand complexes are possible with the larger lanthanides (Yb, Sm, Nd and Er)⁴⁰ while smaller lanthanoids (Sc) form mono-diketiminato complexes⁴¹. The Sc alkyl complexes have shown to be highly active catalysts when activated to form the cationic species⁴²⁻⁴³. It has been suggested that the high activity is due to improved coordination sphere accessibility facilitated by bulky, yet low coordinate, ligands.



Figure 1.3 β -diketiminato ligand and Ln complex

The use of tridentate “pincer” ligands (chelator that binds to three adjacent coplanar sites on the metal center)¹² in place of bidentate ligands is desirable due to the increase in stability of the lanthanide complexes through the chelate effect²⁷. There is no shortage of pincer ligand-based lanthanide complexes in the literature, chief among these are pybox or

BOPA type ligands⁴⁴⁻⁴⁶, pyridine-based ligands⁴⁷⁻⁴⁹, amidinate ligands⁵⁰⁻⁵¹ and other nitrogen-based imino ligands⁵²⁻⁵⁴ (**Figure 1.4**). Phosphorous containing pincer ligands have also been commonly used⁵⁵⁻⁵⁶ even though it was originally thought that phosphorous was too “soft” of a donor to sufficiently bind to the lanthanide centres. These ligands allow for isolation of discrete five-coordinate lanthanide complexes, and the steric adjustability of the ligand scaffold prevents formation of dimers and bridging structures.

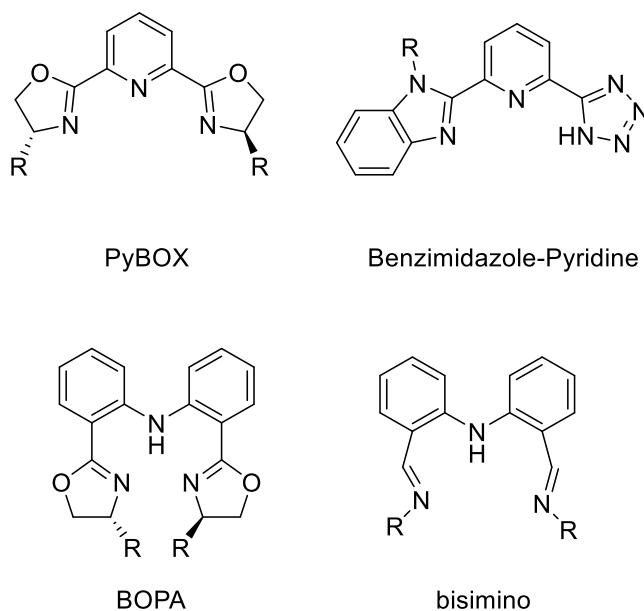


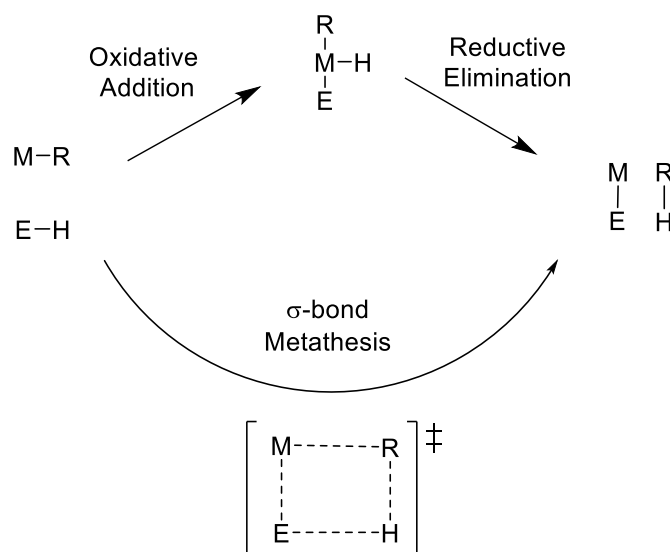
Figure 1.4 Examples of tridentate pincer ligands used in lanthanide complexes

The history of ligands used in lanthanide chemistry demonstrated several important trends and behaviours that will be important when designing a ligand for use in lanthanide catalysts. The use of Cp and Cp* ligands demonstrated the success in using anionic donors, as well as the integration of adjustable substituents to allow for increased solubility. The use of tethered *ansa* ligands, as well as the range of sterically adjustable β -diketiminato

ligands, demonstrated the importance of metal accessibility to accommodate substrate binding for increased reactivity. The use of a range of pincer ligands improves the stability of the lanthanide complexes through the chelate effect and offers an easily tunable ligand scaffold to enable fine adjustment of sterics. The use of these tridentate ligands has allowed for isolation of stable low coordinate lanthanide complexes, many of which have shown to be catalytically active.

1.1.3 Catalytic Reactivity of Lanthanides

As mentioned previously, the lack of several available stable oxidation states among the lanthanides prevents them from oxidative-addition or reductive-elimination reactivity. For this reason the main mechanism used in lanthanide catalysis is σ -bond metathesis (**Scheme 1.1**).



Scheme 1.1 Oxidative-addition and reductive-elimination vs. σ -bond metathesis

While not all catalytic transformations proceed through this mechanism, there are several examples that do such as olefin polymerization¹⁸⁻¹⁹, hydroamination²⁴, hydrosilylation²⁰⁻²¹ and ring opening polymerization⁵⁷. In all of these reactions one of the main mechanistic steps is the binding of a substrate to the lanthanide centre and in some cases insertion into a remaining labile ligand such as an alkyl or an amide^{21, 37}. In several of these transformations there is an observed trend of increased reactivity and turnover frequency with an increase in ionic radius of the lanthanide centre⁵⁸⁻⁶². This has been attributed to better availability of the metal centre to the incoming substrate for binding. Some of the most active lanthanide catalysts for olefin polymerization are lanthanide dialkyl or trialkyl complexes where one of the alkyl groups have been removed by activation with $[\text{Ph}_3\text{C}]^+ [\text{B}(\text{C}_6\text{F}_5)_3]^-$ to form a highly active cationic species. This generates an open coordination site for the substrate to bind, as well as increased Lewis acidity at the metal centre due to the cationic charge. The neutral species show little to no reactivity suggesting the cationic complex is the real active catalyst¹⁹. Okuda¹⁹ has shown that lanthanide tris(alkyls) $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2]$ are highly active pre-catalysts for ethylene polymerization with the most active species being the alkyl dication, $[\text{Ln}(\text{CH}_2\text{SiMe}_3)(\text{THF})_x]^{2+}$. Unfortunately, these lanthanide tris(alkyl) complexes are only accessible for the smaller lanthanides (Tm, Er, Y, Ho, Dy, Tb and Yb)¹⁴. Thus the increased catalytic activity observed with these lanthanide alkyls is limited by the fact they are only accessible synthetically for the smaller lanthanides.

1.1.4 Lanthanide Catalyst Ligand Design

When designing ligands for use in lanthanide catalysis it is important to consider what reactivity is desired. The use of monoanionic pincer ligands is appropriate for several reasons: the monoanionic profile allows for less labile ionic bonding to the lanthanide to ensure the ligand does not easily redistribute while still allowing for two anionic X^- type ligands at the lanthanide centre which may be important for activation and insertion during the catalytic cycle. A rigid, bulky, tridentate ligand scaffold should also assist in formation of discrete complexes rather than dimeric or polymeric structures that ultimately lower catalyst reactivity.

These considerations, along with several successful examples of literature complexes with a similar design, led to the initial design in the Berg group of a carbazole-based oxazoline pincer ligand for use in low coordinate lanthanide complexes (**Figure 1.5**)⁶³⁻⁶⁴. It was thought that the carbazole would offer an easily tunable scaffold while also acting as an anionic nitrogen donor and providing stability in the backbone of the ligand. The oxazoline rings can be synthesized in few steps to provide two additional neutral nitrogen donors and introduce an appropriate size pocket to bind the lanthanide centre. The alkyl groups on the oxazoline ring next to the nitrogens provide both easily adjustable steric bulk as well as a chiral centre that may be helpful in forming a stereoselective catalyst.

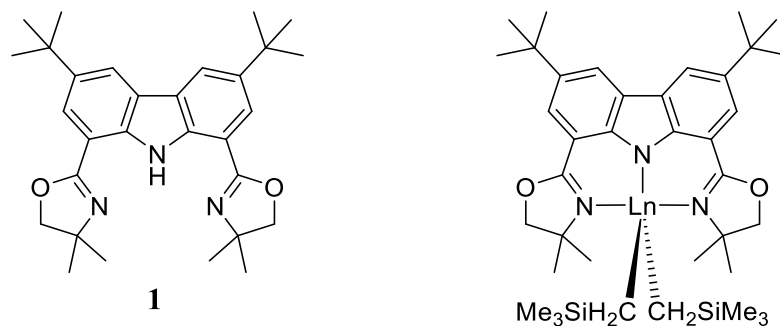


Figure 1.5 1,8-*bis*-(4,4'-dimethyloxazolin-2'-yl)-3,6-di-*tert*-butylcarbazole ligand (HCzx, **1**) and potential lanthanide dialkyl pre-catalyst

A similar carbazole-based pyrazole ligand has been used by the Hayes group⁶⁵ for the successful isolation of stable lanthanide alkyl complexes. The success of our carbazole-based ligand (**1**) and the ligands used by the Hayes group were the motivation for developing the carbazole-*bis*(triazole) and carbazole-*bis*(tetrazole) ligands, HCzTr and HCzT, presented in this thesis (**Figure 1.6**). The complete scope of our ligand design and synthesis will be discussed in Chapter 2 and the use of this ligand in lanthanide chemistry will be presented in Chapter 3.

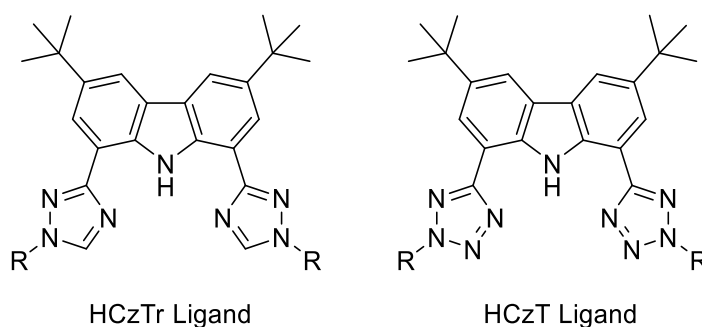


Figure 1.6 Ligands presented in this work

1.2 Transition Metals

The transition metals, also known as the d-block metals, are much more well known and studied compared to the f elements since some of the transition metals such as copper, gold, silver and iron date back all the way to ancient times, while discovery of the remaining transition metals were discovered more recently (18th century)²⁷. Early applications of the transition metals were for use in tools and weapons from their ores, but recent applications are dominated by catalysis for use in industrial applications¹¹. All of the d-block metals except for Tc can be found in the earth's crust, and some of the elements are extremely abundant (Fe is the fourth most abundant element)²⁷.

1.2.1 Transition Metal Properties

The transition metals are located in groups 3-11 of the periodic table and they all have (or readily form) partially filled d orbitals. As mentioned previously, the group 3 metals (Sc, Y) are more commonly studied with the f-elements due to their similar reactivity and although the group 12 metals (Zn, Cd, Hg) are not technically considered transition metals since their d subshell is full, their chemistry will be included in this section. One of the main features of the transition metals that is not observed in the lanthanides is their broad range of accessible oxidation states¹⁵. Access to several of these states, along with the ease of interconversion between these states, make the transition metals powerful tools in catalysis and magnetism-based applications.

Similar to what was seen for the lanthanides, the atomic radius of the transition metals decrease from left to right across a row due to an increase in effective nuclear charge with increasing atomic number. There is also an increase in atomic radius going down a group, but due to the filling of the 4f shell between the second and third row and the

resulting lanthanide contraction, there is little increase in atomic radius seen between the 4d and 5d metals¹⁵. These trends lead to the 4d and 5d metals having more similar chemistry to each other than the 3d metals. In general, the ionic radius of the d-block metals is smaller than those of the lanthanides, but depending on the oxidation state of the transition metal this is not always the case. The natural abundance of the d-block metals varies considerably, but the first row transition metals are drastically more abundant than the second and third row transition metals or the lanthanides (**Table 1.2**). This, along with their low cost, makes first row transition metals (especially iron) extremely attractive for use in industrial level catalysis.

Table 1.2 Estimated abundances of d and f block metals in the earth's crust²⁷ (numerical values are in parts per million)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
26	6600	190	140	1100	63000	30	90	68	79
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
29	130	17	1.1	-	0.001	0.0007	0.0063	0.08	0.15
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
34	3.3	1.7	1.1	0.0026	0.0018	0.0004	0.037	0.0031	0.067
Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er
60	8.7	33	6.0	1.8	5.2	0.94	6.2	1.2	3.0
Tm	Yb	Lu							
0.45	2.8	0.56							

1.2.2 Bonding in Transition Metal Complexes

The main transition metals discussed in this work are the smaller first row transition metals, so this description of the bonding behaviour and characteristics will be limited to the 3d metals. Metal-ligand bonding among the d-block metals is drastically different than what is observed for the lanthanides and is much more well understood and studied. The

main difference between the bonding in the f-block versus the d-block is the covalency of the bonding in the d-block. The valence 3d orbitals of the transition metals are less core-like than the valence 4f orbitals of the lanthanides and they are able to interact more strongly with the ligands. This allows for orbital overlap of the 3d orbitals with s and p orbitals of the ligands to form more covalent bonds. There are several theories that exist to explain the bonding seen among the transition metals, one of the simplest being crystal field theory (CFT) which is an electrostatic model that treats the incoming ligands as point charges¹⁵. CFT predicts that the five d orbitals in a metal complex will not be degenerate and the resulting splitting pattern of the d orbitals will be determined by the type and arrangements of ligands around the metal centre^{15, 27}. These different geometries give rise to different splitting patterns as seen in **Figure 1.7**.

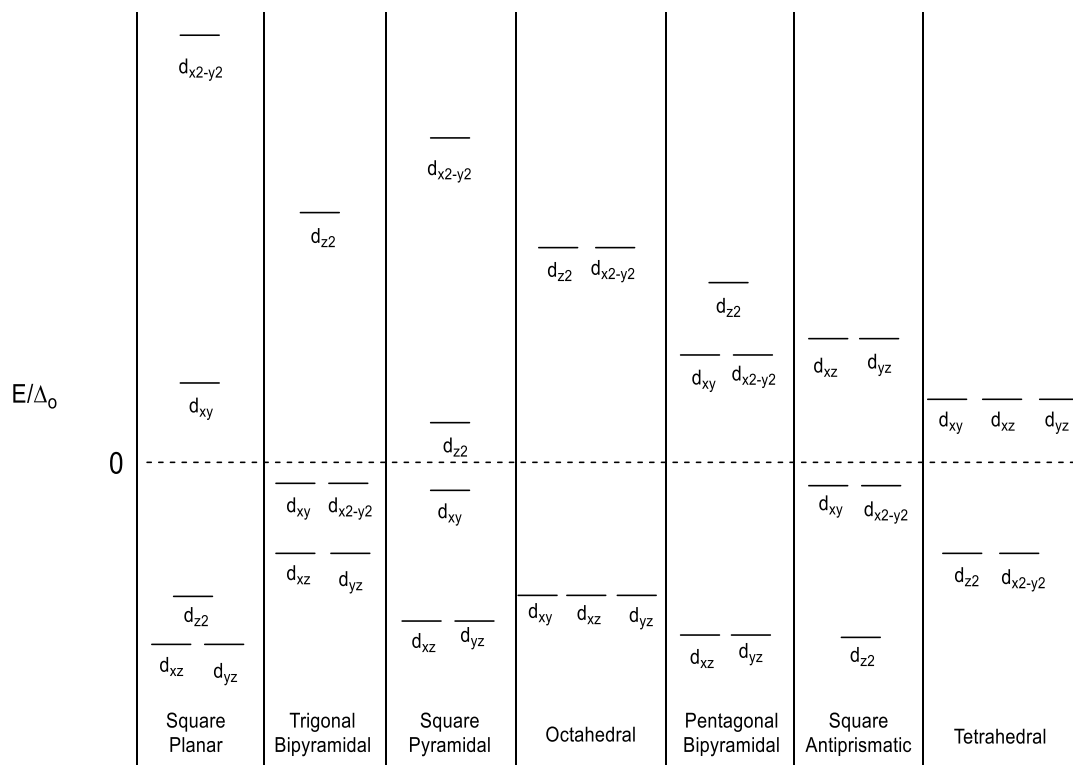


Figure 1.7 CFT orbital splitting diagrams for some common fields¹⁵

The splitting of the d orbitals is a direct effect of the surrounding ligands, and this splitting results in differences in magnetic properties of the metal complexes, such as spin state (this will be discussed in more detail in Chapter 4). This orbital splitting can be quantified by a value known as crystal field splitting (Δ_o); this value is different throughout the d-block with typical Δ_o values for first row transition metals in the range of 10 000 – 30 000 cm^{-1} while for second row transition metals the values are in the range of 20 000 – 40 000 cm^{-1} ²⁷.

While CFT gives useful insight into the geometry and magnetic/electronic properties of transition metal complexes, it is overly simplified and does not take into account covalent interactions. Instead of thinking of the ligands as point charges with

repulsive interactions with metal electrons, a better model to more accurately describe the metal-ligand bonding is molecular orbital (MO) theory. MO theory takes into account orbital overlap between the ligand and the metal in covalent interactions and allows for a range of bonding types through the use of group theory. In MO theory, pairs of atomic orbitals or ligand group orbitals of the same symmetry, similar energy and with significant spatial overlap combine to produce an equal number of molecular orbitals¹⁵. Depending on the symmetry of these orbitals, the interaction can be categorized into either σ or π type overlap (**Figure 1.8**). Ligands can then be differentiated as σ -acceptor, σ -donor or π -acceptor, π -donor in character depending on the interaction with the metal and the distribution of the electrons involved in the bonding. These interactions will be discussed in more detail in Chapter 5 of this work.

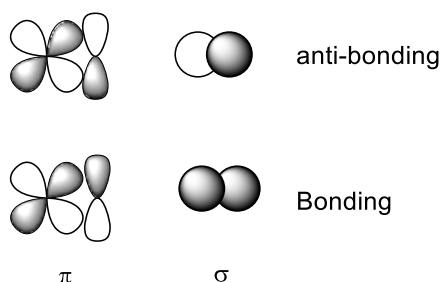


Figure 1.8 Simplified diagram of σ and π type orbital interactions

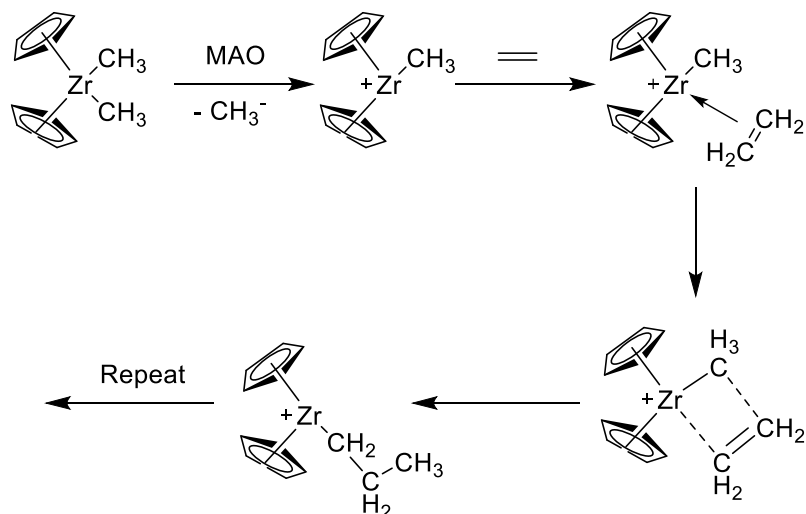
In MO theory, the Δ_O value depends on the type of interaction the ligand is making with the metal, similar to what is seen in CFT. By changing the ligand donor/acceptor type it is possible to directly adjust Δ_O which allows for fine tuning of the electronic and magnetic properties of the complex. MO theory provides a powerful framework to explain the geometry and electronics of transition metal complexes depending on the type of ligand

in the complex. Unlike the lanthanides, the spectroscopic and electronic properties of transition metal complexes are directly affected by the ligand environment making ligand design more involved with the d-block metals.

1.2.3 Catalytic Reactivity of Transition Metals

Unlike the lanthanides, the transition metals show different reactivity trends depending on where in the d-block they are located due to difference in radius, as well as accessible oxidation states. Also unlike the lanthanides, the transition metals are able to undergo both σ -bond metathesis and oxidative-addition and reductive-elimination reaction steps making them more versatile catalysts in industry.

The propensity of early transition metals to undergo σ -bond metathesis catalytic mechanisms is demonstrated by the commercial use of Ti and Zr-based Ziegler-Natta catalysts for olefin polymerization to produce polyolefins^{3-4, 11}. The mechanism of catalysis involves initiation of the pre-catalyst to form the active species by introducing an open coordination site by use of a co-catalyst such as various Al alkyls or methylaluminoxane (MAO). The olefin can then interact with the metal centre and form a four-centred transition state (σ -bond metathesis) to insert into the M-C bond. This creates a new open coordination site so that another olefin can bind and the cycle can continue. This general mechanism is shown in **Scheme 1.2**.

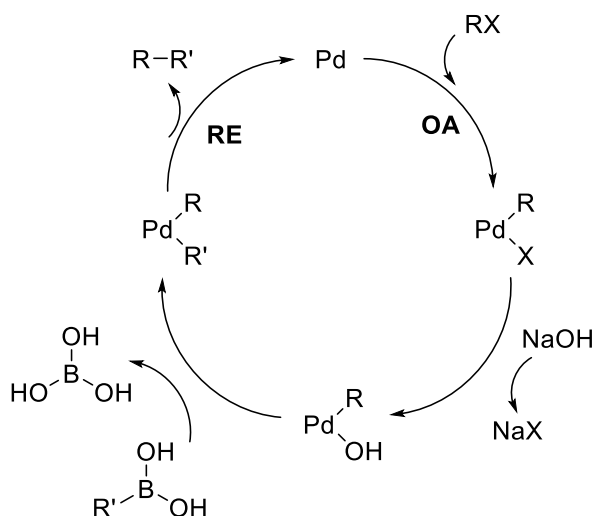


Scheme 1.2 Example of Ziegler-Natta catalyst polymerization mechanism

By adjusting the ligands that surround the metal centre, stereochemical control is possible: isotactic polypropylene can be isolated by use of a C_2 -symmetric *ansa*-metallocene on a Zr catalyst while use of bulkier C_s -symmetric *ansa* ligands (such as fluorenyl) produce syndiotactic polypropylene⁶⁶. This demonstrates both the importance of the metal centre reactivity, as well as the use of the proper ligand to control the catalysis.

Late transition metals, however, undergo oxidative-addition and reductive-elimination mechanistic steps primarily due to their access to several oxidation states. A popular example of a late transition metal catalyst is the use of Pd in cross-coupling reactions. Heck, Negishi and Suzuki were awarded the Nobel prize in 2010 for their work in developing Pd-catalyzed cross-coupling reactions⁶⁷. Cross-coupling reactions give a simple and straightforward route to important C-C bond formation processes that are important in the synthesis of pharmaceuticals⁶⁸. The integral steps in the catalytic mechanisms of cross-coupling reactions involves oxidative-addition and reductive-elimination to transform organic halides into organic compounds with new C-C bonds.

While the mechanism for the different types of Pd cross-coupling reactions (Suzuki, Negishi, Kumada, Sonogashira, etc.) are all slightly different, all involve the use of a Pd(0) catalyst that undergoes oxidative-addition to a Pd(II) species, that eventually undergoes reductive-elimination back to Pd(0) (**Scheme 1.3**)⁶⁷. The main difference between the various reactions is the intermediate transmetalation step, such as the use of boronic acid as the transmetalation agent in the Negishi Suzuki-Miyaura mechanism.



Scheme 1.3 Mechanism for Suzuki cross-coupling reaction

Even though cross-couplings are significantly different from σ -bond metathesis reactions, one common feature important to both is the ligand design, including the steric and electronic properties of the supporting ligands. Kumada discovered that use of bidentate ligands such as bis(1,1'-diphenylphosphino)ferrocene (dppf) accelerate the reductive-elimination step in the cross-coupling reaction, thereby increasing the overall rate of the reaction⁶⁹. In the following years several important ligand-based properties were shown to increase Pd cross-coupling reactivity including the cone angle of the ligand (a

measure of its size) and the electronic properties. It was found that the more sterically encumbered Pd catalyst with tri-*o*-tolylphosphine as a ligand had increased activity over the traditional $[\text{Pd}(\text{PPh}_3)_4]$ catalyst^{67, 70} and Osborn discovered that PCy_3 was a suitable ligand for carbonylation reactions using Pd catalysts and suggested that “*significant catalytic activity is found only with phosphines which are both strongly basic and with well-defined steric volume*”⁷¹. These results again show that both the metal and the ligands present can have a drastic effect on the resulting reactivity.

1.2.4 Ligands Used in Transition Metal Complexes

The ligands used in transition metal complexes can be adapted to the desired application whether that involves magnetism, catalysis or photophysical properties. This work is mainly focused on stoichiometric and catalytic reactivity so the ligand scope discussed in this section will be centred on ligands for use in transition metal catalysts. In contrast to what was observed with the lanthanides, transition metals are able to bind a range of donor ligands¹², both hard and soft, and since the bonding is much more covalent in character there are far more carbon-based ligands seen in the d-block. Unlike the lanthanides, the coordination sphere of the transition metals (especially the first row) is quite a bit smaller and can usually only accommodate coordination numbers between two and six. Transition metals are also able to undergo π -back-donation giving rise to CO and alkene complexes that are unknown in the lanthanides.

The most common ligands used in transition metal complexes are bidentate or tridentate chelating ligands and since there is access to several oxidation states there are examples of mono, di, and trianionic ligands. Unlike in the lanthanides, neutral ligands are

also commonly used due to the less labile metal-ligand bonds formed. There is evidence that has shown a preference to form five-membered chelate ring between the ligand donors and the metal centre⁷²⁻⁷³, especially with the smaller first row transition metals due to increased stability of these complexes. This gives rise to several neutral, mono and dianionic ligands commonly used in transition metal complexes that form stable five (or six in the case of acac) membered chelate rings upon complexation. A small variety of some of the more common ligands are shown in **Figure 1.9**²⁷.

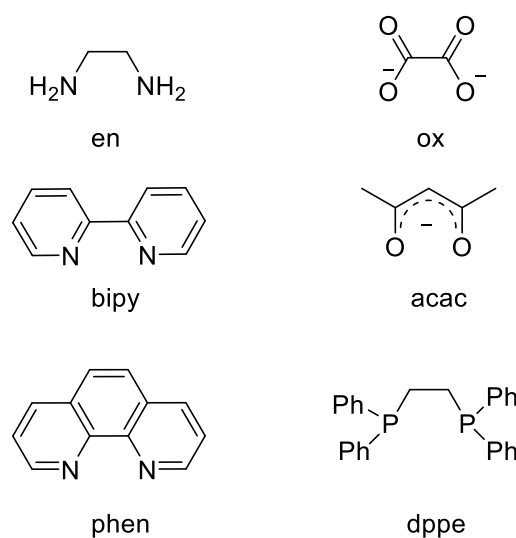


Figure 1.9 Some common bidentate chelating ligands

These ligands are commercially available which enables extensive research to be conducted in coordination complexes using a range of d-block metals of varying size⁷⁴⁻⁷⁷. In order to further tune the steric and electronic profile of the ligand, tridentate pincer ligands are employed using a variety of donor atoms. The number of pincer ligands used in transition metal coordination chemistry is far too widespread to even scratch the surface of in this short introduction^{12, 78-79}. A small selection of especially common and successful

pincer ligand scaffolds is shown in **Figure 1.10**. Common traits of several of these ligands include the use of five or six membered heterocycles, carbenes or imino groups.

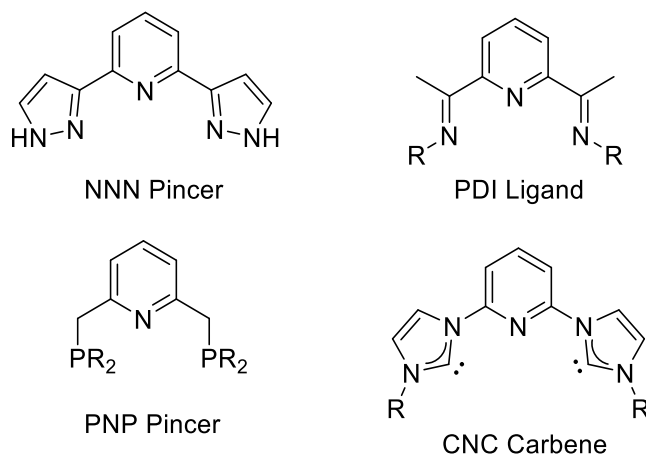
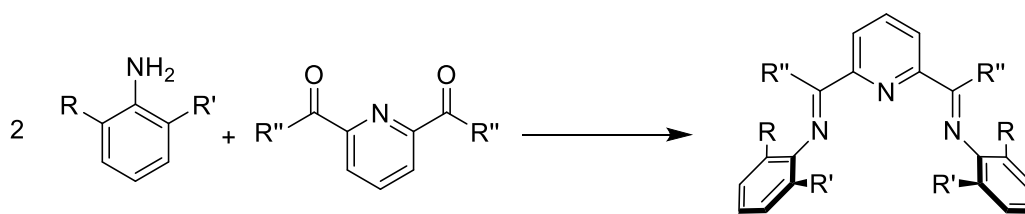


Figure 1.10 Small selection of pincer ligands used in transition metal coordination

All of these ligands allow for complexation of a wide range of transition metals of varying size and oxidation state, while still allowing access to the metal centre for reactivity without steric overcrowding. Carbene-based pincer ligands gained popularity in the late 90s and early 2000s after the emergence of their use in Pd complexes that were found to be highly active Heck reaction catalysts⁸⁰⁻⁸². Their ease of synthesis and the ability to tune the steric and electronic properties make them attractive for use in transition metal complexes. CNC carbene pincer ligands offer two metal-carbon σ bonds that are largely electrostatic which supplies enhanced stability compared to non-organometallic complexes such as phosphine ligands^{81, 83}. Carbene pincer ligands have also been shown to undergo conversion between bidentate and tridentate binding modes that can facilitate metal oxidation state changes as well as the steric and electronic demands of the catalytic reaction^{12, 84}.

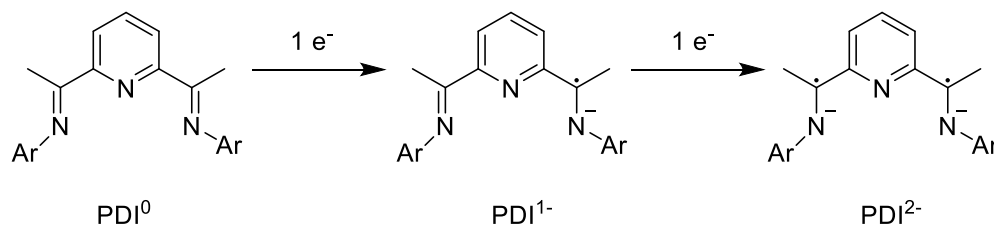
Another extremely successful pincer ligand in transition metal chemistry is the pyridine diimine (PDI) ligand that is easily synthesized in a one step Schiff-base condensation reaction with functionalized aniline and 2,6-diacetylpyridine⁸⁵⁻⁸⁶ (**Scheme 1.4**).



Scheme 1.4 Synthesis of functionalized PDI pincer ligand

The capability to sterically and electronically tune the ligand in several locations in one synthetic step makes this an extremely powerful ligand design for use in transition metal catalysis. Fe and Co complexes with the PDI ligand system exhibit particularly exceptional reactivity in polymerization of olefins^{85, 87-89}. The steric bulk of the ligand is instrumental in stabilizing low coordinate transition metal complexes that display increased reactivity. In addition, the steric bulk of the ligand was also proven to directly affect the catalytic activity as well as the polymer molecular weight⁸⁹. More recently the Chirik group has conducted extensive research on low coordinate Fe complexes of the PDI ligand for use in hydrosilylation and hydrogenation catalysis⁹⁰⁻⁹². Additionally, the PDI ligand system has shown to be redox non-innocent (**Scheme 1.5**) and can exist in the neutral, monoanionic or dianionic form⁹³⁻⁹⁴ which allows the ligand to act as an electron reservoir during catalytic transformations⁹⁵⁻⁹⁷. This is an extremely powerful method to make

cheaper, more environmentally friendly base-metal catalysts that mimic the reactivity of the more expensive noble metals such as Pt.



Scheme 1.5 Ligand-centred reductions in PDI ligands

The emergence of these sterically and electronically adjustable pincer ligand scaffolds has allowed for the development of first row transition metal reactivity that was previously inaccessible. This demonstrates the power and importance of the ligand, not just the metal centre, in catalytic transformations of the d-block metals.

One main distinguishing feature between the transition metal catalyst pincer ligands presented here and the pincer ligands discussed in the lanthanide section earlier in this work (Section 1.1.2) is the charge of the ligand. In general, nitrogen-based pincer ligands used in lanthanide catalysts are anionic³⁷, while a majority of nitrogen-based pincer ligands used in transition metal catalysts (especially Fe) are neutral⁹⁸⁻¹⁰⁰. One explanation for the use of anionic ligands in lanthanide complexes is the increased need to anchor the ligand and prevent redistribution. Another reason is the limited oxidation state range: if the pincer ligand was neutral the complex would require three additional anionic X^- ancillary ligands to satisfy the lanthanide centre. However, while transition metals have access to a large range of oxidation states, they require access to two oxidation states separated by two units in order to be used as catalysts in processes involving oxidative-addition and reductive-

elimination steps. If the pincer ligand used is taking up one of these oxidation states, there is one less available for catalytic reactivity. Moreover, since transition metals form covalent and less labile bonds than the lanthanides there is less need for a strong anchor by use of an anionic donor²⁷.

While the literature on nitrogen-based pincer ligands used in transition metal catalysis is dominated by neutral pincer ligands, the use of anionic nitrogen-based pincer ligands is largely underexplored. The resulting reactivity of transition metal complexes using an anionic ligand will likely be different than the same reactivity with known neutral pincer ligands. For this reason and the strict ligand requirements needed in order to synthesize and stabilize lanthanide complexes, we set out to synthesize tridentate monoanionic ligands (**Figure 1.6**) that may be proficient for use with a variety of metals including both f and d-block metals.

1.3 Scope of Research

Even though lanthanides and transition metals have vastly different bonding, reactivity and behaviour, the use of properly designed ligands enhances the reactivity of the resulting complexes in both cases. Incorporating an easily adjustable rigid ligand scaffold allows for fine tuning of the steric profile which will be important in successfully synthesizing both low coordinate transition metal and lanthanide complexes. The use of hard nitrogen donors in both anionic and neutral forms will help in stabilizing both types of metal complexes and the tridentate nature will increase stabilization through the chelate effect. In this thesis we present the design and synthesis of a new class of carbazole-based pincer ligand and their use in both transition metal and lanthanide chemistry.

In Chapter 2 we present the design, synthesis and development of our novel carbazole-based azole ligands, along with studies on the physical properties of the ligands, such as cyclic voltammetry and fluorescence properties. The use of bis-ligand Zn complexes to further study the electronic properties of these ligands in a metal complex is also discussed.

In Chapter 3 we report the synthesis of several lanthanide complexes with our ligand system and report the capability of the ligands to bind in several unexpected modes including bidentate, bridging and both pseudo *fac* and *mer* tridentate modes. The reactivity of the mono-ligand lanthanide complexes in ring opening polymerization of lactones and the odd redox behaviour of the trivalent lanthanide complexes are also briefly discussed.

Chapter 4 focuses on the use of our ligands to form air-stable bis-ligand complexes of some first row transition metals, mainly iron. The magnetic properties of these complexes are reported including a thermally induced spin crossover observed for the iPr-substituted carbazole-*bis*(tetrazole) Fe complex.

Chapter 5 presents the chemistry of the mono(ligand) iron complexes and hosts most of the reactivity studies in this work. The synthesis and characterization of Fe(II) and Fe(III) complexes with the iPr-substituted carbazole-*bis*(tetrazole) ligand is reported, facilitated by the use of Mössbauer spectroscopy where X-ray crystal structures are lacking. The use of a bulky phenoxide ligand in these iron complexes to limit ligand redistribution is reported. Several adducts of these Fe phenoxide complexes were synthesised and an in-depth study on the sterics and electronics of these complexes is discussed. The preliminary reactivity of these complexes was studied, including their use as hydrosilylation catalysts, where some evidence for ligand non-innocence is presented. Chapter 6 discusses possible

future directions for this research while Chapter 7 presents the experimental details pertaining to Chapters 2-5.

Chapter 2 Ligand Design, Synthesis and Properties

2.1 Background

Previous research in our group focused on design and synthesis of new ligands for exclusive use in lanthanide chemistry⁶³. One ligand Jin Zou (previous Berg group member) developed consisted of a rigid carbazole backbone with two oxazoline rings in the 1 and 8 positions, HCzx, **1**, (**Figure 2.1**)⁶³. Deprotonation of carbazole gives a monoanionic nitrogen donor on a large rigid skeleton. The 3 and 6 positions were blocked with tert-butyl (tBu) groups to allow subsequent functionalization at the 1 and 8 positions. The tBu groups were also thought to aid in crystallization and provide a useful ¹H NMR handle, especially in the case of paramagnetic complexes. The oxazoline rings were attractive as they are relatively easy to make and provide hard neutral nitrogen donors that are good at stabilizing lanthanide centres. Oxazolines are also attractive as ligands because they can be made chiral by varying the substituents on the oxazoline ring thereby allowing access to chiral complexes for use in stereoselective catalysis¹⁰¹.

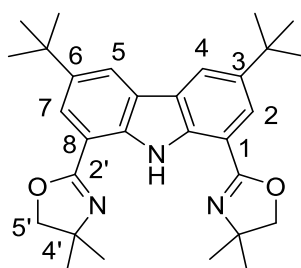


Figure 2.1 HCzx ligand (**1**)

Ligand **1** was synthesised on large scale in good yields and a number of lanthanide complexes of this ligand were successfully synthesized⁶³⁻⁶⁴. The isolation of the dialkyl complexes, $(\text{Czx})\text{Ln}(\text{CH}_2\text{SiMe}_3)_2$, was of particular note because other lanthanide dialkyls are known to function as extremely active alkene polymerization catalysts upon activation with MAO or $[\text{Ph}_3\text{C}]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$. However, these lanthanide complexes failed to polymerize ethylene and isoprene with $[\text{Ph}_3\text{C}]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$ as an initiator. Upon examination of the X-ray crystal structure of $(\text{Czx})\text{Yb}(\text{CH}_2\text{SiMe}_3)_2$ it was seen that the alkyl groups bind in an unanticipated fashion, where both alkyl groups are rotated away from the oxazoline methyl groups in a “folded wing” geometry⁶⁴ (**Figure 2.2**). This is most likely to avoid steric repulsion between the alkyl groups and the oxazoline methyl groups.

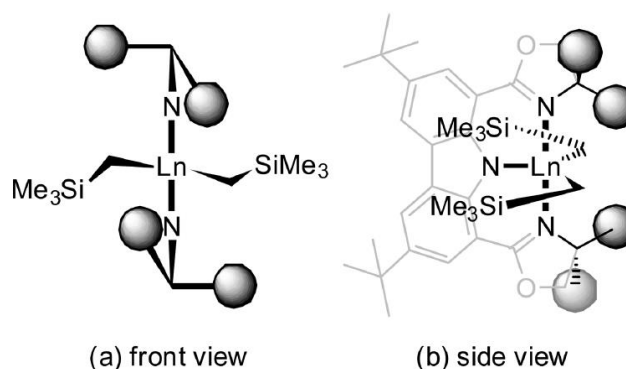


Figure 2.2 Illustration of $(\text{Czx})\text{Yb}(\text{CH}_2\text{SiMe}_3)_2$ structure (reprinted with permission from ⁶⁴)

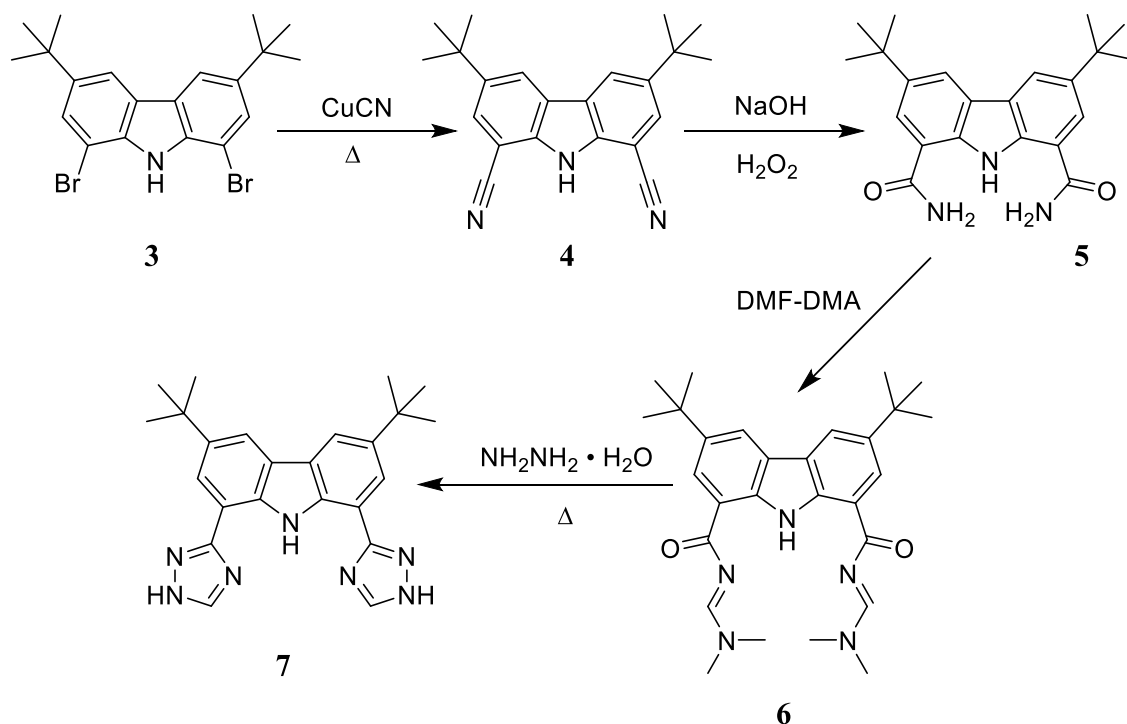
It was hypothesized that the reason for the surprisingly low reactivity of the lanthanide alkyl complexes was the odd geometry of the alkyl groups. This sterically crowded geometry may prevent alkene insertion into the $\text{Ln}-\text{C}$ bond, especially since there is NMR evidence for formation of the cationic species, $[(\text{Czx})\text{Yb}(\text{CH}_2\text{SiMe}_3)]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$

on treatment with $[\text{Ph}_3\text{C}]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^{-63}$. Therefore, the basis of my project was to develop a similar carbazole-based ligand without the bulky substituents on the chelating rings. Since the synthesis of oxazoline rings with only H substituents results in extremely low yields due to the *Thorpe-Ingold* effect¹⁰²⁻¹⁰³, different ring systems were considered. The carbazole backbone is still desirable since it is cheap and easy to make and most importantly, the synthetic path previously developed can readily be modified to make different nitrogen-containing rings of a similar size.

2.2 Carbazole-Bis(Azole) Ligands

2.2.1 Design and Synthesis of Ligands

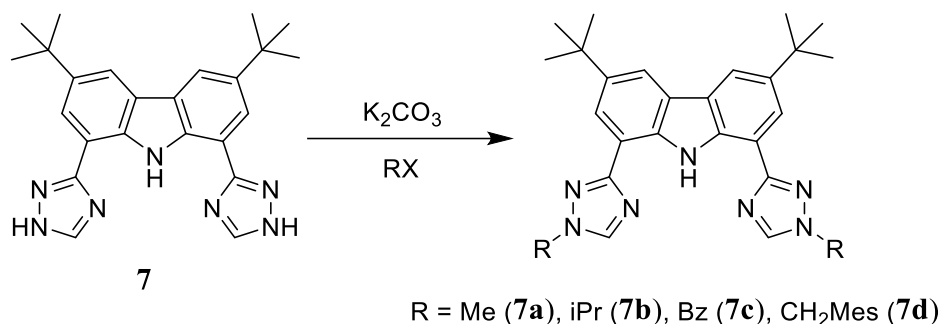
One of the simplest ways to decrease the bulk of the oxazoline rings is to replace them with planar azoles. The precursors to **1** provide convenient entry into the 1,2,4-triazole and 1,2,3,4-tetrazole systems as discussed below. The 1,2,4-triazole derivative can be synthesised from the known di-*t*Bu carbazole¹⁰⁴ (**2**) to form the known dibromo-carbazole precursor¹⁰⁵ **3** by first reacting it with CuCN at elevated temperatures to replace the bromo groups with cyano groups to afford **4**. The aryl cyano groups of **4** can be converted into a simple carboxamide (**5**) by an exothermic reaction using H_2O_2 and NaOH as outlined by McMaster¹⁰⁶. Subsequent reaction of **5** with DMF-DMA affords the dimethylamino derivative **6**. Treating this with hydrazine monohydrate in a ring closing reaction affords the desired unsubstituted 1,2,4-triazole derivative HCzTr^H (**7**) in good overall yield (69 %) as shown in **Scheme 2.1**.



Scheme 2.1 Synthesis of unsubstituted HCzTr^H ligand (7)

The unsubstituted version of the triazole ligand **7**, can be alkylated with several different organic groups by simple deprotonation using a mild base followed by treatment with an alkyl halide RX (R = Me, iPr, Bz, CH₂Mes). This is a nice feature as it is easy to modify the ligand size, steric and electronic properties by simply changing the substituent on the azole ring in one step at the end of the synthesis. Alkylation of the azole ring is required in order to remove the acidic triazole NH proton. This is because triazole NH deprotonation would likely occur during complex formation resulting in unwanted bridging interactions, especially with the lanthanides. The parent 1,2,4-triazole, HCzTr^H, was deprotonated with K₂CO₃ and then treated with MeI, 2-bromopropane, benzyl bromide and bromomethylmesitylene to produce the methyl (**7a**), isopropyl (**7b**), benzyl (**7c**) and methyl mesityl (**7d**) derivatives, respectively (**Scheme 2.2**). It was found that for secondary

bromides such as 2-bromopropane, the reaction needed higher temperatures and longer reaction times compared to the primary halides.



Scheme 2.2 Alkylation of HCzTr^H (**7**)

These new ligands HCzTr^{Me} (**7a**), HCzTr^{iPr} (**7b**), HCzTr^{Bz} (**7c**), and HCzTr^{CH₂Mes} (**7d**) were all characterized by ¹H, ¹³C, 2D NMR, X-ray crystallography (in some cases) and high resolution mass spectrometry. The tBu groups appear as a large singlet in the ¹H NMR spectrum around 1.50 ppm. Similarly, the aromatic carbazole backbone protons always appear as narrow doublets (⁴J_{HH} = 1.8 Hz) in the range of 8-9 ppm. The CH of the triazole ring appears as a downfield resonance at 8.80 ppm and in the parent triazole, **7**, the NH resonance can be seen as an extremely broad singlet at 14.46 ppm. This NH resonance of the carbazole is found around 12 ppm for all ligands when internal hydrogen bonding is present, but shifts upfield (around 8 ppm) when there is no hydrogen bonding. The alkylated ligands show the appropriate resonances in the ¹H NMR spectra as shown in **Figure 2.3** and discussed in Chapter 7.

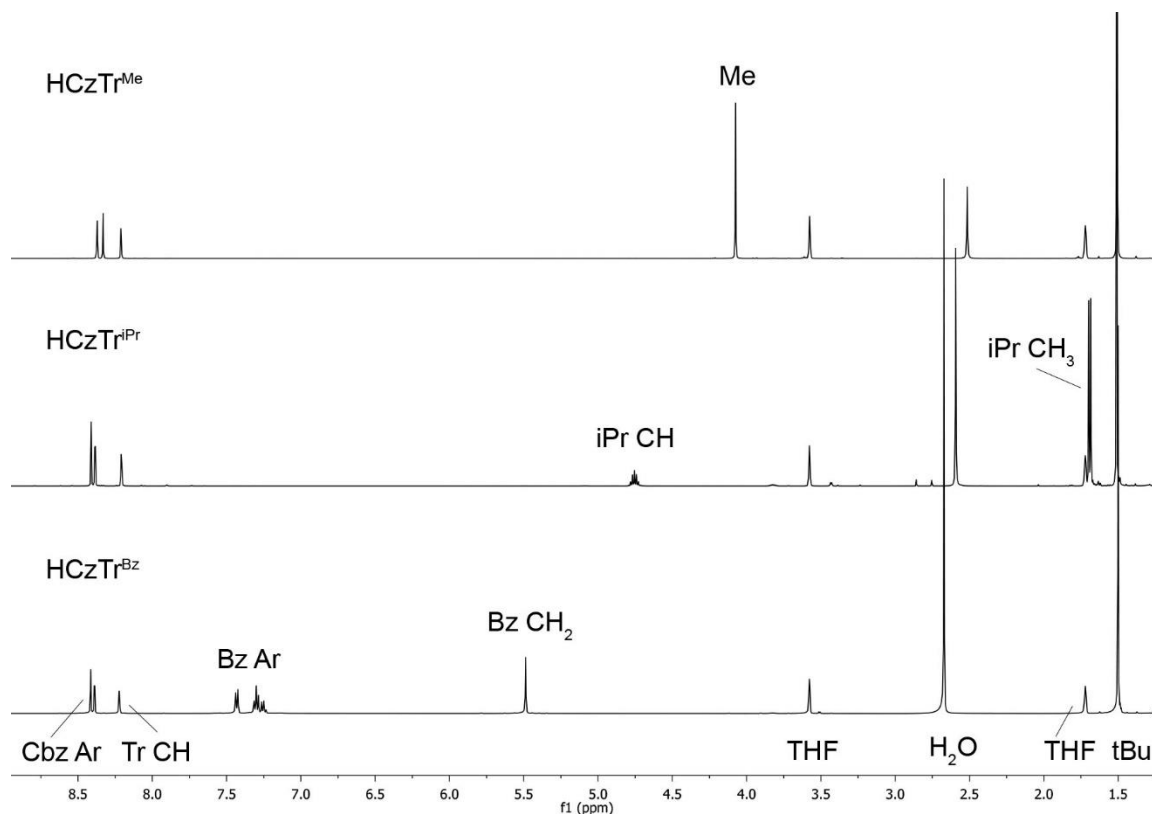


Figure 2.3 Stack plot of HCzTr^{Me} (**7a**), HCzTr^{iPr} (**7b**) and HCzTr^{Bz} (**7c**) ¹H NMR spectra (500 MHz, THF-D₈, 298 K)

While it is clear by the NMR spectra that these new ligands have the correct structure, X-ray quality crystals of **7b** (Figure 2.4) and **7c** (Figure 2.5) were grown that also confirm the structure. Both ligands crystallize in the monoclinic crystal system in the P2₁/n space group. In the isopropyl ligand, **7b**, the unsubstituted nitrogen adjacent to the CH is rotated inwards towards the carbazole NH for one ring (N7) and outward for the other (N4). This results in cant angles¹⁰⁷ of the triazole rings of 9.69° and -16.25°. In contrast, for the benzyl ligand, **7c**, the cant angles are both in the same direction at -10.68° and -6.53°. The fact that the cant angles in the benzyl ligand are smaller illustrates the

triazole rings are slightly more co-planar with carbazole in this case, probably due to packing effects. All crystallographic data can be found in the Appendix.

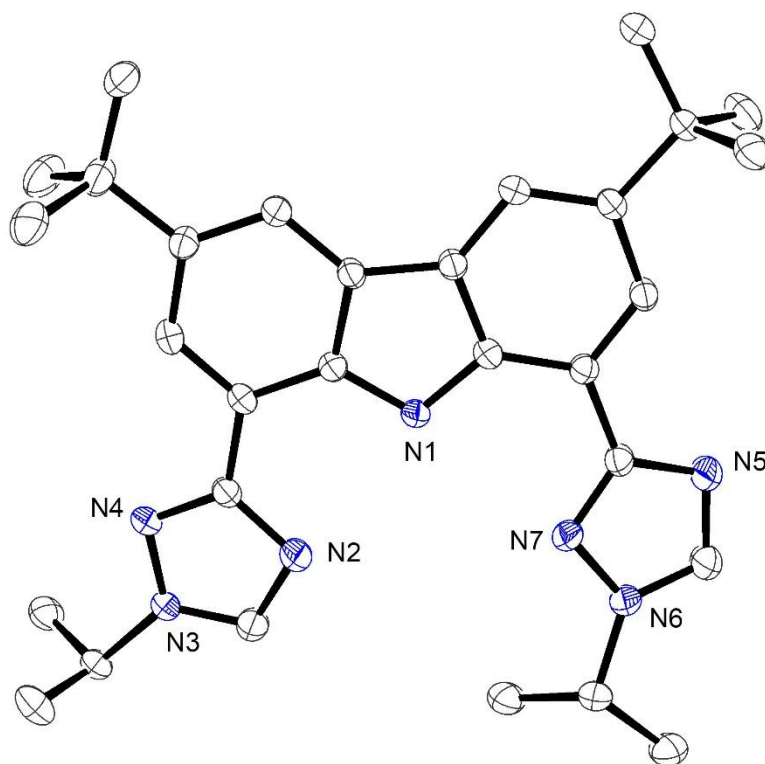


Figure 2.4 ORTEP3¹⁰⁸ plot (50% probability ellipsoids) of HCzTr^{iPr} (**7b**) (H atoms and solvent omitted for clarity)

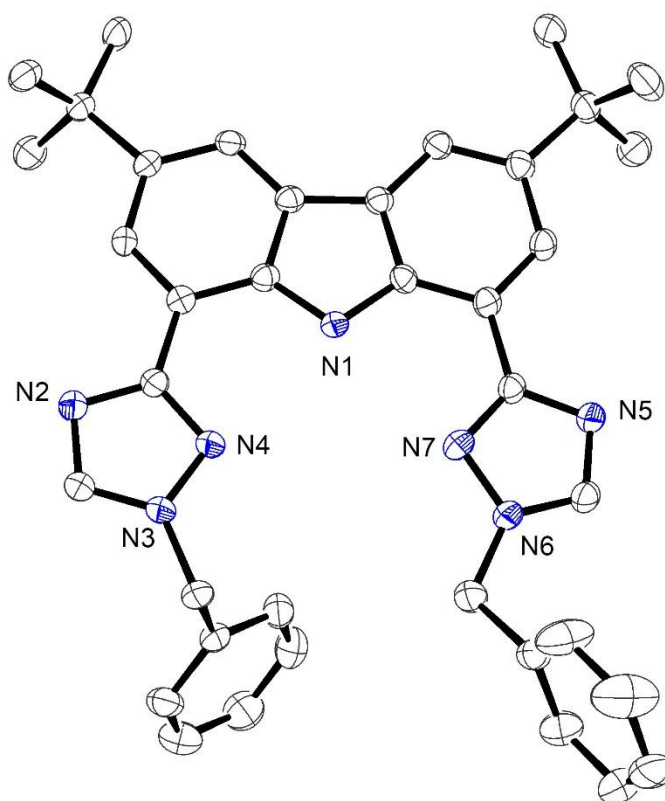
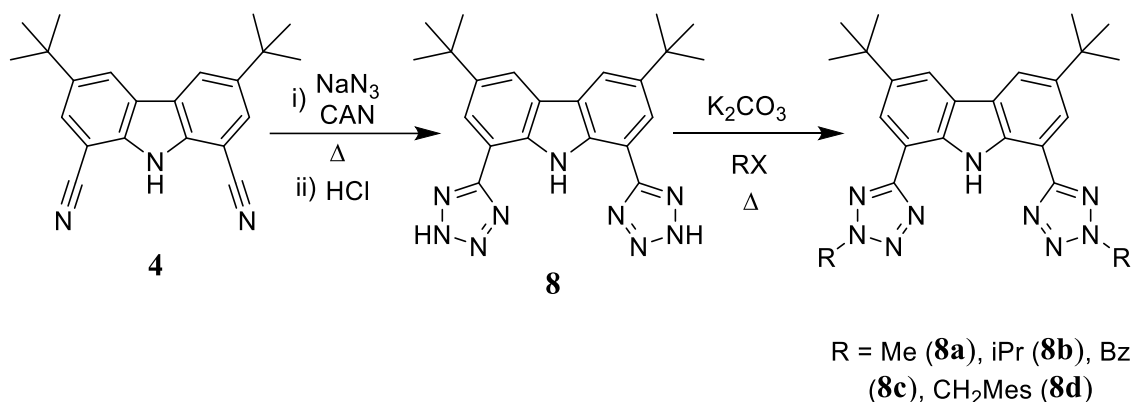


Figure 2.5 ORTEP3¹⁰⁸ plot (50% probability ellipsoids) of HCzTr^{Bz} (**7c**) (H atoms and solvent omitted for clarity)

We were also successful in preparing a similar bis-tetrazole ligand. In this case a simple one-step “click” reaction between **4**, already synthesised for the triazole route, and sodium azide afforded the parent tetrazole ligand HCzT^H (**8**). The reaction proceeds best using **4**, sodium azide and cerium ammonium nitrate (CAN) as a catalyst¹⁰⁹ at 140 °C in DMF for 48 h. Since the sodium salt of the tetrazole is formed *in situ*, the reaction is acidified with 1M HCl to protonate the tetrazole ring. Using the same procedure as for the 1,2,4-triazole, the parent tetrazole **8** can be deprotonated and alkylated to produce the methyl (**8a**), isopropyl (**8b**), benzyl (**8c**) and methyl mesityl (**8d**) derivatives of the ligand (Scheme 2.3).



Scheme 2.3 Synthesis of HCzT^R ligands

The new tetrazole ligands HCzT^{Me} (**8a**), HCzT^{iPr} (**8b**), HCzT^{Bz} (**8c**) and HCzT^{CH₂Mes} (**8d**) were all characterized by ¹H, ¹³C, 2D NMR, X-ray crystallography (in some cases) and high resolution mass spectrometry. NMR characterization was very similar to the triazole derivatives, with the only difference being the lack of the triazole ring CH signal at 8.80 ppm. X-ray quality crystals of **8b** (Figure 2.6) and **8c** (Figure 2.7) were grown from hot isopropanol and characterized by X-ray crystallography. Ligand **8b** crystallizes in the P2₁/n space group and **8c** in the P-1 space group. Similarly, to the triazole instance, the cant angles of the tetrazole rings in the iPr case are larger (-6.74° and 11.68°) compared to the benzyl derivative (-7.20° and 4.66°). The main difference is that in HCzT^{Bz} the tetrazole rings cant in opposing directions, while in **7c** the triazole rings are canted in the same direction.

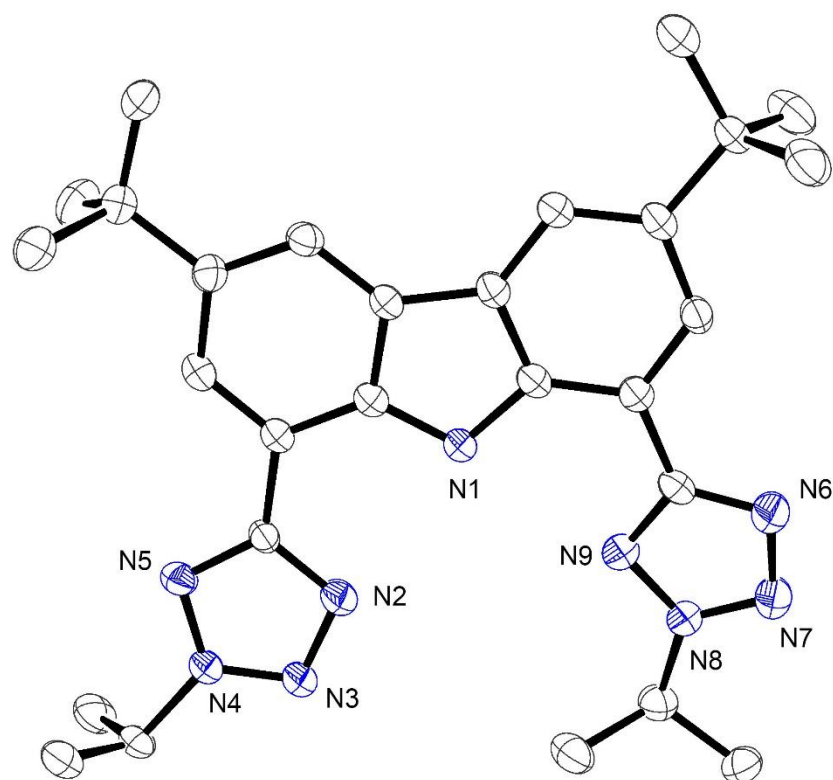


Figure 2.6 ORTEP3¹⁰⁸ plot (50% probability ellipsoids) of HCzT^{iPr} (**8b**) (H atoms and solvent omitted for clarity)

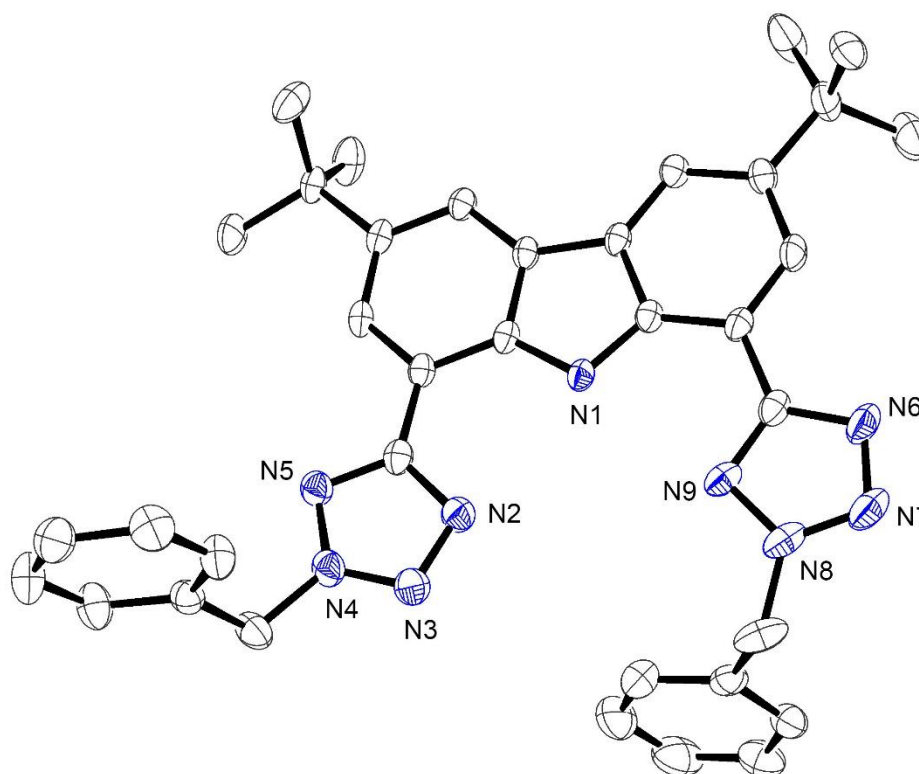


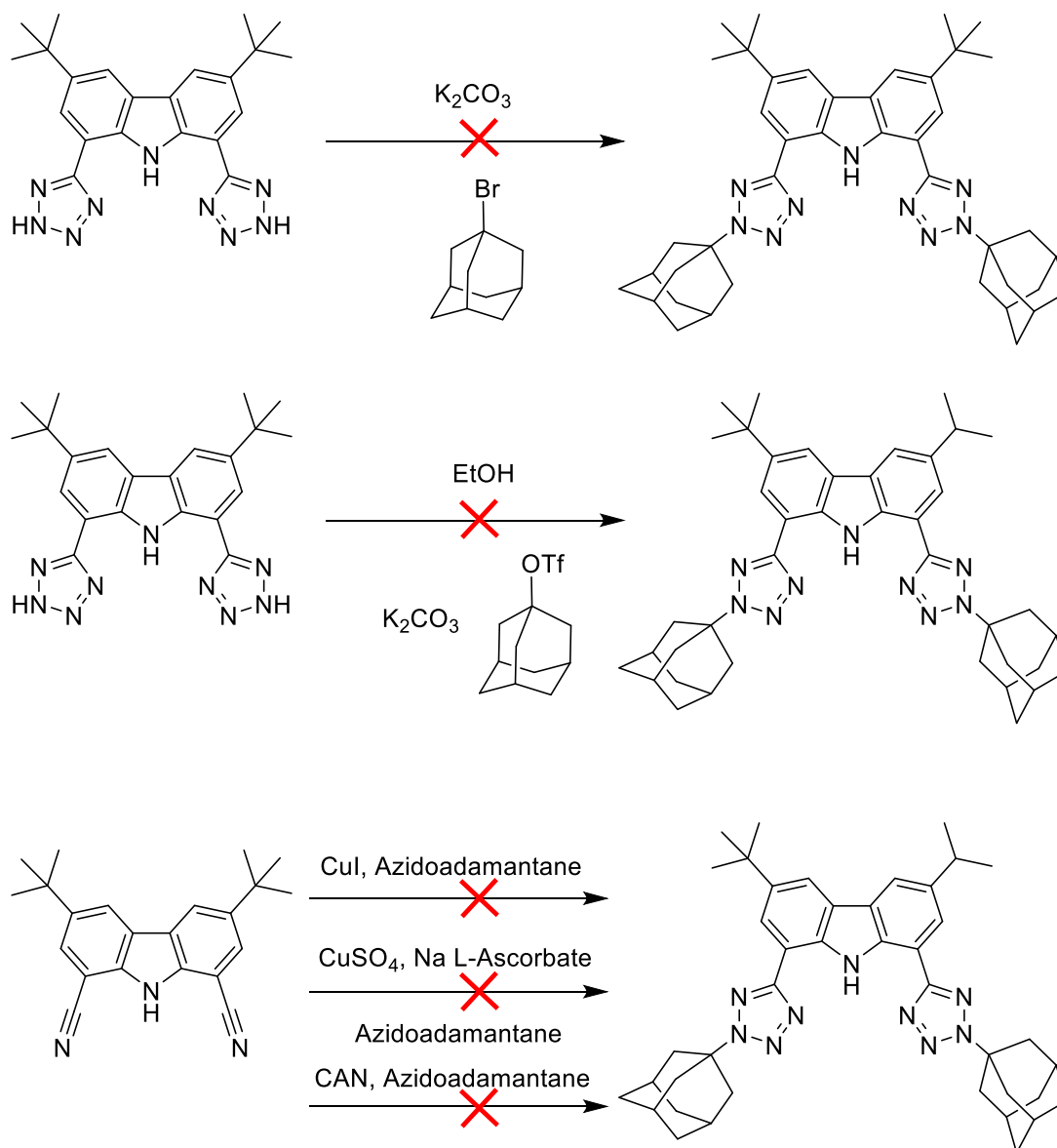
Figure 2.7 ORTEP3¹⁰⁸ plot (50% probability ellipsoids) of HCzT^{Bz} (**8c**) (H atoms and solvent omitted for clarity)

2.2.2 Use and Development of the Ligands

With the goal of synthesizing novel lanthanide and transition metal complexes with our new ligands, it was decided to focus primarily on one ligand rather than on all eight in order to gain insight into the behaviour and reactivity of one ligand before branching out to others. Due to the higher yield and ease of synthesis, the tetrazole scaffold was chosen over the triazole. This also avoids possible agostic interactions (interaction between metal and C-H bond) or a site for metalation that could occur at the 1,2,4-triazole ring CH because the tetrazole ring does not contain a CH moiety¹¹⁰. In terms of substituents, the isopropyl derivative seemed the most attractive due to its distinct ¹H NMR pattern (12 H doublet and

2 H septet), large steric bulk and tendency to improve crystallinity. The latter point is exceedingly important for paramagnetic complexes as the NMR spectra may not be as useful in characterization, increasing our reliance on X-ray crystallography. The isopropyl tetrazole ligand **8b** proved successful in the synthesis of a wide array of lanthanide and first row transition metal complexes to be discussed in detail later in this thesis.

We also briefly explored larger substituents to see if very crowded ligands could be made by this route. One of the largest organic groups commonly used in ligands is adamantyl. It is desirable not only for its large bulk, but also for its high symmetry which simplifies the NMR spectrum. Several potential adamantyl precursors are also available making it a good candidate. The most straightforward way to synthesize this target is by using the deprotonation/alkylation protocol outlined in **Scheme 2.2** and illustrated for adamantyl bromide in **Scheme 2.4**. Several attempts at synthesising the adamantyl ligand HCzT^{Ad} were unsuccessful. It was found that simple deprotonation of the tetrazole ring and substitution with bromoadamantane was not possible even at elevated temperatures, most likely because the bromo-substituted carbon on the adamantane is tertiary and the mechanism of the reaction is likely $\text{S}_{\text{N}}2$. Attempts to make the reaction more $\text{S}_{\text{N}}1$ -like were conducted by replacing the bromide on the adamantyl with a better leaving group such as a triflate and doing the reaction in a polar protic solvent such as ethanol, but still no reaction took place (**Scheme 2.4**). It was clear that an adamantyl group could not be added to the tetrazole ring by the same procedure previously used, so methods that did not involve alkylation were explored.



Scheme 2.4 Attempted synthesis of HCzT^{Ad}

The cyano carbazole, **4**, was reacted in “click”-type chemistry with azidoadamantane to see if the tetrazole ring could be formed with the adamantyl substituent already in place in order to avoid tertiary carbon substitution. Several different “click” reaction conditions were used with varying solvents and catalysts, but again no desired product was ever formed (**Scheme 2.4**). A quick scan of the literature revealed that

although “click” reactions are now considered common and reliable protocols in organic chemistry, the “click” reaction between an organic azide and a nitrile to form a substituted tetrazole has no precedent^{109, 111-112} even though similar reactions with sodium azide produce the parent tetrazole **8**.

2.3 Ligand Properties

With these new ligands in hand we decided to research the physical and electronic properties of the ligands themselves before attempting to coordinate them to a variety of metals. It is important to understand the properties and behaviour of the parent ligands so that we can better understand the behaviour of complexes derived from them.

2.3.1 Cyclic Voltammetry

In order to study the electronic properties of the ligands and differences between them the cyclic voltammograms (CV) of each were recorded. This simple technique allows us to determine if there are any oxidations or reductions of the ligand in the absence of metal complexation. CVs were recorded for the methyl, isopropyl and benzyl versions of both the triazole and tetrazole ligands; the methyl mesityl ligands **8d** and **7d** were not investigated as it was assumed they would be very similar to the benzyl derivatives. The CVs were run at room temperature in dry THF with tetrabutylammonium hexafluorophosphate [$\text{nBuN}^+ \text{PF}_6^-$] as supporting electrolyte at a scan rate of 100 mV/s. The stack plot of all CVs is seen in **Figure 2.8**. The full redox window from -2 V to 1.6 V was examined but only the positive range is shown in **Figure 2.8** because there were no reduction peaks between -2 and 0 V for any of the ligands. It should also be mentioned that

the second oxidation peak seen in **7a** is due to oxygen and is also seen in the blank (indicated by a * in **Figure 2.8**).

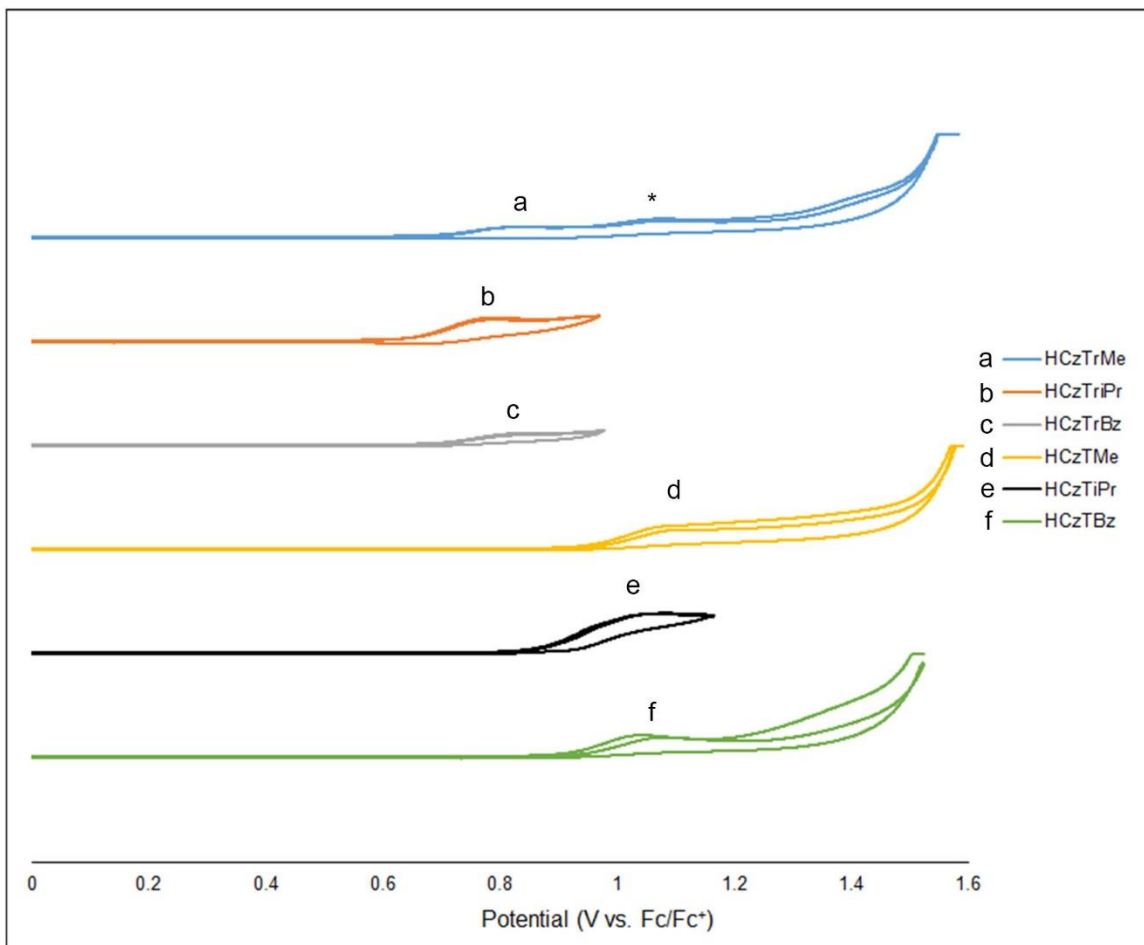


Figure 2.8 Cyclic voltammogram of selected ligands vs. Fc/Fc⁺ in THF with [nBu₄N⁺PF₆⁻] as supporting electrolyte. Scan rate is 100 mV/s.

Each ligand shows one irreversible oxidation peak at varying potentials. The oxidation is likely carbazole-based and it is irreversible possibly because the carbazole cation ejects a proton leaving a neutral ligand that cannot be similarly reduced. There is little dependence on the ligand substituent. For example, all substituted tetrazole ligands show peaks around 1.06 V and similarly all three triazole ligands show a peak around 0.8

V. There is, however, a fairly large difference in oxidation potential between the tetrazole and the triazole ligands, with the triazole ligands oxidizing at a lower potential compared to the tetrazole ligands. If the oxidation is carbazole-based, the shift in oxidation potential could be due to the triazole being less electron withdrawing than the tetrazole. This would make the carbazole moiety of the triazole-based ligands more electron rich and easier to oxidize. This result also suggests a high degree of resonance between the carbazole backbone and the azole rings. This is consistent with the planarity of the ligand observed in the solid state, although packing effects no doubt play a role in the coplanarity of the azole and carbazole rings. The CV experiments on the parent ligands suggest that the ligands themselves are redox non-innocent and are capable of being oxidized within a reasonably modest positive potential window. This is important because the oxidation of the ligands may play a role in the redox behaviour of their metal complexes.

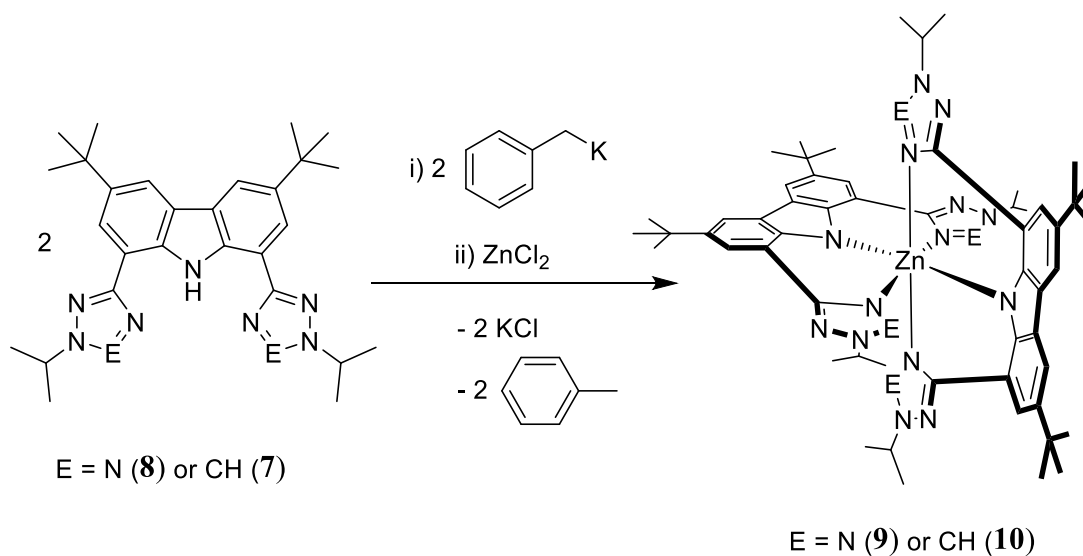
2.4 Zinc Complexes

While the CV data of the protonated ligands showed some insight into the electronic properties of the ligands, it is not a perfect comparison to ligand behaviour in a metal complex where the ligand is deprotonated. In order to study more relevant electronic properties and redox potentials of the ligands, we needed to synthesize an air-stable complex with a redox inactive metal of a suitable size. Preliminary studies showed that mono-ligand metal complexes with our ligands are not very robust or air stable making them difficult to study. However, two carbazole-bis(azole) ligands fit around first row transition metals (see Chapter 4) forming air-stable metal complexes that do not oxidize or degrade in air over an extended period of time. With this knowledge, we synthesized the

bis-ligand Zn complexes of our ligands to use as an air-stable, metal-redox-inactive electronic model to study how the ligands behave in a metal complex. Zn is a group 12 metal most stable in the Zn(II) oxidation state due to its d^{10} electron count. Because of this Zn is not able to adopt a Zn(I) or Zn(III) state and is “redox inactive” within the redox window of interest^{15, 113-114}. Thus the redox activity of a Zn complex is solely due to oxidation or reduction of the CzT or CzTr ligands themselves.

2.4.1 Synthesis and Characterization of Zinc Carbazole-bis(azole) Complexes

Synthesis of the Zn complexes was conducted in the glovebox under an inert atmosphere, although this may not be necessary. Using a general salt metathesis method, two equivalents of deprotonated ligand were reacted with ZnCl_2 to produce fluorescent yellow-green powders as the crude products (**Scheme 2.5**).



Scheme 2.5 Synthesis of $(\text{CzT}^{\text{iPr}})_2\text{Zn}$ (**9**) and $(\text{CzTr}^{\text{iPr}})_2\text{Zn}$ (**10**)

The fluorescent yellow-green solids (CzT^{iPr})₂Zn (**9**) and (CzTr^{iPr})₂Zn (**10**) are air stable and diamagnetic. The ¹H and ¹³C NMR spectra of **9** and **10** are extremely simple showing only one set of unique ligand resonances (**Figure 2.9**). This suggests high symmetry complexes and the lack of a carbazole NH resonance around 12 ppm confirms complexation to the metal.

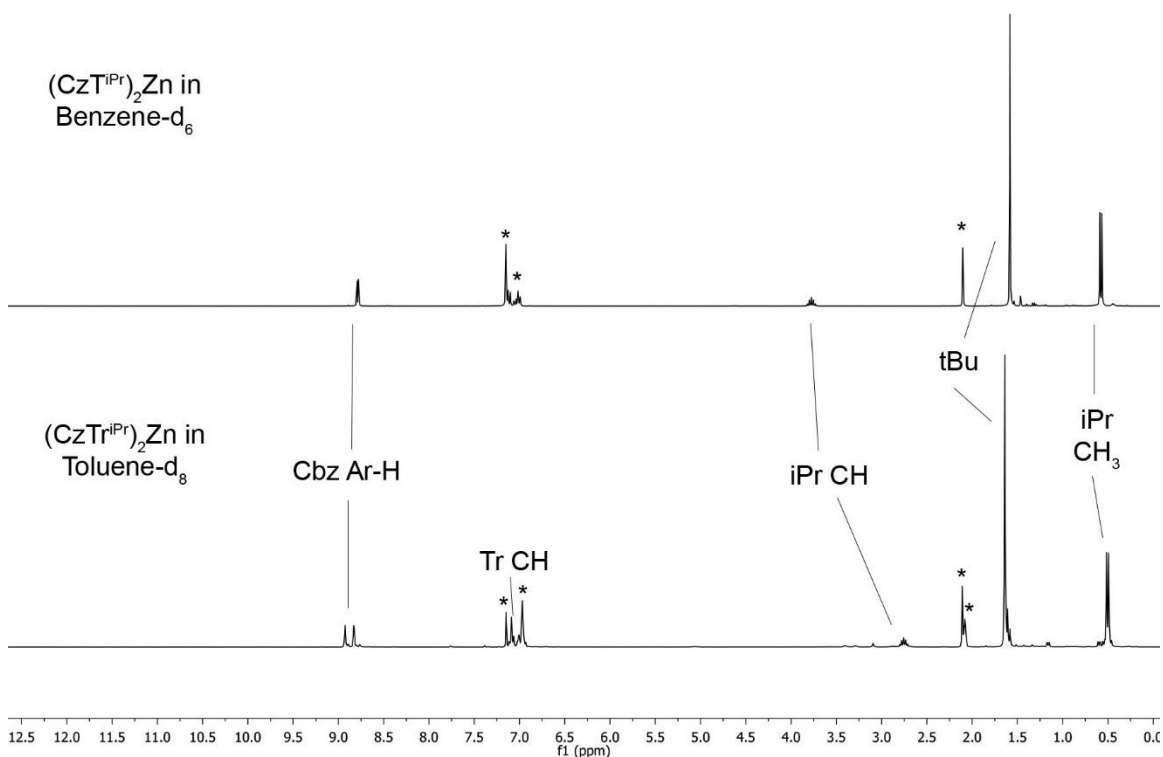


Figure 2.9 Stack plot of bis-carbazole(azole) Zn complexes ¹H NMR spectra (300 MHz, C₆D₆/toluene-D₈, 298 K) (* denotes NMR solvent as well as residual toluene)

2.4.2 Cyclic Voltammetry

The cyclic voltammogram of **9** done at room temperature in dry THF with [nBu₄N⁺PF₆⁻] as supporting electrolyte at a scan rate of 100 mV/s is shown in **Figure 2.10**. The

edge of the spectrum has been adjusted to crop out the solvent window which cuts off at about 1.0 V.

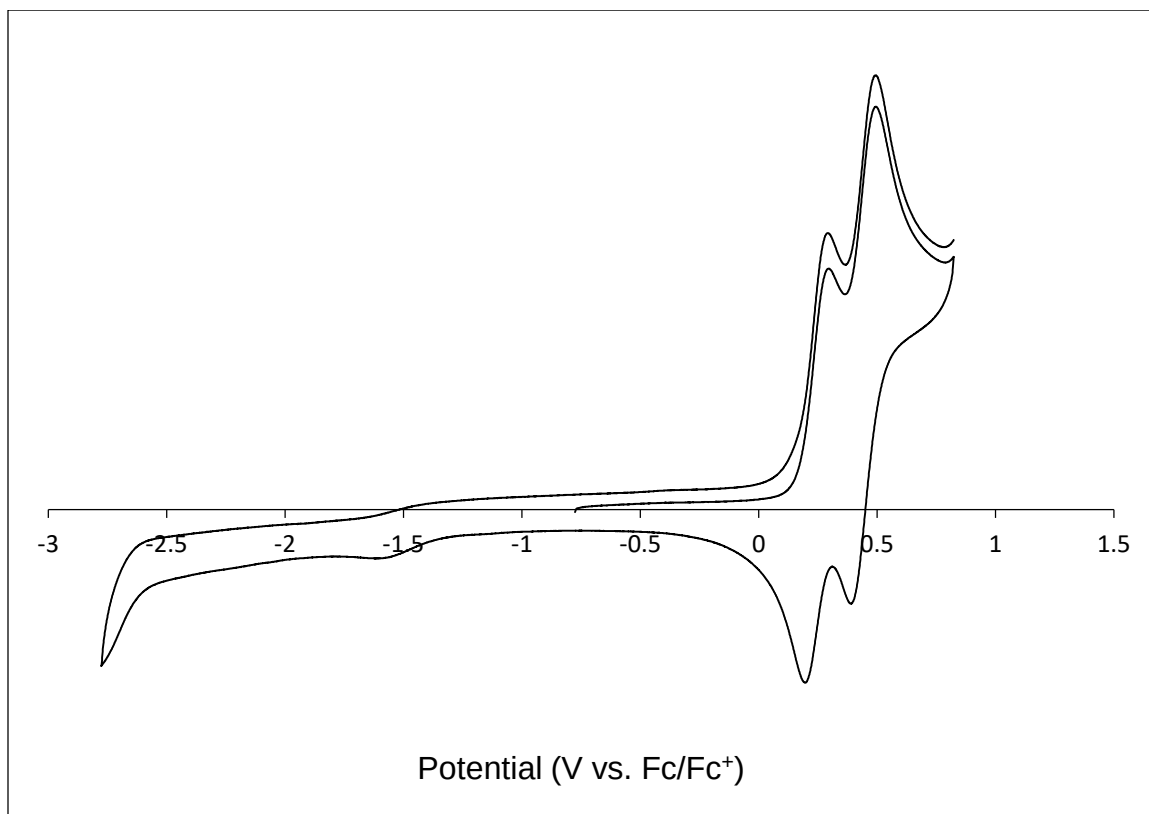


Figure 2.10 Cyclic voltammogram of $(\text{CzT}^{\text{iPr}})_2\text{Zn}$ (**9**) vs. Fc/Fc^+ in THF with $[\text{nBu}_4\text{N}^+ \text{PF}_6^-]$ as supporting electrolyte. Scan rate is 100 mV/s.

The CV confirms oxidation of the ligand as previously shown in the CV of the protonated ligand, but the peaks appear at a less positive potential and they are now reversible. The pattern of two reversible peaks at close potentials is consistent with oxidation of the two ligands in **9** in stepwise fashion. The CV also shows that while the ligand is fairly easy to oxidize, it does not undergo reduction to -2.75 V vs. Fc/Fc^+ . It is likely that the site of the oxidation is carbazole-based rather than tetrazole-based to form a carbazole-based radical cation. Similar $\text{Co}(\text{III})$ complexes ($[\text{Co}^{\text{III}}(\text{L})_2]\text{BF}_4$) with carbazole-

based pincer ligands ($\text{HL}^{\text{R/R}}$: 3,6-di(tert-butyl)-1,8-bis[5-(3-benzyl-1,2,3-triazole)]-9H-carbazole, R = H or tBu) show very similar reversible oxidation peaks¹¹⁵. Brooker and co-workers similarly assigned these oxidations to the carbazole with one reversible peak from each ligand. The CV of **9** was taken in a variety of solvents to open the oxidation side of the window wider. Interestingly when the CV is done in ACN, a new reversible peak at a higher oxidation potential is seen (**Figure 2.11**).

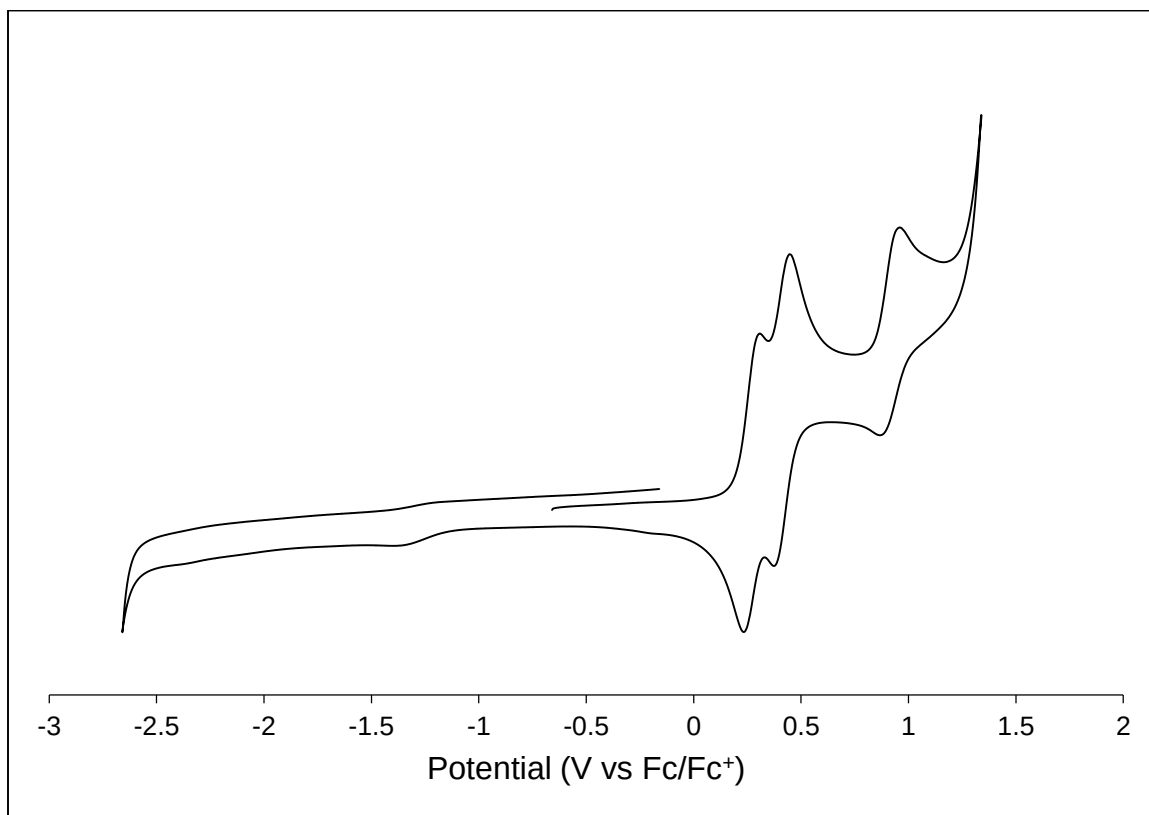


Figure 2.11 Cyclic voltammogram of $(\text{CzT}^{\text{iPr}})_2\text{Zn}$ (**9**) vs. Fc/Fc^+ in ACN with $[\text{nBu}_4\text{N}^+ \text{PF}_6^-]$ as supporting electrolyte. Scan rate is 100 mV/s.

The appearance of an additional reversible oxidation wave is a bit puzzling. It is reasonable to assume the first two redox waves represent oxidation of each ligand, but a third wave is less easily assigned. It is possible that one of the ligands has been oxidized a

second time but we are unsure if this oxidation occurs at the carbazole backbone or at one of the tetrazole rings. A similar third redox couple (besides the two carbazole-based redox couples) is also seen in the CV of **10** run in ACN as seen in **Figure 2.12**.

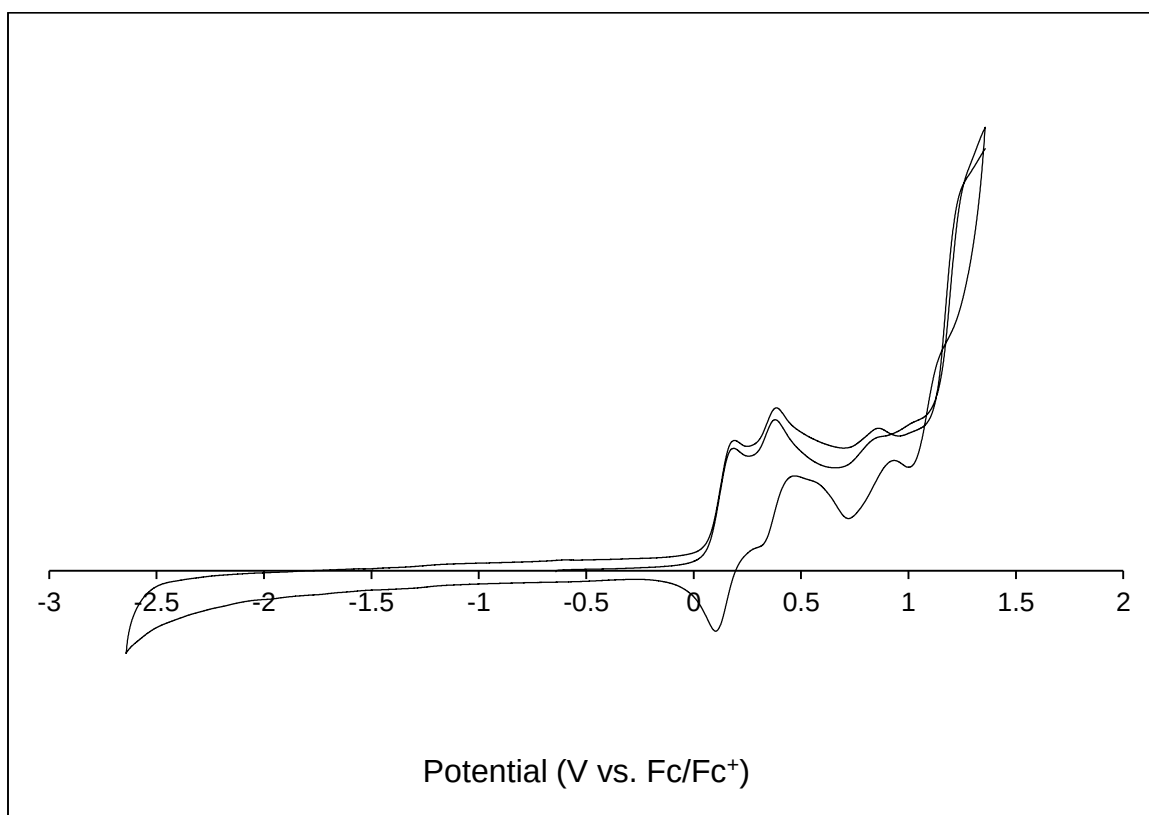


Figure 2.12 Cyclic voltammogram of (CzTr^{iPr})₂Zn (**10**) vs. Fc/Fc⁺ in ACN with [nBu₄N⁺ PF₆⁻] as supporting electrolyte. Scan rate is 100 mV/s.

Both CVs of the tetrazole and triazole bis-ligand Zn complexes run in ACN are almost identical; both show the two overlapping reversible waves assigned as the oxidation of the carbazole moiety of each ligand in the complex and both show a third reversible redox event at a higher potential. The same trend of lower oxidation potentials in the triazole ligand versus the tetrazole ligand is retained in the Zn complexes (**Table 2.1**), as was observed for the free ligands although not quite to the same degree. In the Zn

complexes, the oxidation potential is only slightly lower for the triazole vs. the tetrazole ligand (**Table 2.1**) whereas in the protonated ligands the difference was more profound. While the assignment of the third redox couple in both **9** and **10** is unclear, what we can say definitively is that the carbazole backbone of both the triazole and tetrazole ligands reversibly oxidizes at low potential and neither is easily reduced.

Table 2.1 Electrochemical data of Zn complexes in ACN (V vs. Fc/Fc⁺)

	E_{a1} (E_{c1})/V	E_{a2} (E_{c2})/V	E_{a3} (E_{c3})/V
9	0.34 (0.24)	0.46 (0.30)	0.98 (0.89)
10	0.17 (0.11)	0.41 (0.32)	0.90 (0.73)

2.4.3 Fluorescence

While characterizing the Zn complexes it was noticed that they are fluorescent in both the solid and solution state. In the solid state and in solution they fluoresce yellow-green in visible light but blue under UV light. The UV-Vis of **9** was recorded in spectrophotometric grade dried ACN to determine the wavelengths of the allowed transitions of the complex. The resulting spectrum shows two main absorbance peaks at 313 and 337 nm. Using this data, the emission spectra were recorded while exciting at these different wavelengths in order to determine the energy of emission. The emission spectra were run in the same ACN solution exciting at 313 and 337 nm; both show similar resulting peaks at 380, 442 and 755 nm. The main two peaks in the emission spectra at 380 and 442 nm correlate well with the emitted blue colour seen of the solution under UV light. The plot of the UV-Vis absorption spectrum as well as the emission spectrum exciting at 337 nm are shown in **Figure 2.13**. The excitation spectrum was also run using a sufficiently long emission wavelength of 755 nm and the resulting spectrum is similar to the absorption

spectrum displaying three main peaks at 268, 309 and 369 nm. While not completely consistent, these peaks show the same pattern seen in the UV-Vis spectrum which illustrates absorption peaks at slightly higher wavelengths of 313, 337 and 442 nm.

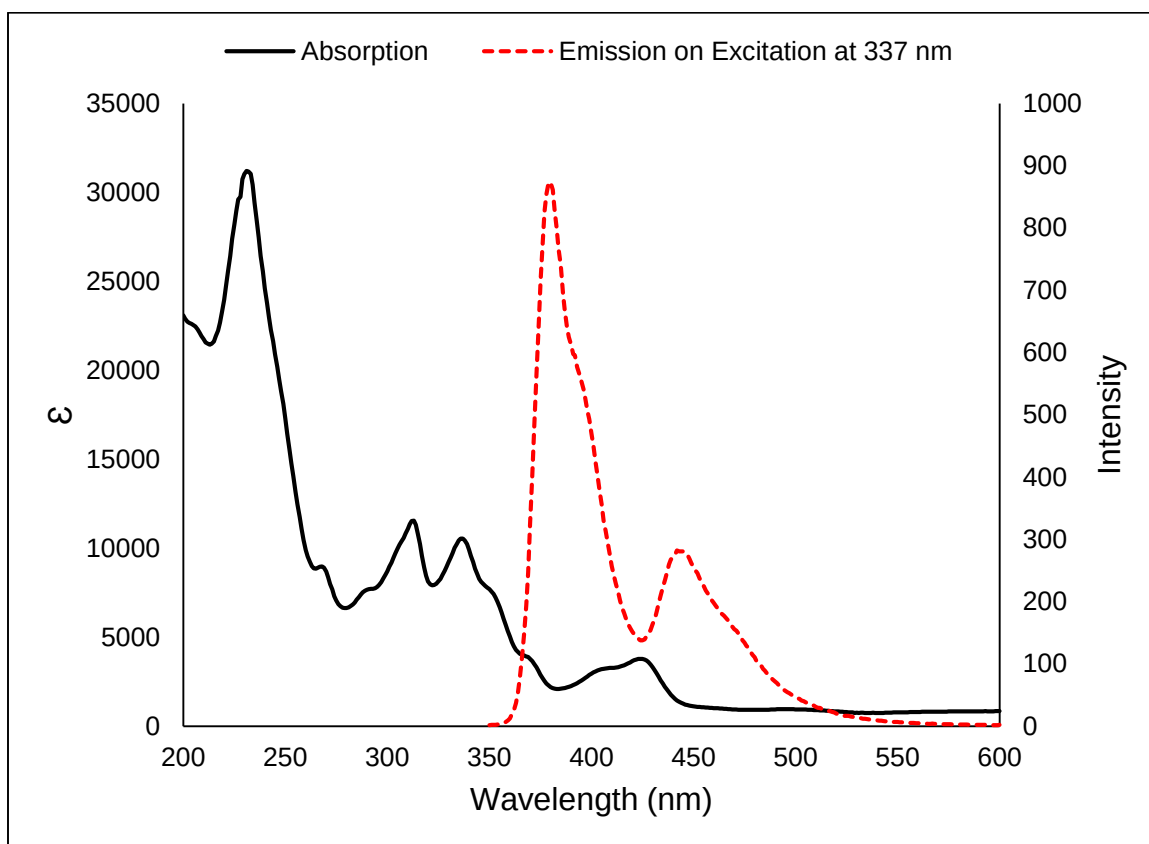


Figure 2.13 UV-Vis absorption and emission spectra of $(\text{CzT}^{\text{iPr}})_2\text{Zn}$ (**9**) ($9.41 \cdot 10^{-5}$ M in ACN)

The overlaid spectra (**Figure 2.13**) should mirror each other based on the “Mirror Image Rule” and show both the excitation and emission processes that are occurring. While the intensities are not equal, the approximate “mirror image” is intact and two different Stokes shifts can be measured¹¹⁶. The Stokes shift arises from the difference in energy between the absorbed and emitted photon. Since some energy of the excited photon is

rapidly lost as non-radiative decay (vibrational relaxation, most likely as heat that is absorbed by neighbouring solvent molecules), the emitted photon will be of a lower energy (longer wavelength) than the excited photon. The difference in energy is a quantifiable measure known as the Stokes shift and is derived from the difference between the emission and excitation wavelength. The two Stokes shifts can be measured as 43 nm and 129 nm. The pattern of both two absorption peaks as well as two emission peaks is likely due to two different transitions. The first higher energy transition with a larger Stokes shift (313 nm excitation and 442 nm emission) may be due to a S_0 to S_2 transition, while the lower energy smaller Stokes shift transition at 337 nm excitation and 380 nm emission is most likely due to an S_0 to S_1 transition. No lifetime or quantum yield experiments were conducted on **9** since the main focus of this complex was not as a fluorophore, but these fluorescence experiments do prove that the solution of **9** is fluorescent, with emissions in the blue range of 380-442 nm.

Similar fluorescence experiments were conducted on the isostructural **10** that also exhibited fluorescence to the naked eye. The UV-Vis spectrum run in ACN is shown in **Figure 2.14** and unsurprisingly confirms very similar absorption peaks at 315, 334 and 420 nm. Similar to **9**, emission spectra were run exciting at 315, 334 and 420 nm, and similar emission peaks were seen in both the 315 nm and 334 nm excitation case, with peaks at 381 nm and 480 nm. The excitation spectrum run at an emission wavelength of 761 nm displayed three peaks at 266, 303 and 368 nm. This again gives two Stokes shifts of 47 nm and 165 nm similar to that seen in the tetrazole case **9**. The fact that both show extremely similar fluorescence properties suggests that the main source of the fluorescence is from the carbazole rather than the azole arms. This result is not surprising based on a literature

search that indicates several carbazole-based complexes and ligands investigated as possible OLED candidates due to their high fluorescence intensity¹¹⁷⁻¹²¹. Several of these carbazole molecules display similar low wavelength absorption spectra and emission spectra in the blue region consistent with our data. This strongly suggests that the fluorescence seen in **9** and **10** is likely carbazole-based and not a unique feature of the complexes themselves. This fluorescence is not seen with the protonated free ligands, but we do note similar fluorescence in the $K^+[CzTr^R]^-$ and $K^+[CzTr^R]^-$ salts that suggests that the deprotonated ligand is responsible for the fluorescence.

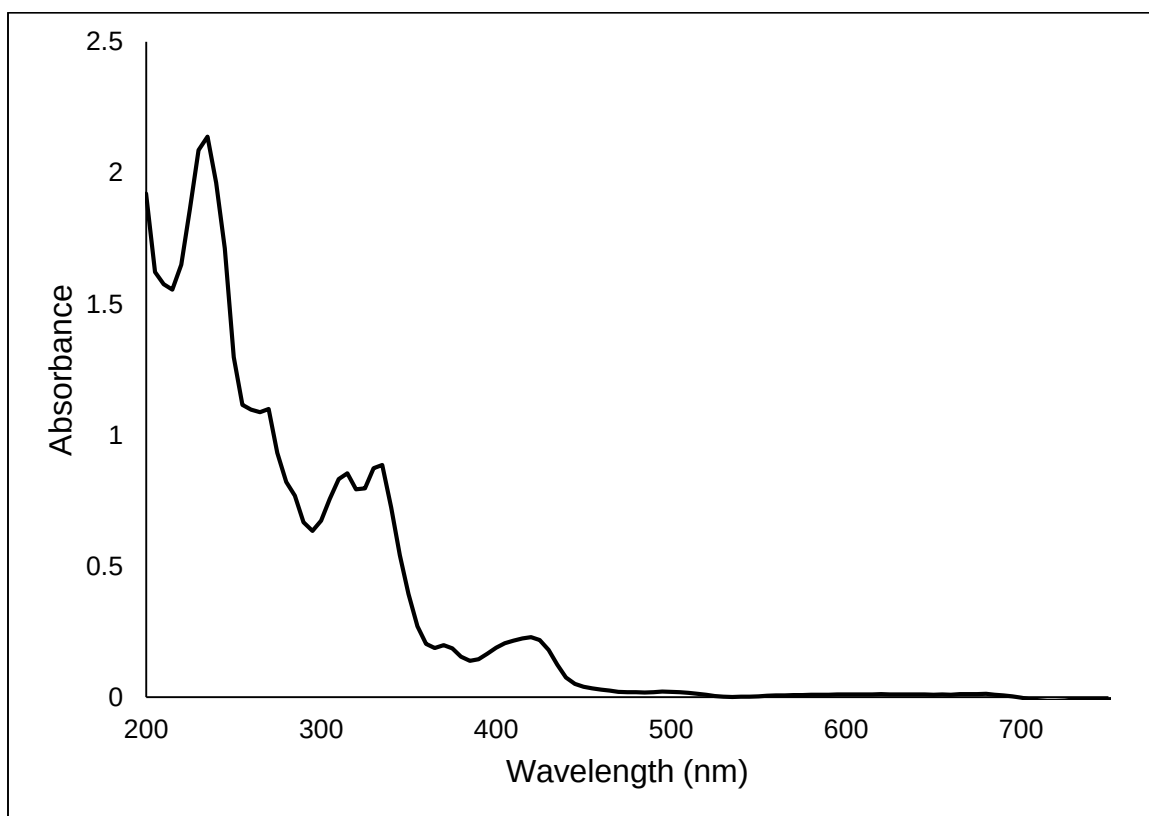


Figure 2.14 UV-Vis absorption spectrum of (CzTr^{iPr})₂Zn (**10**) ($2.27 \cdot 10^{-5}$ M in ACN)

2.5 DDQ Complexes

With the knowledge that our ligands are redox active and seemingly easy to oxidize at a modest potential, attempts were made to synthesize an intact complex with an oxidized ligand in order to better study the oxidation properties of the ligand and how resonance may affect the location of oxidation. Oxidation of the protonated ligand itself will presumably give an unstable product as one electron oxidation would form a carbazole-based radical cation that can eject a proton to become neutral. This is reinforced by the irreversibility of the oxidation peak as seen in the CV discussed earlier. The bis-ligand zinc complexes conversely show reversible oxidation waves, probably because the increased rigidity and metal complexation increases the stability of the oxidized ligand. One difference in using the bis-ligand Zn complexes is that both ligands oxidize as shown by two oxidation peaks at very similar potentials. For this reason, mild oxidants were used in attempts to avoid “over oxidation” of the complexes.

DDQ, chloranil (**Figure 2.15**) and several available Ag salts were tested as oxidizing agents since all of them have oxidation potentials below 0.4 V vs Fc/Fc⁺ (depending on solvent conditions)¹²² and are easy to handle. In most cases, a distinct colour change occurred upon reaction of **9** with the oxidizing agent along with changes in the appearance of the ¹H NMR spectrum. Unfortunately, most of the products gave complicated NMR spectra and proved difficult to purify by crystallization making characterization difficult. However, the reaction of DDQ with **9** did yield pure product after recrystallization from warm toluene to give a blue solid. Surprisingly, the ¹H NMR spectrum of this product showed unequivocally the presence of protonated ligand resonances that directly matched **8b**. The most likely cause of this is that the DDQ was wet

causing hydrolysis of the ligand and de-complexation from Zn; however, the deep blue colour of this product is inconsistent with colourless free ligand **8b**.

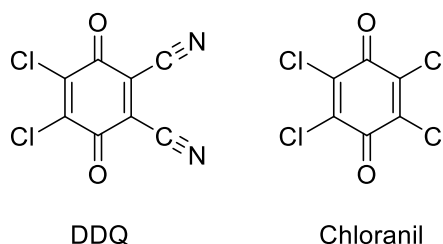


Figure 2.15 Structure of DDQ and chloranil

One possibility to explain the colour of this product is the formation of a charge transfer complex between DDQ and the protonated ligand **8b**. There is literature precedence for the formation of π -stacked charge transfer complexes between various quinones and aromatic donors¹²³. To test this theory, DDQ was reacted with simple protonated parent ligand **8b** in THF; the colour of the solution immediately changed from yellow to dark blue upon mixing of the two solutions suggesting that indeed a charge transfer complex had formed. Again the resulting ¹H NMR spectrum showed a simple set of protonated ligand resonances, but the solution remained an intense blue colour. The proposed charge transfer complex is composed of a 1:1 ratio of ligand to DDQ where the ligand carbazole is the electron donor and the DDQ the electron acceptor giving rise to an intensely coloured complex. A sample of ligands were tested as electron donors with both DDQ and chloranil used as electron acceptors; all give deep coloured solutions varying from green to purple in solution (**Table 2.2**).

Table 2.2 Ligand charge transfer complex colours

	DDQ	Chloranil
HCzT^{Me} (8a)	Dark Green	Blue
HCzT^{iPr} (8b)	Blue	Dark Green
HCzTr^{iPr} (7b)	Blue	Green
HCzT^{Bz} (8c)	Dark Green	Green
HCzT^{CH₂Mes} (8d)	Green-Teal	Dark Brown-Red
HCzTr^{CH₂Mes} (7d)	Dark Red-Purple	Dark Purple-Black

In the case of chloranil and **7d**, poor quality X-ray crystals were grown. While the data obtained was of low quality, refinement was sufficient to establish the basic connectivity of the charge transfer complex. The asymmetric unit is comprised of one ligand and one chloranil molecule (**Figure 2.16**) both sitting in close contact coplanar to each other, so most likely π -stacking interactions are contributing to the structure. When the structure is grown to see the full unit cell the π -stacking continues in a 1:1 ratio of ligand to chloranil in a continuous stack. The chloranil molecules seem centred on the carbazole rather than the triazole arms, possibly due to steric crowding of the bulky “CH₂Mes” substituents which both sit twisted inwards. The stack plot of a small section of the unit cell is shown in **Figure 2.17** to show the π -stacking pattern.

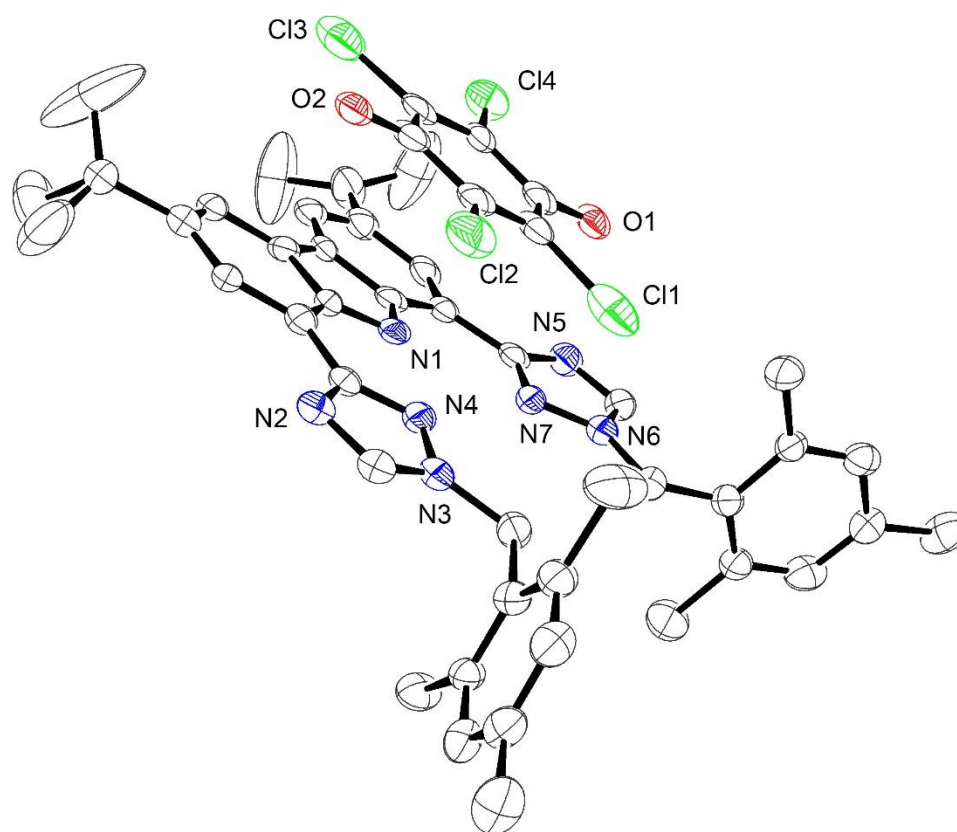


Figure 2.16 ORTEP3¹⁰⁸ plot (25% probability ellipsoids) of chloranil HCzTr^{CH2Mes} (**7d**) charge transfer complex (H atoms omitted for clarity)

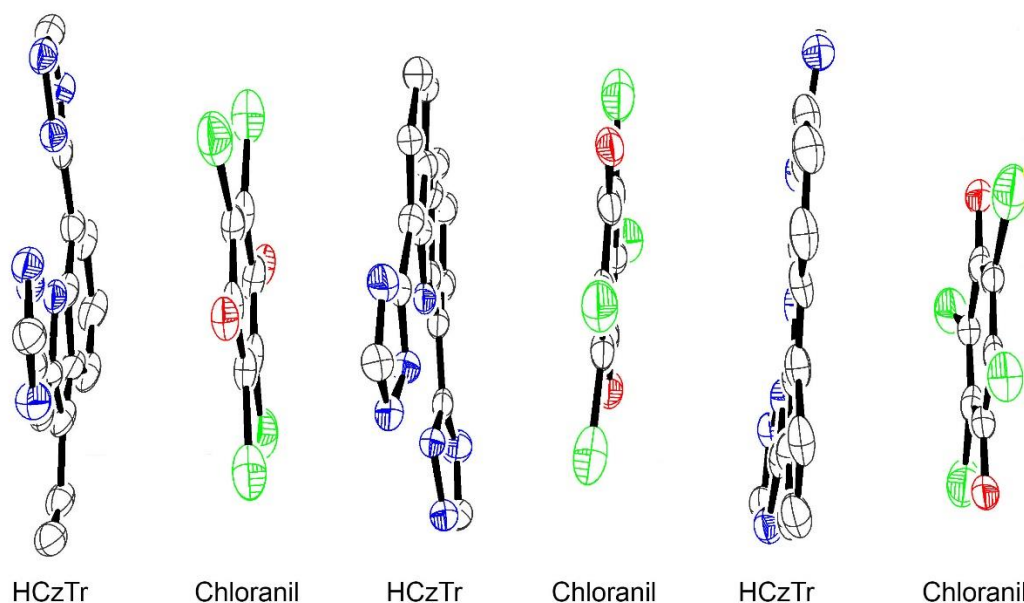
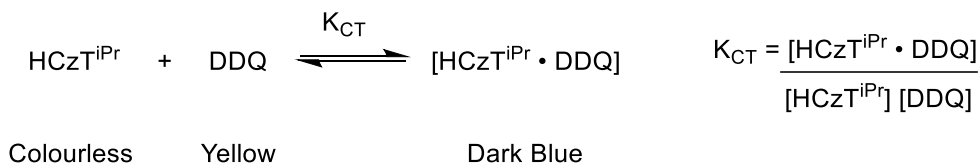


Figure 2.17 ORTEP3¹⁰⁸ plot (25% probability ellipsoids) of chloranil HCzTr^{CH₂Mes} (**7d**) charge transfer complex stack (H atoms, tBu and CH₂Mes groups omitted for clarity)

In solution the behaviour is slightly different: it was noticed that in THF, benzene, toluene, or DCM the charge transfer complexes are thermochromic. For **8b** and DDQ at room temperature (depending on the concentration) the solution is green but on cooling it becomes dark blue and on heating it turns yellow. In the solid state the product is dark blue as it is at low temperature, suggesting that a π -stacked charge transfer dimer is intact at low temperature. The fading of the colour from blue to yellow upon heating is due to the charge transfer complex breaking up in solution (**Scheme 2.6**). This process is presumably entropy driven. In very concentrated samples the solution remains dark blue and shows little evidence for thermochromism when heated while in dilute solutions the colour remains pale green even at low temperatures, consistent with the equilibrium in **Scheme 2.6**.



Scheme 2.6 Charge transfer equilibrium equation

Similar thermochromism was seen in a case with “molecular tweezers” where DDQ was also used¹²⁴ (**Figure 2.18**). Iyoda *et al.* found that their extended fused aromatic ring system formed similar charge transfer complexes with DDQ facilitated by π -stacking and were thermochromic in solution ranging from yellow to blue at high and low temperatures, respectively. In experiments using all eight ligand variations for both DDQ and chloranil there is no redox chemistry seen. While the main goal of the quinone reactivity was to attempt to oxidize the ligand, the resulting charge transfer complexes are interesting and the ability of the ligand π system to engage in fairly strong π -stacking and charge transfer interactions could play a role in how our ligands interact with aromatic rings systems in complexes.

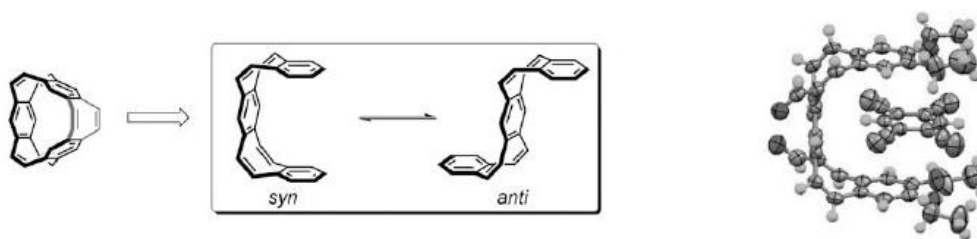


Figure 2.18 Example of “molecular tweezers” π -stacked charge transfer complex with DDQ (reprinted with permission from ¹²⁴)

2.6 Summary

Two new ligand scaffolds were successfully synthesized in good yields using carbazole as the backbone and either triazole (**7**) or tetrazole (**8**) rings to complete the pincer framework. From these two templates, eight new ligands with substituents varying in size from methyl (**7a** and **8a**), isopropyl (**7b** and **8b**), benzyl (**7c** and **8c**), and methyl mesityl (**7d** and **8d**), were synthesized and fully characterized. The physical and electronic properties of these ligands were also investigated. The ligands themselves were shown to be redox active and undergo oxidation at modest potentials with the oxidation centred on the carbazole moiety. The oxidation is irreversible for the protonated ligand, but shifts to lower potentials and becomes reversible in metal complexes of redox-inactive metals such as the Zn complexes, **9** and **10**. In addition, the bis-ligand Zn complexes are fluorescent emitting in the blue region in solution. Finally, the unexpected complexes formed between these ligands and quinones, such as DDQ and chloranil, demonstrate the ability of the ligands to π -stack and form highly coloured charge transfer complexes. With the target ligands in hand, the synthesis, characterization and study of reactivity of both lanthanide (Chapter 3) and transition metal complexes (Chapter 4 and 5) was pursued.

Chapter 3 Lanthanide Complexes and Reactivity

3.1 Introduction

Lanthanide complexes with organic ligands have only somewhat recently been studied and developed (1980s) considering the first lanthanide, cerium, was discovered in the 1750s. This is most likely due to not only the difficulty in separating the lanthanides from one another, but also the extreme air and moisture sensitivity of their organometallic complexes that make them difficult to study and handle¹⁴. Although somewhat challenging to study, organolanthanide complexes have shown to be very reactive in catalytic transformations³⁷ due to their large ionic size and Lewis acidity. The difficulty lies in synthesizing a lanthanide complex that is both reactive and robust; often times ligands that are large enough to stabilize the lanthanide centres are so large that they impede the catalytic activity. Historically, organolanthanide complexes predominantly used Cp and Cp* as ancillary ligands²⁸⁻³¹ due to their size, negative charge and the fact that they do not rely on π -back bonding from the metal to form stable bonds. Cp* is bulky enough to stabilize the larger lanthanides and prevent unwanted bridging interactions. Evans has shown some very interesting reactivity by sterically *over-saturating* the metal centre in his (Cp*)₃Ln complexes such as ring opening of THF¹²⁵ and ethylene polymerization¹²⁶, but many Cp and Cp* lanthanide complexes show limited reactivity due to steric crowding around the lanthanide centre³². For this reason, the use of Cp-free ligands in lanthanide catalysts has attracted growing attention³⁶. Extensive studies by lanthanide-focused research groups such as Lappert⁴¹, Edelmann and Schumann³⁶, Evans³¹, Andersen¹²⁷⁻¹²⁸

and others¹²⁹ have been conducted that tune the lanthanide properties by changing both the steric and electronic profile of the organic ligands used.

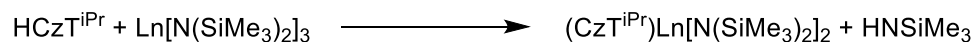
Our ligand **8b** was originally designed for use in lanthanide complexes, as discussed in Chapter 2 of this work. The multidentate structure of this ligand should aid in stabilization of lanthanide complexes and prevent bridging interactions. The use of both neutral and anionic nitrogens as the donor atoms are ideal to bind to the hard, ionic, Lewis acidic lanthanide centre, and the monoanionic charge means that a trivalent lanthanide complex can retain two additional reactive anionic ligands such as alkyls or amides. This design should promote metal-centred substrate binding and insertion into one of the remaining alkyl or amide ligands. This chapter will explore the use of the **8b** ligand in coordination complexes with the lanthanides, and their resulting reactivity.

3.2 Mono-ligand Complexes

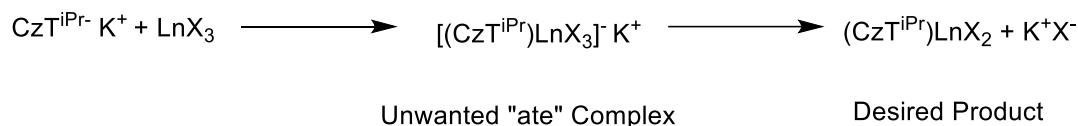
3.2.1 Synthesis Through Protonolysis

The simplest route to prepare lanthanide complexes of **8b** is through an acid-base reaction between the protonated ligand, HCzT^{iPr} , and the lanthanide precursor, $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ (**Scheme 3.1**)³⁷. This reaction is preferred due to the fact that the by-product is the volatile silylamine $\text{HN}(\text{SiMe}_3)_2$ that can be removed under reduced pressure and there is no risk of making the unwanted lanthanide “ate” complex, often observed in salt metathesis reactions (**Scheme 3.1**).

1. Protonolysis



2. Salt Metathesis

**Scheme 3.1** Synthesis of lanthanide complexes

The desired mono-ligand products $(\text{CzTi}^{\text{iPr}})\text{Ln}[\text{N}(\text{SiMe}_3)_2]_2$ ($\text{Ln} = \text{Yb}$ (**11**) or Er (**12**)) were successfully prepared for the smaller lanthanides, Yb and Er, using the protonolysis route. In contrast, the larger lanthanides, Sm and Ce, produced multi-ligand products; these results are discussed later in this Chapter (Section 3.3). Previously in our group, we were unable to synthesize any $(\text{Czx})\text{Ln}[\text{N}(\text{SiMe}_3)_2]_2$ complexes with the more sterically crowded ligand, **1**, even with prolonged heating⁶³. This suggests that **8b** is indeed less sterically crowding around the metal centre than **1** as we had hoped. These complexes (**11** and **12**) can be recrystallized from warm toluene to give pure product as yellow crystals for both the Yb (**11**) and Er (**12**) complexes. The simple ^1H NMR spectra of these paramagnetic complexes (**Figure 3.1**) suggested that they were monomeric with at least C_{2v} symmetry; this was confirmed by X-ray studies as will be discussed in Section 3.2.2. The main distinguishing feature in the NMR spectra that confirms the complexation of only one **8b** ligand is the integration of the silylamide (36 H) relative to one set of ligand

resonances in both cases. This, along with one paramagnetically shifted set of CzT^{iPr} ligand resonances, confirms the formula of $(\text{CzT}^{\text{iPr}})\text{Ln}[\text{N}(\text{SiMe}_3)_2]$ for both Yb (**11**) and Er (**12**).

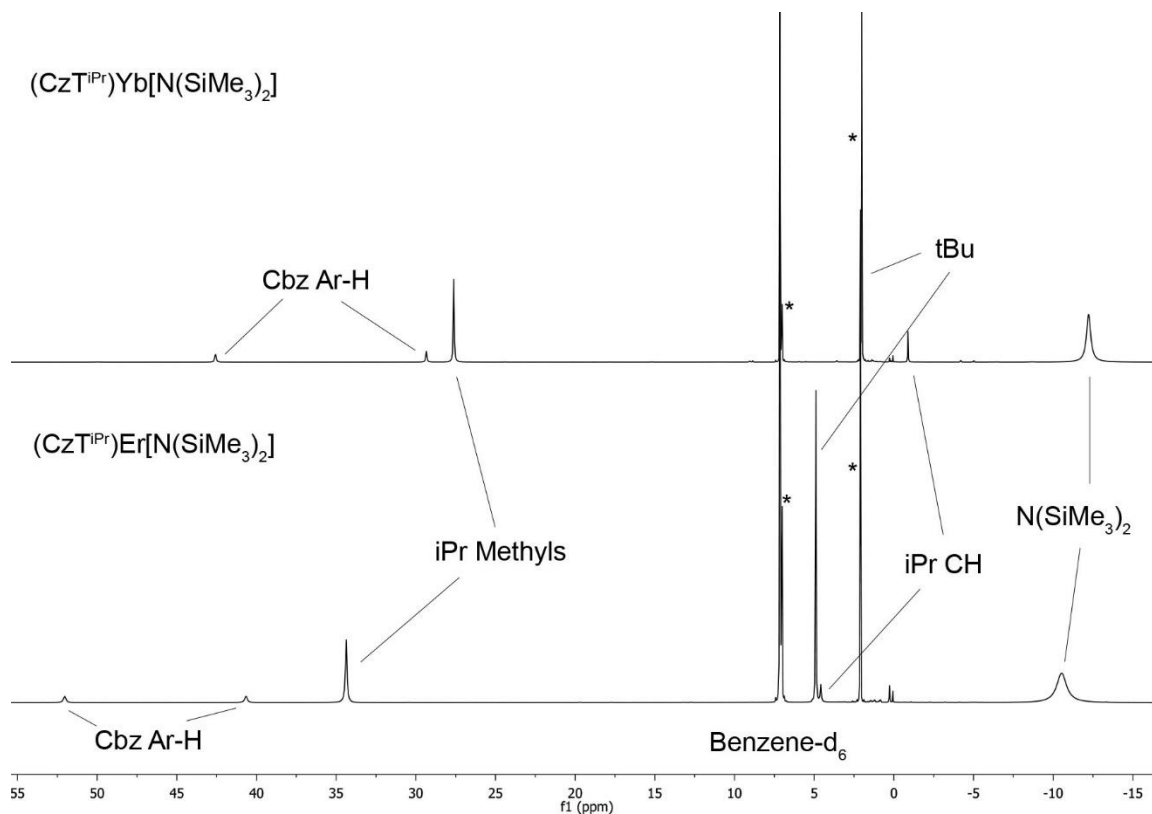
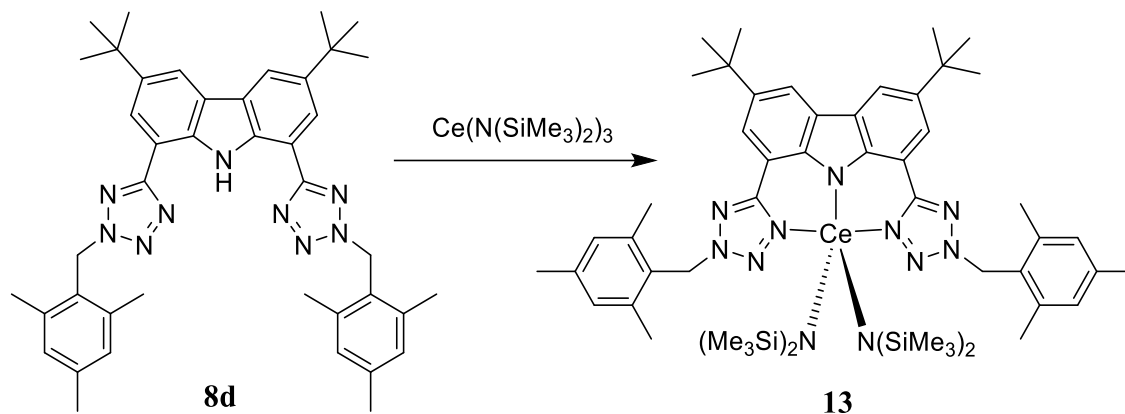


Figure 3.1 ^1H NMR spectra of $(\text{CzT}^{\text{iPr}})\text{Yb}[\text{N}(\text{SiMe}_3)_2]$ (**11**) and $(\text{CzT}^{\text{iPr}})\text{Er}[\text{N}(\text{SiMe}_3)_2]$ (**12**) (300 MHz, C_6D_6 , 298 K) (* denotes residual toluene)

In attempts to stop complexation of a second ligand onto the larger lanthanides, the use of a larger substituent than iPr on the tetrazole rings was employed; this led to the development of the **8d** ligand as discussed in Chapter 2 of this work. A similar protonolysis route with the larger **8d** ligand was employed with Ce (**Scheme 3.2**) to see if the larger substituents would shut down complexation of a second ligand and form the mono-ligand bis-silylamide complex.



Scheme 3.2 Synthesis of $(\text{CzT}^{\text{CH}_2\text{Mes}})\text{Ce}[\text{N}(\text{SiMe}_3)_2]$ (**13**)

The ^1H NMR spectrum of **13** confirmed the formation of a mono-ligand Ce bis-silylamide complex rather than the bis-ligand mono-silylamide Ce complex (Section 3.3). The spectrum of **13** is symmetrical (**Figure 3.2**) with only eight resonances consistent with C_{2v} symmetry. The broad silylamide peak seen at -1.23 ppm integrates to 36 H providing good evidence that only one **8d** ligand is bound with two silylamide groups remaining on the Ce. The additional bulk of the methyl mesityl moiety compared to the *i*Pr on the tetrazole ring is enough to make it too crowded to fit two ligands, even on the larger lanthanide centre.

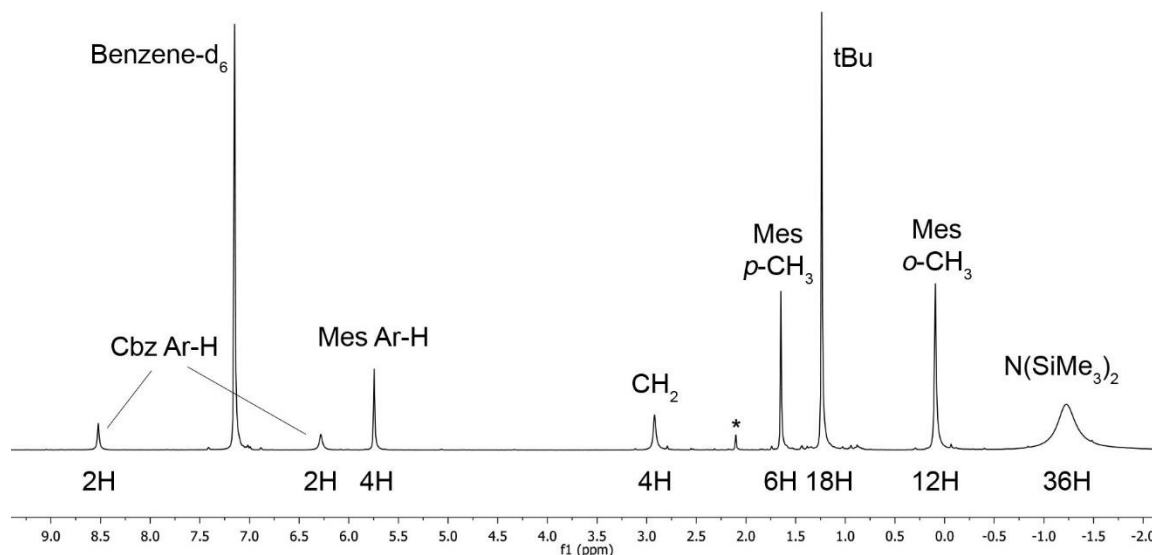
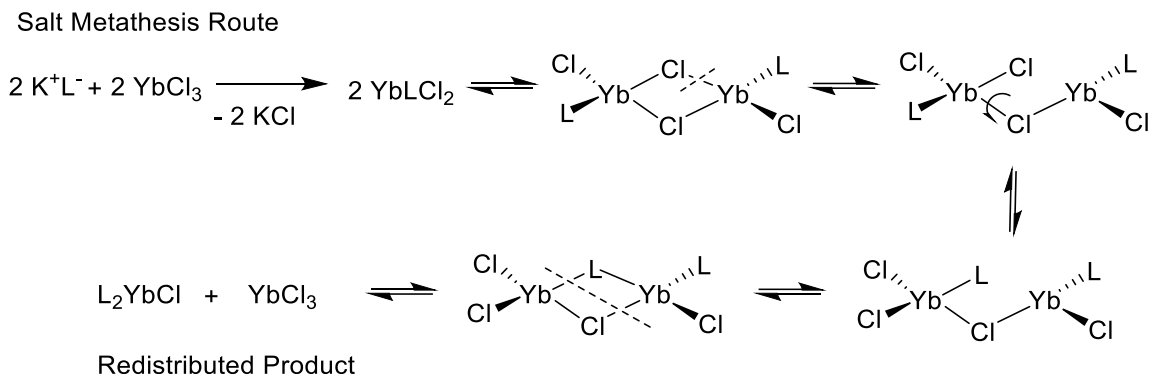


Figure 3.2 ^1H NMR spectrum of $(\text{CzT}^{\text{CH}_2\text{Mes}})\text{Ce}[\text{N}(\text{SiMe}_3)_2]$ (**13**) (300 MHz, C_6D_6 , 298 K) (* denotes residual toluene)

3.2.2 Synthesis Through Salt Metathesis

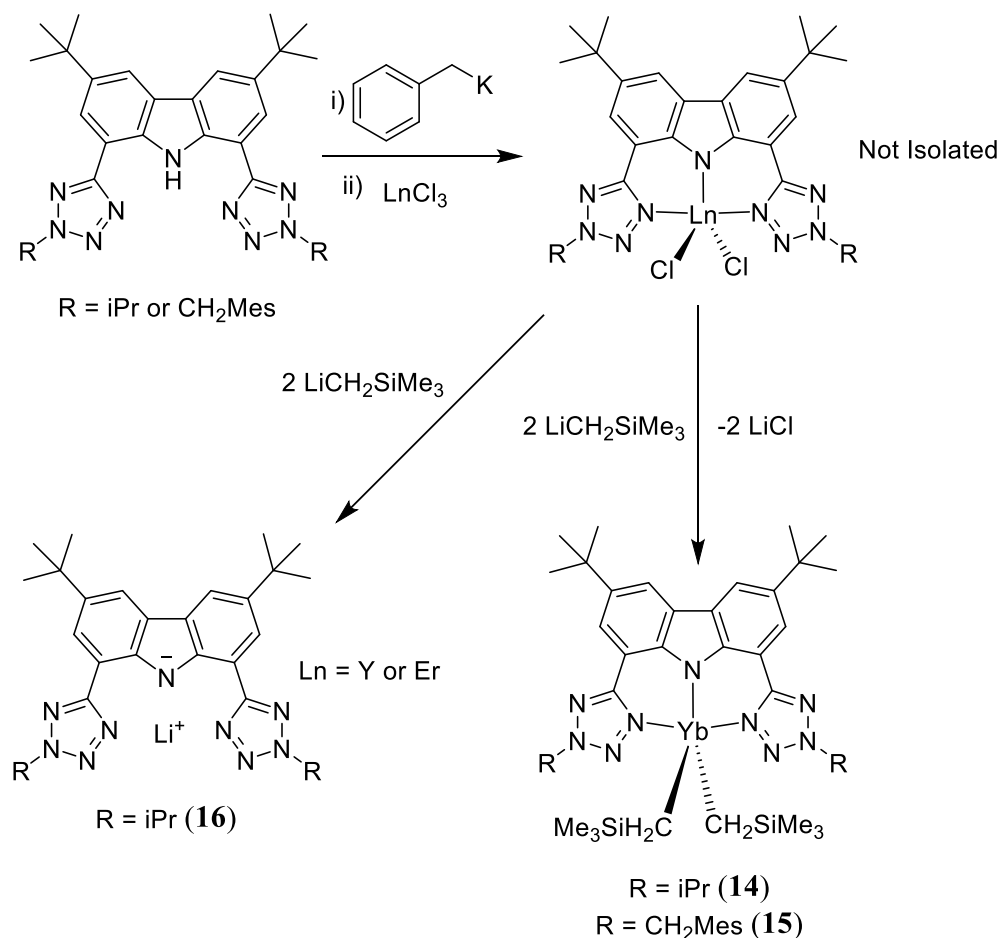
Another common route to synthesizing metal complexes is through salt metathesis³⁷. This technique poses a few problems for lanthanide complexes; mainly the possibility of forming the undesired “ate” complex where a fourth ligand is bound and the complex is ionic (**Scheme 3.1**). This is more common with lanthanides than transition metals as the coordination sphere is much larger and the metal needs more ligands in order to reach electronic and coordinative saturation. Salt metathesis can also facilitate ligand redistribution through bridging groups (**Scheme 3.3**). The possibility of these reactions occurring complicates the synthesis and can lead to product mixtures. However, since there are few Ln starting materials with ligands other than halogens that can be purchased or made, salt metathesis is often a necessary step in order to synthesize lanthanide complexes with substituents that are otherwise unavailable.



Scheme 3.3 Generic ligand redistribution of an Yb complex facilitated through bridging chlorides

Salt metathesis is a necessary route in order to synthesize a direct analogue of $(\text{Czx})\text{Yb}(\text{CH}_2\text{SiMe}_3)_2$ ⁶³ using our new ligands. The three step synthetic sequence to give $(\text{CzT}^{\text{iPr}})\text{Yb}(\text{CH}_2\text{SiMe}_3)_2$ (**14**) and $(\text{CzT}^{\text{CH}_2\text{Mes}})\text{Yb}(\text{CH}_2\text{SiMe}_3)_2$ (**15**) is shown in **Scheme 3.4**. The ^1H NMR spectra of both **14** and **15** are simple and suggest C_{2v} symmetry with one unique set of ligand resonances in each case, along with the lanthanide alkyl CH_3 resonance around -30 ppm and the diagnostic CH_2 resonance extremely shifted to around -240 ppm. These spectra match well with the ^1H NMR spectrum of $(\text{Czx})\text{Yb}(\text{CH}_2\text{SiMe}_3)_2$ further suggesting the desired products were successfully synthesized. In the case of the slightly larger lanthanides Y and Er (ionic radius for six-coordinate $\text{Ln}(\text{III})$: 0.90 Å for Y, 0.89 Å for Er and 0.87 Å for Yb)¹³⁰, the first step to generate $(\text{CzT}^{\text{iPr}})\text{LnCl}_2$ went smoothly, but upon addition of $\text{LiCH}_2\text{SiMe}_3$ the solution turned dark red and a white salt precipitated from solution. In both cases the ^1H NMR spectrum of the red solution showed a symmetric set of deprotonated ligand resonances in the diamagnetic region that does not match the NMR spectrum of the parent ligand **8b**. The pattern of the resonances, dark red colour and the lack of paramagnetic influence (in the case of Er) suggests that the product does not

contain a lanthanide centre, and is most likely the Li salt of the ligand, $\text{Li}^+ [\text{CzT}^{\text{iPr}}]^-$ (**16**) (**Scheme 3.1**). This was later proven by a simple reaction between the protonated parent ligand **8b** and $\text{LiCH}_2\text{SiMe}_3$ to produce a red solution with a ^1H NMR spectrum that exactly matched that observed in the Y and Er reactions. Based on this it seems as though $(\text{CzT}^{\text{iPr}})\text{LnX}_2$ complexes undergo substitution of the $[\text{CzT}^{\text{iPr}}]^-$ ligand in preference to displacement of X^- .



Scheme 3.4 Attempted and successful salt metathesis reactions between $\text{LiCH}_2\text{SiMe}_3$ and *in situ* generated $(\text{CzT}^{\text{R}})\text{LnCl}_2$ ($\text{R} = \text{iPr}$ or CH_2Mes , $\text{Ln} = \text{Y}$, Er or Yb)

One synthetic route to avoid this unwanted salt formation is to use the lanthanide tris-alkyl $\text{Ln}(\text{CH}_2\text{SiMe}_3)_3$ as a starting reagent in an acid-base reaction with the protonated ligand, similar to the reaction used to synthesize **11** and **12**. This route eliminates the possibility of salt or unwanted “ate” complex formation, and offers a much simpler and cleaner reaction. Unfortunately, the lanthanide tris-alkyl starting materials are difficult to synthesize as they are not only extremely water sensitive, but also thermally sensitive. Attempt at synthesizing the $\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ starting complexes where $\text{Ln} = \text{Y}$, Er and Yb were all unsuccessful, even though their synthesis is known in the literature¹³¹⁻¹³³.

3.2.3 X-ray Structural Studies

The solid state structures of **11** and **12** were determined by X-ray crystallography, both complexes are isostructural and crystallize in the P-1 space group with toluenes of solvation in the lattice. A representative ORTEP plot of **11** is shown in **Figure 3.3** and selected bond lengths and angles for **11** and **12** are collected in **Table 3.1**. The $\text{Ln}-\text{N}_{\text{Cbz}}$ bond lengths in **11** and **12** of 2.347(2) and 2.368(3), respectively are on the longer end of other known carbazole-based chelating ligand lanthanide complexes (range corrected to match five coordinate $\text{Yb}(\text{III})$ by use of Shannon Radii¹³⁰: 2.131(3)-2.367(2) Å, median 2.258 Å, $\text{Er}(\text{III})$ ¹³⁰: 2.153(2)-2.389(2) Å, median 2.280 Å)^{56, 64-65, 134-136}. There are no known neutral tetrazole lanthanide complexes that have been crystallographically characterized, but the $\text{Ln}-\text{N}_{\text{Tz}}$ lengths in **11** (2.385(2), 2.393(2) Å) and **12** (2.390(3), 2.401(3) Å) are consistent with $\text{Ln}-\text{N}$ oxazoline bond lengths in our Czx ligand complexes (range corrected to match five coordinate $\text{Yb}(\text{III})$ ¹³⁰: 2.332(3)-2.416(3) Å, median 2.373 Å, $\text{Er}(\text{III})$ ¹³⁰: 2.344(3)-2.438(3) Å, median 2.395 Å)⁶⁴. The $\text{Ln}-\text{N}(\text{SiMe}_3)_2$ bond lengths in

11 (2.189(2), 2.200(2) Å) and **12** (2.207(3), 2.226(3) Å) are on the shorter end of other known lanthanide silylamide complexes (range corrected to match five coordinate Yb(III)¹³⁰: 2.165(2)-2.343(2) Å, median 2.212 Å¹³⁷, Er(III)¹³⁰: 2.220(2)-2.300(4) Å, median 2.249 Å¹³⁸). These short bond lengths suggest that the lanthanide centre is not exceptionally crowded by the CzT ligand.

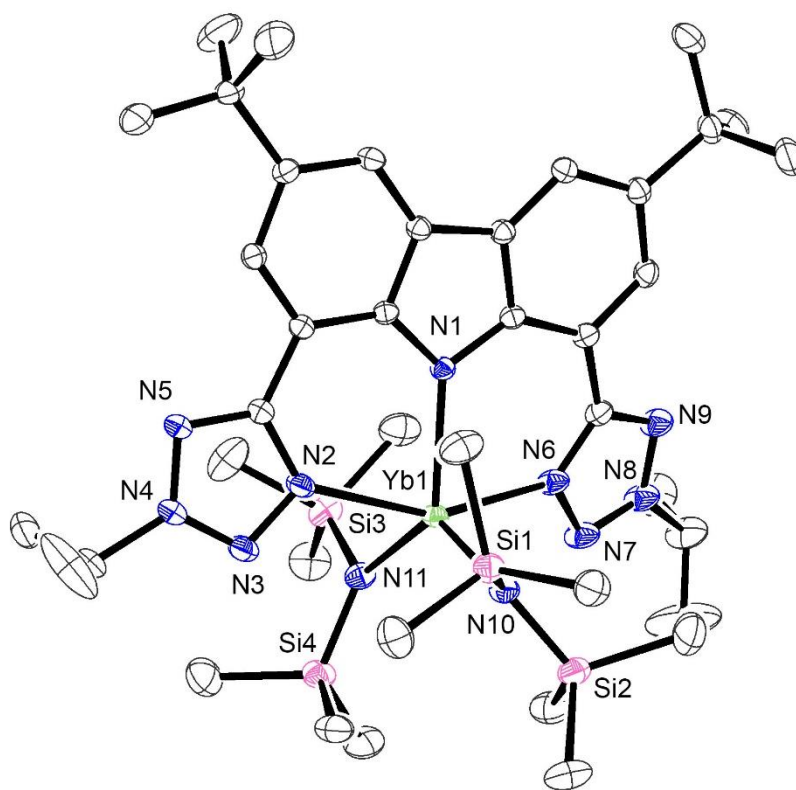


Figure 3.3 ORTEP3¹⁰⁸ plot (40% probability ellipsoids) of (CzT^{iPr})Yb[N(SiMe₃)₂] (**11**) (H atoms omitted for clarity)

An unexpected structural feature in these complexes is the distortion of the CzT ligand from planar; the tetrazole rings are canted (both in the same direction) away from the carbazole plane, this causes the lanthanide centre to sit removed from the carbazole plane by 0.33 and 0.34 Å for **11** and **12**, respectively. The fact that the tetrazole rings are

rotated and the ligand as a whole is not flat even in these five coordinate structures shows that this ligand is capable of different modes of bonding besides a strictly *mer* geometry commonly seen in tridentate pincer ligands. This suggests that in more crowded geometries these ligands will be able to distort and remain bonded to the metal centre.

Table 3.1 Selected bond lengths (Å) and angles (°) of (CzT^{iPr})Yb[N(SiMe₃)₂] (**11**) and (CzT^{iPr})Er[N(SiMe₃)₂] (**12**)^a

	11	12
Ln-N1	2.347(2)	2.368(3)
Ln-N2	2.385(2)	2.390(3)
Ln-N6	2.393(2)	2.401(3)
Ln-N7	2.189(2)	2.207(3)
Ln-N11	2.200(2)	2.226(3)
Ln-Cbz Plane	0.334	0.344
N1-Ln-N2	77.92(6)	77.20(10)
N1-Ln-N6	78.78(6)	78.68(10)
N1-Ln-N7	113.40(6)	113.63(11)
N1-Ln-N11	127.18(6)	123.98(10)
N2-Ln-N6	154.05(6)	153.46(10)
N2-Ln-N7	102.92(7)	102.44(11)
N2-Ln-N11	85.47(7)	84.83(11)
N6-Ln-N7	96.71(7)	97.23(11)
N6-Ln-N11	98.35(7)	99.74(11)
N7-Ln-N11	122.21(7)	121.98(11)
Cant Angle¹⁰⁷ Tz₁	7.91	7.80
Cant Angle¹⁰⁷ Tz₂	-16.46	-16.28

^aCbz plane refers to N1 and C1-C12; Tz₁ refers to C21 and N2-N5; Tz₂ refers to C25 and N6-N9.

3.3 Multi-ligand Complexes

3.3.1 Bis-ligand Complexes with Smaller Lanthanides

In some cases, attempts at making mono-ligand lanthanide complexes resulted in multi-ligand complexes. This result is somewhat surprising as the ligand was designed

specifically to be rigid and multidentate in order to avoid multi-ligand complexation to the lanthanide centre. The previous HCzx ligand never showed complications due to more than one ligand binding to a lanthanide⁶³, but as discussed previously the oxazoline ligand was much more crowding around the metal centre, most likely shutting down multiple ligand complexation to the same metal. In all cases of multi-ligand lanthanide complexes in this work, the synthetic route used was protonolysis of the silylamide lanthanide starting precursors $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ by the protonated ligand **8b**.

The first sign that more than one **8b** ligand could bind to a single lanthanide centre came from the crystal structure of an unexpected product. In the same sealed ampoule that contained crystals of **11** and **12**, smaller, hair-like crystals were found growing on the wall. Dr. Allen Oliver was able to get diffraction data on these thin crystals using the synchrotron source at U. C. Berkeley, that indicated a different unit cell from the mono-ligand complexes or the starting $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$. To our surprise, the structure showed two **8b** ligands on the lanthanide centre, but instead of one remaining silylamide $[\text{N}(\text{SiMe}_3)_2]$ group, a siloxide ligand (OSiMe_3) was found instead. These $(\text{CzT}^{\text{iPr}})_2\text{Ln}(\text{OSiMe}_3)$ ($\text{Ln} = \text{Yb}$ (**17**) and Er (**18**)) species were not detected by NMR or elemental analysis so these products probably arose from trace amounts of oxo containing impurities in the starting $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ or hydrolysis of an $\text{N}(\text{SiMe}_3)_2$ ligand by trace water. Oddly enough this product was observed in both the Yb and Er case, with X-ray quality crystals yielding structures for both.

The solid state structures of the bis-ligand lanthanide siloxide (**17** and **18**) complexes were determined by X-ray crystallography. Selected bond lengths and angles for **17** and **18** are collected in **Table 3.2** and representative ORTEP plots of **17** are shown

in **Figure 3.4**. The two tridentate CzT^{iPr} ligands in both **17** and **18** sit roughly perpendicular to each other (dihedral angle of 81.11° in **17** and 80.72° in **18** between the two carbazole planes), with one linear OSiMe_3 ligand occupying the seventh coordination site forming a mono-capped octahedral geometry.

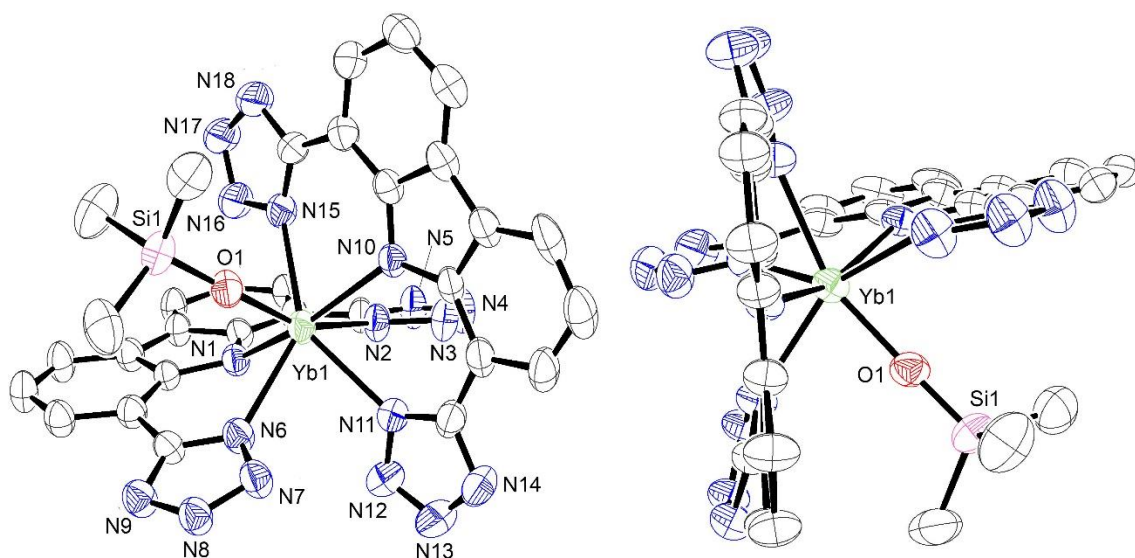


Figure 3.4 ORTEP3¹⁰⁸ plots (50% ellipsoid probability) of $(\text{CzT}^{\text{iPr}})_2\text{Yb}(\text{OSiMe}_3)$ (**17**) (H atoms, tBu and iPr groups omitted for clarity)

The Ln-N_{Cbz} bond lengths in **17** (2.338(4), 2.361(4) Å) and **18** (2.374(3), 2.401(3) Å) are consistent with other chelating lanthanide carbazolide complexes (range corrected for 7 coordinate Yb(III)¹³⁰: 2.248(3)-2.484(2) Å, median 2.375 Å; 7 coordinate Er(III)¹³⁰: 2.268(2)-2.504(2) Å, median 2.395 Å)^{56, 64-65, 134-136}. The Ln-N_{Tz} bond lengths in **17** (2.421(4)-2.491(5) Å) and **18** (2.448(3)-2.530(3) Å) are short compared to carbazole-oxazoline Ln-N distances (range corrected for 7 coordinate Yb(III)¹³⁰: 2.439(3)-2.533(3) Å, median 2.490 Å; 7 coordinate Er(III)¹³⁰: 2.459(3)-2.553(3) Å, median 2.510 Å)^{64, 134}.

Table 3.2 Selected bond lengths (Å) and angles (°) of (CzT^{iPr})₂Yb(OSiMe₃) (**17**) and (CzT^{iPr})₂Er(OSiMe₃) (**18**)

	17	18
Ln-N_{Cbz} (N1)	2.338(4)	2.374(3)
Ln-N_{Cbz} (N7)	2.361(4)	2.401(3)
Ln-N_{Tz} (N2)	2.491(5)	2.464(3)
Ln-N_{Tz} (N6)	2.455(4)	2.530(3)
Ln-N_{Tz} (N11)	2.421(4)	2.448(3)
Ln-N_{Tz} (N15)	2.434(4)	2.451(3)
Ln-O1	2.061(4)	2.086(2)
Ln-Cbz₁ Plane	1.264	1.280
Ln-Cbz₂ Plane	0.607	0.608
N1-Ln-N2	73.54(14)	74.27(9)
N1-Ln-N6	74.74(14)	72.99(9)
N1-Ln-N7	155.37(14)	155.73(9)
N1-Ln-N11	110.42(15)	83.71(9)
N1-Ln-N15	83.79(14)	111.68(10)
N7-Ln-N2	86.09(14)	129.50(9)
N7-Ln-N6	129.27(13)	87.26(9)
N7-Ln-N11	76.49(14)	78.16(9)
N7-Ln-N15	78.31(13)	75.85(10)
N2-Ln-N11	75.33(15)	142.10(9)
N2-Ln-N15	77.60(15)	74.26(10)
N6-Ln-N11	73.87(14)	77.33(9)
N6-Ln-N15	141.99(14)	76.21(10)
N2-Ln-N6	123.64(15)	122.88(10)
N11-Ln-N15	143.93(14)	143.45(10)
O1-Ln-N1	103.91(14)	103.28(9)
O1-Ln-N2	156.65(15)	76.64(9)
O1-Ln-N6	76.27(15)	156.29(9)
O1-Ln-N7	89.25(14)	89.06(9)
O1-Ln-N11	125.65(15)	79.00(9)
O1-Ln-N15	79.05(15)	125.38(10)
Cant angle¹⁰⁷ Tz₁	-15.83	-17.92
Cant angle¹⁰⁷ Tz₂	17.89	15.75
Cant angle¹⁰⁷ Tz₃	-2.79	-4.51
Cant angle¹⁰⁷ Tz₄	4.84	2.99

Cbz₁ refers to N1 and C1-C12; Cbz₂ refers to N10 and C29-C40; Tz₁ refers to C21 and N2-N5; Tz₂ refers to C25 and N6-N9; Tz₃ refers to C 49 and N11-N14; Tz₄ refers to C53 and N15-N18.

The Ln-OSiMe₃ bond length in **17** of 2.061(4) Å and in **18** of 2.086(2) Å is consistent with other seven coordinate lanthanide siloxide structures in the literature (range corrected to match Yb(III)¹³⁰: 1.922(2)-2.150(7) Å, median 2.078 Å, Er(III)¹³⁰: 1.942(2)-2.170(7) Å, median 2.098 Å)¹³⁹⁻¹⁴¹. What is more interesting is the inconsistent distortion of the ligands in each structure. Both **17** and **18** have one CzT ligand that is almost planar (cant angles 2-5°) whereas the second CzT ligand in each structure is drastically distorted with large cant angles (15-18°). This causes the lanthanide centre to sit far removed from the carbazole plane of the distorted ligand (approximately 1.7 Å) while it is only slightly removed from the carbazole plane of the more planar ligand in each case (0.6 Å). This high degree of distortion and twisting of CzT is presumably due to the crowding around the lanthanide centre in order to make room for the siloxide ligand. The ability to fit two **8b** ligands around the smaller lanthanides, such as Yb and Er, was quite unexpected, but the ability of these ligands to deviate from planarity in order to accommodate larger coordination numbers is likely facilitating these bis-ligand structures.

3.3.2 Tris-Ligand Yttrium Complex

The isolation of degradation products **17** and **18** prompted us to examine whether similar degradation products could be observed by ¹H NMR spectroscopy for a diamagnetic yttrium complex. The room temperature reaction of one equivalent of Y[N(SiMe₃)₂]₃ with two equivalents of **8b** gave complex mixtures that could not be separated. However, the product that crystallized out of the reaction mixture on extended heating showed a complicated ¹H NMR spectrum that contained no N(SiMe₃)₂ ligands! Elemental analysis and X-ray crystallography established this as the tris(ligand) complex, (CzT^{iPr})₃Y (**19**).

Selected bond lengths and angles of **19** are collected in **Table 3.3** and representative ORTEP plots are shown in **Figure 3.5** and **Figure 3.6**.

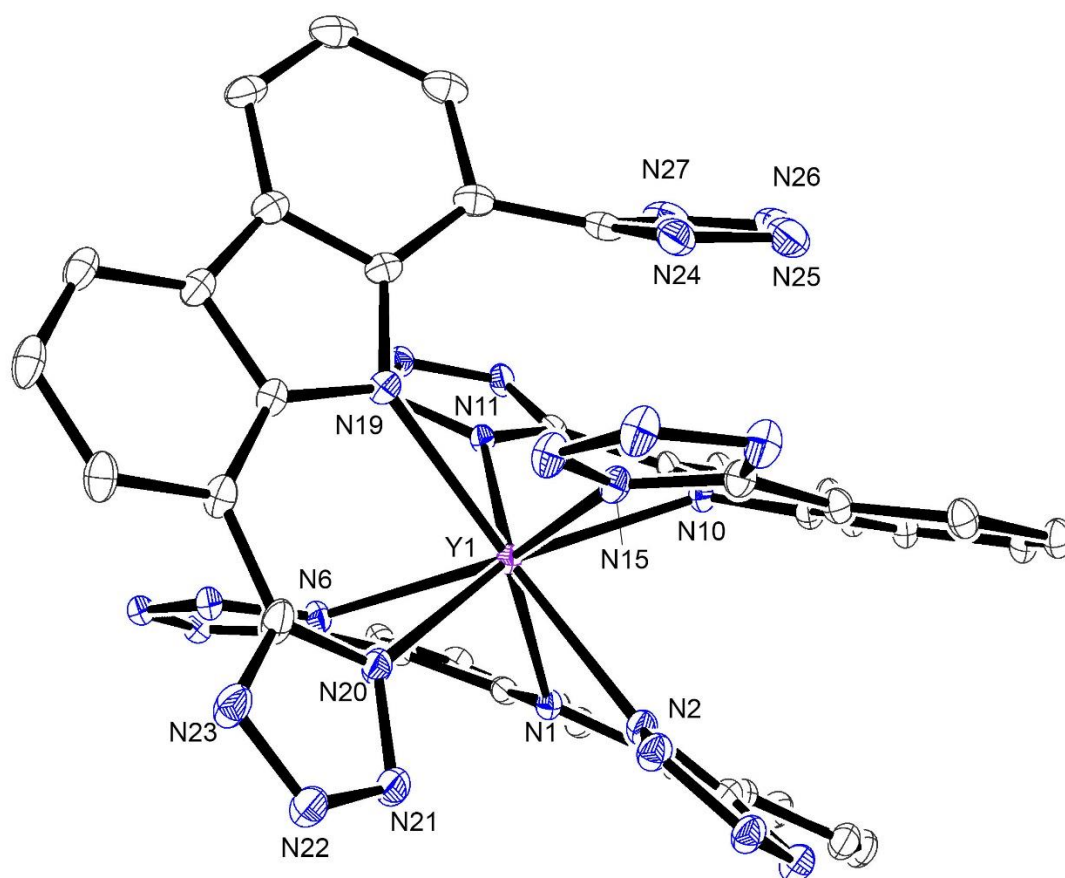


Figure 3.5 ORTEP3¹⁰⁸ plot (30% ellipsoid probability) of (CzT^{iPr})₃Y (**19**) (H atoms, tBu and iPr groups omitted for clarity)

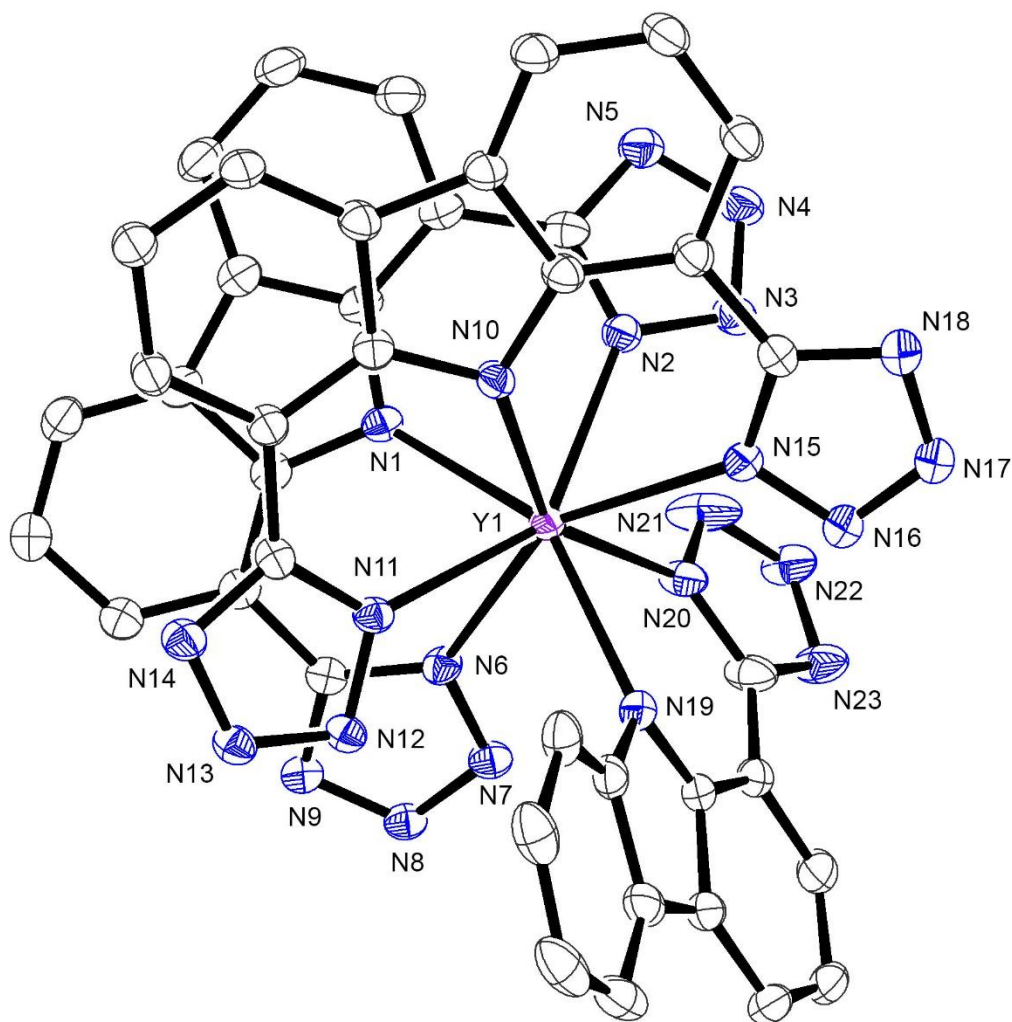


Figure 3.6 ORTEP3¹⁰⁸ plot (30% ellipsoid probability) of (CzT^{iPr})₃Y (**19**) (H atoms, tBu, iPr groups and non-bonding Tz ring omitted for clarity)

The Y-N_{Cbz} bond lengths in **19** (2.465(2), 2.378(2) and 2.466(2) Å) are consistent with other chelating lanthanide carbazolid complexes (range corrected for 8 coordinate Y(III)¹³⁰: 2.342(3)-2.578(2) Å, median 2.469 Å)^{56, 64-65, 134-136}. The Y-N_{Tz} bond lengths in **19** (2.478(2)-2.544(2) Å) are shorter than carbazole-oxazoline Ln-N distances (range corrected for 8 coordinate Y(III)¹³⁰: 2.533(3)-2.627(3) Å, median 2.584 Å)^{64, 134}.

Table 3.3 Selected bond lengths (Å) and angles (°) of (CzT^{iPr})₃Y (**19**)

Y1-N1	2.465(2)	N1-Y1-N2	71.71(6)
Y1-N7	2.378(2)	N1-Y1-N6	70.43(6)
Y1-N19	2.466(2)	N1-Y1-N7	89.98(6)
Y1-N2	2.533(2)	N1-Y1-N11	80.06(6)
Y1-N6	2.544(2)	N1-Y1-N15	136.53(6)
Y1-N11	2.478(2)	N1-Y1-N19	149.67(6)
Y1-N15	2.488(2)	N1-Y1-N20	106.07(7)
Y1-N20	2.483(2)	N7-Y1-N2	78.61(6)
		N7-Y1-N6	137.82(6)
Y1-Cbz₁ Plane	1.383	N7-Y1-N11	74.00(6)
Y1-Cbz₂ Plane	1.157	N7-Y1-N15	73.70(6)
Y1-Cbz₃ Plane	0.814	N7-Y1-N19	111.71(6)
		N7-Y1-N20	147.31(6)
Cant angle¹⁰⁷ Tz₁	-17.84	N19-Y1-N2	136.41(6)
Cant angle¹⁰⁷ Tz₂	20.98	N19-Y1-N6	83.04(6)
Cant angle¹⁰⁷ Tz₃	-20.93	N19-Y1-N11	77.56(6)
Cant angle¹⁰⁷ Tz₄	18.50	N19-Y1-N15	73.62(6)
Cant angle¹⁰⁷ Tz₅	-17.73	N19-Y1-N20	78.50(6)
		N2-Y1-N6	118.49(6)
		N2-Y1-N11	143.20(6)
		N2-Y1-N15	69.07(6)
		N2-Y1-N20	73.80(6)
		N6-Y1-N11	71.07(6)
		N6-Y1-N15	147.11(6)
		N6-Y1-N20	72.50(6)
		N11-Y1-N15	123.93(6)
		N11-Y1-N20	138.26(6)
		N15-Y1-N20	80.26(7)

Cbz₁ refers to N1 and C1-C12; Cbz₂ refers to N10 and C29-C40; Cbz₃ refers to N19 and C57-C68' Tz₁ refers to C 21 and N2-N5; Tz₂ refers to C25 and N6-N9; Tz₃ refers to C49 and N11-N14; Tz₄ refers to C53 and N15-N18; Tz₅ refers to C81 and N20-23.

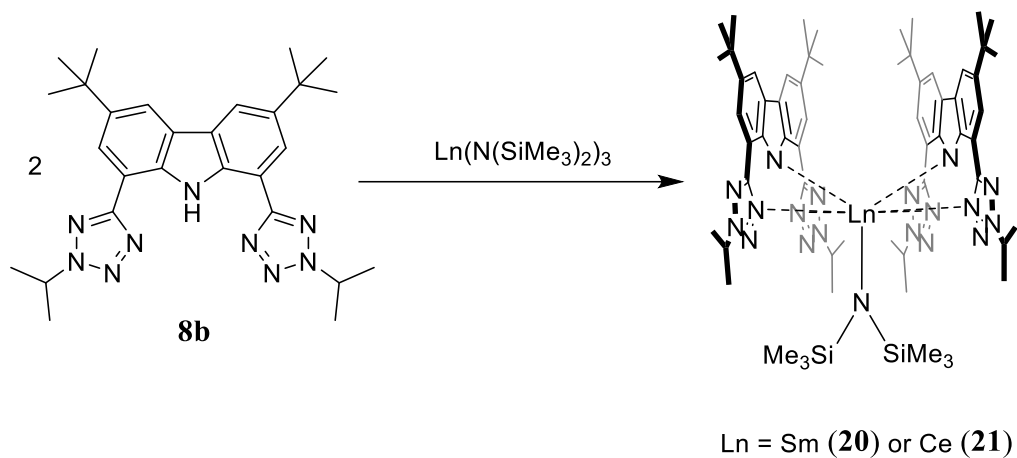
The most interesting structural feature in **19** is that bidentate binding of the **8b** ligand is evident for the first time. Two of the ligands bind in a tridentate mode (although highly distorted from *mer*), but the third ligand is bound only through the Cbz N and one Tz N, with the non-bonded tetrazole ring rotated away from the Y centre, likely due to high steric crowding of the lanthanide centre. Both tridentate ligands are bonded with the Y

sitting out of the carbazole plane by 1.1-1.3 Å. The two tridentate ligands are almost coplanar forming a sandwich-like complex with the Y in the middle. This is an unexpected geometry for tridentate pincer ligands. All bound tetrazole rings are twisted significantly from planarity with the carbazole unit showing large cant angles ranging from 17-21°. Presumably this distortion is necessary to accommodate the high coordination number. While it was surprising to us that two of our CzT ligands could fit around Yb and Er (**17** and **18**) it was even more unexpected that three ligands would bind to any of the lanthanides. This strongly suggests that the iPr substituents on **8b** will not be bulky enough to stabilize mono-ligand complexes of the larger lanthanides.

3.3.3 Bis-ligand Complexes with Larger Lanthanides

With this information in hand we decided to attempt to make multi-ligand lanthanide complexes under forcing conditions on purpose in an attempt to mimic Evans' Cp* *steric-oversaturation* reactivity¹²⁵⁻¹²⁶. Attempts to form (CzT^{iPr})₂Ln[N(SiMe₃)₂] through protonolysis of two molar equivalents of protonated ligand **8b** and one molar equivalent of Ln[N(SiMe₃)₂]₃ with the smaller lanthanides (Ln = Yb or Er) failed, even at elevated temperatures for prolonged periods. This was somewhat surprising as we have evidence of two ligands binding to the smaller lanthanides as seen with **17** and **18**. This result suggests that the increase in steric crowding on going from the siloxide ligand to the silylamide ligand is big enough to prevent binding of a second ligand onto the lanthanide, even under harsher conditions. Additionally, this suggests that three CzT^{iPr} ligands, where two are tridentate and one is bidentate, is less sterically encumbering than two tridentate CzT^{iPr} and one remaining silylamide ligand. In the case of the larger lanthanides this

reaction is successful and $(\text{CzT}^{\text{iPr}})_2\text{Ln}[\text{N}(\text{SiMe}_3)_2]$ ($\text{Ln} = \text{Sm}$ (**20**) or Ce (**21**)) form in good yields, even at room temperature (**Scheme 3.5**).



Scheme 3.5 Synthesis of $(\text{CzT}^{\text{iPr}})_2\text{Ln}[\text{N}(\text{SiMe}_3)_2]$ [$\text{Ln} = \text{Sm}$ (**20**) and Ce (**21**)]

The ^1H NMR spectrum of **21** at room temperature is extremely broad and the resonances are barely discernable. Increasing the temperature to 338 K sharpens the resonances enough to obtain some characterization data, and the integrations are consistent with two **8b** ligands and one silylamide ligand remaining on the Ce centre (**Figure 3.7**). The observation of only five resonances suggests high symmetry (C_{2v}) which is not possible if the CzT ligands are binding in a pseudo *mer* fashion as was seen in **17** and **18**. Variable temperature (VT) NMR experiments were conducted, and the plot of chemical shift (δ) vs. $1/T$ is linear for each resonance suggesting that the complex is showing Curie-Weiss¹⁴² behaviour (**Figure 3.8**) and that the broadness of the resonances is likely due to paramagnetic influence. This is consistent with the pseudo *fac* bonding of the ligands to the lanthanides shown in **Scheme 3.5**. There may also be some broadening due to fluxional processes, but this should show non-linear trends in the δ vs. $1/T$ plot.

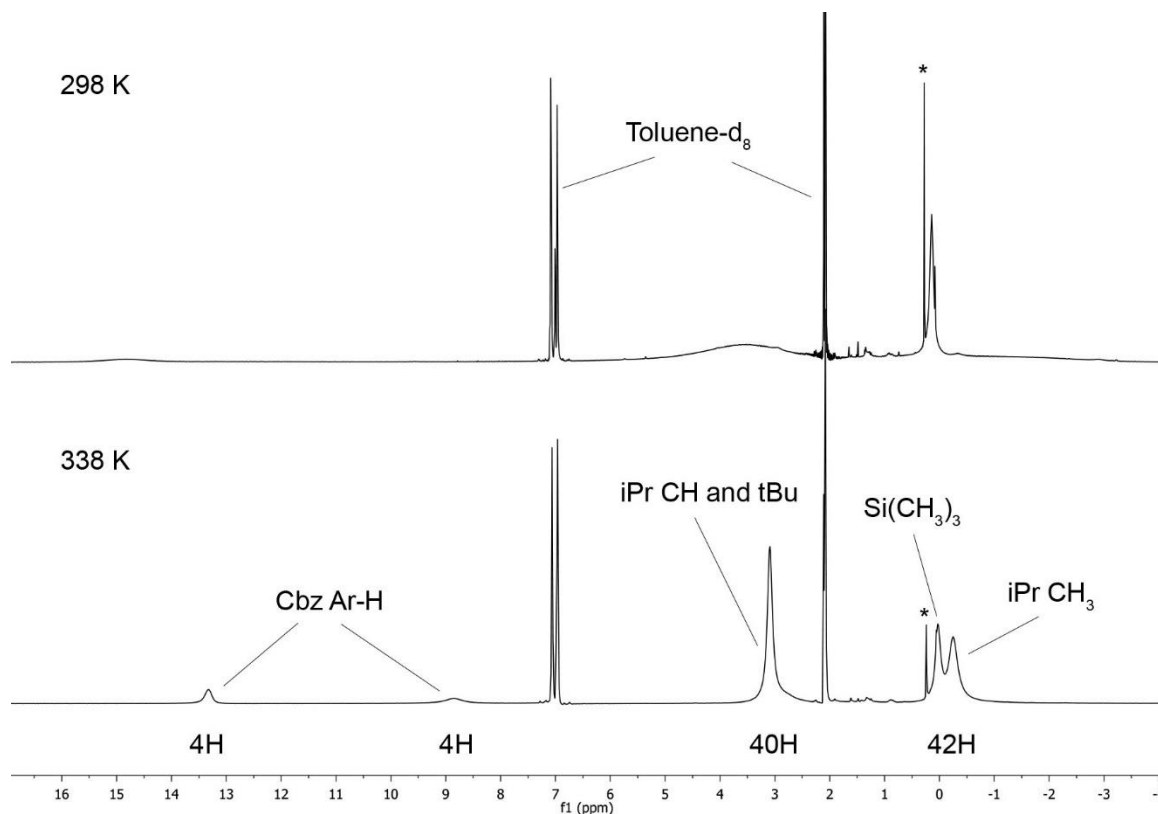


Figure 3.7 Variable temperature ^1H NMR spectra of $(\text{CzTi}^{\text{iPr}})_2\text{Ce}[\text{N}(\text{SiMe}_3)_2]$ (**21**) (360 MHz, toluene-D_8) (* denotes residual grease in sample)

The ^1H NMR spectrum of **20** obtained at 343 K is quite similar to that of **21**, suggesting that the structure is also similar. The main difference is that in the Sm case there are two extra resonances that each integrate to 2 H, consistent with the CH of the iPr group on the ligand. Again the small number of ligand resonances suggests high symmetry for **21** in solution. The separation of the iPr CH peaks in the case of Sm suggests some loss of symmetry in moving to the smaller lanthanide, but unfortunately no X-ray crystal structure of the Sm complex was obtained so it is impossible to compare to the solid state Ce structure (discussed later). The peak widths of the ^1H NMR resonances for both **20** and **21** are comparable ($\nu_{1/2}$ ranges from 25 to 120 Hz for **20** and 36 to 136 Hz for **21**) suggesting

that the appearance of the two new resonances in the Sm case is not solely due to a change in magnetic moment of the lanthanide centre.

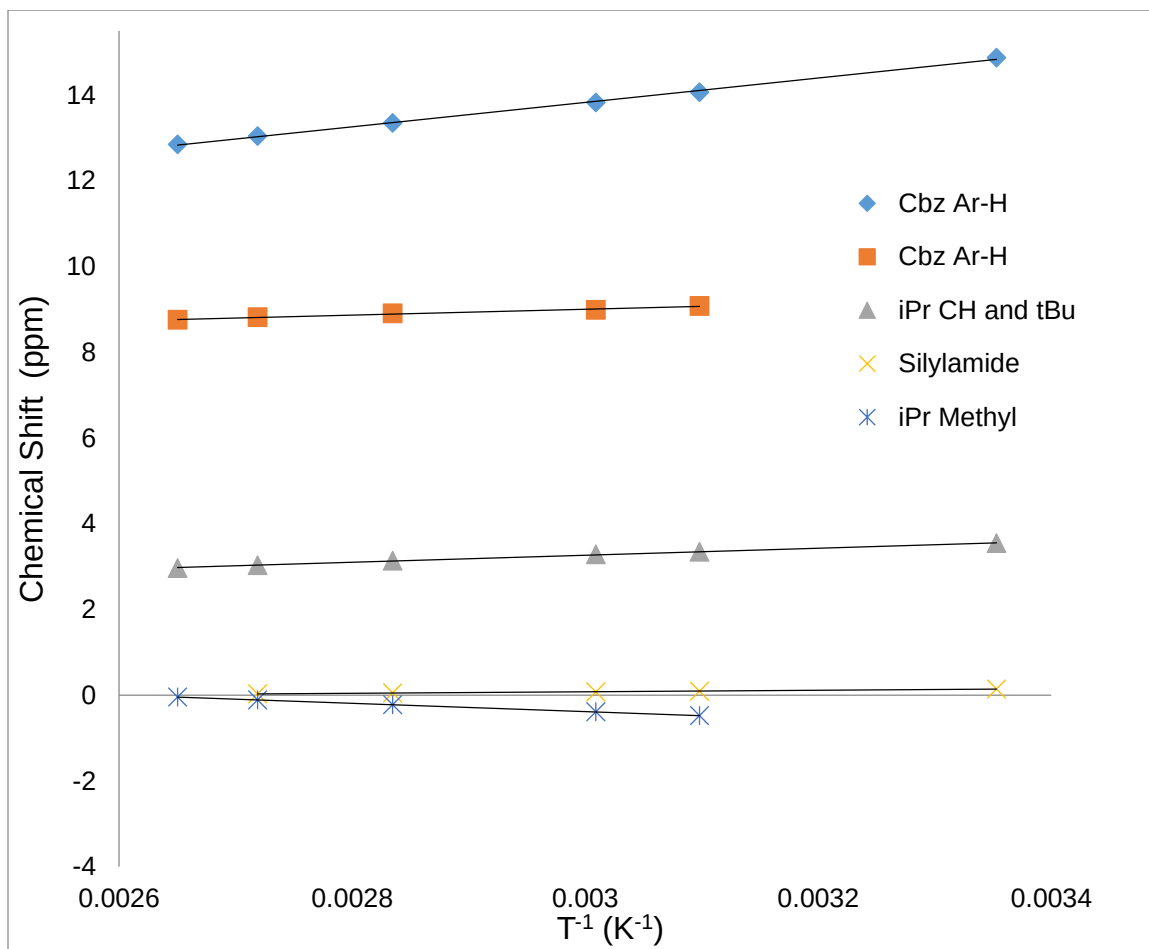


Figure 3.8 δ vs. $1/T$ plot of $(CzT^{iPr})_2Ce[N(SiMe_3)_2]$ (**21**) (360 MHz, toluene- D_8)

X-ray quality crystals of **21** were grown from toluene and the complex was structurally characterized. Selected bond lengths and angles are collected in **Table 3.4** and representative ORTEP plots are shown in **Figure 3.9** and **Figure 3.10**.

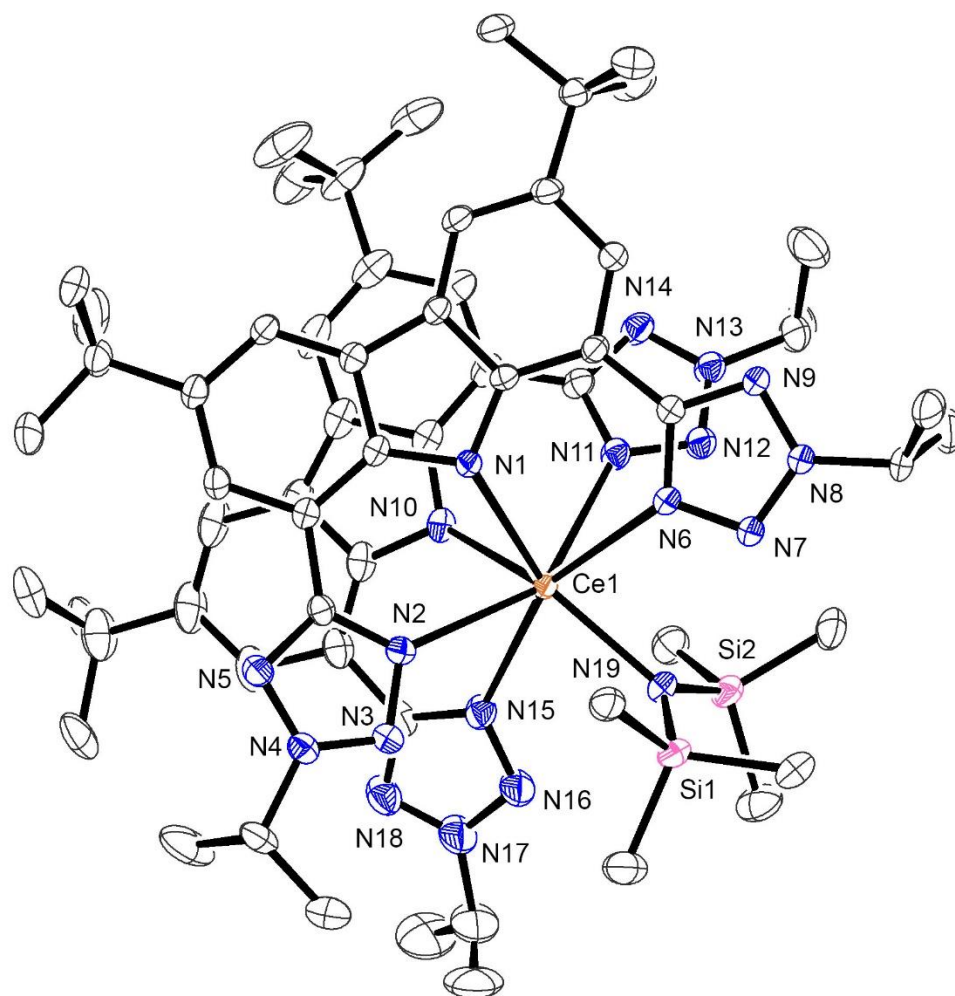
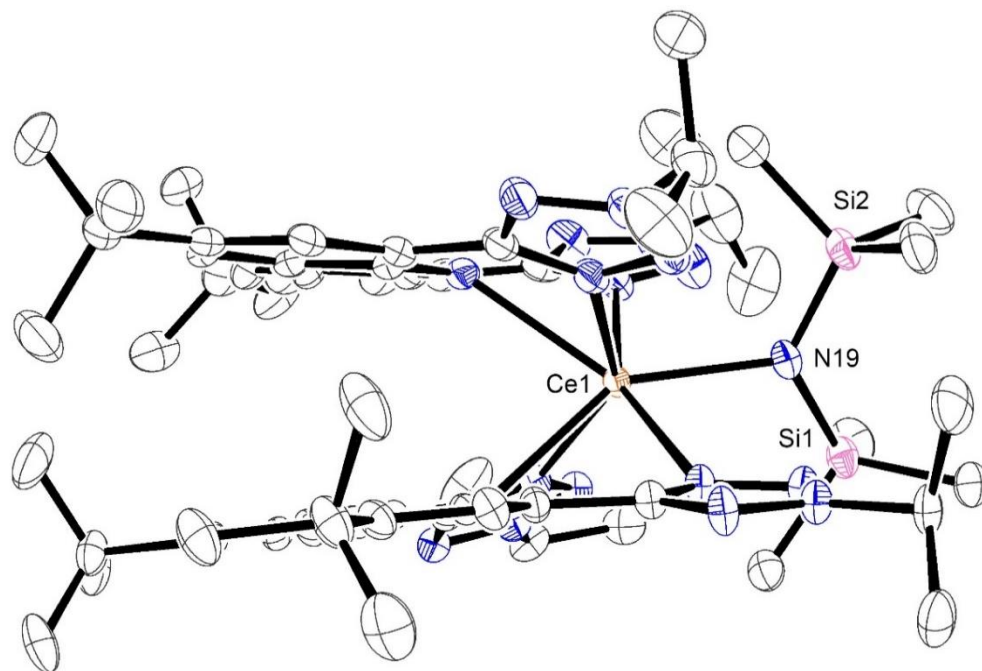


Figure 3.9 ORTEP3¹⁰⁸ plot (50% ellipsoid probability) of (CzTi^{iPr})₂Ce[N(SiMe₃)₂] (**21**) (H atoms omitted for clarity)

Table 3.4 Selected bond lengths (Å) and angles (°) of (CzT^{iPr})₂Ce[N(SiMe₃)₂] (**21**)

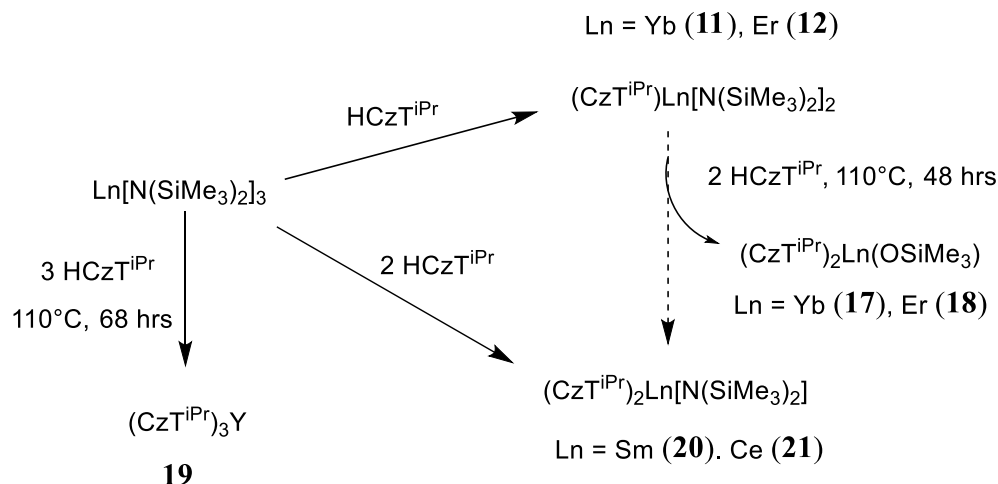
Ce1-N1	2.567(2)	N7-Ce1-N15	69.28(7)
Ce1-N7	2.557(2)	N2-Ce1-N11	146.56(6)
Ce1-N2	2.627(2)	N2-Ce1-N15	70.52(6)
Ce1-N6	2.703(2)	N6-Ce1-N11	68.74(7)
Ce1-N11	2.624(2)	N6-Ce1-N15	157.05(6)
Ce1-N15	2.679(2)	N2-Ce1-N6	118.23(6)
Ce1-N19	2.352(2)	N11-Ce1-N15	116.83(7)
Ce1-Cbz₁ Plane	1.468	N19-Ce1-N1	143.01(7)
Ce1-Cbz₂ Plane	1.437	N19-Ce1-N2	112.26(7)
		N19-Ce1-N6	78.47(7)
N1-Ce1-N2	70.10(6)	N19-Ce1-N7	136.05(7)
N1-Ce1-N6	69.42(6)	N19-Ce1-N11	101.16(7)
N1-Ce1-N7	80.36(6)	N19-Ce1-N15	78.59(7)
N1-Ce1-N11	84.21(6)		
N1-Ce1-N15	131.71(6)	Cant angle¹⁰⁷ Tz₁	-19.60
N7-Ce1-N2	84.76(7)	Cant angle¹⁰⁷ Tz₂	10.38
N7-Ce1-N6	130.25(6)	Cant angle¹⁰⁷ Tz₃	-22.02
N7-Ce1-N11	69.73(7)	Cant angle¹⁰⁷ Tz₄	21.23

Cbz₁ refers to N1 and C1-C12; Cbz₂ refers to N10 and C29-C40; Tz₁ refers to C21 and N2-N5; Tz₂ refers to C25 and N6-N9; Tz₃ refers to C49 and N11-N14; Tz₄ refers to C53 and N15-N18.

**Figure 3.10** ORTEP3¹⁰⁸ plot (50% ellipsoid probability) of (CzT^{iPr})₂Ce[N(SiMe₃)₂] (**21**) (H atoms omitted for clarity)

The Ce-N_{Cbz} bond lengths in **21** (2.557(2) and 2.567(2) Å) are consistent with other chelating lanthanide carbazolid complexes (range corrected for 7 coordinate Ce(III)¹³⁰: 2.393(3)-2.629(2) Å, median 2.520 Å)^{56, 64-65, 134-136}. The Ce-N_{Tz} bond lengths in **21** (2.624(2)-2.703(2) Å) are long compared to carbazole-oxazoline Ln-N distances (range corrected for 7 coordinate Ce(III)¹³⁰: 2.584(3)-2.678(3) Å, median 2.635 Å)^{64, 134}. The Ce-N(SiMe₃)₂ distance in **21** of 2.352(2) Å is consistent with other 7 coordinate lanthanide silylamide complexes (range corrected for Ce(III)¹³⁰: 2.337(2)-2.4588(11) Å, median 2.418 Å)¹⁴³. Similar to what was seen for **19**, the two CzT ligands bind with the Ce metal sitting between the two ligands in a sandwich-like structure. This leaves an open channel or cleft for the bulky silylamide ligand to fit in the seventh coordination site. The Ce sits removed from the carbazole planes by about 1.4 Å, which causes the tetrazole rings to cant significantly (10-22°). There is experimental evidence that **21** is formed preferentially even when there is only one equivalent of **8b** present. This bis-ligand structure demonstrates the need for bulkier ligands in order to stabilize mono-ligand complexes with larger lanthanides such as Ce. The successful formation of a mono-ligand complex of Ce with the bulkier **8d** ligand in complex **13** is further evidence of the effect peripheral ligand bulk has on lanthanide complex formation.

In order to summarize the synthetic results for all mono, bis and tris lanthanide complexes discussed in this work, a complete scheme of all lanthanide complexes and how they were synthesized is shown in **Scheme 3.6**.



Scheme 3.6 Protonolysis of $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ with HCzT^{iPr} (**8b**) (all reactions carried out at room temperature in toluene unless otherwise specified)

3.4 Reactivity and Catalysis

3.4.1 Introduction

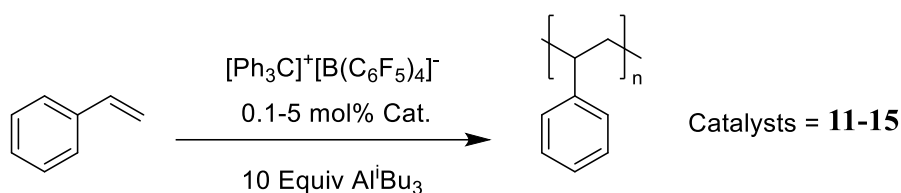
With the mono-ligand lanthanide complexes **11-15** in hand, attempts to explore their catalytic reactivity were conducted. Unlike transition metals, lanthanides do not have the ability to undergo the mechanistic steps involving oxidative-addition and reductive-elimination since they do not have access to both the (II) and (IV) oxidation state on the same metal centre (within a reasonable electronic window). This limits the catalytic bond-forming steps at these metals to σ -bond metathesis, insertion and single electron transfer (SET) processes. While SmI_2 is widely known for its reducing abilities¹⁴⁴ and cerium in the (IV) oxidation state (such as in CAN) is popular as an oxidation catalyst¹⁴⁵, the lanthanide complexes synthesised in this work are not suitable for redox processes because the metals employed are all in their most stable (III) oxidation state. Several lanthanide complexes similar to ours have shown to be efficient catalysts in transformations such as

polymerization of olefins^{59, 146-150}, hydroamination²⁴, hydrosilylation^{20, 61} and ring opening polymerization of lactones/lactides¹⁵¹ to name a few, so we used this as a starting point to probe the comparative reactivity of the complexes in this work.

3.4.2 Polymerization of Styrene

One of the most straightforward and simple olefin polymerization tests is the polymerization of styrene. Styrene itself is easy to handle as it is a liquid, fairly easy to dry, and it is also an extremely easy olefin to polymerize, so much so that it is bottled with stabilizers and kept at cold temperatures so that it does not spontaneously polymerize. While there is no need for a novel lanthanide catalyst to polymerize styrene in industry, it is a good benchmark test to probe the possible catalytic activity of our complexes for polymerization. In order for the styrene substrate to bind to the lanthanide centre, one of the substituents must be removed to create an open coordination site. A common reagent to accomplish this is $[\text{Ph}_3\text{C}]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$. One equivalent of $[\text{Ph}_3\text{C}]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$ was reacted with the lanthanide complex to yield the cationic $[(\text{CzT}^{\text{R}})\text{LnX}]^+ [(\text{B}(\text{C}_6\text{F}_5)_4)]^-$ species as the active catalyst with loss of $\text{Ph}_3\text{C-X}$. Complexes where $\text{X} = \text{N}(\text{SiMe}_3)_2$ (**11**, **12** and **13**) or CH_2SiMe_3 (**14** and **15**) should be able to polymerize styrene at modest activities, but there is debate whether $\text{N}(\text{SiMe}_3)_2$ or CH_2SiMe_3 are suitable groups for substrate insertion as there is experimental evidence of catalysts with these groups not being active^{59, 148}. A common strategy to avoid this problem is to add a co-catalyst such as AlR_3 to act as a chain transfer agent to aid the polymerization further⁵⁸. It has been shown that the sterics of the AlR_3 R group (Me, Et, iPr) affects the selectivity, % conversion and molecular weight of the resulting polymer⁵⁸⁻⁵⁹. Molar amounts between 0.1-5 mol % of

catalyst were tested with complexes **11-15**. In all cases the desired amount of lanthanide pre-catalyst was reacted with equimolar amounts of $[\text{Ph}_3\text{C}]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$ followed by the appropriate amount of dried styrene and Al^iBu_3 , and was allowed to stir at room temperature for an extended time (**Scheme 3.7**).



Scheme 3.7 General procedure for the polymerization of styrene

Surprisingly there was no polystyrene formed with any of the lanthanide pre-catalysts. Based on this result it was postulated that the cationic active catalyst $[(\text{CzT}^{\text{R}})\text{LnX}]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$ may not have formed. To prove the formation of the cationic adduct a test reaction was conducted in which one equivalent of **14** was reacted with one equivalent of $[\text{Ph}_3\text{C}]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$. An orange oil formed that showed dramatic ^1H NMR chemical shift changes from the starting alkyl **14** when dissolved in deuterated bromobenzene. While it is difficult to fully assign the paramagnetic complex ^1H NMR spectrum (**Figure 3.11**), it is clear that a reaction occurs and a new Yb complex formed. Further investigations by ^{19}F , ^{11}B or ^{13}C NMR were unsuccessful due to the paramagnetic Yb centre. These results are very similar to those observed by Zou⁶³ with her analogous Y complex $(\text{Czx})\text{Y}(\text{CH}_2\text{SiMe}_3)_2$ and consistent with formation of the desired cationic species (specifically the formation of a dense orange oil). Since the cationic $[(\text{CzT}^{\text{R}})\text{LnX}]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$ is not very soluble in toluene or benzene, attempts at styrene polymerization

in other solvents (such as bromobenzene) were conducted in order to see if homogeneity was an issue. Unfortunately, no polystyrene was formed even in more polar solvents (THF and bromobenzene) where everything was fully dissolved. At this time, it is unclear why our mono-ligand lanthanide complexes are inactive as olefin polymerization catalysts, but due to their lack of reactivity, olefin polymerization was not pursued further.

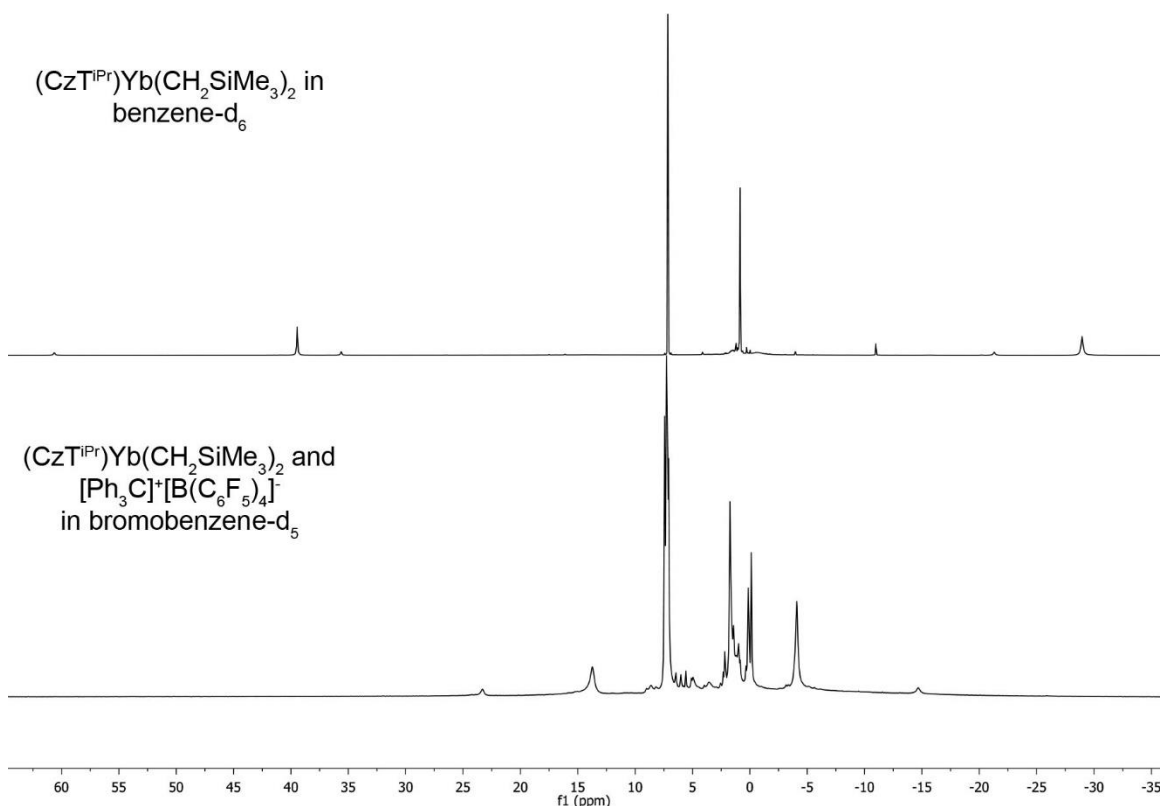
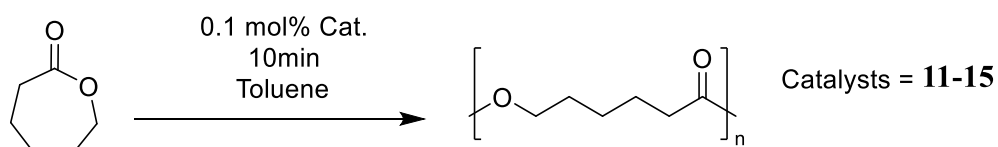


Figure 3.11 ¹H NMR spectra (300 MHz, C₆D₆ and bromobenzene-D₅, 298 K) of (CzTiⁱPr)Yb(CH₂SiMe₃)₂ (**14**) and [Ph₃C]⁺[B(C₆F₅)₄]⁻ reaction with (CzTiⁱPr)Yb(CH₂SiMe₃)₂ (**14**) (CH₂ resonance in **14** observed at -237 ppm omitted from top spectrum for clarity)

3.4.3 Ring-Opening Polymerization of Lactones

Since the lanthanide complexes failed to polymerize simple olefin substrates, different catalytic transformations were pursued in attempts to ascertain the reactive

potential of our complexes. Similar lanthanide complexes are well known to catalyze ring opening polymerization (ROP) of lactones and lactides^{60, 139, 151-159}. This is a reaction of industrial interest, specifically the ROP of lactide (the cyclic dimer of lactic acid) to form biodegradable polymers¹⁶⁰⁻¹⁶². As a test reaction, we chose one of the most common ROP substrates ϵ -caprolactone as it ring opens fairly easily and is convenient to handle. To perform catalytic ROP test reactions, 0.1 mol % of catalyst was stirred with a toluene solution of dry ϵ -caprolactone at room temperature for 10 minutes under N_2 (**Scheme 3.8**), followed by quenching with acidic MeOH to precipitate the polyester from solution as a white solid. All lanthanide complexes tested gave polyester product; the activity and percent conversion for each are summarized in **Table 3.5**.



Scheme 3.8 General procedure for the ring opening polymerization of ϵ -caprolactone

Table 3.5 ROP catalytic data for ϵ -caprolactone

Catalyst	Ln	Ligand	X	Activity (kg mol ⁻¹ h ⁻¹)	% Conversion	Ln(III) Ionic Radius ¹³⁰ (Å)
11	Yb	8b	N(SiMe ₃) ₂	250	36 %	0.808
12	Er	8b	N(SiMe ₃) ₂	690	97 %	0.830
13*	Ce	8d	N(SiMe ₃) ₂	200	88 %	0.950
14	Yb	8b	CH ₂ SiMe ₃	250	36 %	0.808
18	Yb	8d	CH ₂ SiMe ₃	230	34 %	0.808

[lactone]:[cat] is 1000:1, t = 10 min at room temperature. * Catalyst **13** was used in 0.5 mol % and was stirred for 15 minutes rather than 10 minutes.

From this data it is clear that while all complexes are catalytic for the ring opening polymerization of ϵ -caprolactone, the Er complex **12** is superior not only in activity but percent conversion under the same conditions. This is not surprising in comparison to the smaller analogue **11** because activity generally increases with the ionic radius of the lanthanide centre^{60, 152, 163-164}. The Ce complex might be expected to be the most active given its large size, but the larger $\text{CzT}^{\text{CH}_2\text{Mes}}$ ligand used in **13** may affect the expected activity gains. This hypothesis was investigated by comparing the activity of **14** and **15** against each other; and while there is a slight decrease in activity seen with the bulkier ligand, the effect is not drastic. Unfortunately, there is no direct ligand steric comparison for the Ce complex since we are unable to synthesize a mono-ligand complex using ligand **8b**. Another surprise is the identical activity and percent conversion for the Yb case on changing from the generally less reactive silylamide to the more reactive alkyl. Based solely on Pearson's Hard-Soft-Acid-Base (HSAB) principle¹⁶⁵, lanthanide alkyls should be more reactive and easier to insert into than lanthanide amides²⁶ as a Ln-C bond is weaker and more labile than a Ln-N bond. This will affect the activity of catalysts **11** and **14** if initial insertion into the Ln-C or Ln-N bond is the rate determining step, but based on these results it appears that insertion may not be rate limiting. The increase in activity of ROP catalysis seen with increasing lanthanide ionic size is suggestive that the coordination step may in fact be rate determining, although this result goes against literature claims of the activity depending on the insertion ligand present^{60, 153} (amides showed higher activity than aryloxides). While these preliminary results are fairly interesting and show some successful catalytic reactivity with the mono-ligand CzT family of lanthanide complexes, further

reactivity and tests were not pursued due to the relatively low activity compared to other lanthanide systems under similar conditions^{153, 155 166}.

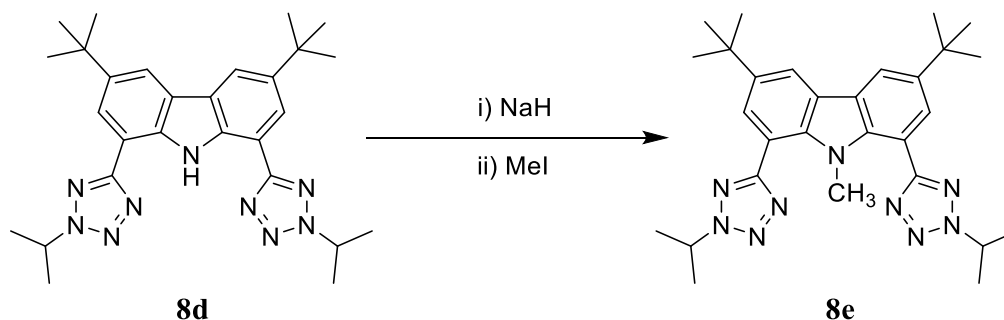
3.5 Single Electron Redox Behaviour

3.5.1 Introduction

While the (III) oxidation state is the most stable and common for all the lanthanides, some lanthanides are able to adopt the (II) or (IV) state within a reasonable redox window. While all lanthanides have been seen in the (II) state¹⁶⁷⁻¹⁷⁰, the most stable (II) states in the lanthanide series are those where the electronic configuration is either a half filled shell (Eu(II), f^7) or a full shell (Yb(II), f^{14}). Sm also possesses a readily accessible (II) state, although at a slightly lower reduction potential of -1.55 V vs SHE compared to -0.35 V for Eu and -1.15 V for Yb¹⁷¹. The (IV) oxidation state within the lanthanide series is much less common. For an extended period of time, only Ce was known to adopt the (IV) state¹⁷², but recently Tb was isolated in the (IV) state¹⁷³. While sometimes difficult to attain, lanthanide complexes in these unusual oxidation states show some greater oxidizing [Ce(IV)] or reducing [Sm(II)] power. Along with their interesting redox properties, Yb(II) and Ce(IV) are especially attractive due to their diamagnetism making characterization much simpler by NMR spectroscopy. Although Ce(IV) complexes might be interesting to explore, the fact that the CzT ligands are easy to oxidize makes them less compatible with this ion. On the other hand, Jin Zou was able to synthesize Yb(II) complexes of the Czx ligand⁶³ and discovered interesting oxidative coupling of primary phosphines¹³⁴. With this information it was thought that the similar CzT ligands would also be good candidates for forming Yb(II) complexes, so this chemistry was explored.

3.5.2 Divalent Lanthanide Complexes

Initial attempts to synthesize a divalent Yb complex of **8b** focused on the protonolysis route, as salt metathesis reactions often yield unwanted side products as discussed previously. Reaction of the convenient divalent Yb starting material, $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2(\text{THF})_2$, with **8b** at room temperature in toluene immediately produced a dark green solution, but upon stirring for a few minutes, the solution slowly lightened in colour and eventually turns yellow. This result is inconsistent with the divalent dark green $(\text{CzX})\text{Yb}[\text{N}(\text{SiMe}_3)_2](\text{THF})$ obtained by Zou. The colour change from dark green to yellow strongly suggests oxidation has taken place from Yb(II) to Yb(III). This was confirmed by ^1H NMR spectroscopy since the resulting spectrum was of a paramagnetic complex, consistent with trivalent Yb. The most obvious explanation for this redox reaction is that the ligand is being reduced (most likely the NH of the carbazole) while the Yb is being oxidized. In order to test this hypothesis, we removed the possibility of carbazole NH reduction by methylating the carbazole nitrogen to give a methyl version of the ligand $^{\text{Me}}\text{CzT}^{\text{iPr}}$, **8e** (Scheme 3.9).



Scheme 3.9 Methylation of carbazole NH

The same reaction was then repeated on NMR scale using the new methylated ligand with $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2(\text{THF})_2$ in benzene- d_6 . In this case the solution was dark red-purple and the ^1H NMR spectrum, while broad, showed only resonances within the diamagnetic window (0-9 ppm). The ^1H NMR spectrum of the product suggests the ligand is bound to the Yb through the neutral tetrazole nitrogens while the silylamide ligands are retained producing $(^{\text{Me}}\text{CzT}^{\text{iPr}})\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2$ (**22**) as the product. This sample was left for several days and no change in colour from dark red-purple or in the diamagnetic ^1H NMR spectrum were observed suggesting that no oxidation process was occurring. Complex **22** was never purified, but this simple test clearly suggests that NH reduction of **8b** by Yb(II) is faster than the acid-base reaction with $\text{N}(\text{SiMe}_3)_2$ in this case. Unfortunately, this redox phenomenon prevented us from isolating the desired divalent $(\text{CzT}^{\text{iPr}})\text{Yb}[\text{N}(\text{SiMe}_3)_2]$ complex by use of protonolysis.

Although sometimes plagued by “ate” complex formation, metathesis is another route to synthesize a divalent Yb complexes especially since the base-free starting material YbI_2 is readily available. Also, in the case of salt metathesis, there is no carbazole NH present so the ligand cannot be reduced at that site by Yb(II). Reaction of YbI_2 with one equivalent of $\text{Li}^+[\text{CzT}^{\text{iPr}}]^-$ (**16**) in THF at room temperature produced a dark green solution that yielded a pale green-brown crude product after filtration and removal of solvent. Initially, the ^1H NMR spectrum of this product displayed broad resonances in the diamagnetic region, but over time the solution slowly turns yellow and the NMR shows the growth of paramagnetic peaks. This observation was consistent over multiple trials in varying NMR solvents (toluene and benzene) and the colour change also occurred in small test reactions in the glovebox suggesting that hydrolysis is not the culprit. The appearance

of the paramagnetic peaks and the colour change from dark green to yellow suggests that the final product formed is in fact Yb(III). An obvious explanation for this result is that the Yb(II) is being oxidized while the ligand is again being reduced but at a site other than the carbazole NH (which is not present here). To support this hypothesis, the redox potential of the ligand **8b** itself was investigated in the form of the zinc complex **9** (as discussed in Section 2.4.2). The CV of **9** showed that while the ligand itself is quite easily oxidized, it showed no reduction peaks within the solvent window of the cyclic voltammogram (to -2.5 V vs. Fc/Fc^+). Unfortunately, we were unable to obtain a CV directly on the actual Yb product due to its high air sensitivity so it is impossible to say for sure that the ligand is not reduced as the reduction potential of the ligand will be somewhat different on Yb than on Zn. However, it is unlikely that the reduction potential would change enough to be within the Yb(II)/Yb(III) oxidation window (-1.15 V vs. SHE, or approximately -1.77 vs Fc/Fc^+)^{174, 171, 175}.

While attempts to grow X-ray quality crystals of the $(\text{CzT}^{\text{iPr}})\text{YbI}$ product were unsuccessful, poor quality crystals were grown from the same reaction using the related CzTr^{Me} ligand (**Figure 3.12**) that showed similar characteristics of Yb(III) such as the yellow-orange colour and paramagnetic complex NMR spectrum in the final product. The high R value of this crystal structure renders any bond lengths or angles unreliable, but the refinement is sufficient to give basic connectivity information (**Figure 3.12**). Surprisingly, the structure shows two CzTr^{Me} ligands around each Yb centre with one iodide ligand remaining. This is consistent with a Yb(III) oxidation state showing that the metal has in fact been oxidized from Yb(II) to Yb(III). What is perplexing is the lack of any reduction product, especially since it seems the ligand is unlikely to be reduced.

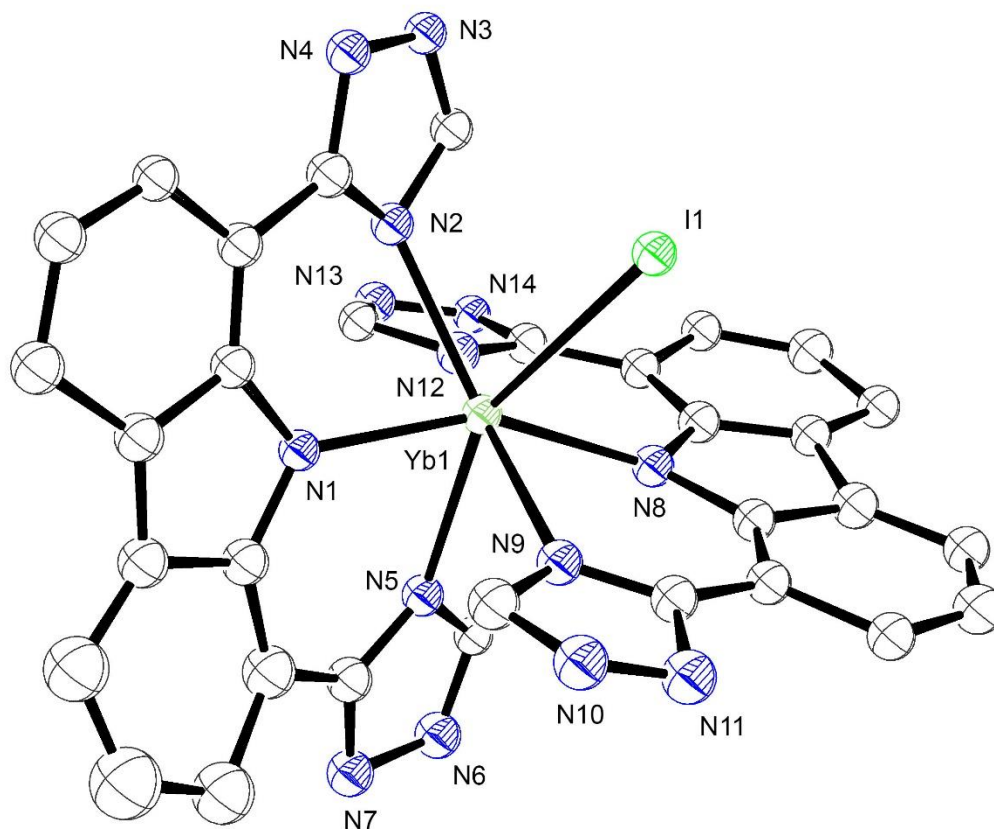
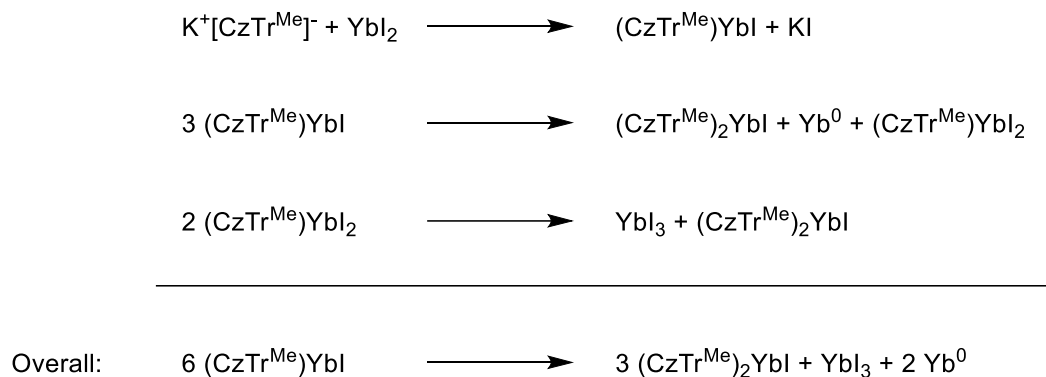


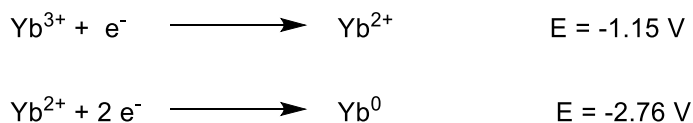
Figure 3.12 ORTEP3¹⁰⁸ plot (10% probability ellipsoids, isotropic refinement) of $(\text{CzTr}^{\text{Me}})_2\text{YbI}$ (t-Bu and Me groups omitted for clarity)

One explanation to account for an Yb(III) product is a disproportionation reaction where the ligand oxidation state remains the same, but Yb(II) disproportionates to Yb(III) and Yb(0) in the final products (**Scheme 3.10**). This reaction pathway would give the isolated $(\text{CzTr}^{\text{Me}})_2\text{YbI}$ as one of the main products, along with YbI_3 (presumably removed by filtration as an insoluble salt) and Yb(0) metal which would be extremely difficult to isolate.



Scheme 3.10 Possible disproportionation pathway

These results are highly speculative and based solely on the crystal structure and evidence of Yb oxidation from Yb(II) to Yb(III) clearly evident by the paramagnetic complex ^1H NMR spectrum. This is one possible redox route that would explain the crystal structure of the bis-ligand Yb(III) complex and no other discernible products by NMR (which is the case for both YbI_3 and $\text{Yb}(0)$). The redox couple involved in this type of disproportionation is unfavourable by about 1.71 V (**Scheme 3.11**) which means in order for this to occur the preferential stabilization of the Yb(III) oxidation state must be significant.



Scheme 3.11 Redox potentials of Yb and Yb ions vs. SHE^{15, 175}

A literature search reveals no reports of Yb(II) complex disproportionation in the solution phase even though the reaction in the solid state is known¹⁷⁶⁻¹⁷⁷. This disproportionation event is impossible to prove without isolation of the Yb(0) reduction

product, which in itself is extremely difficult to achieve. While the postulated Yb(II) disproportionation event seems unlikely, it is hard to ignore similar results found for the Cz_x ligand system⁶³. Upon reacting the divalent Yb complex (Cz_x)YbI(THF)₂ with LiCH₂SiMe₃, a similar colour change from dark green to orange was observed and the product was identified as the (Cz_x)Yb(CH₂SiMe₃)₂ complex which was independently prepared by a metathesis reaction with Yb(III)⁶³. As far as we know LiCH₂SiMe₃ has not been reported to function as an oxidizing agent and in fact Li alkyls are well known reducing agents during metathesis reactions with reducible metal salts¹⁷⁸. The Cz_x ligand system is similar to the CzT and CzTr systems, so the observation of similar results between the two with regards to Yb(II) is consistent. So far, attempts at isolating divalent lanthanide complexes with the CzT or CzTr ligands have been unsuccessful, but Yb(II) complexes of the Cz_x ligand, obtained through both protonolysis and metathesis reaction, (**Figure 3.13**) suggests some electronic differences between the two ligand systems. The fact that in both the CzT and Cz_x ligand systems oxidation to Yb(III) occurs seems like more than just a coincidence. While these results are inconclusive, there may be interesting underlying electronic properties between these ligands and divalent lanthanides. Unfortunately, at this stage it is extremely difficult to understand all the redox events that are occurring.

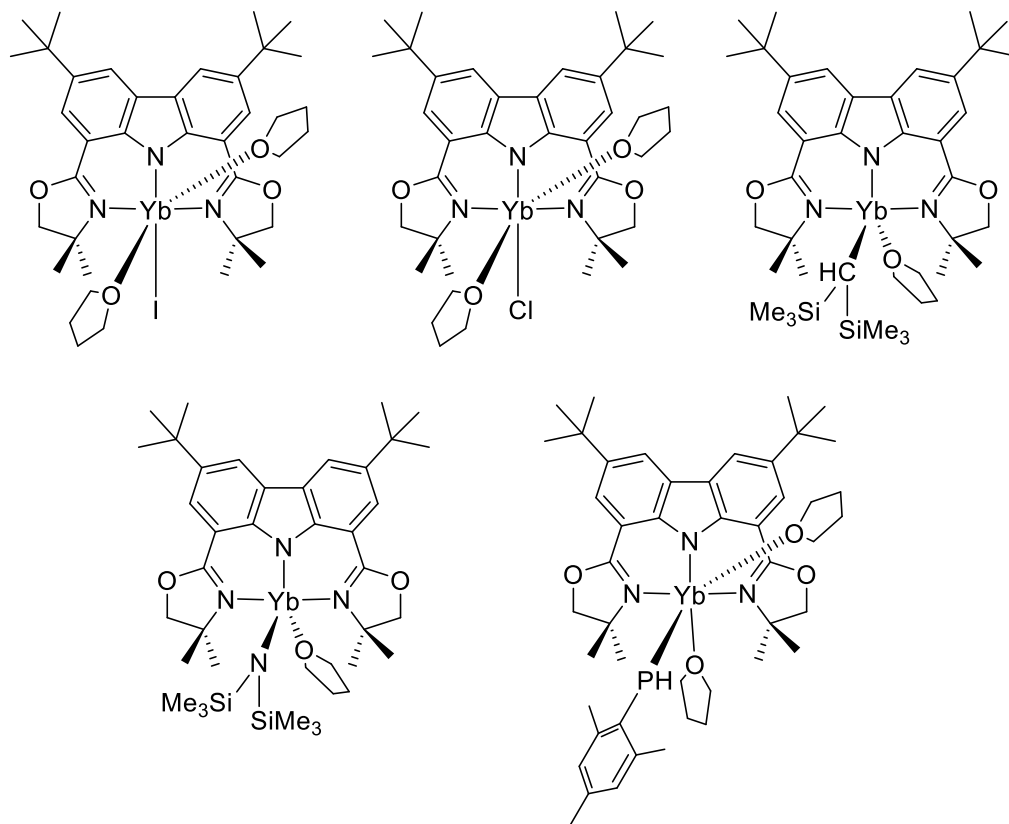


Figure 3.13 Selection of divalent Yb complexes with Czx (**1**)⁶³

3.6 Summary

The use of our novel ligand **8b** to form lanthanide complexes was successful, although not all results were as expected. While the ligand forms simple mono-ligand complexes with the smaller lanthanides in the protonolysis reaction with $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ (**11** and **12**) and salt metathesis reaction in the case of Yb to form the dialkyl **14**, complications arose with the larger lanthanides where $\text{Ln} = \text{Sm}$ and Ce . The unexpected formation of bis-ligand complexes **20** and **21** verified that the ligand set, while less sterically crowding than the previous Czx ligand set, was not bulky enough to prevent further ligand complexation onto the lanthanide centre. Similar multi-ligand products were

also seen in the smaller lanthanides under forcing conditions **19** or when the silylamide ligands were replaced with smaller siloxide ligands **17** and **18**. While these results are less desirable in terms of reactivity, as the lanthanide centre is now too sterically crowded to bind substrates in a catalytic cycle, the crystal structures of these products show the vast binding capabilities of our ligand that were not considered previously in our design. Pincer ligands are generally designed to bind *mer* around a metal centre to aid in stabilization of the complex, but our pincer ligand is able to bind in a pseudo *fac* fashion as well where the metal centre sits well out of the plane of the ligand. In addition, our ligand has shown both tridentate and bidentate binding modes as well as the ability of the tetrazole rings themselves to be canted.

This ligand set also successfully decreased steric bulk around the lanthanide centre in comparison to the previous Czx ligand. The main motivation behind the design of the HCzT and HCzTr ligand family was to remove the steric bulk around the inside of the ring caused by the methyl group in the oxazoline ring to allow better complexation of the lanthanides. This goal was achieved and immediately proven by isolation of **11**, **12** and **13**; the silylamide ligands were too large and bulky for the Czx ligand to accommodate, so in that respect the lanthanide project was a success.

While the mono-ligated complexes did show modest catalytic activity towards ring opening polymerization of ϵ -caprolactone, the complications and undesired complexation of multiple ligands onto the lanthanides suggested that this ligand may not be best suited towards lanthanide chemistry. This caused us to consider the possibility of a better application of this ligand in the smaller metals; mainly first row transition metals as will be discussed in Chapters 4 and 5 in this work.

Chapter 4 Bis-Ligand Transition Metal Complexes

4.1 Introduction

While investigating transition metal chemistry with the CzT^{iPr} ligand it was discovered that two ligands bind preferentially to form air stable bis-ligand octahedral complexes. This was found to be true for several metals across the first row transition metals. While initially bis-ligand complexes were not the desired goal, they proved to be helpful in studying our ligand system further as they gave air stable derivatives. The stability of these complexes allowed us access to characterization techniques, such as CV and solid state magnetic data, that are otherwise unavailable or not practical for the less stable mono-ligand complexes that decompose quickly upon exposure to air. These bis-ligand complexes displayed interesting physical and magnetic properties that may have otherwise gone unnoticed if only the mono-ligand route was pursued. In this chapter the synthesis, characterization and properties of these complexes will be discussed.

4.2 Iron Complexes

The use of Fe in catalysis has attracted growing attention mainly due to its large abundance, low cost and low toxicity compared to some of the larger second and third row transition metals¹⁷⁹⁻¹⁸¹. Fe is a good metal choice for use with our ligands due its smaller size and most stable Fe(II) oxidation state that allows one or two of our anionic ligands to bind. Initially, there were no plans to synthesize bis-ligand Fe complexes of our CzT ligands because we thought there would not be enough room around the metal to

accommodate more than one of our ligands. Furthermore, from a reactivity standpoint, bis-ligand complexes are undesirable because the metal centre is sterically and electronically saturated. Nevertheless, octahedral Fe complexes often possess interesting magnetic behaviour, most notably involving variable spin states in a phenomenon known as spin crossover (SCO) (**Figure 4.1**). Spin crossover is the change in spin state of a complex due to external stimuli such as heat, pressure or light¹⁵. This transition from low spin to high spin states is largely dependant on the ligands that surround the metal centre due to the magnitude of the ligand field splitting. If the energy gap between the t_{2g} and e_g set of orbitals is small enough, thermal population of the e_g orbitals can occur and as the temperature is raised, this population increases. This is possible for first row transition metals with a d^4 through d^7 electron configuration in an octahedral geometry. In the case of Fe(II), d^6 , the ground state is a low spin ($S=0$) state but as the temperature is raised and the e_g orbitals are populated, the spin state eventually becomes high spin ($S=2$). In fact, Fe(II) complexes with N-donor ligands are among the best known SCO complexes in the literature¹⁸². This led us to investigate bis-ligand Fe(II) complexes with our CzT ligands and study the magnetic properties of these complexes.

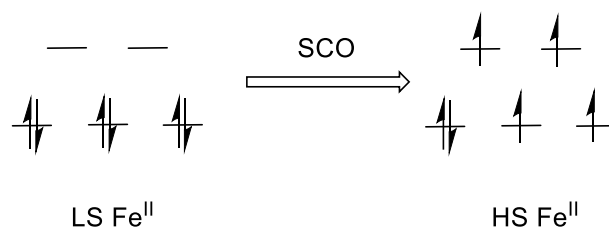
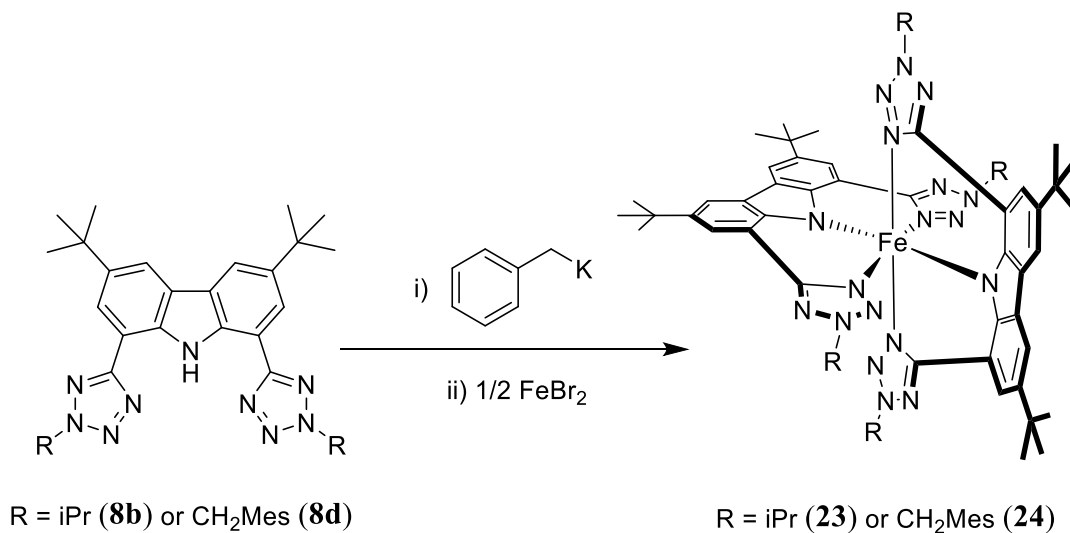


Figure 4.1 Spin crossover (SCO) of Fe(II)

4.2.1 Synthesis and Characterization

Synthesis of the bis-ligand Fe complexes was conducted in the glovebox under an inert atmosphere, although these precautions may not be necessary for their formation. A bis-ligand Fe complex was originally discovered by accident in a salt metathesis reaction between one equivalent of $\text{K}^+[\text{CzT}^{\text{iPr}}]^-$ and anhydrous FeBr_2 . Work-up of the red solution produced deep red crystals that proved to be the bis-ligand complex $(\text{CzT}^{\text{iPr}})_2\text{Fe}$, **23**, by X-ray crystallography. This result was surprising because based on the formation of mono(ligand) complexes with the lanthanides, we felt the ligand was too big to fit twice around the much smaller Fe(II) centre. However, with this knowledge we set out to synthesize the bis-ligand Fe complexes on purpose. Reaction of two equivalents of $\text{K}^+[\text{CzT}^{\text{R}}]^-$ with FeBr_2 (**Scheme 4.1**) produced the desired bis-ligand Fe complexes in high yields as red powders. Interestingly, even the bulkier ligand **8d** produced $(\text{CzT}^{\text{CH}_2\text{Mes}})_2\text{Fe}$, **24**, using the same procedure (**Scheme 4.1**). We had hoped that using a bulky ligand would prevent complexation of a second chelate but this was clearly not the case.



Scheme 4.1 Synthesis of bis-ligand Fe complexes $(\text{CzT}^{\text{iPr}})_2\text{Fe}$ (**23**) and $(\text{CzT}^{\text{CH}_2\text{Mes}})_2\text{Fe}$ (**24**)

While the synthesis of these complexes was carried out in a nitrogen-filled glovebox, complexes **23** and **24** are air stable and do not oxidize or degrade in air over an extended period of time (months). Thermogravimetric analysis (TGA) in air of dry crystals (**Figure 4.2**) shows that **23** is stable to 300 °C. The TGA of ground powdered **23** exposed to air for some time before analysis shows an initial drop in mass (**Figure 4.3**) suggesting that the complex is hygroscopic, picking up about ten water molecules per Fe complex. However, water absorption does not appear to cause complex degradation or ligand protonation.

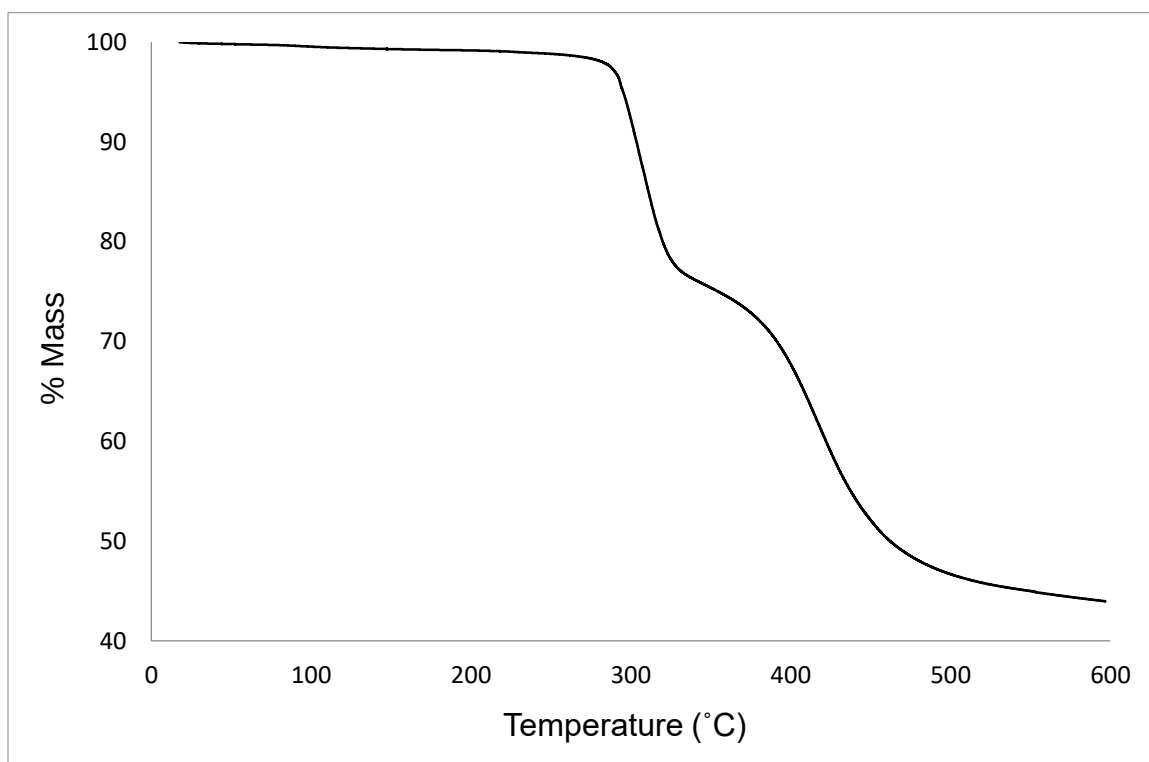


Figure 4.2 TGA of crystals of (CzT^{iPr})₂Fe (**23**)

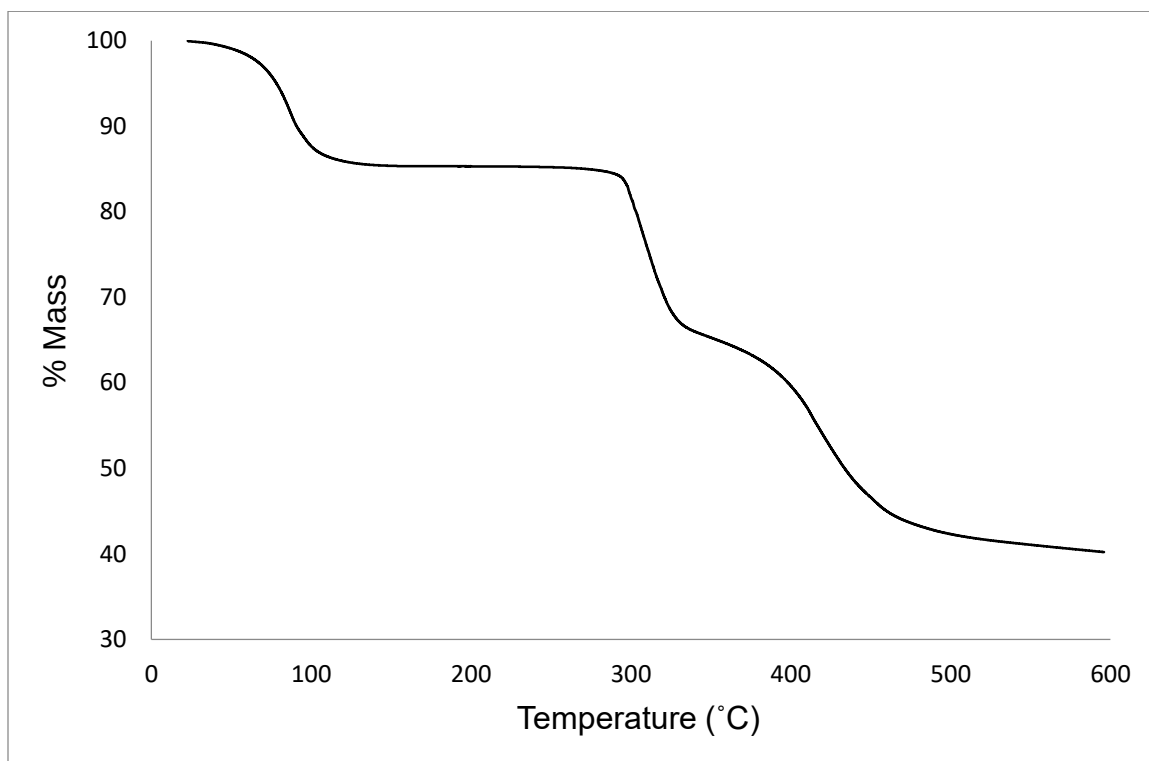


Figure 4.3 TGA of powder sample of (CzT^{iPr})₂Fe (**23**)

The ¹H NMR spectrum of **23** in benzene-D₆ is of a paramagnetic complex (**Figure 4.4**) but very simple suggesting a high spin Fe(II) centre in a high symmetry environment. There is only one resonance for each type of ligand proton indicating overall D_{2d} symmetry. All resonances are broad singlets with line widths ranging from 18-152 Hz (full width at half maximum, $\nu_{1/2}$).

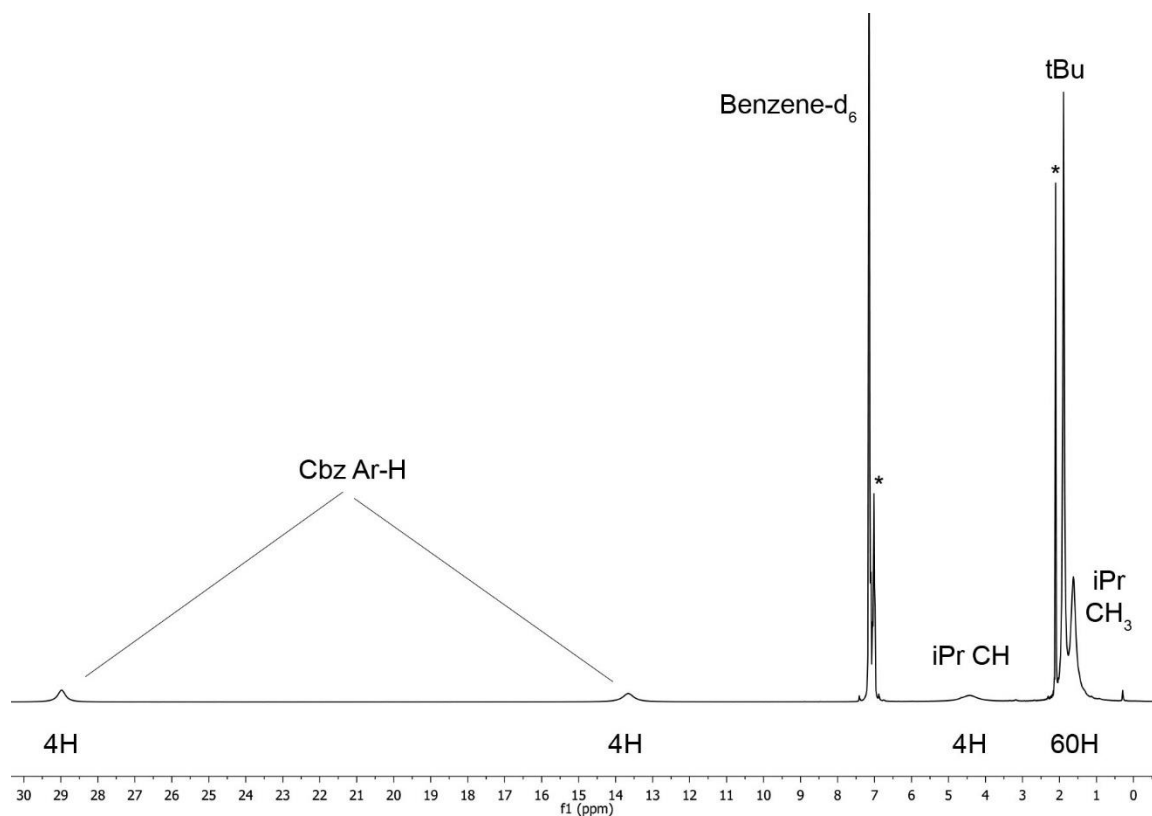


Figure 4.4 ^1H NMR spectrum (300 MHz, C_6D_6 , 298 K) of $(\text{CzT}^{\text{iPr}})_2\text{Fe}$ (**23**) (* denotes residual toluene in the lattice)

The ^1H NMR spectrum of **24** in benzene- D_6 (**Figure 4.5**) is also simple and symmetrical with only one set of ligand resonances, but surprisingly all resonances show modest shifts mostly within the diamagnetic region (0-13 ppm). The sample is clearly not diamagnetic as all resonances are observed as broad singlets ($\nu_{1/2}$ 5-39 Hz) and the carbazole backbone protons in particular are shifted outside the diamagnetic region. Based just on the NMR spectra, the magnetic properties of **23** and **24** are not identical in solution, although both still show some paramagnetism.

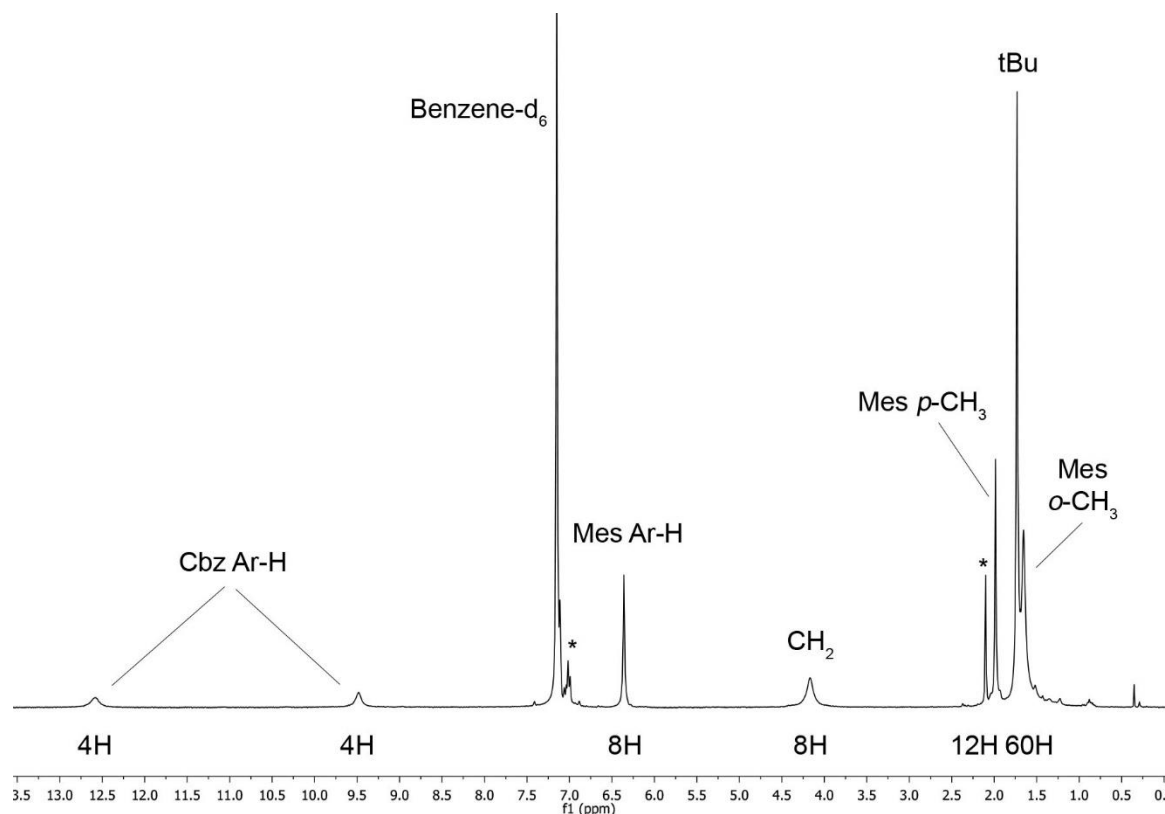


Figure 4.5 ^1H NMR spectrum (300 MHz, C_6D_6 , 298 K) of $(\text{CzT}^{\text{CH}_2\text{Mes}})_2\text{Fe}$ (**24**) (* denotes residual toluene in the lattice)

4.2.2 X-ray Structural Studies

The solid state structures of both **23** and **24** were determined by X-ray crystallography. Selected bond lengths and angles for both structures are collected in **Table 4.1**. Complex **23** crystallizes in the triclinic P-1 space group with seven toluenes of solvation in the lattice and two Fe molecules per unit cell. The structure was determined at low temperatures (120 K) meaning the Fe(II) is in the low spin state (*vide infra*), but this is not necessarily true at higher temperatures (as suggested by the paramagnetic complex NMR spectrum). The full magnetic investigation of **23** will be discussed later in this chapter.

Table 4.1 Selected bond lengths (Å) and angles (°) of (CzT^{iPr})₂Fe (**23**) and (CzT^{CH₂Mes})₂Fe (**24**)

	23		24
Fe1-N1	1.972(2)	Fe1-N1	1.958(2)
Fe1-N7	1.978(2)	Fe1-N6	1.951(2)
Fe1-N2	1.999(2)	Fe1-N2	1.972(2)
Fe1-N6	1.983(2)	Fe1-N7	1.960(2)
Fe1-N11	2.013(2)		
Fe1-N15	2.003(2)		
N1-Fe1-N2	89.85(8)	N1-Fe1-N2	89.81(5)
N1-Fe1-N6	89.36(8)		
N1-Fe1-N7	179.17(7)	N1-Fe1-N6	180.0
N1-Fe1-N11	91.28(8)	N1-Fe1-N7	90.25(5)
N1-Fe1-N15	89.69(7)		
N7-Fe1-N2	89.72(8)	N6-Fe1-N2	90.19(5)
N7-Fe1-N6	91.07(8)		
N7-Fe1-N11	89.44(8)	N6-Fe1-N7	89.75(5)
N7-Fe1-N15	89.60(8)		
N2-Fe1-N6	179.14(8)	N2-Fe1-N2'	179.63(9)
N2-Fe1-N11	91.85(8)	N2-Fe1-N7	90.50(6)
N2-Fe1-N15	90.20(8)		
N6-Fe1-N11	87.82(8)		
N6-Fe1-N15	90.14(8)		
N11-Fe1-N15	177.73(8)		
Cant angle¹⁰⁷ Tz₁	6.25	Cant angle¹⁰⁷ Tz₁	-8.41
Cant angle¹⁰⁷ Tz₂	-1.82		
Cant angle¹⁰⁷ Tz₃	-4.17	Cant angle¹⁰⁷ Tz₂	-9.91
Cant angle¹⁰⁷ Tz₄	3.17		

Tz₁ refers to C21 and N2-N5; Tz₂ refers to C25 and N6-N9; Tz₃ refers to C49 and N11-N14; Tz₄ refers to C53 and N15-N18.

A representative ORTEP plot of the asymmetric unit of **23** is shown in **Figure 4.6**.

The six coordinate geometry around the Fe centre is approximately octahedral, with the bond angles between adjacent nitrogen donors from the ligand on the Fe centre ranging from 87.82(8)°-91.85(8)°. The CzT^{iPr} ligands both bind in a *mer* fashion around the Fe centre, with the two N_{Cbz} trans to each other. The ligands are essentially planar with the

cant angles between 1.8-6.3°. This suggests there is not significant steric crowding in the complex as the pincer ligands are not distorted very much in the tridentate *mer* geometry.

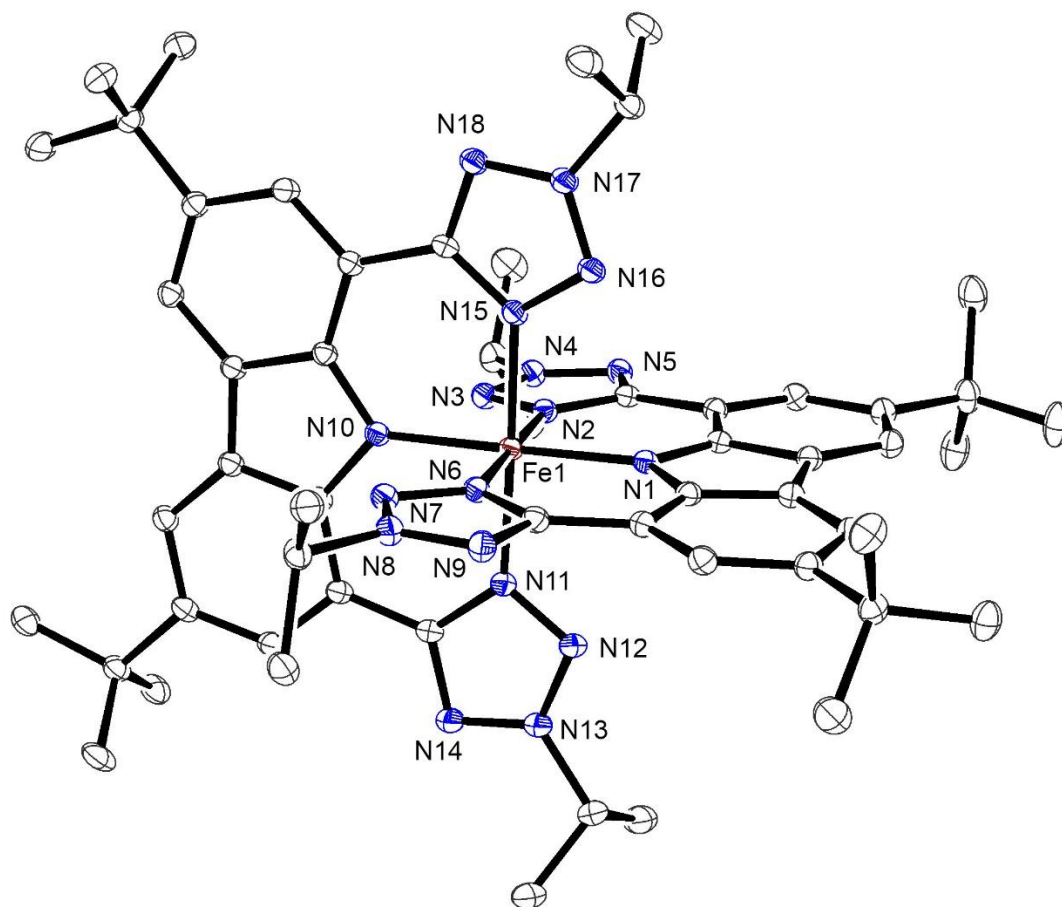


Figure 4.6 ORTEP3¹⁰⁸ plot (30% probability ellipsoids) of (CzT^{iPr})₂Fe (**23**) (solvent and H atoms omitted for clarity)

The Fe-N_{Cbz} bond lengths in **23** of 1.972(2) and 1.978(2) Å are consistent with other known carbazolate Fe complexes (range corrected to match six coordinate low spin Fe(II)¹³⁰: 1.938(4)-2.011(3) Å, median 1.974 Å)¹⁸³⁻¹⁸⁶. The same range corrected for six coordinate high spin Fe(II)¹³⁰ is 2.108(4)-2.181(3) Å with a median of 2.144 Å. The Fe-

N_{Cbz} lengths in **23** being well below 2 Å strongly suggests a low spin state. There are several six coordinate Fe(II) tetrazole complexes known in the literature, most of them being SCO complexes. The Fe- N_{Tz} bond lengths in these complexes can be classified into three categories: low spin, high spin and an intermediate spin state where the complex is undergoing the spin crossover phenomenon and there is thermal equilibrium between the different spin states. The range for LS six coordinate Fe(II) is 1.951(3)-2.038(4) Å (median, 1.983 Å), HS range is 2.010(4)-2.208(4) Å (median, 2.176 Å) and the range for the intermediate spin state is 1.972(2)-2.226(6) Å (median, 2.013 Å)¹⁸⁷⁻¹⁹⁴. Based on these literature values there is some overlap in bond lengths between the three spin states, but in general under 2 Å is low spin and over 2 Å is high spin, with the intermediate spin state having values varying in between. The Fe- N_{Tz} lengths in **23** of 1.983(2)-2.013(2) Å are most consistent with the low spin literature values and along with the short Fe- N_{Cbz} bond lengths, confirm the low spin state of **23** at low temperatures.

A representative ORTEP plot of **24** is shown in **Figure 4.7**. Similar to **23**, the structure was determined at 120 K. Complex **24** crystallizes in the monoclinic C2/c space group with two Fe molecules per unit cell, and half of one molecule of **24** in the asymmetric unit, this leads to some labelling discrepancies between **23** and **24**. Similar to **23**, the geometry of **24** is octahedral with the bond angles between adjacent nitrogen donors from the ligand and the Fe centre ranging from 89.50°-90.50° with the nitrogens from the $\text{CzT}^{\text{CH}_2\text{Mes}}$ ligand binding in a *mer* fashion around the Fe.

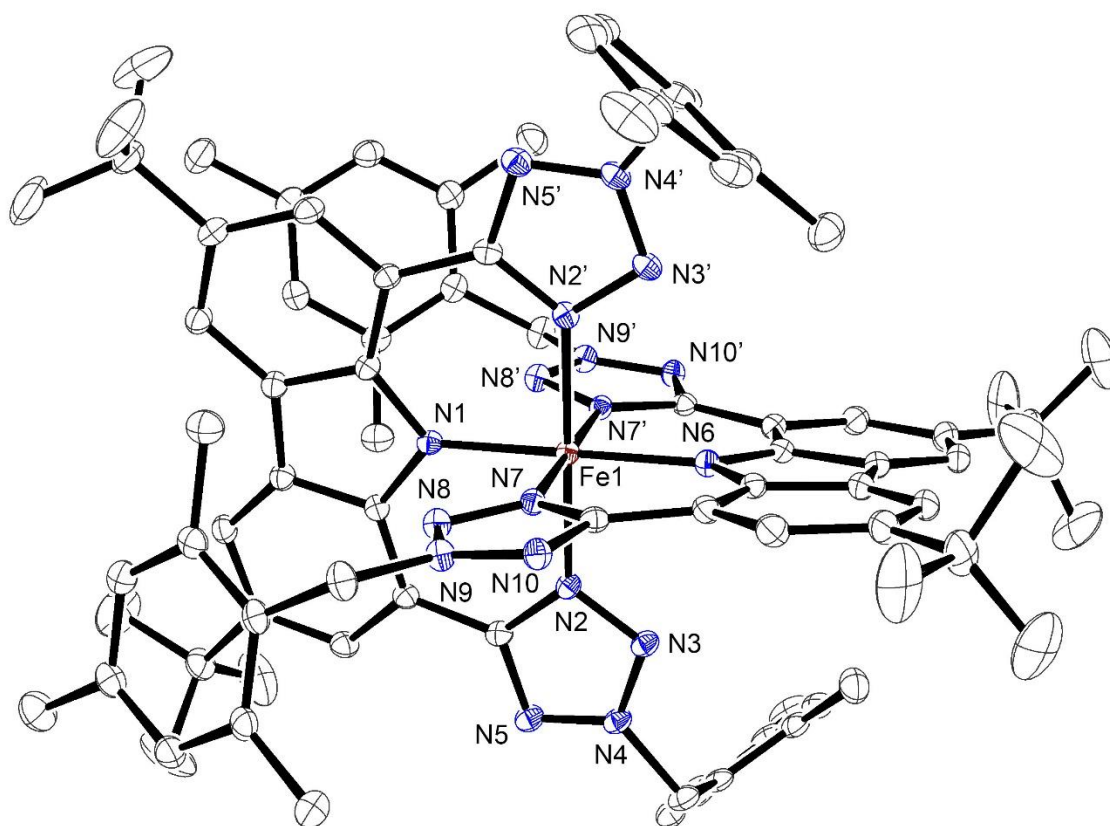


Figure 4.7 ORTEP3¹⁰⁸ plot (30% probability ellipsoids) of (CzT^{CH₂Mes})₂Fe (**24**) (solvent and H atoms omitted for clarity)

The Fe-N bond lengths in **24** are even shorter than in **23** with the N_{Cbz}-Fe bonds at 1.951(2) Å and 1.958(2) Å and the elongated neutral N_{Tz}-Fe bond lengths of 1.960(2) Å and 1.972(2) Å. These lengths are consistent with other low spin Fe(II) carbazolidine and tetrazole complexes as discussed above. These shorter bond lengths in **24** versus **23** also suggests that the bulkier ligands in **24** are not causing increased steric crowding. On the other hand, unlike **23**, the ligands in **24** are twisted somewhat and do not lay completely flat. The measured cant angles between the carbazole and each tetrazole ring in **24** are almost double what was found in **23** at 8.4° and 9.9°. This could be due to the added bulk of the CH₂Mes substituent compared to the iPr. The slight increase in crowding that this

distortion implies makes it even more surprising that the Fe-N bond lengths in **24** are shorter than those in **23** at similar temperatures. However, these short Fe-N bond lengths suggest a low spin Fe(II) centre in the solid state. It is notable that both X-ray bond length data in the solid state and ^1H NMR data in solution suggest that the low spin contribution is greater in **24** than in **23**. These observations prompted us to look at the solid state magnetism of these complexes in more detail.

4.2.3 Magnetic Studies

The inconsistencies between the NMR spectra and X-ray crystal structures for both **23** and **24** led us to further study the magnetic properties of these complexes. The paramagnetic complex ^1H NMR spectrum suggests unpaired electrons as expected for high spin Fe(II) while the short Fe-N bond lengths determined by X-ray crystallography at lower temperatures suggests low spin Fe(II) in both cases. The most likely cause of this discrepancy is a temperature dependant change in spin state (spin crossover) which is common for octahedral d^6 metals. This is especially true for Fe(II) which accounts for most of the SCO occurrences, particularly with nitrogen ligands^{190, 195-204}.

Solution state magnetism can be probed by the Evans' method which relies on the difference in chemical shift of the solvent resonances in the presence and absence of a paramagnetic solute²⁰⁵. The Evans' method was conducted in benzene- D_6 at room temperature for **23** and gave a value of $4.1 \mu_{\text{B}}$. This value is not consistent with either a low spin Fe(II) ($\mu = 0 \mu_{\text{B}}$) or a high spin state with four unpaired electrons ($\mu = 5.0\text{-}5.6 \mu_{\text{B}}$). While there is a fair amount of error associated with the Evans' method (typically $\pm 0.3 \mu_{\text{B}}$), several measurements on different batches of recrystallized compound gave values ranging

from 3.8-4.4 μ_B with an average value of 4.1 μ_B for all measurements. It is possible that the value of 4.1 μ_B represents an intermediate spin state at room temperature where the Fe has not fully transitioned to high spin. To probe this further a variable temperature Evans' method experiment was conducted on a sample of **23** in toluene- D_8 to determine the full range of μ over a range of temperatures. The variable temperature plot of the resulting magnetic data is shown in **Figure 4.8**. As the data clearly shows, there is a smooth transition from $\chi T=0.5$ to $\chi T=2.0$ which translates to magnetic moment values of 2.0 to 4.0 μ_B respectively. While neither of these values equates to low spin or high spin states, it shows a temperature-induced SCO within the temperature range of 200-350 K. This confirms our suspicions that **23** undergoes a SCO near room temperature.

With these interesting solution magnetic results, we sought further solid state magnetic studies to fully understand the magnetic behaviour of **23**. The most obvious course of action to prove a temperature-induced SCO phenomenon in the solid state is through SQUID (superconducting quantum interference device) magnetometry. This gives a similar plot to **Figure 4.8** but over a broader range of temperatures not available in the solution state due to solvent melting point, boiling point and solubility restrictions; the solid state magnetic data for **23** is shown in **Figure 4.9**²⁰⁶. The most striking feature of this data is the clear SCO behaviour including a two-step transition that was not seen in the solution magnetic data. Similar to the solution data there is a clear transition from $\chi T=0.5$ to $\chi T=2.0$ as observed in the solution state, but an intermediate state at approximately $\chi T=1.5$ is observed from 200 K to 330 K.

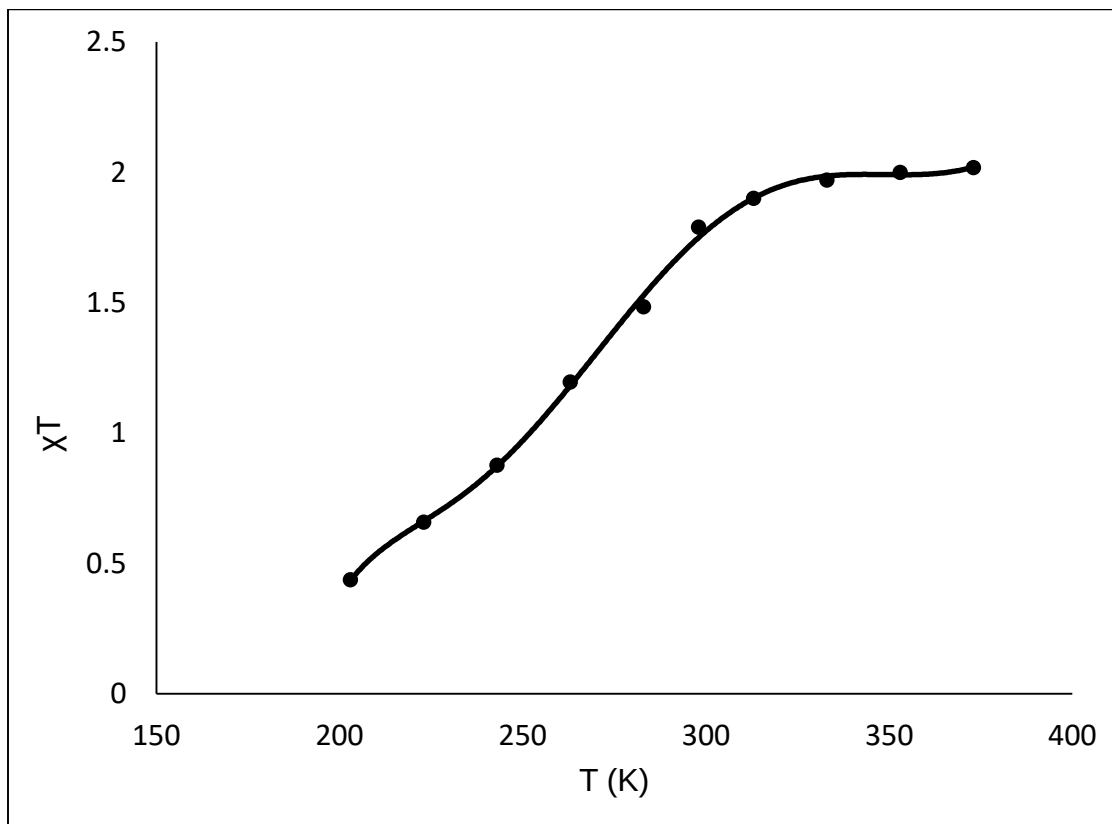


Figure 4.8 Variable temperature solution state magnetic data of $(\text{CzT}^{\text{iPr}})_2\text{Fe}$ (**23**)

This suggests some sort of intermediate spin state that is stable over a 100 °C range consisting of a mixture of low spin and high spin states. While two step transitions in SCO are rare, they are not unknown^{198, 207-211}. This is most commonly seen in polymers or clusters where one Fe centre has transitioned from low spin to high spin, but other Fe centres within the polymer have not yet transitioned. In our case it is more likely explained by some sort of crystal packing effect where one Fe complex has transitioned from low spin to high spin, but the requisite increase in Fe-N bond lengths makes it energetically more difficult for a neighbouring complex to do the same. The high barrier for the second transition is presumably a reflection of the increased energy required to break the crystal packing.

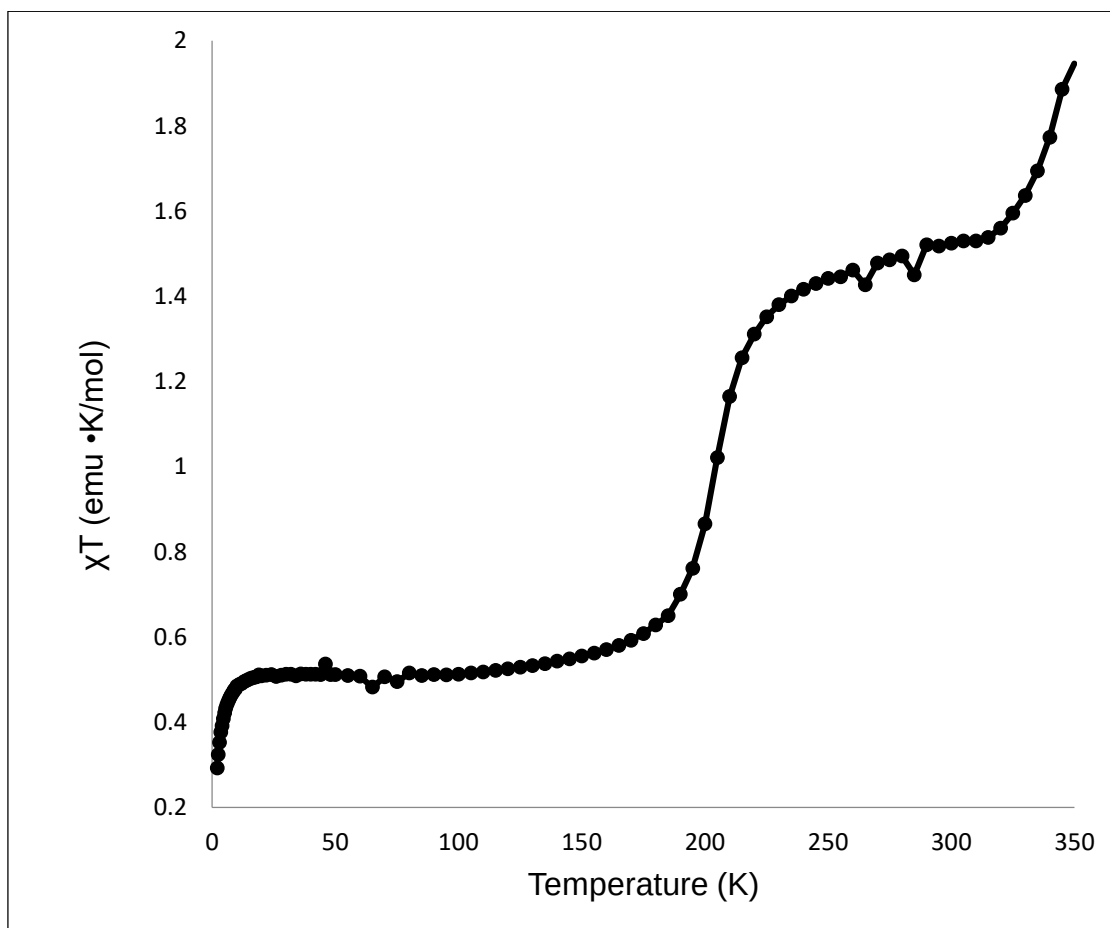


Figure 4.9 Solid state magnetic data of $(\text{CzT}^{\text{iPr}})_2\text{Fe}$ (**23**)

This idea is backed up by the solution data where there is only one SCO transition observed because there are no crystal packing effects in solution. It is also interesting that the two transitions seen are quite abrupt, perhaps suggesting some cooperative effects where the stable arrangement occurs. It can be seen that as the sample approaches 0 K the system becomes fully low spin where the magnetic moment is zero.

Mössbauer (MB) spectroscopy was employed to further investigate the temperature-induced SCO of **23**. Mössbauer spectroscopy is a powerful method to monitor Fe complexes because it gives evidence of the oxidation and spin state as well as the

coordination number around the Fe centre²¹²⁻²¹³. There are two main parameters of importance in Mössbauer spectroscopy: the quadrupole splitting (ΔE_Q) and the isomer shift [$\delta(\text{Fe})$]. The quadrupole splitting is the width of the doublet while the isomer shift is the centre point of the doublet (or singlet if no quadrupole splitting is present). With these two values, the oxidation and spin state of the Fe present can be determined by comparison to a library of known values for similar complexes. For reference, these values have been condensed into a general graph showing the typical values for different types of Fe species (**Figure 4.10**). The low spin state in **Figure 4.10** is denoted by roman numerals [Fe(II)] while the high spin state is denoted by superscript numbers (Fe^{2+}). The coordination number is denoted by the superscript number in square brackets before Fe (eg. $^{[6]}\text{Fe}$). Since the measured Mössbauer values are compared to known literature values rather than derived theoretically there can be some ambiguity associated with the type of Fe complex from Mössbauer. Nevertheless, it is a very useful tool even though there is some overlap in values between different spin and oxidation states of Fe as seen by the overlapping areas in **Figure 4.10**. All Mössbauer results in this thesis were obtained by Dr. Barbara Sawicka, who also helped to analyze and interpret the results using her extensive knowledge of Mössbauer. The circled numbers seen in **Figure 4.10** are correlated to MB spectra throughout this work for ease of assignment, the matching number can be found on the applicable MB spectra of each complex in question. **Figure 4.10** will be referenced several times throughout this work when MB results are discussed.

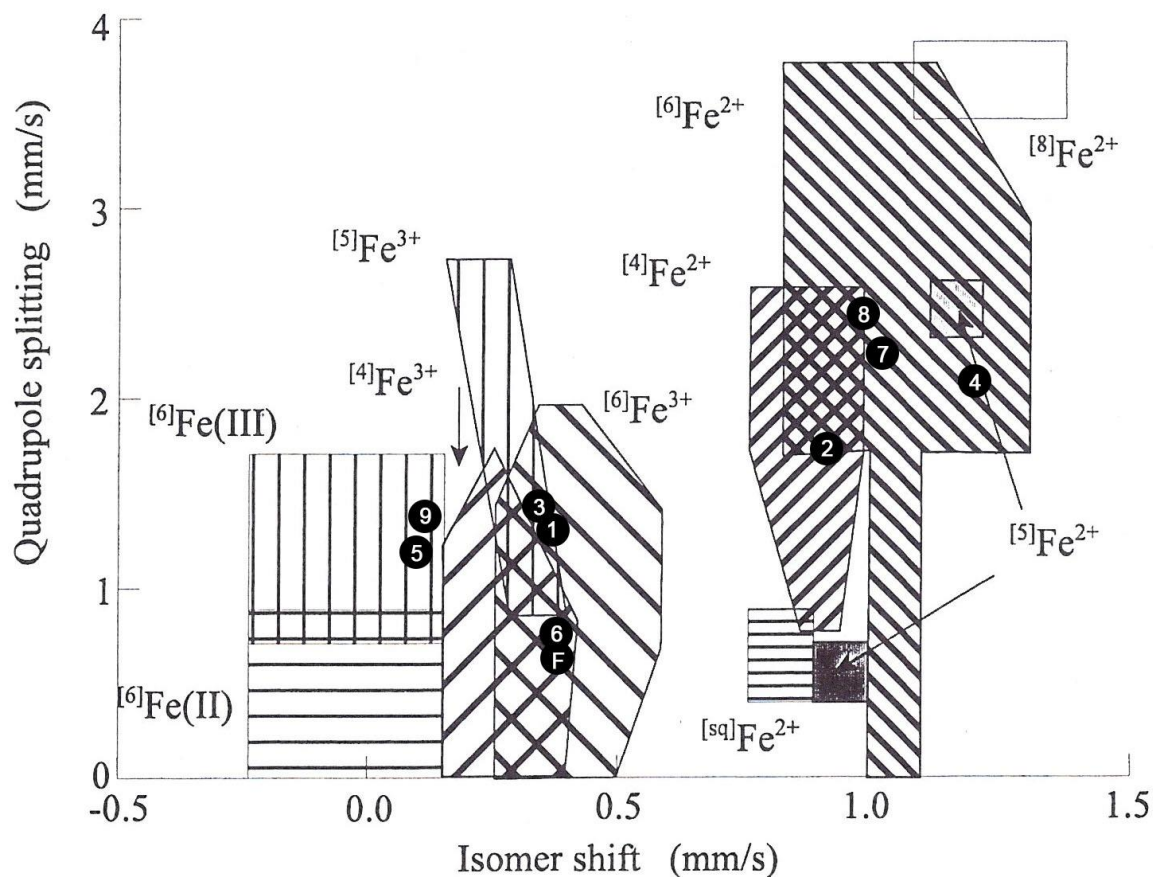


Figure 4.10 Allowed ^{57}Fe quadrupole splitting-isomer shift combinations for different valence states and coordination (reprinted with permission from ²¹²). MB number-complex correlation: 1 and 2: complex **23**, 3: complex **24**, 4-6: complex **25**, 7: complex **28**, 8: complex **30**, 9: complex **36**, F: ferrihydrite.

The room temperature Mössbauer spectrum of **23** is shown in **Figure 4.11**. There are two doublets seen in the spectrum, each one due to a different “type” of Fe present in the sample. The low spin Fe(II) is seen as the doublet with ΔE_Q of 1.30 mm/s and $\delta(\text{Fe})$ of 0.42 mm/s, this doublet accounts for 38% of the Fe present in the sample (solid arrows). The high spin Fe(II) is seen as the doublet with ΔE_Q of 1.89 mm/s and $\delta(\text{Fe})$ of 0.95 mm/s, this doublet accounts for the remaining 62% of the Fe present in the sample (dashed arrows).

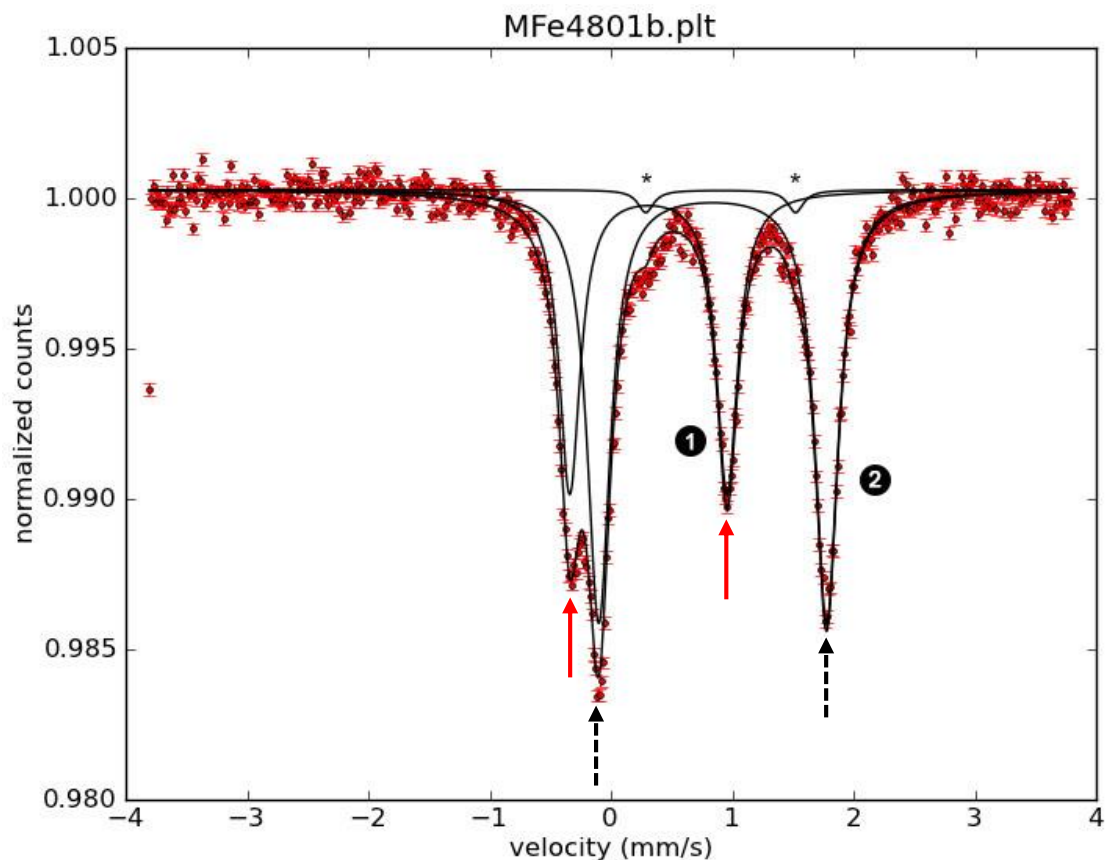


Figure 4.11 Mössbauer spectrum of $(\text{CzT}^{\text{iPr}})_2\text{Fe}$ (**23**) at room temperature (showing actual data (ϕ) and deconvoluted peak fits (solid lines). The small doublet indicated with an asterisk (*) is due to a small unknown impurity in the sample).

While the LS Fe(II) values do not match well with the graph of data shown in **Figure 4.10**, it is consistent with similar six coordinate Fe SCO complexes with nitrogen-based ligands in the literature^{190, 197, 199, 207, 214}. The Mössbauer spectrum clearly demonstrates that there is a mixture of both high spin and low spin Fe(II) present at room temperature which matches both the solid state and solution state magnetic data discussed previously. What is even more helpful is that Mössbauer is able to quantify the amount of both spin states present at a given temperature, which SQUID and Evans' method data are not able to provide directly. To further probe the temperature dependence of the spin

transition, the Mössbauer sample was cooled with liquid nitrogen and the spectrum recorded again. The liquid nitrogen cooled Mössbauer spectrum of **23** is shown in **Figure 4.12**.

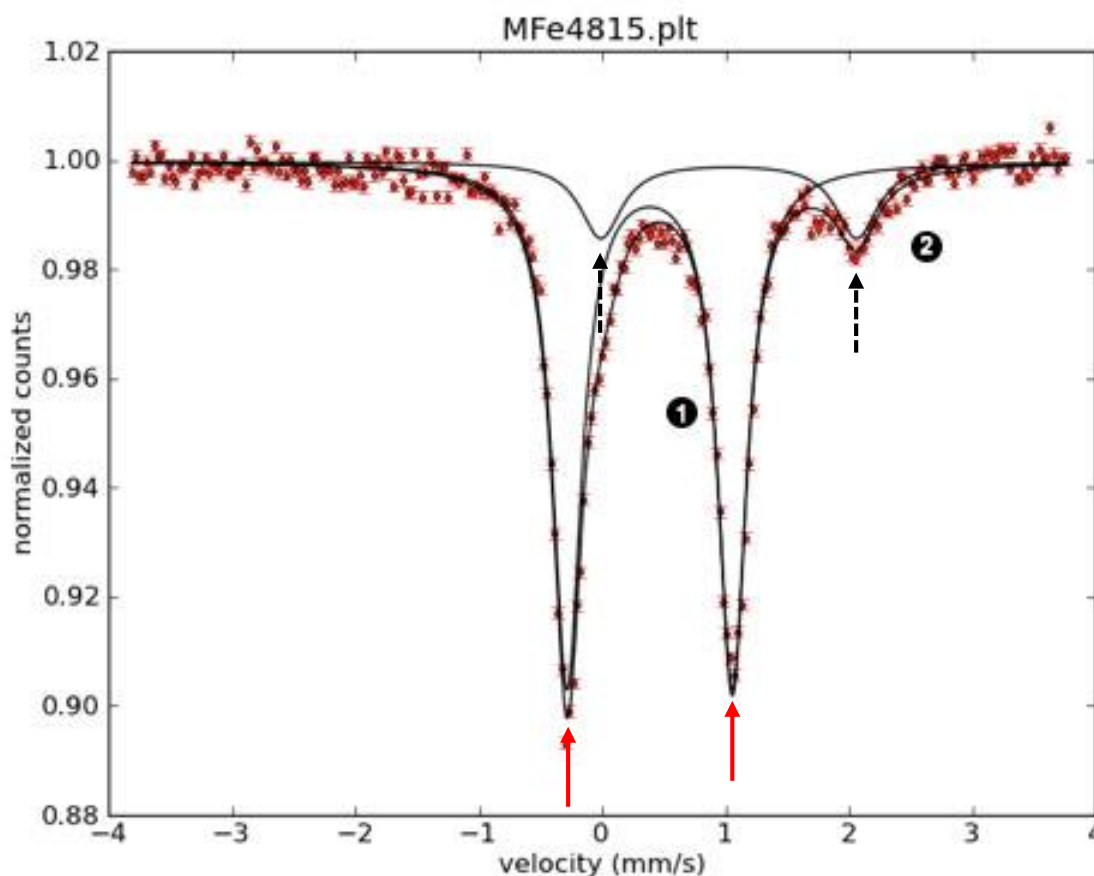


Figure 4.12 Liquid nitrogen cooled low temperature Mössbauer spectrum of $(\text{CzT}^{\text{iPr}})_2\text{Fe}$ (**23**)

At cooler temperatures there is a clear increase in the low spin Fe(II) doublet to 83% and the high spin doublet has decreased to 17%. The low spin doublet is seen at ΔE_Q of 1.34 mm/s and $\delta(\text{Fe})$ of 0.50 mm/s while the high spin doublet is at ΔE_Q of 2.07 mm/s and $\delta(\text{Fe})$ of 1.14 mm/s. This increase in amount of low spin Fe(II) present at lower

temperatures is completely consistent with the solid and solution state magnetic data obtained by other methods. With use of Mössbauer spectroscopy, SQUID magnetometry and variable temperature Evans' method we have determined that **23** goes through a temperature induced spin crossover transition that is one step in solution and two steps in the solid state. With these results we then tested whether the analogous **24** complex displayed similar magnetic tendencies.

The Evans' method was conducted on **24** and gave a value of only $1.86 \mu_B$. This value matches fairly well with the calculated theoretical value of $1.7\text{--}1.8 \mu_B$ for one unpaired electron, which in this case is not possible. While this result verifies that **24** is not diamagnetic, it does not match for a high spin state, and gives a much lower magnetic moment at room temperature in solution than the similar complex **23**. This result alone shows that the magnetic behaviour of **23** and **24** are not identical and simply changing the substituent of the ligand from an iPr to a CH₂Mes impacts the magnetic properties of the complex. It is still possible that **24** undergoes a similar SCO phenomenon to **23**, but just at a higher temperature. This would explain the lower magnetic moment at room temperature while still accounting for the paramagnetic influence seen in the ¹H NMR spectrum. To determine the spin state of the Fe in the solid state at room temperature, Mössbauer spectroscopy was again employed. The Mössbauer spectrum of **24** recorded at room temperature is shown in **Figure 4.13**. Interestingly the spectrum shows only one species of Fe present at room temperature unlike the spectrum of **23**. The ΔE_Q of 1.46 mm/s and $\delta(\text{Fe})$ of 0.39 mm/s are consistent with an six coordinate low spin Fe(II) species. These values are similar to those seen in **23** for the low spin portion of the complex, but there is no high spin fraction present.

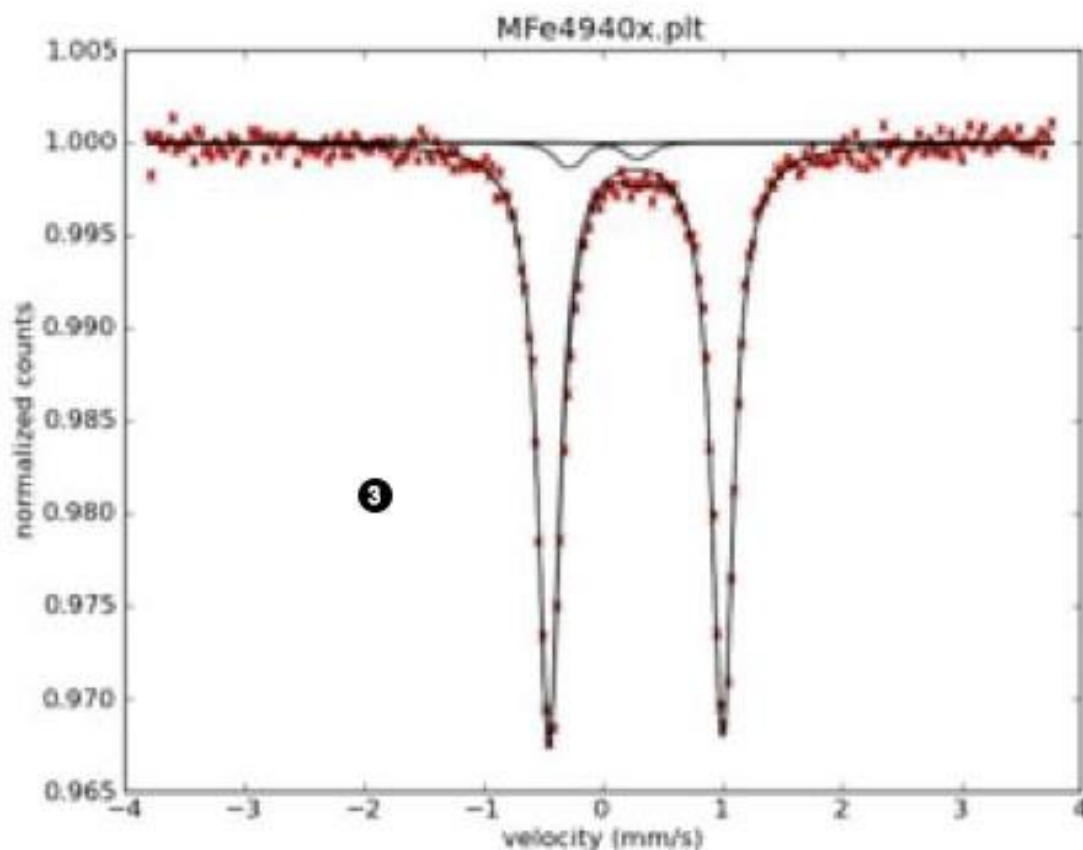


Figure 4.13 Mössbauer spectrum of $(\text{CzT}^{\text{CH}_2\text{Mes}})_2\text{Fe}$ (**24**) at room temperature

This result is not consistent with the solution state magnetic moment determined by Evans' method that verified a paramagnetic contribution in the complex. Both the Mössbauer spectrum at room temperature and the X-ray crystal structure that was determined at low temperatures are consistent with low spin Fe(II), but the ^1H NMR spectrum is not diamagnetic and gives a magnetic moment of $1.86 \mu_{\text{B}}$ suggesting it is not low spin. Two possible explanations can be considered; the magnetic moment seen in the solution state might be due to a paramagnetic or ferromagnetic impurity in the NMR sample causing the paramagnetic shift of the diamagnetic low spin complex. This is unlikely as the solution state magnetic moment has been measured several times on

different batches of recrystallized sample and gives very similar magnetic moments each time. Another explanation could be a possible TIP (temperature independent paramagnetic) contribution, which is known in other low spin Fe(II) complexes²¹⁵⁻²¹⁶. Unfortunately, we were unable to obtain solid state magnetic moment measurements via SQUID magnetometry due to the demise of the departmental SQUID instrument and inability to access a working magnetometer. Ideally solid state magnetic data should be obtained on **24** to prove or disprove the TIP theory.

4.2.4 Cyclic Voltammetry

Since **23** is an air stable complex we decided to investigate its electronic properties by cyclic voltammetry. The CV of the complex would hopefully give us good insight into any possible redox processes of the metal or ligand. Additionally, this could provide insight into the redox behaviour of the air sensitive mono-ligand complexes (Chapter 5). The cyclic voltammogram of **23** done at room temperature in THF is shown in **Figure 4.14**. The CV clearly shows three reversible peaks within the solvent window with $E_{1/2}$ values of approximately -1.7, -0.5 and 0.3 V, with respect to an internal Fc/Fc⁺ redox couple. The two reversible peaks at -0.5 and 0.3 V are very similar in shape and size and based on CV data of **9** from Chapter 2 it is possible these peaks are due to the CzT ligands themselves. This would mean the reduction wave around -1.7 V may be due to the Fe(II)/Fe(I) reduction which has been reported between -1.82 to -2.21 V in other Fe complexes²¹⁷⁻²¹⁹. While it is fairly uncommon to observe this Fe(I) redox peak, it is less likely that the Fe(II)/Fe(0) peak would be observed at that positive of a potential as the Fe(I)/Fe(0) reduction has been observed between -2.28 to -2.45 V²¹⁸⁻²¹⁹. Unfortunately, THF has a fairly limited solvent

window on the oxidation side so no redox processes at potentials more positive than 0.6 V can be seen. This limitation prevents us from observing the possible Fe(II)/(III) redox couple. In order to check if there are additional redox processes occurring past 0.6 V, DCM was used as the solvent in order to open the solvent window wider on the oxidation side. The cyclic voltammogram of **23** done at room temperature in DCM is shown in **Figure 4.15**.

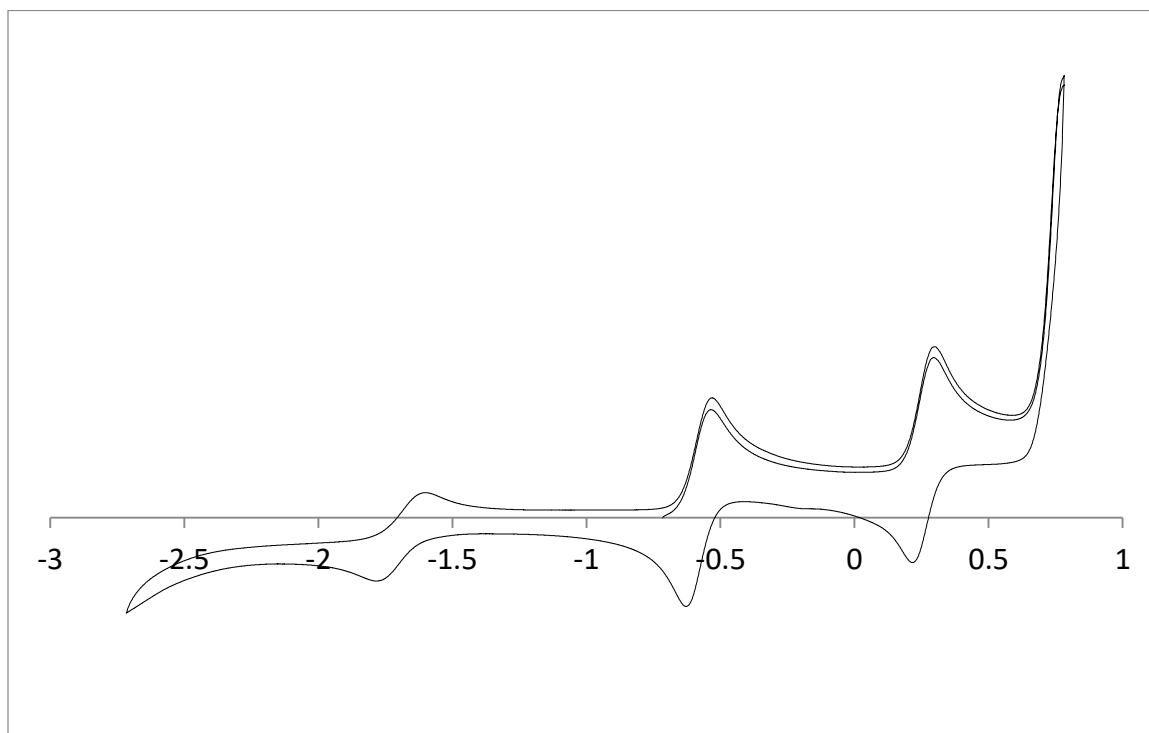


Figure 4.14 Cyclic voltammogram of $(\text{CzT}^{\text{iPr}})_2\text{Fe}$ (**23**) in THF at room temperature vs. Fc/Fc^+ with $[\text{nBu}_4\text{NPF}_6]$ as supporting electrolyte. Scan rate is 100 mV/s.

With the wider oxidation potential window in DCM, it is now clear that there is an additional peak at a more positive potential of approximately 1.1 V. The other three peaks are still seen in the DCM experiment, but they are slightly shifted and look more quasi-reversible than reversible compared to the THF experiment. This additional redox peak

may be attributed to the Fe(II)/(III) redox couple that has been observed between 0.78-1.28 V vs. Fc/Fc⁺ in similar Fe complexes²²⁰⁻²²².

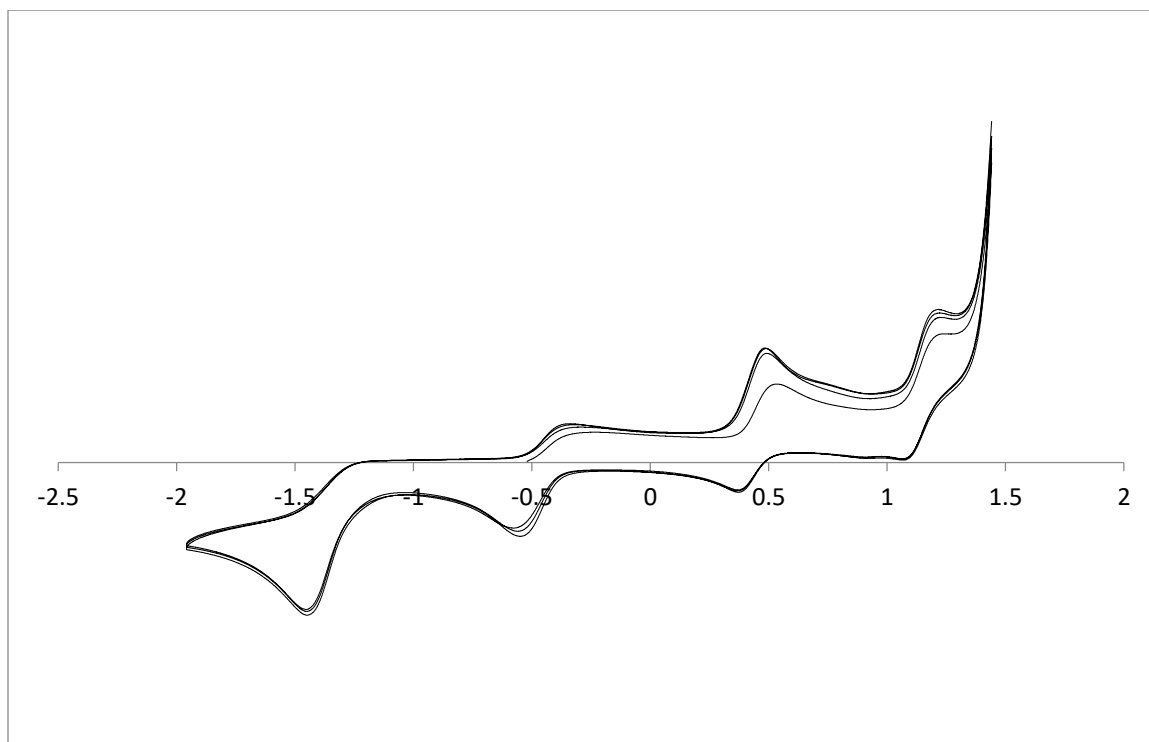


Figure 4.15 Cyclic voltammogram of (CzT^{iPr})₂Fe (**23**) in DCM at room temperature vs. Fc/Fc⁺ with [nBu₄NPF₆] as supporting electrolyte. Scan rate is 100 mV/s.

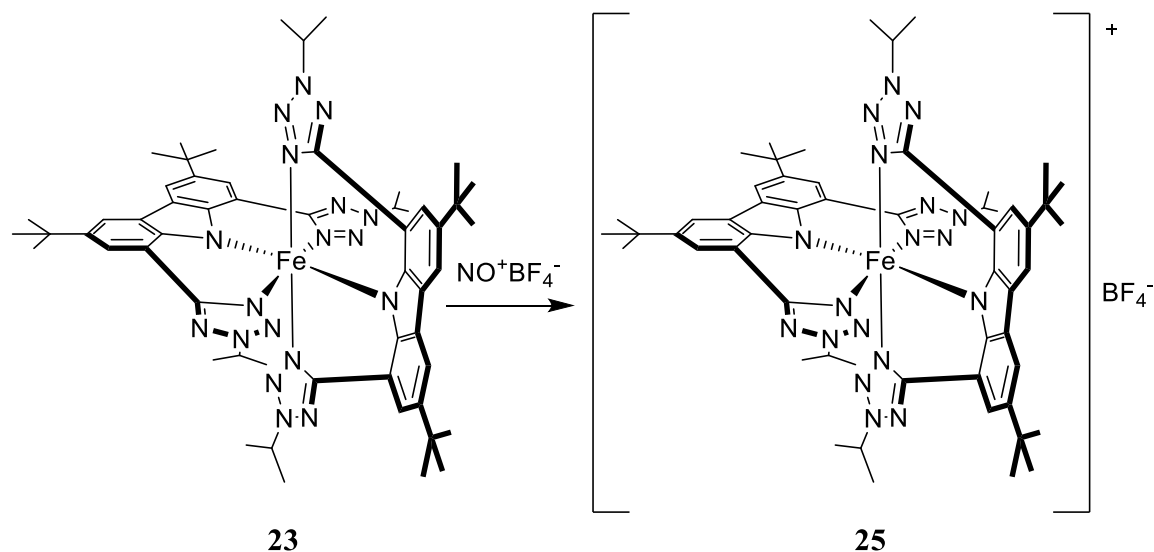
Although definitive assignments of these redox events based on this CV data is not possible, we can draw some tentative conclusions: the two middle, quasi-reversible redox couples in **Figure 4.15** (0.4 V and -0.4 V) are from oxidation of each of the two CzT ligands sequentially, the highest quasi-reversible redox couple at 1.1 V is the Fe(II)/Fe(III) oxidation, and the irreversible peak at -1.4 V is due to an Fe(II)/Fe(I) reduction. There are similar bis-ligand transition metal complexes known in the literature with carbazole-based pincer ligands that show similar ligand-based redox couples (one redox event per carbazole ligand in each complex). The redox potentials of these ligand-based oxidations vary

depending on the metal used: Ni (-0.23 and 0.01 V), Zn (0.10 and 0.11 V), and Ru (-0.06 and 0.74 V)²²³. A small family of Co complexes with varying substituents on the carbazole and triazole rings $[\text{Co}^{\text{III}}(\text{L}^{\text{R/R}})_2]\text{BF}_4$ ($\text{L} = 3,6\text{-di(R)-1,8-bis[5-(3-(4-R)\text{benzyl-1,2,3-triazole})]-9H-carbazole}$, $\text{R} = \text{H, tBu}$) gave potentials ranging from 0.36 to 0.72 V depending on the substituents¹¹⁵. These values are consistent with what has been assigned as the ligand-based oxidations in **23**. From Chapter 2, the ligand-based redox couples in Zn complex **9** are only separated by 0.1 V whereas in **23** they are separated by 0.9 V. The fact that the gap is small in the Zn complex suggests that the oxidation of the first ligand does not affect the oxidation of the second ligand very much. The disruption of this pattern in the Fe complex strongly suggests there is electronic communication between the two ligands, such that oxidation of the first ligand makes oxidation of the second ligand more difficult giving rise to the large gap in potential. This observation is not unexpected since Zn is a d^{10} metal and is unable to connect the two ligands electronically. With the Fe complex there is likely delocalization of the valence electrons between the Fe centre and both ligands leading to electronic communication between the two ligands. From this data it is apparent that ligand-based oxidation is still observed in **23** along with the Fe(II)/(III) oxidation and Fe(II)/(I) reduction within the solvent window.

4.2.5 One Electron Oxidation

Through the course of testing reactivity of some of the mono-ligand Fe complexes (as will be discussed in Chapter 5 of this work) an unexpected oxidized bis-ligand Fe complex was discovered. In attempts to form an Fe nitrosyl complex by use of NO^+BF_4^- with a mono-ligand Fe precursor, redistribution occurred to form a bis-ligand cation

$(\text{CzT}^{\text{iPr}})_2\text{Fe}^+$, with a BF_4^- counter ion present as demonstrated by X-ray crystallography. NO^+BF_4^- has commonly been used as an oxidizing agent in the literature so the oxidation of the complex is not unexpected. The $[(\text{CzT}^{\text{iPr}})_2\text{Fe}]^+ \text{BF}_4^-$ complex, **25**, can be synthesized intentionally by reacting **23** in THF with NO^+BF_4^- at room temperature overnight (**Scheme 4.2**). The solution slowly changes colour from red to brown as the reaction proceeds. Removal of the solvent under reduced pressure gives brown powder as crude product. Unlike the neutral bis-ligand **23**, the oxidized product seems to be extremely air sensitive and turns a dark brown-black colour immediately upon exposure to air. A representative ORTEP of the asymmetric unit of **25** is shown in **Figure 4.16** and a table of selected bond lengths and angles is included in **Table 4.2**.



Scheme 4.2 Synthesis of $[(\text{CzT}^{\text{iPr}})_2\text{Fe}]^+ \text{BF}_4^-$ (**25**)

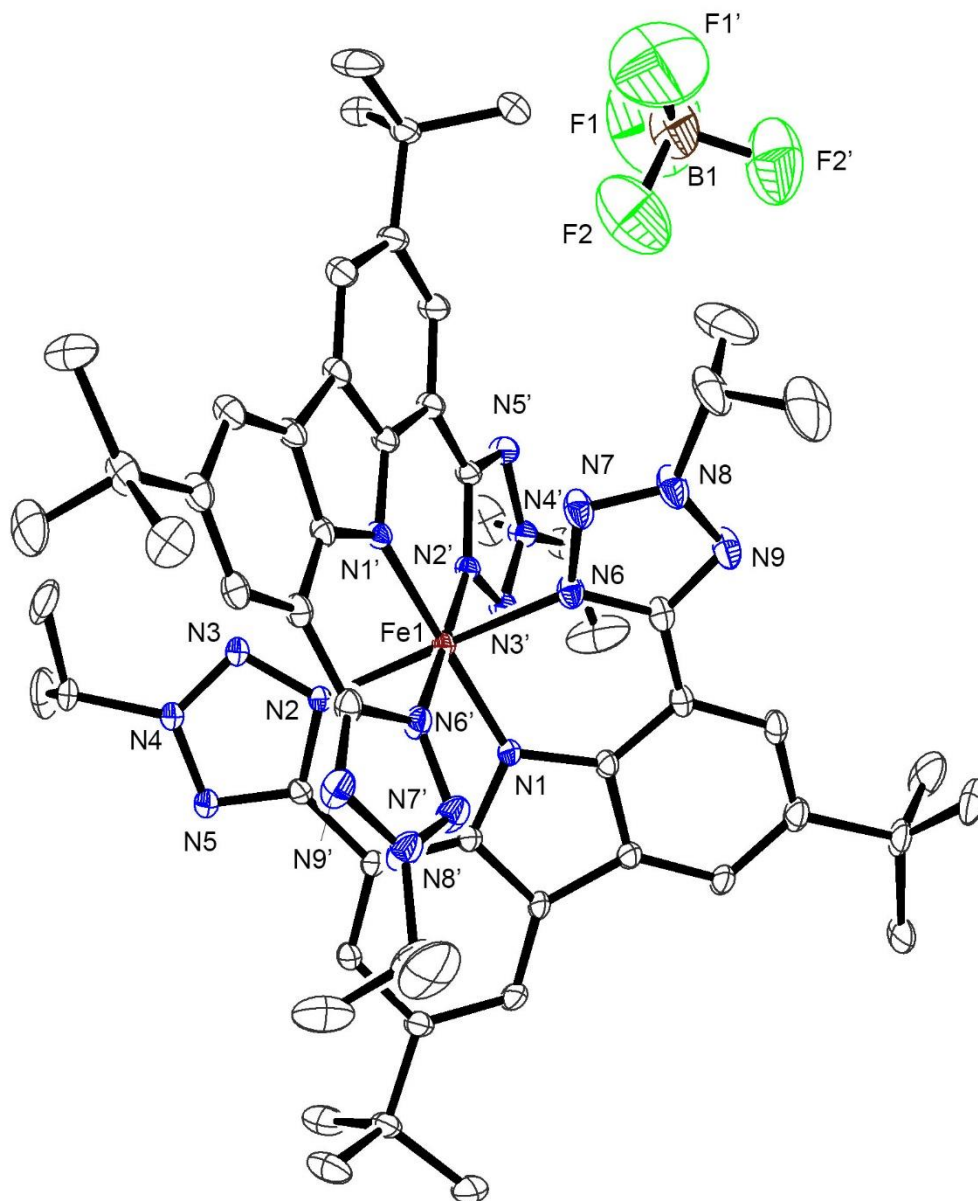


Figure 4.16 ORTEP3¹⁰⁸ plot (30% probability ellipsoids) of $[(\text{CzT}^{\text{iPr}})_2\text{Fe}]^+ \text{BF}_4^-$ (25) (H atoms omitted for clarity)

Table 4.2 Selected bond lengths (Å) and angles (°) of [(CzT^{iPr})₂Fe]⁺ BF₄⁻ (**25**)

Fe1-N1	1.908(2)	Fe1-N2	1.979(2)
		Fe1-N6	1.977(2)
N1-Fe1-N2	89.54(8)	N2-Fe1-N1'	91.35(9)
N1-Fe1-N6	89.46(9)	N2-Fe1-N2'	95.40(12)
N1-Fe1-N1'	178.68(13)	N2-Fe1-N6'	84.54(8)
N1-Fe1-N2'	91.35(9)	N6-Fe1-N1'	89.66(9)
N1-Fe1-N6'	89.66(9)	N6-Fe1-N2'	84.55(8)
N2-Fe1-N6	178.99(10)	N6-Fe1-N6'	95.53(13)
Cant angle¹⁰⁷ Tz₁	-9.27	Cant angle¹⁰⁷ Tz₂	17.16

Tz₁ refers to C21 and N2-N5; Tz₂ refers to C25 and N6-N9.

Complex **25** crystallizes in the less common trigonal P3₁21 space group containing three Fe molecules and three BF₄⁻ counter ions per unit cell (one half of a complex and one half of a BF₄⁻ counterion per asymmetric unit) with a highly disordered toluene molecule removed from the structure through the SQUEEZE function. The ratio of one BF₄⁻ counter ion per one (CzT^{iPr})₂Fe molecule indicated that the charge of the bis-ligand Fe moiety is +1. However, this could mean there are two neutral ligands on an Fe(III) centre or one oxidized and one non-oxidized ligand on an Fe(II) centre. As discussed previously, both the Fe and the ligand are able to be oxidized but the ligand likely oxidizes at a lower potential than the Fe. It is difficult to assign the site of oxidation based solely on the crystal structure as the spin state of the Fe is also unknown and that will directly affect the expected Fe-N bond lengths. The crystal structure was obtained at 120 K. The Fe-N_{Cbz} distance in **25** of 1.908(2) Å is significantly shorter than those found in **23** (1.972(2) and 1.978(2) Å) and **24** (1.958(2) and 1.951(2) Å) suggesting Fe(III) rather than Fe(II). There are few Fe(III) carbazolidine complexes known in the literature, and the few that are known are all HS five coordinate complexes. The Fe-N_{Cbz} bond lengths in these complexes range from

2.024(3)-2.036(4) Å, (median, 2.029 Å) when corrected to six coordinate high spin Fe(III)¹³⁰ and 1.929(3)-1.941(4) Å, (median, 1.934 Å) when corrected to six coordinate low spin Fe(III)^{105, 130, 184, 224}. Based on these literature values, the Fe-N_{Cbz} length in **25** is most consistent with a low spin Fe(III) state, but the bond length observed is even shorter than those reported. The Fe-N_{Tz} lengths in **25** are 1.979(2) and 1.977(2) Å, the Fe-N_{Tz} bond lengths in **23** of 1.983(2)-2.013(2) Å can be corrected to LS Fe(III) (1.923(2)-1.953(2) Å) and HS Fe(III) (2.018(2)-2.048(2) Å). The observed Fe-N_{Tz} bond lengths in **25** are intermediate between high and low spin Fe(III) literature complexes^{225,187-194} as well as complex **23**, so it is not possible to assign the spin state confidently from low temperature structural data alone.

Another structural difference in **25** not seen in **23** or **24** is the twisting and distortion of the CzT ligands. In **25** the cant angles of the tetrazole rings range from 9-17° where in **23** and **24** they are significantly smaller ranging from 1-6° and 8-9° respectively. This distortion from planarity could be due to oxidation of the ligand rather than the metal. If one of the ligands is oxidized and the Fe is in the Fe(II) oxidation state this would affect the bonding and structure as the ligand is now a radical. This distortion may also explain the longer than expected Fe-N_{Tz} bond lengths in **25** compared to the short Fe-N_{Cbz} length because the increased canting and twisting of the tetrazole rings increases the bond lengths. Conversely, if the Fe centre is Fe(III) (as suggested by the short Fe-N_{Cbz} lengths) this could also cause distortion from planarity of the ligands due to an increase in steric crowding with a decrease in ionic radius from Fe(II) to Fe(III). The tetrazole rings may be twisting slightly in order to alleviate some of the steric pressure caused by the shortening of the Fe-N_{Cbz} bond lengths. The disruption in planarity of the ligands is probably a result of some

sort of oxidation, but it is difficult to assign the site of oxidation using only crystal structure data. The oxidation potential of NO^+ is around 1.0 V vs Fc/Fc^+ (depending on the solvent)¹²² which may be strong enough to oxidize either the ligand or the Fe centre (based on the CV of **23**) so it is difficult to say which has been oxidized.

In attempts to better understand the oxidation state of the Fe (and possibly the ligands), Mössbauer spectroscopy was employed. The room temperature Mössbauer spectra recorded over several days on **25** is shown in **Figure 4.17**. It is clear that the spectrum is changing over the period that it was recorded. The sample is air sensitive so this could be due to sample degradation over time if the holder was not sealed properly. We specifically designed Mössbauer sample holders for our samples comprised of two 0.5 cm² acrylic pieces that fit tightly together. After loading in the glovebox, the two pieces are fit together and epoxy glue used around the seam to fully seal the sample. The glue is left to dry/harden for a few days before the sample is taken out of the glovebox to ensure an optimal seal, but oxygen exposure of the sample due to a non-perfect seal is not uncommon based on our experience. Three main doublets are observed due to three types of Fe present in the sample: six coordinate high spin Fe(II) (ΔE_Q 2.11 mm/s; $\delta(\text{Fe})$ 1.29 mm/s), six coordinate low spin Fe(III) (ΔE_Q 1.28 mm/s; $\delta(\text{Fe})$ 0.12 mm/s) and six coordinate high spin Fe(III) (ΔE_Q 0.87 mm/s; $\delta(\text{Fe})$ 0.41 mm/s). These assignments are based on correlating the values to the chart on **Figure 4.10** along with the expertise of Dr. Barbara Sawicka.

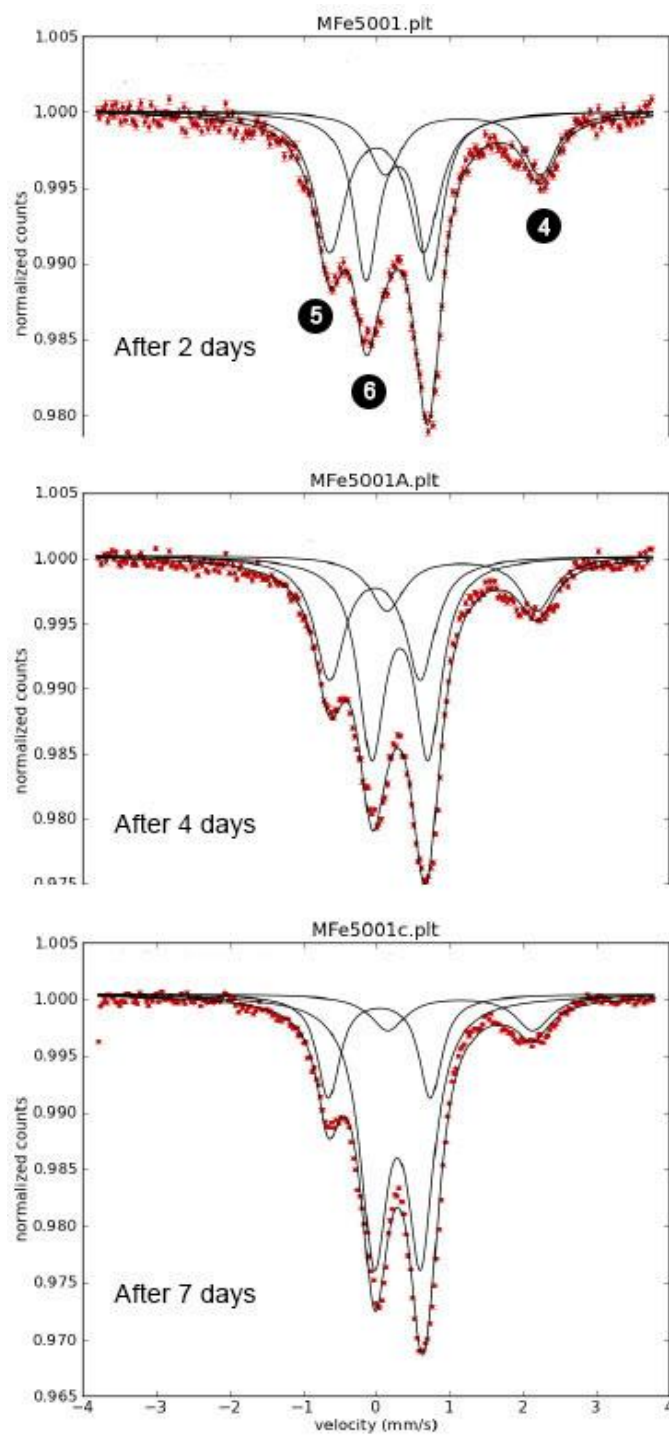


Figure 4.17 Room temperature Mössbauer spectra of $[(\text{CzT}^{\text{iPr}})_2\text{Fe}]^+ \text{BF}_4^-$ (25) recorded over seven days

The amount (%) of each species present throughout the seven days is as follows: LS Fe(III) decreases from 42 % to 34 % to 23 %, HS Fe(II) decreases from 20 % to 17 % to 12 % and HS Fe(III) increases from 38 % to 48 % to 65 %. The trend clearly shows an increase in HS Fe(III) over time and conversely, a decrease in both HS Fe(II) and LS Fe(III) over time. Another trend that can be seen in this data is that the two decreasing Fe species are decreasing at similar rates over the seven days, this data is shown visually in graph form in **Figure 4.18**.

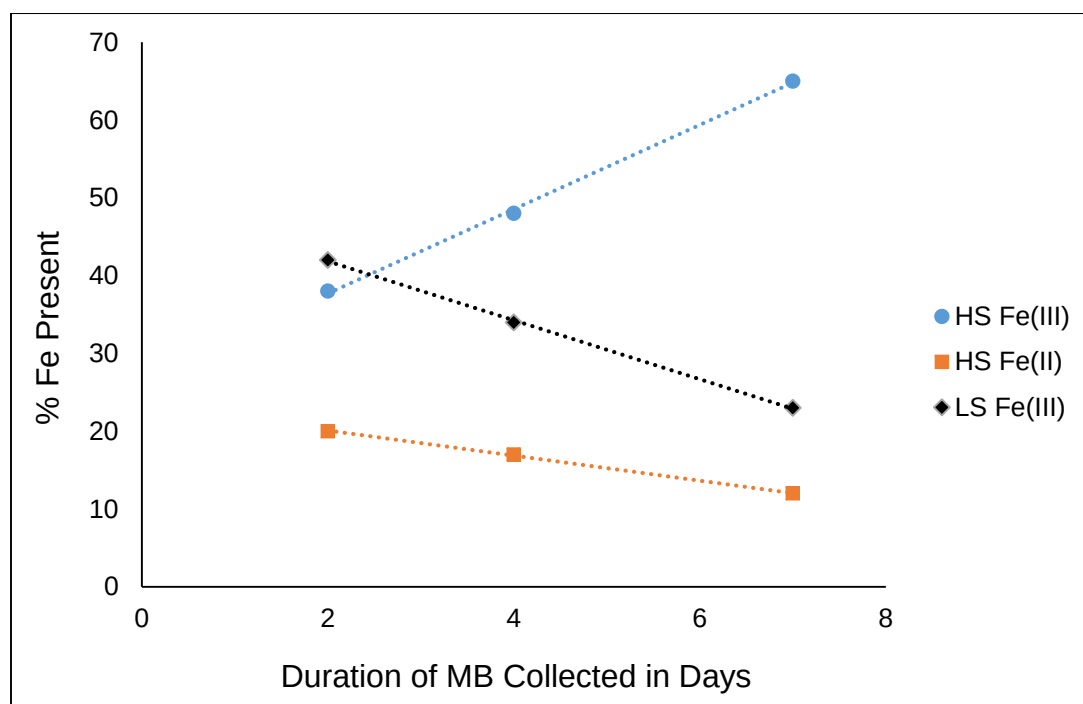
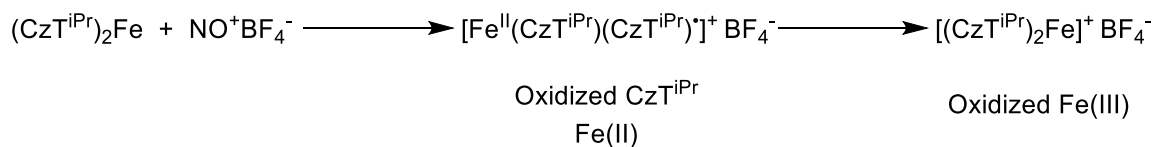


Figure 4.18 Visual representation of Mössbauer spectrum recorded over seven days of $[(\text{CzT}^{\text{iPr}})_2\text{Fe}]^+ \text{BF}_4^-$ (25)

From this data it seems that the LS Fe(III) and HS Fe(II) species are decreasing and being converted into the HS Fe(III) species slowly over time. Based on similar quadrupole splitting and isomer shift values seen in this work (discussed later in Chapter 5, **Figure 5.4**

and **Figure 5.22**), the likely assignment of this increasing HS Fe(III) species is ferrihydrite caused by oxygen exposure of the sample. This explains the slow degradation/decrease in the other Fe species present and growth of one HS Fe(III) species as the data was collected. The remaining two Fe species that were more prevalent in the first two MB spectra are likely from complex **25** itself before being oxidized and destroyed by oxygen exposure. The observation of both Fe(II) and Fe(III) present in this sample suggests that oxidation of the Fe(II) centre is not straightforward. The Fe(III) values of ΔE_Q 1.28 mm/s; $\delta(\text{Fe})$ 0.12 mm/s are very similar to another Fe(III) complex in this work (**36**) suggesting a similar CzT Fe(III) complex. If the sample was simply a mixture of oxidized complex **25** and unoxidized starting complex **23** we would expect to see the same two SCO Fe(II) species (**Figure 4.11**) in the MB spectra; the fact that we only see one Fe(II) species disproves this theory. Complex **23** is also not oxygen sensitive so we would expect the Fe(II) species to remain intact and prevalent in the MB spectrum even if the sample holder is leaking, which again is not observed. One possible explanation for this result could be that initially the CzT ligand is oxidized by NO^+ in which case the Fe would be in the (II) oxidation state. Over time an electron transfer occurs where now the Fe is oxidized to Fe(III) and the ligand is now no longer oxidized. A possible reaction scheme for this electron transfer process is shown in **Scheme 4.3**.



Scheme 4.3 Possible reaction pathway of $(\text{CzT}^{\text{iPr}})_2\text{Fe}$ (**23**) oxidation

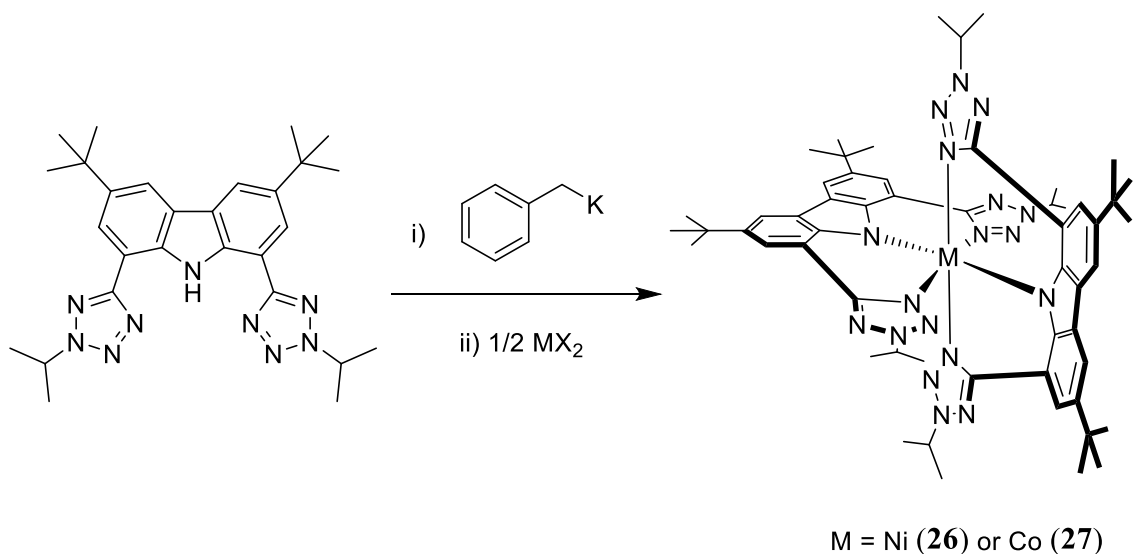
It is reasonable to expect CzT^{iPr} ligand oxidation over Fe(II) because the CV supports ligand oxidation at a lower potential by about 1.4 V (**Figure 4.15** and **Table 4.4**). A reaction pathway involving first oxidation of the ligand and then an electron transfer from Fe(II) to form Fe(III) would explain the complicated MB spectrum. However, it is unclear why an electron transfer would occur from the metal to the ligand. It is possible that the oxidized version of the ligand is simply not very stable and there is preference for the Fe to be oxidized. Perhaps initially the ligand is oxidized due to its lower oxidation potential, this forms an intact bis-ligand Fe complex where one ligand is now a radical. The ligand oxidation disrupts the planarity of the complex and the ligand is now twisted and deformed around the Fe centre, but still bound. This may not be very stable so in order to relieve some electronic and steric pressure caused by the twisting, electron transfer occurs from the metal to the ligand in order to re-reduce the ligand and cause the structure to become more planar. The final, most stable resting state of this oxidized complex would then be the Fe(III) bis-ligand complex where both ligands are neutral. Further MB experiments are needed in order to understand this oxidation process better.

4.3 Zinc, Nickel and Cobalt Complexes

4.3.1 Synthesis and Characterization

All bis-ligand transition metal complexes were made in the glovebox under an inert atmosphere and anhydrous conditions. The synthesis and characterization of $(\text{CzT}^{\text{iPr}})_2\text{Zn}$, **9**, was already discussed in Chapter 2 of this work. Both $(\text{CzT}^{\text{iPr}})_2\text{Ni}$ (**26**) and $(\text{CzT}^{\text{iPr}})_2\text{Co}$ (**27**) were synthesized using the same synthetic method as **9** except using NiCl_2 and CoBr_2

as anhydrous metal salts (**Scheme 4.4**). Both were synthesized in good yields giving yellow (Ni) and orange (Co) powders as crude products.



Scheme 4.4 Synthesis of (CzT^{iPr})₂Ni (**26**) and (CzT^{iPr})₂Co (**27**)

Both the Ni and Co bis-ligand complexes show ¹H NMR spectra consistent with paramagnetic complexes with one set of ligand resonances due to the high symmetry (D_{2d}). Nickel complex **26** has an extremely broad set of resonances with the furthest shifted resonance at 28.55 ppm and the $\nu_{1/2}$ values ranging from 195-26 Hz. The ¹H NMR spectrum of cobalt complex **27** is shown in **Figure 4.19**. All expected resonances were observed and are fairly sharp compared to **26** (not shown).

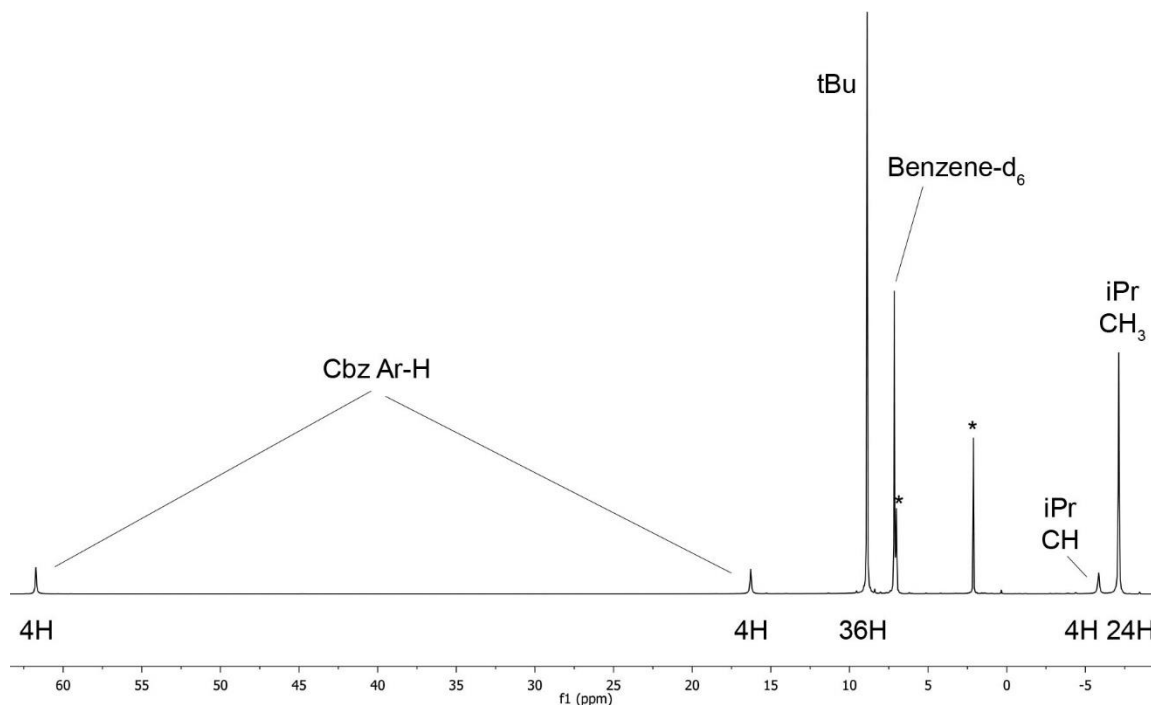


Figure 4.19 ^1H NMR spectrum (300 MHz, C_6D_6 , 298 K) of $(\text{CzT}^{\text{iPr}})_2\text{Co}$ (**27**) (* denotes residual toluene in the lattice)

4.3.2 X-ray Structural Studies

The solid state structures of **9**, **26** and **27** were determined by X-ray crystallography. Selected bond lengths and angles for all three structures are included in **Table 4.3**. Zinc complex **9** crystallizes in the triclinic P-1 space group with seven toluenes of solvation in the lattice; a representative ORTEP plot of **9** is shown in **Figure 4.20**. The geometry around the Zn is best described as octahedral with both CzT^{iPr} ligands binding in a *mer* orientation around the metal. The Zn- N_{Cbz} lengths in **9** of 2.043(2) and 2.042(2) Å are slightly shorter than a similar six coordinate bis-carbazole-based oxazoline ligand Zn(II) complex with Zn-N lengths of 2.054(3) and 2.052(3) Å²²⁶ and are also shorter compared to the Fe- N_{Cbz} lengths of LS Fe(II) in **23** (when corrected¹³⁰ for Zn(II) 2.102(2) and 2.108(2) Å). The Zn- N_{Tz} distances in our structure (2.190(3)-2.225(3) Å) are a bit on the longer side of other

reported six coordinate Zn(II) tetrazole complexes (range 2.111(4)-2.210(2) Å, median 2.161 Å)²²⁷, as well as with the Fe-N_{Tz} lengths in **23** (corrected¹³⁰ for Zn(II) 2.113(2)-2.143(2) Å) There is some canting of the tetrazole rings with the measured cant angles varying from 2° to 7.9°.

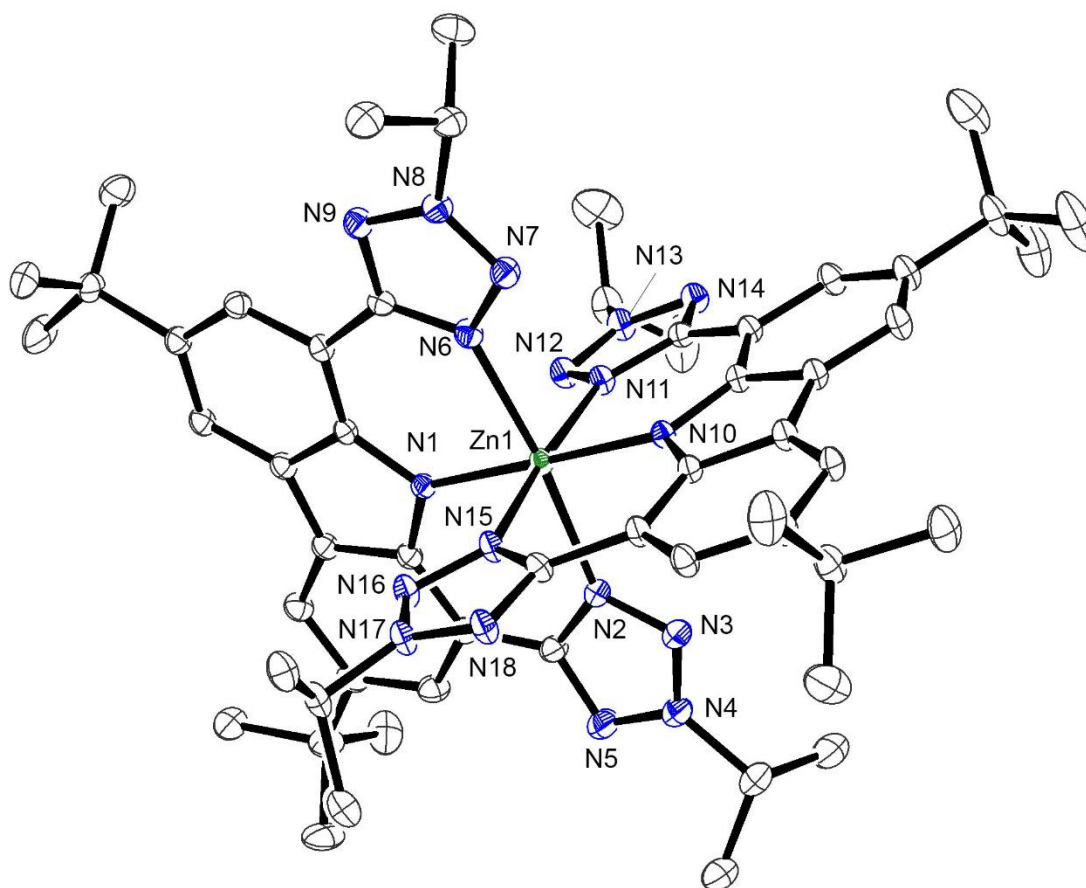


Figure 4.20 ORTEP3¹⁰⁸ plot (30% ellipsoids) of (CzT^{iPr})₂Zn (**9**) (solvent molecules and H atoms omitted for clarity)

The crystal structure of Nickel complex **26** was also obtained on marginal crystals using synchrotron radiation. Although there are three independent molecules in the unit cell, the structure of all three molecules are very similar to the Zn and Co complexes **9** and

27 shown in **Figure 4.20** and **Figure 4.21**, respectively. The only notable difference is that the tetrazole cant angle range is larger in **26** (3.2–22.1°) compared to the other bis-ligand metal complexes **9**, **23** and **27**. Cobalt complex **27** crystallizes in the triclinic P-1 space group with six toluene of solvation in the lattice; a representative ORTEP plot of **27** is shown in **Figure 4.21**.

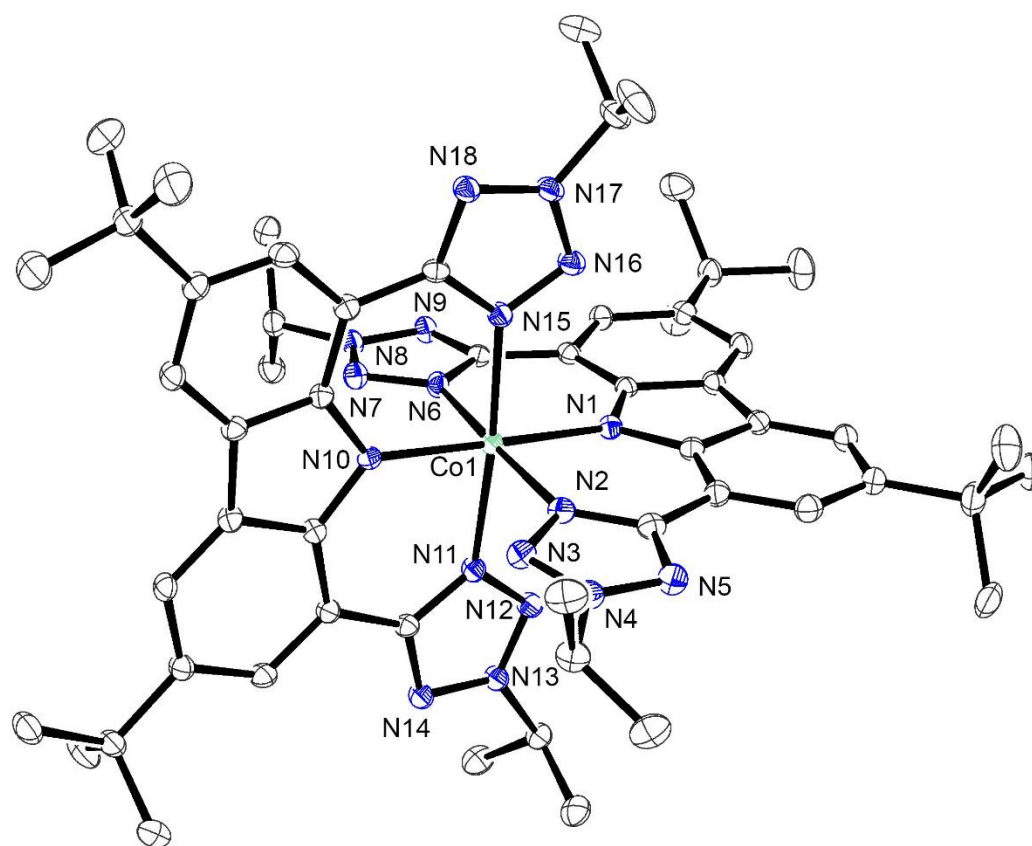


Figure 4.21 ORTEP3¹⁰⁸ plot (30% ellipsoids) of (CzT^{iPr})₂Co (**27**) (solvent molecules and H atoms omitted for clarity)

The Co–N_{Cbz} bond lengths in **27** are 2.050(2) and 2.053(2) Å, these are intermediate between high spin and low spin Co(II) literature complexes¹¹⁵, a better comparison to determine spin state is with our own isostructural complexes **9** and **23**. The M–N_{Cbz} lengths

in **9** and **23** can be corrected to match LS Co(II)¹³⁰ to give a range of 1.952(2)-2.018(2) Å, which are shorter than those found in **27**. The same range corrected¹³⁰ to match HS Co(II) gives values of 2.047(2)-2.113(2) Å which is fairly consistent with those found in **27** suggesting a high spin state.

Table 4.3 Selected bond lengths (Å) and angles (°) of (CzTⁱPr)₂Zn (**9**), (CzTⁱPr)₂Ni (**26**) and (CzTⁱPr)₂Co (**27**)

	A*	26 B*	C*	27	9
M-N1	2.041(3)	2.019(2)	2.047(3)	2.050(2)	2.043(2)
M-N7	2.043(3)	2.029(2)	2.046(3)	2.053(2)	2.042(2)
M-N2	2.076(3)	2.115(2)	2.122(3)	2.183(2)	2.223(2)
M-N6	2.084(3)	2.101(2)	2.117(3)	2.181(2)	2.225(2)
M-N11	2.137(3)	2.170(3)	2.111(3)	2.152(2)	2.213(2)
M-N15	2.135(3)	2.108(3)	2.091(3)	2.166(2)	2.190(2)
N1-M-N2	87.64(10)	87.95(9)	86.63(10)	87.50(7)	87.43(8)
N1-M-N6	86.92(10)	88.04(9)	87.71(10)	87.21(7)	87.24(8)
N7-M-N11	87.27(10)	87.17(10)	87.25(10)	87.10(7)	87.34(8)
N7-M-N15	86.23(10)	87.67(10)	87.22(10)	87.47(7)	87.34(8)
N6-M-N11	85.04(10)	96.54(10)	86.13(11)	90.34(8)	91.21(8)
N11-M-N2	90.82(11)	81.76(10)	91.24(11)	87.24(8)	91.55(8)
N2-M-N15	92.84(11)	92.72(10)	94.46(11)	92.51(7)	87.85(8)
N15-M-N6	91.98(11)	89.33(9)	88.76(11)	90.41(8)	89.90(8)
N1-M-N11	98.82(10)	88.66(10)	94.04(10)	93.51(7)	91.83(8)
N1-M-N15	87.75(10)	96.33(10)	92.06(10)	91.93(7)	93.50(8)
N7-M-N2	91.30(11)	89.86(9)	87.67(10)	93.30(8)	93.26(8)
N7-M-N6	94.64(10)	94.03(9)	98.05(10)	92.02(7)	92.11(8)
Cant angle¹⁰⁷ Tz₁	-22.11	11.77	-10.67	-5.82	-6.33
Cant angle¹⁰⁷ Tz₂	-16.13	13.79	-3.24	4.13	4.30
Cant angle¹⁰⁷ Tz₃	11.90	-18.47	13.05	2.95	7.94
Cant angle¹⁰⁷ Tz₄	18.98	-18.17	10.88	-7.57	-1.97

*Molecule A, B and C represent three unique molecules in the asymmetric unit. Tz₁ refers to C21 and N2-N5; Tz₂ refers to C25 and N6-N9; Tz₃ refers to C49 and N11-N14; Tz₄ refers to C53 and N15-N18.

4.3.3 Cyclic Voltammetry

The CV of **9** was already presented and discussed in Chapter 2 of this work; it revealed that the ligand is redox active and in the bis-ligand complexes, each ligand showed reversible oxidation with $E_{1/2}$ around 0.3 V vs Fc/Fc⁺. The CV of both **27** and **26** were run in dry ACN at room temperature with [nBu₄N⁺ PF₆⁻] as supporting electrolyte at a scan rate of 100 mV/s. The CV of **27** is seen in **Figure 4.22** as a stack plot; the bottom spectrum is the full potential window to the solvent limit at -2.5 V while the top spectrum is the same solution but with the window decreased. The CV of **26** is seen in **Figure 4.23**.

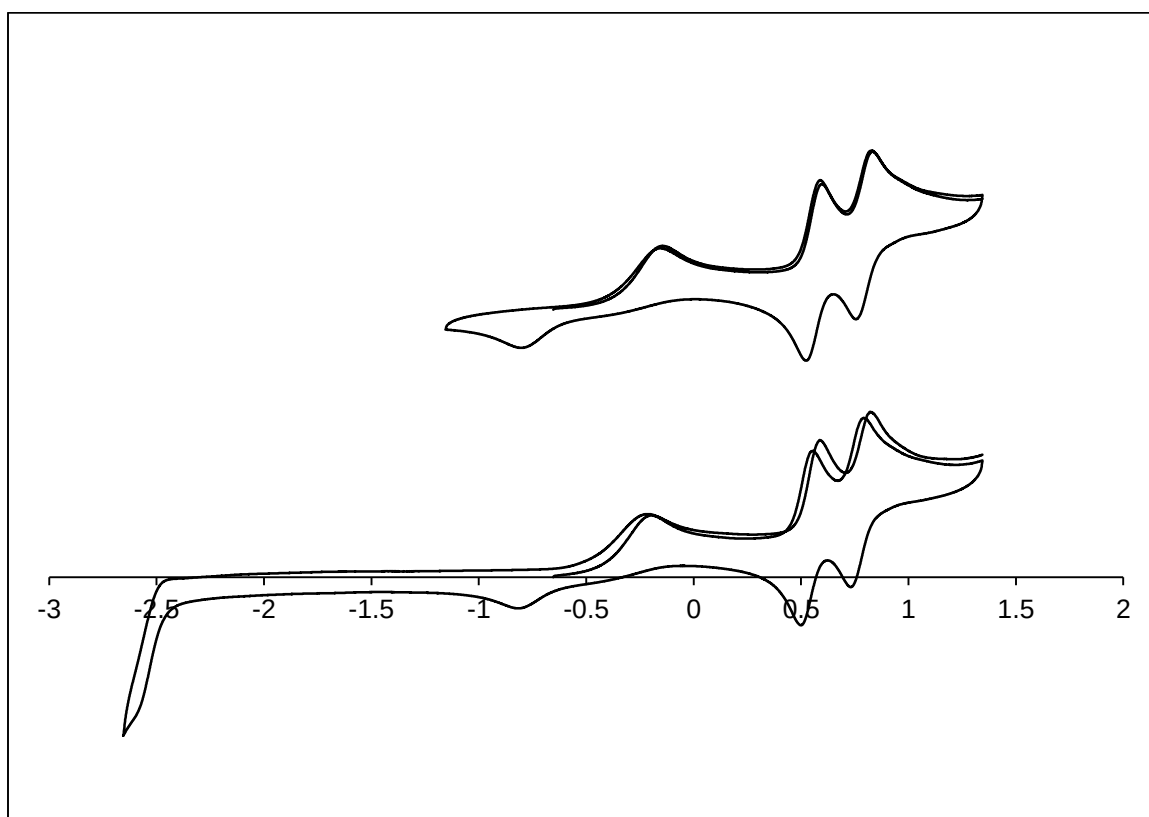


Figure 4.22 Cyclic voltammogram of (CzT^{iPr})₂Co (**27**) vs. Fc/Fc⁺ in ACN with [nBu₄N⁺ PF₆⁻] as supporting electrolyte. Scan rate is 100 mV/s.

The CVs of both **26** and **27** show a familiar pattern of two reversible oxidation peaks close to each other, most likely from oxidation of each CzT ligand sequentially. The CV of **27** also shows an irreversible reduction at -0.79 V. This can be assigned as the Co(II)/Co(III) redox couple based on similar literature values^{115, 122}. The oxidation potential of the ligands in the Co complex is quite a bit higher than in the case of both Zn and Ni under the same conditions (all done in ACN with [nBu₄N⁺ PF₆⁻] as supporting electrolyte). In the Zn complex **9**, the ligand oxidation potentials are at $E_{1/2}$ of 0.38 V and 0.29 V, these are shifted to slightly lower potentials in the Ni complex (0.33 V and 0.16 V) and in the Co complex these peaks are shifted to much higher potentials at 0.8 V and 0.57 V.

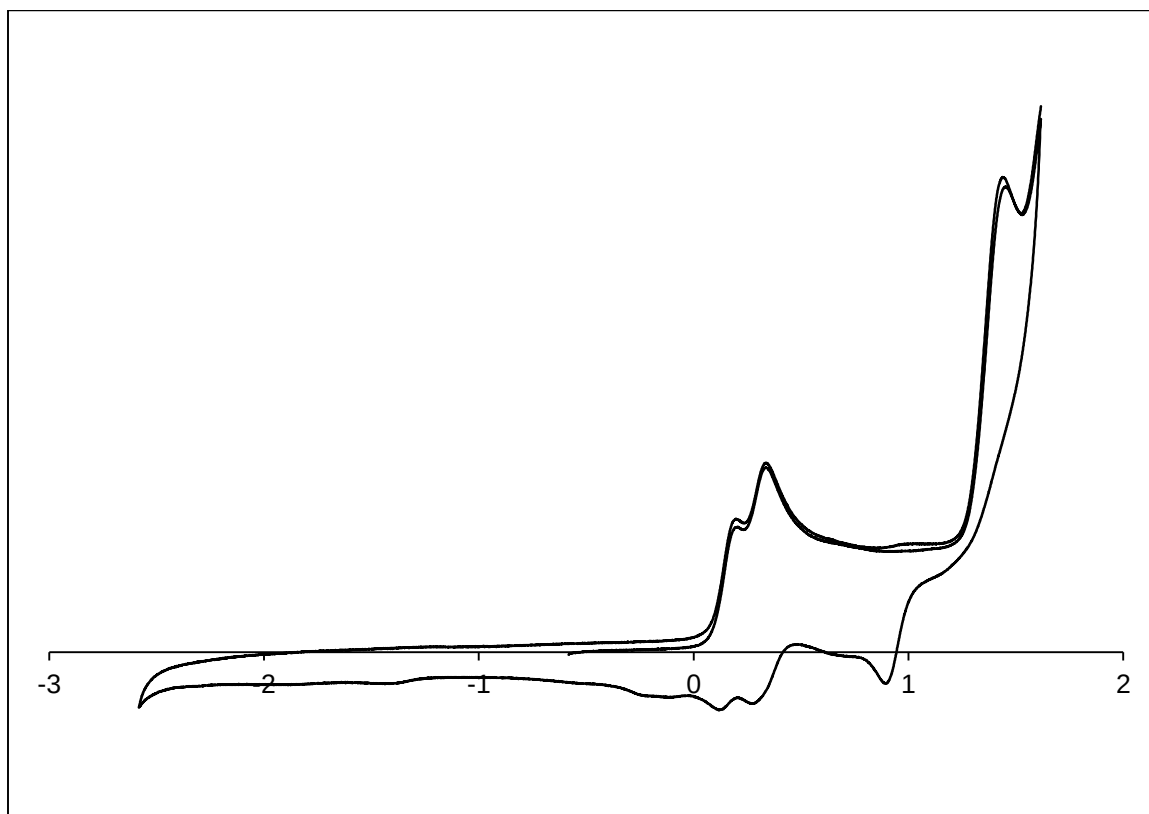


Figure 4.23 Cyclic voltammogram of (CzT^{iPr})₂Ni (**26**) vs. Fc/Fc⁺ in ACN with [nBu₄N⁺ PF₆⁻] as supporting electrolyte. Scan rate is 100 mV/s.

Using **9** as the benchmark, since the metal is redox inactive within the window of interest, it seems that Ni lowers the oxidation potential of the ligands while Co raises the oxidation potential of the ligands quite a bit (**Table 4.4**). In the Co case this could be due to the fact that the Co is oxidized before the ligands are oxidized: the Co is in the Co(III) oxidation state when the ligand oxidation is occurring. This changes the overall charge of the complex compared to the other metals where the oxidation state of the metal is (II) when the ligand oxidation occurs. In the Ni CV (**Figure 4.23**) there is similarly additional redox activity other than just the ligand oxidations. There is an irreversible oxidation that occurs right before the solvent window cut-off at 1.4 V. The reduction portion of this redox couple is smaller and seen at 0.9 V. Literature values for Ni(II)/Ni(III) are reported in a large range from -0.105-1.09 V²²⁸⁻²³⁰ (corrected to match Fc/Fc⁺ standard)¹⁷⁴ whereas Ni(IV) is reported at higher potentials ranging from 0.13-1.82 V^{228, 231} (corrected to match Fc/Fc⁺ standard)¹⁷⁴. Based on the size of the oxidation wave in **26** at 1.4 V it is possible that it is Ni(II)/Ni(IV), but this redox couple is much less commonly observed so it is difficult to assign this redox event definitively. We are confident it is Ni-based but whether it is Ni(III) or Ni(IV) is uncertain. As discussed previously with the CV of **23**, the fact that in both **27** and **26** the ligand redox couples are close in potential to each other suggests that one ligand oxidation has little affect on the oxidation of the remaining ligand. It also suggests that the Co and Ni metal redox activities have little to no affect on the ligand cooperativity, unlike the Fe case where the ligand redox couples were drastically different in potential from one another. A summary of the electrochemical data of selected bis-ligand transition metal complexes in this work is collected in **Table 4.4**.

Table 4.4 Electrochemical data of bis-ligand complexes in varying solvents (V vs. Fc/Fc⁺)

	E _{a1} (E _{c1})/V	E _{a2} (E _{c2})/V	E _{a3} (E _{c3})/V	E _{a4} (E _{c4})/V
	M(II)→M(I)	Cbz _{ox1}	Cbz _{ox2}	M(II)→M(III)
9 (ACN)	-	0.34(0.24)	0.46(0.30)	0.98(0.89) [*]
23 (THF)	-1.58(-1.76)	-0.48(-0.62)	0.32(0.23)	-
23 (DCM)	(-1.43)	-0.36(-0.54)	0.51(0.39)	1.12(1.08)
26 (ACN)	-	0.23(0.14)	0.36(0.29)	1.47(0.90)
27 (ACN)	-0.13(-0.79)	0.61(0.53)	0.84(0.77)	-

^{*} Due to an additional ligand oxidation, not metal-based

4.3.4 Magnetic Studies

Co(II) has the potential to exist in either the high spin or low spin magnetic state since it is a d⁷ metal and many Co(II) complexes undergo spin crossover similar to Fe(II)^{199, 232-233}. Our work with Fe(II) suggested that the CzT^{iPr} ligand system is neither a strong field nor a weak field ligand and as a result the metal can exist in either the high spin or low spin state. An investigation into the spin state of **27** in the solid state and solution was conducted to determine whether a similar spin crossover occurs or if the spin state is constant.

The solution state magnetic moment of **27** was determined by the Evans' method at room temperature in benzene-D₆ to give a value of 3.66 μ_B. This value is consistent with the spin-only magnetic moment of a high spin d⁷ system with three unpaired electrons (3.87 μ_B), although it is lower than typical μ_{eff} values observed for most high spin Co(II) (4.3-5.2 μ_B)¹⁵. If the complex was low spin Co(II), the expected magnetic moment would be much closer to 1.7 μ_B due to only one unpaired electron. The value observed for **27** suggests a high spin Co(II) where the orbital contribution to the magnetic moment is quenched.

The solid state magnetic data was obtained with the use of a SQUID magnetometer. The resulting data are shown in **Figure 4.24**. Based on this data there are a few key features to note; first, the spin state of the complex is clearly high spin with the χT value of 5 giving a μ_{eff} of $6.3 \mu_{\text{B}}$ and secondly there is hysteresis present. The effective magnetic moment observed here is a bit high for the expected spin-only magnetic moment¹⁵, but it leaves no doubt this is a high spin complex. At low temperatures (approaching 4 K) the effective magnetic moment drops to $5.3 \mu_{\text{B}}$. Based on this, the complex clearly does not exhibit spin crossover, unlike the isostructural **23** and remains high spin even at lower temperatures. In this experiment the temperature was varied from low to high and back to low again. The fact that the magnetic moment of the complex is different at the same temperature for the increasing and decreasing temperature sweep depicts the hysteresis of the complex.

Magnetic data were not obtained on **26** because octahedral d^8 complexes only exist in one spin state with two unpaired electrons. The solid state magnetic data of the Zn complex **9** was obtained to ensure that there was no ligand contribution to any of the magnetic data found in the Fe or Co complexes. The resulting data showed complete diamagnetic behaviour consistent with the NMR data, suggesting that all solid state and solution magnetic contributions are purely from the metal centre.

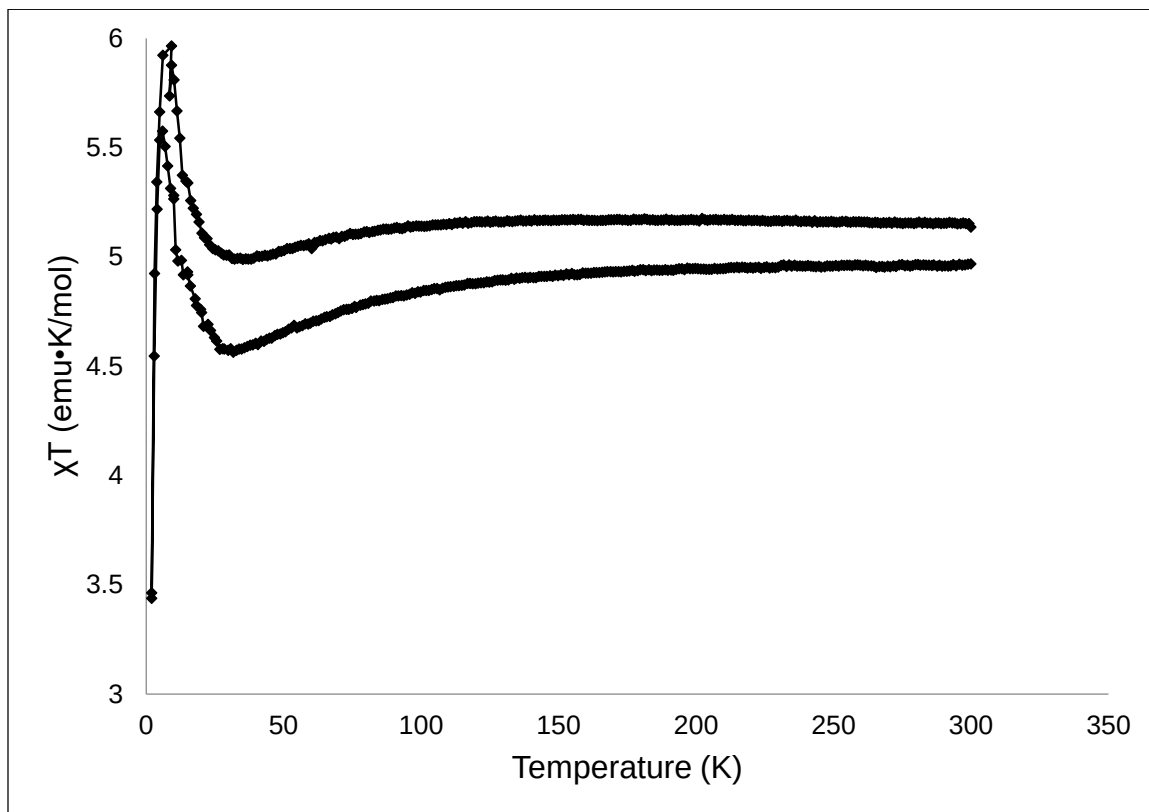


Figure 4.24 Solid state magnetic data of $(\text{CzT}^{\text{iPr}})_2\text{Co}$ (**27**)

4.4 Summary and Conclusion

Complexation of two CzT^{iPr} ligands to a single metal centre is possible for many first row transition metals to form air stable octahedral complexes. The use of the bulkier ligand $\text{CzT}^{\text{CH}_2\text{Mes}}$ in an attempt to stop complexation of a second ligand to the metal centre was unsuccessful, at least in the case of Fe. These bis-ligand Fe complexes (**23** and **24**) are common redistribution products, initially discovered during exploration of the mono- CzT Fe chemistry (Chapter 5). Upon further inspection, it was found that **23** displayed a thermally-induced spin crossover. This spin transition is smooth in solution but in the solid state an abrupt two-step process is observed, likely due to cooperative intermolecular effects. Conversely **24** shows dramatically different magnetism where no spin crossover is

present and the Fe(II) low spin state shows temperature independent paramagnetism. The neutral **23** complex can be oxidized to give **25** as an air sensitive complex. Investigation into the oxidation state of this complex suggests that initially the ligand is oxidized and over time electron transfer occurs from Fe(II) to re-reduce the ligand and oxidize the metal to Fe(III).

Bis-ligand complexes using the CzT^{iPr} ligand were also synthesized for Co, Ni and Zn. The cyclic voltammetry of these complexes was investigated and compared to the redox properties of the ligand itself, discussed in Chapter 2. The Co complex is high spin over a broad temperature range and unlike the analogous Fe complex no spin crossover process is observed although the complex does show marked hysteresis. While these bis-ligand complexes are relatively unreactive, their physical and magnetic properties proved very interesting. Knowing that two ligands can easily bind to one metal centre, we set out to design and synthesize mono-ligand Fe complexes that would not redistribute and would hopefully show catalytic reactivity. These results are discussed in Chapter 5.

Chapter 5 Mono-Ligand Iron Complexes

5.1 Introduction

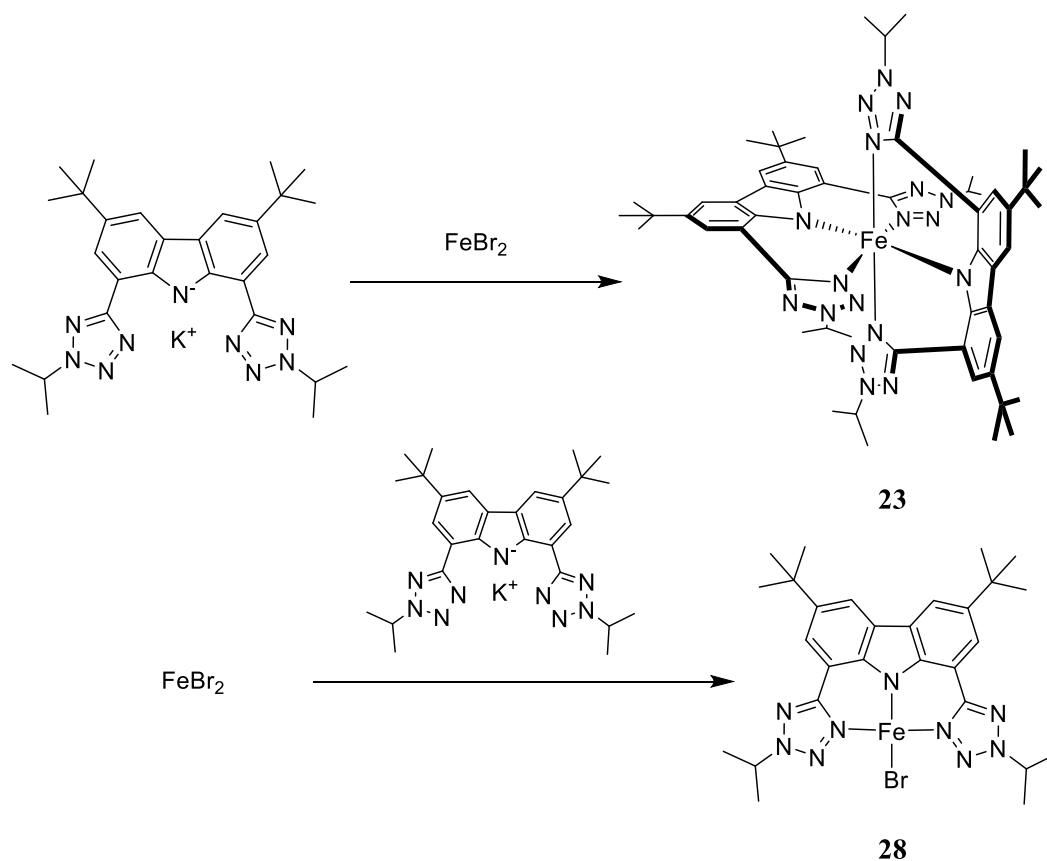
Chapter 4 showed the interesting magnetic properties of Fe complexes with two of our CzT ligands, but in order to unlock the potential reactivity of Fe complexes we need to form less sterically hindered mono-ligand complexes. Low coordinate Fe complexes have been shown to be good catalysts for hydrosilylation⁹², hydrogenation²³⁴, epoxidation²²⁴ and polymerization²³⁵⁻²³⁶, to name a few. There is a lot of interest in Fe-based catalysts due to the low toxicity, high natural abundance and most importantly, low cost of Fe compared to some of the precious metals that are generally used in catalysis (Pd, Pt, Ir, Ru, Rh, etc.)¹⁷⁹⁻¹⁸¹. While there are many nitrogen-based tridentate pincer ligands used in Fe chemistry, a large majority of these are neutral^{100, 234, 236-240}. There are far fewer examples of anionic nitrogen-based pincer ligands similar to our CzT ligands in use^{184, 241}. This led us to explore the use of **8b** in low coordinate mono-ligand complexes of Fe(II) and Fe(III) to determine if similar reactivity is seen with an anionic ligand in place of a neutral ligand.

5.2 Divalent Iron Halide Complexes

5.2.1 Synthesis and Characterization of (CzT^{iPr})FeBr

As discussed in Chapter 4, initial attempts to synthesize a mono-ligand Fe(II) complex produced the bis-ligand complex **23** by the salt metathesis reaction shown in **Scheme 5.1**. However, the mono-ligand Fe complex (CzT^{iPr})FeBr, **28**, can be formed preferentially when the order of addition is reversed. It was discovered that when the FeBr₂

was added slowly to a solution of the potassium salt of the ligand, $\text{K}^+ [\text{CzT}^{\text{iPr}}]^-$, the bis-ligand complex was the main product, but when the FeBr_2 was kept in excess by adding the ligand salt slowly to the Fe solution, the main product formed was **28** (**Scheme 5.1**).



Scheme 5.1 Synthesis of $(\text{CzT}^{\text{iPr}})\text{FeBr}$ (**28**) (all reactions done in THF at room temperature)

Unlike the bis-ligand Fe complex **23**, **28** is extremely oxygen sensitive: upon exposure to air there is an immediate colour change from orange-yellow to dark red-black. This is true both in solution and in the solid state. Also, surprisingly, **28** is much less soluble than **23** and is not soluble at all in warm toluene or benzene; the only available solvent in the glovebox that **28** dissolves in is THF. As a solid, **28** is an orange powder, but in THF

the solution is yellow suggesting the formation of a THF adduct in solution. The room temperature ^1H NMR spectrum is of a paramagnetic complex and contains a simple set of ligand resonances consistent with C_{2v} symmetry between 2.5 and 30 ppm with $\nu_{1/2}$ varying from 13 to 191 Hz. Interestingly, when the NMR solution is cooled several more paramagnetic peaks appear suggesting that THF exchange is occurring faster than the NMR time scale at room temperature. A stack plot of the NMR spectra are shown in **Figure 5.1**, only the downfield section is shown to simplify the spectra; the upfield section is complicated by the presence of sharp diamagnetic solvent resonances.

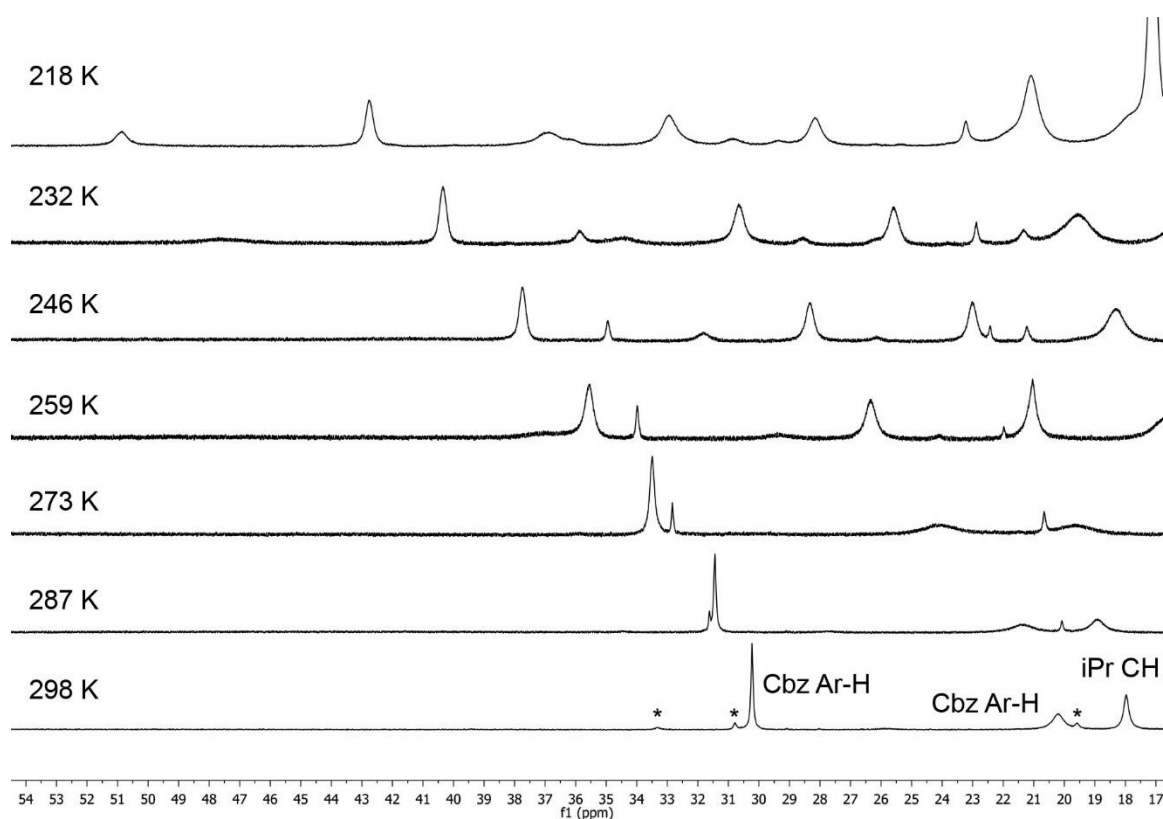
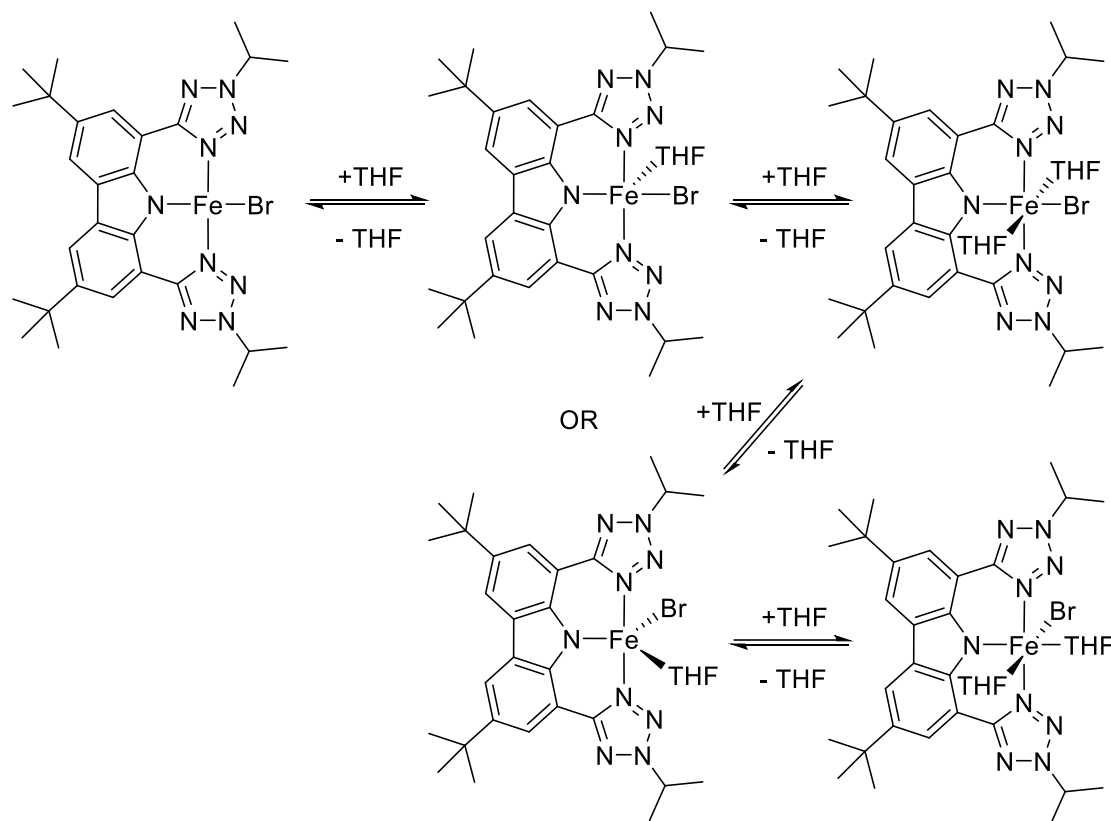


Figure 5.1 Downfield region of the ^1H NMR spectrum (300 MHz, THF-D_8) of $(\text{CzT}^{\text{iPr}})\text{FeBr}$ (**28**) at varying temperatures (* denotes small amount of unknown paramagnetic complex)

Each of the Cbz Ar-H resonances integrate to two protons as does the iPr CH resonance in the room temperature spectrum. The correlated 18 H integrated resonance for the tBu protons as well as the 12 H resonance for the methyl groups on the iPr are present further upfield. The 218 K ^1H NMR spectrum is difficult to assign as there are several overlapping peaks, many of which are quite broad and it is possible that some may also be lost in the baseline. Based on the large number of new resonances seen at low temperature it is possible that both five and six coordinate complexes exist. With only one CzT^{iPr} ligand bound there are presumably two open coordination sites on the Fe centre in solution that can be occupied by THF. Thus several different geometries are possible as illustrated in **Scheme 5.2** and slow interconversion between these on the NMR timescale could explain the complexity of the low temperature spectra.

Attempts to grow X-ray quality crystals of **28** from THF in order to determine how many THF molecules bind were unsuccessful. The Evans' method susceptibility measurement, conducted in THF-D_8 at room temperature, gave a value of $6.02 \mu_{\text{B}}$ which is consistent with high spin Fe(II).



Scheme 5.2 Possible THF exchange between different (CzT^{iPr})FeBr (**28**) solvates

5.2.2 Solid State Structure Determination

In the absence of a crystal structure, determination of the solid state structure of **28** was inferred from the Mössbauer spectrum (**Figure 5.2**). The MB values $\delta(\text{Fe})$ of 1.07 mm/s and ΔE_Q of 2.26 mm/s are consistent with a high spin Fe(II) centre (**Figure 4.10**) as observed in solution. As discussed in Chapter 4, Mössbauer spectroscopy is able to determine the oxidation state, spin state and coordination number of the Fe centre; these isomer shift and quadrupole splitting values are consistent with a six coordinate, high spin Fe(II) complex (**Figure 4.10**). While the solid state structure cannot be determined unequivocally by MB, six coordinate high spin Fe(II) is inconsistent with the simple four

coordinate structure shown in **Scheme 5.1**. A six coordinate structure in the solid state suggests some sort of bridging interaction such as through a CzT tetrazole nitrogen or the bromide atoms (**Figure 5.3**). This polymeric structure matches well with the MB values and it may also help to explain the low solubility of **28**. It is possible that **28** is only soluble in THF because a coordinating solvent is needed to break up the polymer and in solution it exists as a THF adduct to fill the vacant coordination sites. Four coordinate Fe complexes are fairly rare, especially when the ligand is not bulky enough to stabilize a low coordinate Fe environment. The four coordinate Fe(II) complex, as shown in **Scheme 5.1**, is only a 14 electron complex (assuming there is no extra electron donation from the tetrazole units), so it is reasonable to postulate a polymeric form (**Figure 5.3**) where bridging provides both steric and electronic saturation.

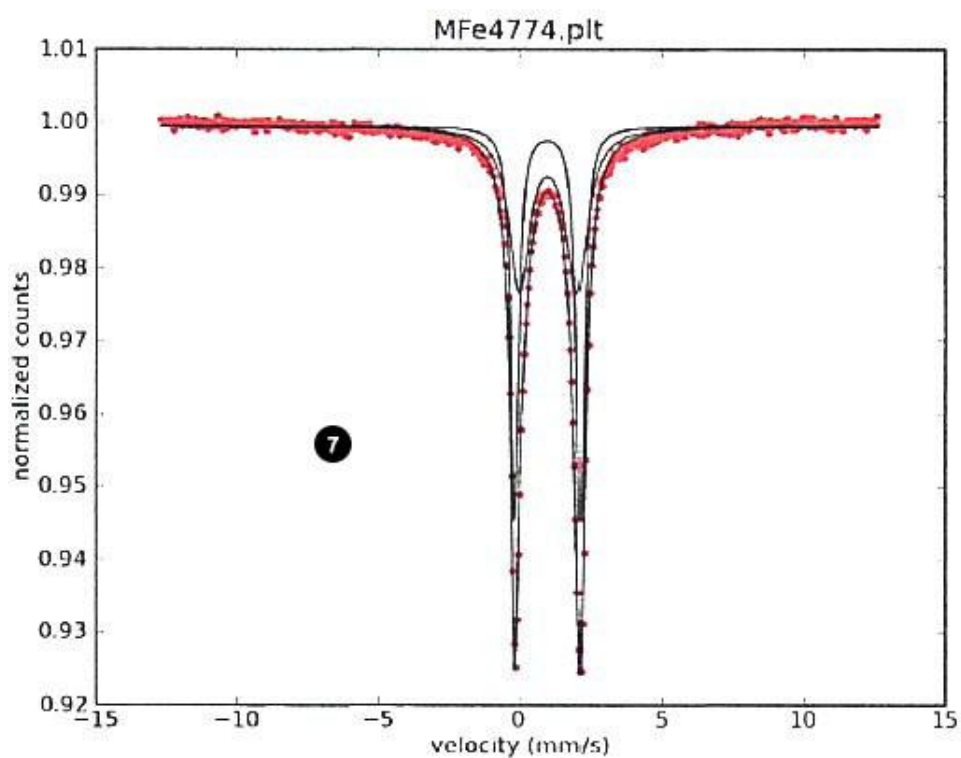


Figure 5.2 Room temperature Mössbauer spectrum of (CzT^{iPr})FeBr (**28**)

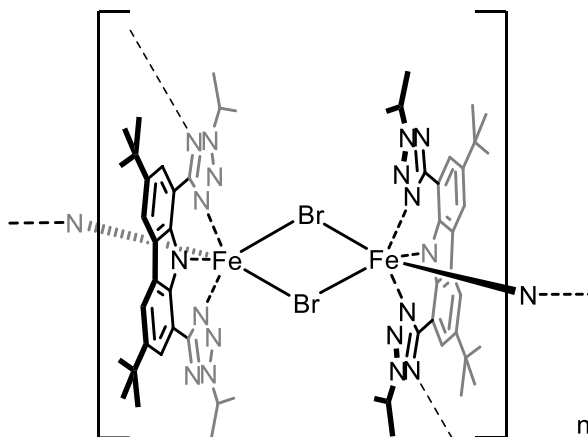


Figure 5.3 One possible six coordinate structure of (CzT^{iPr})FeBr (**28**)

Given the propensity of **23** to form during the synthesis of **28**, we conducted a test to see if **28** redistributes spontaneously in solution. A sample of **28** in THF-D₈ was monitored over several days by NMR spectroscopy to see if redistribution occurred. After several days at room temperature followed by several days at 50°C, there was no change in the ¹H NMR spectrum. The stability of **28** in THF solution, even after further heating, suggests that THF adduct formation helps stabilize the complex. However, when the THF solution is exposed to air, an immediate colour change to dark red is observed and the paramagnetic NMR resonances due to **28** disappear. This sensitivity is clearly due to oxygen and not moisture in the air because addition of deoxygenated D₂O results in no change in either the NMR spectrum or the colour of the solution.

This oxygen sensitivity is also present in the solid state: upon exposure to air a powdered sample changed from orange to black within seconds. In an attempt to monitor and characterize the oxidation product, the MB spectrum was recorded on a sealed sample then exposed to air by drilling holes in the sample container and the MB spectrum recorded again (**Figure 5.4**). There is a clear change in the quadrupole splitting and isomer shift

values for the oxidized sample and the values observed are consistent with ferrihydrite, a common hydrous ferric oxyhydroxide mineral $\text{Fe}_2\text{O}_3 \cdot 1/2 \text{H}_2\text{O}$. So presumably on exposure to air the CzT ligand dissociates and the Fe(II) centre is oxidized to Fe(III) in the form of ferrihydrite. Although it seems air oxidation is rapid, one positive outcome of this observation is it suggests that **28** may be highly reactive with other substrates.

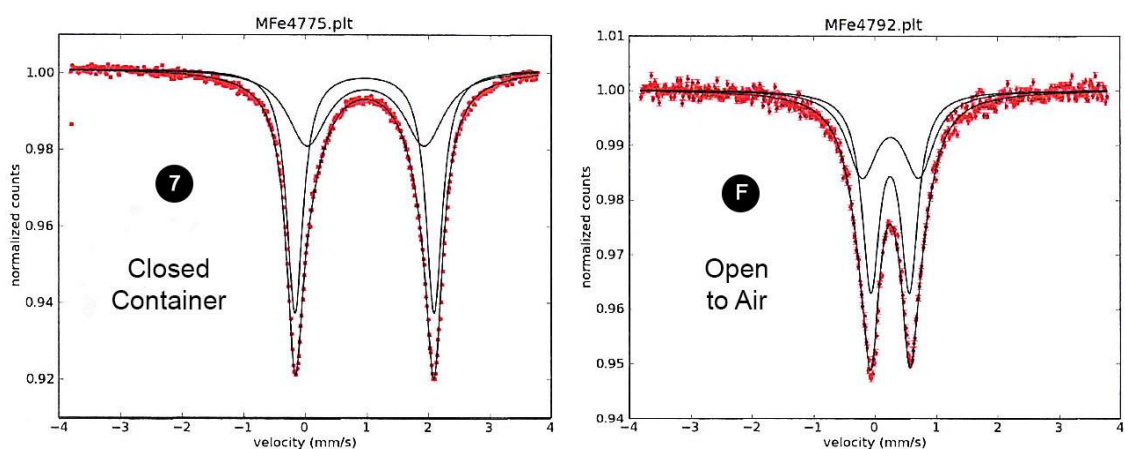
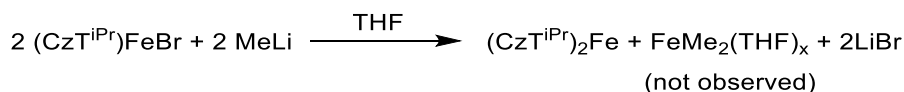


Figure 5.4 Mössbauer spectra of $(\text{CzT}^{\text{iPr}})\text{FeBr}$ (**28**) before and after exposure to air

5.2.3 Reactivity of $(\text{CzT}^{\text{iPr}})\text{FeBr}$

The first reaction conducted on **28** was an attempt to replace the bromide ligand with something more reactive, such as an alkyl. All reactions with **28** were done in THF since that is the only available anhydrous and deoxygenated solvent that the complex dissolves in, which means that the reactivity is likely that of a THF adduct of **28**. However, for simplicity and because we do not know the extent of solvation, all subsequent reactions show the Lewis base-free complex. Reaction of **28** with MeLi gave immediate and complete redistribution to the bis-ligand complex **23**, as shown in **Scheme 5.3**.

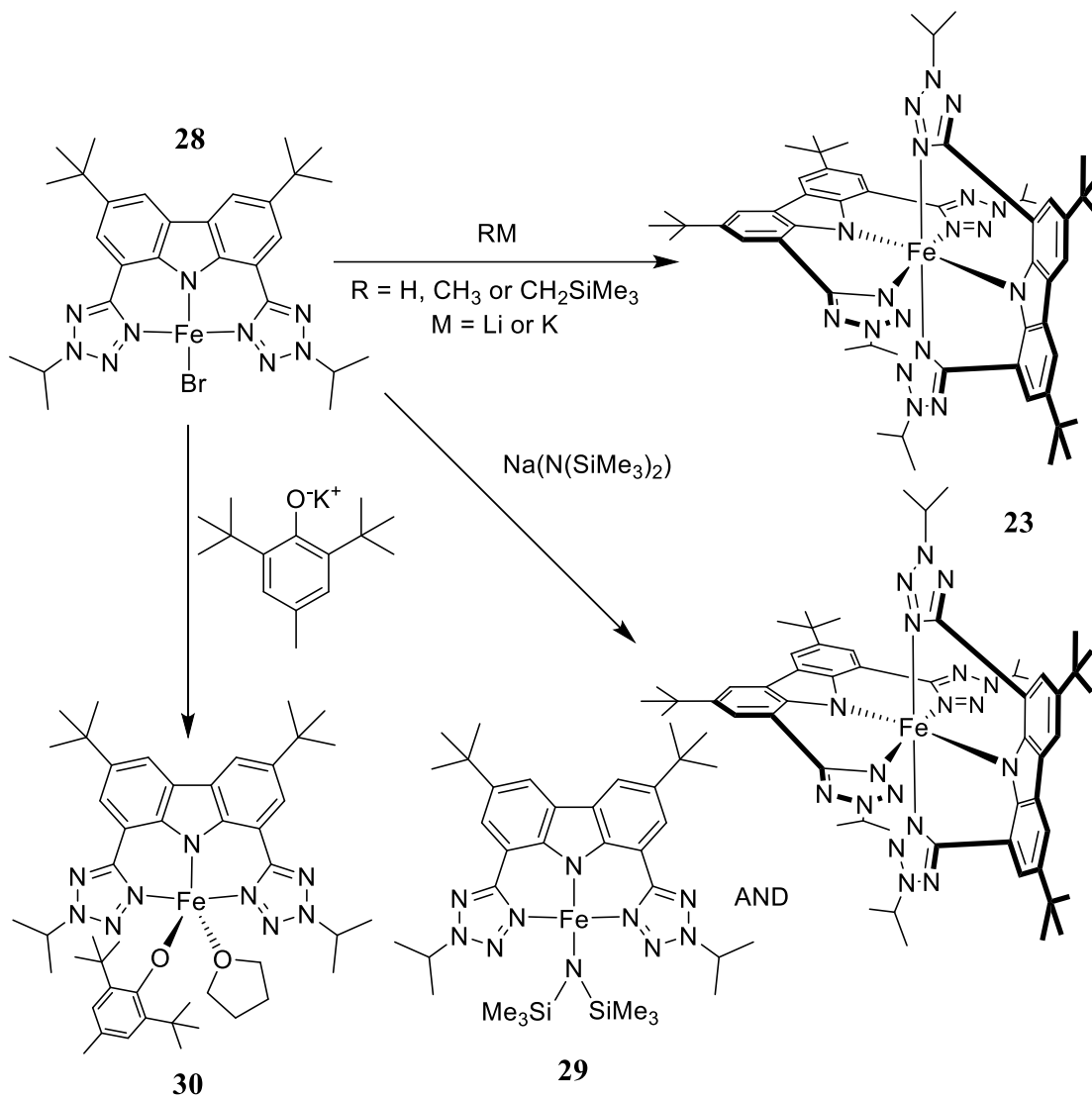


Scheme 5.3 Redistribution of $(\text{CzT}^{\text{iPr}})\text{FeBr}$ (**28**) to $(\text{CzT}^{\text{iPr}})_2\text{Fe}$ (**23**)

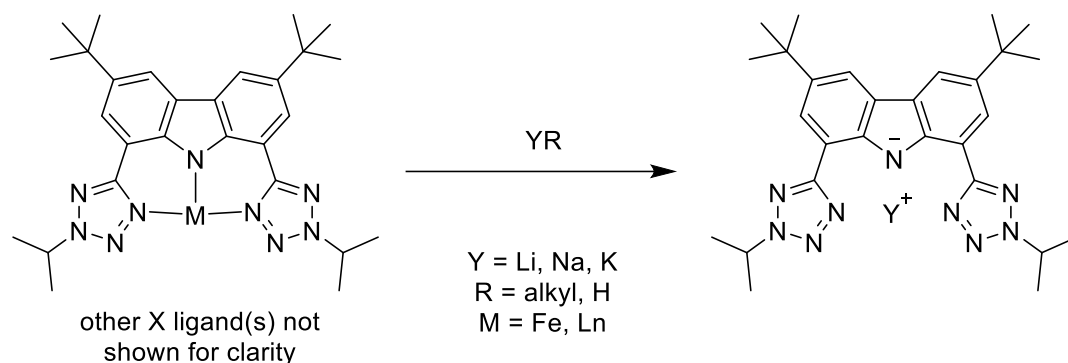
Attempts to shut down this redistribution pathway by use of larger and more sterically crowding alkyl groups such as $\text{LiCH}_2\text{SiMe}_3$ were unsuccessful as were attempts to form an Fe hydride complex through a salt metathesis reaction with KH. Reaction of **28** with $\text{Na}[\text{N}(\text{SiMe}_3)_2]$ did show new paramagnetic resonances in the ^1H NMR spectrum that match those expected for $(\text{CzT}^{\text{iPr}})\text{Fe}[\text{N}(\text{SiMe}_3)_2]$ (**29**), but about 50% of the Fe product formed (based on NMR integration) was the bis-ligand redistribution product. Due to the difficulty in separating the two products by crystallization, no further research was conducted on $(\text{CzT}^{\text{iPr}})\text{Fe}[\text{N}(\text{SiMe}_3)_2]$. A summary of these redistribution reactions is shown in **Scheme 5.4**. Changing the electronic and steric properties of the incoming ligand by using a bulky phenoxide finally gave a new mono-ligand Fe complex $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})(\text{THF})$ (**30**) (**Scheme 5.4**). The chemistry of the phenoxide product is discussed in Section 5.3 below, but the successful formation of the Fe phenoxide product proves that the right combination of donor and ligand bulk can shut down the redistribution pathway.

Along with ligand substitution reactions, the redox chemistry of **28** was briefly explored to see if it was possible to generate different oxidation states of Fe. In a simple attempt to reduce the Fe(II) to Fe(I), a THF solution of **28** was stirred with a Na amalgam. An immediate colour change occurred from yellow to red, but the resulting ^1H NMR

spectrum showed that the product was **23**. This result, along with attempts at ligand substitution, suggests that formation of Na^+ , K^+ or Li^+ adducts of the CzT ligand facilitates ligand redistribution. Similar results were discussed in Chapter 3 with lanthanide complexes suggesting the ligand preferentially binds Li^+ resulting in elimination of LiCzT from the lanthanide coordination sphere. Thus it seems that in most cases where an electrophile is present ($\text{Y}^+ = \text{Na}^+, \text{K}^+, \text{Li}^+$), elimination of CzT^{iPr} from the metal centre occurs preferentially to form a salt with the alkali cation (**Scheme 5.5**). In the case of Fe this results in ligand redistribution to form **23** as the final product, with the formation of $[\text{CzT}^{\text{iPr}}]^- \text{Y}^+$ as a by-product facilitating the redistribution. This hypothesis is supported by the fact that **28** does not undergo spontaneous ligand redistribution even at elevated temperatures, but rather redistribution occurs when a salt metathesis reagent is added that initiates the redistribution.



Scheme 5.4 Ligand substitution and redistribution reactions of $(\text{CzT}^{\text{iPr}})\text{FeBr}$ (**28**)



Scheme 5.5 Possible electrophile induced ligand loss

5.3 Divalent Iron Phenoxide Complexes

In order to explore the chemistry of a reactive mono-ligand Fe complex we need a complex that is sterically and electronically stable enough so that ligand redistribution does not occur, but not so stable that it is inert for further reactivity. In order to shut down the redistribution pathway steric bulk is needed so that a second CzT ligand can not physically fit around the Fe centre. This bulk can be achieved by using a bulkier CzT ligand, or by replacing the bromide with a bulkier ancillary ligand. As discussed in Chapter 2 of this work, synthesizing a new bulky CzT ligand is more difficult than we initially thought and would involve drastically changing the current ligand synthesis which would be extremely time consuming and involve several extra synthetic steps. To avoid this, we decided to use the original **28** complex and adjust the ancillary ligand. Since the only reagent that did not result in ligand redistribution was the bulky phenoxide, 2,6-di-tert-butyl-4-methylphenoxide (OAr), we decided to explore the chemistry of (CzT^{iPr})Fe(OAr)(THF), **30**, in more detail.

5.3.1 Characterization of (CzT^{iPr})Fe(OAr)(THF)

The synthesis of (CzT^{iPr})Fe(OAr)(THF), **30**, was conducted in THF giving rise to the THF adduct as a yellow powder (**Scheme 5.4**). Complex **30** was characterized by ¹H NMR spectroscopy, magnetic susceptibility (Evans' method), Mössbauer spectroscopy as well as X-ray crystallography. Like its bromide precursor **28**, complex **30** is extremely oxygen sensitive and changes from yellow to dark green immediately upon exposure to oxygen. This is true in both the solid and solution state. Unlike **28**, **30** is soluble in benzene and toluene at room temperature as well as THF. This increase in solubility suggests this complex is monomeric rather than polymeric, a fact confirmed by the X-ray structure (*vide infra*).

The ¹H NMR spectrum at room temperature in benzene-D₆ is consistent with C_{2v} symmetry (**Figure 5.5**) which suggests that THF exchange is rapid on the NMR timescale. No bound THF resonances were seen at room temperature. Variable temperature NMR was conducted in an attempt to slow THF exchange and confirm the formation of a C_s symmetric five coordinate Fe complex. This would be evident by decoalescence of the 12 H iPr methyl resonance into two 6 H resonances. **Figure 5.6** shows the NMR spectra of **30** between 183 and 373 K. Although it is hard to see from this figure, the iPr methyl resonance (12 H) does not decoalesce even at 183 K. However, it does broaden significantly which may suggest it is close to decoalescence.

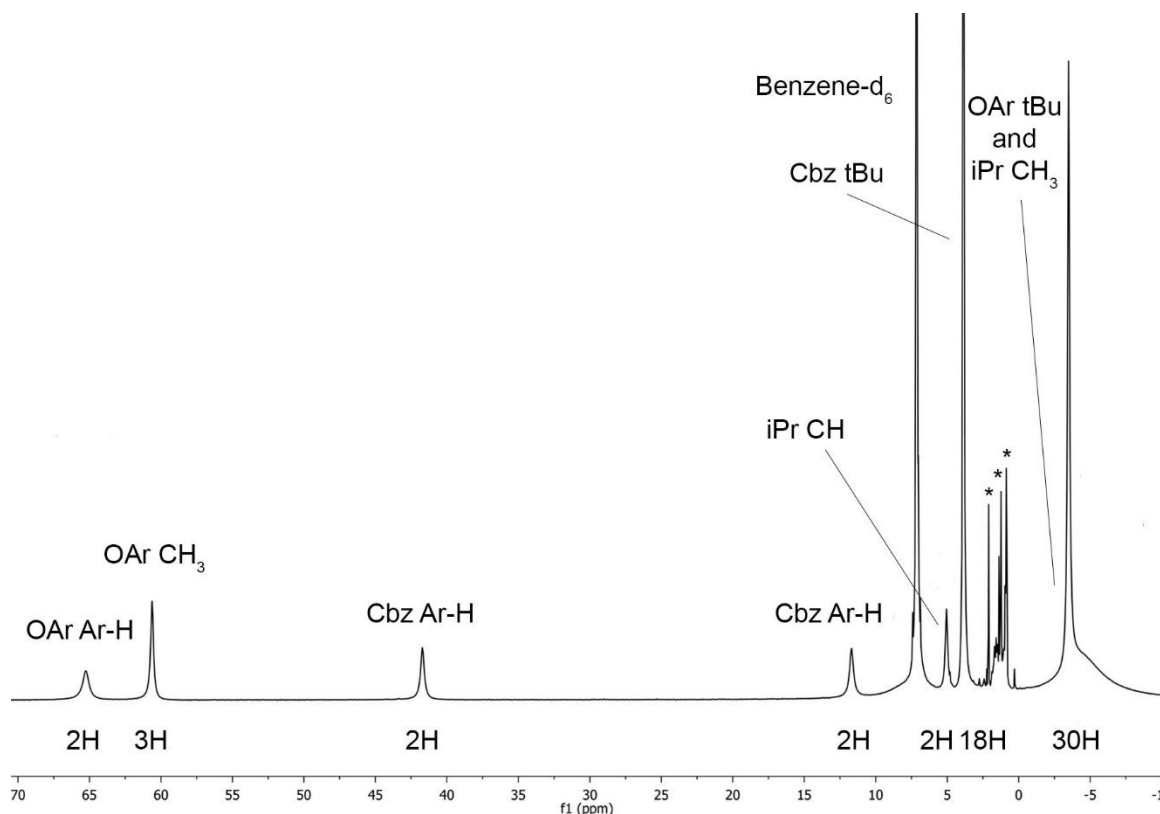


Figure 5.5 ^1H NMR spectrum (300 MHz, C_6D_6) of $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})(\text{THF})$ (**30**) at 298 K (* residual hexanes and grease resonances)

The THF resonances shift from close to their diamagnetic positions at high temperature (2.00 and 3.85 ppm at 373 K for the β and α protons, respectively) and broaden considerably as the temperature is lowered (around 16 ppm at 193 K for both β and α protons). The only resonance that appears to decoalesce at low temperature is a 2 H resonance assigned to the OAr aryl CH protons (indicated by red dashed line on **Figure 5.6**). This is consistent with restricted rotation of the Fe-O or O-C bond for the FeOAr unit. Decoalescence of the tBu groups of the OAr ligand is not observed but this may be because the difference in chemical shift between the tBu groups in the decoalescence spectrum is very small.

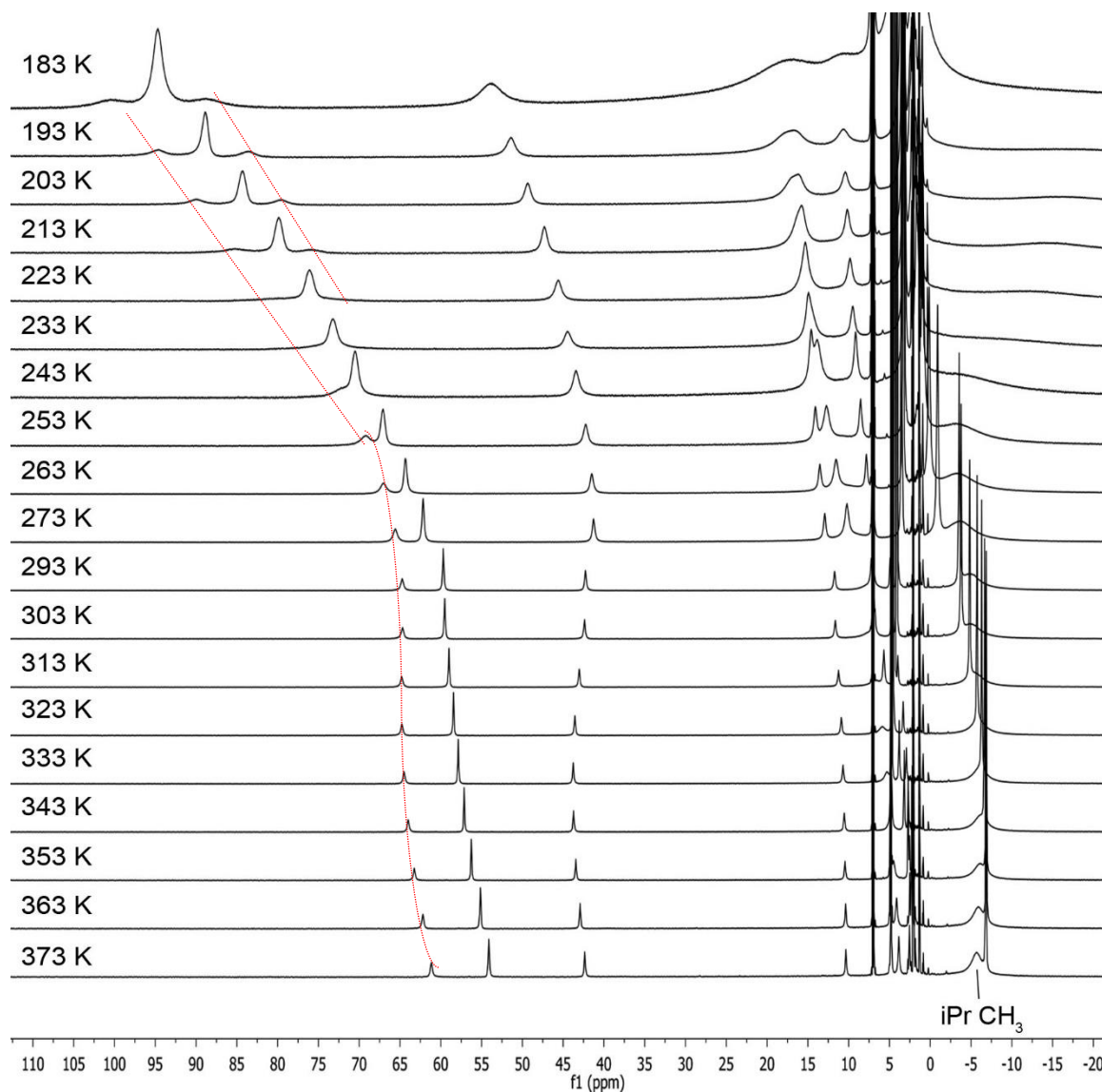


Figure 5.6 Variable temperature ^1H NMR spectra (360 MHz, $\text{toluene-}D_8$) of $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})(\text{THF})$ (30)

A similar variable temperature ^1H NMR experiment was conducted in $\text{THF-}D_8$, and shows a second set of complex resonances in smaller amounts. This is most clearly demonstrated in the downfield region of the spectrum (**Figure 5.7**) as the diamagnetic region is quite broad and contains several overlapping resonances. This is possibly attributed to the formation of a bis-THF adduct formed in solution when excess THF is

present giving a six coordinate Fe structure. This suggests that the Fe complex is not exceptionally crowded, and is able to accommodate coordination of a second THF molecule in the coordination sphere through an octahedral geometry. The fact that the second set of complex resonances is so small suggests that even with excess THF present and at lower temperatures the five coordinate Fe structure is dominant. These observations could be explained by the equilibria shown in **Scheme 5.6**.

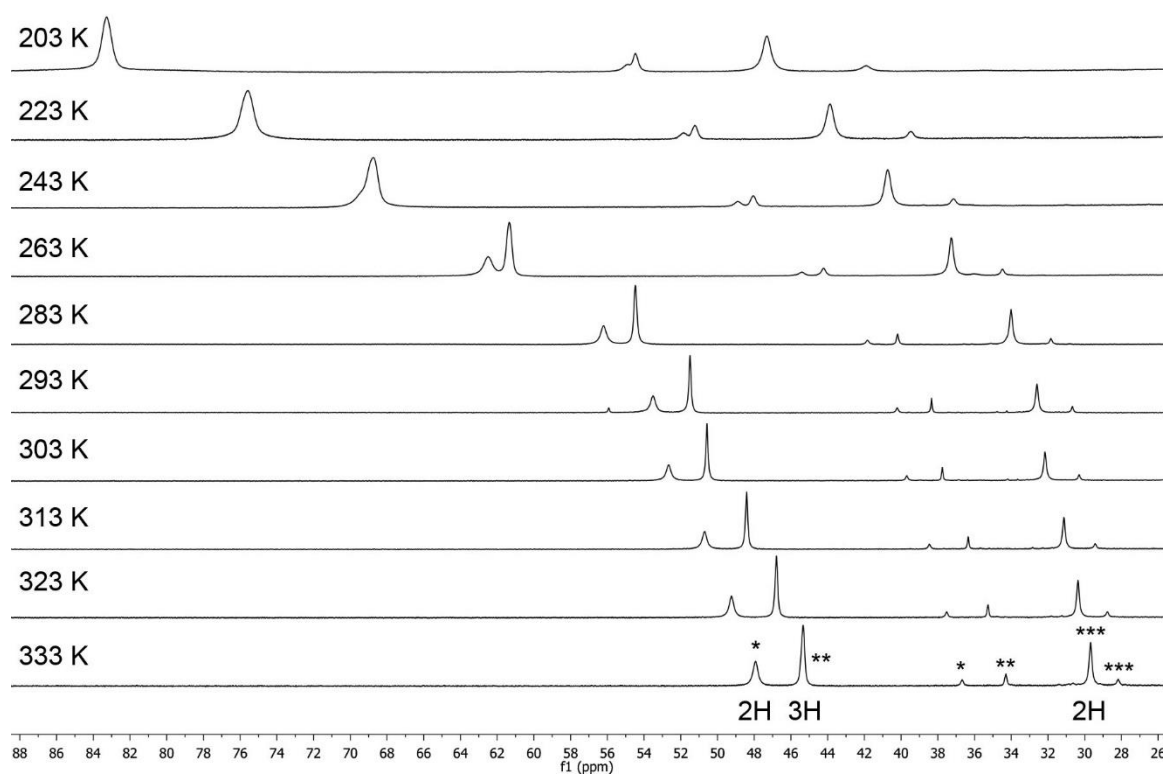
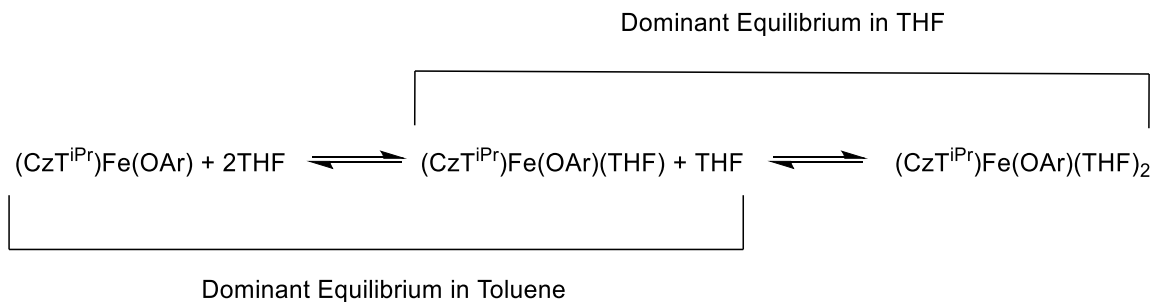


Figure 5.7 Downfield region of variable temperature ^1H NMR spectra (360 MHz, $\text{THF-}d_8$) of $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})(\text{THF})$ (**30**) (* denotes OAr Ar-H resonances, ** denotes OAr CH_3 resonance, *** denotes Cbz Ar-H resonance)



Scheme 5.6 THF exchange equilibria of $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})(\text{THF})$ (**30**) in solution

The Evans' method was conducted in benzene- D_6 and the magnetic moment calculated was $5.26 \mu_{\text{B}}$ which is consistent with a high spin Fe(II) centre. This is in agreement with all other Fe complexes of CzT^{iPr} and suggests that the CzT pincer is a relatively weak field ligand. The solid state Mössbauer spectrum in **Figure 5.8**, shows similar parameters to **28** [$\delta(\text{Fe}) = 1.02 \text{ mm/s}$; $\Delta E_{\text{Q}} = 2.56 \text{ mm/s}$] consistent with a five-coordinate high spin Fe(II) centre (**Figure 4.10**).

The solid state structure of **30** was determined by X-ray crystallography (**Figure 5.9**); selected bond lengths and angles for **30** are collected in **Table 5.5**. The geometry around the Fe is best described as trigonal bipyramidal with the CzT^{iPr} ligand binding in a pseudo-*mer* orientation. The Fe- N_{Cbz} distance of $2.065(2) \text{ \AA}$ in **30** is longer than other reported Fe carbazolid complexes (range corrected to match five coordinate high spin Fe(II)^{130, 242}: range $1.989(3)$ - $2.027(4) \text{ \AA}$, median $2.020 \text{ \AA}$)^{105, 183-184, 224}.

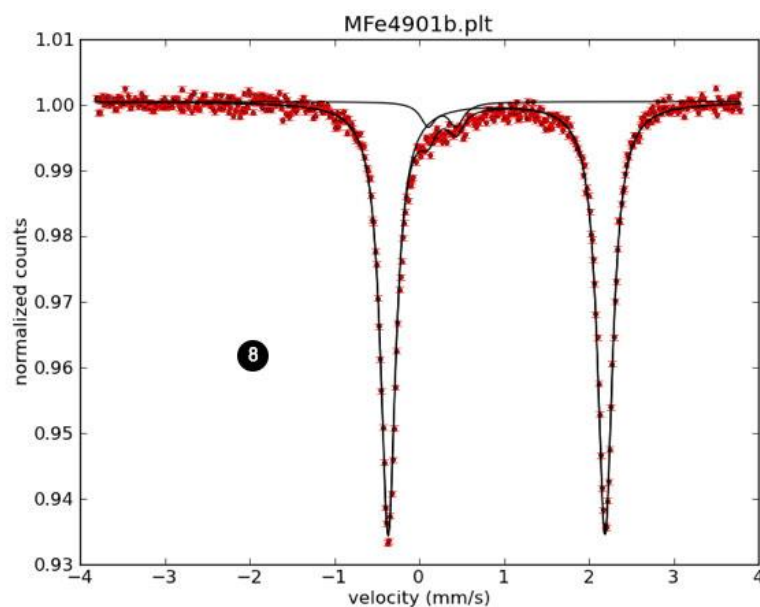


Figure 5.8 Mössbauer spectrum of $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})(\text{THF})$ (**30**) at room temperature

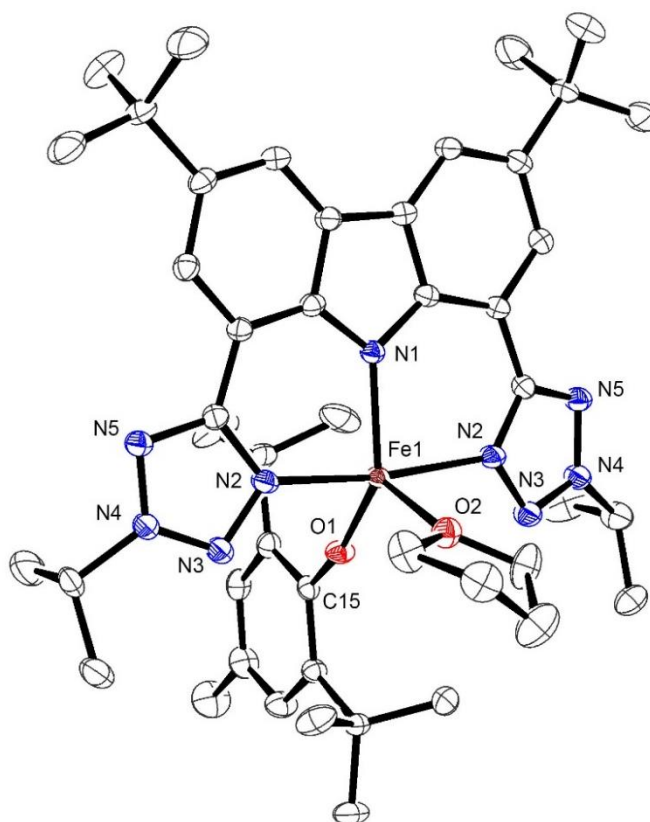


Figure 5.9 ORTEP3¹⁰⁸ plot (50% probability ellipsoids) of $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})(\text{THF})$ (**30**) (H atoms omitted for clarity)

Table 5.1 Selected bond lengths (Å) and angles (°) of (CzT^{iPr})Fe(OAr)(THF) (**30**)

Fe1-N1	2.065(2)	Fe1-O1	1.8977(13)
Fe1-N2	2.1991(12)	Fe1-O2	2.1494(14)
N1-Fe1-N2	86.20(3)	N2-Fe1-O2	89.14(3)
N1-Fe1-O1	135.28(6)	N2-Fe1-N2'	171.06(6)
N1-Fe1-O2	110.67(6)	O1-Fe1-O2	114.04(6)
N2-Fe1-O1	94.36(3)	Fe1-O1-C15	167.18(12)

The Fe-N_{Tz} distance of 2.1991(12) in **30** is longer than other reported tetrazolyl Fe complexes (range corrected to match five coordinate high spin Fe(II)¹³⁰: range 1.870(4)-2.076(2) Å, median 2.05 Å)^{187, 192, 243}. The fact that the CzT ligand N-Fe bond lengths are all on the longer end of the range of known values suggests high spin Fe(II). The Fe-O_{THF} distance in **30** matches well with other five coordinate high spin Fe(II) THF complexes (range 2.058(1)-2.368(1) Å, median 2.16 Å)²⁴⁴. The Fe-OAr distance of 1.898(1) Å in **30** matches well with other known five coordinate high spin Fe(II) complexes with terminal phenoxide groups (range 1.815(2)-1.9840(11) Å, median 1.921 Å)^{239, 245-248}. Interestingly, the Fe-O-C angle in these terminal phenoxides are quite bent (range 126.9(2)-148.7(3)°) compared to the angle in **30**. The linear phenoxide angle in **30** could be sterically or electronically driven. The phenoxide oxygen could act as a π -donor and donate extra electron density to the Fe centre causing the angle to become more linear. Based on a literature search of all crystallographically characterized terminal Fe phenoxides (all coordination numbers, oxidation states and spin states) the data shows a large range of angles (99.7(3)-176.7(2)°) as well as Fe-O distances (1.773(2)-2.000(2) Å)²⁴⁹. A scatter plot of this data shows a weak correlation between bond length and angle suggesting that the Fe-O-C phenoxide angle is sterically driven rather than electronic (**Figure 5.10**) because if it was electronically driven, one would expect a substantial negative correlation.

From the data in **Figure 5.10** the correlation coefficient was calculated to be -0.46 showing a moderate correlation.

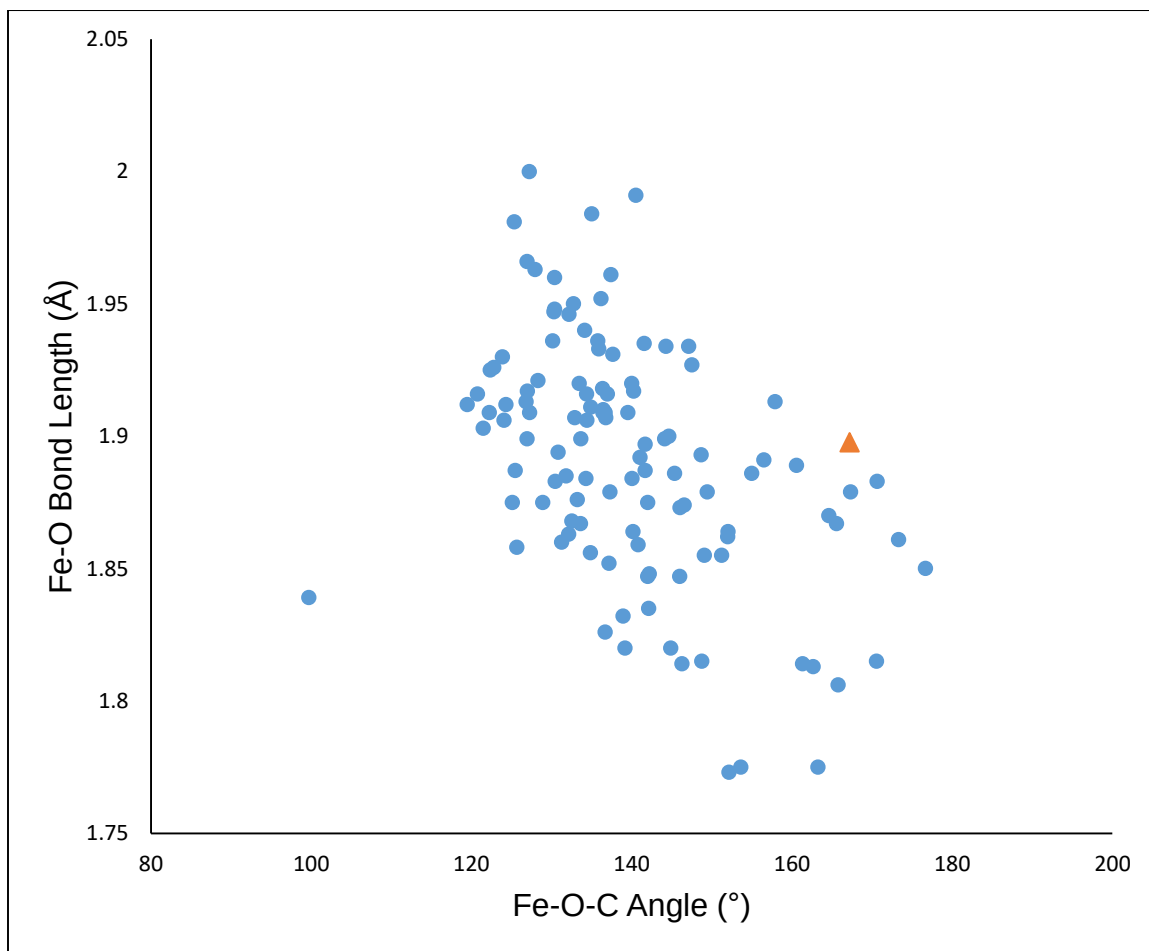


Figure 5.10 Scatter correlation plot of known terminal Fe phenoxide complexes $[(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})(\text{THF})]$ (**30**) denoted by orange triangle]

Most complexes with Fe-O bond lengths similar to that in **30** have significantly bent phenoxide angles (**Figure 5.10**). This suggests that our complex is more sterically crowded and the phenoxide is forced to sit in a linear orientation in order to relieve some steric congestion. A more in-depth crystallographic comparison of the Fe phenoxide moiety will be discussed later in this Chapter.

5.3.2 (CzT^{iPr})Fe(OAr) Adducts

With **30** being the only crystallographically characterized mono-ligand Fe complex in this work up until now, we decided to use it as the main platform for testing reactivity and behaviour of mono-ligand Fe complexes with our CzT class of ligand. While the crystal structure gives us good insight into the bonding, sterics and geometry of the complex, it gives little information on the electronic properties of the Fe centre itself. In order to determine what class of catalysis or reactivity is available to this complex it is important to understand more about the electronics of the Fe centre and the complex as a whole. One simple experiment that divulges the electronics of the metal centre in an organometallic complex is to form a CO complex and use the resulting IR CO stretching frequency as an indicator if the metal is electron rich or poor¹⁵. Transition metal carbonyl complexes are extremely common and the use of their CO stretching frequencies to determine the electron density at the metal has been widespread among inorganic chemists for many decades.

Attempts to form a mono-ligand Fe carbonyl complex with **30** were conducted by simply charging a Kontes flask with **30** in toluene under CO gas, and stirring for several hours at room temperature. Upon addition of CO there was an immediate colour change from yellow to dark green and unlike the case with oxygen exposure, the dark green colour persists and the final product is dark green. The resulting paramagnetic complex ¹H NMR spectrum shows the same pattern of peaks that was seen in the spectrum of **30**, but all the resonances have shifted (**Figure 5.11**). This pattern is consistent with replacement of THF by CO, although it was somewhat surprising that the NMR spectrum was of a paramagnetic complex as CO is a strong field ligand and the resulting complexes are generally low spin²⁵⁰⁻²⁵².

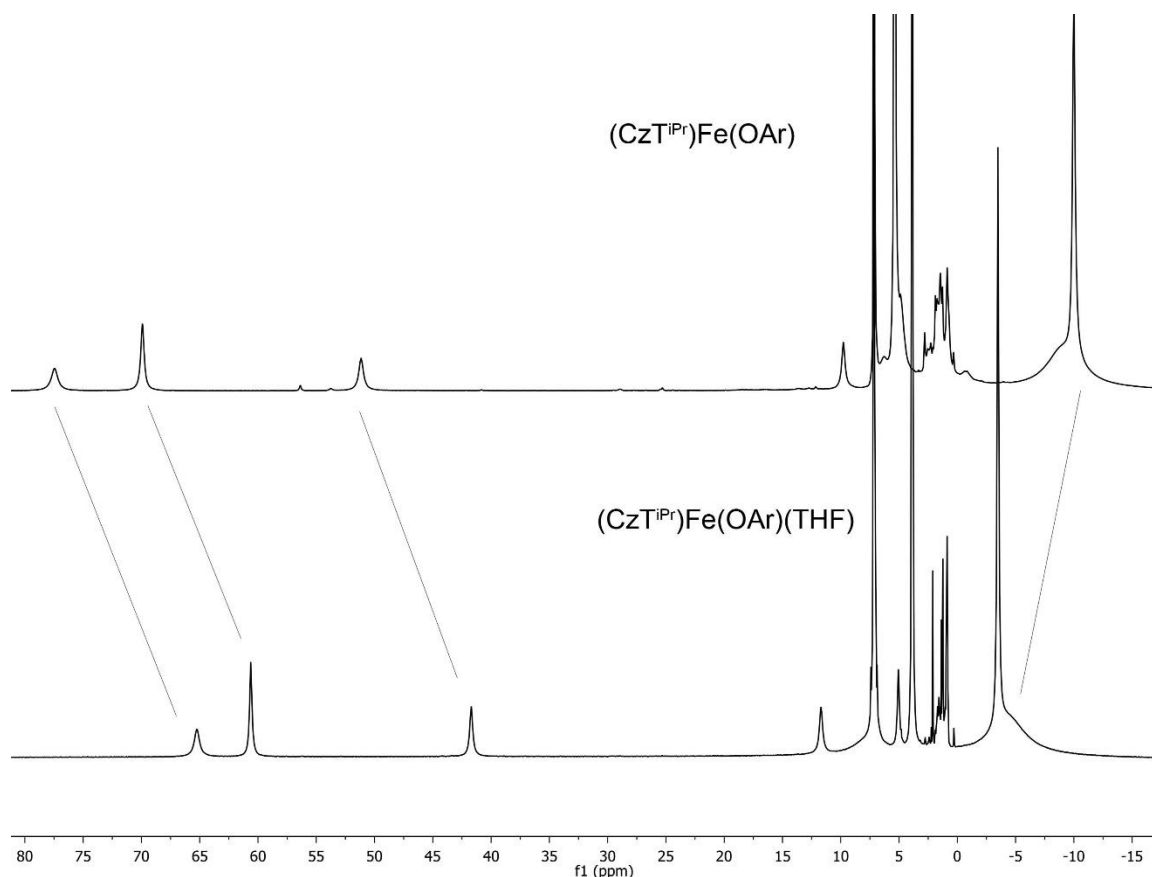
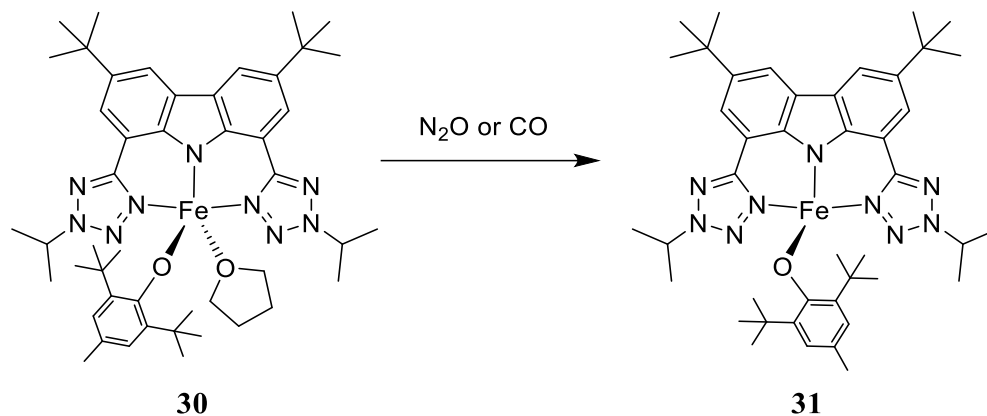


Figure 5.11 ^1H NMR spectrum (300 MHz, C_6D_6) stack plot of $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})(\text{THF})$ (**30**) and $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})$ (**31**) at 298 K

To our surprise, the IR spectrum of the dark green product showed no peaks in the carbonyl region! Since carbonyl stretching frequencies are generally very strong and sharp, the IR spectrum suggested that the product contained no carbonyl groups. This result was initially very confusing as there is clear evidence for some sort of transformation given the drastic colour change and shift in NMR resonances. It is also unlikely that the “ $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})$ ” moiety has been destroyed or the geometry significantly changed since the NMR spectrum shows the same pattern of resonances as in the THF adduct. While attempting to grow X-ray quality crystals it was also determined that this product is quite

thermally sensitive; gentle heating of a solution of the dark green product showed no additional colour change, but resulted in a drastic change in the NMR spectrum. After heating there were no discernable ligand or phenoxide peaks present so it appears as though the complex was completely destroyed.

Our surprise increased when it was found that reaction of **30** with N₂O gave the exact same product. Initially N₂O was reacted with **30** in attempts to oxidize Fe and form an Fe=O complex. The Evans' method was conducted on the dark green product and it was determined to have a magnetic moment of 5.16 μ_B , consistent with high spin Fe(II). These results along with the NMR spectrum suggested that the (CzT^{iPr})Fe(OAr) complex is still intact, but has changed in some way and is no longer **30**. This mystery was finally solved when X-ray quality crystals of the dark green product were grown from room temperature hexanes and a structure determined. Shockingly the X-ray structure showed a four coordinate Fe complex that retained the CzT^{iPr} and OAr ligands around the Fe with an open coordination site where the THF had been bound. The synthesis of this Lewis base-free (CzT^{iPr})Fe(OAr) complex, **31**, is shown in **Scheme 5.7** and a representative ORTEP diagram is shown in **Figure 5.12** with selected bond lengths and angles in **Table 5.2**.



Scheme 5.7 Synthesis of (CzT^{iPr})Fe(OAr) (**31**)

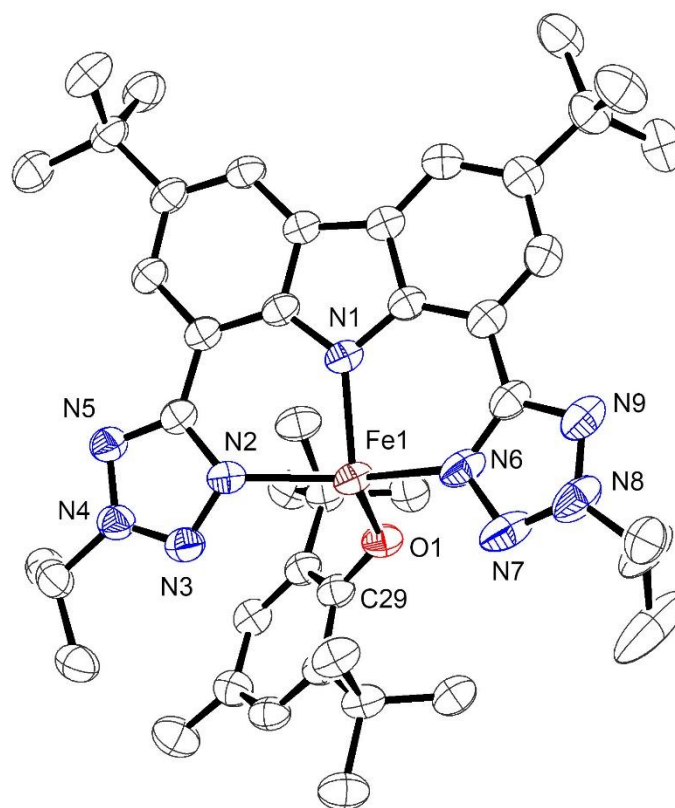


Figure 5.12 ORTEP¹⁰⁸ plot (50% probability ellipsoids) of (CzT^{iPr})Fe(OAr) (**31**) (H atoms omitted for clarity)

Table 5.2 Selected bond lengths (Å) and angles (°) of (CzT^{iPr})Fe(OAr) (**31**)

Fe1-N1	2.036(2)	Fe1-N6	2.122(2)
Fe1-N2	2.108(2)	Fe1-O1	1.894(2)
N1-Fe1-N2	85.57(8)	N2-Fe1-O1	103.80(8)
N1-Fe1-N6	85.89(8)	N6-Fe1-O1	104.03(8)
N1-Fe1-O1	131.04(7)	Fe1-O1-C29	126.16(2)
N2-Fe1-N6	149.30(8)		

The geometry around the Fe is somewhere between a trigonal bipyramid missing an equatorial ligand and a distorted tetrahedron with the CzT ligand folded somewhat and binding in a tridentate pseudo-*mer* orientation with the phenoxide occupying the fourth site. Looking closely at the packing in the unit cell, it shows a repeating pattern of two molecules of **31** positioned “back to back” to each other with the phenoxide groups pointing outwards (**Figure 5.13**); this packing is likely facilitated by π -stacking of the tetrazole aromatic rings. The Fe-N_{Cbz} distance of 2.036(2) Å in **31** is longer than other reported four coordinate high spin Fe(II) carbazolidine complexes (range 1.958(4)-2.019(2) Å, median 1.994 Å)^{183, 185-186}, as was also seen in the THF adduct crystal structure. There are no structurally characterized four coordinate Fe tetrazole or triazole complexes to compare to, but the Fe-N_{Tz} distances in **31** (2.108(2), 2.11(3) Å) are longer than other Fe tetrazole complexes when the range has been corrected to match four coordinate high spin Fe(II)¹³⁰ (range 1.860(2)-2.069(2) Å, median 2.036 Å)^{187, 192, 243}. The Fe-O distance of 1.894(2) Å in **31** is consistent with other reported four coordinate high spin Fe(II) terminal phenoxide complexes (range: 1.874(4)-1.948(3) Å, median 1.899 Å)²⁵³. The most striking feature of the crystal structure of **31** is that the Fe-O-C angle of the phenoxide is now significantly bent (126.16(2)°) compared to the THF adduct complex (167.18(1)°). The Fe-OAr angle in **31** is also smaller than all other reported four coordinate, high spin Fe(II)

complexes with similar terminal phenoxides (range of 130.2(3)-170.6(2)°, median 139.5°)²⁵³.

Upon closer inspection, one methyl of a tBu group on the phenoxide is pointed towards the Fe centre and one hydrogen atom (H42A) approaches the Fe centre quite closely (2.097 Å) as illustrated in **Figure 5.14**. The Fe-H close contact observed here falls within what are generally referred to as agostic or “remote agostic” interactions based on other Fe structures with close Fe-H contacts (Fe-H bond length range: 1.874-2.750 Å)²⁵⁴⁻²⁵⁸. The highly bent Fe-O-C phenoxide angle in **31** could be the result of this Fe-H agostic interaction.

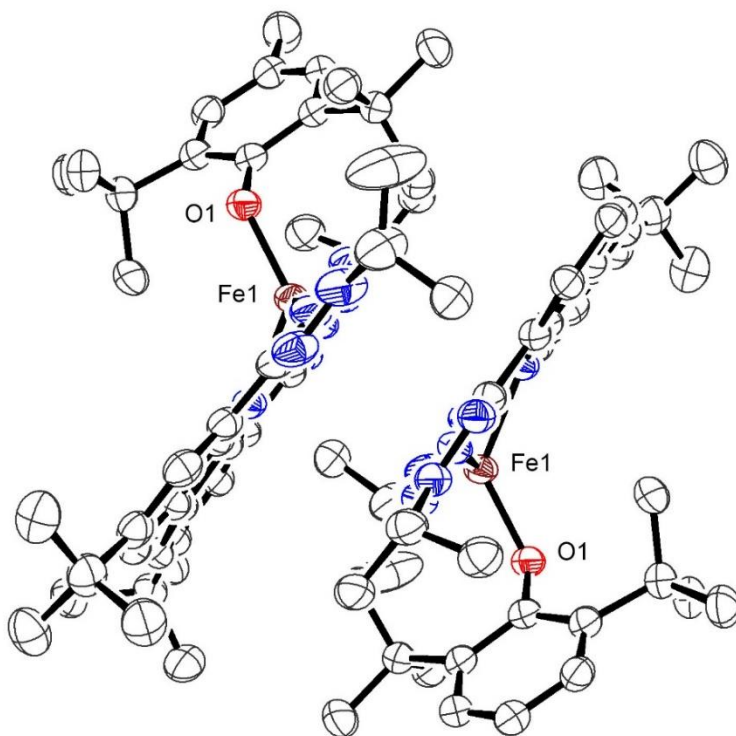


Figure 5.13 Stacking of (CzT^{iPr})Fe(OAr) (**31**) in crystal structure

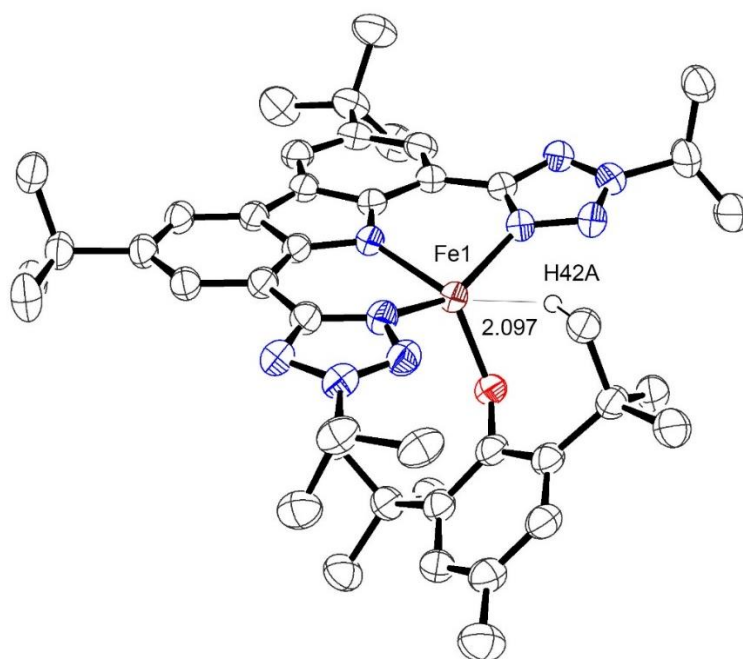
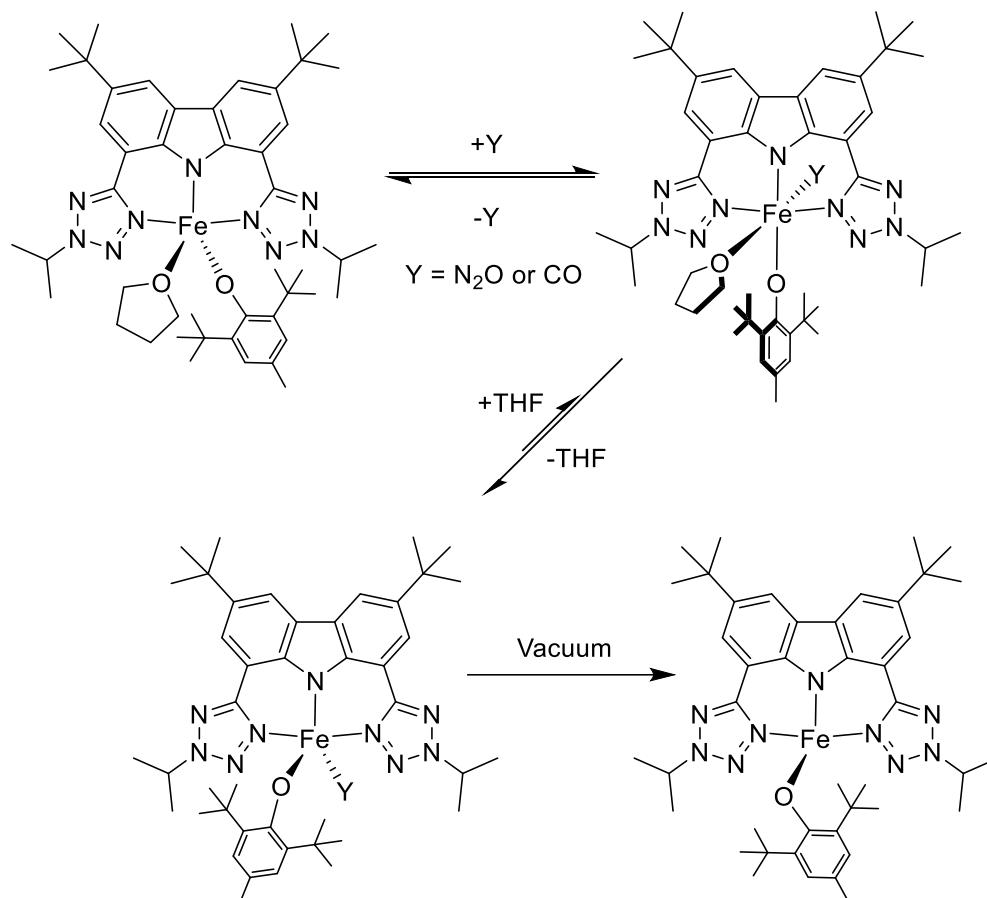


Figure 5.14 Agostic interaction in $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})$ (**31**)

CO is an excellent π -acceptor ligand, so the fact that it does not bind to the Fe centre in **31** at the vacant site suggests that there is little if any π back-donation from the Fe centre to CO. N_2O is also a π -acceptor ligand but a poor σ -donor ligand and again we see displacement of THF, but no permanent binding of the N_2O to the Fe centre. The Fe complex would seemingly rather be four coordinate and have an open coordination site (or an agostic interaction) than bind CO or N_2O . When **31** is dissolved in THF there is a slow conversion from dark green to yellow and the original five coordinate **30** complex is regenerated; presumably in this transformation the phenoxide Fe-O-C angle returns to linear. THF is a σ -donor ligand and binds to the Fe centre, albeit fairly weakly, given the fact it is readily displaced in the presence of poor competitors (CO, N_2O) in non-coordinating solvents. These observations suggest that the Fe centre is not particularly

electron poor and likely lacks appropriate filled π symmetry orbitals at the vacant site to bond with π -acceptors.

Since it seems as though the only function of CO or N₂O gas in the reaction with **30** is to displace the THF, attempts were made to synthesize **31** by simply removing the weakly bound THF under vacuum. A finely ground powder sample of **30** was placed under full vacuum for several hours and gently heated to promote removal of the THF. While there was a colour change of the sample from yellow to dark red, the resulting product was not **31** but rather some sort of oxidized degradation product. This possibly suggests that **31** is synthesized through an associative mechanism (**Scheme 5.8**) with the N₂O/CO binding to form a six coordinate Fe complex before the THF and fifth ligand dissociate (upon exposure to vacuum to remove solvent) leaving a four coordinate complex. This N₂O associative mechanism is speculative at this point, but would be a reasonable explanation for the observed results. The N₂O would likely be extremely labile as it is a poor σ -donor ligand and known transition metal complexes with an intact N₂O moiety are extremely rare²⁵⁹⁻²⁶⁰. There is one example in the literature with a bound N₂O ligand on an Fe centre but this complex is a metal-organic framework (MOF) and the presence of bound N₂O was inferred from powder neutron diffraction data²⁶¹.



Scheme 5.8 Synthesis of $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})$ (**31**) through an associative mechanism

While the reaction of **30** with N_2O and CO give the same final product, it was found that in the case of N_2O a significant amount of another product was formed during the reaction. In almost every reaction of **30** with N_2O there is a second set of paramagnetic resonances seen in the NMR spectrum and the amount of this other product fluctuates from reaction to reaction. This second product is considerably less soluble than **31** and is yellow, not dark green. A stack plot containing the ^1H NMR spectrum of the pure dark green product **31**, a mixture of both products and the pure yellow unknown product is shown in **Figure 5.15**.

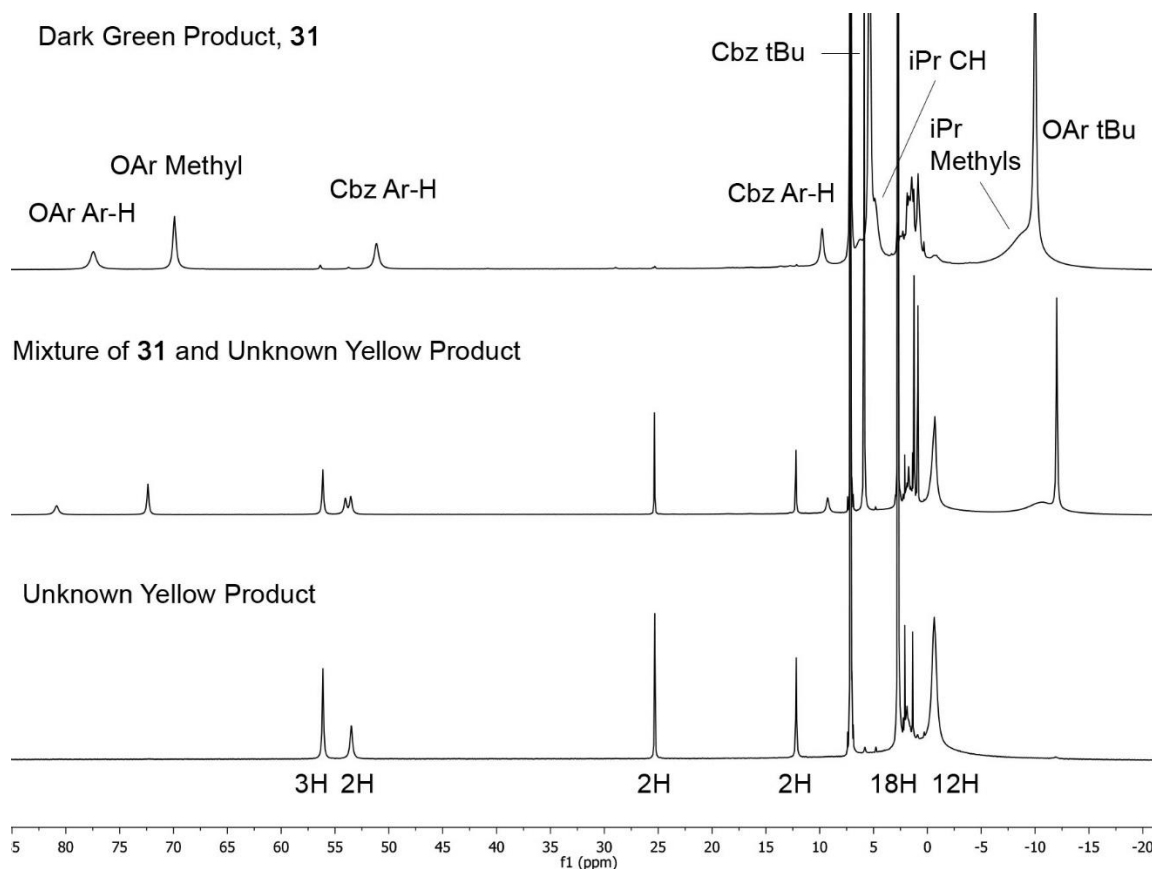


Figure 5.15 ^1H NMR spectrum (300 MHz, C_6D_6) stack plot of $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})$ (**31**) and unknown yellow N_2O product at 298 K

Upon closer inspection of the yellow product NMR spectrum, there is a pattern consistent with a full set of resonances for one CzT^{iPr} ligand (three 2 H, one 12 H and one 18 H resonances) and then one remaining resonance that integrates to three protons. This pattern and the paramagnetic nature of the spectrum suggests that it is some sort of Fe complex containing one bound CzT^{iPr} . No structural data was ever obtained on this product so the final characterization was never achieved.

Since it appears **31** preferentially binds σ -donors and not π -acceptors, different adducts were synthesized from the starting THF adduct **30**. Isonitriles are isoelectronic with CO, but are easier to work with since they are liquids or solids and are slightly better

σ -donors and poorer π -acceptors than CO. The isonitrile tBuNC was reacted with **30** in toluene to produce a fairly insoluble lime green product even in THF. The ^1H NMR spectrum in THF- D_8 is complicated but matches well with the ^1H NMR spectrum of **30** in THF- D_8 . This suggests, not surprisingly, that some displacement of tBuNC by the solvent is occurring.

Fortunately, an X-ray quality crystal was grown from the crude reaction mixture and the structure shows that tBuNC is bound to the Fe centre. A representative ORTEP diagram of $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})(\text{tBuNC})$, **32** is shown in **Figure 5.16**, and selected bond lengths and angles are collected in **Table 5.3**.

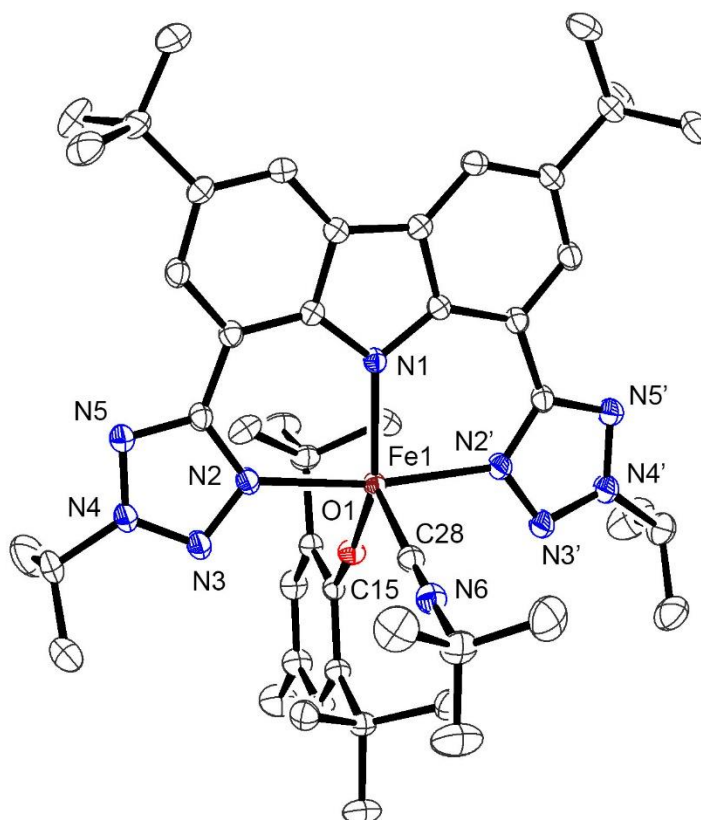


Figure 5.16 ORTEP3¹⁰⁸ plot (50% probability ellipsoids) of (CzT^{iPr})Fe(OAr)(tBuNC) (**32**) (H atoms omitted for clarity)

Table 5.3 Selected bond lengths (Å) and angles (°) of (CzT^{iPr})Fe(OAr)(tBuNC) (**32**)

Fe1-N1	2.082(2)	Fe1-O1	1.8956(14)
Fe1-N2	2.2076(12)	Fe1-C28	2.135(2)
N1-Fe1-N2	85.34(3)	N2-Fe1-C28	91.80(3)
N1-Fe1-O1	137.96(6)	N2-Fe1-N2'	170.67(6)
N1-Fe1-C28	114.30(7)	O1-Fe1-C28	107.74(7)
N2-Fe1-O1	93.55(3)	Fe1-O1-C15	171.21(13)

The geometry around the Fe centre is trigonal bipyramidal with the CzT^{iPr} ligand binding in a *mer* orientation. The Fe-N_{Cbz} distance of 2.082(2) Å in **32** is longer than other reported Fe carbazolidate complexes (range corrected to match five coordinate high spin Fe(II)¹³⁰: range 1.989(3)-2.027(4) Å, median 2.020 Å)^{105, 183-184, 224}. There is only one structurally characterized high spin five coordinate Fe(II) tBuNC complex in the literature, and the Fe-CNtBu bond length (2.094(6) Å)²⁶² is shorter than the bond length in **32** (2.135(2) Å). There are several structurally characterized six coordinate Fe(II) tBuNC structures, but they are all low spin, and the lengths reported are much shorter than our reported values (corrected to match five coordinate high spin Fe(II)¹³⁰: range 1.868(4) – 1.938(5) Å, median 1.9125 Å)²⁶³⁻²⁷⁰. Similar to CO, tBuNC is a strong field ligand so it is not surprising that high spin Fe complexes of isonitriles are rare. The ability of tBuNC to bind to Fe in **30** but not to drop the spin state to low spin strongly suggests that there is little to no π -backdonation from the metal to the isonitriles and that the Fe-C bond is clearly labile. We are unable to compare the NC bond length in our complex to that of free tBuNC since there appears to be no structurally characterized free tBuNC (based on a CSD search). The closest approximation is from a bridged tBuNC between two Cr centres where the NC bond length is 1.151(3) Å²⁷¹. The authors suggest very little π -backdonation from the metal to the isonitrile in this structure based on a very slight shift in the CN IR stretching frequency (2150 cm⁻¹ vs 2135 cm⁻¹). The nitrile NC triple bond length in **32** of 1.139(3) Å is actually shorter than the closest approximation of free tBuNC [1.151(3) Å]²⁷¹. If there was any π -backdonation from the metal to the isocyanide it would increase the NC bond length due to populating antibonding orbitals. All of this data is consistent with tBuNC acting solely as a weak sigma donor in **32** which is highly unusual for a strong field ligand

such as an isonitrile. Another notable feature of the crystal structure is that the Fe-O-C bond angle of the phenoxide is again linear with an angle of $171.21(1)^\circ$, similar to that seen in the THF adduct. As discussed in the case of the THF adduct, this bond angle is most likely controlled by steric rather than electronic factors.

As one further test of the binding capabilities of **30** with σ -donor ligands, triphenylphosphine oxide (TPPO) was reacted with the starting THF adduct **30**. Upon addition of the phosphine oxide to a toluene solution of **30** there is a colour change from yellow to pale orange. The resulting paramagnetic complex ^1H NMR spectrum of the product $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})(\text{TPPO})$ (**33**) taken in benzene- D_6 is shown in **Figure 5.17**.

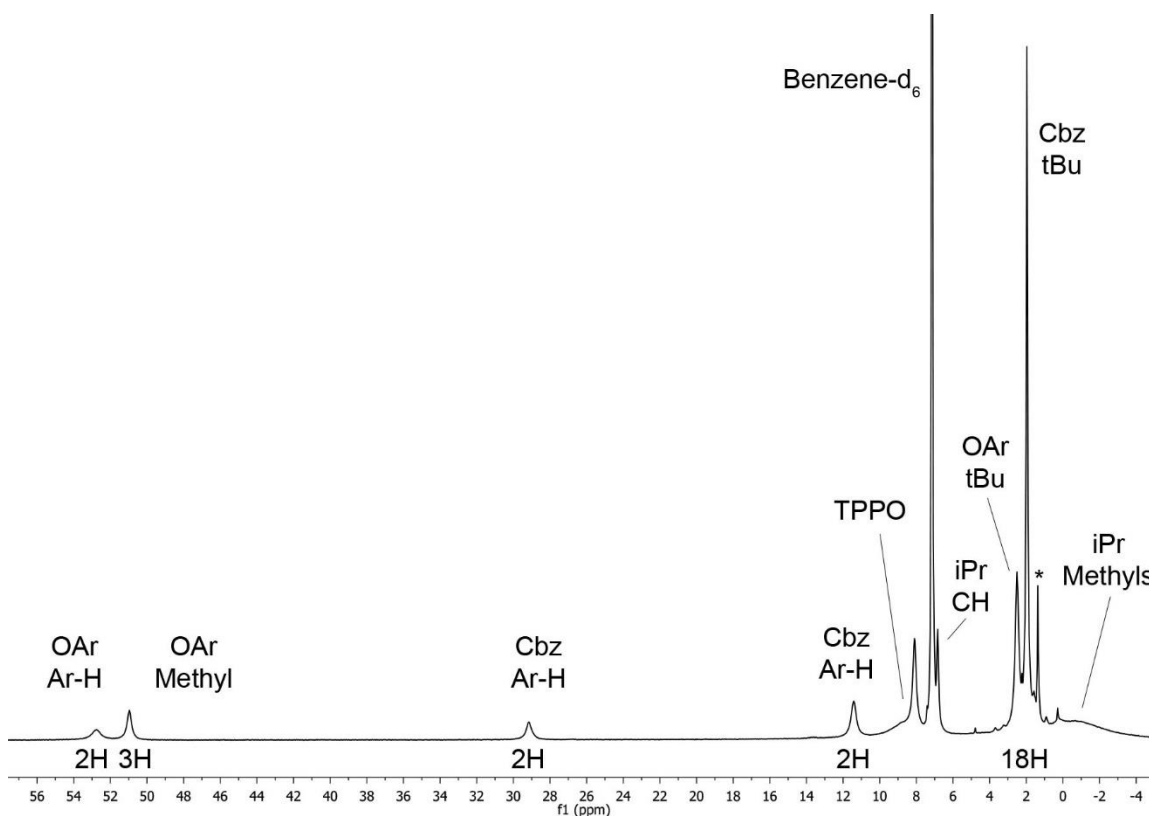


Figure 5.17 ^1H NMR spectrum (300 MHz, C_6D_6) of $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})(\text{TPPO})$ (**33**) at 298 K (* denotes residual hexanes resonances)

The spectrum shows a familiar pattern of resonances consistent with **30** and other adducts, but there are clearly broad resonances, most likely due to the aromatic protons of TPPO, under the sharper CzT iPr and tBu resonances. X-ray quality crystals of the TPPO adduct (CzT^{iPr})Fe(OAr)(TPPO) (**33**) were grown from the reaction mixture and the solid state structure was obtained. A representative ORTEP diagram of **33** is shown in **Figure 5.18** and selected bond lengths and angles are collected in **Table 5.4**.

The geometry around the Fe centre is trigonal bipyramidal with the CzT^{iPr} ligand binding in a pseudo *mer* orientation although the N2-Fe1-N6 angle is somewhat folded at 161.58(7)°. The Fe-N_{Cbz} distance of 2.081(2) Å in **33** is longer than other reported Fe carbazolidine complexes (range corrected to match five coordinate high spin Fe(II)¹³⁰: range 1.989(3)-2.027(4) Å, median 2.020 Å)^{105, 183-184, 224}. The Fe1-O2 bond length of 2.0857(14) Å in **33** is also longer than other reported Fe TPPO complexes (corrected to match five coordinate high spin Fe(II)¹³⁰ range: 1.941(2)-2.038(4) Å, median 1.986 Å)²⁷²⁻²⁷⁶. The Fe1-O2-P1 angle in **33** of 150.81(9)° is fairly consistent with other reported Fe complexes (range: 137.9(1)-164.2(2)°, median 154.42°)²⁷²⁻²⁷⁶, although these complexes range from three to six coordinate and are a mix of high spin Fe(II) and Fe(III).

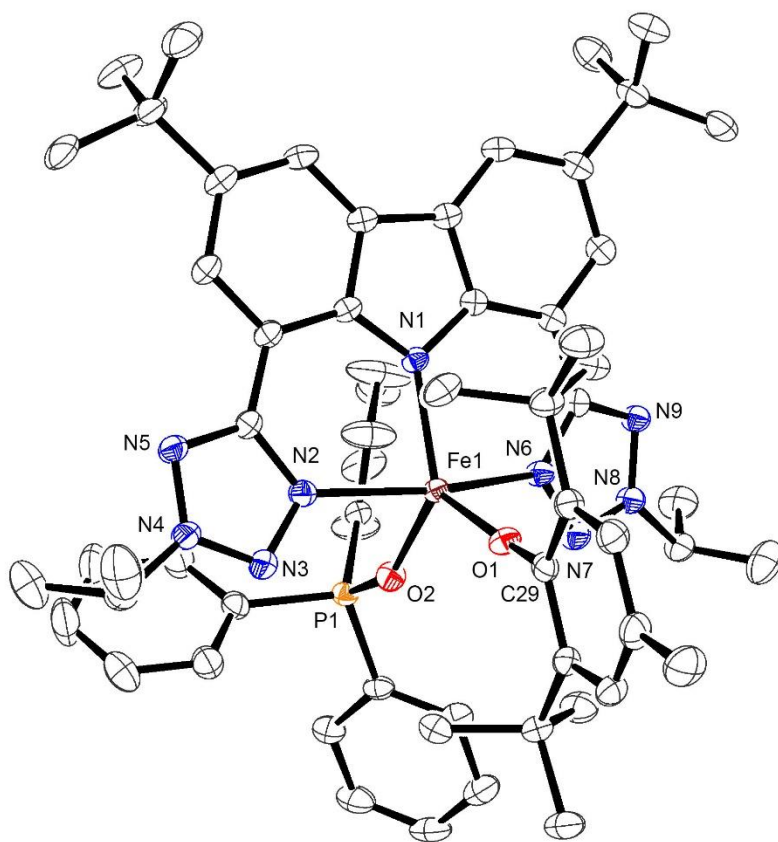


Figure 5.18 ORTEP3¹⁰⁸ plot (50% probability ellipsoids) of (CzT^{iPr})Fe(OAr)(TPPO) (**33**) (H atoms omitted for clarity)

Table 5.4 Selected bond lengths (Å) and angles (°) of (CzT^{iPr})Fe(OAr)(TPPO) (**33**)

Fe1-N1	2.081(2)	Fe1-O1	1.8907(14)
Fe1-N2	2.215(2)	Fe1-O2	2.0857(14)
Fe1-N6	2.184(2)		
N1-Fe1-N2	86.00(6)	N2-Fe1-N6	161.58(7)
N1-Fe1-N6	84.75(6)	N6-Fe1-O1	96.12(6)
N1-Fe1-O1	125.93(6)	N6-Fe1-O2	84.64(6)
N1-Fe1-O2	119.48(6)	O1-Fe1-O2	114.39(6)
N2-Fe1-O1	102.21(6)	Fe1-O1-C29	168.34(13)
N2-Fe1-O2	86.11(6)	Fe1-O2-P1	150.81(9)

The only five coordinate Fe TPPO complexes that are structurally characterized are porphyrins where the oxidation state is Fe(III) and the geometry is completely different. Based on the fairly long Fe-O2 bond length and the bent angle of the TPPO it seems that the TPPO is acting as a σ -donor ligand and there are no π interactions occurring either from or to the metal centre. The Fe-O-C phenoxide angle in **33** is again fairly linear with an angle of 168.31(1)° similar to those of the THF and tBuNC adduct presented in this work.

Based on a structure search in the Cambridge Structural Database (CSD) there are very few five or four coordinate Fe complexes with a terminal phenoxide and none of the structures contain a tridentate mono-anionic pincer ligand analogous to CzT discussed in this work. This makes it extremely difficult to structurally and electronically compare the results found in our work with similar known Fe complexes. Due to this, the best structural comparison to make is to compare all four Fe(OAr) complexes from this work with each other. All four of the structures discussed in this chapter are high spin Fe(II) terminal phenoxides with a coordination number of four or five, but the variance in the Fe-O-C bond angle of the phenoxide is not negligible. A comparison of selected bond lengths and angles from all four Fe phenoxide complexes has been collected in **Table 5.5**.

Table 5.5 Selected bond lengths (Å) and angles (°) of (CzT^{iPr})Fe(OAr)L (L = THF, open coordination site, tBuNC, TPPO)

L	Fe-N_{Cbz}	Fe-N_{Tz}	Fe-O_{Ar}	Fe-O-C	N_{Tz}-Fe-N_{Tz}
Lewis Base-Free (31)	2.036(2)	2.108(2) 2.122(2)	1.894(2)	126.16(2)	149.30(8)
THF (30)	2.065(2)	2.1992(12)	1.8977(13)	167.18(12)	171.06(6)
tBuNC (32)	2.082(2)	2.2075(12)	1.8956(14)	171.21(13)	170.67(6)
TPPO (33)	2.081(2)	2.215(2) 2.184(2)	1.8907(14)	168.34(13)	161.58(7)

Comparing the data from **Table 5.5** there are no unexpected trends or deviations (apart from the phenoxide angle, *vide infra*). All three five coordinate structures show fairly consistent bond lengths and angles and those involving the CzT ligand are considerably longer than those in the four coordinate Lewis base-free complex as might be expected. However, the Fe-OAr bond is the *same* length in the four coordinate bent structure. This could be a reflection of less π -donation from O in this bent form or it could reflect a necessary lengthening to allow the close approach of the agostic C-H interaction. Whichever effect predominates, the Fe-OAr distance is substantially longer in the Lewis base-free complex than expected.

5.3.3 DFT Calculations

It has been experimentally proven that **30** binds σ -donors fairly well, but is poor at binding π -acceptors such as CO and N₂O. Four coordinate Fe complexes are fairly rare and usually extremely oxygen and sometimes even thermally sensitive. The fact that our Fe complex **31** would rather be four coordinate with an empty coordination site than bind a small π -acceptor ligand such as CO strongly suggests that the appropriate π orbitals are not available for back-donation. The binding of a bulky σ -donor ligands (TPPO) suggests that empty σ orbitals are accessible on Fe at this site. By studying the reactivity, chemical behaviour and solid state structures of the four Fe(OAr) adducts we were able to determine the elementary bonding picture of these complexes as well as what ligands are appropriate versus what bonding and reactivity would not be possible.

Using the four X-ray crystal structures obtained of all the (CzT^{iPr})Fe(OAr)L adducts, single point DFT calculations were conducted to visualize the frontier orbitals available for bonding. All calculations were done at the B3LYP level using the coordinates from the solid state structures to obtain the electronic structures. All four complexes showed four singly occupied molecular orbitals (SOMOs). The smallest SOMO-LUMO gap (SOMO4-LUMO, **Table 5.6**) is similar for all with values of 3.06 eV (405 nm), 2.95 eV (420 nm), 2.93 eV (423 nm) and 2.57 eV (493 nm) for the Lewis base-free, THF, tBuNC and TPPO complexes, respectively.

Table 5.6 MO energy levels (in eV) of (CzT^{iPr})Fe(OAr)L (L = open site, THF, tBuNC or TPPO)

	Open Site	THF	tBuNC	TPPO
LUMO +1	-1.398	-1.239	-1.113	-1.231
LUMO	-1.522	-1.360	-1.240	-1.267
SOMO4	-4.583	-4.315	-4.171	-3.780
SOMO3	-5.026	-4.780	-4.755	-4.673
SOMO2	-5.529	-5.502	-5.428	-5.017
SOMO1	-5.690	-5.553	-5.483	-5.137
HOMO	-5.913	-5.609	-5.568	-5.287

For the Lewis base-free complex, SOMO1 and SOMO3 are primarily carbazole π -bonding in character (**Figure 5.19**). SOMO2 is Fe-ligand σ -antibonding to all four donor atoms while SOMO4 is primarily phenoxide π -bonding in character. The LUMO is tetrazole π -bonding while the HOMO is phenoxide π -bonding. The bonding picture for the five coordinate adducts, also shown in **Figure 5.19**, is quite similar with some re-ordering of SOMO1 and SOMO2 for the tBuNC and TPPO adducts.

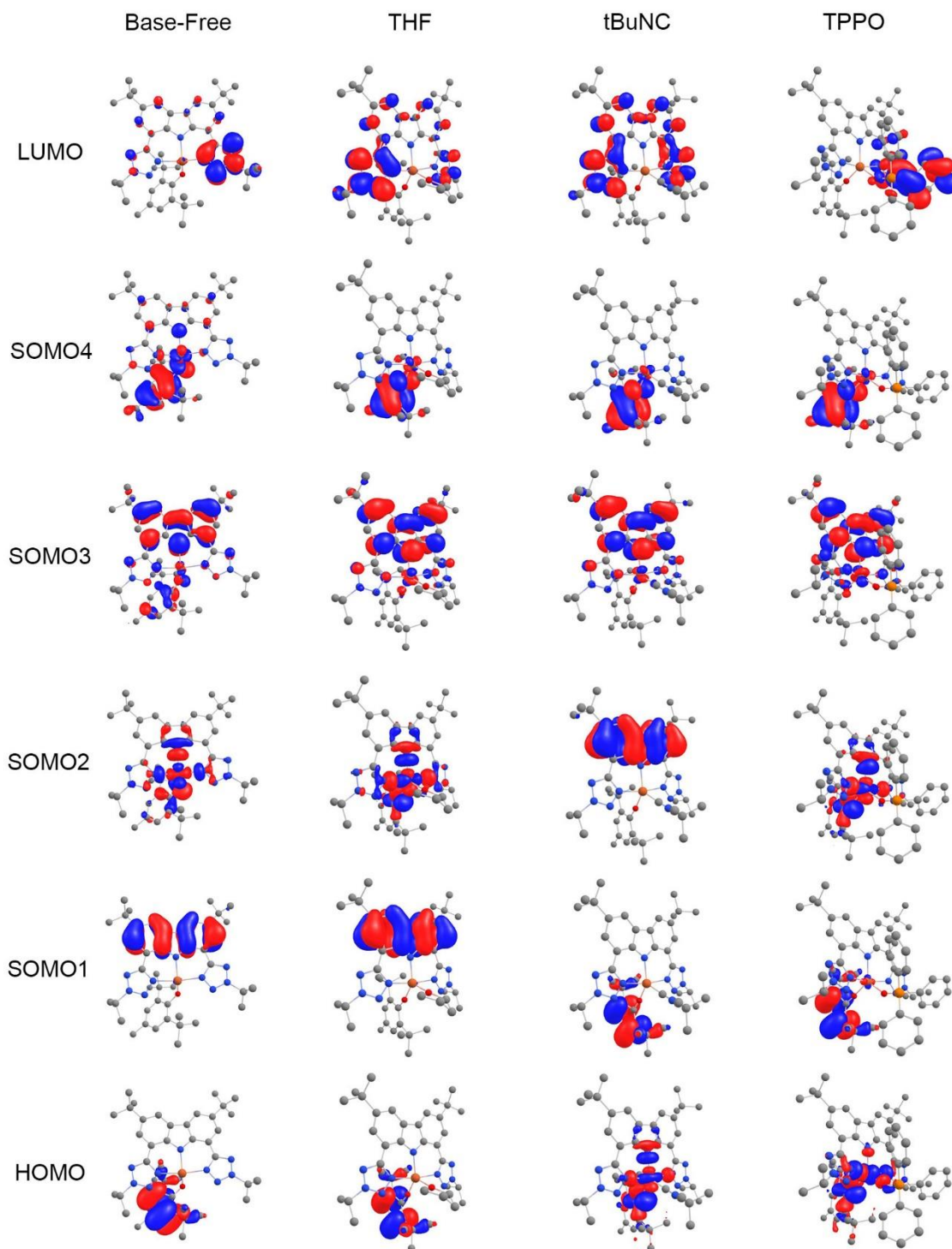


Figure 5.19 Frontier orbital diagrams of $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})(\text{THF})$ (**30**) adducts

Most notably, none of these orbitals have significant Fe character at the empty site. In fact, the lowest orbital with σ -acceptor character at the vacant site (in the Lewis base-free complex) is LUMO+14 (LUMO-LUMO+14 gap of 3.07 eV) while the highest energy filled orbital with potential π -donor character is HOMO-7 (HOMO-HOMO-7 gap of 1.39 eV). These orbital energies may explain the reactivity of these (CzT^{iPr})Fe(OAr)L complexes. The Lewis base-free complex is a relatively poor σ -Lewis acid because the σ -acceptor orbital is so high in energy while it also shows no tendency to form complexes with π -acceptors such as CO because the π -donor orbital is low in energy and a poor energy match with the CO acceptor orbital.

Interestingly when a geometry optimization calculation was done on the Lewis base-free complex, the resulting phenoxide angle becomes linear (169.3°) and the Fe-O bond length shortens to 1.859 Å. The solid state structure compared to the geometry optimized structure is shown in **Figure 5.20**. In terms of the difference in electronic structure between the geometry optimized and the population-based calculations, all four SOMOs are fairly similar. In the lowest energy level SOMO of the geometry-optimized structure there is some phenoxide and carbazole π -orbital character and the highest energy SOMO has more metal-based σ -antibonding character to all ligands that is not seen in the non-optimized structure. The biggest electronic difference between the two is in the HOMO. The HOMO of the geometry-optimized structure has both carbazole and phenoxide π -orbital character, whereas the solid state structure has only phenoxide π -orbital character. Also the SOMO-LUMO gap is slightly larger at 2.87 eV (433 nm) in the geometry optimized structure.

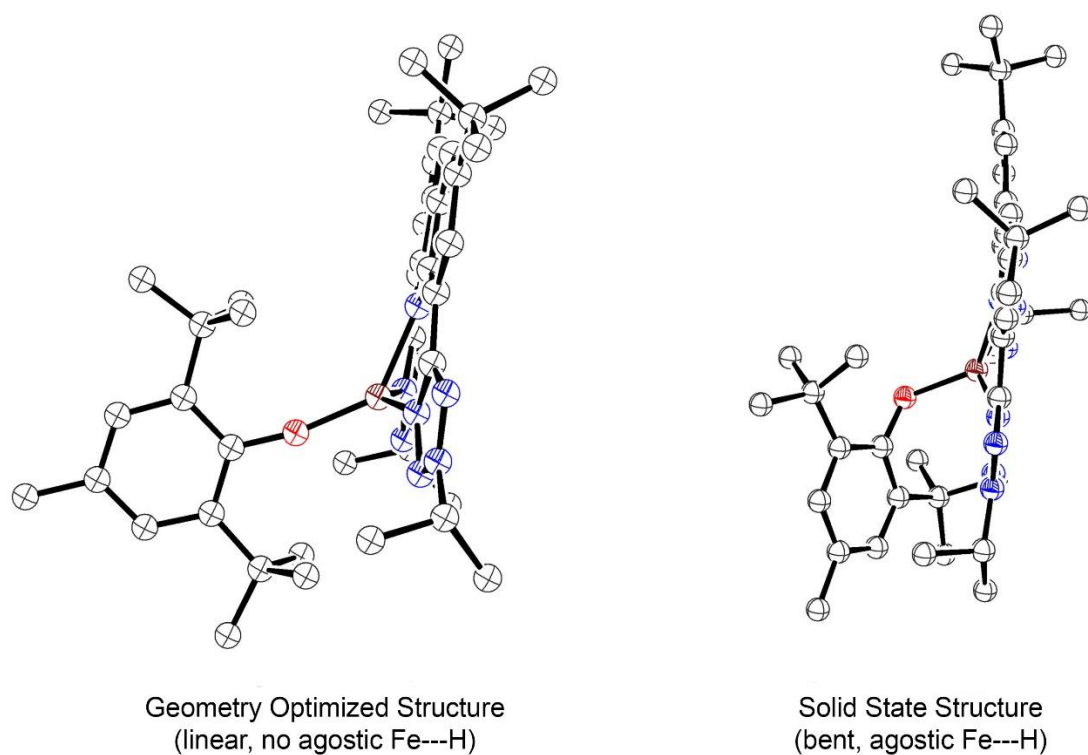


Figure 5.20 Solid state vs. geometry optimized structural comparison of $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})$ (**31**)

The discrepancy between the crystal structure and the geometry-optimized structure from DFT suggests that the phenoxide angle seen in the solid state is sterically, rather than electronically, driven. Crystal packing effects, π -stacking and agostic interactions may play an important role in the solid state. It is also possible that the phenoxide angle is more linear in solution for the Lewis base-free adduct than what was observed in the solid state. The shortened Fe-O bond length in the geometry optimized structure however does suggest some extra electron donation from the oxygen to the Fe that is not seen in the solid state structure.

5.3.4 Reactivity of (CzTⁱPr)Fe(OAr)(THF)

Successful isolation of a series of mono-ligand Fe phenoxide complexes that do not readily redistribute enabled us to attempt some reactivity studies. We decided to test the reactivity of the THF adduct because of its ease of synthesis, increased solubility and THF lability. Solid **30** reacts immediately upon exposure to air, the colour changing from yellow to dark red-black within seconds. In hydrocarbon solvents (benzene or toluene) the yellow solution turns dark green immediately on exposure to air, remains dark green for about an hour after which the solution eventually turns and remains dark red. **Figure 5.21** illustrates the changes that occur in the paramagnetic region of the ¹H NMR spectrum on exposure to air. Free phenol resonances are observed in the diamagnetic region at the green stage. The NMR spectrum at the dark red stage does not show any paramagnetic resonances outside the range of 8 ppm to 0 ppm.

The Evans' method was also conducted as the reaction progressed in an attempt to assign the Fe oxidation and spin state at each stage. The magnetic moment calculated by the Evans' method declines progressively from 5.26 μ_B at the initial yellow stage to 3.46 μ_B at the intermediate green stage and finally 1.98 μ_B at the final dark red end state. This data suggests the initial **30** complex reacts with atmospheric oxygen to generate a short-lived intermediate complex that undergoes further conversion to an air stable dark red product. While free phenol shows that the phenoxide group has been lost, the lack of diamagnetic, protonated HCzTⁱPr resonances in either the intermediate or final state suggests that this ligand is still complexed to Fe. The most obvious product that could form is the bis-ligand complex **23**. While there is some evidence for traces of **23** at the intermediate stage, there is no significant amount of this compound in the final red product.

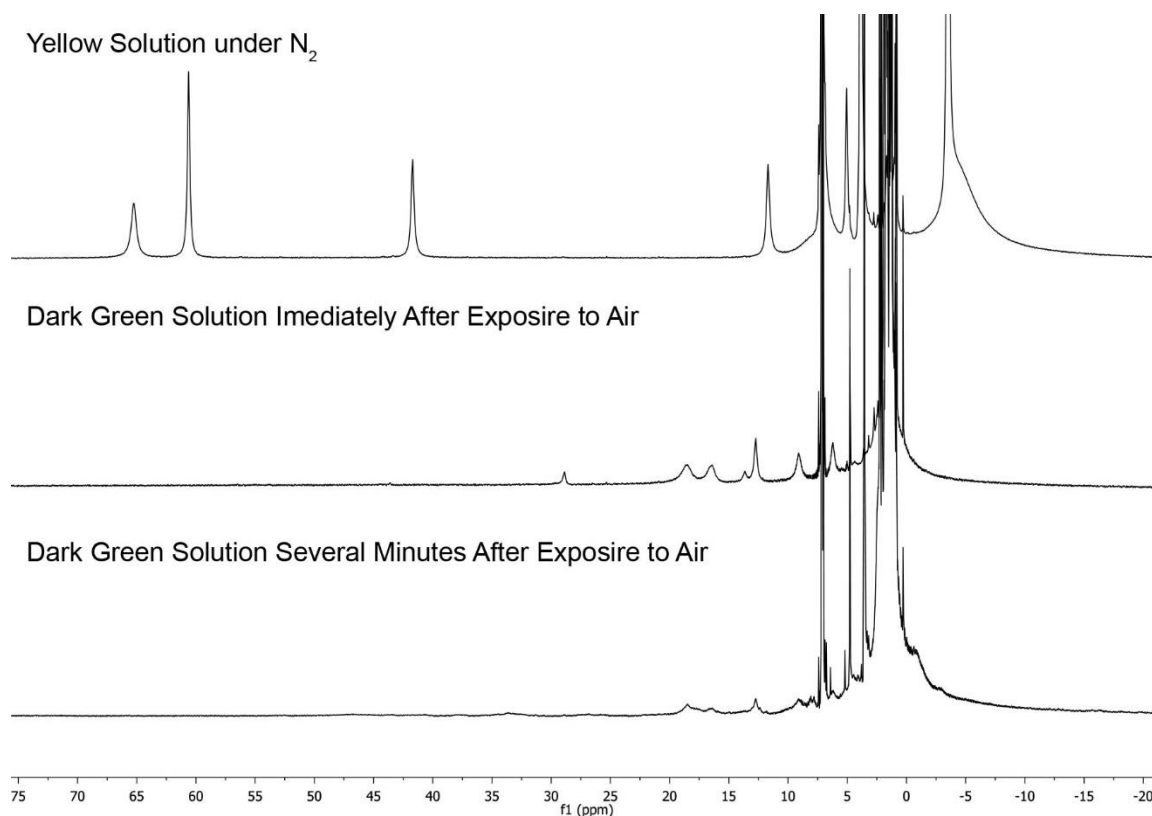


Figure 5.21 Stack plot of ^1H NMR spectrum (300 MHz, C_6D_6) of $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})(\text{THF})$ (**30**) at 298 K after immediate exposure to air

The oxidation reaction was also followed in the solid state by Mössbauer spectroscopy. A sealed Mössbauer sample holder containing **30** was monitored at room temperature for several days to make sure no air was leaking into the system. After establishing that the system was fully sealed, a small hole was punctured in the holder to oxidize the complex and the Mössbauer spectrum was recorded again (**Figure 5.22**). Unfortunately, MB spectra take several days to record so the intermediate dark green complex is probably too short lived to appear in the spectra.

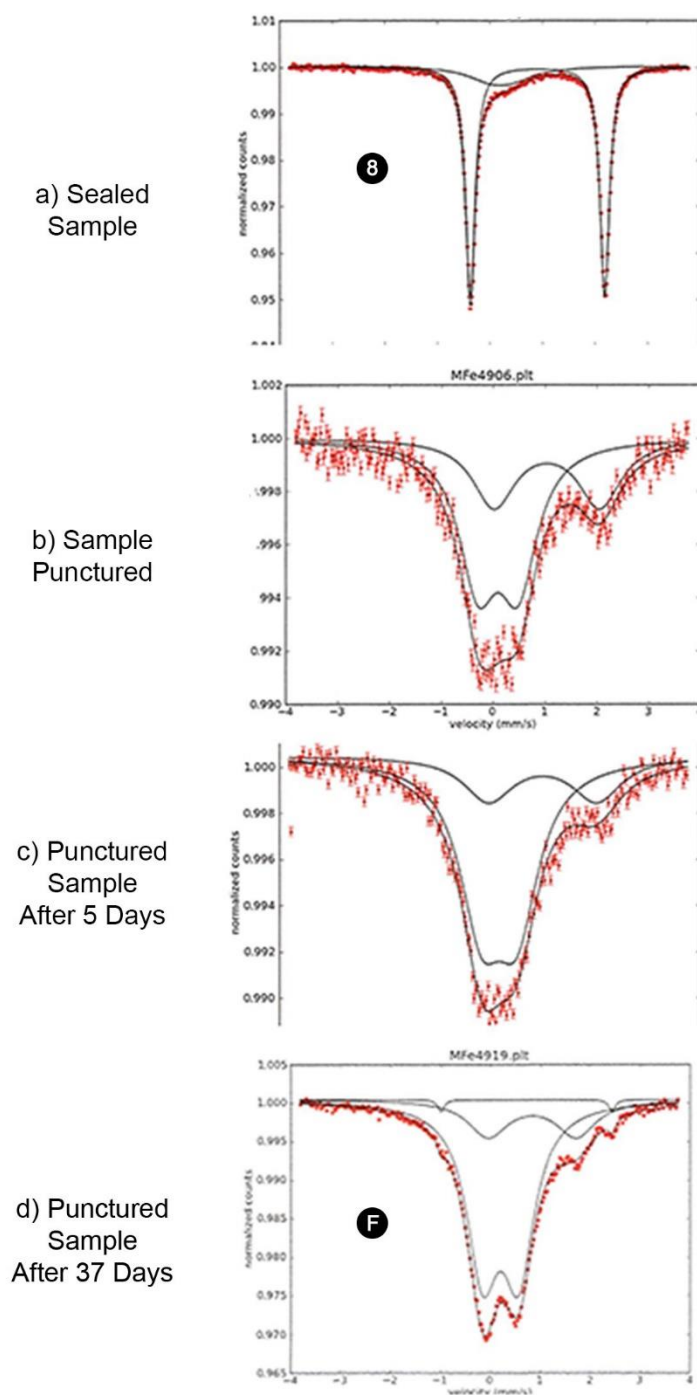
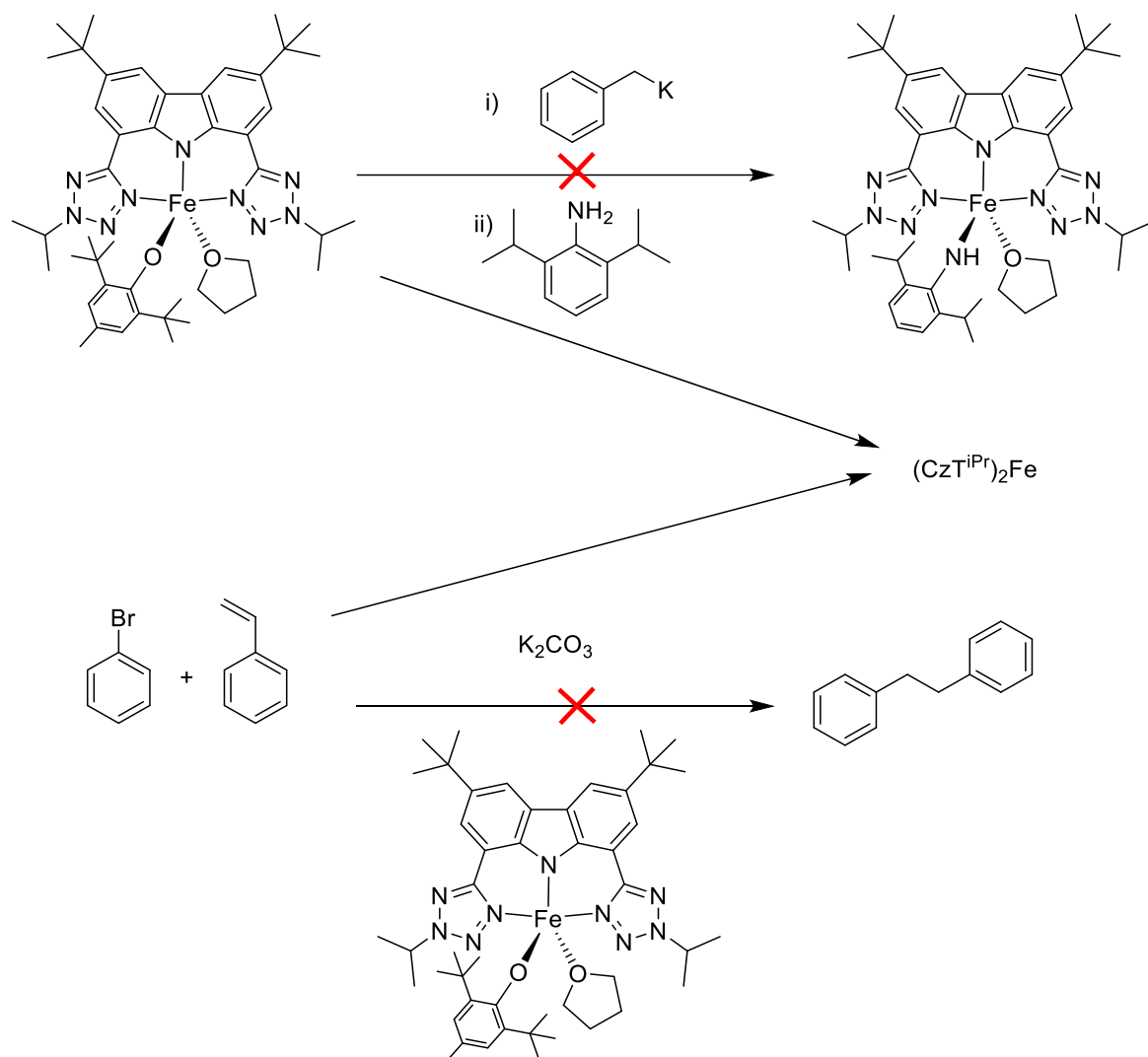


Figure 5.22 Mössbauer spectrum of $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})(\text{THF})$ (**30**), before and after exposure to air

There was an immediate change in the MB spectrum in terms of isomer shift and quadrupole splitting values as soon as the hole was punctured (**Figure 5.22(b)**) and the colour of the sample changed from yellow to dark red-black immediately. By day 37 (**Figure 5.22(d)**) the MB spectrum contained very little starting **30** and was mostly the oxidized product. The oxidized product peaks are consistent with an Fe(III) centre and are similar to the spectrum seen in **Figure 5.4** for the MB spectrum of **28** after exposure to air. In the case of **28** it was proposed that the oxidized product formed is likely ferrihydrite based on the isomer shift and quadrupole splitting values seen in the MB spectrum so that also appears to be the ultimate oxidation product here.

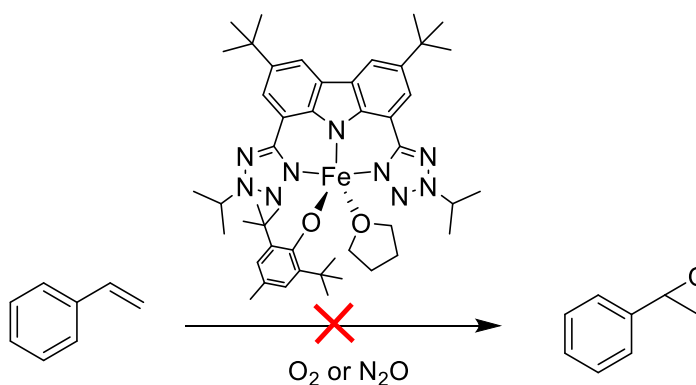
While **30** does not redistribute to the bis-ligand complex spontaneously, it was found that certain reagents caused the seemingly stable mono-ligand complex to redistribute to **23**. During initial attempts to form an aniline complex by first displacing the phenoxide through a salt metathesis reaction with benzyl potassium to form the benzyl complex *in situ* and then reacting with an aniline resulted in formation of the redistribution product **23** (**Scheme 5.9**). The same result was also found in attempts at a Heck-type cross coupling reaction of styrene and bromobenzene using **30** as a catalyst (**Scheme 5.9**). The common feature of these two reactions is that they use a potassium salt of a base. As previously mentioned, the presence of electrophiles such as Li^+ , Na^+ or K^+ with our CzT class of ligands seems to preferentially form the ionic salt of the ligand, $[\text{CzT}]^-\text{Y}^+$ and this likely facilitates redistribution to the bis-ligand Fe complex. Even though the use of the bulky phenoxide was sufficiently crowding to shut down direct redistribution, it is not able to suppress redistribution in the presence of an alkali metal ion.



Scheme 5.9 Redistribution of $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})(\text{THF})$ (**30**) when base is present

Knowing that **30** is extremely oxygen sensitive, we thought that a short lived Fe(IV) oxo species might form that could catalyze alkene epoxidation reactions²⁷⁷⁻²⁷⁸. To test this a mixture of **30** and styrene was dissolved in benzene- D_6 and monitored by NMR before and after exposure to oxygen. Styrene alone does not bind to the Fe complex and the ^1H NMR spectrum remains unchanged before oxygen exposure. After oxygen exposure the NMR was monitored for several hours, and while the paramagnetic Fe complex peaks

changed completely, the styrene peaks remained unchanged. The same reaction was also tested using N_2O as a potential oxygen source, but no epoxide was formed in this case either (**Scheme 5.10**). From these results it seems that the Fe complex is not suitable as an oxidation catalyst possibly because any Fe(IV) oxo species is too unstable to conduct any reactivity. This is not altogether surprising as non-porphyrin high oxidation state Fe oxo species are quite rare and extremely unstable²⁷⁹⁻²⁸².



Scheme 5.10 Attempted epoxidation with $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})(\text{THF})$ (**30**)

Along the same theme, we reacted **30** with several organic azides (RN_3 : $\text{R} = \text{PhCH}_2$, 2,6-diisopropyl phenyl, adamantyl) in an attempt to form Fe(IV) imido species. Metal complexes with fully intact organic azido groups are very rare²⁸³⁻²⁸⁵ and there are no examples of a structurally characterized Fe complex with an intact organic azido group. The more likely product would be an Fe imido species by elimination of nitrogen as there are several structurally characterized complexes in the literature, although due to their non-trivial synthesis, they are also considered uncommon. While there are several examples of Fe(II) and Fe(III) terminal imido complexes²⁸⁶⁻²⁹¹ Fe(IV) imido species are less

common²⁹²⁻²⁹⁴ and the most common geometry for a terminal Fe=NR is four-coordinate pseudo tetrahedral usually through the use of tripodal ligands.

Reaction of **30** with one equivalent of RN₃ at room temperature resulted in a slow colour change from yellow to dark brown and the resulting ¹H NMR spectrum showed new paramagnetic resonances. The crude reaction mixtures were very complicated and contained some unreacted **30**, but the reaction product with azidoadamantane was successfully recrystallized from warm toluene to give a brown solid. The ¹H NMR spectrum of this clean product is shown in **Figure 5.23**.

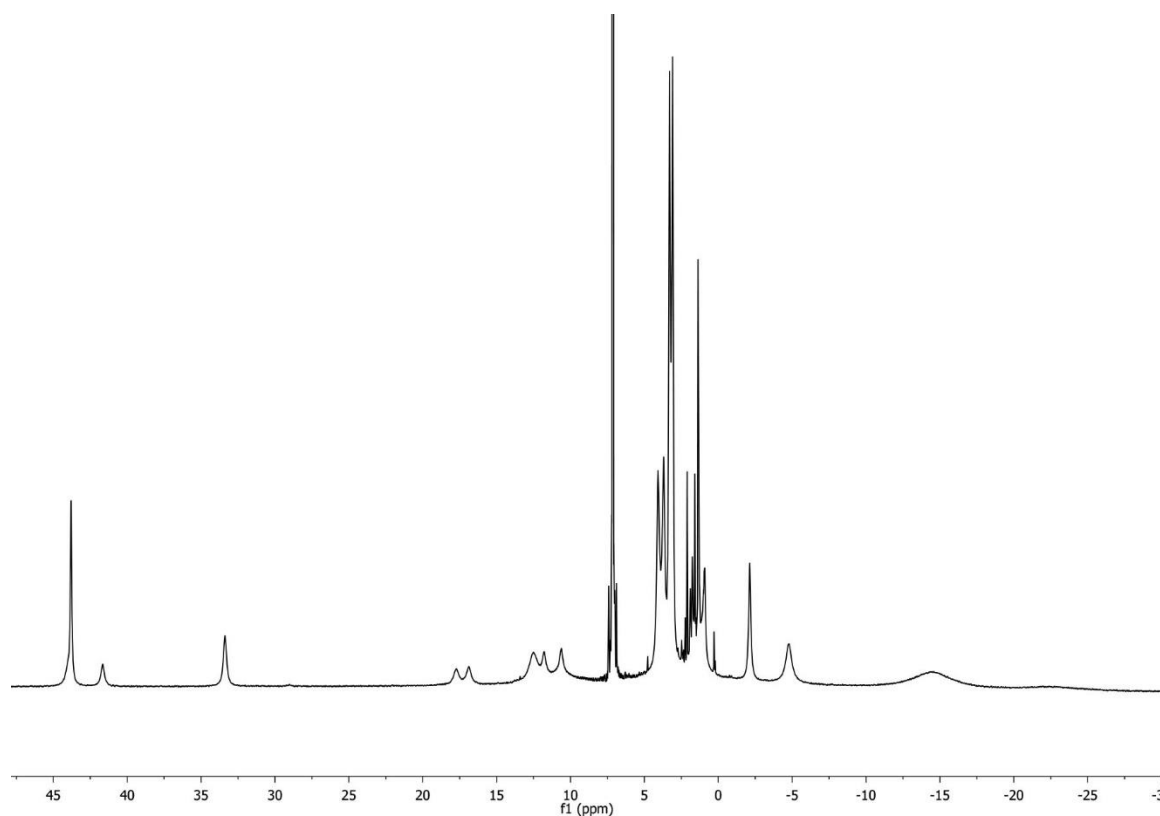
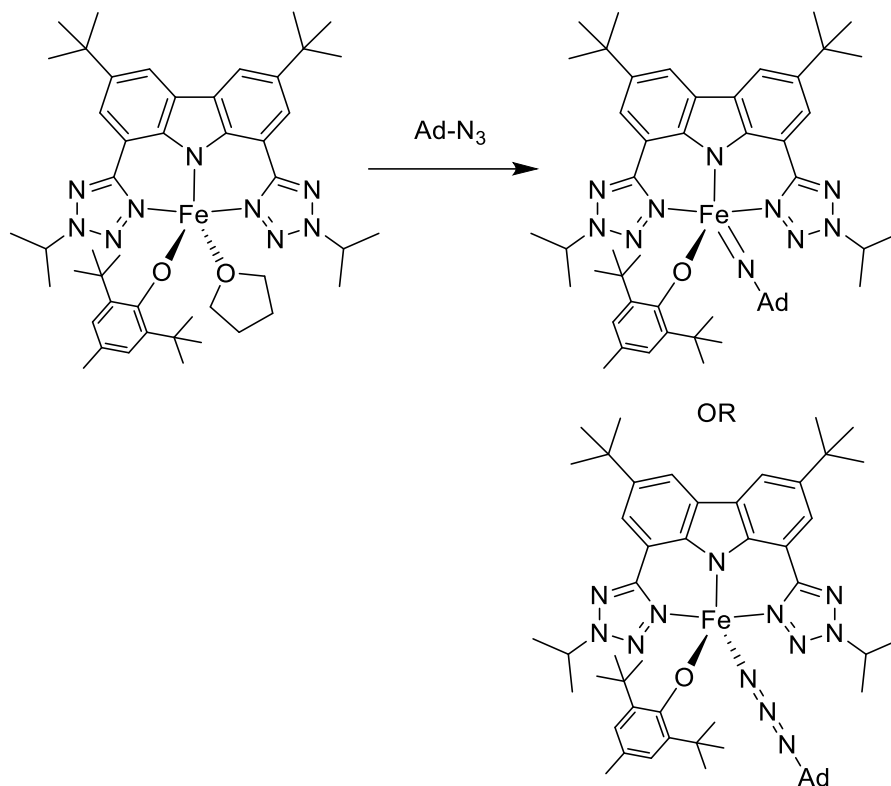


Figure 5.23 ¹H NMR spectrum (300 MHz, C₆D₆) of recrystallized (CzT^{iPr})Fe(OAr)(THF) (**30**) azidoadamantane product at 298 K (a very small broad resonance at 113 ppm has been omitted for clarity)

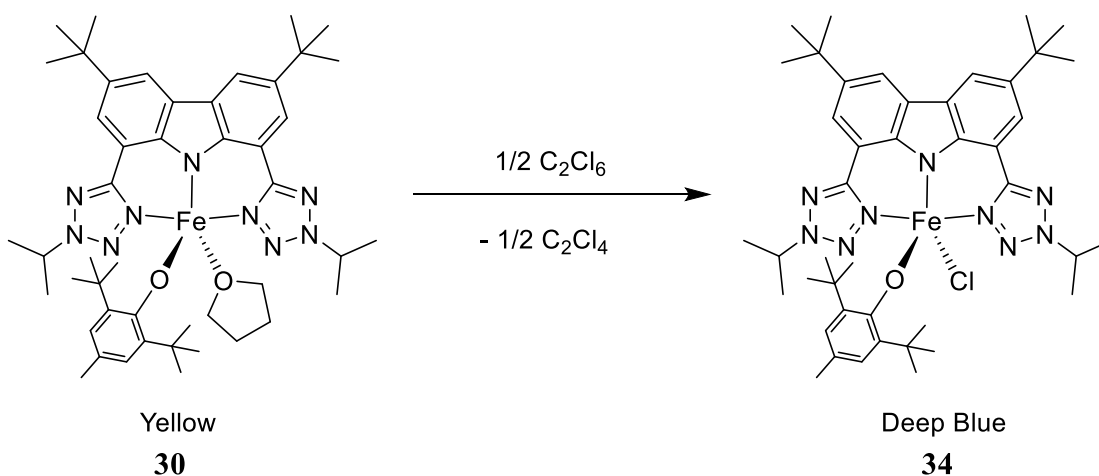
The NMR spectrum is clearly of a paramagnetic complex and contains several more resonances than what was observed for the starting **30** complex. There are several resonances reminiscent of the starting phenoxide complex but they have all shifted and some resonances are missing. In addition, there are four sets of doublet-like features (at approximately 17, 12, 4 and 3 ppm) that may suggest a lower symmetry structure. There are also extremely broad and highly shifted resonances (113 ppm, $\nu_{1/2}$ 1090 Hz not shown in **Figure 5.23**), that have not been observed for any of the Fe(II) complexes in this work. These resonances are generally more consistent with the Fe(III) NMR spectra seen in this work (complexes **34** and **36** discussed later in this chapter, for NMR details see Chapter 7). Alternatively, the large shift and broadening could indicate closer contact with the paramagnetic Fe centre rather than a change in metal oxidation state. Unfortunately, X-ray quality crystals were not obtained for this product, so whether the structure includes an intact azido group or formation of a terminal (or even bridging) imido complex as shown in **Scheme 5.11** is unknown. Very similar results were found with reactivity of **28** with organic azides that also gave brown products with similar paramagnetic complex ^1H NMR spectra. In no case was redistributed **23** formed in these reactions. This reactivity was ultimately not pursued due to our inability to isolate pure Fe(IV) species or X-ray quality crystals, but it remains an intriguing area for future studies.



Scheme 5.11 Possible reaction products with azidoadamantane (Ad-N₃)

The one electron oxidation chemistry of **30** was also explored to see whether the smaller ionic radius of Fe(III) causes any change in the structure. Hexachloroethane is a well known chlorinating agent that undergoes reduction to form tetrachloroethene with a reduction potential of approximately -2.0 V vs Fc/Fc⁺²⁹⁵. Reaction of half an equivalent of hexachloroethane with **30** resulted in an immediate colour change from yellow to deep blue (**Scheme 5.12**). The resulting blue product was extremely soluble and fully dissolved in hexanes at room temperature. Crystals of **34** were grown from room temperature hexanes solution, but they did not diffract likely due to solvent loss. Attempts to avoid solvent loss by coating solvated crystals of **34** in Krytox oil failed because they even dissolved in this oil. This product was found to be very thermally sensitive: when heated a colour change

occurs from dark blue to dark green and the ^1H NMR spectrum completely changes. The NMR spectrum of the dark blue product shows a set of extremely broad resonances with large shifts not seen in previous Fe(II) complexes of this type (max. shifted resonance at 157 ppm). An Evans' method magnetic susceptibility measurement was conducted on this complex at room temperature and gave a value of $5.58 \mu_{\text{B}}$ which rules out low spin Fe(III), this value is consistent with either high spin Fe(II) or Fe(III). There is little usable characterization data obtained from the NMR spectrum due to the extreme broadening of the resonances, but the NMR behaviour and colour is consistent with a similar high spin Fe(III) complex (as will be discussed in Section 5.3). Based on this, the likely product is a chlorinated complex $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})\text{Cl}$, **34**.



Scheme 5.12 Oxidation of $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})(\text{THF})$ (**30**) with hexachloroethane

In one trial, X-ray quality red crystals slowly deposited out of the dark blue solution of **34**. Surprisingly, these proved to be the oxidized redistribution product $[(\text{CzT}^{\text{iPr}})_2\text{Fe}]^+[(\text{OAr})\text{FeCl}_3]^-$, **35**. A representative ORTEP diagram of **35** is shown in

Figure 5.24 and selected bond length and angles are collected in **Table 5.7**. The oxidation state of the Fe in this structure is Fe(III) based on the redistribution pathway suggested in **Scheme 5.13**, but the spin state of the Fe(III) is unknown at this point as there is no characterization data other than the solid state structure. Complex **35** crystallizes in the P-1 space group, with two CzT ligands binding around the Fe centre in a pseudo octahedral geometry.

Table 5.7 Selected bond lengths (Å) and angles (°) of [(CzT^{iPr})₂Fe]⁺[(OAr)FeCl₃]⁻ (**35**)

Fe1-N1	1.923(3)	Fe1-N6	1.981(3)
Fe1-N10	1.936(3)	Fe1-N11	1.961(3)
Fe1-N2	1.974(3)	Fe1-N15	1.956(3)
N1-Fe1-N2	89.28(12)	N10-Fe1-N15	89.36(12)
N1-Fe1-N6	89.81(11)	N2-Fe1-N6	176.91(12)
N1-Fe1-N10	176.91(12)	N2-Fe1-N11	90.27(12)
N1-Fe1-N11	88.58(12)	N2-Fe1-N15	90.56(12)
N1-Fe1-N15	92.36(12)	N6-Fe1-N11	92.62(12)
N10-Fe1-N2	88.13(12)	N6-Fe1-N15	86.57(12)
N10-Fe1-N6	92.86(11)	N11-Fe1-N15	178.75(12)
N10-Fe1-N11	89.73(12)		
Cant angle¹⁰⁷ Tz₁	12.98	Cant angle¹⁰⁷ Tz₃	-17.06
Cant angle¹⁰⁷ Tz₂	-6.23	Cant angle¹⁰⁷ Tz₄	-11.61

Tz₁ refers to C21 and N2-N5; Tz₂ refers to C25 and N6-N9; Tz₃ refers to C49 and N11-N14; Tz₄ refers to C53 and N15-N18.

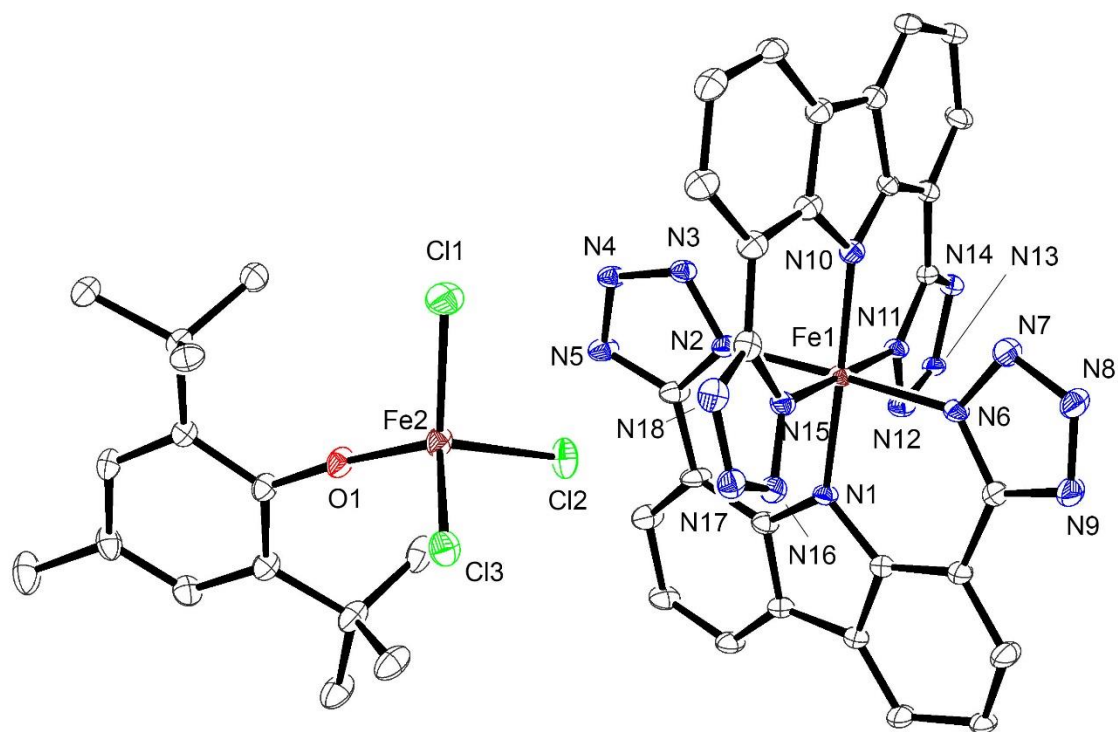
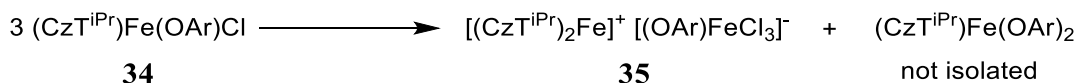


Figure 5.24 ORTEP3¹⁰⁸ plot (30% probability ellipsoids) of $[(\text{CzT}^{\text{iPr}})_2\text{Fe}]^+[(\text{OAr})\text{FeCl}_3]^-$ (**35**) (H atoms, tBu and iPr groups omitted for clarity)

As mentioned in Chapter 4, there are few Fe(III) carbazolidine complexes known in the literature, and the few that are known are all HS five coordinate complexes. The Fe- N_{Cbz} bond lengths in these complexes range from 2.024(3)-2.036(4) Å, median of 2.029 Å when corrected to match six coordinate high spin Fe(III)¹³⁰ and 1.929(3)-1.941(4) Å, median of 1.934 Å when corrected to match six coordinate low spin Fe(III)^{105, 130, 184, 224}. The Fe- N_{Cbz} distances in **35** of 1.923(3) and 1.936(3) Å match well with those of the low spin Fe(III) distances strongly suggesting the Fe(III) is in the low spin state. Literature values for Fe- N_{Tz} of six-coordinate high spin Fe(III) complexes range from 2.139(2)-2.200(6) Å with a median of 2.166 Å, the range corrected to match low spin Fe(III)¹³⁰ gives a range of 2.044(2)-2.105(6) Å, median 2.071 Å²²⁵. The Fe- N_{Tz} lengths in **35** range from

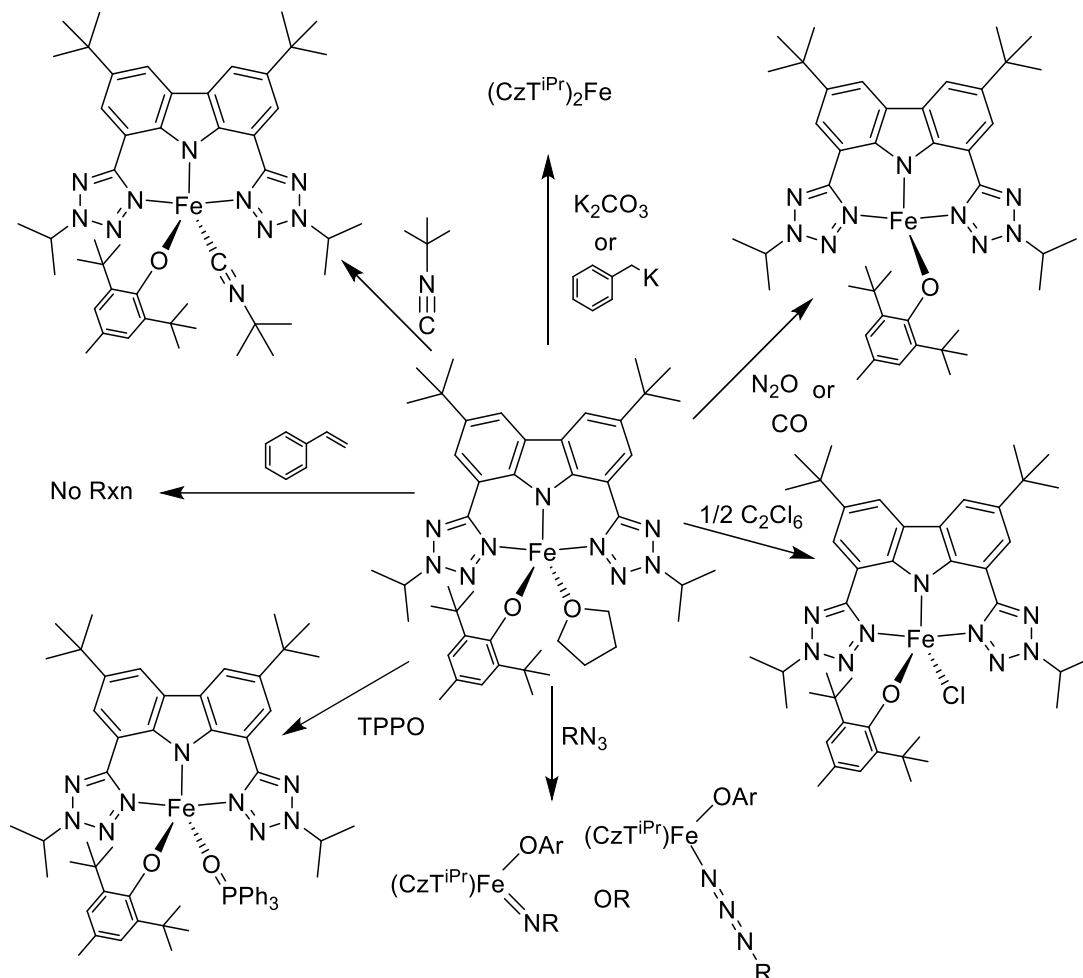
1.956(3)-1.981(3) Å and are significantly shorter than either range obtained from the literature, but they are closer to the low spin range.

The Fe-N distances in **35** are not dissimilar to those of **25** as was discussed in Chapter 4. The cant angle of the tetrazole rings in **35** (6-17°) are also in the same range as was observed for **25** (9-17°). This data suggests that the spin state and oxidation state of the Fe is likely the same for both **25** and **35**, although the Fe-N_{Cbz} distances in **35** are slightly longer than those observed in **25** (1.908(2) Å). Using only the solid state data, the most likely state of the Fe in both structures is low spin Fe(III). Presumably **35** forms by redistribution of **34** in solution at room temperature as shown in **Scheme 5.13**. This suggests that the monomeric (CzT^{iPr})Fe(OAr)Cl (**34**) is not particularly stable, which is not surprising based on its thermal sensitivity.



Scheme 5.13 Possible redistribution of (CzT^{iPr})Fe(OAr)Cl (**34**)

A summary of all the reactivity of **30** discussed in this chapter is collected in **Scheme 5.14**, this includes the adducts discussed in Section 5.3.2 as well as the reactivity discussed in Section 5.3.3.



Scheme 5.14 Reactivity summary for $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})(\text{THF})$ (**30**)

5.3.5 Hydrosilylation Catalysis

With several low coordinate $\text{Fe}(\text{II})$ complexes in hand we set out to test them as catalysts for some common reactions. Hydrosilylation is an attractive choice since the most widely known and industrially relevant hydrosilylation catalysts are Pt-based (Karstedt's and Speier's catalysts) and it has been estimated that approximately 5.6 metric tons/year of Pt is consumed by the silicone industry, and most of this Pt is not recoverable⁹². The high cost, high toxicity and low abundance of Pt makes this an important issue to overcome and

as a result, considerable research has been recently dedicated to finding a more abundant and cost effective metal for hydrosilylation catalysis. There are several Fe(II) pincer ligand complexes that have shown to be catalytic in olefin hydrosilylation, but a majority of these require a reductant as an activator to form an active Fe(0) catalyst^{238, 240, 296-303}. Other similar Fe(II) pre-catalysts use ligands such as amines³⁰⁴ and isonitriles³⁰⁵⁻³⁰⁶ as activators to form the active catalyst *in situ*, some of which are Fe(0) and some are suggested to be Fe(II). A selection of five coordinate Fe hydrosilylation pre-catalysts are shown in **Figure 5.25**.

Fe(0) is widely accepted as the active catalyst centre in olefin hydrosilylation transformations based on the well-known Chalk-Harrod mechanism³⁰⁷. There are several examples of Fe(0) catalysts that do not require any reductant or initiator, the most common being CO complexes of Fe³⁰⁸⁻³¹⁰. Perhaps the most famous and active Fe olefin hydrosilylation catalyst is the five coordinate Fe(0) pincer complex (both monomer and dimer form) with two N₂ ligands developed by Chirik^{90, 92} (**Figure 5.25**). While several of the five coordinate pincer complexes shown in **Figure 5.25** share several features with our Fe(OAr) complexes, the distinguishing feature is that all of these catalysts contain neutral tridentate pincer ligands with two additional anionic ligands (usually halogens).

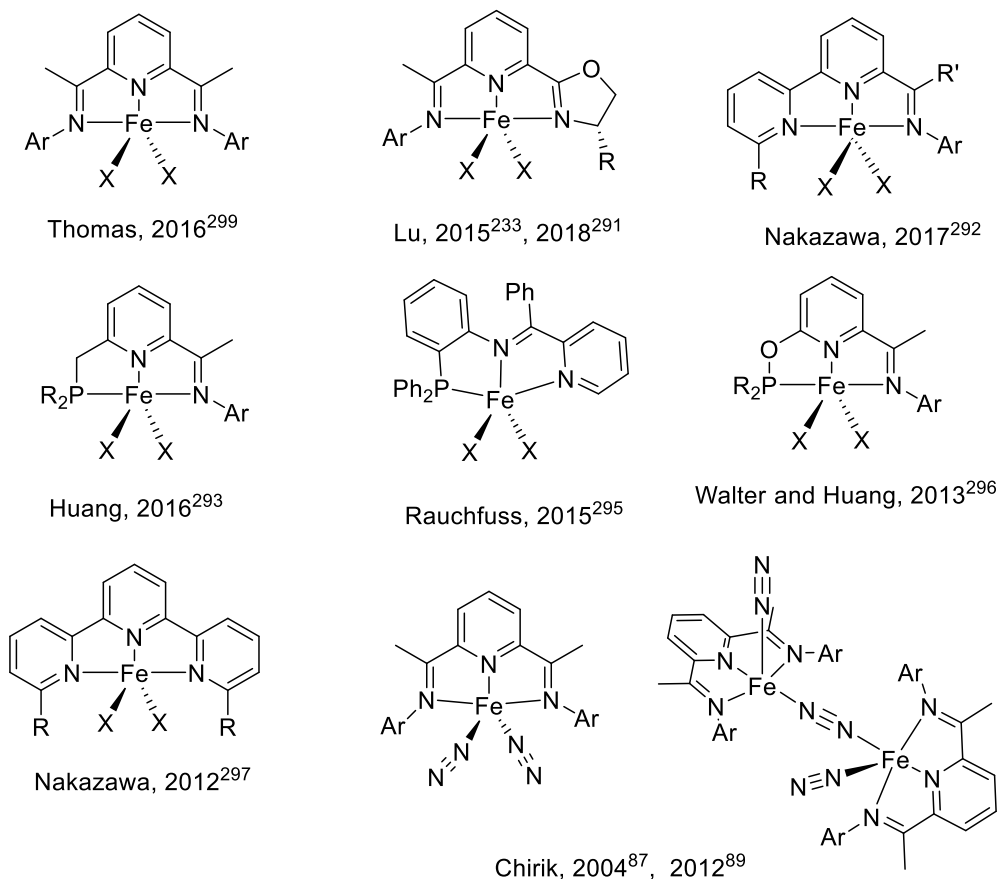


Figure 5.25 Similar five coordinate Fe(II) complexes that are active hydrosilylation pre-catalysts

Our CzT ligand however is anionic so only one X-type ligand (OAr) is left to form the four and five coordinate Fe(II) complexes. We were unsure if our Fe phenoxide complexes (**30-33**) would be suitable for hydrosilylation catalysis, especially if the active catalyst is Fe(0). We have also shown that redistribution is the main pathway when bases are present, so activation of the catalyst to form an Fe(0) centre with the widely used reductants NaBHET₃ or EtMgBr is not an option as it would likely cause redistribution to the bis-ligand Fe product, **23**.

Despite all of these potential downfalls, we decided to test the hydrosilylation of styrene with phenylsilane using our Fe(OAr) adducts (**30**, **31** and **33**) as catalysts without any reductant or initiator. Initial attempts involved monitoring the reactions by ^1H NMR with high catalyst loading (5 mol%) of the THF adduct **30** in toluene- D_8 with a large excess of styrene and phenylsilane. Shockingly, in the time it took to submit and run the ^1H NMR spectrum (approximately 15 minutes) at room temperature there were resonances in the resulting spectrum consistent with both the Markovnikov (M) and anti-Markovnikov (aM) hydrosilylation products (**Figure 5.26**)!

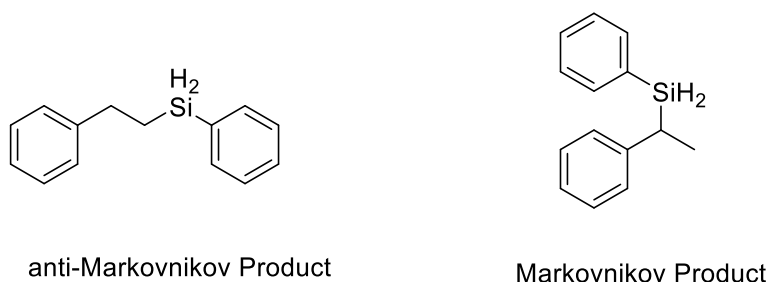


Figure 5.26 anti-Markovnikov (aM) and Markovnikov (M) hydrosilylation products

After 24 hours at room temperature, the resulting ^1H NMR spectrum showed complete consumption of the styrene with larger amounts of the M and aM products; paramagnetic resonances for the catalyst **30** remained unchanged. To be confident that our Fe complex was catalysing this transformation a control run with equimolar amounts of styrene and phenylsilane in benzene- D_6 and without added catalyst was also run. After 24 hours no discernable amount of either hydrosilylation product was formed in the control run.

The hydrosilylation reactions were repeated using 1.0 mol% of **30** as catalyst with equimolar amounts of styrene and phenylsilane in benzene- D_6 at room temperature. The reaction was monitored by ^1H NMR spectroscopy and the stack plot of the spectra taken after 15 minutes, two hours, four hours, seven hours and 24 hours is shown in **Figure 5.27**.

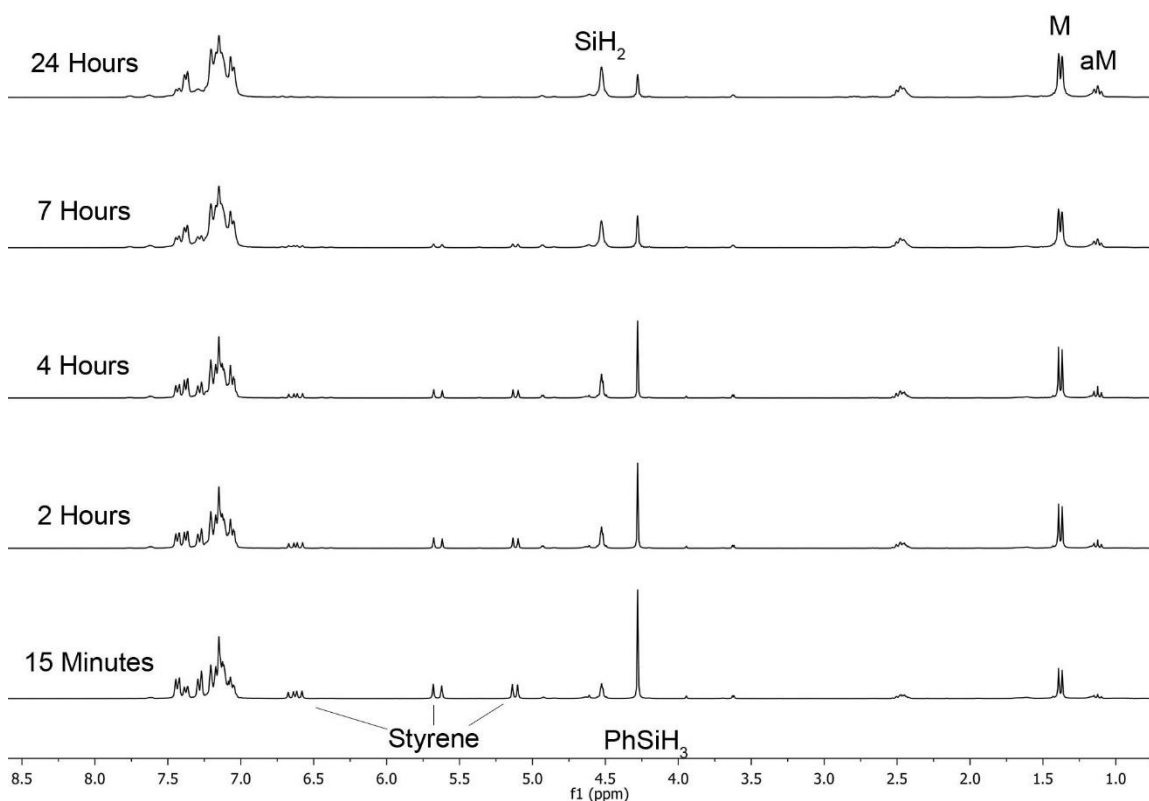


Figure 5.27 Stack plot of ^1H NMR spectrum (300 MHz, C_6D_6) of styrene and phenylsilane hydrosilylation catalyzed by $(CzTi^{iPr})Fe(OAr)(THF)$ (**30**) at 298 K

The phenyl region is complicated due to overlapping resonances for styrene, phenylsilane and the hydrosilylation products so there is little information available in this region. However, the styrene olefin peaks clearly diminish with reaction time and are barely discernable after 24 hours suggesting that all of the styrene has been consumed. The

phenylsilane resonance at 4.28 ppm similarly diminishes over the reaction period, but is never fully consumed. The M and aM hydrosilylation products can be quantified by the distinct CH_2Si triplet found at 1.14 ppm for the aM product and the CHCH_3 doublet at 1.37 ppm for the M product. The remaining resonances overlap each other and are more difficult to distinguish; the SiH_2 resonance is at 4.59 ppm for the M product and 4.86 ppm for the aM product. The CHCH_3 quartet for the M product is found at 2.53 ppm overlapping with the PhCH_2 from the aM product at 2.54 ppm. Based on integration of the aM triplet and M doublet, the ratio of aM to M product formed is approximately 1:3 showing selectivity for the M product. This is somewhat surprising as it has been shown that Fe-based hydrosilylation catalysts are generally more selective for the aM product than the M product: out of all the aforementioned Fe-based hydrosilylation catalysts, only two were shown to be selective for the M product^{297, 303}. One publication reports the exact same ligand for use in Fe and Co-based hydrosilylation catalysts and the Fe catalyst showed selectivity for the aM product while the Co catalyst was selective for the M product exclusively²⁹⁸.

A ^1H NMR kinetic experiment was also conducted using 1.0 mol% of **30** as catalyst with hexamethylbenzene as an internal standard. The spectra were run every 10 minutes for approximately 10.8 hours with the first spectrum run after 20 minutes of initial mixing. The concentration vs. time plot for selected resonances is shown in **Figure 5.28**. After all of the styrene was consumed, residual phenylsilane remained. This suggests that the styrene is being consumed in other reactions such as oligomerization and there are several small resonances in the diamagnetic region at complete conversion that could be due to styrene side reactions. Based on **Figure 5.28**, the reaction is complete after about 3 hours

at room temperature, this gives a TOF of approximately 0.010 s^{-1} or an activity of $335\text{ mol}_{\text{prod}}\text{ mol}_{\text{cat}}^{-1}\text{ h}^{-1}$.

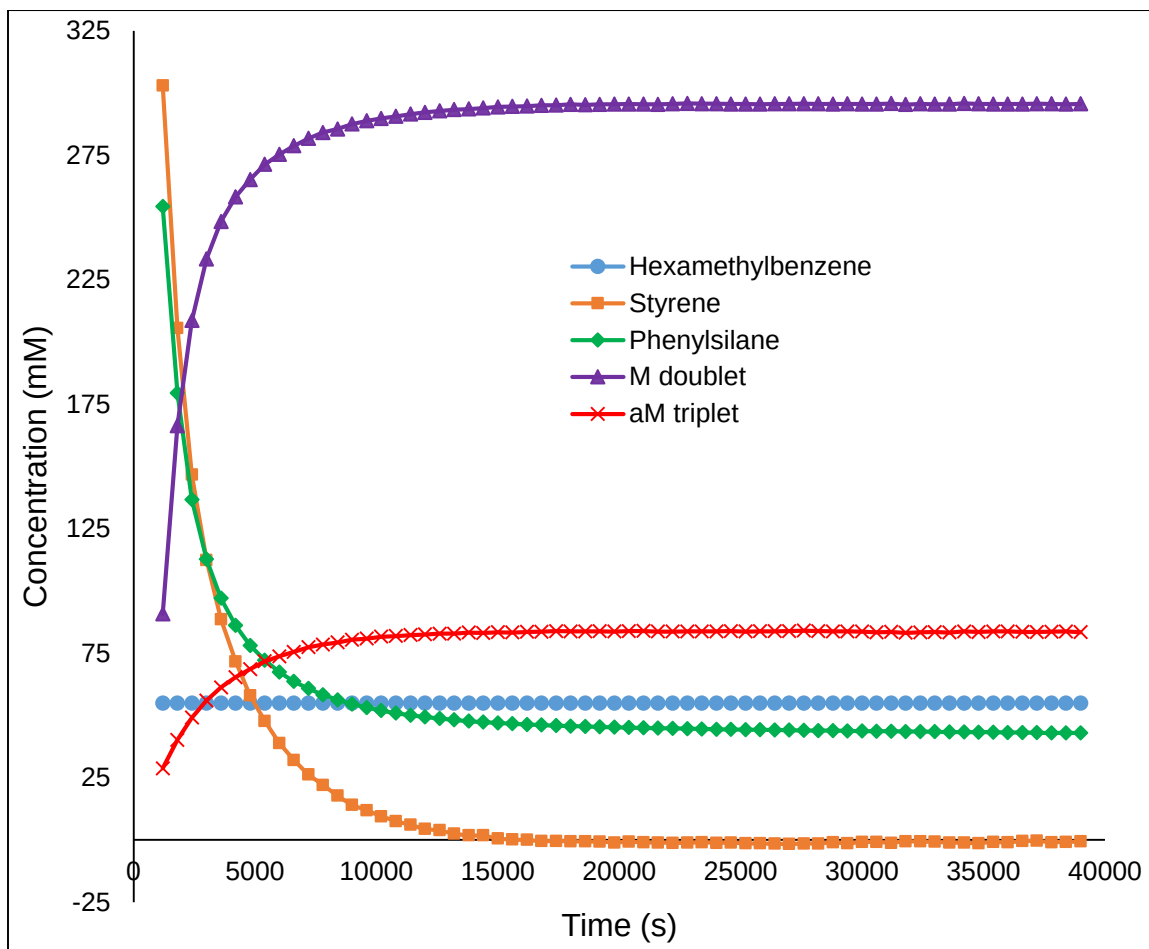


Figure 5.28 Kinetics ^1H NMR monitoring (360 MHz, benzene- D_6 , 298 K) of hydrosilylation of styrene and phenylsilane

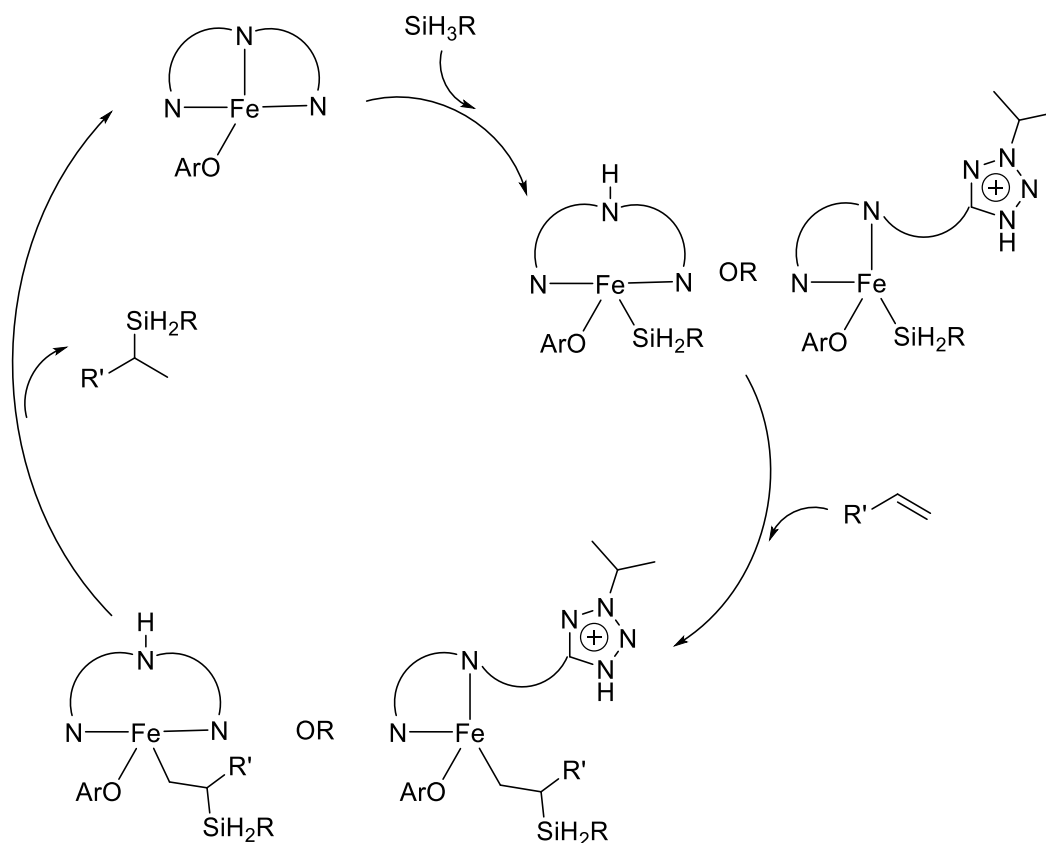
Lewis base-free **31** and TPPO adduct **33** were also tested to see if there was any variation in rate or selectivity. The tBuNC adduct **32** was not tested due to its very low solubility in benzene or toluene. The reaction conducted with 1.0 mol% **31** as the catalyst showed similar selectivity with the M product being favoured by a 3:1 ratio over the aM product after 24 hours. The Lewis base-free catalyst consumed all of the styrene at about

three times the rate of the THF adduct. On the other hand, 1.0 mol% **33** while still showing the same selectivity, consumed the styrene much more slowly with some still present in solution after 24 h at room temperature.

From these results there is a clear trend in reaction rate with the fastest being the Lewis base-free, then THF and finally TPPO adduct. This trend could be explained one of two ways: either the rate is dependant on the bulk of the fifth coordinated ligand or it could be due to the ability to generate a vacant site. Both of these would predict the rate to be quickest with the Lewis base-free catalyst that already has a vacant coordination site, then second quickest with the THF adduct and finally slowest with the TPPO adduct as it is both the bulkiest and most strongly bound ligand. The observation that the catalyst ^1H NMR resonances remain unchanged at the end of the transformation suggests that there is no degradation of the catalyst, but since the THF or TPPO ligand dissociation is likely in equilibrium it does not verify which mechanism is more likely.

If the reaction proceeded by the classic Chalk-Harrod mechanism³⁰⁷ with oxidative addition and reductive elimination, the phenoxide would need to dissociate to allow reduction of the Fe(II) to Fe(0) and would likely not reform the pre-catalyst. Conversely, if the reaction proceeds through a σ -bond metathesis mechanism (as is seen with lanthanide catalysts in hydrosilylation), the phenoxide again would need to detach from the Fe to form a siloxide leaving an Fe hydride that would then be the active catalyst. Again it would be highly unlikely that the Fe(II) phenoxide complex would re-form to the initial complex after this reaction. Based on our preliminary results, the mechanism is likely occurring with no change in Fe oxidation state, this suggests that the ligand may be non-innocent in this transformation and act as a proton reservoir to maintain the phenoxide Fe-O bond. One

possible mechanism that could explain this reactivity is shown in **Scheme 5.15** (only the Lewis base-free Fe complex as the catalyst and the Markovnikov product are shown for clarity).



Scheme 5.15 A possible ligand assisted silane addition mechanism for olefin hydrosilylation (shown with $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})$ (**31**) as catalyst and Markovnikov hydrosilylation product)

Throughout this mechanism, Fe stays in the Fe(II) oxidation state and the phenoxide remains bound the entire time. The key step in this mechanism involves a ligand assisted silane addition where the SiH_2Ph adds to the metal and the H (effectively H^+) is added to the ligand by either protonating the carbazole N or adding to a tetrazole ring to form a tetrazolium ion. This is followed by insertion of styrene into the Fe-Si bond followed by

protonation of the Fe-C bond by the carbazole NH or tetrazolium proton to regenerate the Fe complex and liberate the product. This proposed mechanism may or may not require a vacant site at the Fe centre. The ancillary ligand steric size or lability would both predict the slowest rate for the TPPO adduct and the fastest rate for the Lewis base-free catalyst based on this proposed mechanism.

There is one carbazole pincer ligand-based Fe(II) pre-catalyst known in the literature that bears a striking resemblance to our CzT ligand system (**Figure 5.29**), but interestingly, while it showed to be active for ketone hydrosilylation, it showed no reactivity at all towards styrene hydrosilylation¹⁸⁴. The authors suggest that the active catalyst is the Fe hydrido formed by loss of $\text{PhSiH}_2\text{N}(\text{SiMe}_3)_2$ when the pre-catalyst is reacted with PhSiH_3 . We can not completely eliminate loss of ArOSiH_2Ph in our case but the fact that we see no change in our catalyst seems to rule out phenoxide loss.

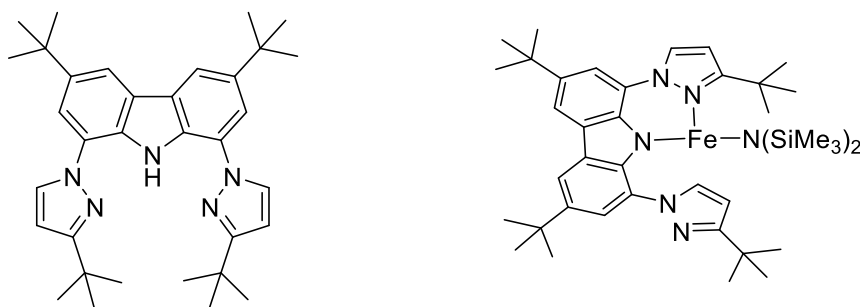


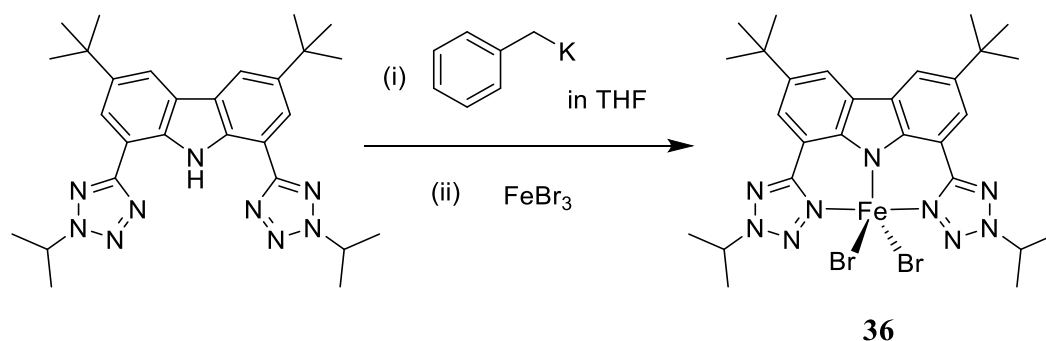
Figure 5.29 Carbazole-based pincer ligand and Fe(II) complex

5.4 Trivalent Iron Halide Complexes

The mono-ligand chemistry with Fe(II) proved to be more complicated and difficult than expected, mostly due to the high tendency for redistribution. It was hoped that the use of Fe(III) would stop redistribution since the ionic radius of Fe(III) is smaller than that of Fe(II) and presumably less able to accommodate a six coordinate structure with two CzT^{iPr} ligands.

5.4.1 Synthesis and Characterization of (CzT^{iPr})FeBr₂

The same synthetic method that was used to synthesize **28** was used to make the analogous Fe(III) complex (CzT^{iPr})FeBr₂, **36**. The salt metathesis reaction with the ligand and anhydrous FeBr₃ (**Scheme 5.16**) gave a dark red-brown powder as crude product in good yield.



Scheme 5.16 Synthesis of (CzT^{iPr})FeBr₂ (**36**)

This product was characterized in solution using ¹H NMR as well as an Evans' method susceptibility measurement and in the solid state using Mössbauer spectroscopy in the absence of a crystal structure. Several batches of dark red crystals were grown from

toluene solution, but in all cases these did not diffract. The MB data will be discussed in detail later, but the isomer shift and quadrupole splitting values suggest a low spin, six coordinate Fe(III) complex. Similar to the Fe(II) complex **28** discussed earlier in this chapter, the coordination number obtained from the MB data is consistent with a six-coordinate Fe centre (**Scheme 5.16**). This is most easily accommodated by a dimeric structure with bridging bromide ions between the two Fe(III) centres (**Figure 5.30**), similar to that proposed for polymeric $[(\text{CzT}^{\text{iPr}})\text{FeBr}]_n$ in the solid state.

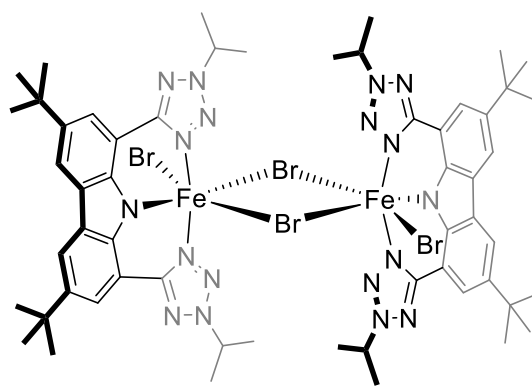


Figure 5.30 Possible six coordinate structure of $(\text{CzT}^{\text{iPr}})\text{FeBr}_2$ (**36**)

The solution state data is more complicated and contradicts the solid state data. It should first be noted that it is fairly unusual to obtain an NMR spectrum of an Fe(III) complex: based on a literature search, EPR is usually more appropriate and an NMR spectrum cannot be obtained^{105, 311-313}. In our case we were able to obtain a NMR spectra for paramagnetic **36**, and the Evans' method gave a magnetic moment of $5.94 \mu_B$ which is suggestive of high spin Fe(III). The ^1H NMR spectra run in toluene- D_8 were not consistent each time the spectrum was run and proved to be concentration dependant. In dilute

solutions there are two sets of paramagnetic resonances, whereas in more concentrated solutions this simplifies to one set of paramagnetic resonances (**Figure 5.31**). There is also a colour change observed with varying concentrations: dilute solutions of **36** are dark blue-green while concentrated solutions are dark red.

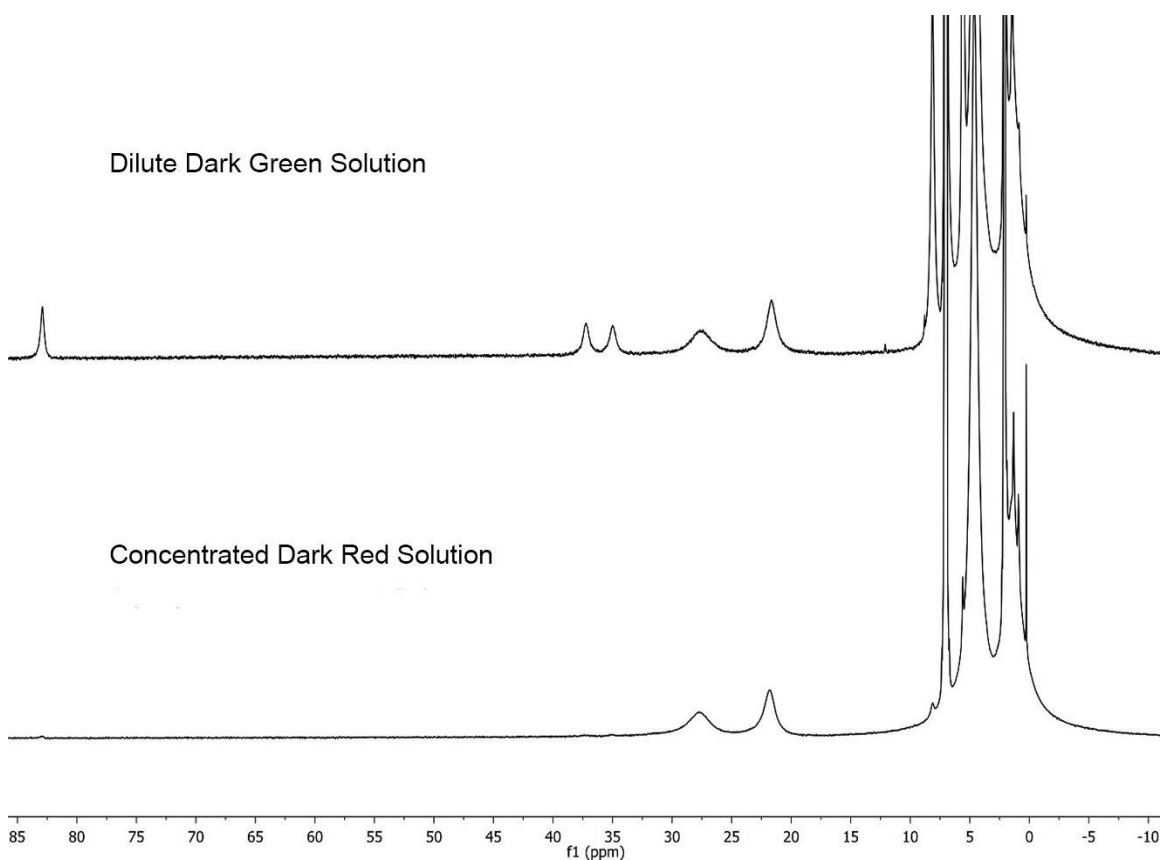


Figure 5.31 Stack plot ^1H NMR spectrum (300 MHz, toluene- D_8) of $(\text{CzTi}^{\text{iPr}})\text{FeBr}_2$ (**36**) at 298 K

Both spectra shown in **Figure 5.31** are from the same batch of recrystallized **36** so the extra resonances are not simply due to an impurity. In the more concentrated red spectrum there are four paramagnetic resonances that are extremely broad ($\nu_{1/2}$ between 213-604 Hz); two of the resonances integrate to 2 H each (likely from the carbazole

backbone), one resonance integrates to 12 H likely from the iPr groups of the ligand and the final resonance integrates to 20 H which would account for the remaining 18 tBu protons as well as the two protons from the iPr group. The dilute blue-green solution contains all of these resonances along with one full additional set of paramagnetic CzT^{Pr} resonances (three 2 H resonances, one 12 H and one 18 H resonance). This suggests that there are two magnetically inequivalent CzT^{iPr} Fe complexes that exist in dilute solutions, but only one of these exists in concentrated solutions. The most evident explanation for this is that a monomer-dimer equilibrium is operative that shifts almost completely to dimer in more concentrated solutions (**Figure 5.32**). Based on this hypothesis, the more upfield resonances are due to the dimer while the downfield resonances, only seen in dilute solutions, are from the monomer. This is consistent with the dimeric structure postulated in the solid state (**Figure 5.30**) which is also dark red in colour. Further evidence that the downfield resonances are due to the dark blue-green monomer is that the Fe(III) complex **34**, discussed in Section 5.3, is also deep blue in colour and has similarly shifted broad resonances (max. shifted resonance at 80 ppm).

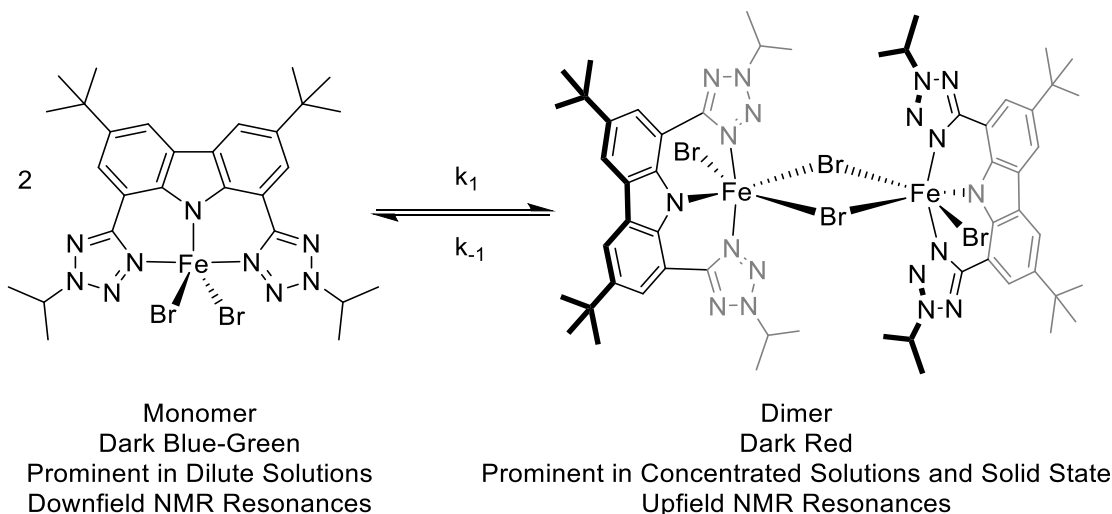


Figure 5.32 Monomer-dimer equilibrium of $(\text{CzT}^{\text{iPr}})\text{FeBr}_2$ (**36**)

To further test the postulate that a monomer-dimer equilibrium exists in dilute solutions, VT NMR was employed to observe the temperature dependence of the assigned resonances. Since going from the dimer to the monomer will have a positive change in entropy, there should be an increase in monomer compared to dimer at elevated temperatures. An NMR sample of **36** in benzene- D_6 was run at room temperature and then again at 343 K and the integrations of the monomer and dimer resonances were monitored. The stack plot showing the downfield region of the VT NMR spectra including integrations is shown in **Figure 5.33**. From this it is clear that there is an increase of resonances assigned to the monomer at elevated temperature compared to room temperature consistent with our hypothesis. The fact that we also see both the monomer and dimer resonances at higher temperatures suggests that the rate of monomer association and dimer dissociation are slow on the NMR timescale.

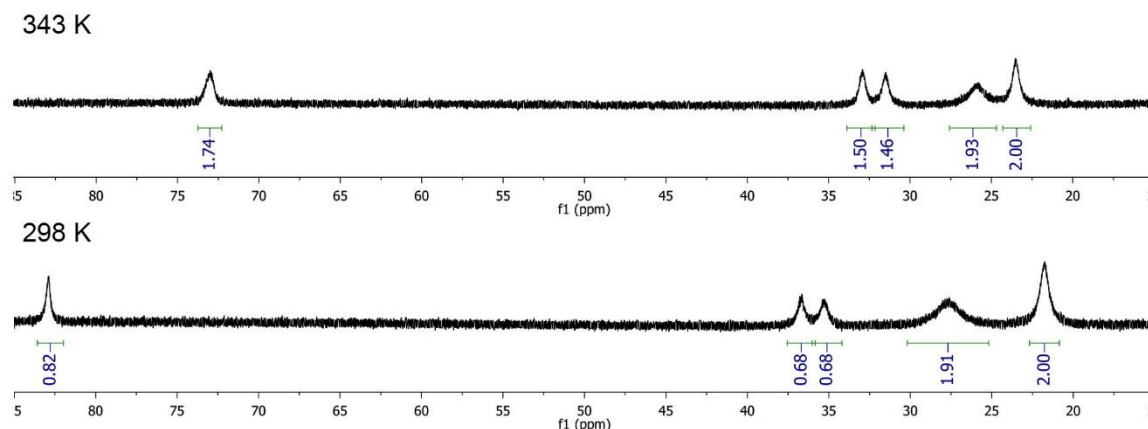


Figure 5.33 Integrated VT ^1H NMR spectra (360 MHz, C_6D_6) of $(\text{CzT}^{\text{iPr}})\text{FeBr}_2$ (**36**)

An Evans' method magnetic moment of $5.94 \mu_{\text{B}}$ for **36** was calculated assuming a monomeric structure. The fact that the magnetic moment is consistent with a high spin Fe(III) even with dimer present in solution suggests that the two Fe centres in the dimer are not magnetically coupled. If the two Fe centres were antiferromagnetically coupled or if an Fe-Fe bond was present, the expected magnetic moment value would be much lower. This solution state magnetic data contradicts the solid state magnetic data obtained by Mössbauer spectroscopy that suggested a low spin Fe(III) centre. The $\delta(\text{Fe})$ value of 0.16 mm/s and ΔE_{Q} value of 1.39 mm/s (**Figure 5.34**) are consistent with a six coordinate, low spin Fe(III) complex based on the data chart shown in **Figure 4.10**³¹⁴. General $\delta(\text{Fe})$ values for low spin Fe(III) are in the range of 0.12-.17 mm/s³¹⁴ while for high spin Fe(III) these values are shifted much higher in the range of 0.4-0.85 mm/s³¹⁴⁻³¹⁵.

Based solely on this data trend it seems that **36** is low spin in the solid state, but since MB values are inferred from literature values for known structures, there is some ambiguity in assignment of spin state and coordination number using MB values alone. At this time, without access to a SQUID magnetometer, the solid state magnetic moment of

36 is not fully understood. From our preliminary results all that can be concluded is that **36** exists in the high spin Fe(III) state in solution and the data we have now suggests that it exists in the low spin Fe(III) state in the solid state.

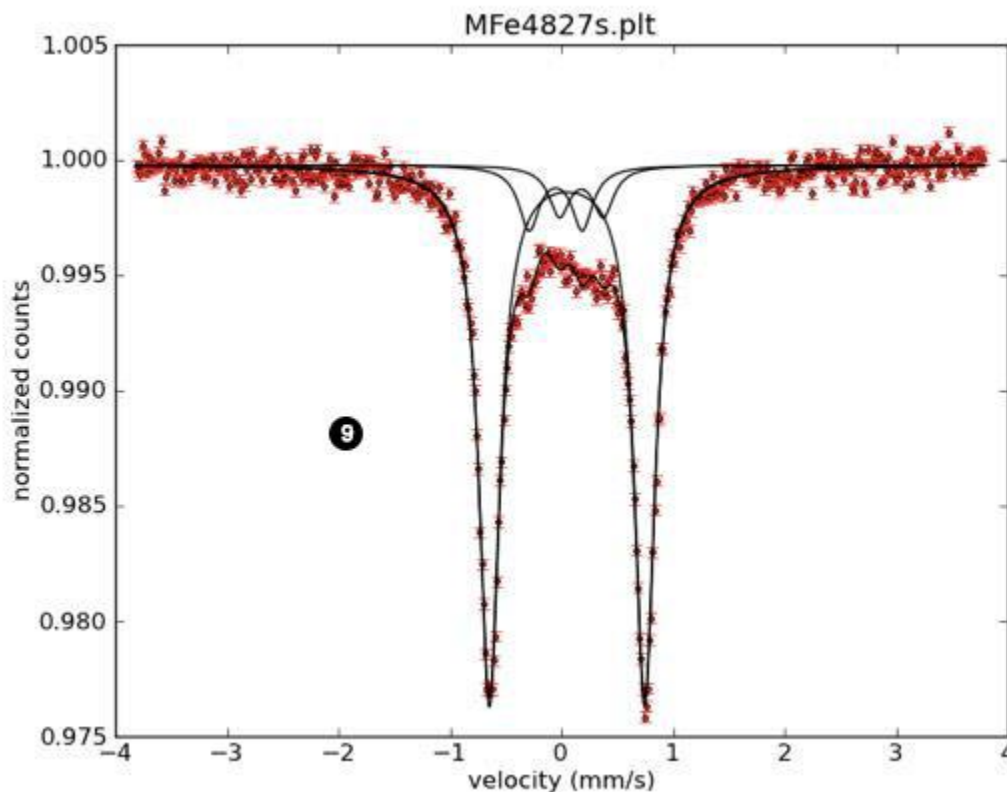


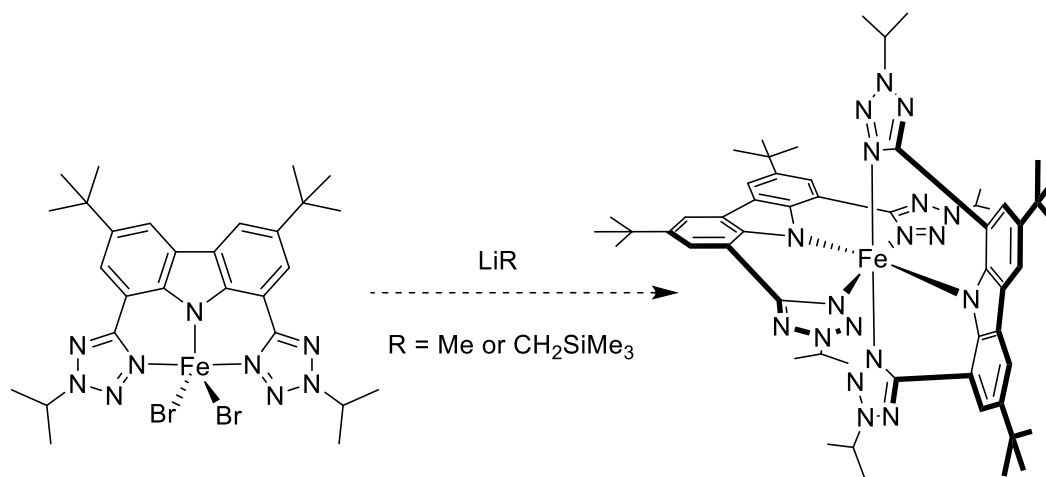
Figure 5.34 Mössbauer spectrum of $(\text{CzT}^{\text{iPr}})\text{FeBr}_2$ (**36**) at room temperature

5.4.2 Reactivity of $(\text{CzT}^{\text{iPr}})\text{FeBr}_2$

Similar to the mono-ligand Fe(II) complex discussed earlier, attempts were made to substitute the Br ligands for something more reactive such as an alkyl. MeLi was added in a salt metathesis reaction with **36** in attempts to form the dimethyl complex. Inspection of the resulting ^1H NMR spectrum showed the ligand redistribution product **23** (**Scheme**

5.17). Attempts to avoid reduction and ligand redistribution by using larger alkyl groups also failed and resulted in formation of **23** (Scheme 5.17).

Alkyl lithiums are known to be reducing agents so reduction of Fe(III) is not altogether unexpected, and to this date there are no crystallographically characterized Fe(III) dialkyls so the failure of this reaction is not surprising. Since it seems difficult to synthesize an Fe(III) dialkyl with our system we attempted to test the reactivity of **36** itself without first completing ligand substitution.



Scheme 5.17 Reduction and ligand redistribution of (CzT^{iPr})FeBr₂ (**36**)

In order to test if **36** is reactive in any sort of catalytic transformation, initial attempts to see if whether a substrate could bind were pursued. A simple small scale reaction was tested with **36**, styrene and several thousand equivalents of MAO to see if any polystyrene was formed. After stirring the solution for several hours at room temperature and quenching the solution, no polystyrene was formed. This suggests that **36** may not be well suited as a polymerization catalyst since styrene is an extremely easy olefin to

polymerize. Due to this lack of reactivity along with the persistent problem of ligand redistribution to form the bis-ligand Fe(II) complex, further reactivity and chemistry with our Fe(III) complex was not pursued.

5.5 Conclusion

The exploration of mono-ligand Fe complexes with our CzT^{iPr} ligand proved to be the most fruitful venture in comparison to the results of Chapter 3 and 4. The use of Mössbauer spectroscopy allowed us to determine the polymeric structure of **28** which ties in to the variable bonding capability and versatility of our CzT ligands as demonstrated in Chapter 3 with the lanthanides. The reactivity studies of **28** were challenging due to the increased tendency to redistribute into the bis-ligand **23** which prevents further reactivity. These results did however successfully shed some light into the behaviour and reactivity of mono-ligand Fe complexes with our ligand. Reactions with sterically unhindered electrophiles result in redistribution facilitated by the formation of $\text{Y}^+ [\text{CzT}^{\text{iPr}}]^-$ ($\text{Y} = \text{Na}, \text{Li}, \text{K}$) but redistribution can be shut down with the proper mix of steric and electronic properties in the ancillary ligands. Oxidation chemistry also seems feasible with both the Fe(III) and possibly Fe(IV) oxidation states available.

These results enabled us to further pursue the chemistry and reactivity of the most promising complex, the mono-ligand Fe phenoxide, **30**. This proved to be the only mono-ligand Fe structure that generally resisted redistribution. The odd electronic structure of **30** enabled formation of σ -bond donor adducts (TPPO and tBuNC), while attempts to form an adduct using π -acceptor ligands led to formation of the four coordinate Lewis base-free complex **31**. This gave rise to a small family of $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})\text{L}$ complexes (**30**, **32**, **33**)

that were all structurally characterized. The Fe-O-C angle varies in the solid state for these complexes although we believe this to be sterically, rather than electronically, motivated. In addition to the different adducts formed, one electron oxidation on **30** successfully formed an Fe(III) complex **34**.

Perhaps the most exciting result in this thesis was the discovery that three of the four Fe(OAr) adducts function as hydrosilylation catalyst giving rise to both the anti-Markovnikov and the less commonly seen Markovnikov hydrosilylation products of styrene and phenylsilane with a TOF of 0.010 s^{-1} . The use of an intact Fe(II) catalyst is inconsistent with currently accepted mechanisms for Fe-based hydrosilylation. We postulated a ligand non-innocent mechanism that involves the CzT ligand acting as a proton shuttle to keep the Fe in the Fe(II) oxidation state throughout the transformation.

Finally, we were able to successfully synthesize and characterize an Fe(III) complex with our CzT^{iPr} ligand. Extensive NMR studies determined that **36** exists in a dimeric form in the solid state, but exists in a monomer-dimer equilibrium in dilute solutions.

Chapter 6 Conclusions and Future Work

6.1 Summary

Extensive research was conducted to develop a new class of carbazole-based *bis*(triazole) (CzTr^R) and *bis*(tetrazole) (CzT^R) ligands and explore their applications in transition metal and lanthanide chemistry. These ligands proved to be redox active, fluorescent and capable of forming π -stacked charge transfer complexes (with quinones). In addition, these ligands displayed several different bonding modes, particularly in lanthanide complexes. The behaviour and properties of their lanthanide and transition metal complexes proved to be highly ligand dependant.

The HCzTr^R and HCzT^R family of ligands are fairly simple to synthesize starting from inexpensive carbazole and are produced in good overall yields (**Figure 6.1**). The HCzT^R ligands can be synthesized in five steps with overall yields ranging from 50-62 % depending on the substituent and the HCzTr^R ligands can be synthesized in seven steps with overall yields ranging from 47-64 % depending on the substituent. The protonated HCzT^H and HCzTr^H ligands can be easily functionalized on the azole ring in one step to offer a variety of substituents allowing simple electronic and steric adjustments of the ligand. In this work the substituents included methyl, benzyl, isopropyl and methyl mesityl offering a range of sterics within our class of ligand.

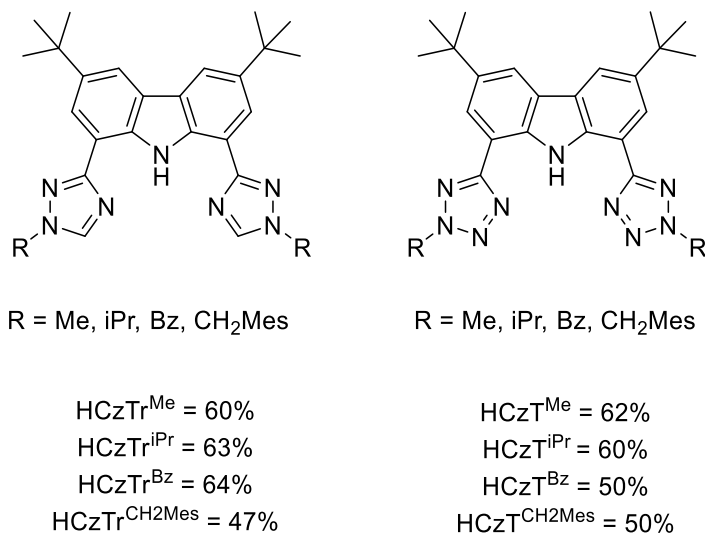


Figure 6.1 Overall yields of HCzTr^R and HCzT^R ligands

The physical properties of these ligands were explored and proved quite interesting. The ligands are all redox active with a carbazole-based oxidation at modest potentials. The bis-ligand Zn complexes demonstrated that this oxidation is retained in metal complexes and is reversible. These complexes also showed that the deprotonated ligands are fluorescent, emitting in the blue region. Attempts to oxidize the ligands with quinones resulted in highly coloured, charge transfer complexes displaying extensive π -stacking in the solid state.

Successful synthesis of lanthanide complexes with our CzT^R ligands was achieved using both salt metathesis and protonolysis reactions. The salt metathesis route enabled us to synthesize mono-ligand Yb dialkyl complexes with our CzT^{iPr} and CzT^{CH₂Mes} ligands. The protonolysis products with lanthanide silylamides gave rise to mono, di and tri ligated lanthanide complexes in the forms of (CzT^{iPr})Ln[N(SiMe₃)₂]₂, (CzT^{iPr})₂Ln[N(SiMe₃)₂] and (CzT^{iPr})₃Ln. The smaller lanthanides (Yb and Er) gave the expected mono-ligand products

while the larger lanthanides (Ce and Sm) gave the unexpected bis-ligand complexes. It was also discovered that use of the bulkier ligand $\text{CzT}^{\text{CH}_2\text{Mes}}$ allows for formation of the mono-ligand complex with Ce, $(\text{CzT}^{\text{CH}_2\text{Mes}})\text{Ce}[\text{N}(\text{SiMe}_3)_2]_2$, due to the increased steric bulk of this ligand. Under forcing conditions (extended heating) the tris-ligand complex $(\text{CzT}^{\text{iPr}})_3\text{Y}$ was formed with Y, but in this case one ligand binds in a bidentate fashion while the other two are tridentate. Hydrolysis products involving two tridentate ligands were observed by X-ray crystallography in lanthanide siloxide complexes of the smaller lanthanides, $(\text{CzT}^{\text{iPr}})_2\text{Ln}(\text{OSiMe}_3)$ ($\text{Ln} = \text{Yb}, \text{Er}$). These results clearly show that our CzT ligands are much less sterically crowding than the carbazole-*bis*(oxazoline) (Czx) ligands developed previously because these ligands are unable to form lanthanide silylamide complexes even under forcing conditions. These lanthanide results also demonstrated the variable bonding capability of our CzT ligands: they are able to bind in the expected tridentate *mer* geometry, but also in a *fac* type tridentate bonding mode where the lanthanide centre sits far removed from the ligand pocket and in a bidentate mode where one of the tetrazole rings is non-coordinating.

Reactivity studies were conducted on the mono-ligand lanthanide complexes, $(\text{CzT}^{\text{R}})\text{LnX}$ ($\text{R} = \text{iPr}, \text{CH}_2\text{Mes}$. $\text{X} = \text{N}(\text{SiMe}_3)_2, \text{CH}_2\text{SiMe}_3$). All of these complexes were active catalysts for the ring opening polymerization of ϵ -caprolactone at room temperature with 0.1 mol% catalyst loading. In attempts to stabilize a divalent lanthanide centre with our CzT ligands, it was found that the metal is oxidized to the trivalent state. Reaction of divalent diamagnetic Yb(II) consistently resulted in a paramagnetic Yb(III) product. In the protonolysis case it was determined that the carbazole NH was being reduced in concert with Yb oxidation. However, in the salt metathesis reactions with Yb(II) where the

carbazole NH is not available for reduction, oxidation to Yb(III) still occurs. This observation was tentatively assigned to a disproportionation reaction where the initial Yb(II) starting material is converted to both a Yb(III) complex with the CzT ligand and Yb(0). These results suggest that the CzT ligand system acts as a hard donor that is better suited towards trivalent lanthanide complexes.

Air stable bis-ligand transition metal complexes were obtained with our CzT^{iPr} , CzTr^{iPr} , and $\text{CzT}^{\text{CH}_2\text{Mes}}$ ligands for several first row metals (Fe, Co, Ni and Zn). The most interesting of these complexes is that of $(\text{CzT}^{\text{iPr}})_2\text{Fe}$ which showed a smooth thermally-induced SCO transition in the solution state and a more notable two-step SCO transition in the solid state facilitated by crystal packing effects. When the ligand bulk is increased to form $(\text{CzT}^{\text{CH}_2\text{Mes}})_2\text{Fe}$ this SCO phenomenon is no longer present and instead TIP contributions are seen. This demonstrates the high degree of magnetic tunability available by simply adjusting the peripheral steric bulk of the CzT ligand in these Fe complexes. Additional ligand effects in these bis-ligand structures were observed in the oxidized product $[(\text{CzT}^{\text{iPr}})_2\text{Fe}]^+ \text{BF}_4^-$. This complex showed a possible electron transfer process where the ligand is initially oxidized, but over time the Fe(II) centre is slowly oxidized to Fe(III) and the ligand is reduced to its monoanionic state.

Several mono-ligand Fe(II) and Fe(III) complexes were successfully synthesized with our CzT^{iPr} ligand. These complexes prefer to form polymeric $[(\text{CzT}^{\text{iPr}})\text{FeBr}]$ or dimeric structures $[(\text{CzT}^{\text{iPr}})\text{FeBr}_2]$ in the solid state in order to saturate the coordination sphere around the Fe centre. The Fe(III) complex, $(\text{CzT}^{\text{iPr}})\text{FeBr}_2$, also showed an interesting monomer-dimer equilibrium in dilute solutions. These sterically unsaturated complexes undergo rapid ligand redistribution in solution to form $(\text{CzT}^{\text{iPr}})_2\text{Fe}$ in the

presence of electrophiles which limits further reactivity. This redistribution was successfully prevented with the right balance of steric and electronic effects provided by a bulky phenoxide in $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})(\text{THF})$. Reactions of this phenoxide complex with σ -donor ligands resulted in displacement of THF and formation of tBuNC and TPPO adducts while reactions with π -acceptor ligands such as CO and N_2O resulted in formation of a four coordinate Lewis base-free complex, $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})$. These four Fe phenoxide complexes were all structurally and electronically characterized and compared to explain the unusual variation in the phenoxide geometry from bent (Lewis base-free) to linear (base adducts) in these complexes. The electronic structures of the complexes calculated by DFT, along with experimental results, demonstrated the lack of π -back donation available from the Fe centre leading to the inability of $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})(\text{THF})$ to bind π -acceptor ligands. The THF and TPPO adducts along with the Lewis base-free Fe phenoxide all catalyze the hydrosilylation of a simple olefin substrate (styrene) by phenylsilane without the use of initiators or reductants. The formation of a 3:1 ratio of Markovnikov versus anti-Markovnikov product is fairly unusual for Fe catalysts, as is the catalytic activity of the unreduced Fe(II) complex. These results prompted us to suggest a catalytic mechanism that employs the CzT^{iPr} ligand to act as a proton shuttle in order to maintain the structure and oxidation state of the Fe catalyst. These preliminary results demonstrate the powerful reactivity our redox active ligands are capable of in association with inexpensive, readily available and non-toxic transition metals. This mono-ligand Fe complex proved to be the most promising branch of reactivity attempted with our CzT class of ligands, and suggests a plethora of undiscovered reactivity available with these complexes.

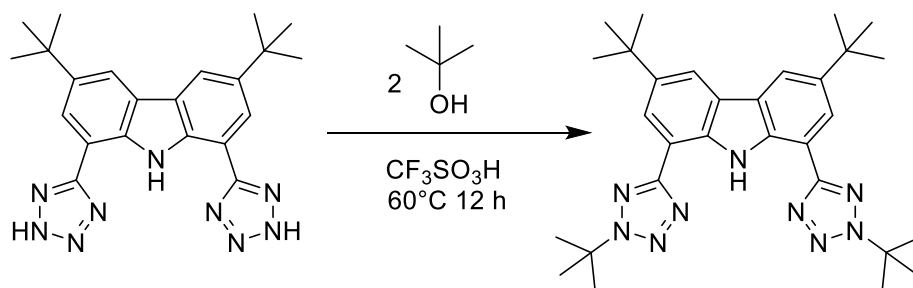
6.2 Conclusions and Future Work

The results discussed in this work demonstrate the capabilities of our new CzT and CzTr ligands. The most promising chemistry from this work is the hydrosilylation catalysis demonstrated by our mono-ligand Fe complexes. More research is needed on these preliminary results in order to understand the mechanism and to optimize the catalyst. While hydrosilylation of styrene and phenylsilane is a good proof of concept, neither of these substrates are relevant for industry-based applications. Tertiary silanes (R_3SiH) as well as unactivated terminal alkenes, such as 1-octene, are much more commercially relevant to industrial hydrosilylation applications. Future work should focus on testing a greater variety of substrates to see if hydrosilylation occurs with secondary or tertiary silanes, and unactivated terminal and internal alkenes.

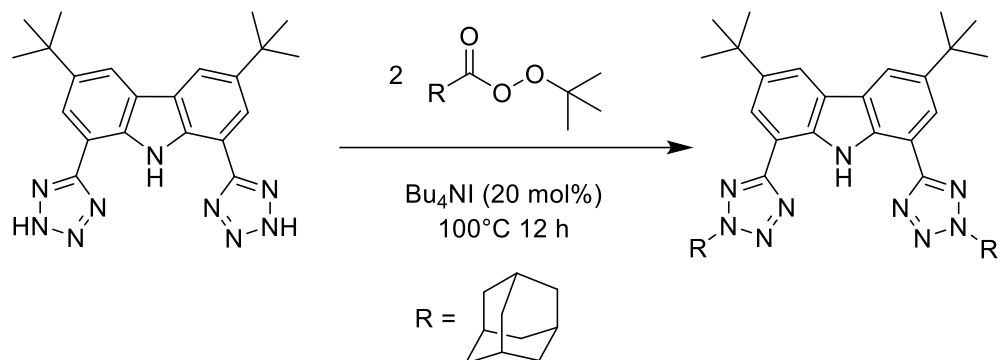
The selectivity of the catalyst should also be considered; since the modest 3:1 selectivity for the Markovnikov product is unusual. The ligand steric bulk may play a role in product selectivity so research with a variety of ligand substituents in the catalyst will be needed. It would be interesting to vary the bulk of the ancillary phenoxide ligand to see if activity and selectivity are affected. Replacing this phenoxide ligand with other phenoxides or different bulky anions is fairly trivial since this is the last synthetic step in forming the catalyst.

While the mono-ligand Fe complexes proved to be quite successful as hydrosilylation catalysts and demonstrate some interesting and unusual electronic properties, there is a need for a more sterically crowding ligand in order to successfully synthesize more reactive mono-ligand complexes. This need for increased steric bulk on the ligand was demonstrated in both the lanthanide and Fe chemistry. The commonly

observed redistribution to the bis-ligand Fe complex **23** continued to hinder progress on reactivity. It would be preferable to adjust the steric and electronic properties of the complex by adjusting the bulk of the CzT ligand rather than the X^- (e.g. phenoxide) ancillary ligand. Simple substitution of a tertiary carbon group on the azole rings is not available through simple deprotonation and alkylation due to the reaction proceeding through an S_N2 mechanism. However, it has been shown in the literature that it is possible to alkylate a protonated tetrazole ring with a tertiary carbon substituent by reaction with alcohols in a super acid medium such as CF_3SO_3H , $HClO_4$, or H_2SO_4 ³¹⁶⁻³¹⁸. A possible reaction scheme to synthesize a new bulkier CzT ligand is shown in **Scheme 6.1**. Another possible synthetic pathway to a tertiary carbon substituent directly on the tetrazole ring is through a radical induced alkylation with the use of Bu_4NI and organic peroxides and peresters³¹⁹. This route has been shown to allow isolation of tBu-substituted tetrazole rings and more promisingly adamantyl-substituted tetrazole rings in good yields. The proposed reaction scheme to synthesize $HCzT^{Ad}$ is shown in **Scheme 6.2**.



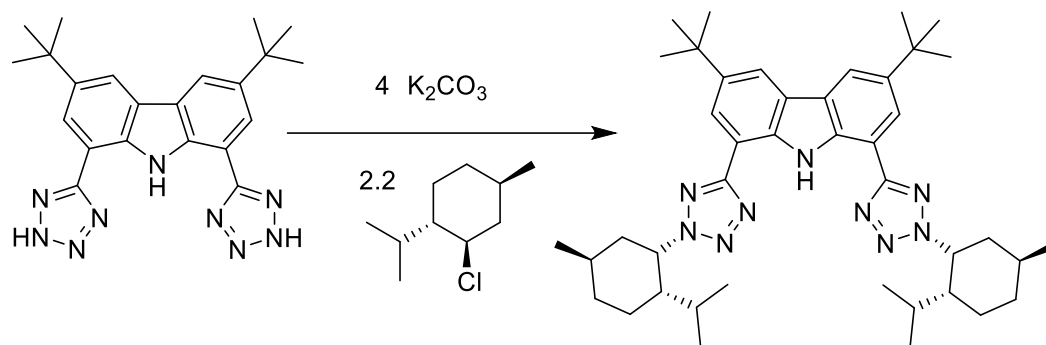
Scheme 6.1 Proposed synthesis of $HCzT^{tBu}$



Scheme 6.2 Proposed synthesis of HCzT^{Ad}

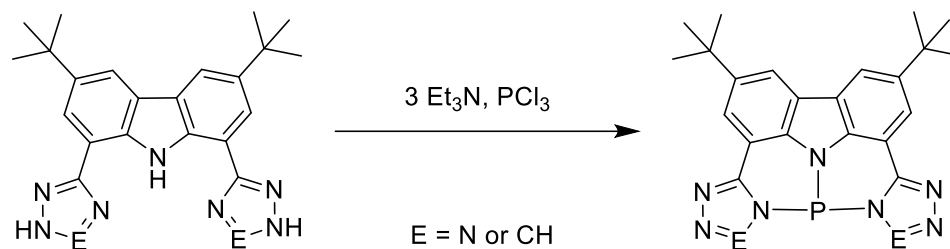
The successful synthesis of these bulky new ligands would allow for more sterically crowded metal complexes that will promote mono-ligand structures (in the case of the lanthanides) and prevent redistribution (in the case of Fe). It has been shown that increased ligand sterics is an important factor in synthesizing low coordinate metal complexes and these complexes will hopefully show increased reactivity at the metal centre.

The introduction of a chiral centre on the ligand would allow for stereoselective transformations at the metal centre. The most trivial way to incorporate a chiral centre on the CzT ligand framework is to use the existing synthetic procedure and alkylate with a halogenated chiral organic substituent, such as (-)-menthyl chloride (**Scheme 6.3**).



Scheme 6.3 Proposed synthesis of a chiral HCzT ligand

While several synthetic options are available to alter our existing ligands, there is also the option of using the non-alkylated HCzT^H and HCzTr^H ligands as trianionic donors. The use of our ligand scaffold as a trianionic ligand may be useful in main group complexes or with early transition metals such as V or Mo. The Radosevich group has shown some very interesting reactivity with their nontrigonal phosphorous compounds with a trianionic nitrogen-based ligand³²⁰⁻³²³. More interestingly, they proved the importance of the ligand binding in a nontrigonal geometry, where non-rigidity increases the reactivity at the phosphorous centre. The lanthanide work showed the CzT ligands offer a range of different binding modes and are not as rigid as initially thought. This phosphorous chemistry may be very well suited towards our CzT and CzTr ligands as we have already proven that they are able to bind in a variety of bonding modes and not solely in the planar *mer* geometry expected of a pincer ligand. The proposed synthesis of these phosphorous complexes is shown in **Scheme 6.4**.



Scheme 6.4 Proposed synthesis of (CzT)P or (CzTr)P complexes

This thesis demonstrates that carbazole-*bis*(azole) ligands, CzT^R and CzTr^R, form a wide range of metal complexes with a variety of coordination modes. The observation of interesting electronic and magnetic properties that depends on the ligand substituents demonstrates the tunability of these systems. Finally, the brief exploration of the catalytic reactivity of these complexes hint at the rich chemistry that may be accessible by further ligand modifications.

Chapter 7 Experimental

General Procedures: All reactions were carried out under a nitrogen atmosphere using Schlenk or glovebox methods (Braun MB150-GII). All solvents and reagents were purchased from Sigma Aldrich Chemicals and used as received except as noted below. All non-anhydrous solid reagents used in the glovebox were dissolved in solvent and dried over activated 4 Å sieves before using. All liquid reagents were dried by passing through a column of alumina and then made into a stock solution of known concentration before being deoxygenated by several freeze-pump-thaw cycles prior to use in the glovebox. Tetrahydrofuran, hexanes and toluene were dried by distillation from sodium metal and benzophenone, ACN and DCM were distilled from CaH₂. Solvents were stored in the glovebox over activated 4 Å sieves. Anhydrous LnCl₃ salts were purchased from Aldrich and converted to their THF solvates, LnCl₃(THF)_x by refluxing in anhydrous THF. Ln[N(SiMe₃)₂]₃, Ln[N(SiMe₃)₂]₂(THF)₂, benzyl potassium, LiCH₂SiMe₃ and bromomethylmesityl were prepared according to literature procedures³²⁴⁻³²⁷. K⁺[2,6-di-tert-butyl-4-methylphenoxide]⁻ was prepared from 2,6-di-tert-butyl-4-methylphenol and KH. ε-caprolactone was purchased from Sigma Aldrich and vacuum distilled from CaH₂ before use. Styrene was purchased from Sigma Aldrich and washed repeatedly with aqueous NaOH and water to remove inhibitors and then passed through a column of alumina and stored over MgSO₄ in the freezer.

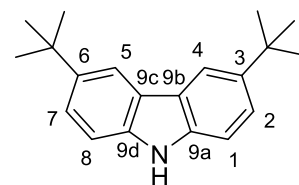
All NMR spectra were recorded on either Bruker AVANCE AMX-500, AVANCE AMX-360 or AVANCE AMX-300 spectrometers. The ¹H NMR spectra were recorded at 500, 360 or 300 MHz, ¹³C NMR spectra were recorded at 125, 90 or 75 MHz. Benzene-*D*₆

and toluene- D_8 were dried over potassium metal and stored in sealed Erlenmeyer flasks; 1 mL ampoules of THF- D_8 were bought from Aldrich and used as received. Air sensitive NMR samples were sealed in 5 mm tubes fitted with a J Young valve and further sealed with parafilm. Final NMR assignments of the diamagnetic ligands were accomplished with the help of 2D techniques (COSY, NOESY, HSQC, HMBC). Melting points were carried out in sealed capillary tubes using a Gallenkamp MFB 600 030W instrument and are uncorrected. +ESI-MS data were collected on a Q-TOF II instrument by MicroMass. Cyclic voltammetry was carried out on a Bioanalytical Systems Epsilon Voltammetric Analyzer in acetonitrile, THF or DCM using $n\text{-Bu}_4\text{N}^+\text{PF}_6^-$ as supporting electrolyte (0.1 M). Elemental analyses (C, H, N) were carried out by Canadian Microanalytical Ltd., Delta, B.C or Guelph Chemical Laboratories Ltd. Guelph Ontario. Thermogravimetric analysis (TGA) was completed on a Q600 SDT instrument from TA Instruments and analyzed using TA Universal Analysis, under an N_2 atmosphere at a heating rate of 10 $^\circ\text{C}/\text{min}$ up to 600 $^\circ\text{C}$ using a ceramic pan with approximately 10 mg of sample. UV-vis spectra were recorded on a Varian Cary 50 Scan spectrometer and fluorescence spectra were recorded on an Agilent Cary Eclipse fluorimeter. Magnetic measurements were performed on a Quantum Design SQUID SPMS-5S magnetometer; the temperature dependant magnetic susceptibility was measured over 2-350 K with an applied field of 10000 Oe. Diamagnetic corrections were made by subtracting the appropriate Pascal's constants³²⁸. X-ray diffraction data was collected on a Bruker Kappa X8-Apex II diffractometer using Mo and Cu $K\alpha$ radiation at the University of Notre Dame or at the Advanced Light Source (ALS) synchrotron facility at Lawrence Berkeley National Laboratory, Berkeley, CA. DFT calculations were carried out using Gaussian 16

implemented on the WestGrid computing network. Calculations were performed either using single point calculations or geometry optimized calculations at the B3LYP level using the 6-311G basis set³²⁹⁻³³⁰. Frequency calculations were carried out on geometry optimized calculations to ensure convergence to a true minimum rather than a saddle point.

3,6-Di-*tert*-butylcarbazole (**2**)

The synthesis of **2** was conducted as previously reported¹⁰⁴ except for the following changes: ZnCl₂ (40.50 g, 297.2 mmol)

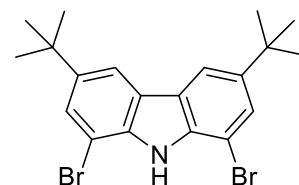


was dehydrated under vacuum in a 1 L round bottom flask by heating until molten with a Bunsen burner. On cooling, carbazole (16.50 g, 98.70 mmol) and nitromethane (500 mL) were added to the flask, and the solution was stirred under N₂ until thoroughly mixed and dark green in colour. 2-Chloro-2-methylpropane (33.0 mL, 300 mmol) was added dropwise by dropping funnel resulting in a colour change from dark green to green-brown with formation of a white precipitate. The white precipitate dissolved upon further stirring and the solution changed to opaque and light green. After stirring overnight at room temperature, 500 mL of H₂O was added to the reaction mixture and stirring was continued for 30 minutes. The solution changed to dark green and large emulsions were formed. The reaction mixture was extracted with DCM (3 x 300 mL) and the combined organic layers were washed with water (2 x 750 mL) and dried over MgSO₄. After filtration, the solvent was removed under reduced pressure to yield a light brown-yellow powder as the crude product. Purification of the crude product, if desired, was achieved by stirring in minimal hexanes overnight to yield a white powder. Yield: 27.3 g (99.0 %). MP. 220-223 °C. ¹H NMR (300 MHz, CDCl₃, 298 K): δ 8.10 (d, *J* = 2.0 Hz, 2 H, 4,5-Ar-*H*), 7.84 (br s, 1 H,

NH (Cbz)), 7.49 (dd, $J = 2.0, 8.5$ Hz, 2 H, 2,7-Ar-*H*), 7.36 (dd, $J = 0.5, 8.5$ Hz, 2 H, 1,8-Ar-*H*), 1.48 (s, 18 H, C(CH₃)₃). ¹³C {¹H} NMR (75 MHz, CDCl₃, 298 K): δ 142.2 (3,6-aryl-C), 138.0 (9a,9d-aryl-C), 123.5 (9b,9c-aryl-C), 123.4 (2,7-aryl-C), 116.3 (4,5-aryl-C), 110.1 (1,8-aryl-C), 34.7 (C(CH₃)₃), 32.2 (C(CH₃)₃).

1,8-dibromo-3,6-di-*tert*-butylcarbazole (**3**)

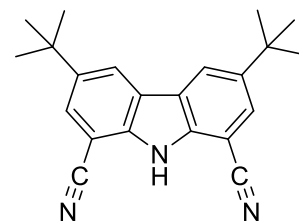
The synthesis of **3** was conducted as previously reported¹⁰⁵ except for the following changes: 3,6-Di-*tert*-butylcarbazole (**2**)



(10.01 g, 35.80 mmol) was dissolved in glacial acetic acid (300 mL). Once fully dissolved, bromine (4.1 mL, 80 mmol) was added drop-wise by dropping funnel in the dark and the solution changed from light brown to dark orange. The reaction was left to stir for 3 hours at room temperature in the dark and a white precipitate of pure product formed. The precipitate was removed by vacuum filtration and washed with distilled H₂O to yield a white powder as the pure product. 300 mL H₂O was added to the filtrate and a second crop of **3** was collected after storage in the fridge overnight. A further crop was precipitated out by mixing this filtrate with water. Recrystallization of the product, if desired, was achieved in hot isopropanol to yield pale purple crystals. Yield: 15.6 g (99.7 %). MP. 172-174 °C. ¹H NMR (300 MHz, CDCl₃, 298 K): δ 8.11 (br s, 1H, NH (Cbz)), 7.95 (d, $J = 1.3$ Hz, 2H, 4,5-Ar-*H*), 7.62 (d, $J = 1.7$ Hz, 2H, 2,7-Ar-*H*), 1.42 (s, 18H, C(CH₃)₃). ¹³C {¹H} NMR (75 MHz, CDCl₃, 298 K): δ 144.8 (3,6-aryl-C), 136.4 (9a,9d-aryl-C), 126.6 (2,7-aryl-C), 125.0 (9b,9c-aryl-C), 116.0 (4,5-aryl-C), 104.0 (1,8-aryl-C), 34.9 (C(CH₃)₃), 31.9 (C(CH₃)₃).

1,8-Dicyano-3,6-di-*tert*-butylcarbazole (4)

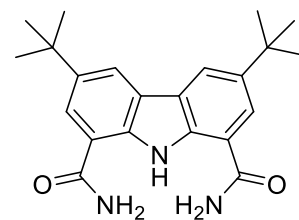
The synthesis of **7** was conducted as previously reported⁶⁴ except for the following changes: 1,8-Dibromo-3,6-di-*tert*-butylcarbazole (**3**) (10.02 g, 22.90 mmol) was dissolved in NMP



(180 mL), to give a light brown solution. CuCN (5.33 g, 59.5 mmol) was added, and the reaction was left to reflux at 180 °C overnight. As it was heated the solution turned very dark. After cooling to room temperature, the solution was added to a beaker containing EtOAc (200 mL) and NH₄OH (400 mL) and stirred for 30 minutes. The solution was filtered through Celite to remove the white Cu salt precipitate that had formed. The resulting filtrate was extracted with EtOAc (3 x 500 mL) and washed with 1 M HCl (2 x 300 mL), brine (2 x 300 mL), H₂O (2 x 300 mL) and dried over MgSO₄. After filtration, the solvent was removed under reduced pressure to yield a light brown powder as the crude product. The crude product was recrystallized from a mixture of isopropanol and EtOAc to yield light brown crystals. Yield: 6.68 g (88.7 %). MP. 320 °C (dec). ¹H NMR (300 MHz, CDCl₃, 298 K): δ 9.92 (br s, 1H, NH (Cbz)), 8.29 (d, *J* = 1.8 Hz, 2H, 4,5-Ar-*H*), 7.82 (d, *J* = 1.8 Hz, 2H, 2,7-Ar-*H*), 1.43 (s, 18H, C(CH₃)₃). ¹³C{¹H} NMR (75 MHz, CDCl₃, 298 K): δ 144.02 (3,6-aryl-C), 139.36 (9a,9d-aryl-C), 128.70 (2,7-aryl-C), 123.99 (9b,9c-aryl-C), 122.33 (4,5-aryl-C), 117.24 (C≡N), 94.33 (1,8-aryl-C), 35.12 (C(CH₃)₃), 31.92 (C(CH₃)₃).

1,8-Diamido-3,6-di-*tert*-butylcarbazole (5)

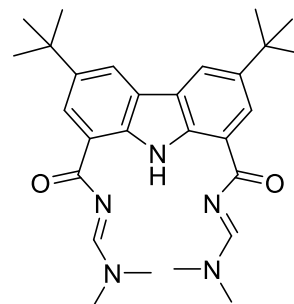
1,8-Dicyano-3,6-di-*tert*-butylcarbazole (**4**) (2.00 g, 6.07 mmol) was added to a 2 L round bottom flask and dissolved in DMF (50 mL). NaOH (5.0 g) was dissolved in H₂O (50 mL) to give a 2.5



M solution. This was added slowly to 30 % H₂O₂ (150 mL) for a final concentration of 0.5 M and stirred manually to allow some gas to be released. This basic solution was added slowly to the round bottom flask in 10-15 mL portions over the course of 30 minutes. As the solution was added, large amounts of heat and gas were produced and a pale yellow froth formed that floated on the surface. If the basic solution was added too quickly, the reaction mixture was liable to boil continuously resulting in product decomposition; however, if it was added too slowly the basic solution reacted and generated large amounts of gas and heat before mixing with the reaction mixture and no product formed. The reaction was left to stir overnight at room temperature after which product was removed by vacuum filtration and washed with distilled H₂O to yield a yellow powder as the crude product. Yield: 2.11 g (95.1 %). MP. 308-310 °C. ¹H NMR (300 MHz, DMSO-D₆, 298 K): δ 11.59 (br s, 1H, NH (Cbz)), 8.43 (d, *J* = 1.6 Hz, 2H, 4,5-Ar-*H*), 8.29 (br s, 2H, NH (amide)), 8.03 (d, *J* = 1.7 Hz, 2H, 2,7-Ar-*H*), 7.44 (br s, 2H NH (amide)), 1.44 (s, 18H, C(CH₃)₃). ¹³C {¹H} NMR (75 MHz, DMSO-D₆, 298 K): δ 169.3 (amido-C), 141.3 (3,6-aryl-C), 137.6 (9a,9d-aryl-C), 123.1 (2,7-aryl-C), 122.8 (9b,9c-aryl-C), 120.5 (4,5-aryl-C), 115.1 (1,8-aryl-C), 34.8 (C(CH₃)₃), 31.9 (C(CH₃)₃).

1,8-Bis[[(N,N-dimethylamino)methylene]carboxamide]-3,6-di-*tert*-butylcarbazole (6)

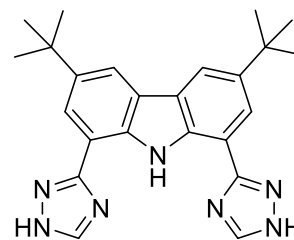
1,8-Diamido-3,6-di-*tert*-butylcarbazole (**5**) (4.00 g, 11.7 mmol) was dissolved in THF (50 mL). DMF-DMA (8.72 mL, 65.6 mmol) was added to the solution at room temperature. As DMF-



DMA was added, the solution changed from light orange to dark orange. The solution was sealed and allowed to stir at room temperature for 48 h after which the solvent was removed under reduced pressure to yield a reddish-white powder as crude product. The crude product was recrystallized from isopropanol to yield a bright yellow powder. Yield: 4.89 g (93.9 %). MP. 267-270 °C. ¹H NMR (300 MHz, DMSO-D₆, 298 K): δ 11.94 (br s, 1H, NH (Cbz)), 8.75 (s, 2H, CH), 8.49 (d, *J* = 2.3 Hz, 2H, 4,5-Ar-*H*), 8.28 (d, *J* = 1.9 Hz, 2H, 2,7-Ar-*H*), 3.42 (s, 6H, [NCH₃]), 3.24 (s, 6H, [NCH₃]), 1.49 (s, 18H, C(CH₃)₃). ¹³C NMR (75 MHz, DMSO-D₆, 298 K) δ 176.6 (C=O), 160.5 (C=N), 140.9 (3,6-aryl-C), 138.0 (9a,9d-aryl-C), 125.2 (2,7-aryl-C), 123.5 (9b,9c-aryl-C), 121.5 (4,5-aryl-C), 118.3 (1,8-aryl-C), 35.6 (N(CH₃)₂), 34.5 (C(CH₃)₃), 31.9 (C(CH₃)₃).

1,8-Bis(2'-H-1',2',4'-triazo-5'-yl)-3,6-di-*tert*-butylcarbazole (HCzTr^H, 7)

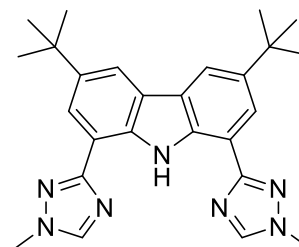
1,8-Bis[[(N,N-dimethylamino)methylene]carboxamide]-3,6-di-*tert*-butylcarbazole (**6**) (4.00 g, 9.44 mmol) was dissolved in



glacial acetic acid (45 mL). Hydrazine monohydrate (1.06 mL, 21.7 mmol) was added and the solution changed from dark orange to opaque yellow. The solution was heated to 120 °C and stirred at reflux for 3 hours. As the solution heated, it changed to a transparent

yellow solution. The solution was cooled to room temperature and diluted with ethyl acetate (150 mL) and then neutralized with saturated sodium bicarbonate solution (750 mL). After the solution no longer produced CO₂, the aqueous layer was removed by separation and the organic layer was washed with distilled H₂O (3 x 200 mL) and brine (3 x 200 mL). The organic layer was dried over MgSO₄, filtered and the solvent removed from the filtrate under reduced pressure to yield a yellow powder as the crude product. The crude product was recrystallized in toluene to yield a white powder. Yield: 3.27 g (94.0 %). MP. 325 °C (dec). ¹H NMR (300 MHz, DMSO-D₆, 298 K): δ 14.46 (br s, 2H, NH (Tr)), 11.75 (br s, 1H, NH (Cbz)), 8.80 (br s, 2H, CH (Tr)), 8.41 (s, 2H, 4,5-Ar-H), 8.29 (s, 2H, 2,7-Ar-H), 1.48 (s, 18H, C(CH₃)₃). ¹³C {¹H} NMR (75 MHz, DMSO-D₆, 298 K): δ 160.6 (Tr-C), 144.3 (Tr-CH), 141.6 (3,6-aryl-C), 136.1 (9a,9d-aryl-C), 123.4 (9b,9c-aryl-C) 120.8 (2,7-aryl-C), 117.9 (4,5-aryl-C), 113.2 (1,8-aryl-C), 34.6 (C(CH₃)₃), 31.9 (C(CH₃)₃).

1,8-Bis(2'-methyl-1',2',4'-triazolo-5'-yl)-3,6-di-tert-butylcarbazole (HCzTr^{Me}, 7a)

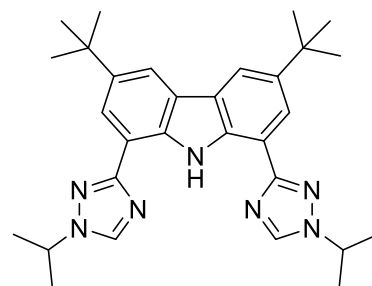


A Schlenk tube was charged with finely ground K₂CO₃ (0.662 g, 4.83 mmol) and DMF (30 mL) and the suspension placed under a nitrogen atmosphere. In a separate flask pure 1,8-bis(2'-H-1',2',4'-triazolo-5'-yl)-3,6-di-tert-butylcarbazole (**7**) (0.500 g, 1.21 mmol) was dissolved in DMF (20 mL) and this solution was added to the Schlenk tube. Iodomethane (0.180 mL, 2.89 mmol) was added to the reaction mixture and the solution was stirred at room temperature for 24 h. The yellow solution was diluted with EtOAc (200 mL) in air and washed repeatedly with

H₂O to remove the DMF. The organic layer was dried over MgSO₄, filtered and the solvent removed from the filtrate under reduced pressure to yield a yellow solid as crude product. The crude yellow powder was recrystallized from hot isopropanol to yield white crystalline solid. Yield: 0.459 g (86.0 %). MP. 311-312 °C. ¹H NMR (500 MHz, THF-D₈, 298 K): δ 11.81 (br s, 1H, NH (Cbz)), 8.37 (d, *J* = 1.9 Hz, 2H, 4,5-Ar-*H*), 8.33 (s, 2H, CH (Tr)), 8.21 (d, *J* = 1.7 Hz, 2H, 2,7-Ar-*H*), 4.07 (s, 6H, [CH₃ (Tr)]), 1.50 (s, 18H, C(CH₃)₃). ¹³C{¹H} NMR (125 MHz, THF-D₈, 298 K): δ 162.9 (Tr-C), 144.9 (Tr-CH), 141.8 (3,6-aryl-C), 136.9 (9a,9d-aryl-C), 124.6 (9b, 9c-aryl-C), 121.7 (2,7-aryl-C), 117.7 (4,5-aryl-C), 114.1 (1,8-aryl-C), 36.0 (Tr-CH₃), 35.2 (C(CH₃)₃), 32.3 (C(CH₃)₃). +ESI-MS: *m/z* 442.271 (M⁺ +H calcd. 442.272).

1,8-Bis(2'-isopropyl-1',2',4'-triazol-5'-yl)-3,6-di-tert-butylcarbazole (HCzTr^{iPr}, 7b)

Ligand **7b** was prepared from 1,8-bis(2'-H-1',2',4'-triazol-5'-yl)-3,6-di-tert-butylcarbazole (**7**) (0.500 g, 1.21 mmol) and 2-bromopropane (0.250 mL, 2.64 mmol) using a

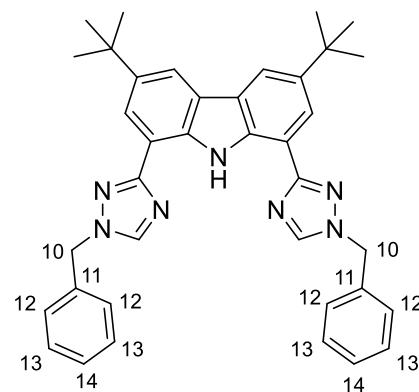


procedure analogous to that for **7a** except that the reaction mixture was heated at 100 °C for 48 h. Yield: 0.548 g (91.1 %). MP. 251-252 °C. ¹H NMR (500 MHz, THF-D₈, 298 K): δ 11.89 (br s, 1H, NH (Cbz)), 8.41 (s, 2H, CH (Tr)), 8.39 (d, *J* = 2.1 Hz, 2H, 4,5-Ar-*H*), 8.21 (d, *J* = 2.0 Hz, 2H, 2,7-Ar-*H*), 4.76 (septet, *J* = 6.7 Hz, 2H, CH(CH₃)₂), 1.69 (d, *J* = 6.7 Hz, 12H, CH(CH₃)₂), 1.51 (s, 18H C(CH₃)₃). ¹³C{¹H} NMR (125 MHz, THF-D₈, 298 K): δ 162.6 (Tr-C), 142.3 (Tr-CH), 141.7 (3,6-aryl-C), 136.9 (9a,9d-aryl-C), 124.53 (9b, 9c-aryl-C), 121.6 (2,7-aryl-C), 117.6 (4,5-aryl-C), 114.3 (1,8-aryl-C), 52.8 (CH(CH₃)₂),

35.2 ($C(CH_3)_3$), 32.3 ($C(CH_3)_3$), 22.7 ($CH(CH_3)_2$). +ESI-MS: m/z 498.334 ($M^+ + H$ calcd. 498.335).

1,8-Bis(2'-benzyl-1',2',4'-triazolo-5'-yl)-3,6-di-tert-butylcarbazole (HCzTr^{Bz}, 7c)

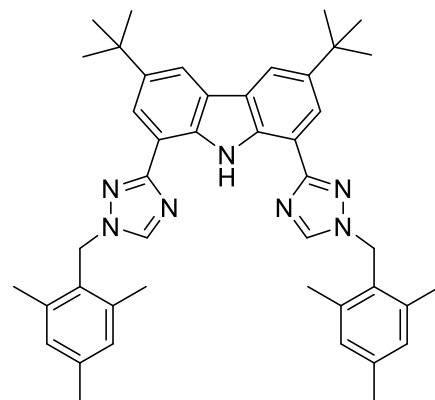
Ligand **7c** was prepared from 1,8-bis(2'-H-1',2',4'-triazolo-5'-yl)-3,6-di-tert-butylcarbazole (**7**) (0.500 g, 1.21 mmol) and benzyl bromide (0.320 mL, 2.69 mmol) using a procedure analogous to that for **7a**. Yield: 0.661



g (92.1 %). MP. 253-255 °C. ^1H NMR (500 MHz, THF- D_8 , 298 K): δ 11.87 (br s, 1H, NH (Cbz)), 8.41 (s, 2H, CH (Tr)), 8.39 (d, J = 1.7 Hz, 2H, 4,5-Ar-H), 8.22 (d, J = 1.9 Hz, 2H, 2,7-Ar-H), 7.44-7.25 (m, 10H, Ar-Benzyl H), 5.48 (s, 4H, Benzyl CH_2), 1.50 (s, 18H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (125 MHz, THF- D_8 , 298 K): δ 163.0 (Tr-C), 144.7 (Tr-CH), 141.9 (3,6-aryl-C), 137.2 (9a,9d-aryl-C), 136.9 (11 benzyl-C), 129.3 (12 benzyl-C), 128.6 (13 benzyl-C), 128.5 (14 benzyl-C), 124.6 (9b, 9c-aryl-C), 121.8 (2,7-aryl-C), 117.8 (4,5-aryl-C), 114.0 (1,8-aryl-C), 53.6 (10 CH_2), 35.2 ($C(CH_3)_3$), 32.3 ($C(CH_3)_3$). +ESI-MS: m/z 594.334 ($M^+ + H$ calcd. 594.334).

1,8-Bis(2'-(2'',4'',6''-trimethylphenyl)methyl-1',2',4'-triazol-5'-yl)-3,6-di-tert-butylcarbazole (HCzTr^{CH₂Mes}, 7d)

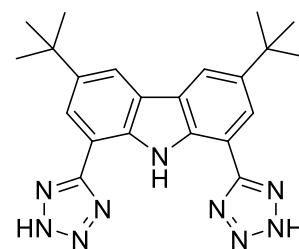
Ligand **7d** was prepared from 1,8-bis(2'-H-1',2',4'-triazol-5'-yl)-3,6-di-tert-butylcarbazole (**7**) (2.00 g, 4.84 mmol) and 1-(bromomethyl)-2,4,6-benzene (2.27



g, 10.7 mmol) using a procedure analogous to that for **7a**. Yield: 2.52 g (76.9 %). MP. 207-209 °C. ¹H NMR (500 MHz, DMSO-D₆, 298 K): δ 11.57 (br s, 1H, NH (Cbz)), 8.48 (s, 2H, CH (Tr)), 8.36 (d, ⁴J_{HH} = 1.5 Hz, 2H, 4,5-Ar-H), 8.18 (d, ⁴J_{HH} = 1.5 Hz, 2H, 2,7-Ar-H), 6.91 (s, 4H, Mes Ar-H), 5.56 (s, 4H, CH₂), 2.41 (s, 12H, Mes o-CH₃), 2.22 (s, 6H, Mes p-CH₃), 1.45 (s, 18H, C(CH₃)). ¹³C{¹H} (125 MHz, DMSO-D₆, 298 K): δ 160.7 (Tr-C), 144.3 (Tr-CH), 141.6 (9a,9d-aryl-C), 137.9 (3,6-aryl-C), 137.7 (11 Mes-C), 135.2 (12 Mes-C), 129.1 (13 Mes-C), 128.5 (14 Mes-C), 123.4 (9b,9c-aryl-C), 120.4 (2,7-aryl-C), 118.1 (4,5-aryl-C), 112.6 (1,8-aryl-C), 47.5 (10 CH₂), 34.5 (C(CH₃)₃), 31.9 (C(CH₃)₃), 20.6 (Mes p-CH₃), 19.6 (Mes o-CH₃).

1,8-Bis(2'-H-tetrazo-5'-yl)-3,6-di-tert-butylcarbazole (HCzT^H, 8)

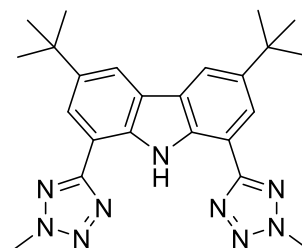
1,8-Dicyano-3,6-di-tert-butylcarbazole (**4**) (4.14 g, 12.6 mmol) was dissolved in DMF (60 mL). Under nitrogen, CAN (1.39 g,



2.54 mmol) was added to the solution. The solution was heated to 140 °C and NaN₃ (2.11 g, 32.5 mmol) was added to the solution; causing the solution to change colour from light orange to dark brown. The reaction mixture was left to reflux for 48 hours then cooled to

room temperature and extracted with EtOAc. The combined organic layers were washed with 1 M HCl (2 x 100 mL), brine (2 x 100 mL), H₂O (2 x 100 mL) and dried over MgSO₄. The mixture was filtered and the solvent was removed from the filtrate under reduced pressure to yield a light yellow-brown powder as the crude product. The product was washed with minimal amounts of EtOAc to remove impurities and then vacuum filtered to yield a light yellow powder. Yield: 4.60 g (88.1 %). MP. 240 °C (dec). ¹H NMR (300 Hz, THF-D₈, 298 K): δ 15.99 (br s, 2H, 2'-NH), 11.89 (br s, 1H, NH (Cbz)), 8.44 (d, *J* = 1.4 Hz, 2H, 4,5-Ar-*H*), 8.29 (d, *J* = 1.4 Hz, 2H, 2,7-Ar-*H*), 1.54 (s, 18H, C(CH₃)₃). ¹³C {¹H} NMR (75 MHz, THF-D₈, 298 K): δ 170.3 (T-C), 143.1 (3,6-aryl-C), 136.9 (9a,9d-aryl-C), 125.0 (9b,9c-aryl-C), 122.4 (2,7-aryl-C), 120.2 (4,5-aryl-C), 114.1 (1,8-aryl-C), 35.4 (C(CH₃)₃), 32.1 (C(CH₃)₃).

1,8-Bis(2'-methyltetrazo-5'-yl)-3,6-di-tert-butylcarbazole
(HCzT^{Me}, 8a)

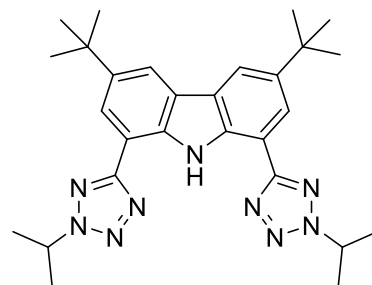


Ligand **8a** was prepared from 1,8-bis(2'-H-tetrazo-5'-yl)-3,6-di-tert-butylcarbazole (**8**) (0.500 g, 1.20 mmol) and iodomethane (0.170 mL, 2.73 mmol) using a procedure analogous to that for **7a**. Yield: 0.454 g (85.1 %). MP. 231-232 °C. ¹H NMR (500 MHz, THF-D₈, 298 K): δ 11.48 (br s, 1H, NH (Cbz)), 8.40 (d, *J* = 2.1 Hz, 2H, 4,5-Ar-*H*), 8.37 (d, *J* = 1.8 Hz, 2H, 2,7-Ar-*H*), 4.53 (s, 6H, CH₃ (T)), 1.52 (s, 18H, C(CH₃)₃). ¹³C {¹H} NMR (125 MHz, THF-D₈, 298 K) δ 165.1 (T-C), 143.0 (3,6-aryl-C), 136.7 (9a,9d-aryl-C), 124.9 (9b,9c-aryl-C), 122.3 (2,7-aryl-C), 119.5 (4,5-aryl-C), 110.3 (1,8-aryl-C), 39.5 (T-CH₃), 35.3 (C(CH₃)₃), 32.2 (C(CH₃)₃). +ESI-MS: *m/z* 444.262 (M⁺ +H calcd. 422.262), 466.244 (M⁺ +Na calcd. 466.244).

1,8-Bis(2'-isopropyltetrazo-5'-yl)-3,6-di-tert-

butylcarbazole (HCzT^{iPr}, **8b**)

Ligand **8b** was prepared from 1,8-bis(2'-H-tetrazo-5'-yl)-3,6-di-tert-butylcarbazole (**8**) (0.500 g, 1.20 mmol) and 2-bromopropane (0.250 mL, 2.66 mmol) using a procedure



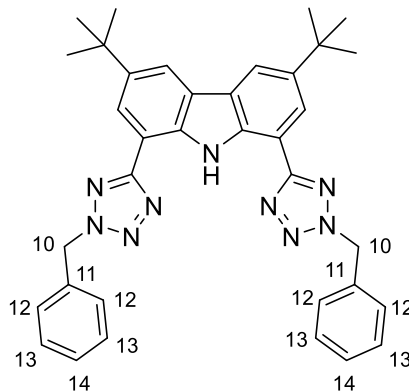
analogous to that for **7a** except that the reaction mixture was heated at 100 °C for 48 h.

Yield: 0.499 g (83.0 %). MP. 204-206 °C. ¹H NMR (500 MHz, THF-D₈, 298 K): δ 11.65 (br s, 1H, NH (Cbz)), 8.41 (d, *J* = 1.7 Hz, 2H, 4,5-Ar-*H*), 8.37 (d, *J* = 1.7 Hz, 2H, 2,7-Ar-*H*), 5.28 (septet, *J* = 6.7 Hz, 2H, CH(CH₃)₂), 1.81 (d, *J* = 6.8 Hz, 12H, (CH(CH₃)₂)), 1.52 (s, 18H, C(CH₃)₃). ¹³C {¹H} NMR (125 MHz, THF-D₈, 298 K): δ 164.9 (T-C), 143.1 (3,6-aryl-C), 137.0 (9a,9d-aryl-C), 125.1 (9b, 9c-aryl-C), 122.3 (2,7-aryl-C), 119.7 (4,5-aryl-C), 110.7 (1,8-aryl-C), 57.6 (CH(CH₃)₂), 35.5 (C(CH₃)₃), 32.4 (C(CH₃)₃), 22.5 (CH(CH₃)₂). +ESI-MS: *m/z* 522.306 (M⁺ + Na calcd. 522.307).

1,8-Bis(2'-benzyltetrazo-5'-yl)-3,6-di-tert-

butylcarbazole (HCzT^{Bz}, **8c**)

Ligand **8c** was prepared from 1,8-bis(2'-H-tetrazo-5'-yl)-3,6-di-tert-butylcarbazole (**8**) (0.500 g, 1.21 mmol) and benzyl bromide (0.310 mL, 2.69 mmol) using a procedure analogous to that for **7a**. Yield: 0.495 g (69.0



%). MP. 220-221 °C. ¹H NMR (500 MHz, THF-D₈, 298 K): δ 11.57 (br s, 1H, NH (Cbz)), 8.40 (d, *J* = 1.8 Hz, 2H, 4,5-Ar-*H*), 8.36 (d, *J* = 1.6 Hz, 2H, 2,7-Ar-*H*), 7.61-7.27 (m, 10H,

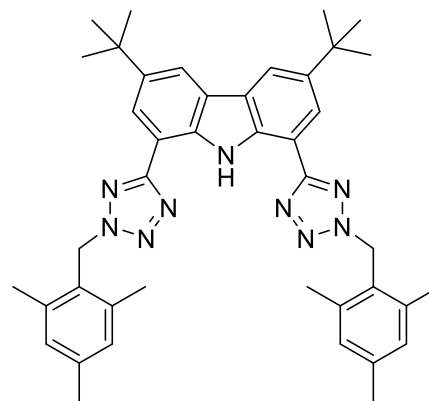
Ar-Benzyl *H*), 6.04 (s, 4H, Benzyl CH_2), 1.51 (s, 18H, $\text{C}(\text{CH}_3)_3$). ^{13}C $\{^1\text{H}\}$ NMR (125 MHz, THF- D_8 , 298 K): δ 165.5 (T-C), 143.2 (3,6-aryl-C), 136.9 (9a,9d-aryl-C), 135.3 (11 benzyl-C), 129.7 (12 benzyl-C), 129.5 (13 benzyl-C), 129.4 (14 benzyl-C), 125.1 (9b, 9c-aryl-C), 122.4 (2,7-aryl-C), 119.8 (4,5-aryl-C), 110.4 (1,8-aryl-C), 57.5 (10 CH_2), 35.5 ($\text{C}(\text{CH}_3)_3$), 32.3 ($\text{C}(\text{CH}_3)_3$). +ESI-MS: m/z 618.306 (M^+ +Na calcd. 618.307)

1,8-Bis(2'-(2'',4'',6''-

trimethylphenyl)methyltetrazo-5'-yl)-3,6-di-tert-

butylcarbazole ($\text{HCzT}^{\text{CH}_2\text{Mes}}$, **8d**)

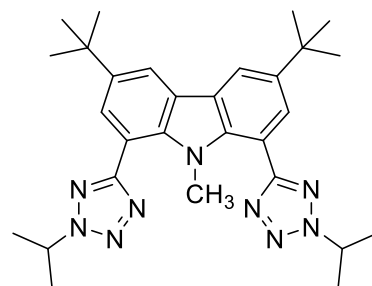
Ligand **8d** was prepared from 1,8-bis(2'-H-tetrazo-5'-yl)-3,6-di-tert-butylcarbazole (**8**) (0.500 g, 1.20 mmol) and bromomethylmesityl (0.568 g, 2.67 mmol)



using a procedure analogous to that for **7a**. Yield: 0.560 g (68.4 %). MP. 173-174 °C. ^1H NMR (300 MHz, CDCl_3 , 298 K): δ 11.25 (br s, 1H, *NH* (Cbz)), 8.36 (d, J = 1.7 Hz, 2H, 4,5-Ar-*H*), 8.23 (d, J = 1.7 Hz, 2H, 2,7-Ar-*H*), 6.92 (s, 4H, Mes Ar-*H*), 5.96 (s, 4H, CH_2), 2.61 (s, 12H, Mes *o*- CH_3), 2.26 (s, 6H, Mes *p*- CH_3), 1.51 (s, 18H $\text{C}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ (75.5 MHz, CDCl_3 , 298 K): δ 164.12 (T-C), 142.5 (3,6-aryl-C), 139.1 (14 Mes-C), 138.6 (12 Mes-C), 136.1 (9a,9d-aryl-C), 129.6 (13 Mes-C), 127.3 (11 Mes-C), 124.1 (9b,9c-aryl-C), 122.2 (4,5-aryl-C), 118.8 (2,7-aryl-C), 109.6 (1,8-aryl-C), 51.4 (10 CH_2), 35.0 ($\text{C}(\text{CH}_3)_3$), 32.2 ($\text{C}(\text{CH}_3)_3$), 22.2 (Mes *p*- CH_3), 20.3 (Mes *o*- CH_3).

MeCzTⁱPr (8e)

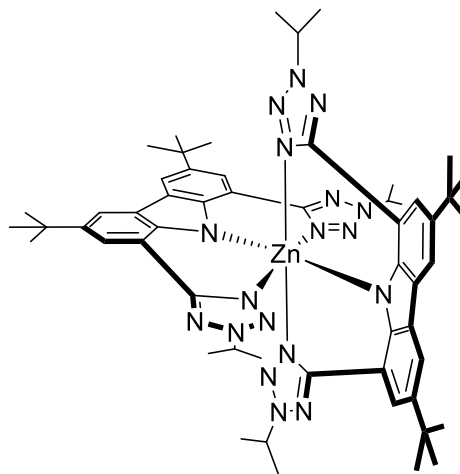
A Schlenk flask was charged with dried HCzTⁱPr (**8b**) (0.100 g, 0.200 mmol) dissolved in dry THF and the solution was stirred under a nitrogen atmosphere. NaH (0.019 g, 0.79 mmol) was added to the reaction mixture



producing a fluorescent yellow solution. After stirring at room temperature for 1 h, iodomethane (0.015 mL, 0.24 mmol) was added to the reaction mixture by syringe. This solution was allowed to stir overnight at room temperature then was filtered through Celite to remove the salt precipitate and the solvent removed from the filtrate under reduced pressure. The crude yellow residue was washed in hexanes to yield a beige powder. Recrystallization from hot IPA yielded a pale yellow solid. Yield: 0.088 g (86 %). MP. 132-135 °C. ¹H NMR (300 MHz, C₆D₆, 298 K): δ 8.39 (br 2nd order approx. d, 4H, both Ar-*H*), 4.55 (septet, *J* = 6.8 Hz, 2H, CH(CH₃)₂), 3.30 (s, 3H, CH₃), 1.40 (s, 18H, C(CH₃)₃), 1.20 (d, *J* = 6.8 Hz, 12H, (CH(CH₃)₂)). ¹³C {¹H} NMR (75 MHz, C₆D₆, 298 K): δ 165.2 (T-C), 143.0 (3,6-aryl-C), 140.9 (9a,9d-aryl-C), 127.7 (9b, 9c-aryl-C), 126.1 (2,7-aryl-C), 118.5 (4,5-aryl-C), 112.6 (1,8-aryl-C), 56.3 (CH(CH₃)₂), 37.9 (C(CH₃)₃), 34.8 (CH₃), 32.0 (C(CH₃)₃), 21.9 (CH(CH₃)₂).

(CzTⁱPr)₂Zn (9)

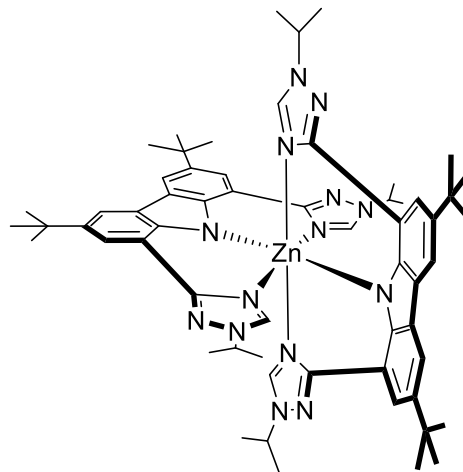
In the glovebox, HCzTⁱPr (**8**) (0.200 g, 0.400 mmol) was dissolved in THF and stirred. Benzyl potassium (0.052 g, 0.40 mmol) was dissolved in THF and added dropwise to the ligand solution resulting in a colour change to fluorescent yellow with a precipitate. ZnCl₂ (0.027 g, 0.20 mmol) was



added to the reaction mixture; the fluorescent colour remained unchanged but a white precipitate now formed. The solution was allowed to stir overnight after which the solution was filtered through Celite to remove the salt precipitate and the solvent was removed from the filtrate under reduced pressure. The crude product was washed with hexanes to yield a fluorescent yellow-green powder. Recrystallization of this powder from warm toluene yielded fluorescent yellow crystals. Yield: 0.204 g (96.9 %). MP. 255-258 °C. ¹H NMR (300 MHz, C₆D₆, 298 K): δ 8.80 (d, J = 2.1, 2H, 4,5-Ar-*H*), 8.78 (d, J = 2.0, 2H, 2,7-Ar-*H*), 3.78 (septet, J = 6.7, 2H, CH(CH₃)₂), 1.58 (s, 18H C(CH₃)₃), 0.58 (d, J = 6.7, 12H, CH(CH₃)₂). ¹³C {¹H} NMR (75 MHz, C₆D₆, 298 K): δ 165.3 (T-C), 148.3 (3,6-aryl-C), 137.7 (9a,9d-aryl-C), 125.5 (9b, 9c-aryl-C), 121.9 (2,7-aryl-C), 119.5 (4,5-aryl-C), 109.8 (1,8-aryl-C), 56.2 (CH(CH₃)₂), 34.7 (C(CH₃)₃), 32.4 (C(CH₃)₃), 21.0 (CH(CH₃)₂). Anal. Calcd. for C₅₆H₇₂N₁₈Zn: C 63.29, H 6.83, N 23.73; found: C 63.90, H 7.09, N 22.47. Anal calcd. for the 0.25 toluene 0.25 hexane solvate, C 64.27, H 7.05, N 22.77.

(CzTrⁱPr)₂Zn (10)

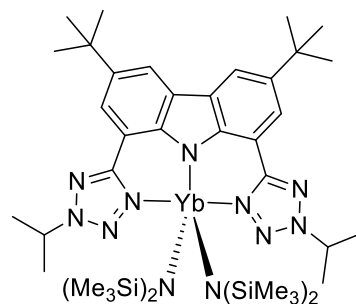
10 was prepared from HCzTrⁱPr (**7b**) (0.200 g, 0.402 mmol) and ZnCl₂ (0.027 g, 0.20 mmol) using a procedure analogous to that for **9**. The crude product was isolated as a fluorescent yellow powder and recrystallization from warm toluene yielded fluorescent yellow-green crystals. Yield:



0.197 g (93.9 %). MP. 267-269 °C. ¹H NMR (300 MHz, Toluene-D₈, 298 K): δ 8.93 (d, J = 2.1, 2H, 4,5-Ar-H), 8.83 (d, J = 2.0, 2H, 2,7-Ar-H), 7.15 (s, 2H, CH (Tr)), 2.76 (septet, J = 6.7, 2H, CH(CH₃)₂), 1.64 (s, 18H C(CH₃)₃), 0.50 (d, J = 6.7, 12H, CH(CH₃)₂). ¹³C {¹H} NMR (75 MHz, Toluene-D₈, 298 K): δ 161.6 (Tr-C), 147.5 (Tr-CH), 141.4 (3,6-aryl-C), 138.2 (9a,9d-aryl-C), 128.5 (9b, 9c-aryl-C), 121.4 (2,7-aryl-C), 118.2 (4,5-aryl-C), 114.3 (1,8-aryl-C), 51.7 (CH(CH₃)₂), 35.0 (C(CH₃)₃), 32.6 (C(CH₃)₃), 21.6 (CH(CH₃)₂). Anal. Calcd. for C₆₀H₇₆N₁₄Zn: C 68.06, H 7.24, N 18.52; found: C 68.24, H 7.06, N 18.80.

(CzTⁱPr)Yb[N(SiMe₃)₂]₂ (11)

In the glovebox, HCzTⁱPr (**8b**) (0.200 g, 0.400 mmol) dissolved in toluene was added to a solution of Yb[N(SiMe₃)₂]₃ (0.261 g, 0.400 mmol) dissolved in toluene, resulting in a yellow solution. After stirring at room

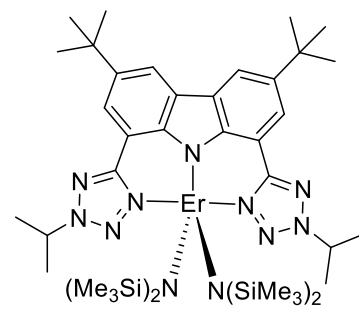


temperature for 36 hours, the solution turned a dark orange colour. The solvent was removed under reduced pressure and the crude product was washed in hexanes to yield an

orange powder. Recrystallization of the crude product from warm toluene yielded yellow crystals. Yield: 0.325 g (81.8 %). MP. 241-244 °C. ^1H NMR (300 MHz, C_6D_6 , 298 K): δ 42.57 (s, 2H, $\nu_{1/2}$ = 35 Hz, Ar-*H*), 29.34 (s, 2H, $\nu_{1/2}$ = 24 Hz, Ar-*H*), 27.62 (s, 12H, $\nu_{1/2}$ = 20 Hz, $\text{CH}(\text{CH}_3)_2$), 2.02 (s, 18H, $\nu_{1/2}$ = 7 Hz, $\text{C}(\text{CH}_3)_3$), -0.89 (s, 2H, $\nu_{1/2}$ = 9 Hz, $\text{CH}(\text{CH}_3)_2$), -12.22 (s, 36H, $\nu_{1/2}$ = 95 Hz, $\text{Si}(\text{CH}_3)_3$). Anal. Calcd. for $\text{C}_{40}\text{H}_{72}\text{N}_{11}\text{Si}_4\text{Yb}$: C 48.41, H 7.31, N 15.52; found: C 49.06, H 6.98, N 13.75.

(CzTⁱPr)Er[N(SiMe₃)₂]₂ (12**)**

12 was prepared from HCzTⁱPr (**8b**) (0.100 g, 0.200 mmol) and $\text{Er}[\text{N}(\text{SiMe}_3)_2]_3$ (0.130 g, 0.200 mmol) using a procedure analogous to that for **11**. **12** was isolated as an orange powder and was recrystallized from warm toluene to yield orange



crystals. Yield: 0.191 g (96.7 %). MP. 240-243 °C. ^1H NMR (300 MHz, C_6D_6 , 298 K): δ 52.03 (s, 2H, $\nu_{1/2}$ = 60 Hz, Ar-*H*), 40.66 (s, 2H, $\nu_{1/2}$ = 60 Hz, Ar-*H*), 34.37 (s, 12H, $\nu_{1/2}$ = 27 Hz, $\text{CH}(\text{CH}_3)_2$), 4.89 (s, 18H, $\nu_{1/2}$ = 10 Hz, $\text{C}(\text{CH}_3)_3$), 4.58 (s, 2H, $\nu_{1/2}$ = 16 Hz, $\text{CH}(\text{CH}_3)_2$), -10.53 (s, 36H, $\nu_{1/2}$ = 220 Hz, $\text{Si}(\text{CH}_3)_3$). Anal. Calcd. for $\text{C}_{40}\text{H}_{72}\text{ErN}_{11}\text{Si}_4$: C 48.69, H 7.35, N 15.62; found: C 53.48, H 7.82, N 13.76. Anal calcd. for the 1.30 toluene solvate, C 53.30, H 7.51, N 13.93.

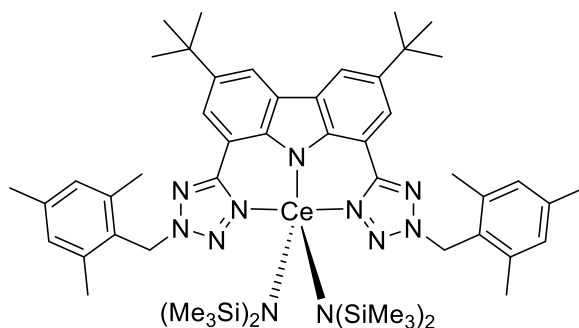
(CzT^{CH₂Mes})Ce[N(SiMe₃)₂] (13)

13 was prepared from HCzT^{CH₂Mes} (**8d**)

(0.100 g, 0.147 mmol) and

Ce[N(SiMe₃)₂]₃ (0.091 g, 0.15 mmol)

using a procedure analogous to that for **11**.



13 was isolated as an orange powder and was recrystallized from warm toluene to yield yellow-orange crystalline solid. Yield: 0.149 g (88.9 %). MP. 240-244 °C. ¹H NMR (300 MHz, C₆D₆, 298 K): δ 8.52 (s, 2H, *v*_{1/2} = 10 Hz, Cbz Ar-*H*), 6.28 (s, 2H, *v*_{1/2} = 14 Hz, Cbz Ar-*H*), 5.74 (s, 4H, *v*_{1/2} = 9 Hz, Mes Ar *H*), 2.92 (s, 4H, *v*_{1/2} = 14 Hz, CH₂), 1.65 (s, 6H, *v*_{1/2} = 7 Hz, Mes *p*-CH₃), 1.24 (s, 18H, *v*_{1/2} = 8 Hz, C(CH₃)₃), 0.09 (s, 12H, *v*_{1/2} = 12 Hz, Mes *o*-CH₃), -1.22 (s, 36H, *v*_{1/2} = 76 Hz, Si(CH₃)₃).

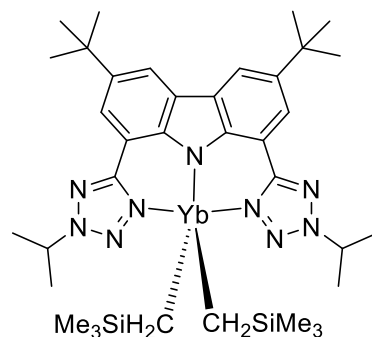
(CzT^{iPr})Yb[CH₂SiMe₃]₂ (14)

In the glovebox HCzT^{iPr} (**8b**) (0.200 g, 0.400 mmol) was

dissolved in THF and stirred. Benzyl potassium (0.052 g,

0.40 mmol) dissolved in THF was added dropwise to the

solution which immediately turned fluorescent yellow with



deposition of a precipitate. Solid YbCl₃ (0.112 g, 0.400 mmol) was added to the reaction

mixture resulting in a yellow-orange solution with a white salt precipitate. This solution

was let stir for 2 h at room temperature after which it was filtered through Celite to remove

the salt precipitate. To this filtrate, solid LiCH₂SiMe₃ (0.075 g, 0.797 mmol) was added

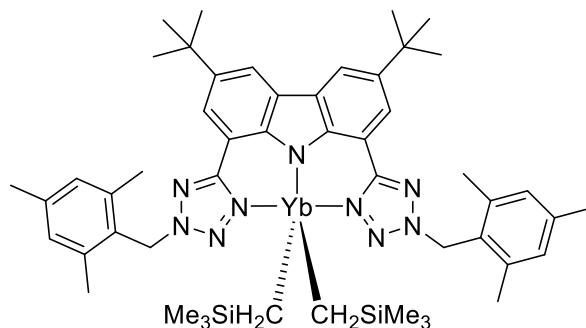
and the solution changed colour to dark orange and a white salt precipitate formed. The

solution was then allowed to stir overnight at room temperature. Filtration of the reaction

mixture through Celite to remove the precipitate and removal of the solvent from the filtrate afforded a dark orange solid. Yield: 0.312 g (92.1 %). MP. 260 °C (dec). ^1H NMR (300 MHz, C_6D_6 , 298 K): δ 60.63 (s, 2H, $\nu_{1/2}$ = 42 Hz, Ar-*H*), 39.46 (s, 12H, $\nu_{1/2}$ = 26 Hz, $\text{CH}(\text{CH}_3)_2$), 35.63 (s, 2H, $\nu_{1/2}$ = 33 Hz, Ar-*H*), 0.85 (s, 18H, $\nu_{1/2}$ = 7 Hz, $\text{C}(\text{CH}_3)_3$), -10.98 (s, 2H, $\nu_{1/2}$ = 11 Hz, $\text{CH}(\text{CH}_3)_2$), -28.96 (s, 18H, $\nu_{1/2}$ = 63 Hz, $\text{CH}_2\text{Si}(\text{CH}_3)_3$), -237.8 (s, 4H, $\nu_{1/2}$ = 885 Hz, $\text{CH}_2\text{Si}(\text{CH}_3)_3$). Elemental analysis was not obtained as the product is thermally sensitive and decomposes at room temperature over an extended period of time.

(CzT^{CH₂Mes})Yb[CH₂SiMe₃]₂ (15)

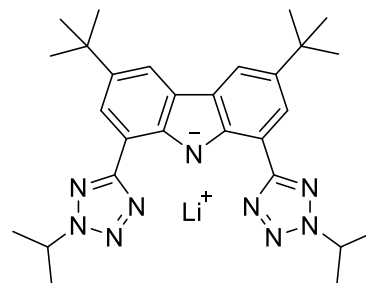
15 was prepared from HCzT^{CH₂Mes} (**8d**) (0.200 g, 0.294 mmol), YbCl₃ (0.082 g, 0.29 mmol) and LiCH₂SiMe₃ (0.055 g, 0.58 mmol) using a procedure analogous



to that for **14**. **15** was isolated as a dark red-orange solid. Yield: 0.261 g (86.4 %). MP. 284 °C (dec). ^1H NMR (300 MHz, C_6D_6 , 298 K): δ 65.35 (s, 4H, $\nu_{1/2}$ = 51 Hz, CH_2), 36.03 (s, 2H, $\nu_{1/2}$ = 39 Hz, Cbz Ar-*H*), 2.88 (s, 12H, $\nu_{1/2}$ = 29 Hz, Mes *o*- CH_3), 16.84 (s, 4H, $\nu_{1/2}$ = 11 Hz, Mes Ar *H*), 6.30 (s, 6H, $\nu_{1/2}$ = 8 Hz, Mes *p*- CH_3), 0.86 (s, 18H, $\nu_{1/2}$ = 8 Hz, $\text{C}(\text{CH}_3)_3$), -11.19 (s, 2H, $\nu_{1/2}$ = 14 Hz, Cbz Ar-*H*), -30.55 (s, 18H, $\nu_{1/2}$ = 75 Hz, $\text{CH}_2\text{Si}(\text{CH}_3)_3$), -239.3 (s, 4H, $\nu_{1/2}$ = 921 Hz, $\text{CH}_2\text{Si}(\text{CH}_3)_3$). Elemental analysis was not obtained as the product is thermally sensitive and decomposes at room temperature over an extended period of time.

Li⁺[CzTⁱPr]⁻ (16)

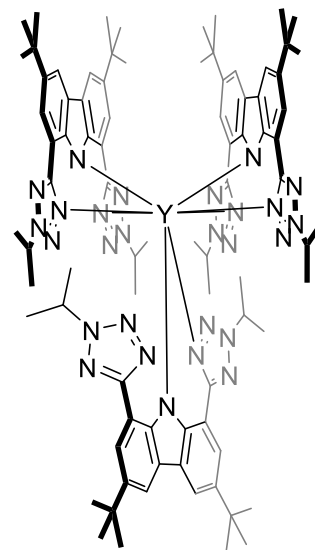
In the glovebox, HCzTⁱPr (**8b**) (0.025 g, 0.050 mmol) was dissolved in toluene and stirred. A 1.6 M MeLi solution (0.030 mL, 0.048 mmol) was added to the reaction mixture resulting in an immediate colour change to



fluorescent yellow. The solution was allowed to stir for 2 h at room temperature after which time the solvent was removed under reduced pressure and the product washed with hexanes to give a fluorescent yellow powder. Yield: 0.023 g (91 %). MP. 300-302 °C. ¹H NMR (300 MHz, Toluene-D₈, 298 K): δ 8.63 (br d, *J* = 6.8 Hz, 4H, both Ar-*H*), 4.52 (septet, *J* = 6.6 Hz, 2H, CH(CH₃)₂), 1.55 (s, 18H, C(CH₃)₃), 0.79 (d, *J* = 6.4 Hz, 12H, (CH(CH₃)₂)). ¹³C {¹H} NMR (75 MHz, Toluene-D₈, 298 K): δ 167.1 (T-C), 149.9 (3,6-aryl-C), 137.5 (9a,9d-aryl-C), 127.8 (9b, 9c-aryl-C), 121.1 (2,7-aryl-C), 119.7 (4,5-aryl-C), 110.1 (1,8-aryl-C), 56.9 (CH(CH₃)₂), 35.0 (C(CH₃)₃), 32.7 (C(CH₃)₃), 21.7 (CH(CH₃)₂).

$[(\text{CzT}^{\text{iPr}})_3\text{Y}]$ (**19**)

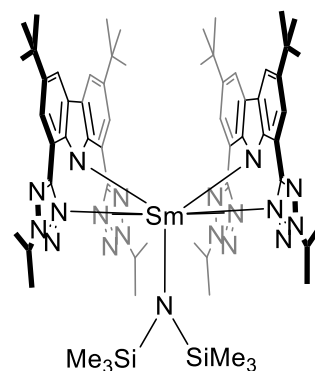
In the glovebox, HCzT^{iPr} (**8b**) (0.200 g, 0.400 mmol) was dissolved in toluene and added to a solution of $\text{Y}[\text{N}(\text{SiMe}_3)_2]_3$ (0.114 g, 0.200 mmol) dissolved in toluene in a Kontes flask to give a yellow solution. The solution was stirred in a sealed Kontes flask at 110 °C for 48 hours, cooled and the solvent removed under reduced pressure. The crude product was washed with hexanes to yield a yellow powder.



Recrystallization of this product from warm toluene yielded yellow crystals. Yield: 0.291 g (91.8 %). MP. 292 °C (dec). ^1H NMR (300 MHz, C_6D_6 , 298 K): δ 8.64 (m, 1H, aryl-*H*), 8.55 (m, 2H, aryl-*H*), 8.41 (m, 1H, aryl-*H*), 8.05 (m, 2H, aryl-*H*), 7.91 (m, 2H, aryl-*H*), 7.81 (m, 2H, aryl-*H*), 7.75 (m, 1H, aryl-*H*), 7.61 (m, 1H, aryl-*H*), 4.17 (br m, 1H, $\text{CH}(\text{CH}_3)_2$), 4.04 (br m, 3H, $\text{CH}(\text{CH}_3)_2$), 3.84 (br m, 1H, $\text{CH}(\text{CH}_3)_2$), 3.13 (br m, 1H, $\text{CH}(\text{CH}_3)_2$), 1.42-1.62 (br overlapping s, 54H, $\text{C}(\text{CH}_3)_3$), 1.15 (br m, 6H, $\text{CH}(\text{CH}_3)_2$), 1.06 (br m, 6H, $\text{CH}(\text{CH}_3)_2$), 0.91-0.97 (br m, 6H, $\text{CH}(\text{CH}_3)_2$), 0.86 (br m, 12H, $\text{CH}(\text{CH}_3)_2$), 0.60 (br m, 6H, $\text{CH}(\text{CH}_3)_2$). Anal. Calcd. for $\text{C}_{84}\text{H}_{108}\text{N}_{27}\text{Y}$: C 63.66, H 6.87, N 23.86; found: C 62.80, H 6.26, N 22.55.

$(\text{CzT}^{\text{iPr}})_2\text{Sm}[\text{N}(\text{SiMe}_3)_2]$ (**20**)

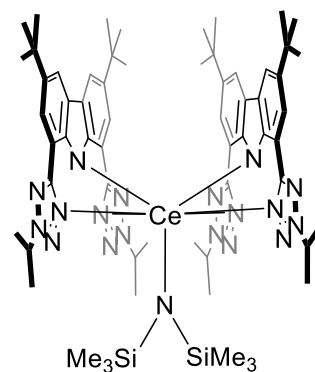
20 was prepared from HCzT^{iPr} (**8b**) (0.200 g, 0.400 mmol) and $\text{Sm}[\text{N}(\text{SiMe}_3)_2]_3$ (0.126 g, 0.200 mmol) using a procedure analogous to that for **19** except that the reaction mixture was stirred for 24 h at room temperature. **20** was isolated as a yellow



powder and was recrystallized from warm toluene to yield yellow crystals. Yield: 0.237 g (91.0 %). MP. 312 °C (dec). ^1H NMR (360 MHz, C_6D_6 , 343 K): δ 9.05 (s, 4H, $\nu_{1/2}$ = 40 Hz, Ar-*H*), δ 8.49 (s, 4H, $\nu_{1/2}$ = 50 Hz, Ar-*H*), 4.70 (s, 2H, $\nu_{1/2}$ = 90 Hz, $\text{CH}(\text{CH}_3)_2$), 2.02 (s, 36H, $\nu_{1/2}$ = 25 Hz, $\text{C}(\text{CH}_3)_3$), 1.31 (s, 24H, $\nu_{1/2}$ = 55 Hz, $\text{CH}(\text{CH}_3)_2$), -0.81 (s, 18H, $\nu_{1/2}$ = 35 Hz, $\text{Si}(\text{CH}_3)_3$), -2.38 (s, 2H, $\nu_{1/2}$ = 120 Hz, $\text{CH}(\text{CH}_3)_2$). Anal. Calcd. for $\text{C}_{62}\text{H}_{90}\text{SmN}_{19}\text{Si}_2$: C 57.32, H 6.87, N 20.16; found: C 58.10, H 7.41, N 19.05. Anal calcd. for the 0.5 toluene 0.25 hexane solvate, C 58.86, H 7.08, N 19.18.

(CzTⁱPr)₂Ce[N(SiMe₃)₂] (21)

21 was prepared from HCzTⁱPr (**8b**) (0.500 g, 1.00 mmol) and $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3$ (0.310 g, 0.500 mmol) using a procedure analogous to that for **19** except that the reaction mixture was stirred for 24 h at room temperature. **21** was isolated as a yellow powder and was recrystallized from warm toluene to yield



yellow crystals. Yield: 0.632 g (97.6 %). MP. 290 °C (dec). ^1H NMR (360 MHz, Toluene- D_8 , 353 K): δ 13.34 (s, 4H, $\nu_{1/2}$ = 65 Hz, Ar-*H*), 8.88 (s, 4H, $\nu_{1/2}$ = 136 Hz, Ar-*H*), 3.12 (s, 40H, $\nu_{1/2}$ = 45 Hz, $\text{C}(\text{CH}_3)_3$ and $\text{CH}(\text{CH}_3)_2$), 0.06 (s, 18H, $\nu_{1/2}$ = 36 Hz, $\text{Si}(\text{CH}_3)_3$), -0.22 (s, 24H, $\nu_{1/2}$ = 60 Hz, $\text{CH}(\text{CH}_3)_2$). Anal. Calcd. for $\text{C}_{62}\text{H}_{90}\text{CeN}_{19}\text{Si}_2$: C 57.38, H 6.99, N 20.51; found: C 61.10, H 7.73, N 18.40. Anal calcd. for the 1.75 toluene solvate, C 61.12, H 7.18, N 18.24.

General Procedure for Styrene Polymerization

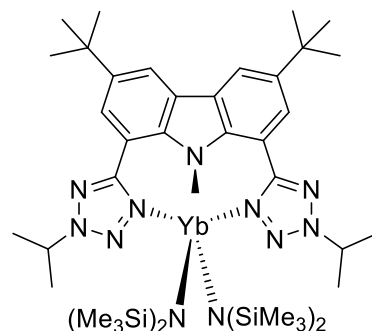
In the glovebox, a 15 mL Schlenk flask was charged with a stir bar and equimolar amounts of the catalyst and $[\text{Ph}_3\text{C}]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$ dissolved in a few mL of toluene. The Schlenk was transferred to the vacuum line and the solution was stirred at room temperature under an atmosphere of N_2 . The desired amount of 0.1 M styrene solution was added to the Schlenk by syringe and stirring continued. Finally, 10 molar equivalents of Al^iBu_3 solution was added to the Schlenk by syringe and the solution was stirred at room temperature under N_2 for 1 h. The reaction mixture was quenched with acidic MeOH. In all cases a negligible amount of white solid precipitated from solution and any polystyrene produced was collected as a white solid by filtration.

General Procedure for ROP of ϵ -Caprolactone

In the glovebox a 15 mL Schlenk flask was charged with a stir bar and the desired amount of catalyst dissolved in toluene. The Schlenk was transferred to the vacuum line and the solution was stirred at room temperature under an atmosphere of N_2 . The desired amount of dried ϵ -caprolactone was added to the Schlenk by syringe and the reaction mixture was stirred for 10 minutes after which the reaction is quenched with acidic MeOH to precipitate the polymer. The white solid was collected by filtration and dried under vacuum until a constant mass was reached.

(MeCzTⁱPr)Yb[N(SiMe₃)₂]₂ (22)

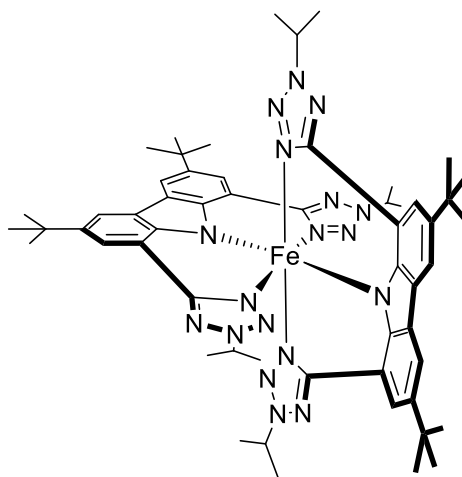
This reaction was only conducted on NMR-scale and the product was never isolated. MeCzTⁱPr (**8e**) (0.015 g, 0.029 mmol) and Yb[N(SiMe₃)₂]₂(THF)₂ (0.019 g, 0.030 mmol) were dissolved in C₆D₆ and the solutions were mixed by



Pasteur pipette resulting in a red-purple solution. ¹H NMR (300 MHz, C₆D₆, 298 K): δ 8.37 (br s, 2H, 4,5-Ar-*H*), 8.32 (br s, 2H, 2,7-Ar-*H*), 4.55 (br s, 2H, CH(CH₃)₂), 3.00 (br s, 3H, CH₃), 1.36 (br s, 18H, C(CH₃)₃), 1.26 (br s, 12H, (CH(CH₃)₂), 0.33 (s, 36H, Si(CH₃)₃).

(CzTⁱPr)₂Fe (23)

23 was prepared from HCzTⁱPr (**8b**) (0.200 g, 0.400 mmol) and FeBr₂ (0.043 g, 0.20 mmol) using a procedure analogous to that for **9**. The crude product was isolated as a dark red powder and recrystallization from warm toluene yielded dark red crystals. Yield: 0.208 g (99.0 %). MP. 238-240 °C. ¹H NMR (300 MHz, C₆D₆, 298 K): δ 28.98 (s,

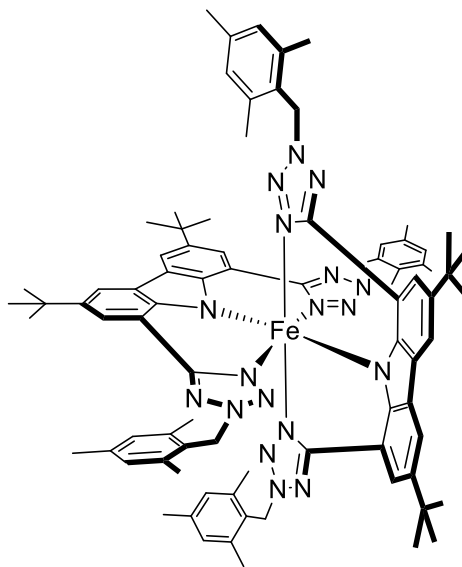


4H, $\nu_{1/2}$ = 82 Hz, Ar-*H*), 13.66 (s, 4H, $\nu_{1/2}$ = 114 Hz, Ar-*H*), 4.42 (s, 4H, $\nu_{1/2}$ = 152 Hz, CH(CH₃)₂), 1.89 (s, 36H, $\nu_{1/2}$ = 18 Hz, C(CH₃)₃), 1.63 (s, 24H, $\nu_{1/2}$ = 38 Hz, CH(CH₃)₂). μ_{eff} (C₆D₆, 298 K) = 4.06 μ_{B} as determined by the Evans' method. Anal. Calcd. for C₅₆H₇₂FeN₁₈: C 63.87, H 6.89, N 23.94; found: C 61.00, H 6.80, N 22.08. Anal calcd. for

the 0.25 toluene, 3 H₂O solvate, C 61.37, H 7.13, N 22.31. EA sample was stored outside of the glovebox for an extended period of time.

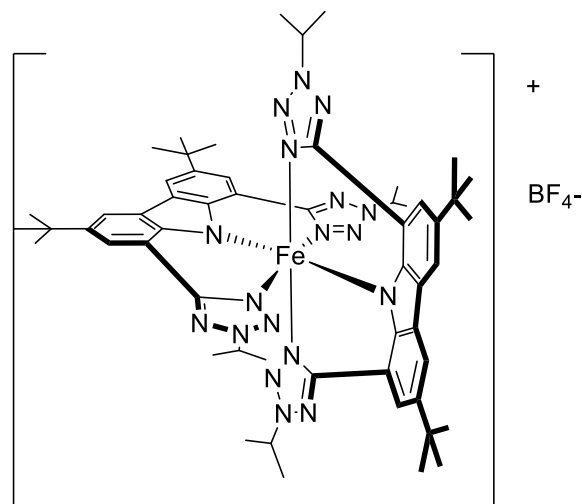
(CzT^{CH₂Mes})₂Fe (24)

24 was prepared from HCzT^{CH₂Mes} (**8d**) (0.300 g, 0.441 mmol) and FeBr₂ (0.048 g, 0.22 mmol) using a procedure analogous to that for **9**. Yield: 0.280 g (89.0 %). MP. 162-165 °C. ¹H NMR (300 MHz, Toluene-D₈, 298 K): δ 12.50 (s, 4H, *v*_{1/2} = 45 Hz, Cbz Ar-*H*), 9.41 (s, 4H, *v*_{1/2} = 29 Hz, Cbz Ar-*H*), 6.32 (s, 8H, *v*_{1/2} = 5 Hz, Mes Ar *H*), 4.20 (s, 8H, *v*_{1/2} = 28 Hz, CH₂), 1.97 (s, 12H, *v*_{1/2} = 4 Hz, Mes *p*-CH₃), 1.74 (s, 36H, *v*_{1/2} = 5 Hz, C(CH₃)₃), 1.63 (s, 24H, *v*_{1/2} = 15 Hz, Mes *o*-CH₃). *μ*_{eff} (C₆D₆, 298 K) = 1.86 *μ*_B as determined by the Evans' method. Anal. Calcd. for C₈₄H₉₆FeN₁₈: C 71.37, H 6.84, N 17.84; found: C 71.29, H 6.56, N 17.72.



$[(\text{CzT}^{\text{iPr}})_2\text{Fe}]^+\text{BF}_4^-$ (25)

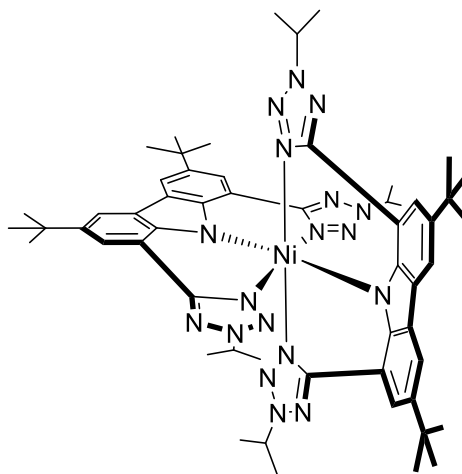
$(\text{CzT}^{\text{iPr}})_2\text{Fe}$ (**23**) was synthesised *in situ* from HCzT^{iPr} (**8b**) (0.200 g, 0.400 mmol) and FeBr_2 (0.043 g, 0.20 mmol) using a procedure analogous to that for **9**. Once the solution was filtered through Celite to remove the salt precipitate, $\text{NO}^+ \text{BF}_4^-$ (0.023 g, 0.20 mmol) was added to the



reaction mixture resulting in an immediate colour change to dark brown. The solution was allowed to stir overnight at room temperature after which the solvent was removed under reduced pressure and the crude product washed repeatedly with hexanes to yield a brown powder. Recrystallization from a warm toluene-hexanes mixture yielded dark brown crystals. Yield: 0.213 g (93.7 %). MP. 241 °C (dec). Two sets of resonances are seen in the NMR spectra; each have been assigned to a different complex labelled A or B. The amount of complex A and B are not consistent between NMR spectra runs so the following assignments are tentative: ^1H NMR (300 MHz, THF-D_8 , 298 K) **Complex A**: δ 26.20 (s, 4H, $\nu_{1/2}$ = 228 Hz, Ar-H), 21.55 (s, 4H, $\nu_{1/2}$ = 154 Hz, Ar-H), 6.06 (s, 4H, $\nu_{1/2}$ = 108 Hz, $\text{CH}(\text{CH}_3)_2$), 4.04 (s, 36H, $\nu_{1/2}$ = 71 Hz, $\text{C}(\text{CH}_3)_3$). 24H resonance for $\text{CH}(\text{CH}_3)_2$ not observable for complex A; **Complex B**: δ 11.67 (s, 4H, $\nu_{1/2}$ = 44 Hz, Ar-H), 11.04 (s, 4H, $\nu_{1/2}$ = 156 Hz, Ar-H), 8.40 (s, 24H, $\nu_{1/2}$ = 50 Hz, $\text{CH}(\text{CH}_3)_2$), 5.28 (s, 4H, $\nu_{1/2}$ = 48 Hz, $\text{CH}(\text{CH}_3)_2$), 1.54 (s, 36H, $\nu_{1/2}$ = 48 Hz, $\text{C}(\text{CH}_3)_3$).

(CzTⁱPr)₂Ni (26)

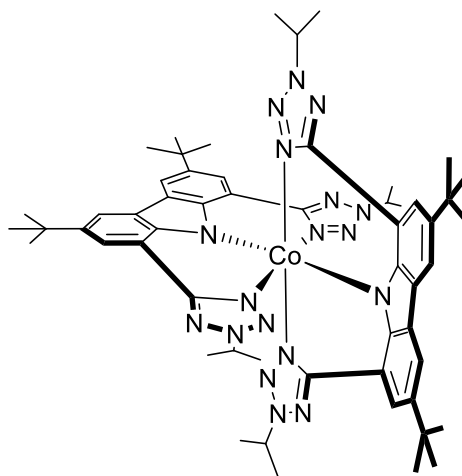
26 was prepared from HCzTⁱPr (**8b**) (0.200 g, 0.400 mmol) and NiCl₂ (0.026 g, 0.20 mmol) using a procedure analogous to that for **9**. The crude product was isolated as a yellow powder and recrystallization from warm toluene yielded yellow crystals. Yield: 0.178 g (84.0 %). MP. 266-268 °C.



¹H NMR (300 MHz, DMSO-D₆, 298 K): δ 28.55 (s, 4H, *v*_{1/2} = 195 Hz, Ar-*H*), 8.26 (s, 4H, *v*_{1/2} = 186 Hz, Ar-*H*), 6.63 (s, 4H, *v*_{1/2} = 163 Hz, CH(CH₃)₂), 1.74 (s, 36H, *v*_{1/2} = 26 Hz, C(CH₃)₃). 24H resonance for CH(CH₃)₂ not observable.

(CzTⁱPr)₂Co (27)

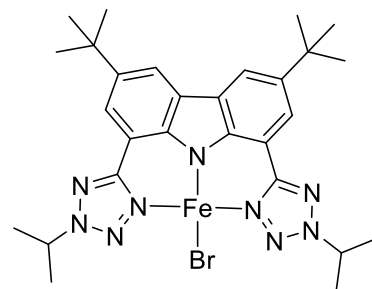
27 was prepared from HCzTⁱPr (**8b**) (0.200 g, 0.400 mmol) and CoBr₂ (0.044 g, 0.20 mmol) using a procedure analogous to that for **9**. The crude product was isolated as an orange powder and recrystallization from warm toluene yielded orange crystals. Yield: 0.195 g (91.8 %). MP. 294-296 °C.



¹H NMR (300 MHz, C₆D₆, 298 K): δ 61.73 (s, 4H, *v*_{1/2} = 25 Hz, Ar-*H*), 16.28 (s, 4H, *v*_{1/2} = 28 Hz, Ar-*H*), 8.88 (s, 36H, *v*_{1/2} = 13 Hz, C(CH₃)₃), -5.85 (s, 4H, *v*_{1/2} = 36 Hz, CH(CH₃)₂), -7.12 (s, 24H, *v*_{1/2} = 20 Hz, CH(CH₃)₂). *μ*_{eff} (C₆D₆, 298 K) = 3.66 *μ*_B as determined by the Evans' method. Anal. Calcd. for C₅₆H₇₂CoN₁₈: C 63.68, H 6.87, N 23.87; found: C 63.43, H 7.04, N 23.51.

(CzTⁱPr)FeBr (28)

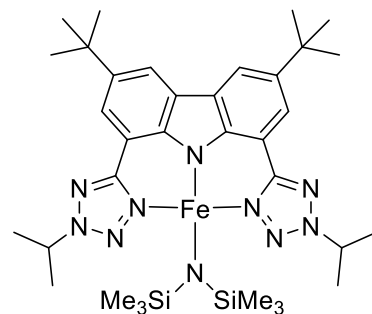
In the glovebox, HCzTⁱPr (**8b**) (0.500 g, 1.00 mmol) was dissolved in THF with stirring. Benzyl potassium (0.130 g, 1.00 mmol) dissolved in THF, was added dropwise to the ligand solution producing a fluorescent yellow solution and



a white salt precipitate. In a separate Erlenmeyer flask, anhydrous FeBr₂ (0.216 g, 1.00 mmol) was dissolved in THF with stirring to give an orange solution. The deprotonated ligand solution was added dropwise to the FeBr₂ solution resulting in an immediate colour change from fluorescent yellow to orange with a white salt precipitate. The solution was allowed to stir overnight, filtered through Celite to remove the salt precipitate and the solvent removed from the filtrate under reduced pressure to leave crude product as a red-orange oily residue. Addition of toluene to this residue induced immediate precipitation of an orange powder that was isolated on a frit by vacuum filtration. Yield: 0.622 g (98.0 %). MP. 322-324 °C. ¹H NMR (300 MHz, THF-D₈, 298 K): δ 30.44 (s, 2H, *v*_{1/2} = 23 Hz, Ar-*H*), 19.58 (s, 2H, *v*_{1/2} = 66 Hz, Ar-*H*), 18.31 (s, 2H, *v*_{1/2} = 191 Hz, CH(CH₃)₂), 9.32 (s, 12H, *v*_{1/2} = 48 Hz, CH(CH₃)₂), 2.51 (s, 18H, *v*_{1/2} = 13 Hz, C(CH₃)₃). *μ*_{eff} (THF-D₈, 298 K) = 6.02 *μ*_B as determined by the Evans' method. Anal. Calcd. for C₂₈H₃₆BrFeN₉: C 53.01, H 5.72, N 19.87; found: C 52.80, H 5.55, N 20.21.

(CzT^{iPr})Fe[N(SiMe₃)₂] (29)

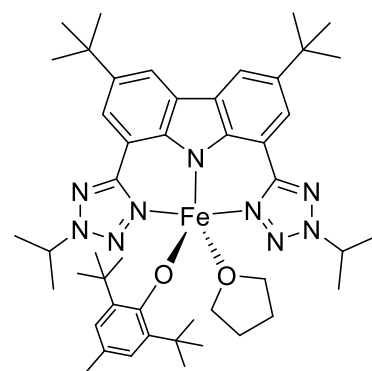
In the glovebox, (CzT^{iPr})FeBr (**28**) (0.100 g, 0.158 mmol) was dissolved in THF with stirring and Na⁺[N(SiMe₃)₂]⁻ (0.029 g, 0.16 mmol) added as a solid to the solution. The solution turned orange-yellow and a white salt precipitate formed. The solution was allowed to stir overnight, filtered



through Celite to remove the salt precipitate and the solvent removed from the filtrate under reduced pressure to give crude product as an orange solid. This product was a mixture of (CzT^{iPr})Fe[N(SiMe₃)₂] and (CzT^{iPr})₂Fe by NMR; attempts at separating the products by crystallization were unsuccessful. ¹H NMR (300 MHz, C₆D₆, 298 K): δ 55.94 (s, 2H, *v*_{1/2} = 71 Hz, Ar-*H*), 22.45 (s, 18H, *v*_{1/2} = 511 Hz, Si(CH₃)₃), 8.34 (s, 2H, *v*_{1/2} = 78 Hz, Ar-*H*), 6.23 (s, 18H, *v*_{1/2} = 15 Hz, C(CH₃)₃), -3.92 (s, 2H, *v*_{1/2} = 37 Hz, CH(CH₃)₂), -14.44 (s, 12H, *v*_{1/2} = 29 Hz, CH(CH₃)₂).

(CzT^{iPr})Fe(OAr)(THF) (30)

In the glovebox, (CzT^{iPr})FeBr (**28**) (0.200 g, 0.315 mmol) was dissolved in THF and stirred. K⁺[2,6-di-*tert*-butyl-4-methylphenoxide]⁻ (0.081 g, 0.31 mmol) was added to the solution. The solution turned orange-yellow and a white salt precipitate formed. The solution was allowed to stir

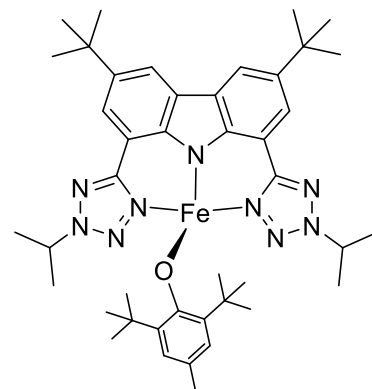


overnight, filtered through Celite to remove the salt precipitate and the solvent removed from the filtrate under reduced pressure to afford the crude product as an orange-yellow solid. Recrystallization of the crude product from warm toluene yielded yellow crystals.

Yield: 0.215 g (80.6 %). MP. 190 °C (dec). ^1H NMR (300 MHz, C_6D_6 , 298 K): δ 65.25 (s, 2H, $\nu_{1/2}$ = 176 Hz, OAr Ar-*H*), 60.62 (s, 3H, $\nu_{1/2}$ = 68 Hz, OAr CH_3), 41.71 (s, 2H, $\nu_{1/2}$ = 112 Hz, Ar-*H*), 11.69 (s, 2H, $\nu_{1/2}$ = 97 Hz, Ar-*H*), 5.05 (s, 2H, $\nu_{1/2}$ = 62 Hz, $\text{CH}(\text{CH}_3)_2$), 3.87 (s, 18H, $\nu_{1/2}$ = 20 Hz, $\text{C}(\text{CH}_3)_3$), -3.49 (s, 18H, $\nu_{1/2}$ = 45 Hz, OAr $\text{C}(\text{CH}_3)_3$), -4.33 (s, 12H, $\nu_{1/2}$ = 890 Hz, $\text{CH}(\text{CH}_3)_2$). μ_{eff} (C_6D_6 , 298 K) = 5.26 μ_{B} as determined by the Evans' method. Anal. Calcd. for $\text{C}_{47}\text{H}_{67}\text{FeN}_9\text{O}_2$: C 66.73, H 7.98, N 14.90; found: C 66.64, H 8.15, N 15.22.

(CzTⁱPr)Fe(OAr) (31)

In a glovebox a Kontes flask was charged with a stir bar and (CzTⁱPr)Fe(OAr)(THF) (**30**) (0.242 g, 0.286 mmol) dissolved in toluene. The sealed flask was transferred to a vacuum line in a fumehood, the reaction vessel immersed in liquid N_2 , the head space evacuated under full vacuum, and then backfilled with N_2O or CO gas. The solution was allowed to thaw and as it melted the colour changed from yellow to deep green. The solution was stirred at room temperature under a constant flow of gas for 3 hours after which the solvent was removed under reduced pressure and the Kontes flask transferred back into the glovebox under vacuum. Once in the glovebox, the dark green residue was dissolved in toluene, transferred to an Erlenmeyer flask and the solvent again removed under reduced pressure. The dark green residue is washed with hexanes to yield a dark green solid as the crude product. Recrystallization from room temperature hexanes gave dark green crystals. Yield: 0.142 g (64.1 %). ^1H NMR (300 MHz, C_6D_6 , 298 K): δ 77.45 (s, 2H, $\nu_{1/2}$ = 201 Hz, OAr Ar-*H*),

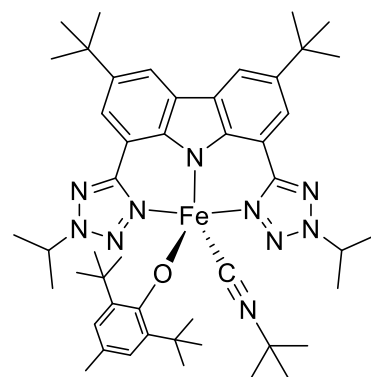


69.91 (s, 3H, $\nu_{1/2}$ = 126 Hz, OAr CH_3), 51.15 (s, 2H, $\nu_{1/2}$ = 149 Hz, Ar-*H*), 9.78 (s, 2H, $\nu_{1/2}$ = 101 Hz, Ar-*H*), 5.38 (s, 18H, $\nu_{1/2}$ = 41 Hz, $\text{C}(\text{CH}_3)_3$), 4.88 (s, 2H, $\nu_{1/2}$ = 131 Hz, $\text{CH}(\text{CH}_3)_2$), -8.70 (s, 12H, $\nu_{1/2}$ = 872 Hz, $\text{CH}(\text{CH}_3)_2$), -10.00 (s, 18H, $\nu_{1/2}$ = 79 Hz, OAr $\text{C}(\text{CH}_3)_3$). μ_{eff} (C_6D_6 , 298 K) = 5.16 μ_{B} as determined by the Evans' method. Elemental analysis was not obtained as the product is thermally sensitive and decomposes at room temperature over an extended period of time.

Occasionally, a hexanes-insoluble product was also obtained in inconsistent amounts. This product can be recrystallized from warm toluene to give yellow crystals. The identity of this compound is unknown at this time. ^1H NMR (300 MHz, C_6D_6 , 298 K): δ 56.13 (s, 3H, $\nu_{1/2}$ = 53 Hz, Unknown CH_3 (?)), 53.50 (s, 2H, $\nu_{1/2}$ = 97 Hz, Ar-*H*), 25.32 (s, 2H, $\nu_{1/2}$ = 20 Hz, Ar-*H*), 12.18 (s, 2H, $\nu_{1/2}$ = 31 Hz, $\text{CH}(\text{CH}_3)_2$), 2.73 (s, 18H, $\nu_{1/2}$ = 17 Hz, $\text{C}(\text{CH}_3)_3$), -0.63 (s, 12H, $\nu_{1/2}$ = 176 Hz, $\text{CH}(\text{CH}_3)_2$).

(CzTⁱPr)Fe(OAr)(tBuNC) (32)

In the glovebox, (CzTⁱPr)Fe(OAr)(THF) (**30**) (0.200 g, 0.236 mmol) was dissolved in toluene with stirring. tBuNC (2.36 mL of 0.1 M solution, 0.236 mol) was added to the solution by syringe, the solution turned dark yellow-orange and yellow-green powder precipitated from solution. The



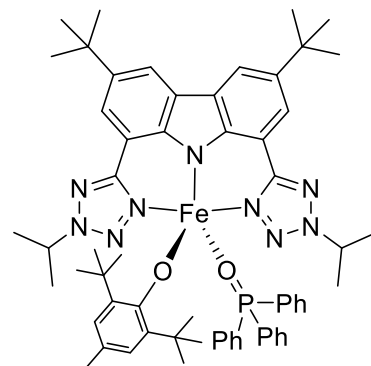
solution was allowed to stir overnight at room temperature, the precipitate was isolated by vacuum filtration on a frit and washed with hexanes to obtain a lime green powder. Recrystallization from warm toluene-THF yielded lime green crystals. Yield: 0.109 g (53.8 %). MP. 242-244 °C. The product was not fully soluble in room temperature THF, and the

^1H NMR spectrum in THF-D_8 matches that of $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})(\text{THF})$ in the same solvent.

Anal. Calcd. for $\text{C}_{48}\text{H}_{68}\text{FeN}_{10}\text{O}$: C 67.27, H 8.00, N 16.35; found: C 67.45, H 7.76, N 15.97.

$(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})(\text{TPPO})$ (33)

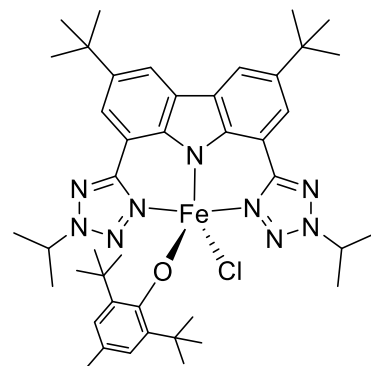
In the glovebox, $(\text{CzT}^{\text{iPr}})\text{Fe}(\text{OAr})(\text{THF})$ (**30**) (0.200 g, 0.236 mmol) was dissolved in toluene with stirring. TPPO (0.066 g, 0.24 mmol) was added to the solution and the solution turned orange. The solution was allowed to stir overnight at room temperature, the solvent removed under



reduced pressure and the orange residue washed with hexanes to afford an orange powder as the crude product. Recrystallization from warm toluene yielded an orange crystalline solid. Yield: 0.214 g (86.0 %). MP. 284-287 °C. ^1H NMR (300 MHz, C_6D_6 , 298 K): δ 52.76 (s, 2H, $\nu_{1/2}$ = 159 Hz, OAr Ar-*H*), 50.96 (s, 3H, $\nu_{1/2}$ = 85 Hz, OAr CH_3), 29.14 (s, 2H, $\nu_{1/2}$ = 119 Hz, Ar-*H*), 11.41 (s, 2H, $\nu_{1/2}$ = 108 Hz, Ar-*H*), 8.10 (s, 10H, $\nu_{1/2}$ = 75 Hz, TPPO Ar-*H*), 6.83 (s, 2H, $\nu_{1/2}$ = 49 Hz, $\text{CH}(\text{CH}_3)_2$), 2.50 (s, 18H, $\nu_{1/2}$ = 82 Hz, OAr $\text{C}(\text{CH}_3)_3$), 1.97 (s, 18H, $\nu_{1/2}$ = 31 Hz, $\text{C}(\text{CH}_3)_3$). Extremely broad resonances hidden in the baseline around 8.78 ppm and -0.60 ppm may be due to missing TPPO Ar-*H* and $\text{CH}(\text{CH}_3)_2$ protons respectively. Anal. Calcd. for $\text{C}_{61}\text{H}_{74}\text{FeN}_9\text{O}_2\text{P}$: C 69.63, H 7.09, N 11.98; found: C 69.44, H 6.89, N 11.66.

(CzTⁱPr)Fe(OAr)Cl (34)

In the glovebox, (CzTⁱPr)Fe(OAr)(THF) (**30**) (0.205 g, 0.242 mmol) was dissolved in toluene with stirring. Solid C₂Cl₆ (0.029 g, 0.12 mmol) was added to the solution resulting in an immediate colour change to deep blue. The solution was allowed to stir overnight at room temperature,



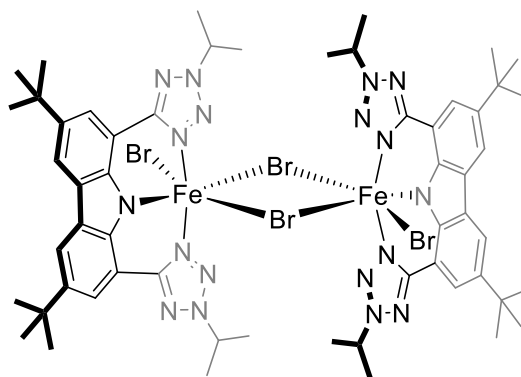
the solvent removed under reduced pressure and the dark blue residue washed with hexanes to afford a dark blue powder as the crude product. Recrystallization from room temperature hexanes yielded dark blue crystals. Yield: 0.180 g (91.8 %). Due to the extreme broadening of the resonances as well as their excessive overlap, integrations are not definitive. ¹H NMR (300 MHz, C₆D₆, 298 K): δ 80.9 (s, 1H, *v*_{1/2} = 587 Hz, OAr Ar-*H*), 66.5 (s, 3H, *v*_{1/2} = 1048 Hz, OAr CH₃), 33.6 (s, 2H, *v*_{1/2} = 1056 Hz, Ar-*H*), 29.9 (s, 2H, *v*_{1/2} = 1102 Hz, Ar-*H*), 22.4 (s, 2H, *v*_{1/2} = 1093 Hz, CH(CH₃)₂), 4.68 (s, *v*_{1/2} = 117 Hz, C(CH₃)₃), 3.52 (s, *v*_{1/2} = 179 Hz, CH(CH₃)₂) both of these integrate to a combined total of 35H, 1.37 (s, 32H, *v*_{1/2} = 88 Hz, OAr C(CH₃)₃). An additional resonance at 158 ppm is extremely broad and blends into the baseline while there is also a resonance at 5.63 ppm that overlaps with surrounding resonances. *μ*_{eff} (C₆D₆, 298 K) = 5.58 *μ*_B as determined by the Evans' method. Elemental analysis was not obtained as the product is thermally sensitive and decomposes at room temperature over an extended period of time.

General Procedure for Hydrosilylation

All hydrosilylation reactions were conducted on NMR scale in J. Young NMR tubes. The desired amount of catalyst was dissolved in C₆D₆ in a small vial. Equimolar amounts of 1.0 M phenylsilane solution and 1.0 M styrene solution were added to the vial and the solution was mixed by pasture pipette and transferred into an NMR tube which was then sealed. The reaction was monitored by NMR spectroscopy at room temperature and the resulting anti-Markovnikov and Markovnikov hydrosilylation products were characterized by the 2H triplet at 1.14 ppm and the 3H doublet at 1.37 ppm, respectively, in C₆D₆.

(CzTiⁱPr)FeBr₂ (36)

In the glovebox, HCzTiⁱPr (**8b**) (0.500 g, 1.00 mmol) was dissolved in THF with stirring. Benzyl potassium (0.130 g, 1.00 mmol) was dissolved in THF and added dropwise to the ligand solution to produce a fluorescent yellow



solution. FeBr₃ (0.296 g, 1.00 mmol) was dissolved in THF with stirring to give a deep red-black solution. The deprotonated ligand solution was added dropwise to the FeBr₃ solution resulting in immediate discharge of the fluorescent yellow colour with formation of a dark red solution and a white salt precipitate. The solution was allowed to stir overnight at room temperature, filtered through Celite to remove the salt precipitate and the solvent was removed from the filtrate under reduced pressure to afford a dark red-black solid as the crude product. Recrystallization from warm toluene-hexanes mixture yielded dark red crystals out of a dark green-blue solution. Yield: 0.693 g (97.0 %). MP. 280-283 °C. ¹H

NMR (300 MHz, Toluene- D_8 , 298 K) **Dimer**: δ 27.81 (s, 2H, $\nu_{1/2}$ = 604 Hz, Ar-*H*), 21.85 (s, 2H, $\nu_{1/2}$ = 338 Hz, Ar-*H*), 4.61 (s, 20H, $\nu_{1/2}$ = 213 Hz, $CH(CH_3)_2$ and $C(CH_3)_3$), 1.44 (s, 12H, $\nu_{1/2}$ = 384 Hz, $CH(CH_3)_2$). μ_{eff} (C_6D_6 , 298 K) = 5.94 μ_B as determined by the Evans' method.

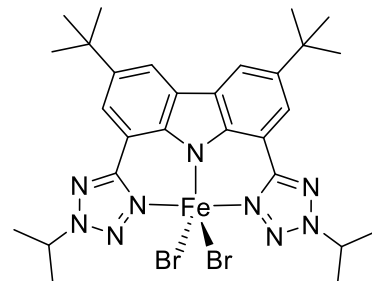
The monomer was also characterized in solution as a blue-green complex with slightly different NMR resonances. ^1H

NMR (300 MHz, Toluene- D_8 , 298 K) **Monomer**: δ 82.90

(s, 2H, $\nu_{1/2}$ = 108 Hz, Ar-*H*), 37.23 (s, 2H, $\nu_{1/2}$ = 176 Hz,

Ar-*H*), 34.99 (s, 2H, $\nu_{1/2}$ = 186 Hz, $CH(CH_3)_2$), 8.12 (s, 12H, $\nu_{1/2}$ = 107 Hz, $CH(CH_3)_2$),

5.58 (s, 18H, $\nu_{1/2}$ = 36 Hz, $C(CH_3)_3$).



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Appendix A. CSD Code Lists

Table A-1 Five-Coordinate Yb(III) Yb-N(SiMe₃)₂ Bond Lengths

BADTIL	GULMEH	KIGQAV	QEGJIY
BAYRID	HESQIF	KIGQUP	WEKSUC
BAYRID01	IYEDUM	KIGRAW	XEZLEW
DECXOA	IYEFOI	LUSNEU	XEZLOG
DIGQUH	JIZVOE	LUSNOE	XEZMAT
DIRSON	KAJMOX	MIPREK	YUXWIZ
FAFXAM	KAJMOX01	NIVFII	ZALFAT
FAFXOA	KAJMOX02	PIFKOG	ZEDJIE

Table A-2 Five-Coordinate Er(III) Er-N(SiMe₃)₂ Bond Lengths

CESQEX	LUSNAQ
EREYEH	MUGYAO
IBUFER	ROHLIL
IBUFUH	WEKTOX
IGITUO	YUXLOU
LUSMOD	ZEDJEA

Table A-3 Seven-Coordinate Ln-N(SiMe₃)₂ Bond Lengths

ASABIG	GUBWEG	IYEDIA	RIVFUA
ENAFII	GUBWIK	QEPKEB	TANVAG
ENAF00	IYEDAS	RIVFEK	WEPYIB
ESIGOD	IYEDEW	RIVFIO	WEPYOH

Table A-4 Six-Coordinate Zn(II) Zn-N_{Tz} Bond Lengths

ACAJIY	SIDMOK
BOVNOQ	XIYKEW
BOVNOQ01	XUQMAX
LOSGOP	XUQMAX01
SIDLUP	YUDKIR

Table A-5 Five-Coordinate High Spin Fe(II) Fe-O_{THF} Bond Lengths

FEKQOE	IDABIY	MASPUT	PAYHIG
FEKSAS	JOGVAE	NAFKUC	SIXQUO
FEKSEW	KARRIH	NAFLAJ	VOPNEW
GEGCED	KASFOC	NAPWUW	XETSIA
GUCBEN	KASFUI	ONUJAJ	XUNFAP

Table A-6 Terminal Fe-OAr Bond Lengths and Angles (all coordination numbers, oxidation states and spin states)

AMAGUR	FESSIG	KUGWOZ	WUWMIM
AMAHAY	FESSOM	LINXEN	XIHVUH
AMAHEC	GOTQAJ	MOBKET	XIJJUX
AMAHIG	GOXDAY	NIMHAU	XIJKAE
AMAHOM	HEVKUP	OBADON	XIKMUB
AMAHUS	ILOCAP	ONUQAR	XIKNAI
AMAJAA	ILOZEP	PAGQAR	XIMNIQ
BOFBAZ	ILOZIT	PAGQEV	YUJQIE
BOFBED	ILOZOZ	PAGQIZ	YUJQUQ
DOGH0Y	ILOZUF	QIPCOJ	YUJRAX
EDIDIH	IXAQII	ROJPOY	YUJREB
EPIMEX	XAQOO	SAPSOR	
FEKREV	IXAQUU	SUCWES	
FEKRIZ	IXARAB	TIXLET	
FEKROF	IXAREF	TUJHEL	
FEKRUL	IXARIJ	TUJHIP	
FEKSAS	IXAROP	UCIVOT	
FEKSEW	IXASAC	UCIVUZ	
FESSAY	IXASEG	WEVRUN	
FESSEC	IXASIK	WUBXEY	

Appendix B. Crystallographic Data

Table B-1 Summary of Crystallographic Data for **7b**, **7c**, **8b** and **8c**

	7b•0.5 IPA^a	7c^b	8b•0.5 IPA^c	8c^c
Emp. Formula	C _{31.5} H ₄₃ N ₇ O _{0.5}	C ₃₈ H ₃₉ N ₇	C _{29.5} H ₄₁ N ₉ O _{0.5}	C ₃₆ H ₃₇ N ₉
Formula wgt.(g/mol)	527.73	593.76	529.71	595.74
Temp. (K)	296.15	296.15	296.15	296.15
Crystal System	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space Group	P2 ₁ /n	P2 ₁ /n	P2 ₁ /n	P-1
a (Å)	11.5280(6)	15.4053(7)	11.5895(14)	11.0597(6)
b (Å)	18.7439(10)	10.6162(4)	18.322(2)	12.4955(6)
c (Å)	14.0981(8)	20.8844(9)	14.4238(18)	12.4982(6)
α (°)	90	90	90	108.642(2)
β (°)	104.106(2)	106.951(2)	104.335(7)	99.016(2)
γ (°)	90	90	90	92.478(2)
Volume (Å³)	2954.5(3)	3267.2(2)	2967.5(6)	1608.31(14)
Z	4	4	4	2
Density (g/cm³)	1.186	1.207	1.186	1.230
Abs. coeff. μ (mm⁻¹)	0.073	0.570	0.075	0.076
F(000)	1140	1264	1140	632
Crystal Size (mm)	0.27 x 0.16 x 0.11	0.11 x 0.09 x 0.02	0.18 x 0.15 x 0.05	0.6 x 0.12 x 0.1
Colour and habit	Colourless rod	Colourless prism	Colourless prism	Brown rod
Theta range (°)	3.688° ≤ 2θ ≤ 56.832°	6.33° ≤ 2θ ≤ 133.544°	3.666° ≤ 2θ ≤ 55.612°	3.496° ≤ 2θ ≤ 56.136°
Refl. Collected	69107	21556	29581	45085
Independent refl.	7384	5770	7007	7757
GooF (F²)	1.028	1.047	1.038	1.050
Final R [I>2σ(I)]	0.0531	0.0552	0.0591	0.0498
Final wR2	0.1361	0.1412	0.1544	0.1312
R (all data)	0.0678	0.0789	0.0942	0.0612
wR2 (all data)	0.1449	0.1562	0.1768	0.1392
Max peak/hole (e/Å³)	0.398/-0.241	0.231/-0.372	0.480/-0.228	0.420/-0.222

^a Data collected on a Bruker Kappa X8-Apex II diffractometer using Mo Kα radiation (λ = 0.71073 Å) at the University of Notre Dame. ^b Data collected on a Bruker Kappa X8-Apex II using Cu Kα radiation (λ = 1.54178 Å) at the University of British Columbia. ^c Data collected on a Bruker Kappa X8-Apex II diffractometer using Mo Kα radiation (λ = 0.71073 Å) at the University of British Columbia.

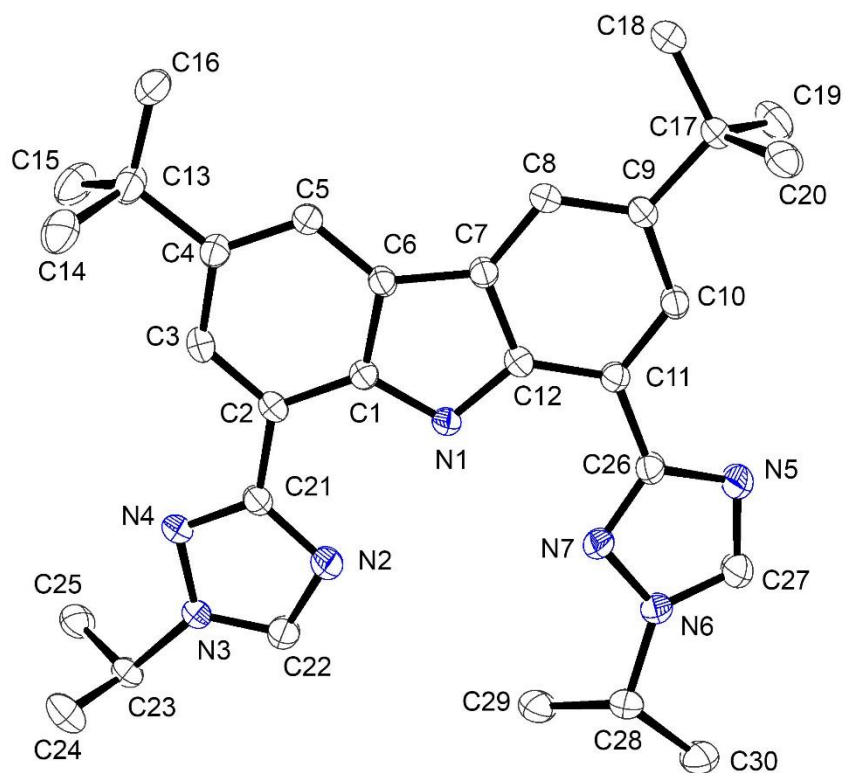


Figure B-1 Labelled ORTEP Drawing of **7b**

H atoms not shown

Disordered tBu carbons C14A, C15A and C16A not shown

Disordered iPrOH of solvation not shown: C31, C32, C33 and O1

Table B-2 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **7b**

Atom	x	y	z	U(eq)
O1	8840(2)	5650.6(13)	4149.1(18)	35.3(5)
N1	3910.6(10)	7242.2(6)	4608.4(8)	19.6(2)
N2	1509.5(12)	7042.5(7)	3689.2(11)	31.0(3)
N3	-300.4(11)	7431.9(7)	3039.0(9)	23.5(3)
N4	252.1(10)	7983.9(7)	3597.5(9)	21.6(3)
N5	6340.6(12)	5568.9(8)	4113.8(11)	34.6(3)
N6	4476.1(11)	5202.3(7)	3656.5(9)	24.4(3)
N7	4434.1(11)	5825.9(7)	4142.6(9)	23.2(3)
C1	3472.0(12)	7880.8(7)	4861.3(10)	18.7(3)
C2	2297.1(12)	8139.1(8)	4621.7(10)	19.9(3)
C3	2097.6(13)	8799.8(8)	5003.6(10)	22.4(3)
C4	3021.6(13)	9215.0(8)	5587.3(10)	22.1(3)
C5	4189.5(13)	8954.8(8)	5782.4(10)	21.5(3)
C6	4423.7(12)	8285.2(7)	5432.8(10)	19.5(3)
C7	5496.4(12)	7858.9(8)	5528.8(10)	19.8(3)
C8	6697.7(12)	7957.1(8)	6010.1(10)	21.2(3)
C9	7538.4(12)	7435.2(8)	5959.3(10)	20.5(3)
C10	7147.3(12)	6812.8(8)	5413.7(10)	21.6(3)
C11	5957.6(12)	6689.4(7)	4937.7(10)	19.9(3)
C12	5127.4(12)	7221.2(8)	5005.4(10)	19.7(3)
C13	2734.9(15)	9934.6(9)	5995.7(12)	29.0(3)
C14	1760(3)	9790.6(18)	6600(2)	38.4(8)
C14A	3253(4)	9924(2)	7142(3)	39.3(11)
C15	2115(3)	10415.0(16)	5125(2)	39.0(8)
C15A	1494(4)	10155(3)	5751(4)	51.9(15)
C16	3752(3)	10301.1(16)	6627(3)	37.2(8)
C16A	3529(4)	10535(2)	5632(4)	43.4(11)
C17	8867.3(12)	7506.3(8)	6482.4(11)	22.9(3)
C18	9134.1(14)	8219.6(9)	7013.4(12)	29.7(3)
C19	9633.8(14)	7450.2(10)	5737.1(13)	33.3(4)
C20	9212.3(14)	6906.0(9)	7248.9(12)	31.6(4)
C21	1340.3(12)	7725.7(8)	3975.9(10)	20.6(3)
C22	449.5(14)	6886.8(9)	3108.8(13)	31.6(4)
C23	-1564.8(13)	7468.6(8)	2496.3(11)	25.2(3)
C24	-2361.0(14)	7382.0(10)	3198.8(13)	34.7(4)
C25	-1795.1(14)	8153.2(9)	1909.1(12)	29.5(3)
C26	5573.3(13)	6027.0(8)	4394.4(10)	22.2(3)
C27	5609.3(14)	5061.5(9)	3658.0(13)	34.6(4)
C28	3377.0(13)	4783.9(8)	3275.2(11)	25.6(3)
C29	2408.1(15)	5252.3(9)	2663.0(13)	34.5(4)
C30	3656.8(15)	4148.7(9)	2706.1(13)	32.9(4)
C31	9089(8)	4456(3)	4823(6)	60(2)

C32	9532(3)	5221(2)	4914(3)	36.6(8)
C33	10821(5)	5278(4)	4859(6)	55.7(17)

Table B-3 Anisotropic Displacement Parameters (U_{ij} , Å² x10³) for **7b**

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
O1	25.2(11)	35.6(13)	45.1(14)	9.6(11)	8.6(10)	4.3(10)
N1	16.7(6)	20.0(6)	21.0(6)	-3.6(4)	2.3(4)	-0.7(4)
N2	20.7(6)	28.4(7)	39.9(8)	-7.7(6)	-0.4(5)	1.1(5)
N3	16.4(6)	22.3(6)	29.9(6)	-2.7(5)	1.9(5)	-0.6(5)
N4	16.9(6)	23.2(6)	23.7(6)	-1.3(5)	3.0(5)	-1.9(5)
N5	23.7(7)	31.4(7)	47.6(8)	-17.0(6)	6.9(6)	2.3(6)
N6	22.7(6)	22.2(6)	26.8(6)	-5.8(5)	3.1(5)	-0.2(5)
N7	23.0(6)	19.7(6)	25.4(6)	-3.9(5)	3.2(5)	0.8(5)
C1	18.0(6)	19.6(7)	18.5(6)	-0.2(5)	4.3(5)	0.2(5)
C2	16.0(6)	23.5(7)	19.4(6)	0.6(5)	3.0(5)	0.1(5)
C3	17.8(6)	25.5(7)	23.5(7)	1.7(6)	4.5(5)	4.2(5)
C4	23.1(7)	20.7(7)	22.2(7)	-0.1(5)	4.9(5)	2.9(6)
C5	19.3(7)	21.2(7)	22.7(7)	-2.1(5)	2.5(5)	0.5(5)
C6	16.0(6)	20.7(7)	21.3(6)	1.0(5)	3.4(5)	1.3(5)
C7	17.9(7)	20.7(7)	20.7(6)	-0.1(5)	4.7(5)	1.1(5)
C8	18.0(7)	21.4(7)	23.4(7)	-1.7(5)	3.5(5)	-2.2(5)
C9	16.1(6)	23.1(7)	21.9(6)	0.9(5)	3.5(5)	0.0(5)
C10	18.0(7)	23.6(7)	23.0(7)	-0.9(5)	4.8(5)	3.2(5)
C11	19.0(7)	20.4(7)	20.3(6)	-1.7(5)	4.8(5)	0.6(5)
C12	17.4(6)	22.4(7)	18.9(6)	0.2(5)	3.8(5)	0.4(5)
C13	32.3(8)	23.7(8)	29.6(8)	-3.0(6)	5.1(6)	7.6(6)
C14	42.4(18)	35.8(17)	41.7(18)	-12.2(14)	19.3(14)	2.3(14)
C14A	45(2)	38(2)	36(2)	-7.1(17)	12.4(18)	13.3(19)
C15	50(2)	24.2(15)	36.3(16)	0.2(12)	-1.3(14)	9.3(14)
C15A	35(2)	44(3)	70(3)	-21(2)	-2(2)	19(2)
C16	32.0(16)	26.9(15)	47.3(19)	-13.6(14)	-0.6(13)	4.6(12)
C16A	58(3)	23(2)	50(3)	-0.9(17)	15(2)	3.9(18)
C17	16.0(6)	24.5(7)	26.4(7)	-2.2(6)	1.6(5)	0.5(5)
C18	19.9(7)	29.0(8)	36.4(8)	-5.4(7)	-0.6(6)	-1.0(6)
C19	18.6(7)	47.9(10)	33.0(8)	-6.7(7)	5.5(6)	-0.4(7)
C20	24.3(8)	31.3(8)	33.8(8)	2.5(7)	-3.2(6)	-0.6(6)
C21	16.8(6)	22.3(7)	22.4(7)	1.3(5)	4.3(5)	-0.1(5)
C22	23.0(8)	26.6(8)	39.9(9)	-9.3(7)	-2.2(7)	2.0(6)
C23	16.5(7)	26.8(8)	29.3(7)	-2.7(6)	-0.5(6)	-1.2(6)
C24	19.5(7)	46.6(10)	36.3(9)	5.4(8)	3.6(6)	-1.6(7)
C25	22.9(7)	31.9(8)	30.2(8)	1.5(6)	-0.2(6)	-0.3(6)
C26	20.2(7)	22.5(7)	22.4(7)	-1.5(5)	2.2(5)	2.9(5)
C27	24.0(8)	31.8(9)	47.1(10)	-16.2(7)	6.7(7)	2.2(7)
C28	22.7(7)	23.9(7)	28.4(7)	-3.2(6)	2.8(6)	-3.4(6)

C29	26.2(8)	29.5(8)	41.8(9)	1.3(7)	-3.2(7)	-3.7(7)
C30	31.5(8)	29.7(8)	37.3(9)	-11.2(7)	8.0(7)	-5.2(7)
C31	60(3)	34(3)	86(6)	18(3)	19(4)	10(3)
C32	34.3(18)	37(2)	37.3(18)	5.2(15)	6.6(15)	7.6(16)
C33	27(2)	61(5)	75(5)	23(3)	5(3)	12(3)

Table B-4 Bond Lengths for **7b**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C32	1.424(4)	C7	C8	1.3979(19)
N1	C1	1.3797(18)	C7	C12	1.4146(19)
N1	C12	1.3783(18)	C8	C9	1.391(2)
N2	C21	1.371(2)	C9	C10	1.410(2)
N2	C22	1.327(2)	C9	C17	1.5355(19)
N3	N4	1.3607(17)	C10	C11	1.3914(19)
N3	C22	1.327(2)	C11	C12	1.4012(19)
N3	C23	1.4735(18)	C11	C26	1.4694(19)
N4	C21	1.3290(18)	C13	C14	1.590(4)
N5	C26	1.3589(19)	C13	C14A	1.580(4)
N5	C27	1.328(2)	C13	C15	1.550(3)
N6	N7	1.3617(17)	C13	C15A	1.447(4)
N6	C27	1.332(2)	C13	C16	1.460(3)
N6	C28	1.4757(19)	C13	C16A	1.610(5)
N7	C26	1.3288(19)	C17	C18	1.527(2)
C1	C2	1.4000(19)	C17	C19	1.532(2)
C1	C6	1.4130(19)	C17	C20	1.544(2)
C2	C3	1.392(2)	C23	C24	1.514(2)
C2	C21	1.4685(19)	C23	C25	1.515(2)
C3	C4	1.411(2)	C28	C29	1.514(2)
C4	C5	1.395(2)	C28	C30	1.514(2)
C4	C13	1.534(2)	C31	C32	1.518(6)
C5	C6	1.399(2)	C32	C33	1.511(7)
C6	C7	1.4506(19)			

Table B-5 Bond Angles for **7b**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C12	N1	C1	108.70(11)	N1	C12	C11	129.57(13)
C22	N2	C21	102.21(13)	C11	C12	C7	120.87(13)
N4	N3	C23	121.96(12)	C4	C13	C14	107.27(16)
C22	N3	N4	109.76(12)	C4	C13	C14A	108.10(18)
C22	N3	C23	128.23(13)	C4	C13	C15	108.27(16)
C21	N4	N3	102.62(11)	C4	C13	C16A	107.68(19)
C27	N5	C26	102.23(13)	C14A	C13	C16A	103.4(3)
N7	N6	C28	120.45(12)	C15	C13	C14	105.9(2)

C27	N6	N7	108.93(12)	C15A	C13	C4	116.9(2)
C27	N6	C28	130.53(13)	C15A	C13	C14A	110.6(3)
C26	N7	N6	102.93(12)	C15A	C13	C16A	109.3(3)
N1	C1	C2	129.18(13)	C16	C13	C4	115.36(17)
N1	C1	C6	109.28(12)	C16	C13	C14	108.7(2)
C2	C1	C6	121.54(13)	C16	C13	C15	110.9(2)
C1	C2	C21	120.22(13)	C9	C17	C20	109.24(12)
C3	C2	C1	117.12(13)	C18	C17	C9	111.70(12)
C3	C2	C21	122.65(13)	C18	C17	C19	108.39(13)
C2	C3	C4	122.97(13)	C18	C17	C20	107.96(13)
C3	C4	C13	120.20(13)	C19	C17	C9	109.83(12)
C5	C4	C3	118.51(13)	C19	C17	C20	109.68(13)
C5	C4	C13	121.29(13)	N2	C21	C2	122.43(13)
C4	C5	C6	120.28(13)	N4	C21	N2	114.20(13)
C1	C6	C7	106.47(12)	N4	C21	C2	123.34(13)
C5	C6	C1	119.51(12)	N3	C22	N2	111.21(14)
C5	C6	C7	134.01(13)	N3	C23	C24	109.63(13)
C8	C7	C6	133.94(13)	N3	C23	C25	110.04(12)
C8	C7	C12	120.05(13)	C24	C23	C25	113.26(14)
C12	C7	C6	106.00(12)	N5	C26	C11	123.41(13)
C9	C8	C7	120.17(13)	N7	C26	N5	114.46(13)
C8	C9	C10	118.42(13)	N7	C26	C11	122.12(13)
C8	C9	C17	122.70(13)	N5	C27	N6	111.44(14)
C10	C9	C17	118.88(12)	N6	C28	C29	110.36(13)
C11	C10	C9	123.18(13)	N6	C28	C30	109.64(13)
C10	C11	C12	117.27(13)	C30	C28	C29	112.13(13)
C10	C11	C26	121.89(13)	O1	C32	C31	110.8(4)
C12	C11	C26	120.83(12)	O1	C32	C33	107.3(4)
N1	C12	C7	109.55(12)	C33	C32	C31	112.1(5)

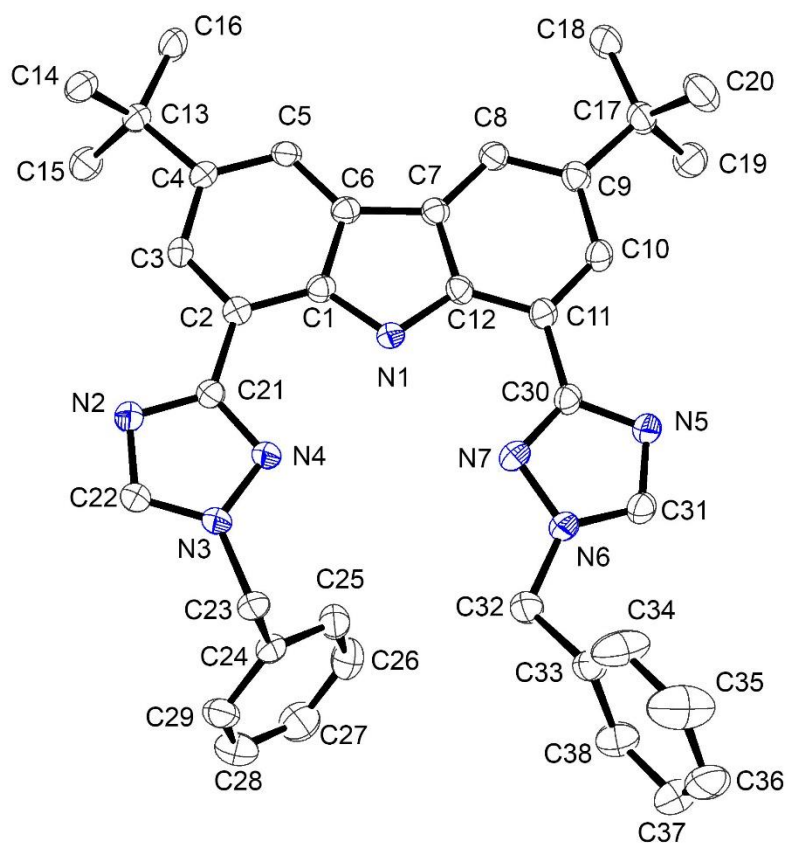


Figure B-2 Labelled ORTEP Drawing of **7c**

H atoms not shown

Disordered tBu carbons C18A, C19A and C20A not shown

Table B-6 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **7c**

Atom	x	y	z	U(eq)
N1	4506.8(12)	6818.2(16)	2775.0(8)	22.4(4)
N2	1914.7(13)	8621.4(18)	1737.7(9)	28.3(4)
N3	2169.7(13)	8649.8(17)	2822.4(9)	25.5(4)
N4	2861.6(12)	7967.7(17)	2727.5(9)	23.9(4)
N5	6199.7(12)	5683.1(18)	4767.8(9)	26.2(4)
N6	5071.6(13)	6879.4(18)	4840.1(9)	26.2(4)
N7	5003.0(13)	6845.1(17)	4172.3(9)	26.7(4)
C1	4113.9(15)	6850.1(19)	2092.6(10)	22.0(5)
C2	3273.2(15)	7343(2)	1728.5(10)	22.9(5)
C3	3020.8(15)	7178(2)	1038.6(10)	23.4(5)
C4	3562.7(15)	6554(2)	703.5(10)	23.7(5)
C5	4406.4(15)	6098(2)	1076.8(10)	23.1(5)
C6	4682.5(15)	6226.0(19)	1773.8(11)	22.3(5)
C7	5456.5(14)	5775.8(19)	2306.6(10)	21.6(4)
C8	6224.4(15)	5065(2)	2318.8(11)	24.6(5)
C9	6844.6(15)	4742(2)	2924.7(11)	25.0(5)
C10	6664.7(15)	5133(2)	3521.4(11)	24.2(5)
C11	5906.7(14)	5817(2)	3529.1(10)	23.1(5)
C12	5309.4(14)	6161.1(19)	2910.1(10)	21.9(4)
C13	3199.3(16)	6397(2)	-62.4(11)	28.6(5)
C14	3160.1(19)	7689(2)	-388.1(12)	36.3(6)
C15	2245.8(17)	5814(3)	-252.0(12)	38.7(6)
C16	3804.0(18)	5536(3)	-334.0(11)	37.9(6)
C17	7705.0(16)	3974(2)	2963.2(12)	30.2(5)
C18	7745(2)	3514(3)	2281.3(16)	36.8(8)
C18A	8280(10)	4783(15)	2568(7)	47(4)
C19	7747(2)	2793(3)	3408.7(16)	41.2(9)
C19A	7396(9)	2768(13)	2580(8)	43(4)
C20	8542(2)	4788(3)	3278.3(18)	41.7(9)
C20A	8315(9)	3771(14)	3645(7)	42(4)
C21	2679.5(15)	7975(2)	2060.8(10)	22.7(5)
C22	1617.3(16)	9022(2)	2236.6(11)	28.8(5)
C23	2077.4(16)	8815(2)	3497.7(11)	28.3(5)
C24	1669.1(16)	7681(2)	3734.2(11)	27.7(5)
C25	2161.9(17)	6574(2)	3908.8(12)	33.6(5)
C26	1782.4(19)	5539(2)	4116.5(13)	40.2(6)
C27	902(2)	5592(3)	4156.2(14)	45.0(7)
C28	402.6(19)	6688(3)	3975.8(14)	43.4(7)
C29	782.7(17)	7724(2)	3766.5(12)	33.6(6)
C30	5700.0(15)	6122(2)	4154.7(10)	23.1(5)
C31	5776.6(15)	6183(2)	5175.4(11)	27.3(5)
C32	4386.9(16)	7537(2)	5071.0(12)	32.0(5)

C33	4768.6(16)	8074(2)	5763.9(11)	27.7(5)
C34	5374(2)	9058(3)	5886.1(15)	52.5(8)
C35	5699(2)	9544(4)	6532.1(18)	70.9(11)
C36	5422(2)	9057(4)	7045.1(15)	58.3(9)
C37	4824(2)	8080(3)	6926.5(13)	47.8(7)
C38	4499.5(19)	7593(2)	6289.6(13)	37.8(6)

Table B-7 Anisotropic Displacement Parameters (U_{ij} , Å² x10³) for **7c**

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
N1	20.9(9)	28.7(9)	18.0(9)	-1.6(7)	6.5(7)	1.9(8)
N2	27.9(11)	34.3(10)	22.2(9)	1.4(8)	6.6(8)	8.6(9)
N3	23.6(10)	31.4(10)	22.8(9)	-2.0(7)	8.8(8)	6.4(8)
N4	21.5(9)	29.2(9)	21.8(9)	-1.9(7)	7.5(7)	3.6(8)
N5	22.6(10)	33.8(10)	21.3(9)	-1.4(7)	4.8(8)	-1.2(8)
N6	24.7(10)	34.3(10)	19.0(9)	-3.9(7)	5.5(8)	-0.5(8)
N7	29.0(10)	31.6(10)	18.7(9)	-3.5(7)	5.7(8)	-0.1(8)
C1	22.9(11)	22.9(10)	20.3(10)	-2.1(8)	6.3(9)	-1.6(9)
C2	22.9(11)	24.5(11)	21.5(11)	0.2(8)	6.8(9)	0.6(9)
C3	22.0(11)	26.5(11)	20.3(10)	2.6(8)	3.9(9)	4.5(9)
C4	25.9(12)	26.7(11)	19.2(10)	3.5(8)	7.9(9)	1.6(9)
C5	22.1(11)	26.6(11)	23.0(11)	-1.1(8)	10.7(9)	0.1(9)
C6	22.4(11)	23.1(10)	22.4(11)	0.0(8)	8.1(9)	-2.2(9)
C7	20.3(11)	23.0(10)	21.6(10)	-1.2(8)	6.4(9)	-1.9(9)
C8	22.9(11)	28.3(11)	22.7(11)	-3.6(8)	6.7(9)	-1.3(9)
C9	21.8(11)	26.9(11)	25.3(11)	-2.8(9)	5.4(9)	-1.5(9)
C10	22.7(11)	25.4(11)	21.6(11)	-2.7(8)	2.1(9)	-1.2(9)
C11	20.0(11)	25.1(11)	22.4(11)	-2.5(8)	3.5(9)	-4.6(9)
C12	17.8(11)	23.3(10)	23.6(11)	-1.3(8)	4.8(9)	-1.6(9)
C13	29.3(13)	37.4(13)	19.5(11)	1.5(9)	7.6(9)	8.4(10)
C14	43.9(15)	44.0(14)	23.9(12)	6.7(10)	14.3(11)	14.8(12)
C15	34.5(14)	55.9(16)	23.0(12)	-7.2(11)	4.2(10)	2.5(12)
C16	40.7(15)	51.6(15)	19.7(11)	0.1(10)	6.2(10)	19.8(12)
C17	24.8(12)	35.9(13)	28.4(12)	-4.2(10)	5.3(10)	5.5(10)
C18	32.9(18)	45.1(19)	32.3(17)	-4.2(14)	9.5(14)	16.8(15)
C18A	42(8)	60(9)	40(8)	4(6)	14(6)	12(7)
C19	45(2)	45.0(19)	34.4(18)	4.5(14)	12.8(15)	21.6(16)
C19A	21(7)	42(8)	65(10)	10(7)	9(6)	13(6)
C20	24.0(16)	52(2)	48(2)	-10.0(16)	8.9(15)	4.2(15)
C20A	26(7)	50(8)	48(8)	-4(6)	4(6)	7(6)
C21	21.6(11)	25.5(11)	20.8(11)	-1.2(8)	5.9(9)	0.0(9)
C22	27.3(12)	35.5(12)	24.8(11)	1.1(9)	9.4(10)	9.2(10)
C23	28.0(12)	36.3(12)	20.8(11)	-4.8(9)	7.7(10)	2.6(10)
C24	29.6(13)	32.9(12)	19.9(11)	-2.8(9)	6.4(9)	3.8(10)
C25	30.1(13)	38.0(13)	29.8(12)	-1.1(10)	4.1(10)	6.2(11)

C26	42.7(16)	35.9(14)	37.1(14)	5.6(11)	3.8(12)	4.2(12)
C27	50.9(17)	41.9(15)	44.4(16)	5.8(12)	17.4(13)	-4.8(13)
C28	41.0(16)	46.2(16)	50.3(16)	-2.1(13)	24.7(13)	-2.5(13)
C29	35.0(14)	34.7(13)	36.1(13)	0.2(10)	18.2(11)	6.1(11)
C30	21.0(11)	25.6(11)	20.6(11)	-1.2(8)	2.9(9)	-2.7(9)
C31	24.0(12)	35.3(12)	21.1(11)	-0.8(9)	3.9(9)	-3.9(10)
C32	28.3(13)	39.6(13)	27.6(12)	-7.1(10)	7.4(10)	3.6(11)
C33	26.3(12)	31.1(12)	26.9(12)	-4.3(9)	9.8(10)	0.1(10)
C34	67(2)	57.3(18)	45.5(16)	-14.9(14)	35.0(16)	-26.3(16)
C35	66(2)	83(2)	75(2)	-49(2)	38.6(19)	-48(2)
C36	42.9(17)	99(3)	33.3(15)	-29.3(16)	12.2(13)	-2.2(17)
C37	51.8(18)	65.4(19)	29.1(14)	2.1(12)	16.5(13)	7.2(15)
C38	45.8(16)	35.8(13)	36.8(14)	0.5(11)	20.0(12)	-3.5(12)

Table B-8 Bond Lengths for 7c

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C1	1.377(3)	C9	C17	1.538(3)
N1	C12	1.375(3)	C10	C11	1.380(3)
N2	C21	1.360(3)	C11	C12	1.399(3)
N2	C22	1.325(3)	C11	C30	1.468(3)
N3	N4	1.350(2)	C13	C14	1.525(3)
N3	C22	1.330(3)	C13	C15	1.535(3)
N3	C23	1.469(3)	C13	C16	1.527(3)
N4	C21	1.338(3)	C17	C18	1.523(4)
N5	C30	1.369(3)	C17	C18A	1.622(15)
N5	C31	1.325(3)	C17	C19	1.551(4)
N6	N7	1.368(2)	C17	C19A	1.512(15)
N6	C31	1.332(3)	C17	C20	1.532(4)
N6	C32	1.459(3)	C17	C20A	1.475(14)
N7	C30	1.329(3)	C23	C24	1.507(3)
C1	C2	1.398(3)	C24	C25	1.389(3)
C1	C6	1.410(3)	C24	C29	1.387(3)
C2	C3	1.390(3)	C25	C26	1.373(4)
C2	C21	1.463(3)	C26	C27	1.383(4)
C3	C4	1.402(3)	C27	C28	1.386(4)
C4	C5	1.393(3)	C28	C29	1.376(4)
C4	C13	1.542(3)	C32	C33	1.506(3)
C5	C6	1.399(3)	C33	C34	1.374(4)
C6	C7	1.454(3)	C33	C38	1.379(3)
C7	C8	1.397(3)	C34	C35	1.394(4)
C7	C12	1.405(3)	C35	C36	1.365(5)
C8	C9	1.388(3)	C36	C37	1.362(4)
C9	C10	1.415(3)	C37	C38	1.378(4)

Table B-9 Bond Angles for **7c**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C12	N1	C1	108.82(17)	C15	C13	C4	110.00(18)
C22	N2	C21	102.70(18)	C16	C13	C4	111.95(18)
N4	N3	C23	120.44(18)	C16	C13	C15	107.7(2)
C22	N3	N4	110.18(18)	C9	C17	C18A	106.4(5)
C22	N3	C23	129.24(19)	C9	C17	C19	110.1(2)
C21	N4	N3	102.40(17)	C18	C17	C9	112.9(2)
C31	N5	C30	102.52(18)	C18	C17	C19	107.2(2)
N7	N6	C32	120.09(18)	C18	C17	C20	108.9(2)
C31	N6	N7	109.26(18)	C19A	C17	C9	106.7(5)
C31	N6	C32	130.49(19)	C19A	C17	C18A	108.2(8)
C30	N7	N6	102.75(17)	C20	C17	C9	109.1(2)
N1	C1	C2	129.05(19)	C20	C17	C19	108.4(2)
N1	C1	C6	109.33(19)	C20A	C17	C9	115.1(6)
C2	C1	C6	121.56(19)	C20A	C17	C18A	106.3(8)
C1	C2	C21	121.47(19)	C20A	C17	C19A	113.7(8)
C3	C2	C1	116.84(19)	N2	C21	C2	124.55(19)
C3	C2	C21	121.68(19)	N4	C21	N2	114.06(18)
C2	C3	C4	123.4(2)	N4	C21	C2	121.39(19)
C3	C4	C13	118.69(19)	N2	C22	N3	110.7(2)
C5	C4	C3	118.61(19)	N3	C23	C24	112.69(18)
C5	C4	C13	122.70(19)	C25	C24	C23	120.9(2)
C4	C5	C6	119.97(19)	C29	C24	C23	120.0(2)
C1	C6	C7	106.07(18)	C29	C24	C25	119.1(2)
C5	C6	C1	119.6(2)	C26	C25	C24	120.6(2)
C5	C6	C7	134.2(2)	C25	C26	C27	120.1(2)
C8	C7	C6	133.83(19)	C26	C27	C28	119.6(3)
C8	C7	C12	119.9(2)	C29	C28	C27	120.3(3)
C12	C7	C6	106.26(18)	C28	C29	C24	120.3(2)
C9	C8	C7	120.3(2)	N5	C30	C11	123.28(19)
C8	C9	C10	118.1(2)	N7	C30	N5	114.15(19)
C8	C9	C17	122.15(19)	N7	C30	C11	122.57(19)
C10	C9	C17	119.75(19)	N5	C31	N6	111.30(19)
C11	C10	C9	123.3(2)	N6	C32	C33	112.41(19)
C10	C11	C12	117.2(2)	C34	C33	C32	121.3(2)
C10	C11	C30	122.02(19)	C34	C33	C38	118.6(2)
C12	C11	C30	120.7(2)	C38	C33	C32	120.1(2)
N1	C12	C7	109.51(18)	C33	C34	C35	119.6(3)
N1	C12	C11	129.18(19)	C36	C35	C34	120.9(3)
C11	C12	C7	121.2(2)	C37	C36	C35	119.7(3)
C14	C13	C4	108.67(19)	C36	C37	C38	119.8(3)
C14	C13	C15	109.7(2)	C37	C38	C33	121.4(3)
C14	C13	C16	108.76(19)				

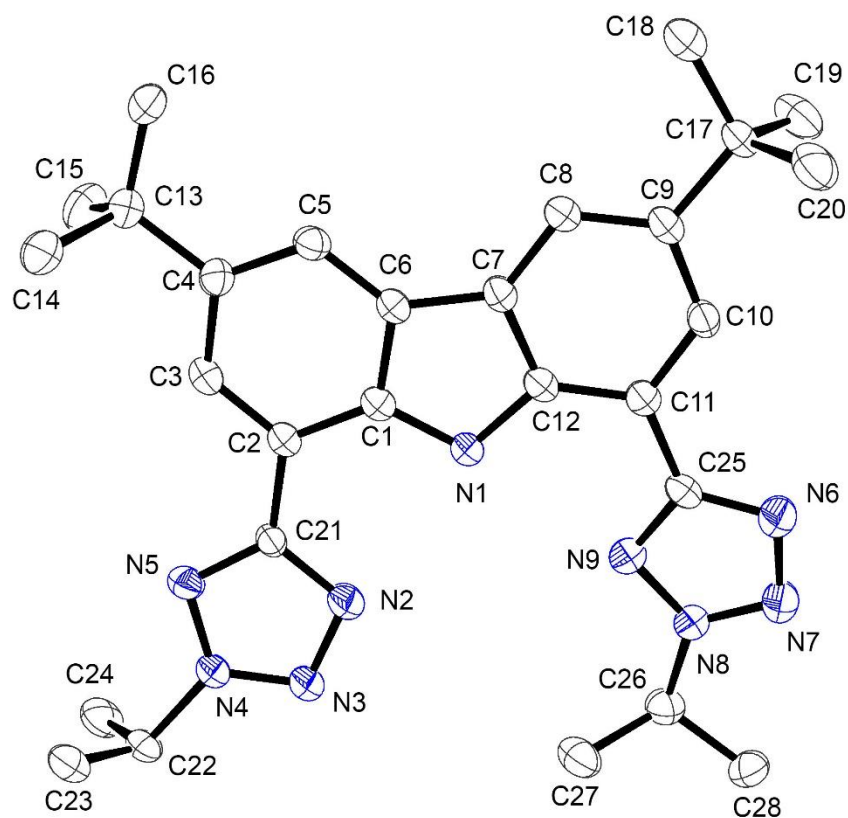


Figure B-3 Labelled ORTEP Drawing of **8b**

H atoms not shown

Disordered tBu carbons C14A, C15A and C16A not shown

Disordered iPr carbons C27A and C28A not shown

Disordered iPrOH of solvation not shown: C29, C30, C31 and O1

Table B-10 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **8b**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
O1	1170(3)	4349.6(19)	5669(3)	61.2(11)
N1	6102.8(13)	2776.0(8)	5427.8(11)	24.3(3)
N2	8492.6(14)	2938.8(9)	6429.7(12)	31.0(4)
N3	9524.5(14)	3121.2(9)	7014.0(12)	30.0(4)
N4	10270.0(13)	2582.2(8)	6972.9(11)	25.5(3)
N5	9788.2(14)	2041.8(9)	6376.4(11)	26.7(4)
N6	3726.1(16)	4522.6(10)	5873.8(15)	45.1(5)
N7	4437.8(16)	5043.2(11)	6346.4(15)	44.4(5)
N8	5538.2(15)	4839.1(9)	6384.1(11)	29.7(4)
N9	5600.8(15)	4201.5(9)	5946.7(12)	30.3(4)
C1	6547.5(16)	2131.8(10)	5158.3(12)	23.4(4)
C2	7724.4(16)	1871.8(10)	5382.1(13)	22.9(4)
C3	7935.0(16)	1209.6(10)	4980.9(13)	26.0(4)
C4	7019.1(17)	793.1(10)	4376.0(13)	26.6(4)
C5	5848.7(16)	1057.5(10)	4187.7(13)	26.0(4)
C6	5604.5(15)	1726.7(10)	4569.4(13)	23.6(4)
C7	4530.0(16)	2159.8(10)	4487.6(13)	24.1(4)
C8	3331.6(16)	2061.7(10)	4008.8(13)	25.0(4)
C9	2484.0(16)	2588.0(10)	4069.6(13)	25.8(4)
C10	2869.2(16)	3217.5(10)	4624.6(13)	25.7(4)
C11	4054.4(16)	3341.8(10)	5100.6(13)	24.8(4)
C12	4886.1(16)	2799.7(10)	5026.6(13)	23.8(4)
C13	7318.6(19)	79.1(11)	3926.6(15)	33.7(5)
C14	7990(4)	-442.0(19)	4707(3)	42.4(10)
C14A	6475(7)	-552(3)	4257(6)	55(2)
C15	8233(3)	291(2)	3299(3)	43.2(10)
C15A	8533(6)	-169(4)	4218(6)	60(2)
C16	6290(3)	-287.1(19)	3294(3)	42.0(11)
C16A	6839(7)	120(4)	2825(5)	56(2)
C17	1158.1(16)	2506.2(11)	3558.2(14)	28.1(4)
C18	903.1(19)	1780.9(12)	3009.6(17)	40.0(5)
C19	778(2)	3129.0(13)	2827.2(17)	43.3(6)
C20	400.7(19)	2524.6(14)	4292.0(17)	43.9(6)
C21	8681.6(16)	2285.4(10)	6042.2(12)	22.0(4)
C22	11533.7(16)	2581.4(11)	7522.1(14)	29.4(4)
C23	11798.2(19)	1881.8(12)	8100.9(15)	36.1(5)
C24	12328.5(18)	2698.3(13)	6838.5(16)	38.5(5)
C25	4449.8(16)	4025.5(10)	5645.4(13)	26.1(4)
C26	6610.2(18)	5278.8(11)	6821.7(15)	33.0(5)
C27	7567(2)	4816.3(15)	7465(2)	38.2(8)
C27A	7640(9)	4934(6)	6751(9)	48(3)
C28	6261(2)	5939.5(15)	7302(2)	35.2(7)
C28A	6546(12)	5334(7)	7928(9)	60(4)

C29	310(6)	4870(4)	5248(5)	77(2)
C30	761(9)	5361(6)	4643(7)	73(3)
C31	-813(10)	4486(6)	4844(9)	98(4)

Table B-11 Anisotropic Displacement Parameters (U_{ij} , Å² x10³) for **8b**

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
O1	35.8(19)	48(2)	103(3)	22(2)	23(2)	13.6(15)
N1	19.9(8)	25.9(8)	25.6(8)	-2.6(6)	3.1(6)	0.7(6)
N2	22.6(8)	31.6(9)	35.7(9)	-4.2(7)	1.4(7)	-0.7(7)
N3	23.7(8)	30.9(9)	32.1(9)	-4.7(7)	0.4(7)	1.9(7)
N4	20.2(8)	27.7(8)	26.8(8)	-1.5(6)	2.5(6)	0.2(6)
N5	22.3(8)	30.2(8)	25.9(8)	-2.1(7)	2.4(6)	-1.6(6)
N6	31.1(10)	42.0(11)	58.4(12)	-20.0(9)	4.0(9)	3.7(8)
N7	31.0(10)	42.8(10)	56.4(12)	-18.0(9)	5.1(9)	5.3(8)
N8	29.2(9)	29.2(9)	29.1(8)	-4.9(7)	3.8(7)	3.0(7)
N9	30.3(9)	27.9(8)	31.2(9)	-4.5(7)	4.9(7)	1.1(7)
C1	21.0(9)	26.1(9)	22.6(9)	1.6(7)	4.7(7)	-0.7(7)
C2	19.5(9)	25.6(9)	23.1(9)	1.6(7)	4.2(7)	0.3(7)
C3	19.9(9)	28.8(9)	28.0(9)	2.3(8)	3.4(7)	1.8(7)
C4	27.6(10)	24.3(9)	27.3(10)	0.9(7)	5.9(8)	2.3(7)
C5	22.7(9)	26.0(9)	27.4(9)	-1.3(7)	2.4(8)	-2.5(7)
C6	18.9(9)	26.1(9)	25.0(9)	0.5(7)	4.2(7)	-0.3(7)
C7	19.7(9)	27.5(9)	24.8(9)	1.4(7)	5.1(7)	1.2(7)
C8	22.2(9)	27.6(9)	24.1(9)	0.3(7)	3.6(7)	-0.5(7)
C9	18.5(9)	32.6(10)	25.2(9)	3.3(8)	3.3(7)	0.8(7)
C10	21.7(9)	30.4(10)	24.2(9)	1.8(7)	4.5(7)	5.2(7)
C11	22.9(9)	26.8(9)	24.3(9)	0.9(7)	5.3(7)	0.4(7)
C12	19.7(9)	28.9(9)	21.8(9)	1.8(7)	3.5(7)	-0.2(7)
C13	33.7(11)	28.8(10)	35.6(11)	-4.2(8)	2.7(9)	6.6(8)
C14	48(2)	25.3(17)	48(2)	-3.7(16)	0.5(18)	4.3(16)
C14A	56(4)	31(3)	80(5)	-6(3)	19(4)	1(3)
C15	46(2)	41(2)	49(2)	-9.7(17)	23.8(18)	2.0(16)
C15A	36(4)	51(4)	84(6)	-27(4)	-2(4)	11(3)
C16	34(2)	31.3(18)	57(2)	-16.8(17)	2.8(17)	4.2(15)
C16A	70(5)	51(4)	51(4)	-12(3)	19(4)	21(4)
C17	18.6(9)	33.1(10)	29.9(10)	0.2(8)	1.2(7)	0.6(7)
C18	25.1(11)	43.0(12)	47.6(13)	-5.1(10)	0.7(9)	0.0(9)
C19	30.6(12)	44.1(13)	47.0(13)	8.2(10)	-5.7(10)	-1.4(10)
C20	25.4(11)	60.3(15)	44.8(13)	-4.9(11)	6.4(10)	-1.3(10)
C21	18.5(9)	24.8(9)	21.7(8)	1.3(7)	2.7(7)	2.8(7)
C22	17.6(9)	36.9(11)	30.0(10)	-6.0(8)	-1.1(8)	-0.6(8)
C23	28.9(11)	40.7(12)	32.9(11)	-0.5(9)	-3.3(9)	1.1(9)
C24	22.4(10)	51.9(13)	39.2(12)	-3.0(10)	3.8(9)	-3.0(9)
C25	22.3(9)	31.1(10)	22.1(9)	3.4(8)	0.5(7)	0.5(8)

C26	31.4(11)	30.1(10)	34.9(11)	-3.5(8)	3.3(9)	-2.4(8)
C27	31.6(15)	33.8(15)	42.6(19)	1.7(13)	-3.3(12)	-2.6(11)
C27A	39(6)	53(7)	46(7)	-8(5)	-3(5)	-7(5)
C28	35.2(15)	33.4(14)	36.8(15)	-10.1(12)	8.1(12)	-2.8(11)
C28A	62(8)	62(8)	54(7)	-17(6)	11(6)	-18(6)
C29	66(4)	74(4)	93(5)	39(4)	26(4)	38(3)
C30	56(4)	81(6)	90(7)	19(5)	31(5)	12(4)
C31	81(6)	82(7)	135(11)	30(8)	35(8)	17(5)

Table B-12 Bond Lengths for **8b**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C29	1.403(6)	C7	C12	1.411(3)
N1	C1	1.382(2)	C8	C9	1.395(3)
N1	C12	1.386(2)	C9	C10	1.412(3)
N2	N3	1.324(2)	C9	C17	1.538(3)
N2	C21	1.362(2)	C10	C11	1.394(3)
N3	N4	1.323(2)	C11	C12	1.406(3)
N4	N5	1.340(2)	C11	C25	1.490(3)
N4	C22	1.483(2)	C13	C14	1.533(4)
N5	C21	1.330(2)	C13	C14A	1.659(7)
N6	N7	1.333(3)	C13	C15	1.602(4)
N6	C25	1.334(3)	C13	C15A	1.440(7)
N7	N8	1.317(2)	C13	C16	1.471(4)
N8	N9	1.338(2)	C13	C16A	1.549(7)
N8	C26	1.484(3)	C17	C18	1.537(3)
N9	C25	1.336(2)	C17	C19	1.542(3)
C1	C2	1.405(2)	C17	C20	1.534(3)
C1	C6	1.417(2)	C22	C23	1.519(3)
C2	C3	1.391(3)	C22	C24	1.522(3)
C2	C21	1.479(2)	C26	C27	1.516(3)
C3	C4	1.418(3)	C26	C27A	1.377(11)
C4	C5	1.402(3)	C26	C28	1.499(3)
C4	C13	1.537(3)	C26	C28A	1.618(12)
C5	C6	1.401(3)	C29	C30	1.440(10)
C6	C7	1.457(2)	C29	C31	1.468(11)
C7	C8	1.401(2)			

Table B-13 Bond Angles for **8b**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	N1	C12	108.72(15)	N1	C12	C11	129.49(17)
N3	N2	C21	105.75(15)	C11	C12	C7	121.08(17)
N4	N3	N2	106.27(15)	C4	C13	C14A	105.2(3)

N3	N4	N5	114.04(15)	C4	C13	C15	106.39(19)
N3	N4	C22	123.13(15)	C4	C13	C16A	109.3(3)
N5	N4	C22	122.82(15)	C14	C13	C4	110.3(2)
C21	N5	N4	101.30(15)	C14	C13	C15	106.2(3)
N7	N6	C25	105.53(17)	C15A	C13	C4	116.9(3)
N8	N7	N6	106.74(16)	C15A	C13	C14A	107.4(5)
N7	N8	N9	113.17(16)	C15A	C13	C16A	113.1(5)
N7	N8	C26	124.29(16)	C16	C13	C4	114.6(2)
N9	N8	C26	122.48(16)	C16	C13	C14	110.9(3)
C25	N9	N8	101.40(15)	C16	C13	C15	107.9(3)
N1	C1	C2	129.32(16)	C16A	C13	C14A	103.9(5)
N1	C1	C6	109.28(15)	C9	C17	C19	109.77(16)
C2	C1	C6	121.40(16)	C18	C17	C9	111.89(16)
C1	C2	C21	120.32(16)	C18	C17	C19	107.56(17)
C3	C2	C1	117.41(16)	C20	C17	C9	109.96(16)
C3	C2	C21	122.24(16)	C20	C17	C18	107.71(17)
C2	C3	C4	122.91(17)	C20	C17	C19	109.88(18)
C3	C4	C13	120.30(17)	N2	C21	C2	122.91(15)
C5	C4	C3	118.30(17)	N5	C21	N2	112.63(15)
C5	C4	C13	121.39(17)	N5	C21	C2	124.29(16)
C6	C5	C4	120.40(17)	N4	C22	C23	109.43(16)
C1	C6	C7	106.27(16)	N4	C22	C24	109.27(16)
C5	C6	C1	119.54(16)	C23	C22	C24	113.75(17)
C5	C6	C7	134.16(17)	N6	C25	N9	113.15(17)
C8	C7	C6	133.88(17)	N6	C25	C11	125.08(17)
C8	C7	C12	119.82(16)	N9	C25	C11	121.77(17)
C12	C7	C6	106.29(15)	N8	C26	C27	111.42(18)
C9	C8	C7	120.52(17)	N8	C26	C28	109.99(18)
C8	C9	C10	118.15(17)	N8	C26	C28A	102.4(5)
C8	C9	C17	122.54(17)	C27A	C26	N8	111.6(5)
C10	C9	C17	119.31(16)	C27A	C26	C28A	110.7(8)
C11	C10	C9	123.19(17)	C28	C26	C27	114.1(2)
C10	C11	C12	117.23(17)	O1	C29	C30	111.2(6)
C10	C11	C25	122.29(17)	O1	C29	C31	108.1(7)
C12	C11	C25	120.46(16)	C30	C29	C31	118.6(7)
N1	C12	C7	109.44(15)				

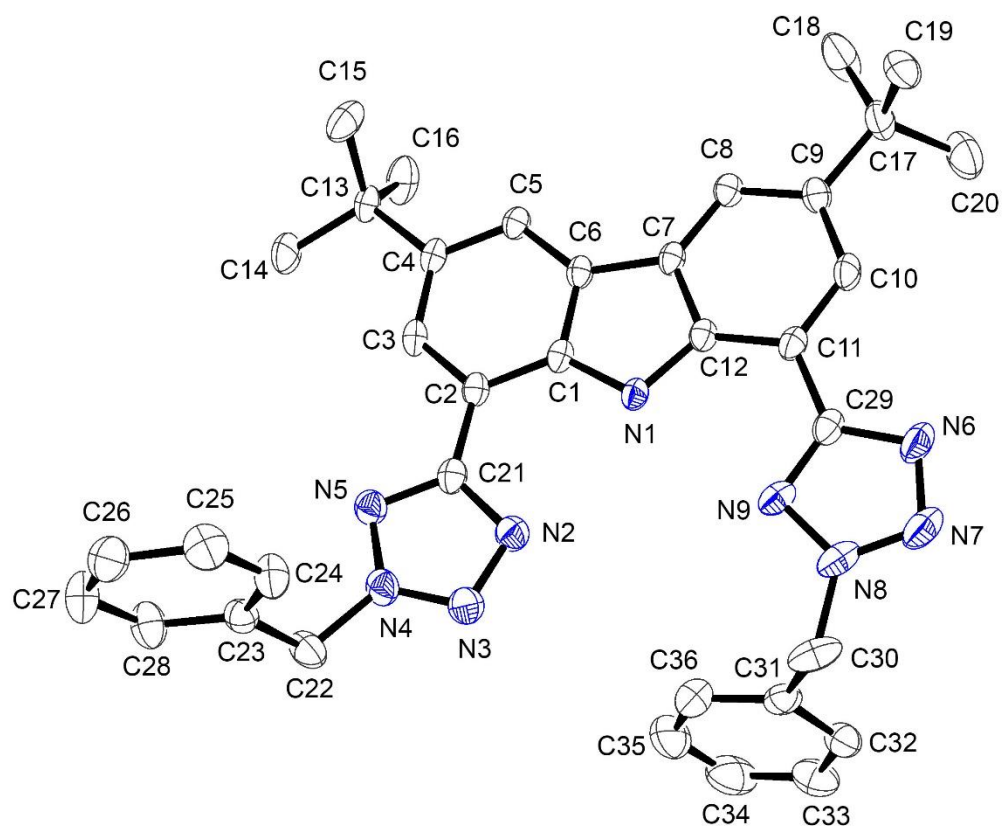


Figure B-4 Labelled ORTEP Drawing of **8c**

H atoms not shown

Table B-14 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **8c**

Atom	x	y	z	U(eq)
N1	3570.5(10)	4016.9(9)	8061.2(9)	22.3(2)
N2	5235.0(11)	4873.3(11)	6952.7(11)	29.4(3)
N3	6118.6(12)	5416.1(11)	6665.0(12)	31.9(3)
N4	6336.4(11)	4706.6(11)	5689.6(11)	29.4(3)
N5	5659.6(11)	3714.1(10)	5312.1(11)	28.3(3)
N6	3008.1(14)	6266.0(11)	11416.3(11)	36.1(3)
N7	3663.7(15)	7234.1(11)	11597.4(12)	40.1(3)
N8	4220.8(13)	7087.2(10)	10710.8(11)	33.1(3)
N9	3971.9(12)	6055.2(10)	9929.4(11)	28.4(3)
C1	3470.8(12)	3103.1(11)	7065.7(11)	21.4(3)
C2	4059.7(12)	2967.8(11)	6125.0(11)	22.5(3)
C3	3751.1(12)	1955.5(12)	5203.4(11)	23.8(3)
C4	2921.5(12)	1076.2(11)	5199.6(11)	23.4(3)
C5	2382.1(12)	1218.3(11)	6171.8(11)	22.6(3)
C6	2643.5(12)	2228.3(11)	7095.9(11)	21.3(3)
C7	2226.2(12)	2651.5(11)	8188.3(11)	21.3(3)
C8	1414.4(12)	2195.2(12)	8714.9(11)	23.2(3)
C9	1211.1(13)	2819.4(12)	9804.6(12)	25.6(3)
C10	1834.4(13)	3909.3(12)	10341.9(12)	26.8(3)
C11	2628.1(13)	4401.4(11)	9835.9(11)	23.9(3)
C12	2824.1(12)	3753.5(11)	8743.7(11)	21.4(3)
C13	2601.3(13)	-27.1(12)	4169.2(12)	26.5(3)
C14	3186.5(17)	29.2(14)	3154.2(13)	38.1(4)
C15	3054.4(18)	-1026.5(14)	4523.0(14)	40.0(4)
C16	1205.3(15)	-245.9(16)	3764.8(14)	41.0(4)
C17	373.2(15)	2333.4(14)	10440.5(13)	32.7(3)
C18	-449.1(19)	1285.6(19)	9633.3(15)	53.1(5)
C19	1191.5(17)	1998.8(15)	11369.1(14)	39.2(4)
C20	-458.7(18)	3216.4(18)	11006.4(17)	49.0(5)
C21	4982.8(12)	3844.9(12)	6121.3(12)	24.0(3)
C22	7296.1(14)	4971.1(14)	5102.3(15)	34.2(3)
C23	8344.5(13)	4246.1(12)	5150.4(13)	26.9(3)
C24	8815.8(15)	4037.1(14)	6155.4(14)	34.1(3)
C25	9815.7(16)	3413.5(15)	6192.3(15)	38.6(4)
C26	10339.7(15)	2993.5(15)	5223.2(16)	40.0(4)
C27	9850.1(16)	3177.1(16)	4226.4(15)	42.4(4)
C28	8857.8(15)	3805.1(15)	4186.9(14)	36.4(4)
C29	3211.6(13)	5563.7(12)	10396.3(12)	26.0(3)
C30	4993.9(16)	7991.0(13)	10559.1(16)	40.9(4)
C31	4398.2(14)	8346.4(12)	9576.8(14)	30.4(3)
C32	3626.3(14)	9208.3(13)	9772.1(14)	31.9(3)
C33	3060.8(17)	9544.0(16)	8882.1(17)	43.2(4)

C34	3244(2)	9021.6(18)	7792.5(18)	56.5(5)
C35	3996(2)	8166.0(19)	7567.9(17)	62.2(6)
C36	4589(2)	7821.1(15)	8462.2(18)	50.3(5)

Table B-15 Anisotropic Displacement Parameters (U_{ij} , Å² x10³) for **8c**

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
N1	25.5(6)	20.8(5)	18.2(5)	2.6(4)	5.0(4)	3.0(4)
N2	26.5(6)	28.9(6)	32.1(7)	7.8(5)	8.1(5)	1.7(5)
N3	27.9(6)	31.4(6)	37.4(7)	11.2(6)	8.9(5)	4.5(5)
N4	24.5(6)	33.0(6)	35.0(7)	14.0(5)	10.3(5)	8.9(5)
N5	26.1(6)	30.0(6)	32.0(7)	12.0(5)	9.3(5)	7.3(5)
N6	55.3(9)	25.4(6)	22.3(6)	0.8(5)	5.3(6)	9.7(6)
N7	61.3(9)	24.2(6)	27.5(7)	1.8(5)	-0.7(6)	9.8(6)
N8	42.9(7)	19.3(6)	30.0(7)	4.5(5)	-6.8(6)	4.2(5)
N9	33.2(7)	19.8(5)	26.5(6)	3.4(5)	-2.0(5)	3.0(5)
C1	21.5(6)	22.9(6)	18.0(6)	4.2(5)	2.6(5)	7.0(5)
C2	20.5(6)	25.5(6)	20.8(6)	5.8(5)	4.6(5)	6.7(5)
C3	22.6(6)	29.4(7)	18.3(6)	4.5(5)	5.9(5)	9.0(5)
C4	23.0(6)	25.2(6)	18.2(6)	2.1(5)	2.2(5)	7.8(5)
C5	23.6(6)	23.2(6)	18.7(6)	4.1(5)	2.2(5)	4.1(5)
C6	22.1(6)	24.4(6)	16.5(6)	5.1(5)	3.0(5)	6.3(5)
C7	23.0(6)	23.2(6)	15.7(6)	4.1(5)	1.9(5)	6.0(5)
C8	24.0(7)	25.2(6)	18.5(6)	5.6(5)	1.3(5)	3.0(5)
C9	27.2(7)	30.9(7)	18.1(6)	7.4(6)	3.8(5)	3.7(5)
C10	33.7(8)	29.1(7)	15.6(6)	3.5(5)	5.6(5)	6.2(6)
C11	29.4(7)	22.0(6)	18.1(6)	3.8(5)	3.1(5)	6.7(5)
C12	23.3(6)	23.5(6)	17.2(6)	6.5(5)	2.7(5)	6.3(5)
C13	28.1(7)	27.4(7)	18.3(6)	-0.4(5)	4.2(5)	5.3(5)
C14	48.8(10)	35.5(8)	22.9(7)	-2.6(6)	12.3(7)	2.2(7)
C15	55.7(11)	28.7(8)	28.3(8)	0.8(6)	2.3(7)	12.0(7)
C16	31.4(8)	49.2(10)	27.4(8)	-5.6(7)	-0.1(6)	3.5(7)
C17	35.8(8)	39.4(8)	21.6(7)	6.8(6)	9.4(6)	-1.0(6)
C18	53.0(11)	68.1(13)	29.7(9)	6.3(9)	12.4(8)	-24.7(10)
C19	52.6(10)	40.4(9)	27.7(8)	14.2(7)	11.2(7)	0.3(7)
C20	45.2(10)	63.6(12)	48.1(11)	23.1(10)	25.1(9)	14.0(9)
C21	23.0(6)	27.4(7)	21.9(6)	7.9(5)	3.5(5)	8.6(5)
C22	28.7(8)	40.5(8)	44.3(9)	24.4(7)	14.5(7)	9.3(6)
C23	23.2(7)	28.5(7)	31.0(7)	11.6(6)	6.5(6)	2.9(5)
C24	34.5(8)	41.3(9)	28.6(8)	11.8(7)	9.7(6)	10.9(7)
C25	35.9(8)	46.7(9)	38.1(9)	21.5(8)	3.1(7)	11.0(7)
C26	30.4(8)	40.9(9)	53.8(11)	19.3(8)	11.7(7)	15.1(7)
C27	39.4(9)	51.2(10)	36.6(9)	8.9(8)	16.1(7)	15.1(8)
C28	34.0(8)	49.8(10)	28.0(8)	14.4(7)	8.1(6)	10.2(7)
C29	32.6(7)	24.6(7)	19.0(6)	5.7(5)	1.5(5)	8.6(5)

C30	37.8(9)	22.5(7)	52.9(11)	9.8(7)	-13.0(8)	-3.3(6)
C31	28.9(7)	23.2(7)	35.1(8)	6.5(6)	3.1(6)	-4.2(5)
C32	32.0(8)	32.8(8)	34.8(8)	15.3(7)	8.6(6)	3.3(6)
C33	39.7(9)	46.2(10)	53.2(11)	30.4(9)	6.5(8)	4.6(7)
C34	76.0(15)	54.2(12)	43.6(11)	27.9(10)	2.1(10)	-9.1(10)
C35	95.0(18)	54.8(12)	33.7(10)	7.0(9)	24.6(11)	-14.6(12)
C36	62.5(12)	30.5(8)	55.8(12)	3.7(8)	27.9(10)	0.9(8)

Table B-16 Bond Lengths for **8c**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C1	1.3791(17)	C9	C10	1.404(2)
N1	C12	1.3762(17)	C9	C17	1.533(2)
N2	N3	1.3241(17)	C10	C11	1.387(2)
N2	C21	1.3540(19)	C11	C12	1.4026(18)
N3	N4	1.3228(18)	C11	C29	1.4640(19)
N4	N5	1.3251(18)	C13	C14	1.531(2)
N4	C22	1.4642(18)	C13	C15	1.531(2)
N5	C21	1.3237(18)	C13	C16	1.531(2)
N6	N7	1.318(2)	C17	C18	1.525(2)
N6	C29	1.3556(18)	C17	C19	1.534(2)
N7	N8	1.317(2)	C17	C20	1.535(2)
N8	N9	1.3313(17)	C22	C23	1.507(2)
N8	C30	1.465(2)	C23	C24	1.391(2)
N9	C29	1.328(2)	C23	C28	1.376(2)
C1	C2	1.3991(18)	C24	C25	1.383(2)
C1	C6	1.4086(19)	C25	C26	1.385(2)
C2	C3	1.3969(19)	C26	C27	1.371(3)
C2	C21	1.4667(19)	C27	C28	1.380(2)
C3	C4	1.399(2)	C30	C31	1.503(2)
C4	C5	1.4009(19)	C31	C32	1.387(2)
C4	C13	1.5376(18)	C31	C36	1.391(2)
C5	C6	1.3936(18)	C32	C33	1.381(2)
C6	C7	1.4539(17)	C33	C34	1.361(3)
C7	C8	1.3946(19)	C34	C35	1.368(3)
C7	C12	1.4077(19)	C35	C36	1.403(3)
C8	C9	1.3949(19)			

Table B-17 Bond Angles for **8c**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C12	N1	C1	108.51(11)	N1	C12	C11	129.63(13)
N3	N2	C21	105.76(12)	C11	C12	C7	120.78(12)
N4	N3	N2	105.41(12)	C14	C13	C4	111.88(12)
N3	N4	N5	114.85(12)	C14	C13	C15	108.73(13)
N3	N4	C22	122.69(13)	C14	C13	C16	107.89(13)
N5	N4	C22	122.39(13)	C15	C13	C4	109.66(12)
C21	N5	N4	100.99(12)	C15	C13	C16	108.65(14)
N7	N6	C29	105.51(13)	C16	C13	C4	109.95(11)
N8	N7	N6	106.50(12)	C9	C17	C19	108.13(13)
N7	N8	N9	114.03(13)	C9	C17	C20	110.89(14)
N7	N8	C30	123.38(13)	C18	C17	C9	111.67(12)
N9	N8	C30	122.51(14)	C18	C17	C19	108.76(15)
C29	N9	N8	101.24(12)	C18	C17	C20	107.99(16)
N1	C1	C2	129.44(13)	C19	C17	C20	109.36(13)
N1	C1	C6	109.64(11)	N2	C21	C2	123.29(12)
C2	C1	C6	120.92(12)	N5	C21	N2	112.98(13)
C1	C2	C21	121.16(12)	N5	C21	C2	123.73(13)
C3	C2	C1	117.28(13)	N4	C22	C23	111.71(12)
C3	C2	C21	121.54(12)	C24	C23	C22	121.19(14)
C2	C3	C4	123.19(12)	C28	C23	C22	119.15(14)
C3	C4	C5	118.21(12)	C28	C23	C24	119.65(14)
C3	C4	C13	121.83(12)	C25	C24	C23	120.04(14)
C5	C4	C13	119.96(13)	C24	C25	C26	119.74(15)
C6	C5	C4	120.22(13)	C27	C26	C25	119.91(15)
C1	C6	C7	105.99(11)	C26	C27	C28	120.58(15)
C5	C6	C1	120.10(12)	C23	C28	C27	120.04(15)
C5	C6	C7	133.90(13)	N6	C29	C11	124.33(14)
C8	C7	C6	133.58(12)	N9	C29	N6	112.72(13)
C8	C7	C12	120.14(12)	N9	C29	C11	122.91(12)
C12	C7	C6	106.27(11)	N8	C30	C31	111.35(13)
C7	C8	C9	120.16(13)	C32	C31	C30	119.82(15)
C8	C9	C10	118.29(13)	C32	C31	C36	118.64(16)
C8	C9	C17	122.05(13)	C36	C31	C30	121.54(16)
C10	C9	C17	119.62(12)	C33	C32	C31	120.90(16)
C11	C10	C9	123.23(13)	C34	C33	C32	120.20(18)
C10	C11	C12	117.37(12)	C33	C34	C35	120.48(19)
C10	C11	C29	121.72(12)	C34	C35	C36	120.17(18)
C12	C11	C29	120.87(13)	C31	C36	C35	119.61(18)
N1	C12	C7	109.59(11)				

Table B-18 Summary of Crystallographic Data for **11** and **12**

	11•2 C₇H₈^a	12•2 C₇H₈^b
Emp. Formula	C ₅₄ H ₈₈ N ₁₁ Si ₄ Yb	C ₅₄ H ₈₈ ErN ₁₁ Si ₄
Formula wgt. (g/mol)	1176.75	1170.97
Temp. (K)	293(2)	120(2)
Crystal System	Triclinic	Triclinic
Space Group	P-1	P-1
a (Å)	11.2711(9)	11.1978(5)
b (Å)	15.7793(12)	15.7727(8)
c (Å)	19.4540(16)	19.3549(9)
α (°)	108.834(2)	108.997(2)
β (°)	104.839(2)	104.761(2)
γ (°)	97.646(2)	97.811(2)
Volume (Å³)	3076.2(4)	3034.7(3)
Z	2	2
Density (g/cm³)	1.270	1.281
Abs. coeff. μ (mm⁻¹)	2.025	1.505
F(000)	1230	1226
Crystal Size (mm)	0.12 x 0.07 x 0.07	0.196 × 0.097 × 0.049
Colour and habit	Yellow needle	Yellow block
Theta range (°)	4.154° ≤ 2Θ ≤ 62.302°	1.406 ° ≤ 2Θ ≤ 27.215°
Refl. Collected	57212	65917
Independent refl.	15021	13522
GooF (F²)	1.046	1.015
Final R [I>2σ(I)]	0.0272	0.0435
Final wR2	0.0625	0.0759
R (all data)	0.316	0.0736
wR2 (all data)	0.0642	0.0846
Max peak/hole (e/Å³)	1.346/-0.818	0.827/-1.274

^a Data collected at the Advanced Light Source (ALS) synchrotron facility ($\lambda = 0.7749$ Å), Lawrence Berkeley National Laboratory, Berkeley, CA. ^b Data collected on a Bruker Kappa X8-Apex II diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å) at the University of Notre Dame.

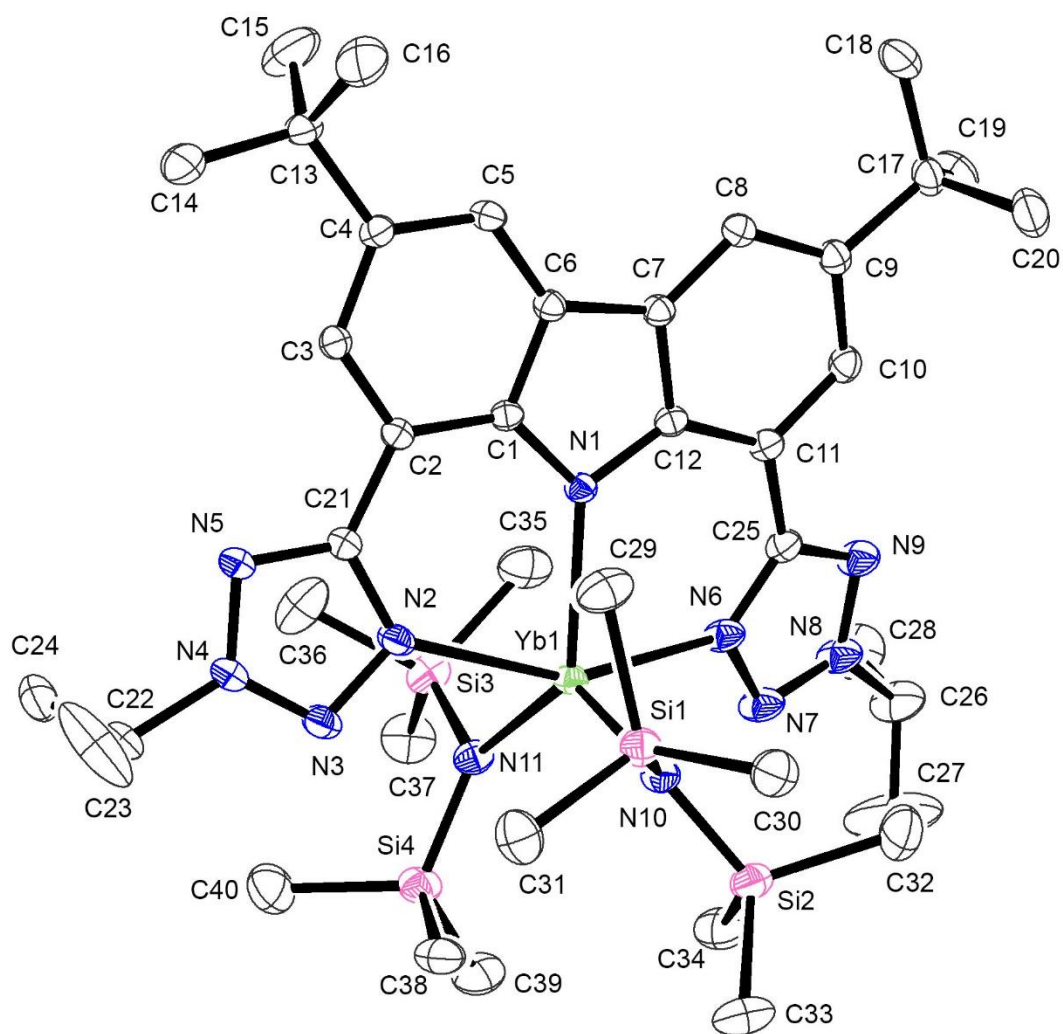


Figure B-5 Labelled ORTEP Drawing of **11**

H atoms not shown

Disordered iPr carbons C23A and C24A not shown

Disordered toluenes of solvation not shown: C41-C54

Table B-19 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **11**

Atom	x	y	z	U(eq)
Yb1	4117.8(2)	1838.0(2)	7886.9(2)	21.17(3)
Si1	5958.2(6)	3226.4(4)	9692.1(4)	27.00(13)
Si2	6169.3(7)	1268.1(5)	9206.5(4)	32.48(14)
Si3	1507.6(7)	508.5(4)	6478.6(4)	33.71(15)
Si4	1715.1(7)	248.4(4)	7943.3(4)	33.53(15)
N1	4564.8(16)	2902.8(11)	7325.9(10)	19.3(3)
N2	2771.7(17)	2842.8(12)	8206.4(11)	25.2(4)
N3	1964.4(18)	2630.1(13)	8553.9(12)	29.0(4)
N4	1275.0(18)	3231.6(13)	8584.2(11)	27.1(4)
N5	1564.8(17)	3847.4(13)	8282.1(11)	25.8(4)
N6	5304.8(19)	1095.3(12)	7115.2(11)	28.0(4)
N7	5319(2)	210.4(13)	6965.0(12)	33.6(5)
N8	6042(2)	37.6(13)	6534.2(12)	35.2(5)
N9	6515(2)	740.9(13)	6376.0(12)	33.9(5)
N10	5512.1(18)	2126.0(12)	8998.8(10)	26.1(4)
N11	2393.7(18)	724.0(12)	7408.2(11)	27.0(4)
C1	4135.6(19)	3707.2(13)	7373.6(11)	18.9(4)
C2	3194.8(19)	4040.6(13)	7669.2(11)	19.8(4)
C3	2899.2(19)	4852.9(14)	7609.3(12)	21.0(4)
C4	3497(2)	5372.9(14)	7280.7(12)	21.5(4)
C5	4459(2)	5062.4(14)	7017.2(12)	22.0(4)
C6	4771.4(19)	4256.4(13)	7065.3(11)	19.8(4)
C7	5672.6(19)	3773.2(13)	6811.7(12)	20.3(4)
C8	6562.2(19)	3981.3(14)	6471.1(12)	22.4(4)
C9	7318.6(19)	3380.2(14)	6268.5(12)	23.0(4)
C10	7116(2)	2558.3(15)	6396.6(12)	24.7(4)
C11	6221(2)	2323.9(14)	6727.6(12)	22.3(4)
C12	5492.5(19)	2955.1(13)	6968.3(11)	19.8(4)
C13	3100(2)	6232.2(15)	7184.0(13)	27.6(5)
C14	2059(3)	6467.1(19)	7524.5(19)	46.7(7)
C15	2601(4)	6048(2)	6331.5(18)	58.7(9)
C16	4232(3)	7055.4(19)	7568(2)	55.9(8)
C17	8367(2)	3591.0(16)	5936.1(13)	27.8(5)
C18	8380(3)	4477.2(19)	5774.2(17)	41.6(6)
C19	8202(3)	2797.5(19)	5186.1(15)	41.7(6)
C20	9643(2)	3714(2)	6521.4(16)	41.3(6)
C21	2516.8(19)	3584.4(14)	8044.6(12)	21.0(4)
C22	276(2)	3243.8(18)	8954.8(14)	33.3(5)
C23	657(14)	4074(9)	9669(8)	88(5)
C23A	870(18)	3846(19)	9749(9)	80(6)
C24	-942(8)	3091(10)	8372(6)	50(2)
C24A	-852(15)	3540(20)	8538(9)	51(4)

C25	6031(2)	1407.6(14)	6751.8(12)	24.5(4)
C26	6262(3)	-897.7(17)	6197.3(17)	48.5(7)
C27	6096(7)	-1423(3)	6685(3)	124(2)
C28	5447(3)	-1315(2)	5363.1(19)	59.5(9)
C29	5883(3)	4137.4(17)	9266.8(15)	41.3(6)
C30	7637(2)	3557.6(18)	10334.6(15)	37.6(6)
C31	4929(3)	3377.7(19)	10314.6(15)	42.0(6)
C32	7773(3)	1321(2)	9084(2)	55.4(8)
C33	6320(3)	1287(2)	10198.0(16)	49.5(7)
C34	5175(3)	83.7(18)	8559.0(17)	44.7(7)
C35	2541(3)	687(2)	5892.7(16)	47.7(7)
C36	423(3)	1308(2)	6429.5(18)	58.4(9)
C37	539(3)	-698.8(19)	5936.7(17)	49.9(7)
C38	2536(3)	850.0(18)	9007.1(15)	39.8(6)
C39	1721(3)	-1004.9(17)	7697.6(18)	47.2(7)
C40	17(3)	308(2)	7810.2(19)	51.5(7)
C41	9243(5)	8728(3)	9192(3)	103.3(17)
C42	8839(4)	7701(3)	8885(2)	65.4(9)
C43	9628(3)	7182(3)	8629.4(18)	59.0(9)
C44	9236(3)	6202(3)	8334.2(18)	60.6(9)
C45	8096(3)	5789(3)	8310.2(18)	62.7(9)
C46	7291(3)	6321(3)	8568(2)	69.9(11)
C47	7663(3)	7251(3)	8840(2)	65.1(10)
C48	2131(3)	3001(2)	5404.9(16)	48.4(7)
C49	2366(2)	3195.5(16)	4735.2(14)	32.3(5)
C50	3542(2)	3681.0(16)	4804.1(14)	30.9(5)
C51	3767(2)	3848.9(17)	4189.5(16)	37.5(6)
C52	2828(3)	3520.7(17)	3485.9(16)	40.2(6)
C53	1661(3)	3042.4(19)	3411.4(16)	45.9(7)
C54	1433(3)	2888.6(19)	4028.2(16)	43.5(7)

Table B-20 Anisotropic Displacement Parameters (U_{ij} , Å² x10³) for **11**

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Yb1	26.41(5)	16.92(4)	22.01(5)	8.78(3)	9.07(3)	4.46(3)
Si1	28.8(3)	27.5(3)	23.6(3)	9.2(2)	7.2(2)	5.7(2)
Si2	37.7(4)	32.2(3)	34.6(4)	19.1(3)	12.4(3)	12.6(3)
Si3	36.0(4)	24.8(3)	31.1(3)	6.8(3)	2.0(3)	3.7(3)
Si4	37.1(4)	24.1(3)	40.8(4)	14.7(3)	14.0(3)	2.5(3)
N1	22.3(8)	16.8(8)	21.2(8)	7.8(7)	9.3(7)	5.8(6)
N2	29.0(9)	23.1(9)	30.1(10)	13.5(8)	15.8(8)	5.4(7)
N3	32.3(10)	27.7(9)	35.8(11)	17.2(8)	18.4(9)	7.3(8)
N4	27.8(9)	31.4(10)	30.1(10)	16.7(8)	15.5(8)	6.9(8)
N5	28.1(9)	30.5(9)	28.4(9)	17.2(8)	15.5(8)	9.5(8)
N6	41.1(11)	19.0(8)	28.3(10)	10.4(8)	14.0(8)	11.1(8)

N7	53.2(13)	21.4(9)	35.7(11)	14.3(8)	21.3(10)	16.9(9)
N8	56.1(14)	24.4(9)	36.9(11)	15.0(9)	24.0(10)	20.7(9)
N9	48.4(12)	26.3(9)	38.7(11)	15.7(9)	23.2(10)	18.8(9)
N10	29.4(9)	26.7(9)	25.1(9)	12.2(8)	10.1(8)	7.0(8)
N11	31.8(10)	17.9(8)	29.1(10)	8.4(7)	7.5(8)	3.6(7)
C1	21.1(9)	16.9(9)	18.1(9)	6.4(7)	5.7(8)	3.9(7)
C2	20.7(9)	20.8(9)	18.6(9)	7.7(8)	7.3(8)	4.4(8)
C3	22.9(10)	22.1(9)	21.1(10)	8.6(8)	10.3(8)	8.2(8)
C4	25.1(10)	20.0(9)	21.3(10)	9.0(8)	7.6(8)	7.4(8)
C5	26.3(10)	20.2(9)	22.7(10)	9.8(8)	11.1(8)	4.2(8)
C6	21.2(9)	18.3(9)	20.2(9)	6.8(8)	7.8(8)	3.9(8)
C7	21.0(9)	18.9(9)	21.1(10)	7.4(8)	7.0(8)	4.2(8)
C8	22.3(10)	21.9(9)	23.2(10)	8.9(8)	7.6(8)	4.1(8)
C9	21.3(10)	26.1(10)	21.7(10)	8.5(8)	7.6(8)	5.5(8)
C10	25.5(10)	24.7(10)	26.0(11)	8.3(9)	10.8(9)	10.8(9)
C11	25.6(10)	21.2(9)	21.5(10)	8.9(8)	7.7(8)	7.2(8)
C12	21.4(9)	18.5(9)	18.7(9)	6.9(8)	5.3(8)	4.3(7)
C13	35.2(12)	24.8(10)	34.4(12)	17.6(9)	18.4(10)	13.7(9)
C14	58.5(18)	39.6(14)	71(2)	35.0(14)	40.8(16)	29.7(13)
C15	86(2)	66(2)	48.8(18)	37.8(16)	26.1(17)	46.3(19)
C16	53.5(18)	30.4(13)	95(3)	30.4(16)	29.5(18)	15.0(13)
C17	24.5(11)	30.9(11)	32.2(12)	11.5(10)	15.1(9)	9.0(9)
C18	42.5(15)	45.1(15)	57.1(17)	28.6(13)	33.6(13)	15.3(12)
C19	48.7(16)	44.4(15)	36.8(14)	11.9(12)	26.2(12)	9.6(12)
C20	26.7(12)	54.0(16)	46.3(15)	20.2(13)	15.3(11)	8.7(11)
C21	22.0(10)	21.0(9)	20.3(10)	7.7(8)	7.9(8)	4.1(8)
C22	30.0(11)	45.0(13)	38.3(12)	23.4(11)	22.1(10)	10.3(10)
C23	77(7)	81(5)	74(5)	-19(4)	57(5)	-31(5)
C23A	37(5)	173(17)	27(4)	20(5)	23(3)	35(8)
C24	30(2)	82(6)	58(4)	43(4)	23(2)	20(4)
C24A	34(5)	100(12)	38(6)	33(7)	22(4)	35(7)
C25	29.9(11)	23.5(10)	22.6(10)	9.7(8)	8.9(9)	10.4(9)
C26	84(2)	26.4(12)	49.8(17)	15.7(12)	35.0(16)	30.7(14)
C27	275(8)	59(2)	111(4)	59(3)	117(5)	100(4)
C28	78(2)	30.1(14)	62(2)	2.3(14)	24.6(18)	17.3(15)
C29	47.4(15)	28.3(12)	37.8(14)	12.5(11)	-0.2(12)	2.0(11)
C30	35.4(13)	39.8(14)	33.8(13)	13.0(11)	7.1(11)	5.7(11)
C31	41.0(14)	44.0(15)	36.3(14)	6.7(12)	15.9(12)	9.1(12)
C32	45.0(17)	54.7(18)	80(2)	32.2(17)	25.4(16)	25.5(14)
C33	67(2)	45.2(16)	39.1(15)	26.8(13)	8.9(14)	11.0(14)
C34	63.1(19)	32.1(13)	44.9(16)	17.0(12)	22.1(14)	14.4(13)
C35	51.7(17)	50.7(16)	32.1(14)	17.7(13)	1.9(12)	0.7(13)
C36	67(2)	55.4(19)	45.3(17)	14.6(15)	2.4(15)	29.9(17)
C37	55.6(18)	35.2(14)	39.1(15)	1.2(12)	5.6(13)	-3.2(13)
C38	52.8(16)	35.6(13)	40.4(14)	21.4(12)	20.7(13)	10.6(12)
C39	56.4(17)	25.7(12)	57.8(18)	19.0(12)	14.4(14)	2.4(12)

C40	41.5(16)	51.3(17)	64(2)	23.4(15)	20.3(14)	4.6(13)
C41	127(4)	71(3)	109(4)	48(3)	23(3)	8(3)
C42	62(2)	81(3)	59(2)	35.4(19)	16.3(17)	15.5(19)
C43	38.6(16)	98(3)	47.6(18)	38.1(19)	12.4(14)	14.9(17)
C44	52.0(19)	91(3)	39.6(16)	21.5(17)	15.6(14)	25.8(19)
C45	59(2)	71(2)	38.7(17)	9.0(16)	3.2(15)	3.2(17)
C46	44.3(18)	98(3)	54(2)	17(2)	16.7(16)	1.5(19)
C47	42.3(17)	90(3)	65(2)	29(2)	21.1(16)	14.3(18)
C48	45.1(16)	53.9(17)	40.2(15)	14.0(13)	16.9(13)	-6.0(13)
C49	36.1(13)	26.1(11)	31.6(12)	7.9(10)	11.7(10)	2.6(10)
C50	31.0(12)	28.3(11)	31.2(12)	9.8(10)	8.6(10)	5.8(9)
C51	35.7(13)	34.7(13)	46.3(15)	17.6(12)	18.0(12)	6.0(11)
C52	55.1(16)	34.0(13)	36.7(14)	18.0(11)	18.0(12)	8.5(12)
C53	50.9(16)	42.9(15)	34.4(14)	16.0(12)	1.9(12)	-0.7(13)
C54	36.7(14)	42.1(15)	41.6(15)	13.8(12)	6.5(12)	-7.2(11)

Table B-21 Bond Lengths for **11**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Yb1	Si1	3.3952(7)	C2	C3	1.399(3)
Yb1	Si2	3.4276(7)	C2	C21	1.454(3)
Yb1	Si3	3.3287(7)	C3	C4	1.396(3)
Yb1	Si4	3.4870(7)	C4	C5	1.394(3)
Yb1	N1	2.3470(16)	C4	C13	1.535(3)
Yb1	N2	2.3851(19)	C5	C6	1.389(3)
Yb1	N6	2.3932(19)	C6	C7	1.441(3)
Yb1	N10	2.1885(19)	C7	C8	1.395(3)
Yb1	N11	2.2001(18)	C7	C12	1.420(3)
Si1	N10	1.7306(19)	C8	C9	1.388(3)
Si1	C29	1.877(3)	C9	C10	1.398(3)
Si1	C30	1.876(3)	C9	C17	1.534(3)
Si1	C31	1.865(3)	C10	C11	1.399(3)
Si2	N10	1.735(2)	C11	C12	1.414(3)
Si2	C32	1.877(3)	C11	C25	1.451(3)
Si2	C33	1.882(3)	C13	C14	1.520(3)
Si2	C34	1.880(3)	C13	C15	1.523(4)
Si3	N11	1.724(2)	C13	C16	1.522(4)
Si3	C35	1.880(3)	C17	C18	1.528(3)
Si3	C36	1.877(3)	C17	C19	1.533(3)
Si3	C37	1.869(3)	C17	C20	1.532(3)
Si4	N11	1.730(2)	C22	C23	1.484(10)
Si4	C38	1.886(3)	C22	C23A	1.446(17)
Si4	C39	1.880(3)	C22	C24	1.471(8)
Si4	C40	1.884(3)	C22	C24A	1.534(14)
N1	C1	1.402(3)	C26	C27	1.476(5)

N1	C12	1.404(3)	C26	C28	1.515(4)
N2	N3	1.333(2)	C41	C42	1.493(6)
N2	C21	1.354(3)	C42	C43	1.365(5)
N3	N4	1.301(3)	C42	C47	1.386(5)
N4	N5	1.334(2)	C43	C44	1.425(5)
N4	C22	1.484(3)	C44	C45	1.343(5)
N5	C21	1.336(3)	C45	C46	1.393(5)
N6	N7	1.334(2)	C46	C47	1.354(5)
N6	C25	1.351(3)	C48	C49	1.508(4)
N7	N8	1.304(3)	C49	C50	1.391(3)
N8	N9	1.326(3)	C49	C54	1.388(4)
N8	C26	1.492(3)	C50	C51	1.381(4)
N9	C25	1.342(3)	C51	C52	1.384(4)
C1	C2	1.413(3)	C52	C53	1.374(4)
C1	C6	1.419(3)	C53	C54	1.376(4)

Table B-22 Bond Angles for **11**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Si1	Yb1	Si2	51.928(17)	N4	N5	C21	101.80(17)
Si1	Yb1	Si4	110.276(17)	N7	N6	Yb1	121.47(15)
Si2	Yb1	Si4	87.367(18)	N7	N6	C25	106.94(18)
Si3	Yb1	Si1	157.830(18)	C25	N6	Yb1	131.59(14)
Si3	Yb1	Si2	128.844(17)	N8	N7	N6	105.04(18)
Si3	Yb1	Si4	51.479(18)	N7	N8	N9	115.34(18)
N1	Yb1	Si1	95.21(4)	N7	N8	C26	122.9(2)
N1	Yb1	Si2	128.41(4)	N9	N8	C26	121.7(2)
N1	Yb1	Si3	96.91(4)	N8	N9	C25	101.60(19)
N1	Yb1	Si4	144.22(4)	Si1	N10	Yb1	119.61(10)
N1	Yb1	N2	77.92(6)	Si1	N10	Si2	119.06(11)
N1	Yb1	N6	78.78(6)	Si2	N10	Yb1	121.32(10)
N2	Yb1	Si1	80.68(5)	Si3	N11	Yb1	115.53(10)
N2	Yb1	Si2	123.49(5)	Si3	N11	Si4	118.22(11)
N2	Yb1	Si3	83.79(5)	Si4	N11	Yb1	124.66(10)
N2	Yb1	Si4	81.80(4)	N1	C1	C2	130.72(18)
N2	Yb1	N6	154.05(6)	N1	C1	C6	112.48(18)
N6	Yb1	Si1	112.78(5)	C2	C1	C6	116.80(18)
N6	Yb1	Si2	80.47(5)	C1	C2	C21	123.16(18)
N6	Yb1	Si3	87.81(5)	C3	C2	C1	119.18(18)
N6	Yb1	Si4	111.64(5)	C3	C2	C21	117.66(18)
N10	Yb1	Si1	26.31(5)	C4	C3	C2	123.73(19)
N10	Yb1	Si2	25.62(5)	C3	C4	C13	122.42(19)
N10	Yb1	Si3	149.66(5)	C5	C4	C3	116.97(19)
N10	Yb1	Si4	99.65(5)	C5	C4	C13	120.58(18)
N10	Yb1	N1	113.40(6)	C6	C5	C4	120.68(19)

N10	Yb1	N2	102.92(7)	C1	C6	C7	105.77(17)
N10	Yb1	N6	96.71(7)	C5	C6	C1	122.55(19)
N10	Yb1	N11	122.21(7)	C5	C6	C7	131.62(19)
N11	Yb1	Si1	134.19(5)	C8	C7	C6	131.84(19)
N11	Yb1	Si2	105.22(5)	C8	C7	C12	122.68(19)
N11	Yb1	Si3	27.86(5)	C12	C7	C6	105.48(17)
N11	Yb1	Si4	24.08(5)	C9	C8	C7	120.35(19)
N11	Yb1	N1	124.18(6)	C8	C9	C10	117.26(19)
N11	Yb1	N2	85.47(7)	C8	C9	C17	123.12(19)
N11	Yb1	N6	98.35(7)	C10	C9	C17	119.60(19)
N10	Si1	Yb1	34.08(6)	C9	C10	C11	123.7(2)
N10	Si1	C29	112.34(11)	C10	C11	C12	119.04(19)
N10	Si1	C30	114.18(11)	C10	C11	C25	117.28(19)
N10	Si1	C31	111.42(11)	C12	C11	C25	123.52(19)
C29	Si1	Yb1	82.49(8)	N1	C12	C7	112.56(17)
C30	Si1	Yb1	140.60(9)	N1	C12	C11	130.61(18)
C30	Si1	C29	103.34(12)	C11	C12	C7	116.80(18)
C31	Si1	Yb1	107.60(9)	C14	C13	C4	112.37(18)
C31	Si1	C29	107.52(14)	C14	C13	C15	107.8(2)
C31	Si1	C30	107.51(12)	C14	C13	C16	108.6(2)
N10	Si2	Yb1	33.05(6)	C15	C13	C4	108.6(2)
N10	Si2	C32	111.43(12)	C16	C13	C4	110.0(2)
N10	Si2	C33	114.37(12)	C16	C13	C15	109.5(2)
N10	Si2	C34	111.99(12)	C18	C17	C9	112.28(19)
C32	Si2	Yb1	112.83(11)	C18	C17	C19	108.3(2)
C32	Si2	C33	108.00(16)	C18	C17	C20	107.8(2)
C32	Si2	C34	106.69(15)	C19	C17	C9	110.37(19)
C33	Si2	Yb1	135.60(11)	C20	C17	C9	108.50(19)
C34	Si2	Yb1	80.73(9)	C20	C17	C19	109.5(2)
C34	Si2	C33	103.82(13)	N2	C21	C2	124.63(19)
N11	Si3	Yb1	36.61(6)	N5	C21	N2	110.94(18)
N11	Si3	C35	111.35(11)	N5	C21	C2	124.44(19)
N11	Si3	C36	112.01(12)	N4	C22	C24A	111.3(6)
N11	Si3	C37	114.56(12)	C23	C22	N4	109.8(5)
C35	Si3	Yb1	80.59(9)	C23A	C22	N4	106.5(8)
C36	Si3	Yb1	103.76(10)	C23A	C22	C24A	113.5(10)
C36	Si3	C35	105.86(16)	C24	C22	N4	108.2(4)
C37	Si3	Yb1	144.85(11)	C24	C22	C23	118.1(6)
C37	Si3	C35	104.49(14)	N6	C25	C11	125.40(19)
C37	Si3	C36	107.95(15)	N9	C25	N6	111.08(19)
N11	Si4	Yb1	31.26(6)	N9	C25	C11	123.4(2)
N11	Si4	C38	112.80(11)	N8	C26	C28	107.7(2)
N11	Si4	C39	112.30(12)	C27	C26	N8	109.4(2)
N11	Si4	C40	113.65(12)	C27	C26	C28	117.3(3)
C38	Si4	Yb1	81.62(8)	C43	C42	C41	120.1(4)
C39	Si4	Yb1	122.57(10)	C43	C42	C47	118.4(4)

C39	Si4	C38	107.06(13)	C47	C42	C41	121.5(4)
C39	Si4	C40	105.81(14)	C42	C43	C44	119.8(3)
C40	Si4	Yb1	127.22(10)	C45	C44	C43	120.1(3)
C40	Si4	C38	104.59(14)	C44	C45	C46	119.9(4)
C1	N1	Yb1	128.78(13)	C47	C46	C45	119.7(3)
C1	N1	C12	103.68(16)	C46	C47	C42	122.0(4)
C12	N1	Yb1	126.80(13)	C50	C49	C48	120.7(2)
N3	N2	Yb1	118.58(13)	C54	C49	C48	121.7(2)
N3	N2	C21	107.03(18)	C54	C49	C50	117.6(2)
C21	N2	Yb1	133.99(14)	C51	C50	C49	121.0(2)
N4	N3	N2	105.24(17)	C50	C51	C52	120.4(2)
N3	N4	N5	114.99(18)	C53	C52	C51	119.1(2)
N3	N4	C22	121.88(19)	C52	C53	C54	120.3(3)
N5	N4	C22	123.09(19)	C53	C54	C49	121.6(2)

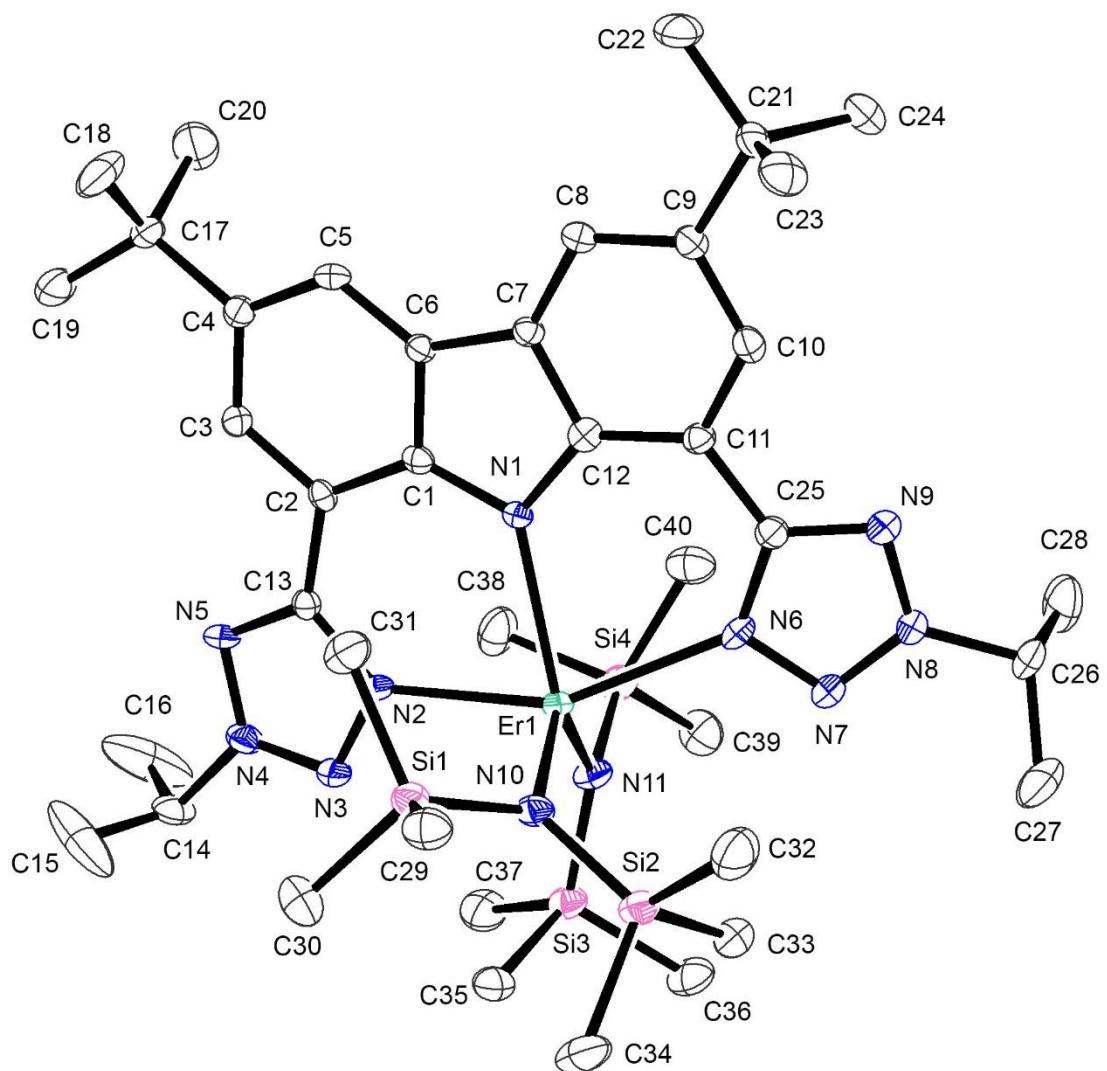


Figure B-6 Labelled ORTEP Drawing of 12

H atoms not shown

Disordered Toluenes of solvation not shown: C41-C54

Table B-23 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **12**

Atom	x	y	z	U(eq)
Er1	4140.2(2)	1824.1(2)	7885.8(2)	14.53(5)
Si1	5976.2(11)	3232.9(8)	9709.7(6)	19.9(3)
Si2	6183.2(11)	1273.8(8)	9226.9(6)	22.6(3)
Si3	1691.6(11)	235.7(8)	7942.9(6)	22.4(3)
Si4	1496.4(11)	497.3(8)	6473.8(6)	22.4(3)
N1	4586(3)	2901(2)	7317.6(16)	12.6(7)
N2	2782(3)	2833(2)	8198.4(17)	17.4(7)
N3	1965(3)	2621(2)	8543.6(18)	20.4(8)
N4	1272(3)	3221(2)	8576.2(18)	20.6(8)
N5	1569(3)	3837(2)	8278.1(17)	18.5(7)
N6	5359(3)	1094(2)	7114.0(18)	18.3(7)
N7	5387(3)	217(2)	6967.6(18)	21.2(8)
N8	6105(3)	43(2)	6526.9(18)	20.5(8)
N9	6559(3)	753(2)	6364.7(18)	21.5(8)
N10	5537(3)	2132(2)	9023.0(17)	18.3(7)
N11	2369(3)	704(2)	7405.7(17)	19.4(7)
C1	4154(3)	3704(2)	7368.0(19)	13.8(8)
C2	3216(3)	4028(2)	7664.5(19)	14.1(8)
C3	2921(4)	4847(2)	7606(2)	15.8(8)
C4	3517(3)	5366(2)	7276(2)	15.9(8)
C5	4483(3)	5055(3)	7015(2)	15.9(8)
C6	4803(3)	4251(2)	7060(2)	13.6(8)
C7	5693(3)	3772(2)	6802(2)	13.9(8)
C8	6593(3)	3982(3)	6462(2)	16.5(8)
C9	7347(3)	3383(3)	6257(2)	16.2(8)
C10	7148(3)	2563(3)	6384(2)	17.1(8)
C11	6250(3)	2329(2)	6711(2)	15.3(8)
C12	5518(3)	2954(3)	6957(2)	16.0(8)
C13	2529(3)	3579(2)	8038(2)	14.6(8)
C14	283(4)	3239(3)	8958(2)	24.4(10)
C15	783(5)	4005(4)	9721(3)	74(2)
C16	-919(5)	3273(5)	8442(3)	78(2)
C17	3113(4)	6219(3)	7181(2)	20.6(9)
C18	4264(4)	7052(3)	7564(3)	37.5(12)
C19	2074(4)	6457(3)	7526(3)	33.8(11)
C20	2610(5)	6028(3)	6313(2)	41.1(13)
C21	8406(4)	3600(3)	5923(2)	18.4(9)
C22	8413(4)	4489(3)	5769(3)	29.5(10)
C23	9687(4)	3716(3)	6510(2)	28.0(10)
C24	8235(4)	2803(3)	5170(2)	29.0(10)
C25	6077(4)	1414(3)	6743(2)	16.6(8)
C26	6320(4)	-886(3)	6188(2)	28.0(10)

C27	6166(7)	-1422(4)	6685(3)	68(2)
C28	5443(5)	-1337(3)	5364(3)	40.2(12)
C29	7656(4)	3577(3)	10353(2)	27.2(10)
C30	4933(4)	3383(3)	10331(2)	31.7(11)
C31	5885(4)	4132(3)	9277(2)	28.0(10)
C32	7802(4)	1334(3)	9127(3)	38.1(12)
C33	5193(4)	94(3)	8564(2)	29.1(10)
C34	6307(4)	1287(3)	10216(2)	35.0(12)
C35	2509(4)	839(3)	9003(2)	28.7(10)
C36	1697(4)	-1015(3)	7701(2)	30.9(11)
C37	-15(4)	297(3)	7812(3)	33.7(11)
C38	417(5)	1305(3)	6431(3)	37.1(12)
C39	509(4)	-705(3)	5928(2)	33.4(11)
C40	2544(4)	683(3)	5894(2)	31.2(11)
C41	2388(4)	3187(3)	4742(2)	22.2(9)
C42	1440(4)	2875(3)	4041(2)	29.1(10)
C43	1647(4)	3050(3)	3419(2)	33.9(11)
C44	2815(4)	3540(3)	3489(2)	27.5(10)
C45	3767(4)	3863(3)	4191(2)	26.6(10)
C46	3558(4)	3689(3)	4809(2)	24.6(10)
C47	2165(4)	2982(3)	5412(2)	32.4(11)
C48	8849(5)	7700(4)	8883(3)	49.3(14)
C49	9634(5)	7183(4)	8620(3)	43.7(13)
C50	9242(5)	6202(4)	8320(3)	44.5(13)
C51	8091(5)	5788(4)	8298(3)	46.0(14)
C52	7298(5)	6326(4)	8566(3)	52.5(15)
C53	7679(5)	7265(4)	8852(3)	48.2(14)
C54	9242(6)	8740(4)	9195(4)	75(2)

Table B-24 Anisotropic Displacement Parameters (U_{ij} , Å² x10³) for **12**

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Er1	17.83(9)	14.23(9)	14.45(9)	7.94(6)	6.54(7)	4.06(6)
Si1	21.7(6)	20.9(6)	17.1(5)	7.7(5)	5.3(5)	5.0(5)
Si2	25.6(6)	24.2(6)	22.4(6)	13.7(5)	7.5(5)	8.1(5)
Si3	24.1(6)	18.9(6)	24.9(6)	10.9(5)	7.7(5)	1.6(5)
Si4	24.4(6)	19.8(6)	19.7(6)	7.3(5)	2.4(5)	3.7(5)
N1	13.1(16)	13.7(16)	11.8(15)	5.5(13)	4.6(13)	2.3(13)
N2	21.4(18)	16.5(17)	19.6(17)	11.4(14)	9.5(15)	4.1(14)
N3	25.6(19)	20.5(18)	23.8(18)	13.0(15)	14.6(16)	8.3(15)
N4	21.1(18)	26.6(19)	21.8(18)	13.6(15)	12.5(15)	8.1(15)
N5	23.2(18)	20.3(18)	18.4(17)	12.4(14)	10.6(15)	4.7(14)
N6	21.6(18)	13.3(17)	22.2(17)	9.4(14)	6.0(15)	6.4(14)
N7	29(2)	16.5(17)	24.6(18)	10.9(15)	12.3(16)	9.2(15)
N8	27.4(19)	17.1(17)	22.8(18)	9.6(15)	12.2(16)	10.4(15)

N9	29(2)	17.8(18)	22.4(18)	9.9(15)	11.6(16)	8.9(15)
N10	20.0(18)	21.7(18)	13.9(16)	9.0(14)	3.3(14)	5.7(14)
N11	20.7(18)	16.5(17)	19.5(17)	9.1(14)	3.0(14)	0.6(14)
C1	14.9(19)	14.2(19)	9.6(17)	3.2(15)	2.5(15)	0.4(15)
C2	15(2)	15.1(19)	9.3(17)	2.1(15)	3.1(15)	3.2(16)
C3	18(2)	14.7(19)	14.6(18)	5.1(15)	5.5(16)	4.5(16)
C4	17(2)	15.7(19)	13.9(18)	5.2(16)	3.8(16)	4.1(16)
C5	17(2)	18(2)	13.8(18)	9.3(16)	4.4(16)	2.3(16)
C6	13.5(19)	15.2(19)	13.6(18)	6.2(15)	5.6(16)	3.8(15)
C7	13.8(19)	15.7(19)	12.9(18)	6.3(15)	3.9(15)	3.9(15)
C8	16(2)	18(2)	16.3(19)	7.7(16)	6.6(16)	3.0(16)
C9	16(2)	19(2)	14.9(19)	6.6(16)	5.7(16)	5.0(16)
C10	17(2)	21(2)	15.1(19)	6.2(16)	5.6(16)	7.4(17)
C11	17(2)	13.6(19)	14.9(19)	5.5(15)	4.6(16)	2.4(16)
C12	14(2)	16(2)	15.4(19)	5.2(16)	2.0(16)	2.2(15)
C13	16(2)	13.2(19)	12.7(18)	3.5(15)	4.5(16)	2.7(16)
C14	22(2)	34(2)	29(2)	20(2)	15.3(19)	8.1(19)
C15	56(4)	97(5)	42(3)	-10(3)	36(3)	-13(3)
C16	23(3)	186(8)	61(4)	82(5)	23(3)	37(4)
C17	26(2)	19(2)	26(2)	13.4(18)	13.4(19)	10.3(18)
C18	40(3)	21(2)	60(3)	23(2)	19(3)	10(2)
C19	43(3)	32(3)	49(3)	27(2)	29(2)	23(2)
C20	58(3)	50(3)	29(3)	23(2)	16(2)	32(3)
C21	17(2)	23(2)	20(2)	10.1(17)	9.2(17)	8.8(17)
C22	29(2)	34(3)	41(3)	25(2)	21(2)	10(2)
C23	19(2)	36(3)	33(2)	16(2)	12(2)	6.7(19)
C24	35(3)	31(3)	27(2)	11(2)	20(2)	10(2)
C25	18(2)	16(2)	13.7(18)	5.1(16)	3.7(16)	3.7(16)
C26	40(3)	18(2)	39(3)	15(2)	21(2)	16(2)
C27	138(6)	37(3)	60(4)	31(3)	51(4)	52(4)
C28	50(3)	24(3)	37(3)	0(2)	12(2)	12(2)
C29	27(2)	28(2)	23(2)	10.6(19)	4.5(19)	1.8(19)
C30	32(3)	34(3)	26(2)	5(2)	12(2)	6(2)
C31	33(3)	22(2)	24(2)	9.0(18)	2(2)	3.6(19)
C32	38(3)	37(3)	51(3)	23(2)	19(2)	19(2)
C33	39(3)	25(2)	28(2)	13(2)	13(2)	13(2)
C34	45(3)	31(3)	32(3)	21(2)	6(2)	8(2)
C35	39(3)	25(2)	27(2)	13.3(19)	16(2)	6(2)
C36	37(3)	21(2)	35(3)	14(2)	9(2)	0(2)
C37	30(3)	33(3)	41(3)	17(2)	15(2)	3(2)
C38	47(3)	33(3)	28(2)	10(2)	3(2)	21(2)
C39	32(3)	31(3)	27(2)	5(2)	5(2)	2(2)
C40	34(3)	33(3)	24(2)	13(2)	5(2)	1(2)
C41	26(2)	20(2)	20(2)	6.3(17)	7.6(18)	2.9(18)
C42	24(2)	31(2)	28(2)	12(2)	5(2)	-2.8(19)
C43	37(3)	35(3)	23(2)	12(2)	-1(2)	2(2)

C44	41(3)	23(2)	24(2)	12.3(19)	14(2)	9(2)
C45	26(2)	25(2)	35(3)	15(2)	15(2)	7.7(19)
C46	27(2)	23(2)	21(2)	5.6(18)	5.5(19)	6.5(19)
C47	32(3)	37(3)	29(2)	13(2)	13(2)	0(2)
C48	44(3)	70(4)	43(3)	34(3)	11(3)	14(3)
C49	26(3)	79(4)	36(3)	30(3)	11(2)	19(3)
C50	38(3)	71(4)	28(3)	21(3)	9(2)	20(3)
C51	42(3)	53(3)	32(3)	9(2)	5(2)	4(3)
C52	30(3)	75(4)	41(3)	13(3)	11(3)	0(3)
C53	30(3)	69(4)	47(3)	22(3)	15(3)	11(3)
C54	82(5)	60(4)	80(5)	40(4)	12(4)	2(4)

Table B-25 Bond Lengths for **12**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Er1	Si4	3.3290(11)	C2	C13	1.445(5)
Er1	N1	2.368(3)	C3	C4	1.389(5)
Er1	N2	2.390(3)	C4	C5	1.388(5)
Er1	N6	2.401(3)	C4	C17	1.528(5)
Er1	N10	2.207(3)	C5	C6	1.388(5)
Er1	N11	2.226(3)	C6	C7	1.424(5)
Si1	N10	1.719(3)	C7	C8	1.395(5)
Si1	C29	1.864(4)	C7	C12	1.416(5)
Si1	C30	1.863(4)	C8	C9	1.380(5)
Si1	C31	1.869(4)	C9	C10	1.394(5)
Si2	N10	1.726(3)	C9	C21	1.539(5)
Si2	C32	1.864(5)	C10	C11	1.387(5)
Si2	C33	1.871(4)	C11	C12	1.408(5)
Si2	C34	1.877(4)	C11	C25	1.453(5)
Si3	N11	1.718(3)	C14	C15	1.479(6)
Si3	C35	1.868(4)	C14	C16	1.477(6)
Si3	C36	1.874(4)	C17	C18	1.536(6)
Si3	C37	1.883(4)	C17	C19	1.514(6)
Si4	N11	1.717(3)	C17	C20	1.541(5)
Si4	C38	1.877(4)	C21	C22	1.525(5)
Si4	C39	1.862(4)	C21	C23	1.531(5)
Si4	C40	1.875(4)	C21	C24	1.530(5)
N1	C1	1.400(5)	C26	C27	1.497(6)
N1	C12	1.403(5)	C26	C28	1.513(6)
N2	N3	1.330(4)	C41	C42	1.378(5)
N2	C13	1.357(5)	C41	C46	1.388(6)
N3	N4	1.298(4)	C41	C47	1.505(5)
N4	N5	1.327(4)	C42	C43	1.385(6)
N4	C14	1.478(5)	C43	C44	1.376(6)
N5	C13	1.337(5)	C44	C45	1.382(6)

N6	N7	1.325(4)	C45	C46	1.377(5)
N6	C25	1.356(5)	C48	C49	1.361(7)
N7	N8	1.306(4)	C48	C53	1.371(7)
N8	N9	1.329(4)	C48	C54	1.507(8)
N8	C26	1.478(5)	C49	C50	1.422(7)
N9	C25	1.332(5)	C50	C51	1.348(7)
C1	C2	1.398(5)	C51	C52	1.389(7)
C1	C6	1.418(5)	C52	C53	1.362(7)
C2	C3	1.408(5)			

Table B-26 Bond Angles for **12**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Er1	Si4	96.71(7)	N1	C1	C6	112.0(3)
N1	Er1	N2	77.20(10)	C2	C1	N1	130.4(3)
N1	Er1	N6	78.68(10)	C2	C1	C6	117.6(3)
N2	Er1	Si4	83.14(8)	C1	C2	C3	118.7(3)
N2	Er1	N6	153.46(10)	C1	C2	C13	124.1(3)
N6	Er1	Si4	88.86(8)	C3	C2	C13	117.2(3)
N10	Er1	Si4	149.66(8)	C4	C3	C2	124.0(4)
N10	Er1	N1	113.63(11)	C3	C4	C17	122.2(4)
N10	Er1	N2	102.44(11)	C5	C4	C3	116.6(3)
N10	Er1	N6	97.23(11)	C5	C4	C17	121.2(3)
N10	Er1	N11	121.98(11)	C6	C5	C4	121.3(3)
N11	Er1	Si4	27.97(8)	C1	C6	C7	106.3(3)
N11	Er1	N1	123.98(10)	C5	C6	C1	121.7(4)
N11	Er1	N2	84.83(11)	C5	C6	C7	131.9(3)
N11	Er1	N6	99.74(11)	C8	C7	C6	132.0(3)
N10	Si1	C29	114.14(18)	C8	C7	C12	122.3(4)
N10	Si1	C30	111.18(18)	C12	C7	C6	105.7(3)
N10	Si1	C31	112.47(17)	C9	C8	C7	120.4(4)
C29	Si1	C31	103.51(19)	C8	C9	C10	117.5(3)
C30	Si1	C29	107.8(2)	C8	C9	C21	122.9(3)
C30	Si1	C31	107.2(2)	C10	C9	C21	119.6(3)
N10	Si2	C32	111.65(19)	C11	C10	C9	123.4(4)
N10	Si2	C33	112.02(18)	C10	C11	C12	119.6(3)
N10	Si2	C34	114.14(19)	C10	C11	C25	116.9(4)
C32	Si2	C33	106.7(2)	C12	C11	C25	123.5(3)
C32	Si2	C34	107.6(2)	N1	C12	C7	112.3(3)
C33	Si2	C34	104.1(2)	N1	C12	C11	131.0(3)
N11	Si3	C35	112.95(17)	C11	C12	C7	116.7(3)
N11	Si3	C36	112.34(19)	N2	C13	C2	124.1(3)
N11	Si3	C37	113.63(18)	N5	C13	N2	110.6(3)
C35	Si3	C36	106.95(19)	N5	C13	C2	125.3(3)
C35	Si3	C37	104.3(2)	N4	C14	C15	108.5(4)

C36	Si3	C37	106.0(2)	C16	C14	N4	109.7(3)
N11	Si4	Er1	37.47(10)	C16	C14	C15	115.2(5)
N11	Si4	C38	111.76(19)	C4	C17	C18	109.8(3)
N11	Si4	C39	114.13(18)	C4	C17	C20	108.4(3)
N11	Si4	C40	111.63(18)	C18	C17	C20	108.8(4)
C38	Si4	Er1	103.70(15)	C19	C17	C4	112.9(3)
C39	Si4	Er1	145.02(15)	C19	C17	C18	108.7(4)
C39	Si4	C38	107.9(2)	C19	C17	C20	108.2(4)
C39	Si4	C40	105.2(2)	C22	C21	C9	111.9(3)
C40	Si4	Er1	79.85(13)	C22	C21	C23	108.5(3)
C40	Si4	C38	105.7(2)	C22	C21	C24	109.1(3)
C1	N1	Er1	128.9(2)	C23	C21	C9	108.2(3)
C1	N1	C12	103.7(3)	C24	C21	C9	110.0(3)
C12	N1	Er1	126.6(2)	C24	C21	C23	109.2(3)
N3	N2	Er1	118.4(2)	N6	C25	C11	125.9(4)
N3	N2	C13	106.8(3)	N9	C25	N6	110.6(3)
C13	N2	Er1	134.5(3)	N9	C25	C11	123.5(3)
N4	N3	N2	105.7(3)	N8	C26	C27	109.8(4)
N3	N4	N5	114.8(3)	N8	C26	C28	108.3(3)
N3	N4	C14	121.9(3)	C27	C26	C28	114.5(4)
N5	N4	C14	123.2(3)	C42	C41	C46	117.9(4)
N4	N5	C13	102.2(3)	C42	C41	C47	121.1(4)
N7	N6	Er1	121.3(2)	C46	C41	C47	121.0(4)
N7	N6	C25	107.3(3)	C41	C42	C43	121.3(4)
C25	N6	Er1	131.4(2)	C44	C43	C42	120.4(4)
N8	N7	N6	105.2(3)	C43	C44	C45	118.7(4)
N7	N8	N9	114.6(3)	C46	C45	C44	120.7(4)
N7	N8	C26	122.8(3)	C45	C46	C41	121.0(4)
N9	N8	C26	122.5(3)	C49	C48	C53	119.2(6)
N8	N9	C25	102.3(3)	C49	C48	C54	120.9(5)
Si1	N10	Er1	119.65(16)	C53	C48	C54	119.9(6)
Si1	N10	Si2	119.95(17)	C48	C49	C50	120.1(5)
Si2	N10	Er1	120.40(16)	C51	C50	C49	119.7(5)
Si3	N11	Er1	124.79(16)	C50	C51	C52	119.5(5)
Si4	N11	Er1	114.56(16)	C53	C52	C51	120.5(5)
Si4	N11	Si3	119.17(18)	C52	C53	C48	121.0(6)

Table B-27 Summary of Crystallographic Data for **17** and **18**

	17•2.33 C₇H₈^{a,b}	18•2.5 C₇H₈^c
Emp. Formula	C _{75.31} H _{99.64} N ₁₈ OSiYb	C _{76.5} H ₁₀₁ ErN ₁₈ OSi
Formula wgt. (g/mol)	1474.21	1484.42
Temp. (K)	150.15	90.0
Crystal System	Triclinic	Triclinic
Space Group	P-1	P-1
a (Å)	13.0237(13)	13.0938(7)
b (Å)	15.8464(15)	15.8303(8)
c (Å)	18.8408(19)	18.8202(9)
α (°)	82.905(3)	82.643(3)
β (°)	88.389(3)	88.231(3)
γ (°)	87.902(3)	88.254(3)
Volume (Å³)	3854.9(7)	3865.7(3)
Z	2	2
Density (g/cm³)	1.270	1.275
Abs. coeff. μ (mm⁻¹)	1.580	1.156
F(000)	1539	1552
Crystal Size (mm)	0.11 x 0.035 x 0.02	0.25 x 0.24 x 0.08
Colour and habit	Yellow rod	Yellow block
Theta range (°)	3.908° ≤ 2θ ≤ 58.448°	3.598° ≤ 2θ ≤ 56.594°
Refl. Collected	59476	74280
Independent refl.	15886	19078
GooF (F²)	1.055	1.072
Final R [I > 2σ(I)]	0.0558	0.0443
Final wR2	0.1263	0.0977
R (all data)	0.0781	0.0595
wR2 (all data)	0.1417	0.1055
Max peak/hole (e/Å³)	2.222/-1.079	3.296/-0.817

^a Data collected at the Advanced Light Source (ALS) synchrotron facility ($\lambda = 0.7749$ Å), Lawrence Berkeley National Laboratory, Berkeley, CA. ^b SQUEEZED solvent is included in the formula which leads to fractional equivalents of solvent as noted. ^c Data collected on a Bruker Kappa X8-Apex II diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å) at the University of Notre Dame.

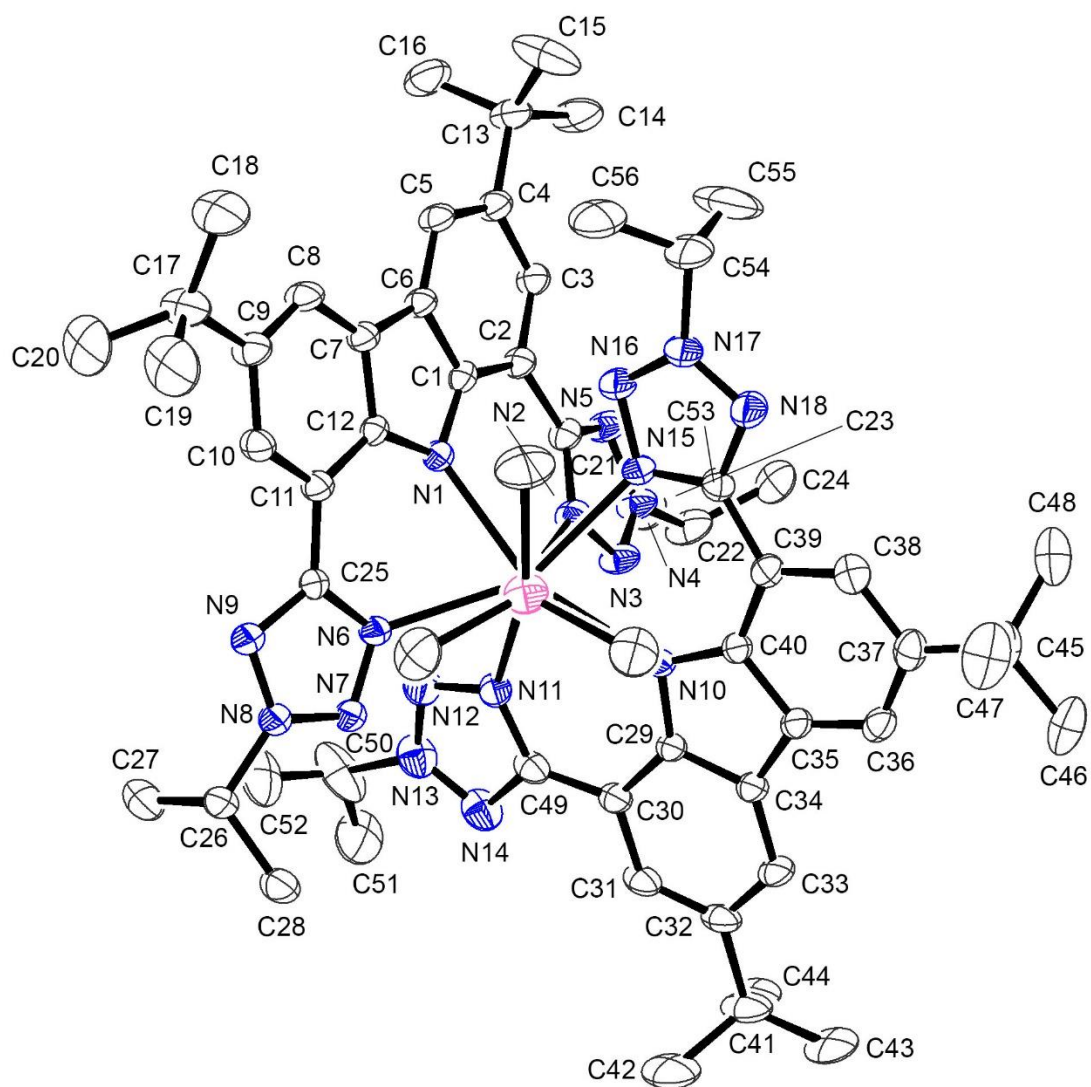


Figure B-7 Labelled ORTEP Drawing of 17

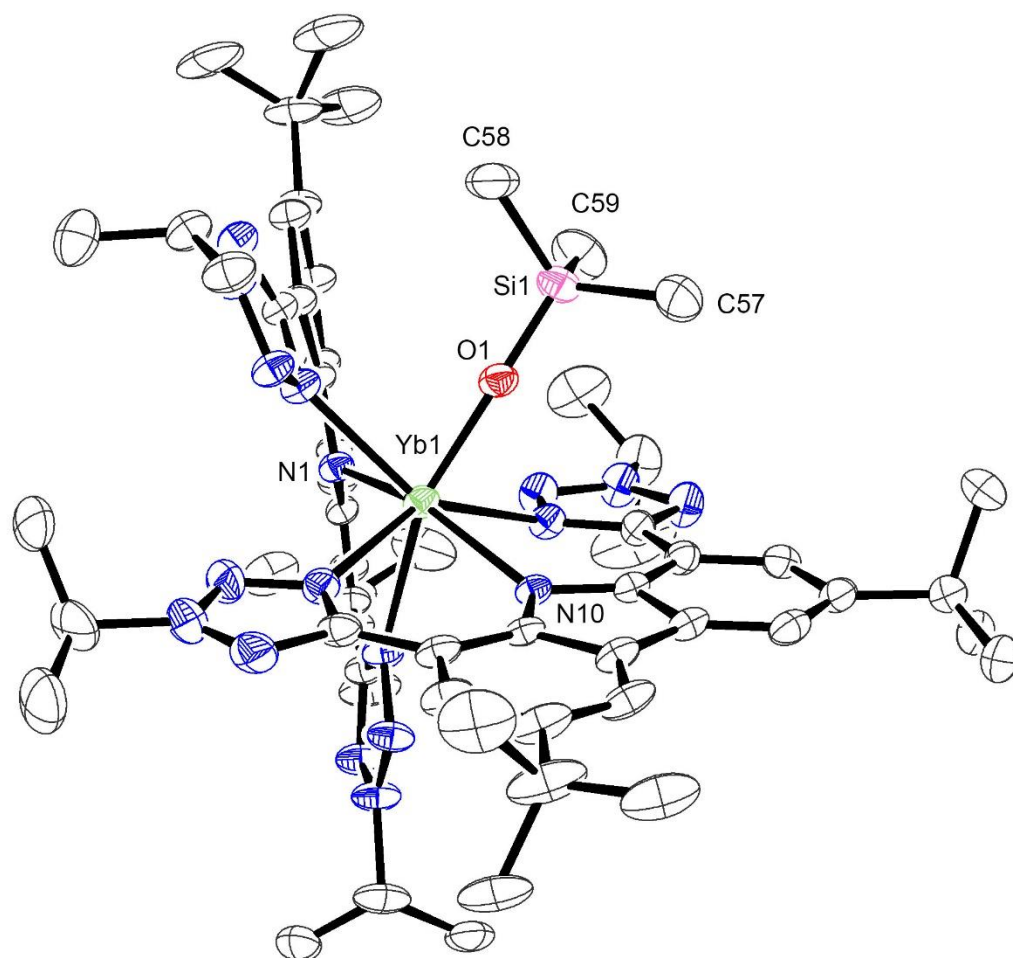


Figure B-8 Labelled ORTEP Drawing of **17** Alternate Perspective

H atoms not shown

Disordered tBu carbons C18A, C19A, C20A, C42A, C43A and C44A not shown

Disordered iPr carbons C23A, C24A, C51A and C52A not shown

Table B-28 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **17**

Atom	x	y	z	U(eq)
Yb1	7669.6(2)	6298.1(2)	3236.2(2)	40.50(8)
Si1	9946.8(14)	7526.6(10)	3391.0(10)	55.5(4)
O1	9016(3)	6905(2)	3353.4(19)	47.4(9)
N1	6384(3)	7291(2)	3496(2)	38.7(9)
N2	6101(4)	5941(3)	2624(2)	45.6(11)
N3	6014(4)	5189(3)	2375(3)	50.5(12)
N4	5164(4)	5262(3)	2022(3)	55.1(13)
N5	4660(4)	6016(3)	2010(3)	54.8(13)
N6	7744(4)	6345(3)	4531(2)	42.3(10)
N7	8204(4)	5755(3)	4982(2)	46.2(11)
N8	8418(4)	6132(3)	5540(2)	46.8(11)
N9	8110(4)	6948(3)	5486(2)	46.6(11)
N10	8573(3)	5386(2)	2517(2)	35.4(9)
N11	7256(4)	4889(3)	3796(2)	46.2(11)
N12	6560(4)	4807(3)	4326(3)	62.1(14)
N13	6618(5)	4010(4)	4592(3)	67.3(15)
N14	7323(5)	3547(3)	4273(3)	67.2(15)
N15	7793(4)	7197(2)	2094(2)	43.0(10)
N16	7336(4)	7969(3)	1990(3)	54.8(13)
N17	7825(4)	8368(3)	1448(3)	58.8(14)
N18	8583(4)	7921(3)	1174(3)	60.6(14)
C1	5634(4)	7668(3)	3043(3)	38.5(11)
C2	5074(4)	7315(3)	2538(3)	41.7(12)
C3	4340(4)	7815(3)	2144(3)	45.7(13)
C4	4132(4)	8673(3)	2221(3)	48.0(13)
C5	4686(4)	9019(3)	2734(3)	46.1(13)
C6	5424(4)	8531(3)	3141(3)	39.6(11)
C7	6082(4)	8709(3)	3695(3)	42.0(12)
C8	6258(5)	9437(3)	4015(3)	51.2(14)
C9	6937(5)	9408(3)	4567(3)	50.7(14)
C10	7403(4)	8620(3)	4816(3)	45.6(13)
C11	7244(4)	7880(3)	4506(3)	40.0(11)
C12	6611(4)	7931(3)	3908(3)	33.9(10)
C13	3337(5)	9229(4)	1780(4)	59.7(17)
C14	2863(6)	8752(5)	1222(4)	88(3)
C15	3855(8)	10001(5)	1380(5)	115(4)
C16	2491(6)	9516(5)	2280(4)	90(3)
C17	7196(6)	10198(4)	4915(4)	75(2)
C18	7110(50)	11000(30)	4390(30)	106(14)
C19	8282(11)	10204(15)	5186(11)	124(5)
C20	7062(19)	10065(15)	5719(6)	121(5)
C18A	6720(50)	11000(30)	4520(30)	108(14)

C19A	8363(10)	10268(11)	4811(8)	100(5)
C20A	6458(17)	10215(15)	5549(9)	131(6)
C21	5271(4)	6429(3)	2396(3)	44.1(12)
C22	4809(6)	4562(4)	1639(4)	71(2)
C23	3778(9)	4335(7)	1861(6)	67(3)
C24	4915(9)	4826(6)	807(6)	70(3)
C23A	3731(19)	4758(15)	1415(14)	75(4)
C24A	5552(18)	4263(14)	1280(13)	77(4)
C25	7698(4)	7071(3)	4835(3)	38.0(11)
C26	8886(5)	5688(4)	6191(3)	52.0(14)
C27	8065(6)	5500(5)	6761(4)	79(2)
C28	9507(5)	4908(4)	6024(3)	60.9(17)
C29	8859(4)	4536(3)	2686(3)	37.7(11)
C30	8509(5)	3923(3)	3245(3)	46.0(13)
C31	8926(5)	3093(3)	3298(3)	57.1(17)
C32	9690(6)	2827(4)	2838(3)	64.1(19)
C33	10051(5)	3427(4)	2304(3)	59.7(17)
C34	9650(5)	4261(3)	2229(3)	45.5(13)
C35	9890(4)	4997(3)	1739(3)	42.3(12)
C36	10591(4)	5125(4)	1175(3)	49.2(14)
C37	10659(5)	5908(4)	766(3)	51.2(14)
C38	9977(5)	6552(4)	946(3)	50.0(14)
C39	9245(4)	6454(3)	1507(3)	43.2(12)
C40	9198(4)	5658(3)	1936(3)	37.5(11)
C41	10070(6)	1886(4)	2921(4)	92(3)
C42	10340(20)	1619(16)	3706(7)	106(6)
C43	10980(11)	1714(8)	2429(9)	96(4)
C44	9155(10)	1334(6)	2755(8)	80(4)
C42A	9920(20)	1435(17)	3681(8)	117(7)
C43A	11261(9)	1946(9)	2916(11)	109(4)
C44A	10052(17)	1568(9)	2183(7)	101(4)
C45	11442(5)	6095(5)	154(4)	65.8(18)
C46	11918(6)	5270(5)	-90(4)	84(2)
C47	12290(6)	6627(6)	403(5)	94(3)
C48	10927(6)	6591(5)	-499(4)	81(2)
C49	7715(5)	4113(3)	3764(3)	49.2(14)
C50	5939(8)	3695(6)	5236(4)	111(4)
C51	5868(18)	2767(8)	5307(11)	113(5)
C52	6195(16)	4120(10)	5858(7)	101(5)
C51A	6659(12)	3190(11)	5744(8)	103(4)
C52A	5114(16)	3249(15)	4939(12)	145(6)
C53	8545(4)	7180(3)	1595(3)	44.3(12)
C54	7520(7)	9250(4)	1123(4)	83(2)
C55	6675(11)	9194(6)	623(6)	160(6)
C56	7260(9)	9776(5)	1700(5)	112(3)
C57	11076(6)	7199(5)	2836(4)	78(2)

C58	10357(6)	7519(5)	4341(4)	79(2)
C59	9535(7)	8645(4)	3036(5)	89(3)

Table B-29 Anisotropic Displacement Parameters (U_{ij} , Å² x10³) for **17**

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Yb1	50.99(15)	29.43(11)	41.59(14)	-7.39(8)	-1.44(10)	2.20(9)
Si1	58.9(11)	40.0(8)	69.0(11)	-8.7(7)	-3.9(9)	-10.9(7)
O1	59(2)	39.4(19)	45(2)	-	-3.5(18)	-4.9(17)
				10.7(16)		
N1	48(3)	32(2)	38(2)	-7.8(17)	-3.6(19)	0.2(18)
N2	57(3)	29(2)	53(3)	-	-8(2)	1.8(19)
				12.4(19)		
N3	52(3)	32(2)	70(3)	-14(2)	-18(2)	1(2)
N4	61(3)	35(2)	73(3)	-22(2)	-22(3)	5(2)
N5	61(3)	36(2)	71(3)	-19(2)	-19(3)	6(2)
N6	55(3)	34(2)	39(2)	-6.0(18)	-8(2)	6.5(19)
N7	60(3)	39(2)	41(2)	-	-8(2)	8(2)
				11.5(19)		
N8	61(3)	38(2)	42(2)	-8.0(19)	-7(2)	7(2)
N9	56(3)	40(2)	44(3)	-7.9(19)	-5(2)	9(2)
N10	45(2)	28.3(19)	34(2)	-6.1(16)	-6.2(18)	2.5(17)
N11	59(3)	36(2)	43(3)	-5.5(19)	1(2)	-5(2)
N12	74(4)	51(3)	60(3)	-2(2)	12(3)	-15(3)
N13	79(4)	58(3)	64(3)	3(3)	8(3)	-22(3)
N14	98(5)	41(3)	62(3)	1(2)	-4(3)	-21(3)
N15	54(3)	30(2)	45(2)	-4.3(18)	-1(2)	4.8(19)
N16	73(4)	33(2)	56(3)	0(2)	5(3)	8(2)
N17	83(4)	33(2)	56(3)	6(2)	8(3)	7(2)
N18	82(4)	38(2)	59(3)	-1(2)	18(3)	4(2)
C1	43(3)	35(2)	39(3)	-12(2)	1(2)	0(2)
C2	48(3)	32(2)	47(3)	-10(2)	-5(2)	-3(2)
C3	50(3)	41(3)	48(3)	-14(2)	-11(3)	1(2)
C4	52(3)	40(3)	54(3)	-13(2)	-10(3)	6(2)
C5	53(3)	30(2)	57(3)	-12(2)	-11(3)	6(2)
C6	44(3)	31(2)	45(3)	-10(2)	-6(2)	2(2)
C7	49(3)	34(2)	43(3)	-8(2)	-7(2)	4(2)
C8	68(4)	31(3)	57(3)	-12(2)	-21(3)	9(2)
C9	59(4)	36(3)	60(4)	-15(2)	-18(3)	1(2)
C10	56(4)	40(3)	43(3)	-8(2)	-16(3)	2(2)
C11	45(3)	35(2)	41(3)	-6(2)	-5(2)	1(2)
C12	38(3)	30(2)	36(3)	-8.9(19)	1(2)	-1.3(19)
C13	65(4)	44(3)	73(4)	-15(3)	-28(3)	13(3)
C14	94(6)	74(5)	102(6)	-33(4)	-67(5)	33(4)
C15	143(9)	76(5)	120(7)	38(5)	-79(7)	-26(5)

C16	89(6)	89(5)	98(6)	-35(5)	-37(5)	48(5)
C17	112(6)	37(3)	80(5)	-19(3)	-49(5)	-2(3)
C18	180(40)	39(6)	105(17)	-23(8)	-50(20)	-3(13)
C19	213(13)	73(6)	98(9)	-41(8)	-49(8)	-26(8)
C20	217(13)	71(7)	88(8)	-49(7)	-39(8)	-23(9)
C18A	190(40)	38(6)	106(17)	-30(8)	-70(20)	6(13)
C19A	191(13)	58(7)	61(9)	-28(8)	-46(9)	-37(8)
C20A	237(16)	80(9)	93(10)	-62(8)	-1(11)	-40(11)
C21	54(3)	31(2)	50(3)	-13(2)	-5(3)	-4(2)
C22	77(5)	38(3)	105(6)	-34(3)	-28(4)	3(3)
C23	74(6)	50(5)	81(7)	-21(5)	1(6)	-14(5)
C24	80(6)	56(5)	84(6)	-38(5)	-8(5)	-10(4)
C23A	82(8)	60(7)	89(8)	-33(6)	-9(7)	-9(7)
C24A	85(10)	62(8)	93(10)	-40(8)	-1(9)	-11(8)
C25	42(3)	39(3)	34(3)	-8(2)	-5(2)	4(2)
C26	61(4)	51(3)	44(3)	-8(3)	-14(3)	13(3)
C27	89(6)	93(5)	51(4)	9(4)	-3(4)	12(4)
C28	82(5)	50(3)	52(4)	-8(3)	-23(3)	8(3)
C29	52(3)	28(2)	35(3)	-	-11(2)	4(2)
				10.6(19)		
C30	68(4)	31(2)	41(3)	-10(2)	-15(3)	4(2)
C31	96(5)	28(3)	48(3)	-4(2)	-22(3)	5(3)
C32	104(6)	37(3)	53(4)	-13(3)	-34(4)	23(3)
C33	84(5)	47(3)	52(3)	-26(3)	-22(3)	28(3)
C34	63(4)	37(3)	38(3)	-12(2)	-11(3)	11(2)
C35	48(3)	43(3)	39(3)	-15(2)	-11(2)	10(2)
C36	46(3)	56(3)	48(3)	-22(3)	-9(3)	11(3)
C37	49(4)	64(4)	45(3)	-20(3)	-2(3)	-4(3)
C38	55(4)	47(3)	50(3)	-10(3)	-1(3)	-12(3)
C39	49(3)	38(3)	44(3)	-9(2)	0(2)	0(2)
C40	41(3)	38(3)	35(3)	-10(2)	-7(2)	2(2)
C41	143(8)	47(4)	92(6)	-32(4)	-63(5)	42(4)
C42	144(14)	40(9)	131(9)	1(6)	-31(8)	28(9)
C43	139(10)	36(5)	118(9)	-41(5)	-41(7)	36(6)
C44	127(11)	25(5)	94(9)	-27(5)	-51(7)	21(6)
C42A	146(17)	45(11)	150(10)	21(8)	-12(10)	35(10)
C43A	154(11)	51(6)	121(9)	-19(6)	-24(8)	42(7)
C44A	147(10)	49(6)	113(9)	-34(6)	-41(7)	27(7)
C45	55(4)	88(5)	61(4)	-31(4)	8(3)	-18(3)
C46	63(5)	111(6)	87(5)	-47(5)	26(4)	-11(4)
C47	64(5)	122(7)	107(6)	-47(5)	16(5)	-43(5)
C48	87(6)	100(6)	60(4)	-24(4)	22(4)	-28(5)
C49	72(4)	31(3)	45(3)	-2(2)	-13(3)	-8(3)
C50	153(9)	108(7)	67(5)	30(5)	-5(5)	-83(7)
C51	149(12)	81(9)	102(9)	11(7)	42(9)	-26(8)
C52	149(12)	85(8)	68(8)	2(7)	33(8)	-48(9)

C51A	140(11)	90(8)	77(8)	2(7)	37(8)	-44(8)
C52A	177(15)	118(11)	132(12)	19(10)	33(11)	-23(11)
C53	58(4)	33(3)	41(3)	-1(2)	3(3)	-3(2)
C54	115(7)	32(3)	95(6)	11(3)	17(5)	10(3)
C55	295(17)	64(5)	120(8)	-2(5)	-108(10)	59(8)
C56	179(10)	41(4)	115(7)	-7(4)	-23(7)	23(5)
C57	82(5)	66(4)	85(5)	-8(4)	5(4)	-16(4)
C58	75(5)	84(5)	85(5)	-37(4)	-16(4)	-12(4)
C59	94(6)	45(4)	128(7)	0(4)	-3(5)	-8(4)

Table B-30 Bond Lengths for **17**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Yb1	O1	2.061(4)	C9	C17	1.536(7)
Yb1	N1	2.338(4)	C10	C11	1.397(7)
Yb1	N2	2.491(5)	C11	C12	1.408(7)
Yb1	N6	2.455(4)	C11	C25	1.464(7)
Yb1	N10	2.361(4)	C13	C14	1.525(9)
Yb1	N11	2.421(4)	C13	C15	1.525(10)
Yb1	N15	2.434(4)	C13	C16	1.524(10)
Si1	O1	1.598(4)	C17	C18	1.513(10)
Si1	C57	1.876(8)	C17	C19	1.517(10)
Si1	C58	1.881(7)	C17	C20	1.509(10)
Si1	C59	1.880(7)	C17	C18A	1.512(10)
N1	C1	1.385(6)	C17	C19A	1.533(10)
N1	C12	1.396(6)	C17	C20A	1.515(10)
N2	N3	1.342(6)	C19	C20	1.86(3)
N2	C21	1.354(7)	C22	C23	1.441(13)
N3	N4	1.302(6)	C22	C24	1.574(13)
N4	N5	1.340(6)	C22	C23A	1.49(2)
N4	C22	1.491(7)	C22	C24A	1.27(2)
N5	C21	1.334(7)	C26	C27	1.505(9)
N6	N7	1.322(6)	C26	C28	1.513(8)
N6	C25	1.347(6)	C29	C30	1.419(7)
N7	N8	1.313(6)	C29	C34	1.415(7)
N8	N9	1.332(6)	C30	C31	1.397(7)
N8	C26	1.473(7)	C30	C49	1.453(8)
N9	C25	1.341(6)	C31	C32	1.390(9)
N10	C29	1.385(6)	C32	C33	1.381(10)
N10	C40	1.381(6)	C32	C41	1.544(8)
N11	N12	1.327(7)	C33	C34	1.395(7)
N11	C49	1.356(7)	C34	C35	1.433(8)
N12	N13	1.301(7)	C35	C36	1.382(8)
N13	N14	1.330(8)	C35	C40	1.434(7)
N13	C50	1.526(9)	C36	C37	1.381(8)

N14	C49	1.334(7)	C37	C38	1.395(8)
N15	N16	1.335(6)	C37	C45	1.528(9)
N15	C53	1.341(7)	C38	C39	1.402(8)
N16	N17	1.296(7)	C39	C40	1.413(7)
N17	N18	1.324(7)	C39	C53	1.464(7)
N17	C54	1.499(7)	C41	C42	1.536(9)
N18	C53	1.335(7)	C41	C43	1.521(9)
C1	C2	1.397(7)	C41	C44	1.565(9)
C1	C6	1.418(6)	C41	C42A	1.531(9)
C2	C3	1.390(7)	C41	C43A	1.556(9)
C2	C21	1.474(7)	C41	C44A	1.537(9)
C3	C4	1.401(7)	C45	C46	1.541(10)
C4	C5	1.398(7)	C45	C47	1.531(9)
C4	C13	1.529(8)	C45	C48	1.532(10)
C5	C6	1.396(7)	C50	C51	1.467(11)
C6	C7	1.429(7)	C50	C52	1.474(11)
C7	C8	1.396(7)	C50	C51A	1.497(11)
C7	C12	1.410(7)	C50	C52A	1.468(12)
C8	C9	1.379(8)	C54	C55	1.480(13)
C9	C10	1.400(7)	C54	C56	1.475(11)

Table B-31 Bond Angles for **17**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Yb1	N1	103.91(14)	C15	C13	C4	109.5(6)
O1	Yb1	N2	156.65(15)	C15	C13	C14	107.3(7)
O1	Yb1	N6	76.27(15)	C16	C13	C4	109.0(5)
O1	Yb1	N10	89.25(14)	C16	C13	C14	109.2(6)
O1	Yb1	N11	125.65(15)	C16	C13	C15	110.0(7)
O1	Yb1	N15	79.05(15)	C18	C17	C9	112(3)
N1	Yb1	N2	73.54(14)	C18	C17	C19	104(3)
N1	Yb1	N6	74.74(14)	C19	C17	C9	115.4(9)
N1	Yb1	N10	155.37(14)	C20	C17	C9	112.5(9)
N1	Yb1	N11	110.42(15)	C20	C17	C18	131(3)
N1	Yb1	N15	83.79(14)	C20	C17	C19	75.9(12)
N6	Yb1	N2	123.64(15)	C18A	C17	C9	112(3)
N10	Yb1	N2	86.09(14)	C18A	C17	C19A	106(3)
N10	Yb1	N6	129.27(13)	C18A	C17	C20A	93(3)
N10	Yb1	N11	76.49(14)	C19A	C17	C9	104.7(7)
N10	Yb1	N15	78.31(13)	C20A	C17	C9	105.7(9)
N11	Yb1	N2	75.33(15)	C20A	C17	C19A	134.4(12)
N11	Yb1	N6	73.87(14)	C17	C19	C20	51.9(7)
N11	Yb1	N15	143.93(14)	C17	C20	C19	52.3(7)
N15	Yb1	N2	77.60(15)	N2	C21	C2	124.6(5)
N15	Yb1	N6	141.99(14)	N5	C21	N2	111.7(4)

O1	Si1	C57	110.8(3)	N5	C21	C2	123.7(5)
O1	Si1	C58	110.7(3)	N4	C22	C24	109.5(6)
O1	Si1	C59	109.8(3)	N4	C22	C23A	109.0(9)
C57	Si1	C58	108.9(4)	C23	C22	N4	111.2(7)
C57	Si1	C59	108.2(4)	C23	C22	C24	112.3(8)
C59	Si1	C58	108.4(4)	C24A	C22	N4	110.2(11)
Si1	O1	Yb1	169.8(2)	C24A	C22	C23A	128.2(15)
C1	N1	Yb1	127.3(3)	N6	C25	C11	124.7(4)
C1	N1	C12	103.6(4)	N9	C25	N6	110.5(4)
C12	N1	Yb1	119.7(3)	N9	C25	C11	124.8(4)
N3	N2	Yb1	122.0(3)	N8	C26	C27	109.4(5)
N3	N2	C21	106.6(4)	N8	C26	C28	110.8(5)
C21	N2	Yb1	130.9(3)	C27	C26	C28	113.7(6)
N4	N3	N2	105.1(4)	N10	C29	C30	130.5(5)
N3	N4	N5	115.2(4)	N10	C29	C34	113.1(4)
N3	N4	C22	121.7(5)	C34	C29	C30	116.4(4)
N5	N4	C22	123.0(5)	C29	C30	C49	122.9(4)
C21	N5	N4	101.4(4)	C31	C30	C29	119.3(5)
N7	N6	Yb1	124.3(3)	C31	C30	C49	117.8(5)
N7	N6	C25	107.5(4)	C32	C31	C30	123.7(6)
C25	N6	Yb1	123.6(3)	C31	C32	C41	119.9(6)
N8	N7	N6	105.7(4)	C33	C32	C31	117.2(5)
N7	N8	N9	113.8(4)	C33	C32	C41	122.9(6)
N7	N8	C26	123.6(4)	C32	C33	C34	120.9(6)
N9	N8	C26	122.5(4)	C29	C34	C35	105.4(4)
N8	N9	C25	102.4(4)	C33	C34	C29	122.5(5)
C29	N10	Yb1	128.6(3)	C33	C34	C35	132.2(6)
C40	N10	Yb1	124.6(3)	C34	C35	C40	105.0(5)
C40	N10	C29	104.0(4)	C36	C35	C34	132.4(5)
N12	N11	Yb1	119.3(3)	C36	C35	C40	122.6(5)
N12	N11	C49	107.4(5)	C37	C36	C35	121.2(5)
C49	N11	Yb1	132.4(4)	C36	C37	C38	116.7(5)
N13	N12	N11	105.5(5)	C36	C37	C45	123.5(6)
N12	N13	N14	114.3(5)	C38	C37	C45	119.8(6)
N12	N13	C50	119.6(7)	C37	C38	C39	124.4(5)
N14	N13	C50	126.0(6)	C38	C39	C40	118.7(5)
N13	N14	C49	102.7(5)	C38	C39	C53	117.4(5)
N16	N15	Yb1	122.0(3)	C40	C39	C53	123.9(5)
N16	N15	C53	106.8(4)	N10	C40	C35	112.5(4)
C53	N15	Yb1	127.1(3)	N10	C40	C39	131.1(4)
N17	N16	N15	105.2(4)	C39	C40	C35	116.4(5)
N16	N17	N18	115.0(4)	C32	C41	C44	108.0(6)
N16	N17	C54	122.9(5)	C32	C41	C43A	103.2(8)
N18	N17	C54	122.0(5)	C42	C41	C32	108.4(11)
N17	N18	C53	101.8(5)	C42	C41	C44	107.0(12)
N1	C1	C2	129.4(4)	C43	C41	C32	113.5(7)

N1	C1	C6	112.2(4)	C43	C41	C42	110.6(14)
C2	C1	C6	118.4(5)	C43	C41	C44	109.1(9)
C1	C2	C21	121.2(5)	C42A	C41	C32	113.2(12)
C3	C2	C1	119.5(4)	C42A	C41	C43A	98.2(14)
C3	C2	C21	119.2(5)	C42A	C41	C44A	132.3(13)
C2	C3	C4	123.2(5)	C44A	C41	C32	108.2(7)
C3	C4	C13	123.3(5)	C44A	C41	C43A	94.3(12)
C5	C4	C3	116.9(5)	C37	C45	C46	111.7(6)
C5	C4	C13	119.8(5)	C37	C45	C47	108.7(5)
C6	C5	C4	121.2(5)	C37	C45	C48	110.5(6)
C1	C6	C7	106.1(4)	C47	C45	C46	109.7(6)
C5	C6	C1	120.7(5)	C48	C45	C46	106.9(6)
C5	C6	C7	133.1(4)	C48	C45	C47	109.3(7)
C8	C7	C6	133.8(5)	N11	C49	C30	124.9(5)
C8	C7	C12	121.3(5)	N14	C49	N11	110.1(6)
C12	C7	C6	104.8(4)	N14	C49	C30	125.0(5)
C9	C8	C7	120.7(5)	C51	C50	N13	110.7(10)
C8	C9	C10	118.0(5)	C51	C50	C52	120.3(12)
C8	C9	C17	122.7(5)	C52	C50	N13	110.2(8)
C10	C9	C17	119.3(5)	C51A	C50	N13	104.5(9)
C11	C10	C9	122.7(5)	C52A	C50	N13	104.8(11)
C10	C11	C12	118.8(4)	C52A	C50	C51A	118.3(13)
C10	C11	C25	119.0(5)	N15	C53	C39	125.6(5)
C12	C11	C25	122.1(4)	N18	C53	N15	111.1(5)
N1	C12	C7	113.1(4)	N18	C53	C39	123.2(5)
N1	C12	C11	128.7(4)	C55	C54	N17	108.7(6)
C11	C12	C7	118.2(4)	C56	C54	N17	109.0(6)
C14	C13	C4	111.8(5)	C56	C54	C55	114.1(8)

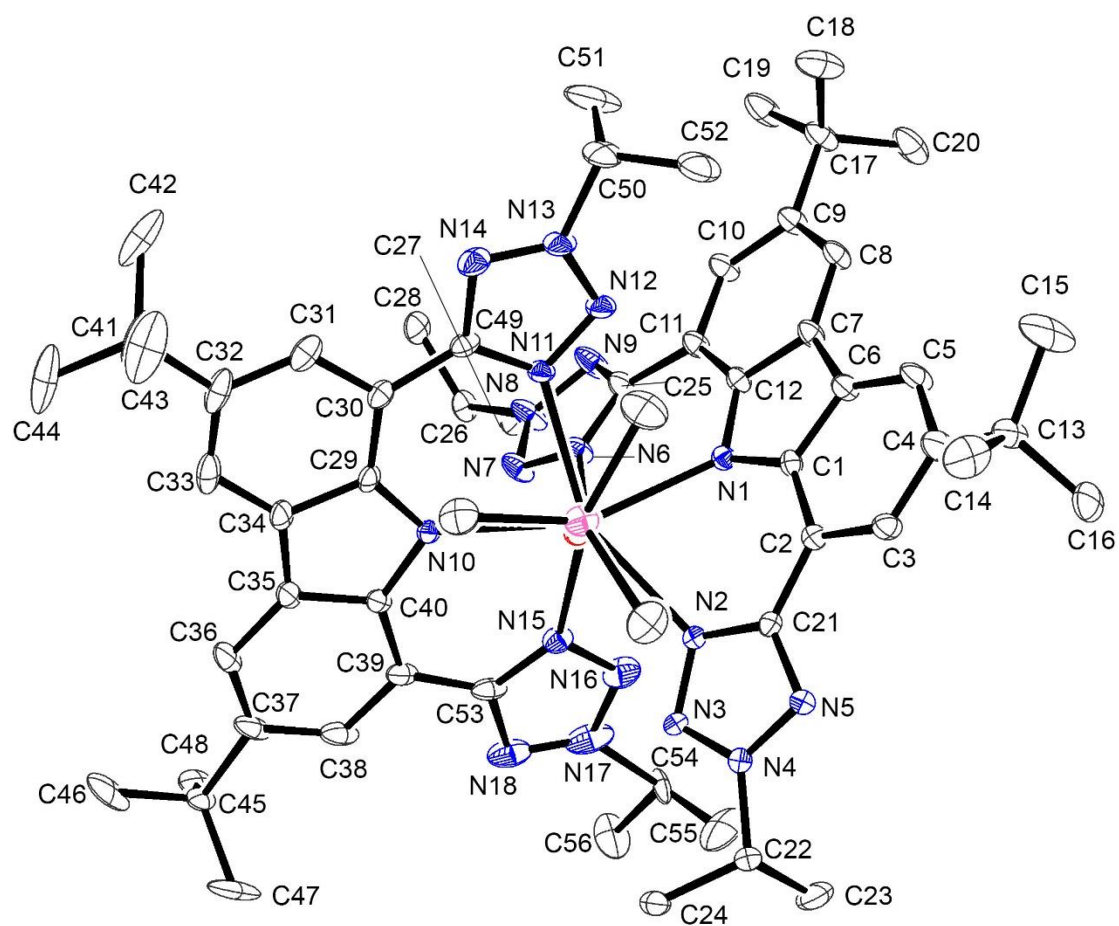


Figure B-9 Labelled ORTEP Drawing of **18**

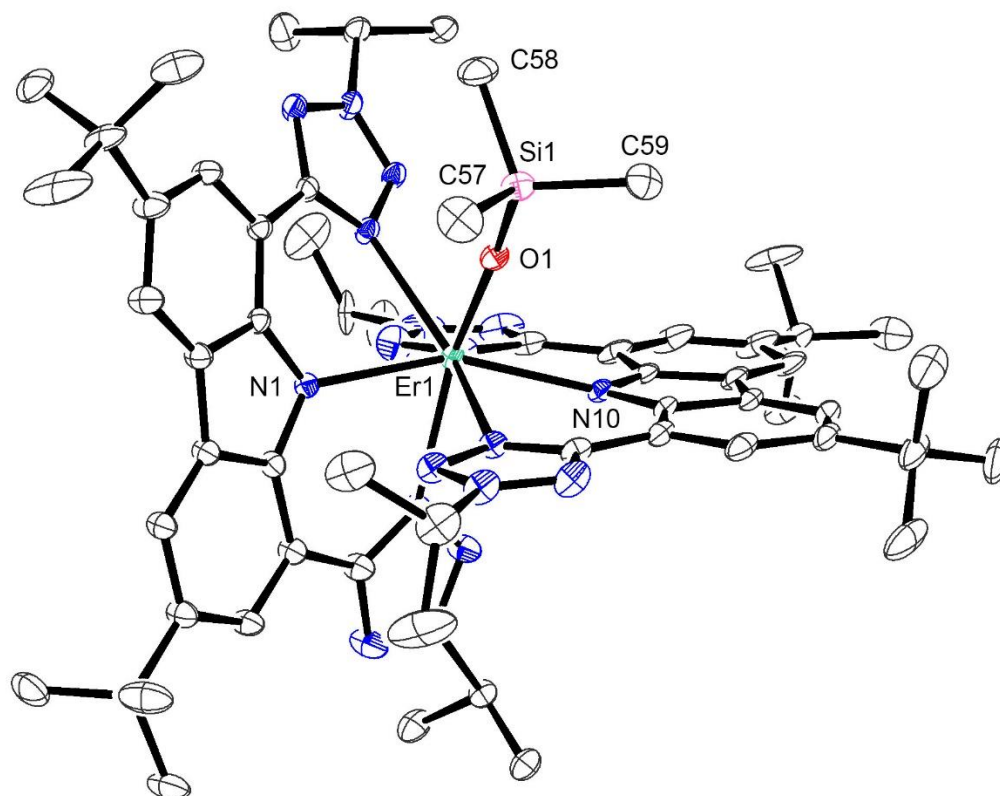


Figure B-10 Labelled ORTEP Drawing of **18** Alternate Perspective

H atoms not shown

Disordered toluenes of solvation not shown: C01-C07, C100-C142

Disordered tBu carbons C13B, C14B, C15B, C16B, C45B, C46B, C47B and C48B not shown

Disordered iPr carbons C26B, C27B, C28B, C54B, C55B and C56B not shown

Table B-32 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **18**

Atom	x	y	z	U(eq)
C12	4362(2)	2337(2)	6955.4(18)	25.5(7)
C40	1105(3)	5486(2)	7315.3(17)	28.4(7)
C11	4919(3)	2690(2)	7468.9(19)	29.5(7)
C39	1446(3)	6105(2)	6757.7(18)	37.2(9)
C10	5650(3)	2179(2)	7862(2)	33.8(8)
C38	1020(4)	6936(2)	6700(2)	55.3(13)
C9	5848(3)	1319(2)	7781(2)	34.5(8)
C37	251(5)	7193(3)	7163(2)	63.7(16)
C8	5291(3)	973(2)	7267(2)	32.5(8)
C36	-105(4)	6583(3)	7702(2)	54.5(13)
C7	4570(3)	1468(2)	6860.3(19)	29.1(7)
C35	304(3)	5746(2)	7781.1(18)	37.6(9)
C17	6629(3)	756(2)	8226(2)	41.3(9)
C45	65(6)	8198(4)	6993(4)	35.4(15)
C19	7116(4)	1233(3)	8792(3)	56.9(13)
C48	936(6)	8738(4)	7206(4)	48(2)
C20	7489(4)	465(3)	7727(3)	57.3(13)
C47	-230(11)	8455(6)	6206(5)	87(5)
C18	6105(4)	-25(3)	8626(3)	62.3(14)
C46	-884(7)	8357(5)	7477(5)	66(3)
C25	4736(3)	3576(2)	7607(2)	34.5(8)
C53	2240(3)	5927(2)	6233.7(19)	35.8(8)
C26	5124(11)	5415(9)	8471(6)	33(3)
C54	4091(9)	6283(7)	4726(6)	42(3)
C28	5070(6)	5145(4)	9273(4)	40.6(19)
C55	3795(12)	5911(8)	4108(6)	80(5)
C27	6207(6)	5654(5)	8193(4)	45(2)
C56	4170(10)	7247(6)	4661(7)	75(5)
C6	3909(3)	1292(2)	6299.3(19)	29.6(7)
C29	776(3)	4352(2)	8080.4(16)	25.9(7)
C5	3734(3)	564(2)	5982(2)	39.1(9)
C30	740(3)	3551(2)	8509.3(17)	29.3(7)
C4	3057(3)	597(2)	5420(2)	40.0(9)
C31	21(3)	3441(3)	9077.4(19)	37.9(9)
C3	2604(3)	1388(2)	5171.7(18)	31.1(7)
C32	-666(3)	4082(3)	9259(2)	43.7(10)
C2	2755(3)	2133(2)	5481.9(17)	26.0(7)
C33	-617(3)	4870(3)	8848(2)	42.4(10)
C1	3390(2)	2071(2)	6086.9(17)	24.1(6)
C34	83(3)	5007(2)	8275.5(18)	33.4(8)
C13	2718(8)	-200(7)	5128(5)	45(2)
C41	-1440(3)	3889(4)	9888(3)	65.2(16)

C15	3157(13)	-1009(8)	5553(8)	100(6)
C42	-903(4)	3388(4)	10534(2)	77.6(19)
C16	3093(7)	-120(5)	4349(4)	56(2)
C44	-1923(4)	4710(4)	10121(3)	85(2)
C14	1537(6)	-256(5)	5159(4)	62(2)
C43	-2288(4)	3340(5)	9644(3)	89(2)
C21	2311(2)	2943(2)	5154.0(16)	25.3(7)
C49	1435(3)	2827(2)	8415.5(17)	28.5(7)
C22	1149(3)	4329(2)	3786.3(18)	36.4(8)
C50	2473(4)	757(2)	8887(2)	51.0(11)
C24	509(3)	5104(2)	3960.4(19)	35.9(8)
C51	3337(6)	824(3)	9387(3)	101(3)
C23	1984(4)	4545(4)	3221(2)	64.5(15)
C52	2741(5)	223(3)	8309(3)	61.7(14)
C58	-366(4)	2448(3)	5669(2)	51.9(11)
C59	-1083(3)	2765(3)	7175(2)	45.7(10)
C57	452(4)	1332(3)	6964(3)	60.8(13)
C45B	-427(7)	8018(5)	7200(5)	35.4(15)
C48B	-38(10)	8584(7)	6525(7)	55(3)
C46B	-1598(7)	7957(6)	7142(6)	50(3)
C47B	-188(8)	8397(6)	7876(5)	50(3)
C13B	2996(17)	-193(15)	4967(11)	45(2)
C15B	2142(12)	-76(8)	4420(8)	61(4)
C16B	3980(10)	-402(8)	4565(7)	53(4)
C14B	2786(16)	-978(14)	5531(9)	52(5)
C26B	5358(13)	5485(12)	8245(8)	28(3)
C28B	4472(8)	5750(6)	8734(5)	40(2)
C27B	6297(7)	5194(6)	8650(5)	38(2)
C54B	3862(7)	6625(7)	4854(5)	40(2)
C56B	3188(6)	6970(5)	4236(4)	46(2)
C55B	4692(10)	6074(7)	4659(7)	81(4)
Er1	2326.2(2)	3719.9(2)	6760.4(2)	22.38(5)
N1	3620(2)	2713.2(17)	6498.6(14)	23.8(5)
N10	1396(2)	4635.1(16)	7489.3(13)	23.7(5)
N9	5355(3)	3985.7(19)	7999(2)	46.8(9)
N18	2614(3)	6523(2)	5727(2)	52.6(10)
N6	3919(2)	4071.6(17)	7378.4(16)	31.0(6)
N15	2717(2)	5161.7(19)	6199.2(16)	32.9(7)
N7	4012(2)	4819.8(18)	7631.6(19)	38.1(7)
N16	3418(3)	5272(2)	5673.9(19)	48.4(9)
N8	4863(3)	4742.5(19)	7991(2)	45.3(9)
N17	3325(3)	6080(3)	5413(2)	59.9(11)
N5	1909(2)	3063.4(19)	4499.9(15)	31.0(6)
N14	1397(3)	2079(2)	8842.0(16)	39.7(8)
N2	2274(2)	3673.8(17)	5458.1(14)	26.8(6)
N11	2200(2)	2812.7(17)	7913.5(14)	26.2(6)

N3	1820(2)	4269.8(19)	5000.0(14)	30.3(6)
N12	2653(2)	2040.9(18)	8019.3(15)	31.8(6)
N4	1612(2)	3886.0(19)	4441.5(15)	31.9(7)
N13	2156(3)	1631.9(18)	8565.9(16)	36.9(7)
O1	976.7(18)	3090.1(14)	6643.3(12)	28.0(5)
Si1	45.3(8)	2449.2(6)	6614.0(5)	33.0(2)
C122	5407(5)	1952(4)	10671(4)	50(3)
C123	4399(5)	2371(3)	10446(3)	35(3)
C124	4289(5)	2825(4)	9761(3)	39(2)
C125	3362(6)	3229(4)	9556(3)	41(3)
C126	2523(5)	3185(4)	10035(4)	46(3)
C127	2618(5)	2732(4)	10718(3)	43(2)
C128	3549(5)	2330(3)	10919(2)	36(2)
C129	5940(20)	7510(30)	6438(16)	66(4)
C130	5024(14)	7648(13)	6913(9)	54(4)
C131	4253(18)	7061(11)	7057(11)	60.7(17)
C132	3428(16)	7230(13)	7504(12)	61(5)
C133	3374(14)	7986(14)	7809(11)	67(6)
C134	4145(18)	8572(11)	7665(12)	58(5)
C142	4970(15)	8404(12)	7218(12)	55.2(16)
C100	3047(6)	7600(6)	7796(5)	143(6)
C101	4013(5)	7651(4)	7338(3)	63.3(18)
C102	4624(5)	8370(4)	7284(3)	55.2(16)
C103	5532(5)	8412(4)	6874(3)	52(2)
C104	5846(5)	7731(4)	6507(4)	59(2)
C105	5244(6)	7012(4)	6554(5)	61.4(16)
C106	4337(5)	6975(4)	6965(4)	60.7(17)
C107	2258(8)	2479(7)	11019(6)	66(3)
C108	3167(8)	2647(5)	10531(5)	39(2)
C109	3075(9)	3079(6)	9830(5)	36(2)
C110	3898(8)	3202(6)	9383(5)	39(2)
C111	4852(7)	2915(5)	9591(4)	39(2)
C112	4986(8)	2489(5)	10281(5)	41(2)
C113	4136(9)	2375(5)	10732(5)	38(2)
C115	5420(30)	6367(16)	6174(14)	46(4)
C116	5150(30)	7120(20)	6570(30)	61.4(16)
C121	4200(20)	7180(20)	6910(20)	60.7(17)
C120	4000(30)	7820(30)	7340(20)	63.3(18)
C119	4740(30)	8400(20)	7433(19)	55.2(16)
C118	5690(30)	8340(20)	7089(17)	46(4)
C117	5900(20)	7710(20)	6660(20)	66(4)
C07	576(18)	-1222(11)	9711(10)	132(8)
C01	254(7)	-531(5)	10105(4)	62(3)
C02	-155(7)	184(6)	9693(3)	66(3)
C03	-476(6)	892(4)	10016(3)	63(3)
C04	-387(5)	885(4)	10751(3)	60(2)

C05	22(5)	170(4)	11163(2)	45.6(18)
C06	343(5)	-538(4)	10840(4)	59(2)

Table B-33 Anisotropic Displacement Parameters (U_{ij} , Å² x10³) for **18**

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C12	24.1(16)	19.9(15)	33.1(17)	-4.8(13)	-1.9(13)	-0.9(12)
C40	43(2)	22.0(16)	22.0(15)	-9.9(12)	-12.3(14)	5.4(14)
C11	31.5(18)	19.0(16)	39.0(19)	-6.2(14)	-7.3(15)	-1.2(13)
C39	68(3)	19.3(16)	25.5(17)	-5.8(13)	-18.0(17)	2.7(16)
C10	37(2)	21.0(16)	45(2)	-8.2(15)	-16.7(16)	-0.2(14)
C38	111(4)	21.6(18)	36(2)	-7.7(16)	-33(2)	13(2)
C9	36(2)	24.9(17)	44(2)	-6.3(15)	-13.3(16)	2.6(15)
C37	122(4)	33(2)	41(2)	-21.4(19)	-46(3)	40(3)
C8	34.4(19)	19.7(16)	45(2)	-9.6(14)	-12.9(16)	3.9(14)
C36	78(3)	52(3)	39(2)	-33(2)	-32(2)	40(2)
C7	29.6(18)	19.9(16)	39.3(19)	-8.2(14)	-8.6(14)	0.6(13)
C35	52(2)	39(2)	24.8(17)	-17.2(15)	-15.0(16)	18.9(17)
C17	43(2)	28.2(19)	55(2)	-8.9(17)	-26.3(19)	5.1(16)
C45	61(5)	14(3)	31(4)	-3(3)	-9(3)	8(3)
C19	62(3)	38(2)	74(3)	-18(2)	-45(3)	16(2)
C48	85(6)	18(3)	41(4)	-8(3)	-19(4)	9(3)
C20	49(3)	46(3)	81(3)	-18(2)	-29(2)	20(2)
C47	176(13)	24(4)	65(6)	-16(4)	-87(8)	35(6)
C18	77(3)	41(2)	68(3)	9(2)	-40(3)	-8(2)
C46	84(7)	22(4)	99(7)	-27(4)	-43(6)	25(4)
C25	37(2)	20.4(16)	48(2)	-8.0(15)	-12.5(16)	-1.8(14)
C53	56(2)	21.1(17)	29.9(17)	4.1(13)	-16.2(17)	-10.6(16)
C26	36(7)	24(5)	44(7)	-18(5)	-5(5)	-6(4)
C54	45(7)	19(5)	57(6)	1(4)	37(5)	5(4)
C28	52(4)	32(4)	42(4)	-19(3)	-2(3)	-4(3)
C55	125(12)	65(8)	46(6)	5(5)	28(7)	-40(8)
C27	55(5)	38(4)	45(4)	-16(4)	2(4)	-16(4)
C56	89(9)	28(5)	101(10)	11(5)	51(8)	-11(5)
C6	31.2(18)	24.1(16)	34.1(18)	-5.0(14)	-7.0(14)	2.7(14)
C29	29.2(17)	31.7(17)	18.6(14)	-10.7(12)	-1.6(12)	0.0(13)
C5	52(2)	19.8(17)	48(2)	-8.3(15)	-22.0(18)	7.5(16)
C30	34.6(19)	32.8(18)	22.1(15)	-8.5(13)	0.5(13)	-5.1(14)
C4	52(2)	25.4(18)	46(2)	-10.7(16)	-19.2(18)	-0.5(16)
C31	40(2)	49(2)	27.5(17)	-13.3(16)	2.4(15)	-19.0(17)
C3	35.9(19)	28.9(18)	29.3(17)	-4.3(14)	-10.5(14)	0.9(14)
C32	28.0(19)	76(3)	34(2)	-31(2)	6.7(15)	-17.1(19)
C2	27.7(17)	24.4(16)	25.8(16)	-3.5(12)	-1.2(13)	0.6(13)
C33	31(2)	66(3)	38(2)	-34(2)	-4.0(16)	4.0(18)
C1	25.7(16)	20.2(15)	27.2(16)	-6.7(12)	0.7(12)	-0.8(12)

C34	35.7(19)	43(2)	24.3(16)	-17.5(15)	-8.2(14)	9.9(16)
C13	76(6)	20.6(19)	41(5)	-10(3)	-27(4)	1(4)
C41	39(2)	116(4)	53(3)	-53(3)	21(2)	-37(3)
C15	190(15)	18(4)	101(9)	-22(4)	-94(10)	9(7)
C42	73(4)	133(5)	35(2)	-33(3)	26(2)	-60(4)
C16	77(6)	43(4)	53(4)	-28(3)	-19(4)	12(4)
C44	40(3)	147(6)	85(4)	-82(4)	31(3)	-29(3)
C14	88(5)	43(4)	58(5)	-13(3)	-18(4)	-33(4)
C43	50(3)	145(6)	89(4)	-74(4)	28(3)	-59(3)
C21	25.6(16)	29.3(17)	20.4(15)	-2.8(12)	2.3(12)	2.2(13)
C49	36.9(19)	26.3(17)	21.8(15)	0.4(13)	-0.6(13)	-9.5(14)
C22	46(2)	40(2)	22.9(16)	-4.0(14)	-7.4(15)	14.9(17)
C50	82(3)	19.3(18)	49(2)	10.1(17)	-3(2)	-4.7(19)
C24	49(2)	29.3(18)	29.4(18)	-1.5(14)	-10.1(16)	7.6(16)
C51	195(8)	35(3)	74(4)	1(3)	-77(5)	23(4)
C23	62(3)	100(4)	24(2)	10(2)	4.5(19)	29(3)
C52	100(4)	26(2)	58(3)	1.7(19)	-22(3)	4(2)
C58	52(3)	58(3)	50(2)	-19(2)	-12(2)	-16(2)
C59	40(2)	47(2)	48(2)	1.5(19)	3.6(18)	-12.6(18)
C57	69(3)	30(2)	80(4)	7(2)	-2(3)	-11(2)
C45B	61(5)	14(3)	31(4)	-3(3)	-9(3)	8(3)
C48B	63(8)	31(6)	71(9)	-4(6)	-6(7)	17(5)
C46B	57(6)	41(5)	54(6)	-22(5)	-11(5)	21(5)
C47B	58(6)	33(5)	63(6)	-24(4)	-7(5)	11(4)
C13B	76(6)	20.6(19)	41(5)	-10(3)	-27(4)	1(4)
C15B	73(10)	50(7)	67(9)	-32(7)	-34(7)	0(7)
C16B	59(8)	51(8)	55(7)	-32(6)	2(6)	0(6)
C14B	78(12)	53(10)	28(7)	-7(6)	7(8)	-41(9)
C26B	35(9)	20(5)	29(7)	-7(5)	1(5)	-5(5)
C28B	47(6)	32(5)	45(5)	-18(4)	1(4)	-1(4)
C27B	42(5)	30(5)	46(6)	-17(4)	-11(4)	-4(4)
C54B	36(5)	40(6)	42(5)	2(4)	15(3)	-1(4)
C56B	39(4)	60(5)	35(4)	13(3)	5(3)	-8(4)
C55B	76(8)	66(7)	87(8)	35(6)	46(7)	2(6)
Er1	27.50(8)	18.45(7)	20.83(7)	-1.93(5)	1.73(5)	0.29(5)
N1	23.9(14)	22.7(13)	24.8(13)	-3.0(10)	-0.4(10)	-0.7(11)
N10	32.4(15)	19.8(13)	19.6(12)	-5.2(10)	-3.8(11)	1.4(11)
N9	48(2)	22.0(15)	74(2)	-14.6(15)	-29.7(18)	5.8(14)
N18	79(3)	34.3(19)	43(2)	9.7(16)	-16(2)	-24.5(19)
N6	36.8(16)	15.6(13)	41.6(17)	-5.7(12)	-9.1(13)	-0.4(11)
N15	39.2(17)	28.1(15)	30.4(15)	1.4(12)	1.5(13)	-9.6(13)
N7	41.1(18)	18.9(14)	56(2)	-9.1(13)	-17.8(15)	0.7(13)
N16	48(2)	50(2)	42.7(19)	11.0(16)	10.2(16)	-16.6(17)
N8	48(2)	21.3(15)	71(2)	-14.3(15)	-34.0(18)	3.8(14)
N17	71(3)	59(3)	45(2)	20.8(19)	-8(2)	-38(2)
N5	36.2(16)	30.6(15)	25.1(14)	-2.2(11)	-1.8(12)	9.7(12)

N14	59(2)	28.3(16)	30.3(16)	1.6(13)	6.3(15)	-10.2(15)
N2	35.3(16)	24.4(14)	20.1(13)	-2.0(10)	0.1(11)	5.7(12)
N11	33.7(15)	19.7(13)	24.2(13)	1.9(10)	-2.3(11)	-0.7(11)
N3	39.5(17)	32.9(16)	17.3(12)	-0.9(11)	-0.1(11)	9.7(13)
N12	43.7(18)	22.0(14)	28.1(14)	3.2(11)	-2.5(13)	-1.2(12)
N4	41.4(17)	30.8(15)	22.7(14)	-3.5(11)	0.4(12)	11.3(13)
N13	58(2)	19.6(14)	31.5(16)	4.7(12)	-1.0(14)	-5.0(14)
O1	34.6(13)	23.6(12)	26.6(11)	-4.6(9)	-1.3(10)	-4.3(10)
Si1	39.0(6)	25.1(5)	35.2(5)	-1.8(4)	-3.5(4)	-10.5(4)
C122	53(6)	45(5)	52(6)	-2(4)	-9(4)	-6(4)
C123	32(6)	35(5)	40(6)	-11(5)	5(5)	-11(4)
C124	45(6)	35(5)	37(5)	1(4)	2(4)	-19(4)
C125	58(10)	33(5)	33(7)	1(5)	-3(6)	-8(6)
C126	55(7)	40(5)	46(6)	-12(4)	-7(5)	-8(5)
C127	45(7)	44(6)	41(6)	-11(4)	10(5)	-7(5)
C128	46(6)	33(5)	30(5)	-3(4)	6(4)	-5(4)
C129	85(8)	66(8)	47(10)	-13(7)	-1(7)	2(6)
C130	73(8)	47(7)	41(8)	-3(6)	-11(7)	2(6)
C131	90(4)	48(4)	44(3)	0(3)	-22(2)	-15(3)
C132	73(10)	60(10)	53(11)	-8(9)	-23(8)	-19(8)
C133	72(11)	67(11)	63(13)	-14(10)	3(10)	-18(9)
C134	69(10)	54(10)	56(11)	-22(9)	3(8)	-10(8)
C142	59(4)	59(3)	52(4)	-17(3)	0(3)	-12(3)
C100	108(8)	204(14)	135(10)	-84(10)	52(7)	-94(9)
C101	74(4)	75(4)	45(3)	-16(3)	-2(3)	-29(3)
C102	59(4)	59(3)	52(4)	-17(3)	0(3)	-12(3)
C103	59(4)	42(3)	54(5)	-2(3)	4(3)	-5(3)
C104	76(5)	58(4)	39(4)	-2(3)	6(4)	8(3)
C105	97(4)	45(3)	45(3)	-12(3)	-28(3)	13(3)
C106	90(4)	48(4)	44(3)	0(3)	-22(2)	-15(3)
C107	59(6)	67(7)	74(8)	-20(6)	31(5)	-13(5)
C108	51(6)	27(4)	42(5)	-12(3)	16(4)	-15(4)
C109	47(6)	31(5)	33(6)	-14(4)	-7(4)	-3(4)
C110	49(6)	36(4)	37(5)	-17(4)	-5(4)	5(4)
C111	50(5)	35(4)	36(4)	-13(3)	8(4)	-15(4)
C112	42(5)	33(4)	52(5)	-16(4)	-12(4)	-1(4)
C113	52(6)	22(4)	39(6)	-4(4)	2(5)	-8(4)
C115	66(8)	37(7)	32(8)	10(6)	-4(7)	2(6)
C116	97(4)	45(3)	45(3)	-12(3)	-28(3)	13(3)
C121	90(4)	48(4)	44(3)	0(3)	-22(2)	-15(3)
C120	74(4)	75(4)	45(3)	-16(3)	-2(3)	-29(3)
C119	59(4)	59(3)	52(4)	-17(3)	0(3)	-12(3)
C118	66(8)	37(7)	32(8)	10(6)	-4(7)	2(6)
C117	85(8)	66(8)	47(10)	-13(7)	-1(7)	2(6)
C07	180(20)	111(15)	113(16)	-42(12)	59(14)	-44(13)
C01	45(6)	82(10)	64(6)	-35(5)	18(5)	-15(6)

C02	46(6)	101(10)	53(6)	-16(5)	10(5)	-31(6)
C03	50(7)	86(10)	50(6)	4(5)	-2(5)	-15(7)
C04	58(6)	72(6)	48(5)	-4(4)	-1(4)	-13(5)
C05	35(4)	65(5)	38(4)	-10(3)	-5(3)	-8(4)
C06	39(5)	76(6)	67(5)	-22(5)	-9(4)	-1(4)

Table B-34 Bond Lengths for **18**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C12	C11	1.408(5)	C45B	C48B	1.541(11)
C12	C7	1.428(4)	C45B	C46B	1.546(11)
C12	N1	1.387(4)	C45B	C47B	1.521(10)
C40	C39	1.413(5)	C13B	C15B	1.53(3)
C40	C35	1.431(5)	C13B	C16B	1.52(2)
C40	N10	1.389(4)	C13B	C14B	1.55(3)
C11	C10	1.401(5)	C26B	C28B	1.539(15)
C11	C25	1.470(5)	C26B	C27B	1.50(2)
C39	C38	1.405(5)	C26B	N8	1.497(19)
C39	C53	1.457(6)	C54B	C56B	1.518(11)
C10	C9	1.404(5)	C54B	C55B	1.442(14)
C38	C37	1.397(7)	C54B	N17	1.450(9)
C9	C8	1.404(5)	Er1	N1	2.374(3)
C9	C17	1.532(5)	Er1	N10	2.401(3)
C37	C36	1.388(7)	Er1	N6	2.530(3)
C37	C45	1.595(7)	Er1	N15	2.451(3)
C37	C45B	1.564(8)	Er1	N2	2.464(3)
C8	C7	1.391(5)	Er1	N11	2.448(3)
C36	C35	1.405(5)	Er1	O1	2.086(2)
C7	C6	1.445(5)	N9	N8	1.342(4)
C35	C34	1.429(6)	N18	N17	1.320(6)
C17	C19	1.546(5)	N6	N7	1.342(4)
C17	C20	1.541(7)	N15	N16	1.327(4)
C17	C18	1.533(6)	N7	N8	1.315(4)
C45	C48	1.540(9)	N16	N17	1.313(5)
C45	C47	1.543(9)	N5	N4	1.339(4)
C45	C46	1.552(10)	N14	N13	1.332(5)
C25	N9	1.346(5)	N2	N3	1.333(4)
C25	N6	1.355(5)	N11	N12	1.336(4)
C53	N18	1.344(5)	N3	N4	1.319(4)
C53	N15	1.353(5)	N12	N13	1.310(4)
C26	C28	1.515(13)	O1	Si1	1.617(2)
C26	C27	1.537(13)	C122	C123	1.5071
C26	N8	1.534(14)	C123	C124	1.4026
C54	C55	1.438(17)	C123	C128	1.4017
C54	C56	1.522(14)	C124	C125	1.3970

C54	N17	1.616(11)	C125	C126	1.3973
C6	C5	1.393(5)	C126	C127	1.3967
C6	C1	1.408(4)	C127	C128	1.3976
C29	C30	1.414(5)	C129	C130	1.502(18)
C29	C34	1.432(5)	C130	C131	1.3900
C29	N10	1.391(4)	C130	C142	1.3900
C5	C4	1.395(5)	C131	C132	1.3900
C30	C31	1.400(5)	C132	C133	1.3900
C30	C49	1.467(5)	C133	C134	1.3900
C4	C3	1.401(5)	C134	C142	1.3900
C4	C13	1.522(11)	C100	C101	1.5067
C4	C13B	1.61(2)	C101	C102	1.4024
C31	C32	1.403(6)	C101	C106	1.4020
C3	C2	1.403(5)	C102	C103	1.3960
C32	C33	1.384(6)	C103	C104	1.3970
C32	C41	1.540(5)	C104	C105	1.3961
C2	C1	1.422(5)	C105	C106	1.3968
C2	C21	1.463(4)	C107	C108	1.489(13)
C33	C34	1.393(5)	C108	C109	1.413(13)
C1	N1	1.399(4)	C108	C113	1.375(14)
C13	C15	1.527(12)	C109	C110	1.351(13)
C13	C16	1.523(10)	C110	C111	1.368(12)
C13	C14	1.550(11)	C111	C112	1.398(12)
C41	C42	1.541(8)	C112	C113	1.381(13)
C41	C44	1.536(8)	C115	C116	1.513(14)
C41	C43	1.546(6)	C116	C121	1.3900
C21	N5	1.342(4)	C116	C117	1.3900
C21	N2	1.353(4)	C121	C120	1.3900
C49	N14	1.344(4)	C120	C119	1.3900
C49	N11	1.357(4)	C119	C118	1.3900
C22	C24	1.529(5)	C118	C117	1.3900
C22	C23	1.518(6)	C07	C01	1.444(13)
C22	N4	1.477(4)	C01	C02	1.3900
C50	C51	1.508(7)	C01	C06	1.3900
C50	C52	1.488(6)	C02	C03	1.3900
C50	N13	1.491(5)	C03	C04	1.3900
C58	Si1	1.875(4)	C04	C05	1.3900
C59	Si1	1.881(4)	C05	C06	1.3900
C57	Si1	1.874(4)			

Table B-35 Bond Angles for **18**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C11	C12	C7	118.1(3)	N8	C26B	C28B	97.8(10)
N1	C12	C11	129.7(3)	C55B	C54B	C56B	114.0(9)
N1	C12	C7	112.2(3)	C55B	C54B	N17	102.2(7)
C39	C40	C35	116.7(3)	N17	C54B	C56B	113.1(6)
N10	C40	C39	131.0(3)	N1	Er1	N10	155.73(9)
N10	C40	C35	112.3(3)	N1	Er1	N6	72.99(9)
C12	C11	C25	121.4(3)	N1	Er1	N15	111.68(10)
C10	C11	C12	119.0(3)	N1	Er1	N2	74.27(9)
C10	C11	C25	119.6(3)	N1	Er1	N11	83.71(9)
C40	C39	C53	122.8(3)	N10	Er1	N6	87.26(9)
C38	C39	C40	119.6(4)	N10	Er1	N15	75.85(10)
C38	C39	C53	117.5(4)	N10	Er1	N2	129.50(9)
C11	C10	C9	123.3(3)	N10	Er1	N11	78.16(9)
C37	C38	C39	123.6(4)	N15	Er1	N6	76.21(10)
C10	C9	C17	123.1(3)	N15	Er1	N2	74.26(10)
C8	C9	C10	117.3(3)	N2	Er1	N6	122.88(10)
C8	C9	C17	119.6(3)	N11	Er1	N6	77.32(9)
C38	C37	C45	109.0(5)	N11	Er1	N15	143.45(10)
C38	C37	C45B	135.5(5)	N11	Er1	N2	142.10(9)
C36	C37	C38	117.1(3)	O1	Er1	N1	103.28(9)
C36	C37	C45	133.4(5)	O1	Er1	N10	89.06(9)
C36	C37	C45B	107.1(5)	O1	Er1	N6	156.29(9)
C7	C8	C9	120.8(3)	O1	Er1	N15	125.38(10)
C37	C36	C35	121.2(4)	O1	Er1	N2	76.64(9)
C12	C7	C6	105.7(3)	O1	Er1	N11	79.00(9)
C8	C7	C12	121.4(3)	C12	N1	C1	103.8(3)
C8	C7	C6	132.8(3)	C12	N1	Er1	127.1(2)
C36	C35	C40	121.7(4)	C1	N1	Er1	119.6(2)
C36	C35	C34	132.6(4)	C40	N10	C29	104.4(3)
C34	C35	C40	105.6(3)	C40	N10	Er1	128.4(2)
C9	C17	C19	112.0(3)	C29	N10	Er1	124.6(2)
C9	C17	C20	109.5(3)	N8	N9	C25	101.4(3)
C9	C17	C18	109.9(3)	N17	N18	C53	101.4(3)
C20	C17	C19	108.3(4)	C25	N6	Er1	130.9(2)
C18	C17	C19	107.5(4)	N7	N6	C25	106.8(3)
C18	C17	C20	109.7(4)	N7	N6	Er1	121.8(2)
C48	C45	C37	114.9(5)	C53	N15	Er1	132.2(2)
C48	C45	C47	111.8(7)	N16	N15	C53	107.1(3)
C48	C45	C46	107.8(6)	N16	N15	Er1	119.9(2)
C47	C45	C37	111.3(5)	N8	N7	N6	105.3(3)
C47	C45	C46	108.0(8)	N17	N16	N15	104.9(4)
C46	C45	C37	102.3(5)	N9	N8	C26	124.0(6)
N9	C25	C11	123.5(3)	N9	N8	C26B	121.4(8)

N9	C25	N6	111.7(3)	N7	N8	C26	120.1(6)
N6	C25	C11	124.8(3)	N7	N8	C26B	122.7(8)
N18	C53	C39	123.4(4)	N7	N8	N9	114.8(3)
N18	C53	N15	111.1(4)	N18	N17	C54	134.6(5)
N15	C53	C39	125.5(3)	N18	N17	C54B	110.4(5)
C28	C26	C27	112.7(10)	N16	N17	C54	109.8(5)
C28	C26	N8	116.8(9)	N16	N17	C54B	134.1(6)
N8	C26	C27	101.6(7)	N16	N17	N18	115.5(3)
C55	C54	C56	118.3(11)	N4	N5	C21	102.0(3)
C55	C54	N17	113.7(9)	N13	N14	C49	101.9(3)
C56	C54	N17	102.6(8)	C21	N2	Er1	123.7(2)
C5	C6	C7	133.4(3)	N3	N2	C21	107.3(3)
C5	C6	C1	121.7(3)	N3	N2	Er1	124.1(2)
C1	C6	C7	104.8(3)	C49	N11	Er1	126.8(2)
C30	C29	C34	116.9(3)	N12	N11	C49	107.0(3)
N10	C29	C30	130.8(3)	N12	N11	Er1	122.0(2)
N10	C29	C34	112.2(3)	N4	N3	N2	105.3(3)
C6	C5	C4	120.4(3)	N13	N12	N11	105.2(3)
C29	C30	C49	124.3(3)	N5	N4	C22	122.2(3)
C31	C30	C29	118.6(3)	N3	N4	C22	123.4(3)
C31	C30	C49	117.1(3)	N3	N4	N5	114.3(3)
C5	C4	C3	117.8(3)	N14	N13	C50	122.8(3)
C5	C4	C13	122.5(5)	N12	N13	C50	122.0(3)
C5	C4	C13B	120.3(9)	N12	N13	N14	115.0(3)
C3	C4	C13	119.5(5)	Si1	O1	Er1	169.59(15)
C3	C4	C13B	120.5(9)	C58	Si1	C59	108.9(2)
C30	C31	C32	124.2(4)	C57	Si1	C58	107.6(2)
C4	C3	C2	123.4(3)	C57	Si1	C59	108.2(2)
C31	C32	C41	120.0(4)	O1	Si1	C58	110.73(17)
C33	C32	C31	117.2(3)	O1	Si1	C59	110.90(16)
C33	C32	C41	122.8(4)	O1	Si1	C57	110.46(19)
C3	C2	C1	117.8(3)	C124	C123	C122	120.9
C3	C2	C21	119.6(3)	C128	C123	C122	121.0
C1	C2	C21	122.5(3)	C128	C123	C124	118.1
C32	C33	C34	120.6(4)	C125	C124	C123	121.1
C6	C1	C2	118.5(3)	C124	C125	C126	120.1
N1	C1	C6	113.3(3)	C127	C126	C125	119.5
N1	C1	C2	128.1(3)	C126	C127	C128	120.0
C35	C34	C29	105.5(3)	C127	C128	C123	121.2
C33	C34	C35	132.0(4)	C131	C130	C129	123(2)
C33	C34	C29	122.5(4)	C131	C130	C142	120.0
C4	C13	C15	111.6(9)	C142	C130	C129	117(2)
C4	C13	C16	106.2(7)	C130	C131	C132	120.0
C4	C13	C14	111.1(7)	C133	C132	C131	120.0
C15	C13	C14	107.9(10)	C132	C133	C134	120.0
C16	C13	C15	110.9(10)	C133	C134	C142	120.0

C16	C13	C14	109.2(8)	C134	C142	C130	120.0
C32	C41	C42	109.9(4)	C102	C101	C100	120.9
C32	C41	C43	108.3(3)	C106	C101	C100	120.9
C42	C41	C43	109.2(5)	C106	C101	C102	118.1
C44	C41	C32	111.6(5)	C103	C102	C101	121.1
C44	C41	C42	108.6(4)	C102	C103	C104	120.1
C44	C41	C43	109.3(4)	C105	C104	C103	119.5
N5	C21	C2	124.1(3)	C104	C105	C106	120.1
N5	C21	N2	111.1(3)	C105	C106	C101	121.1
N2	C21	C2	124.8(3)	C109	C108	C107	121.6(10)
N14	C49	C30	123.0(3)	C113	C108	C107	121.9(10)
N14	C49	N11	110.9(3)	C113	C108	C109	116.4(8)
N11	C49	C30	126.1(3)	C110	C109	C108	121.2(10)
C23	C22	C24	113.6(4)	C109	C110	C111	121.3(10)
N4	C22	C24	110.4(3)	C110	C111	C112	119.8(8)
N4	C22	C23	109.1(3)	C113	C112	C111	118.0(8)
C52	C50	C51	113.3(5)	C108	C113	C112	123.2(9)
C52	C50	N13	109.8(3)	C121	C116	C115	119.9(8)
N13	C50	C51	108.7(4)	C121	C116	C117	120.0
C48B	C45B	C37	101.0(7)	C117	C116	C115	119.7(8)
C48B	C45B	C46B	107.4(8)	C120	C121	C116	120.0
C46B	C45B	C37	118.4(7)	C119	C120	C121	120.0
C47B	C45B	C37	109.0(6)	C118	C119	C120	120.0
C47B	C45B	C48B	111.1(9)	C119	C118	C117	120.0
C47B	C45B	C46B	109.6(7)	C118	C117	C116	120.0
C15B	C13B	C4	112.8(15)	C02	C01	C07	115.2(10)
C15B	C13B	C14B	109.9(17)	C02	C01	C06	120.0
C16B	C13B	C4	115.0(14)	C06	C01	C07	124.8(10)
C16B	C13B	C15B	107.3(15)	C03	C02	C01	120.0
C16B	C13B	C14B	106.4(16)	C02	C03	C04	120.0
C14B	C13B	C4	105.2(15)	C05	C04	C03	120.0
C27B	C26B	C28B	112.8(11)	C04	C05	C06	120.0
C27B	C26B	N8	110.2(13)	C05	C06	C01	120.0

Table B-36 Summary of Crystallographic Data for **19** and **21**

	19•0.87 C₇H₈^{a,b,c}	21•C₇H₈^a
Emp. Formula	C _{90.09} H _{114.96} N ₂₇ Y	C ₆₉ H ₉₈ CeN ₁₉ Si ₂
Formula wgt. (g/mol)	1665.03	1389.96
Temp. (K)	120(2)	119.9
Crystal System	Monoclinic	Monoclinic
Space Group	C2/c	C2/c
a (Å)	36.2178(14)	40.053(7)
b (Å)	16.7410(7)	18.203(3)
c (Å)	31.6549(12)	28.621(5)
α (°)	90	90
β (°)	102.2743(13)	128.185(4)
γ (°)	90	90
Volume (Å³)	18754.3(13)	16401(5)
Z	8	8
Density (g/cm³)	1.179	1.126
Abs. coeff. μ (mm⁻¹)	0.680	0.632
F(000)	7068	5848
Crystal Size (mm)	0.170 x 0.166 x 0.137	0.305 x 0.221 x 0.167
Colour and habit	Yellow block	Yellow block
Theta range (°)	2.886° ≤ 2θ ≤ 52.086°	2.658° ≤ 2θ ≤ 54.21°
Refl. Collected	214690	175945
Independent refl.	18490	18106
GooF (F²)	1.044	1.046
Final R [I>2σ(I)]	0.0453	0.0374
Final wR2	0.1189	0.0866
R (all data)	0.0635	0.0489
wR2 (all data)	0.1294	0.0925
Max peak/hole (e/Å³)	0.69/-0.40	1.386/-0.676

^a Data collected on a Bruker Kappa X8-Apex II diffractometer using Mo Kα radiation (λ = 0.71073 Å) at the University of Notre Dame. ^b SQUEEZED solvent is included in the formula which leads to fractional equivalents of solvent as noted. ^c Formula contains one 0.67 occupancy toluene that was modelled and residual solvent equating to 0.2 equivalents of toluene per asymmetric unit (masked) for a total of 0.87 equivalents of toluene.

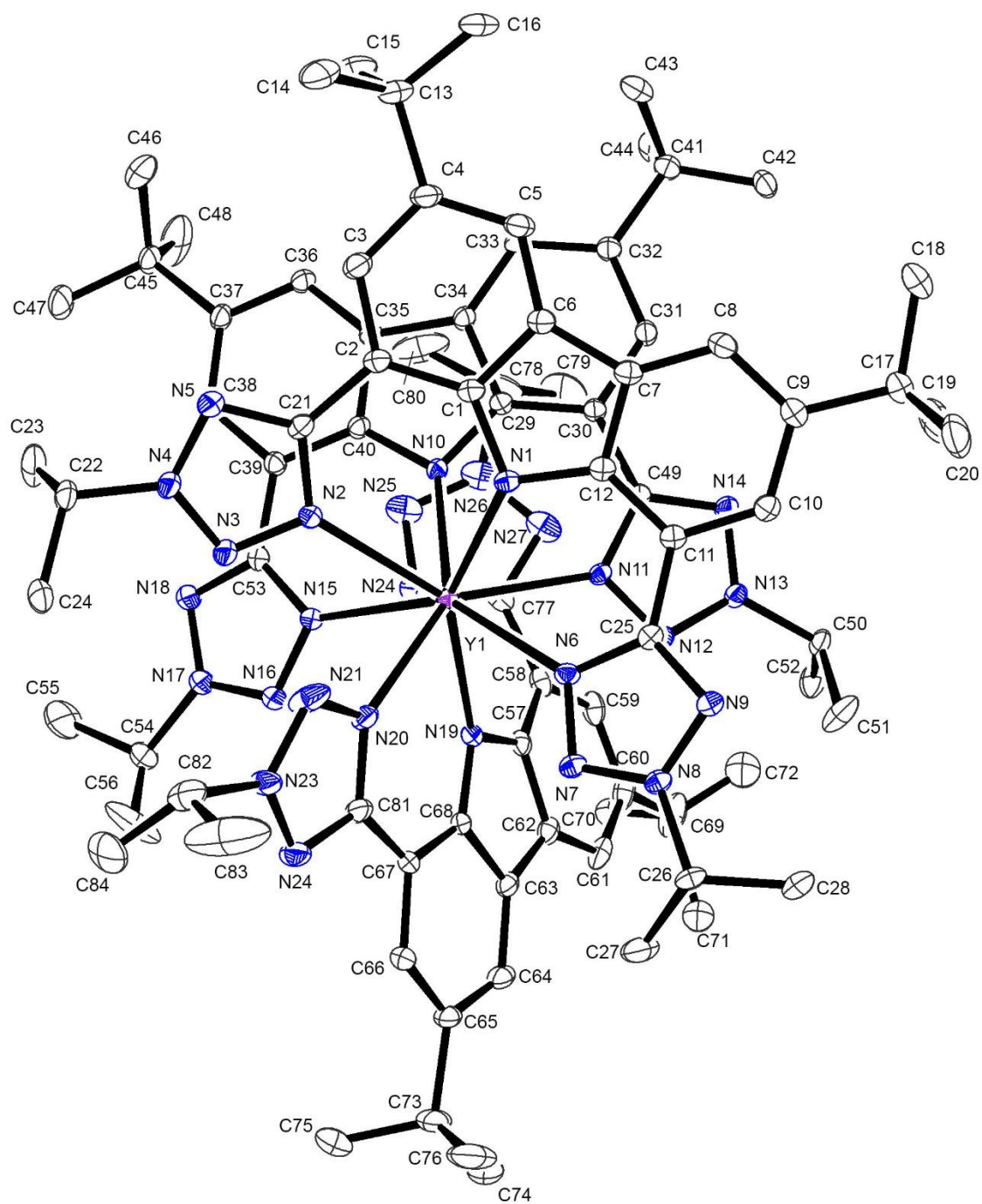


Figure B-11 Labelled ORTEP Drawing of **19**

H atoms not shown

Disordered toluene of solvation not shown: C1S-C7S

Disordered tBu carbons C42A, C43A, C44A, C70A, C71A and C72A not shown

Disordered iPr carbons C79A, C80A, C82A, C83A and C84A not shown

Disordered tetrazole ring nitrogens N22A and N23A not shown

Table B-37 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **19**

Atom	x	y	z	U(eq)
Y1	3031.2(2)	5933.1(2)	3615.3(2)	17.00(7)
N1	3367.0(5)	7149.6(11)	3923.5(6)	20.6(4)
N2	3049.2(5)	6896.5(12)	3002.8(6)	21.9(4)
N3	2811.8(6)	6841.6(12)	2619.6(6)	25.6(4)
N4	2941.7(6)	7340.2(12)	2367.5(6)	25.9(4)
N5	3254.0(6)	7729.5(12)	2555.5(7)	27.3(5)
N6	2760.6(5)	6417.3(11)	4248.4(6)	20.5(4)
N7	2420.2(5)	6222.3(12)	4305.7(6)	22.5(4)
N8	2422.5(5)	6386.6(11)	4711.5(6)	21.0(4)
N9	2747.1(5)	6693.2(11)	4930.8(6)	21.1(4)
N10	3635.3(5)	5652.4(11)	3469.1(6)	18.9(4)
N11	3415.4(5)	5378.8(11)	4294.0(6)	18.3(4)
N12	3265.9(5)	5082.1(11)	4610.1(6)	19.6(4)
N13	3550.9(5)	4994.0(11)	4937.9(6)	21.2(4)
N14	3886.0(5)	5205.8(12)	4864.4(6)	22.6(4)
N15	2913.6(5)	5224.4(12)	2908.5(6)	22.1(4)
N16	2581.0(6)	4899.7(13)	2742.3(6)	27.6(5)
N17	2602.2(6)	4670.1(14)	2352.0(7)	31.3(5)
N18	2933.8(6)	4820.5(13)	2246.9(7)	30.3(5)
N19	2686.4(5)	4699.6(11)	3712.0(6)	20.9(4)
N20	2366.7(5)	6342.0(12)	3324.2(6)	25.4(4)
N21	2268.9(7)	7028.5(15)	3120.1(9)	45.0(7)
N22	1892.4(9)	6953(2)	2961.6(14)	33.7(9)
N23	1738.0(11)	6290(3)	3074.9(15)	35.2(10)
N22A	1968(3)	7271(8)	3193(5)	33(3)
N23A	1777(4)	6611(10)	3265(5)	40(4)
N24	3424.0(6)	3818.4(13)	3276.2(7)	32.3(5)
N25	3759.3(7)	3883.9(14)	3180.3(9)	39.6(6)
N26	4004.4(7)	3919.5(14)	3552.9(9)	41.6(6)
N27	3849.3(7)	3883.7(13)	3897.9(8)	38.2(6)
C1	3632.9(6)	7544.0(13)	3739.1(8)	21.7(5)

C2	3629.1(6)	7682.3(14)	3299.8(8)	23.3(5)
C3	3927.7(7)	8094.6(15)	3190.8(8)	29.5(6)
C4	4235.7(7)	8387.3(16)	3496.5(9)	31.3(6)
C5	4237.0(7)	8257.1(15)	3929.8(9)	29.7(6)
C6	3940.9(7)	7846.9(14)	4051.5(8)	25.1(5)
C7	3859.9(7)	7639.7(14)	4463.0(8)	24.1(5)
C8	4057.7(7)	7730.7(15)	4888.2(8)	27.5(5)
C9	3909.0(7)	7445.0(15)	5229.7(8)	27.4(5)
C10	3548.2(7)	7100.2(14)	5129.7(8)	23.3(5)
C11	3341.8(6)	7003.8(13)	4707.9(7)	20.5(5)
C12	3506.3(6)	7240.6(13)	4363.9(7)	20.7(5)
C13	4549.1(8)	8836(2)	3335.4(10)	44.3(7)
C14	4375.4(10)	9533(2)	3046.0(12)	62.4(10)
C15	4744.7(9)	8257(3)	3076.9(12)	63.8(10)
C16	4843.0(9)	9180(2)	3711.0(11)	56.3(9)
C17	4123.5(8)	7474.9(17)	5703.2(8)	35.3(6)
C18	4494.8(10)	7935(2)	5757.2(10)	60.1(10)
C19	4206.4(11)	6624(2)	5866.1(11)	58.9(10)
C20	3883.3(10)	7904(2)	5979.3(10)	55.4(9)
C21	3316.3(7)	7436.4(14)	2958.2(8)	22.8(5)
C22	2765.6(7)	7430.6(16)	1903.8(8)	30.3(6)
C23	2962.5(9)	6863(2)	1651.7(9)	46.7(8)
C24	2345.4(8)	7290(2)	1838.2(9)	41.1(7)
C25	2955.6(6)	6704.4(13)	4630.9(7)	19.4(5)
C26	2080.3(7)	6304.5(14)	4896.2(8)	24.8(5)
C27	1837.6(8)	5640.2(18)	4663.5(10)	41.0(7)
C28	2192.1(8)	6183.7(17)	5379.7(8)	32.7(6)
C29	3971.9(6)	5819.5(13)	3758.2(7)	19.3(5)
C30	4061.0(6)	5752.9(14)	4210.5(7)	20.2(5)
C31	4427.4(7)	5937.4(15)	4432.5(8)	24.3(5)
C32	4713.2(7)	6177.3(16)	4226.0(8)	27.3(5)
C33	4626.4(7)	6216.2(15)	3775.8(8)	25.4(5)
C34	4266.3(6)	6034.2(14)	3546.7(7)	21.6(5)
C35	4106.3(6)	5943.4(14)	3090.5(7)	21.8(5)
C36	4260.7(7)	5989.9(15)	2727.4(8)	25.2(5)
C37	4045.7(7)	5780.8(15)	2322.4(8)	25.7(5)
C38	3674.9(7)	5528.0(15)	2298.8(7)	24.6(5)
C39	3508.6(6)	5483.6(14)	2656.9(7)	21.8(5)
C40	3726.1(6)	5696.0(14)	3066.1(7)	20.8(5)
C41	5113.6(7)	6350(2)	4480.4(9)	41.7(7)
C42	5157.2(11)	6301(3)	4959.5(12)	40.6(12)
C43	5253.5(19)	7105(4)	4338(2)	50.9(16)
C44	5370.1(10)	5631(3)	4356.2(13)	42.7(12)
C42A	5363(5)	6802(15)	4235(6)	68(6)
C43A	5276(3)	5813(7)	4792(4)	48(3)
C44A	5041(3)	7204(6)	4811(3)	40(3)

C45	4226.0(7)	5790.5(18)	1925.7(8)	32.6(6)
C46	4448.1(11)	6572(3)	1915.9(10)	62.8(10)
C47	3934.6(9)	5748(3)	1505.8(9)	56.6(10)
C48	4497.0(12)	5090(3)	1956.4(11)	70.0(12)
C49	3792.4(6)	5451.6(13)	4453.1(7)	19.0(5)
C50	3509.3(7)	4633.7(14)	5350.8(7)	24.9(5)
C51	3160.8(9)	4966.6(19)	5483.0(10)	47.0(8)
C52	3498.0(9)	3734.5(16)	5303.2(9)	35.9(6)
C53	3124.8(7)	5176.0(14)	2604.0(7)	22.9(5)
C54	2280.2(8)	4246(2)	2068.0(9)	43.5(7)
C55	2357.6(14)	4131(3)	1624.7(12)	98.2(19)
C56	1920.9(10)	4641(3)	2107.1(17)	87.6(15)
C57	2829.6(7)	3983.6(13)	3906.5(7)	22.1(5)
C58	3187.7(7)	3618.2(14)	3951.1(8)	26.5(5)
C59	3256.9(8)	2901.9(15)	4184.2(8)	31.7(6)
C60	2985.4(9)	2496.5(15)	4357.9(8)	35.7(7)
C61	2627.3(8)	2820.6(14)	4283.7(8)	31.8(6)
C62	2549.2(7)	3541.6(14)	4058.0(7)	25.2(5)
C63	2204.2(7)	3959.6(14)	3910.8(7)	25.0(5)
C64	1833.5(7)	3753.7(16)	3913.6(8)	30.3(6)
C65	1538.8(7)	4228.0(17)	3710.4(8)	32.8(6)
C66	1630.7(7)	4932.6(17)	3519.4(8)	30.6(6)
C67	2000.9(7)	5167.5(15)	3512.9(7)	24.8(5)
C68	2302.1(6)	4660.7(14)	3703.1(7)	21.3(5)
C69	3073.0(11)	1678.1(17)	4578.2(10)	49.8(9)
C70	3106(2)	1050(4)	4215(2)	34.9(15)
C71	2695.6(17)	1340(4)	4742(2)	43.1(14)
C72	3374(2)	1654(5)	4920(2)	55.6(18)
C70A	2989(2)	1044(4)	4277(2)	47.1(19)
C71A	2911(2)	1666(5)	4969(2)	58.2(18)
C72A	3541.0(18)	1646(4)	4799(2)	38.5(13)
C73	1120.9(8)	4023.3(19)	3683.1(10)	42.9(7)
C74	1074.0(10)	3218(2)	3900.6(11)	59.5(10)
C75	922.1(9)	3962(2)	3213.0(11)	58.9(10)
C76	945.7(9)	4656(3)	3923.8(14)	66.3(11)
C77	3482.9(7)	3824.1(14)	3712.6(8)	26.4(5)
C78	4417.7(9)	4001(2)	3584.7(17)	67.4(12)
C79	4608.0(14)	3324(5)	3892(2)	86(2)
C80	4518.0(15)	3990(4)	3173(2)	76(2)
C79A	4637(5)	4013(13)	3934(6)	57(6)
C80A	4528(5)	3406(17)	3181(7)	71(7)
C81	2040.2(7)	5932.7(17)	3312.3(9)	32.5(6)
C82	1663.9(11)	7561(3)	2678.7(16)	47.9(13)
C83	1472(3)	8081(7)	2937(4)	130(5)
C84	1413.3(13)	7136(3)	2305.3(17)	73.4(18)
C82A	1782(5)	8055(11)	3064(8)	85(9)

C83A	1405(6)	8010(13)	2916(4)	25(4)
C84A	1763(8)	8480(12)	3508(11)	138(16)
C1S	4209(3)	10952(5)	4176(5)	124(2)
C2S	4010(2)	10248(4)	4204(4)	111(2)
C3S	4109(3)	9901(4)	4593(4)	110(2)
C4S	4375(3)	10155(6)	4937(4)	137(2)
C5S	4562(4)	10769(6)	4888(5)	146(2)
C6S	4472(3)	11218(6)	4473(4)	132(2)
C7S	4079(3)	11339(7)	3793(4)	159(4)

Table B-38 Anisotropic Displacement Parameters (U_{ij} , Å² x10³) for **19**

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Y1	14.22(11)	20.16(11)	17.17(11)	0.92(8)	4.58(8)	-0.53(8)
N1	17.7(10)	21.7(10)	23.5(10)	0.0(8)	7.2(8)	-0.6(8)
N2	17.9(10)	27.0(10)	20.6(10)	2.9(8)	3.5(8)	0.2(8)
N3	23.7(11)	30.5(11)	22.1(10)	6.8(9)	4.2(8)	0.8(9)
N4	25.4(11)	31.0(11)	21.5(10)	7.6(9)	5.4(8)	0.9(9)
N5	26.2(11)	29.8(11)	26.3(11)	4.6(9)	6.3(9)	-2.5(9)
N6	15.1(9)	23.7(10)	23.6(10)	-1.1(8)	6.0(8)	1.0(8)
N7	20.3(10)	23.9(10)	25.4(10)	-0.2(8)	9.7(8)	0.9(8)
N8	21.3(10)	19.3(10)	24.5(10)	0.0(8)	9.3(8)	1.0(8)
N9	21.5(10)	19.0(9)	24.2(10)	0.5(8)	7.7(8)	1.4(8)
N10	18.3(9)	23.1(9)	16.0(9)	-0.5(8)	4.9(7)	0.5(8)
N11	19.2(10)	18.6(9)	18.7(9)	-1.3(7)	7.8(8)	0.2(7)
N12	20.6(10)	21.1(9)	18.1(9)	0.7(8)	6.5(8)	1.2(8)
N13	21.8(10)	23.5(10)	19.4(10)	1.6(8)	7.0(8)	2.4(8)
N14	18.7(10)	28.8(11)	21.5(10)	1.3(8)	7.2(8)	3.2(8)
N15	18.5(10)	26.7(10)	20.7(10)	1.4(8)	3.4(8)	-3.5(8)
N16	23.6(11)	35.8(12)	22.6(10)	-1.6(9)	3.6(8)	-8.0(9)
N17	28.7(12)	41.9(13)	22.4(11)	-3.8(9)	3.1(9)	-12.8(10)
N18	29.4(12)	39.4(12)	22.2(11)	-5.1(9)	5.4(9)	-10.2(10)
N19	19.7(10)	23.0(10)	18.9(9)	0.7(8)	1.5(8)	-2.8(8)
N20	21.1(10)	30.0(11)	26.7(11)	10.4(9)	8.7(8)	3.9(8)
N21	29.6(13)	44.5(14)	67.7(17)	33.0(13)	25.7(12)	16.0(11)
N22	16.6(15)	40(2)	44(2)	20.9(17)	3.4(15)	4.2(13)
N23	19.4(16)	43(2)	42(2)	19.7(18)	4.8(17)	0.2(16)
N22A	21(6)	44(7)	36(7)	25(6)	9(5)	1(5)
N23A	19(6)	58(10)	45(9)	31(7)	16(6)	14(6)
N24	33.2(12)	27.5(11)	37.2(13)	-4.2(10)	9.7(10)	2.6(9)
N25	33.2(13)	32.0(12)	54.9(16)	-6.6(11)	12.7(12)	2.5(10)
N26	29.4(13)	29.9(12)	65.8(18)	-4.1(11)	10.9(12)	6.3(10)
N27	30.3(12)	27.9(12)	52.7(15)	-1.4(11)	0.4(11)	6.0(9)
C1	19.0(11)	19.3(11)	27.8(12)	1.8(9)	7.1(10)	0.4(9)
C2	19.6(12)	22.8(12)	28.6(13)	2.7(10)	7.3(10)	-0.1(9)

C3	27.8(13)	32.0(13)	30.4(13)	6.5(11)	10.2(11)	-1.8(11)
C4	23.1(13)	34.1(14)	37.9(15)	5.7(11)	9.0(11)	-6.3(11)
C5	22.1(13)	31.3(13)	34.9(14)	0.7(11)	4.2(11)	-7.1(10)
C6	23.1(12)	24.2(12)	28.3(13)	0.7(10)	5.7(10)	-1.8(10)
C7	22.3(12)	21.9(12)	28.6(13)	-1.8(10)	6.6(10)	-1.8(9)
C8	22.9(12)	27.1(13)	31.0(13)	-0.7(10)	2.3(10)	-3.8(10)
C9	26.5(13)	28.0(13)	26.0(13)	-2.5(10)	2.0(10)	0.4(10)
C10	23.1(12)	23.3(12)	24.4(12)	-0.7(9)	7.5(10)	3.1(9)
C11	19.7(11)	18.0(11)	24.7(12)	-1.3(9)	6.8(9)	3.3(9)
C12	19.5(11)	18.9(11)	24.3(12)	-1.0(9)	6.0(9)	2.5(9)
C13	31.8(15)	56.8(19)	45.9(17)	11.2(15)	11.8(13)	-17.2(14)
C14	52(2)	68(2)	65(2)	28.1(19)	7.6(17)	-25.6(18)
C15	37.5(18)	95(3)	67(2)	2(2)	31.0(17)	-16.1(18)
C16	33.5(17)	74(2)	59(2)	13.9(18)	6.3(15)	-29.1(16)
C17	31.5(15)	44.3(16)	26.9(14)	1.8(12)	-0.9(11)	-4.3(12)
C18	48(2)	88(3)	34.8(17)	2.6(17)	-10.8(14)	-25.2(19)
C19	60(2)	58(2)	45.3(19)	11.8(16)	-19.1(16)	1.2(17)
C20	54(2)	78(2)	29.0(16)	-15.5(16)	-0.8(14)	-1.5(18)
C21	22.5(12)	22.6(12)	25.0(12)	5.2(9)	8.7(10)	3.0(9)
C22	31.8(14)	37.0(14)	21.0(12)	10.2(11)	2.9(10)	3.8(11)
C23	48.3(18)	67(2)	24.0(14)	7.2(14)	5.3(13)	21.8(16)
C24	31.8(15)	62(2)	26.6(14)	11.8(13)	-1.0(12)	4.4(14)
C25	21.5(12)	15.8(10)	22.0(11)	0.3(9)	7.3(9)	3.8(9)
C26	22.1(12)	24.8(12)	32.0(13)	0.2(10)	15.7(10)	0.8(10)
C27	36.0(16)	44.7(16)	48.5(17)	-9.1(14)	22.9(14)	-15.1(13)
C28	32.9(14)	36.7(14)	33.9(14)	4.0(12)	18.8(12)	0.4(11)
C29	17.1(11)	20.7(11)	20.7(11)	-1.6(9)	5.5(9)	3.0(9)
C30	15.6(11)	25.9(12)	19.6(11)	-0.4(9)	4.8(9)	3.7(9)
C31	19.7(12)	34.8(13)	18.0(11)	-0.7(10)	3.5(9)	3.0(10)
C32	18.5(12)	39.8(14)	23.9(12)	0.1(11)	5.3(10)	0.4(10)
C33	17.1(12)	37.6(14)	23.2(12)	0.5(10)	8.1(9)	-1.1(10)
C34	19.5(11)	27.5(12)	19.1(11)	-0.1(9)	6.8(9)	2.5(9)
C35	18.3(11)	27.8(12)	20.4(11)	0.2(9)	6.7(9)	0.9(9)
C36	19.8(12)	33.9(13)	23.7(12)	2.6(10)	8.3(10)	0.7(10)
C37	25.0(13)	34.7(14)	18.5(11)	2.3(10)	7.3(10)	3.5(10)
C38	23.9(12)	32.8(13)	17.5(11)	-1.3(10)	5.0(9)	3.3(10)
C39	20.1(12)	25.8(12)	19.6(11)	-0.6(9)	4.1(9)	1.5(9)
C40	19.6(11)	24.2(11)	19.4(11)	1.0(9)	6.2(9)	1.9(9)
C41	17.9(13)	77(2)	29.1(14)	9.0(14)	1.1(11)	-8.0(13)
C42	22(2)	77(3)	22.1(19)	-6(2)	1.7(15)	-9(2)
C43	37(4)	65(4)	44(4)	5(3)	-6(3)	-25(3)
C44	20.2(19)	76(3)	32(2)	3(2)	3.8(16)	9.5(19)
C42A	22(8)	140(20)	44(10)	6(10)	-2(6)	-26(10)
C43A	23(5)	61(8)	55(7)	-8(6)	-2(5)	3(5)
C44A	32(5)	46(6)	38(6)	-18(5)	-3(4)	-6(4)
C45	25.5(13)	54.7(17)	19.8(12)	2.1(11)	9.9(10)	4.6(12)

C46	67(2)	93(3)	34.0(17)	4.4(18)	23.8(16)	-25(2)
C47	36.6(17)	114(3)	22.0(14)	4.5(17)	12.5(13)	-0.7(18)
C48	79(3)	99(3)	40.8(19)	9.6(19)	33.8(19)	46(2)
C49	17.9(11)	20.9(11)	18.1(11)	-0.6(9)	4.0(9)	4.2(9)
C50	29.6(13)	28.7(13)	17.4(11)	5.5(9)	7.4(10)	0.9(10)
C51	54.8(19)	50.2(18)	46.4(17)	20.4(15)	34.6(15)	16.9(15)
C52	51.2(18)	29.8(14)	26.2(13)	6.8(11)	6.8(12)	2.0(12)
C53	23.6(12)	26.6(12)	18.3(11)	-0.4(9)	4.3(9)	-1.5(10)
C54	39.6(17)	56.6(19)	30.7(15)	-4.7(13)	-1.0(12)	-24.5(14)
C55	82(3)	164(5)	42(2)	-33(3)	0(2)	-66(3)
C56	35(2)	88(3)	121(4)	-39(3)	-25(2)	-7(2)
C57	27.7(12)	19.4(11)	17.0(11)	-1.9(9)	0.0(9)	-3.5(9)
C58	31.2(14)	21.8(12)	23.1(12)	-4.0(10)	-1.8(10)	0.4(10)
C59	43.7(16)	25.4(13)	22.6(12)	-3.6(10)	-0.6(11)	7.4(11)
C60	64(2)	22.8(13)	19.6(12)	-1.4(10)	8.4(12)	5.9(13)
C61	57.2(18)	19.8(12)	21.4(12)	-1.7(10)	14.9(12)	-6.0(12)
C62	36.0(14)	21.5(12)	18.4(11)	-3.3(9)	6.6(10)	-4.9(10)
C63	31.9(13)	25.5(12)	18.6(11)	-3.8(9)	7.4(10)	-9.6(10)
C64	32.6(14)	32.4(13)	28.1(13)	-5.3(11)	11.3(11)	-15.0(11)
C65	27.3(14)	46.7(16)	26.4(13)	-9.7(12)	10.0(11)	-17.8(12)
C66	20.1(12)	47.4(16)	23.9(12)	-1.3(11)	3.9(10)	-5.5(11)
C67	18.4(12)	36.0(14)	18.7(11)	2.8(10)	1.0(9)	-4.8(10)
C68	20.9(12)	27.0(12)	15.6(11)	-1.5(9)	3.1(9)	-5.6(9)
C69	91(3)	27.4(15)	34.9(16)	10.1(12)	22.1(17)	16.3(15)
C73	27.9(15)	58.0(19)	44.5(17)	-10.1(14)	11.3(13)	-20.4(13)
C74	46.0(19)	81(3)	51(2)	3.2(18)	9.2(16)	-37.7(18)
C75	34.0(17)	84(3)	54(2)	1.3(18)	-2.5(15)	-26.6(17)
C76	30.2(17)	90(3)	84(3)	-27(2)	24.6(18)	-21.3(18)
C77	25.0(13)	17.8(11)	33.1(14)	-3.7(10)	-1.0(10)	4.2(9)
C78	26.1(17)	44(2)	131(4)	-14(2)	15(2)	4.7(14)
C79	36(3)	111(6)	107(5)	8(4)	6(3)	37(3)
C80	51(3)	54(4)	143(6)	7(3)	63(4)	11(3)
C79A	40(9)	67(14)	67(12)	-8(9)	17(8)	5(8)
C80A	37(10)	91(18)	87(14)	-25(12)	20(9)	11(10)
C81	18.9(12)	47.2(16)	31.8(14)	18.3(12)	6.7(10)	3.0(11)
C82	31(2)	50(3)	65(3)	36(2)	15(2)	10.1(18)
C83	56(6)	78(6)	271(14)	93(7)	67(7)	30(5)
C84	48(3)	81(4)	78(4)	52(3)	-19(2)	-4(2)
C82A	46(11)	67(12)	160(20)	92(15)	60(13)	44(9)
C83A	14(7)	52(11)	12(6)	6(6)	7(5)	27(7)
C84A	160(30)	53(12)	260(40)	75(18)	170(30)	67(15)
C1S	133(5)	66(3)	206(6)	-1(4)	111(5)	13(3)
C2S	119(4)	49(3)	201(6)	-13(3)	117(4)	24(3)
C3S	122(4)	42(3)	199(6)	-15(3)	109(4)	17(3)
C4S	155(5)	71(4)	208(6)	-7(4)	93(5)	23(4)
C5S	155(5)	83(4)	221(6)	-9(4)	85(5)	9(4)

C6S	139(5)	69(4)	215(6)	0(4)	95(5)	-9(4)
C7S	172(8)	119(7)	221(9)	-21(7)	117(7)	22(6)

Table B-39 Bond Lengths for **19**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Y1	N10	2.3775(18)	C17	C20	1.537(4)
Y1	N1	2.4647(19)	C22	C24	1.510(4)
Y1	N19	2.4658(19)	C22	C23	1.513(4)
Y1	N11	2.4784(19)	C26	C27	1.509(4)
Y1	N20	2.4831(19)	C26	C28	1.511(4)
Y1	N15	2.4878(19)	C29	C30	1.403(3)
Y1	N2	2.5334(19)	C29	C34	1.420(3)
Y1	N6	2.5436(19)	C30	C31	1.398(3)
N1	C12	1.386(3)	C30	C49	1.452(3)
N1	C1	1.394(3)	C31	C32	1.396(3)
N2	N3	1.332(3)	C32	C33	1.394(3)
N2	C21	1.353(3)	C32	C41	1.530(3)
N3	N4	1.309(3)	C33	C34	1.385(3)
N4	N5	1.331(3)	C34	C35	1.445(3)
N4	C22	1.479(3)	C35	C36	1.383(3)
N5	C21	1.339(3)	C35	C40	1.424(3)
N6	N7	1.324(3)	C36	C37	1.395(3)
N6	C25	1.354(3)	C37	C38	1.395(3)
N7	N8	1.312(3)	C37	C45	1.534(3)
N8	N9	1.334(3)	C38	C39	1.394(3)
N8	C26	1.485(3)	C39	C40	1.411(3)
N9	C25	1.333(3)	C39	C53	1.458(3)
N10	C40	1.385(3)	C41	C43A	1.372(12)
N10	C29	1.388(3)	C41	C43	1.467(8)
N11	N12	1.331(3)	C41	C42	1.493(5)
N11	C49	1.357(3)	C41	C42A	1.514(19)
N12	N13	1.307(3)	C41	C44	1.619(5)
N13	N14	1.331(3)	C41	C44A	1.822(10)
N13	C50	1.476(3)	C45	C47	1.513(4)
N14	C49	1.338(3)	C45	C48	1.520(4)
N15	N16	1.325(3)	C45	C46	1.539(5)
N15	C53	1.354(3)	C50	C52	1.513(4)
N16	N17	1.312(3)	C50	C51	1.518(4)
N17	N18	1.337(3)	C54	C56	1.489(5)
N17	C54	1.492(3)	C54	C55	1.501(5)
N18	C53	1.334(3)	C57	C58	1.414(3)
N19	C68	1.388(3)	C57	C62	1.420(3)
N19	C57	1.396(3)	C58	C59	1.402(3)
N20	N21	1.329(3)	C58	C77	1.475(4)

N20	C81	1.360(3)	C59	C60	1.400(4)
N21	N22A	1.231(11)	C60	C61	1.379(4)
N21	N22	1.355(4)	C60	C69	1.539(4)
N22	N23	1.325(5)	C61	C62	1.401(3)
N22	C82	1.486(5)	C62	C63	1.421(4)
N23	C81	1.331(5)	C63	C64	1.388(3)
N22A	N23A	1.348(19)	C63	C68	1.426(3)
N22A	C82A	1.490(17)	C64	C65	1.375(4)
N23A	C81	1.470(14)	C65	C66	1.398(4)
N24	N25	1.317(3)	C65	C73	1.536(4)
N24	C77	1.352(3)	C66	C67	1.401(3)
N25	N26	1.318(4)	C67	C68	1.412(3)
N26	N27	1.331(4)	C67	C81	1.450(4)
N26	C78	1.485(4)	C69	C72	1.365(8)
N27	C77	1.336(3)	C69	C70A	1.416(8)
C1	C2	1.407(3)	C69	C71A	1.477(8)
C1	C6	1.418(3)	C69	C70	1.581(7)
C2	C3	1.387(3)	C69	C71	1.661(7)
C2	C21	1.450(3)	C69	C72A	1.691(7)
C3	C4	1.401(4)	C73	C75	1.513(4)
C4	C5	1.388(4)	C73	C76	1.520(5)
C4	C13	1.536(4)	C73	C74	1.540(5)
C5	C6	1.395(3)	C78	C79A	1.217(18)
C6	C7	1.437(3)	C78	C80	1.425(7)
C7	C8	1.392(3)	C78	C79	1.556(7)
C7	C12	1.419(3)	C78	C80A	1.73(2)
C8	C9	1.391(4)	C82	C83	1.467(13)
C9	C10	1.402(3)	C82	C84	1.507(7)
C9	C17	1.535(3)	C82A	C83A	1.35(3)
C10	C11	1.394(3)	C82A	C84A	1.59(4)
C11	C12	1.405(3)	C1S	C6S	1.267(15)
C11	C25	1.457(3)	C1S	C7S	1.367(15)
C13	C16	1.529(4)	C1S	C2S	1.394(12)
C13	C14	1.533(5)	C2S	C3S	1.340(13)
C13	C15	1.536(5)	C3S	C4S	1.359(14)
C17	C19	1.523(4)	C4S	C5S	1.259(13)
C17	C18	1.527(4)	C5S	C6S	1.488(16)

Table B-40 Bond Angles for **19**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N10	Y1	N1	80.98(6)	N6	C25	C11	124.9(2)
N10	Y1	N19	111.71(6)	N8	C26	C27	108.93(19)
N1	Y1	N19	149.67(6)	N8	C26	C28	110.2(2)
N10	Y1	N11	74.00(6)	C27	C26	C28	113.5(2)

N1	Y1	N11	80.06(6)	N10	C29	C30	129.5(2)
N19	Y1	N11	77.56(6)	N10	C29	C34	112.47(19)
N10	Y1	N20	147.31(6)	C30	C29	C34	117.9(2)
N1	Y1	N20	106.07(7)	C31	C30	C29	118.9(2)
N19	Y1	N20	78.50(6)	C31	C30	C49	118.8(2)
N11	Y1	N20	138.26(6)	C29	C30	C49	122.2(2)
N10	Y1	N15	73.70(6)	C32	C31	C30	123.2(2)
N1	Y1	N15	136.53(6)	C33	C32	C31	117.6(2)
N19	Y1	N15	73.62(6)	C33	C32	C41	120.8(2)
N11	Y1	N15	123.93(6)	C31	C32	C41	121.5(2)
N20	Y1	N15	80.26(7)	C34	C33	C32	120.5(2)
N10	Y1	N2	78.61(6)	C33	C34	C29	121.8(2)
N1	Y1	N2	71.71(6)	C33	C34	C35	132.8(2)
N19	Y1	N2	136.41(6)	C29	C34	C35	105.2(2)
N11	Y1	N2	143.20(6)	C36	C35	C40	121.9(2)
N20	Y1	N2	73.80(6)	C36	C35	C34	132.7(2)
N15	Y1	N2	69.07(6)	C40	C35	C34	105.20(19)
N10	Y1	N6	137.82(6)	C35	C36	C37	120.3(2)
N1	Y1	N6	70.43(6)	C38	C37	C36	117.9(2)
N19	Y1	N6	83.04(6)	C38	C37	C45	122.1(2)
N11	Y1	N6	71.07(6)	C36	C37	C45	119.9(2)
N20	Y1	N6	72.50(6)	C39	C38	C37	123.4(2)
N15	Y1	N6	147.11(6)	C38	C39	C40	118.7(2)
N2	Y1	N6	118.49(6)	C38	C39	C53	119.4(2)
C12	N1	C1	103.47(18)	C40	C39	C53	121.8(2)
C12	N1	Y1	122.17(14)	N10	C40	C39	129.5(2)
C1	N1	Y1	123.53(14)	N10	C40	C35	112.4(2)
N3	N2	C21	106.76(18)	C39	C40	C35	117.9(2)
N3	N2	Y1	122.42(14)	C43	C41	C42	113.0(4)
C21	N2	Y1	129.82(15)	C43A	C41	C42A	119.0(10)
N4	N3	N2	105.36(19)	C43A	C41	C32	117.9(5)
N3	N4	N5	114.90(19)	C43	C41	C32	110.6(3)
N3	N4	C22	122.4(2)	C42	C41	C32	114.1(2)
N5	N4	C22	122.67(19)	C42A	C41	C32	115.3(8)
N4	N5	C21	101.60(19)	C43	C41	C44	108.2(4)
N7	N6	C25	106.79(18)	C42	C41	C44	105.3(3)
N7	N6	Y1	123.72(14)	C32	C41	C44	105.1(3)
C25	N6	Y1	127.07(14)	C43A	C41	C44A	101.2(7)
N8	N7	N6	105.68(18)	C42A	C41	C44A	94.5(10)
N7	N8	N9	114.29(18)	C32	C41	C44A	102.3(4)
N7	N8	C26	122.28(19)	C47	C45	C48	109.9(3)
N9	N8	C26	123.21(18)	C47	C45	C37	112.3(2)
C25	N9	N8	101.81(18)	C48	C45	C37	108.7(2)
C40	N10	C29	104.43(18)	C47	C45	C46	107.0(3)
C40	N10	Y1	125.26(14)	C48	C45	C46	108.9(3)
C29	N10	Y1	123.19(14)	C37	C45	C46	109.9(2)

N12	N11	C49	107.01(18)	N14	C49	N11	111.10(19)
N12	N11	Y1	123.26(14)	N14	C49	C30	124.2(2)
C49	N11	Y1	128.57(14)	N11	C49	C30	124.7(2)
N13	N12	N11	105.07(17)	N13	C50	C52	108.92(19)
N12	N13	N14	115.26(18)	N13	C50	C51	110.0(2)
N12	N13	C50	122.47(19)	C52	C50	C51	112.7(2)
N14	N13	C50	122.14(19)	N18	C53	N15	111.1(2)
N13	N14	C49	101.55(18)	N18	C53	C39	124.4(2)
N16	N15	C53	107.25(19)	N15	C53	C39	124.5(2)
N16	N15	Y1	121.34(14)	C56	C54	N17	108.9(3)
C53	N15	Y1	130.85(15)	C56	C54	C55	118.4(4)
N17	N16	N15	105.30(19)	N17	C54	C55	110.3(3)
N16	N17	N18	114.51(19)	N19	C57	C58	131.5(2)
N16	N17	C54	120.8(2)	N19	C57	C62	111.8(2)
N18	N17	C54	124.6(2)	C58	C57	C62	116.6(2)
C53	N18	N17	101.81(19)	C59	C58	C57	118.7(2)
C68	N19	C57	104.23(18)	C59	C58	C77	113.7(2)
C68	N19	Y1	124.68(15)	C57	C58	C77	126.7(2)
C57	N19	Y1	128.56(15)	C60	C59	C58	124.0(3)
N21	N20	C81	106.4(2)	C61	C60	C59	117.1(2)
N21	N20	Y1	123.78(16)	C61	C60	C69	121.5(3)
C81	N20	Y1	129.76(16)	C59	C60	C69	121.0(3)
N22A	N21	N20	110.5(5)	C60	C61	C62	120.4(2)
N20	N21	N22	104.0(2)	C61	C62	C57	122.7(2)
N23	N22	N21	115.3(3)	C61	C62	C63	131.3(2)
N23	N22	C82	121.6(3)	C57	C62	C63	105.9(2)
N21	N22	C82	123.2(3)	C64	C63	C62	131.3(2)
N22	N23	C81	100.7(3)	C64	C63	C68	122.9(2)
N21	N22A	N23A	105.5(11)	C62	C63	C68	105.6(2)
N21	N22A	C82A	127.3(10)	C65	C64	C63	120.6(2)
N23A	N22A	C82A	123.4(11)	C64	C65	C66	117.2(2)
N22A	N23A	C81	107.9(10)	C64	C65	C73	123.7(3)
N25	N24	C77	106.4(2)	C66	C65	C73	119.1(3)
N24	N25	N26	106.0(2)	C65	C66	C67	124.0(3)
N25	N26	N27	114.2(2)	C66	C67	C68	118.7(2)
N25	N26	C78	122.8(3)	C66	C67	C81	116.0(2)
N27	N26	C78	122.9(3)	C68	C67	C81	125.4(2)
N26	N27	C77	101.3(2)	N19	C68	C67	131.4(2)
N1	C1	C2	129.0(2)	N19	C68	C63	112.1(2)
N1	C1	C6	112.9(2)	C67	C68	C63	116.5(2)
C2	C1	C6	118.1(2)	C70A	C69	C71A	119.1(5)
C3	C2	C1	118.9(2)	C72	C69	C60	116.1(4)
C3	C2	C21	118.9(2)	C70A	C69	C60	111.6(4)
C1	C2	C21	122.2(2)	C71A	C69	C60	108.1(4)
C2	C3	C4	123.4(2)	C72	C69	C70	112.8(5)
C5	C4	C3	117.6(2)	C60	C69	C70	107.6(3)

C5	C4	C13	123.9(2)	C72	C69	C71	108.3(4)
C3	C4	C13	118.6(2)	C60	C69	C71	109.9(3)
C4	C5	C6	120.6(2)	C70	C69	C71	101.2(4)
C5	C6	C1	121.4(2)	C70A	C69	C72A	107.9(4)
C5	C6	C7	133.3(2)	C71A	C69	C72A	101.3(4)
C1	C6	C7	105.3(2)	C60	C69	C72A	107.9(3)
C8	C7	C12	121.3(2)	C75	C73	C76	112.2(3)
C8	C7	C6	133.4(2)	C75	C73	C65	109.1(2)
C12	C7	C6	105.2(2)	C76	C73	C65	109.1(2)
C9	C8	C7	120.6(2)	C75	C73	C74	107.8(3)
C8	C9	C10	117.5(2)	C76	C73	C74	106.8(3)
C8	C9	C17	123.2(2)	C65	C73	C74	111.8(3)
C10	C9	C17	119.2(2)	N27	C77	N24	112.0(2)
C11	C10	C9	123.3(2)	N27	C77	C58	123.6(2)
C10	C11	C12	118.7(2)	N24	C77	C58	123.2(2)
C10	C11	C25	120.0(2)	C79A	C78	N26	121.2(9)
C12	C11	C25	121.2(2)	C80	C78	N26	112.7(4)
N1	C12	C11	128.7(2)	C80	C78	C79	113.4(4)
N1	C12	C7	113.1(2)	N26	C78	C79	106.3(4)
C11	C12	C7	118.2(2)	C79A	C78	C80A	118.1(11)
C16	C13	C14	107.9(3)	N26	C78	C80A	106.5(7)
C16	C13	C4	111.6(2)	N23	C81	N20	113.2(3)
C14	C13	C4	109.4(2)	N23	C81	C67	120.0(3)
C16	C13	C15	109.2(3)	N20	C81	C67	126.8(2)
C14	C13	C15	109.8(3)	N20	C81	N23A	98.9(6)
C4	C13	C15	108.9(3)	C67	C81	N23A	127.3(5)
C19	C17	C18	109.2(3)	C83	C82	N22	109.9(6)
C19	C17	C9	108.8(2)	C83	C82	C84	116.1(6)
C18	C17	C9	112.1(2)	N22	C82	C84	108.3(4)
C19	C17	C20	109.8(3)	C83A	C82A	N22A	114.2(17)
C18	C17	C20	107.0(3)	C83A	C82A	C84A	95.8(17)
C9	C17	C20	109.9(2)	N22A	C82A	C84A	104.8(16)
N5	C21	N2	111.4(2)	C6S	C1S	C7S	123.5(11)
N5	C21	C2	123.6(2)	C6S	C1S	C2S	124.6(13)
N2	C21	C2	125.1(2)	C7S	C1S	C2S	111.9(13)
N4	C22	C24	109.3(2)	C3S	C2S	C1S	112.6(11)
N4	C22	C23	107.9(2)	C2S	C3S	C4S	127.3(10)
C24	C22	C23	113.8(3)	C5S	C4S	C3S	117.7(13)
N9	C25	N6	111.4(2)	C4S	C5S	C6S	119.9(14)
N9	C25	C11	123.7(2)	C1S	C6S	C5S	117.8(10)

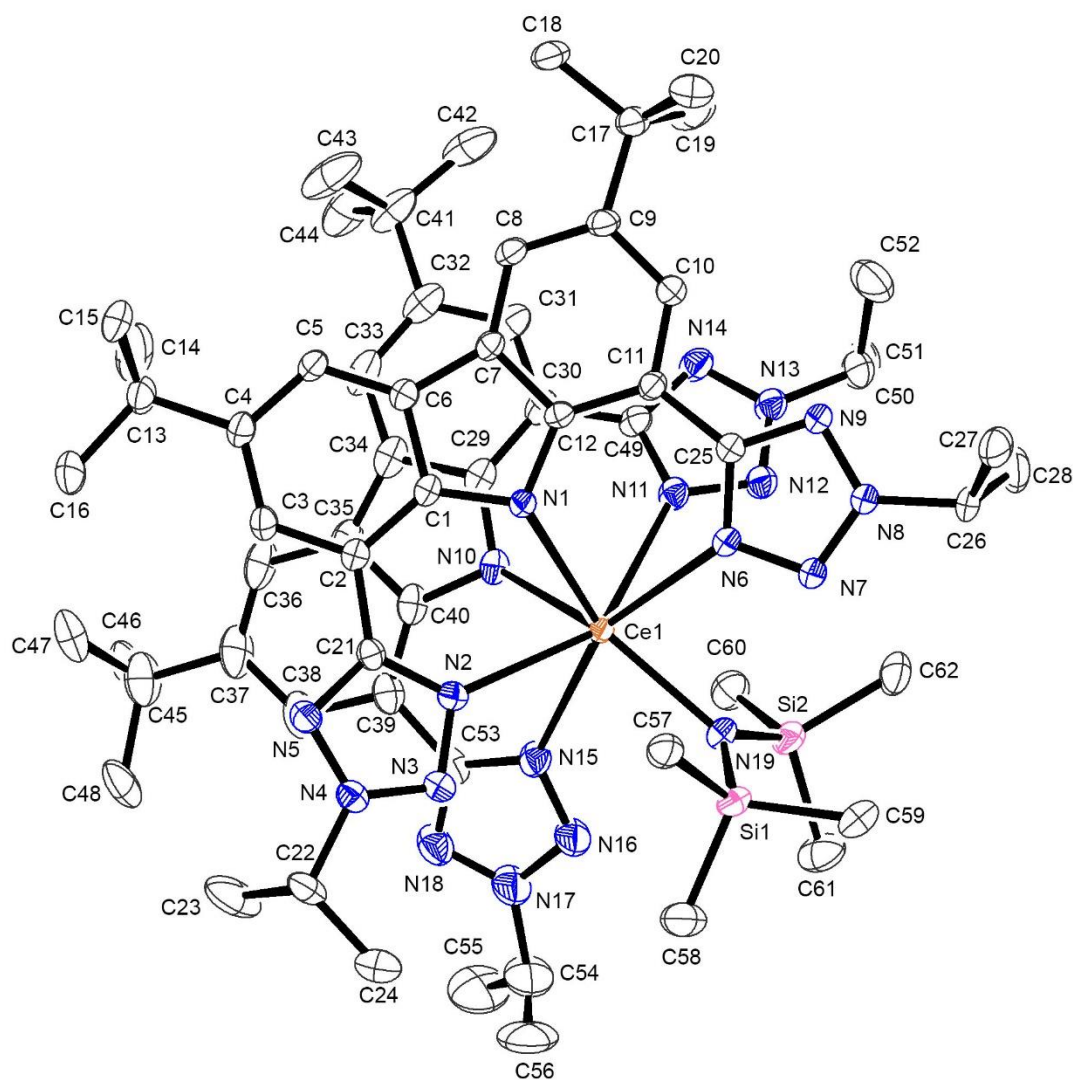


Figure B-12 Labelled ORTEP Drawing of **21**

H atoms not shown

Disordered toluene of solvation not shown: C63-C69

Disordered tBu carbons C46B, C47B and C48B not shown

Disordered iPr carbons C55B and C56B not shown

Table B-41 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **21**

Atom	x	y	z	U(eq)
Ce1	3631.3(2)	6186.3(2)	3960.1(2)	17.35(4)
Si1	3416.9(2)	4719.7(4)	4497.4(3)	26.97(16)
Si2	2821.7(2)	6004.4(4)	4103.7(3)	28.46(16)
N1	3943.4(6)	6021.7(11)	3408.3(8)	17.7(4)
N2	4450.1(6)	5922.8(12)	4725.0(9)	21.0(4)
N3	4628.2(6)	5680.8(12)	5270.5(9)	22.4(4)
N4	5038.8(6)	5718.6(11)	5552.6(9)	21.9(4)
N5	5148.1(6)	5974.5(12)	5227.7(9)	23.3(4)
N6	3146.8(6)	5258.9(11)	3031.3(9)	20.7(4)
N7	2847.7(6)	4831.7(11)	2956.8(9)	21.4(4)
N8	2565.6(6)	4736.8(12)	2380.7(9)	22.1(4)
N9	2656.5(6)	5074.9(12)	2059.4(9)	24.5(4)
N10	3858.7(6)	7509.1(11)	3991.0(9)	22.9(4)
N11	3023.6(6)	6893.5(12)	2997.0(9)	23.2(4)
N12	2618.2(6)	6683.1(12)	2666.3(9)	25.3(5)
N13	2420.5(7)	7095.1(12)	2190.6(10)	26.4(5)
N14	2665.3(7)	7575.8(13)	2179.9(10)	28.3(5)
N15	3944.4(7)	6817.5(13)	5003.3(10)	27.9(5)
N16	3864.1(8)	6596.1(16)	5365.6(11)	38.3(6)
N17	4151.8(8)	6917.0(17)	5875.5(11)	43.5(7)
N18	4422.0(8)	7342.0(15)	5877.4(11)	37.5(6)
N19	3244.2(7)	5579.8(12)	4212.6(9)	24.2(4)
C1	4325.5(7)	6347.2(12)	3608.2(11)	18.1(5)
C2	4711.3(7)	6405.9(13)	4186.6(11)	19.6(5)
C3	5056.8(7)	6754.8(13)	4269.1(11)	21.7(5)
C4	5037.6(8)	7047.6(14)	3801.9(11)	23.0(5)
C5	4657.1(7)	6974.7(13)	3227.6(11)	20.4(5)
C6	4309.7(7)	6625.7(13)	3129.7(10)	19.1(5)
C7	3892.3(7)	6454.9(13)	2597.8(10)	18.9(5)
C8	3689.9(8)	6594.8(13)	2000.7(11)	21.1(5)
C9	3270.9(8)	6371.7(14)	1568.4(11)	22.3(5)
C10	3073.2(8)	5991.8(14)	1759.2(11)	22.5(5)
C11	3267.9(7)	5831.3(13)	2354.8(10)	19.0(5)
C12	3686.3(7)	6081.1(12)	2792.4(10)	17.6(4)
C13	5414.0(8)	7446.2(15)	3895.7(12)	29.6(6)
C14	5297.7(11)	8256.6(18)	3729.1(19)	54.9(10)
C15	5507.2(9)	7104(2)	3499.3(14)	43.3(8)
C16	5819.8(9)	7399(2)	4539.6(14)	43.1(8)
C17	3020.5(8)	6520.8(17)	904.3(11)	29.1(6)
C18	3284.2(9)	6932.0(18)	764.2(12)	33.4(6)
C19	2624.4(10)	6978(2)	677.5(15)	47.0(9)
C20	2877.3(11)	5787(2)	568.0(13)	43.7(8)

C21	4769.6(7)	6104.7(13)	4704.6(10)	19.2(5)
C22	5362.1(8)	5512.8(15)	6186.9(11)	28.7(6)
C23	5615.7(13)	6195(2)	6527.8(14)	60.5(11)
C24	5151.7(10)	5163.8(17)	6424.7(12)	35.4(6)
C25	3028.6(7)	5395.0(13)	2482.5(10)	20.6(5)
C26	2175.4(8)	4292.4(15)	2108.3(12)	26.3(5)
C27	2147.9(10)	3731.2(17)	1692.7(13)	36.5(7)
C28	1791.9(9)	4792.7(18)	1796.8(14)	39.2(7)
C29	3793.1(8)	7844.9(13)	3503.3(12)	24.1(5)
C30	3432.8(8)	7829.5(14)	2901.2(12)	24.1(5)
C31	3435.3(9)	8232.3(15)	2488.5(13)	29.5(6)
C32	3781.9(9)	8658.2(14)	2643.9(14)	31.9(6)
C33	4135.7(9)	8686.2(13)	3245.5(14)	31.2(6)
C34	4142.7(9)	8295.1(14)	3666.1(13)	27.3(5)
C35	4442.3(9)	8248.2(15)	4303.8(13)	31.8(6)
C36	4841.0(10)	8563.8(16)	4722.2(15)	38.1(7)
C37	5060.1(10)	8434.6(17)	5324.4(16)	42.7(8)
C38	4871.3(9)	7989.9(16)	5496.6(14)	37.5(7)
C39	4469.1(8)	7658.6(15)	5086.0(12)	28.7(6)
C40	4253.4(8)	7771.1(14)	4475.9(12)	26.3(5)
C41	3776.5(11)	9084.1(17)	2177.5(16)	42.3(8)
C42	3346.6(12)	9040(2)	1559.4(17)	51.5(9)
C43	4111.9(13)	8753(2)	2135(2)	64.7(12)
C44	3873.2(13)	9893.8(19)	2348(2)	59.7(10)
C45	5498.0(11)	8789.1(19)	5796.0(17)	48.8(8)
C46	5464.6(16)	9584(3)	5843(3)	35.3(13)
C46B	5416(3)	9366(5)	6124(4)	57(3)
C47	5824.9(15)	8597(3)	5681(3)	43.5(15)
C47B	5591(3)	9347(6)	5432(4)	62(3)
C48	5743.2(17)	8458(3)	6469(3)	48.3(17)
C48B	5774(3)	8268(6)	6069(5)	73(4)
C49	3047.7(8)	7433.0(14)	2693.8(11)	23.1(5)
C50	1956.1(8)	7055.4(17)	1718.8(12)	32.7(6)
C51	1760.7(10)	7778.3(18)	1700.6(17)	46.8(8)
C52	1869.1(10)	6853(2)	1139.0(14)	53.4(9)
C53	4282.7(8)	7267.9(15)	5320.0(12)	28.1(6)
C54	4159.4(13)	6832(3)	6398.3(16)	62.3(11)
C55	4642(3)	6831(7)	6974(3)	81(3)
C55B	4294(3)	7580(6)	6738(4)	78(3)
C56	4010(3)	6021(6)	6415(4)	65(2)
C56B	4329(4)	6191(5)	6682(4)	74(3)
C57	3779.8(8)	4370.4(15)	4334.6(12)	29.1(6)
C58	3752.7(10)	4707(2)	5331.4(13)	42.6(8)
C59	2981.8(9)	4026.5(16)	4206.2(14)	33.9(6)
C60	2861.1(10)	7030.0(16)	4066.4(14)	36.1(6)
C61	2776.9(11)	5842(2)	4710.0(15)	45.3(8)

C62	2303.3(9)	5707.1(18)	3393.1(14)	38.6(7)
C63	1808(2)	8935(3)	3188(4)	128(3)
C64	1743.8(15)	8244(3)	3338(3)	83.1(14)
C65	1962.2(18)	8142(4)	3966(3)	101.9(19)
C66	1916(2)	7487(4)	4163(3)	112(2)
C67	1665(2)	6942(4)	3747(3)	126(2)
C68	1450.3(19)	7021(3)	3135(3)	99.0(17)
C69	1512.2(15)	7665(3)	2972(3)	77.5(13)

Table B-42 Anisotropic Displacement Parameters (U_{ij} , Å² x10³) for **21**

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Ce1	16.59(6)	18.82(7)	18.65(7)	-0.83(5)	11.89(5)	-1.77(5)
Si1	27.4(4)	32.4(4)	25.7(4)	5.7(3)	18.7(3)	-1.0(3)
Si2	26.2(4)	36.3(4)	30.6(4)	3.5(3)	21.4(3)	0.2(3)
N1	16.6(9)	20.7(10)	16.9(9)	-1.4(7)	10.9(8)	-1.9(7)
N2	20.1(10)	24.6(10)	17.9(10)	0.4(8)	11.5(8)	-0.1(8)
N3	21.2(10)	24.6(11)	18.7(10)	0.7(8)	10.9(8)	0.1(8)
N4	20.9(10)	20.5(10)	19.7(10)	0.5(8)	10.2(9)	1.2(8)
N5	21.1(10)	24.5(11)	20.4(10)	0.5(8)	10.8(9)	-0.9(8)
N6	20.3(10)	22.9(10)	20.0(10)	0.2(8)	13.0(8)	-4.1(8)
N7	20.6(10)	22.7(10)	20.2(10)	-0.6(8)	12.3(8)	-5.6(8)
N8	20.1(10)	25.9(11)	19.4(10)	-0.6(8)	11.8(8)	-6.1(8)
N9	21.4(10)	33.0(12)	19.8(10)	-1.0(9)	13.2(9)	-8.6(9)
N10	22.1(10)	19.4(10)	28.8(11)	-3.5(8)	16.5(9)	-1.4(8)
N11	20.2(10)	25.2(11)	26.5(11)	2.1(9)	15.5(9)	2.6(8)
N12	21.2(10)	28.8(12)	26.0(11)	3.4(9)	14.5(9)	1.8(9)
N13	21.7(10)	30.6(12)	28.6(11)	5.9(9)	16.5(9)	3.9(9)
N14	25.8(11)	31.6(12)	32.5(12)	8.6(10)	20.6(10)	5.1(9)
N15	24.9(11)	34.2(12)	29.0(12)	-4.8(10)	18.9(10)	-2.3(9)
N16	33.1(13)	58.2(17)	26.5(12)	-12.5(11)	19.8(11)	-10.3(12)
N17	37.7(14)	65.9(19)	28.8(13)	-13.9(12)	21.5(12)	-9.4(13)
N18	30.3(12)	48.7(15)	29.0(12)	-10.7(11)	16.0(11)	-3.9(11)
N19	22.9(10)	29.6(11)	24.9(11)	0.6(9)	17.2(9)	-2.6(9)
C1	18.4(11)	15.6(11)	23.6(11)	-0.8(9)	14.7(10)	-0.6(8)
C2	18.7(11)	18.7(11)	22.7(12)	-0.5(9)	13.4(10)	-0.9(9)
C3	17.6(11)	20.0(12)	24.2(12)	-1.0(10)	11.3(10)	-2.7(9)
C4	20.5(11)	20.9(12)	28.5(13)	0.5(10)	15.6(10)	-2.5(9)
C5	20.4(11)	20.2(12)	25.2(12)	4.0(9)	16.3(10)	1.7(9)
C6	19.5(11)	17.7(11)	22.3(12)	-0.4(9)	14.1(10)	0.9(9)
C7	18.7(11)	20.4(11)	22.1(11)	0.7(9)	14.8(10)	0.7(9)
C8	22.6(11)	24.1(13)	23.1(12)	4.2(10)	17.5(10)	2.4(9)
C9	23.7(12)	28.0(13)	19.5(11)	2.4(10)	15.5(10)	2.7(10)
C10	19.4(11)	29.6(13)	19.6(11)	-0.9(10)	12.5(10)	-1.7(10)
C11	20.1(11)	19.9(12)	20.5(11)	-0.8(9)	14.2(10)	-2.3(9)

C12	19.5(11)	18.3(11)	18.3(11)	1.4(9)	13.4(9)	1.5(9)
C13	21.2(12)	30.9(14)	32.5(14)	5.7(11)	14.4(11)	-4.7(11)
C14	40.5(18)	35.1(17)	81(3)	14.0(17)	33.4(19)	-7.3(14)
C15	23.2(14)	71(2)	40.5(17)	6.1(16)	22.3(13)	-5.7(14)
C16	25.7(14)	54(2)	37.4(16)	1.9(14)	13.7(13)	-17.2(14)
C17	22.7(12)	44.8(16)	21.8(12)	6.0(11)	14.8(11)	2.9(11)
C18	29.1(14)	52.7(18)	24.6(13)	8.5(12)	19.7(12)	3.4(13)
C19	32.1(15)	75(2)	41.3(18)	31.2(17)	26.4(14)	18.7(16)
C20	43.7(17)	65(2)	25.2(15)	-5.6(14)	22.7(14)	-9.7(16)
C21	18.0(10)	17.2(11)	20.0(11)	-2.0(9)	10.5(9)	-0.9(9)
C22	28.7(13)	24.9(13)	16.8(12)	2.1(10)	6.2(11)	0.9(11)
C23	71(2)	43.0(19)	23.3(15)	-4.1(14)	7.0(16)	-21.7(18)
C24	41.9(16)	38.6(16)	24.5(14)	3.8(12)	19.9(13)	6.2(13)
C25	19.7(11)	22.9(12)	19.3(11)	-0.3(9)	12.2(10)	-2.3(9)
C26	20.5(12)	31.8(14)	25.8(13)	-2.9(11)	13.8(11)	-11.9(10)
C27	41.0(16)	39.1(17)	34.7(15)	-13.7(13)	26.1(14)	-21.3(13)
C28	20.5(13)	44.9(18)	41.2(17)	1.5(14)	13.5(13)	-7.5(12)
C29	27.3(12)	15.9(11)	36.6(14)	-1.2(10)	23.4(11)	0.5(10)
C30	25.7(12)	20.8(12)	34.9(14)	2.3(10)	23.4(11)	4.4(10)
C31	33.8(14)	25.4(13)	43.0(16)	8.0(12)	30.5(13)	10.2(11)
C32	42.4(15)	20.2(13)	54.2(17)	9.3(12)	40.4(15)	11.6(11)
C33	34.8(14)	14.2(12)	59.9(18)	2.4(11)	36.9(14)	2.6(10)
C34	32.5(13)	14.4(11)	45.4(15)	-5.6(11)	29.2(13)	-1.1(10)
C35	36.2(15)	22.6(13)	42.8(16)	-10.7(12)	27.4(13)	-11.7(11)
C36	39.1(16)	20.4(13)	61.9(19)	-15.7(13)	34.7(15)	-15.1(12)
C37	38.0(16)	32.4(16)	55.8(19)	-24.7(14)	28.0(15)	-18.0(13)
C38	32.7(15)	31.1(15)	40.2(16)	-18.8(13)	18.3(13)	-13.0(12)
C39	26.4(13)	23.0(13)	32.6(14)	-10.8(11)	16.2(11)	-4.6(10)
C40	26.1(12)	17.1(12)	37.4(14)	-8.7(10)	20.5(11)	-4.3(10)
C41	51.0(18)	32.6(15)	71(2)	23.0(15)	51.4(18)	18.4(14)
C42	69(2)	48(2)	66(2)	28.0(17)	56(2)	20.9(17)
C43	78(3)	70(3)	96(3)	45(2)	78(3)	40(2)
C44	71(3)	34.8(18)	95(3)	27.2(19)	63(2)	10.2(17)
C45	41.8(17)	36.6(17)	57(2)	-21.2(15)	24.7(16)	-20.2(14)
C46	25(2)	27(2)	36(3)	-8(2)	10(2)	-7.2(19)
C46B	45(5)	48(5)	46(5)	-25(4)	12(4)	-27(4)
C47	22(2)	39(3)	45(3)	-7(2)	8(2)	-1(2)
C47B	31(4)	65(6)	62(6)	-15(4)	16(4)	-29(4)
C48	33(3)	34(3)	36(3)	-1(2)	0(2)	-11(2)
C48B	21(4)	54(5)	77(8)	-9(5)	-3(4)	-8(3)
C49	23.2(12)	24.5(13)	27.1(13)	4.1(10)	18.3(11)	5.5(10)
C50	19.8(12)	41.3(16)	32.4(14)	5.4(12)	13.8(11)	3.1(11)
C51	28.0(15)	41.4(18)	65(2)	10.4(16)	26.1(16)	8.3(13)
C52	28.0(15)	89(3)	30.8(16)	-1.1(17)	11.8(14)	3.8(17)
C53	23.7(12)	29.7(14)	25.9(13)	-8.2(11)	12.8(11)	3.0(10)
C54	62(2)	101(3)	32.6(18)	-14.9(19)	33.9(18)	-13(2)

C55	59(5)	131(10)	34(4)	-11(5)	19(4)	12(5)
C55B	96(7)	106(7)	55(5)	-14(5)	58(5)	1(6)
C56	73(6)	90(6)	41(4)	3(4)	40(5)	12(5)
C56B	103(8)	87(6)	28(4)	-4(4)	39(5)	-25(5)
C57	26.4(13)	30.6(14)	29.3(14)	8.7(11)	16.7(12)	3.6(11)
C58	40.9(17)	56(2)	30.7(15)	11.8(14)	22.1(14)	5.7(15)
C59	40.3(16)	33.2(15)	40.0(16)	4.3(12)	30.6(14)	-3.4(12)
C60	35.8(15)	36.9(16)	40.9(17)	1.2(13)	26.3(14)	1.8(13)
C61	46.7(18)	59(2)	49.7(19)	12.8(17)	39.5(17)	12.5(16)
C62	25.3(14)	46.9(18)	45.7(17)	2.1(14)	23.0(13)	-4.8(13)
C63	134(6)	91(4)	228(8)	-16(5)	146(6)	-28(4)
C64	60(3)	61(3)	126(4)	1(3)	57(3)	8(2)
C65	74(3)	154(5)	82(3)	-1(4)	50(3)	40(4)
C66	96(4)	135(5)	80(4)	2(3)	42(3)	44(4)
C67	123(5)	122(5)	80(4)	10(3)	36(4)	51(4)
C68	93(4)	65(3)	110(4)	7(3)	49(3)	10(3)
C69	75(3)	65(3)	103(4)	-17(3)	60(3)	-9(2)

Table B-43 Bond Lengths for **21**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ce1	Si1	3.4440(8)	C8	C9	1.395(3)
Ce1	N1	2.5666(19)	C9	C10	1.392(3)
Ce1	N2	2.627(2)	C9	C17	1.528(3)
Ce1	N6	2.703(2)	C10	C11	1.398(3)
Ce1	N10	2.557(2)	C11	C12	1.410(3)
Ce1	N11	2.624(2)	C11	C25	1.455(3)
Ce1	N15	2.679(2)	C13	C14	1.531(4)
Ce1	N19	2.352(2)	C13	C15	1.529(4)
Si1	N19	1.702(2)	C13	C16	1.530(4)
Si1	C57	1.890(3)	C17	C18	1.536(4)
Si1	C58	1.881(3)	C17	C19	1.536(4)
Si1	C59	1.878(3)	C17	C20	1.535(4)
Si2	N19	1.705(2)	C22	C23	1.517(4)
Si2	C60	1.882(3)	C22	C24	1.512(4)
Si2	C61	1.875(3)	C26	C27	1.520(4)
Si2	C62	1.876(3)	C26	C28	1.513(4)
N1	C1	1.392(3)	C29	C30	1.406(4)
N1	C12	1.391(3)	C29	C34	1.429(3)
N2	N3	1.328(3)	C30	C31	1.395(4)
N2	C21	1.358(3)	C30	C49	1.456(3)
N3	N4	1.311(3)	C31	C32	1.401(4)
N4	N5	1.333(3)	C32	C33	1.400(4)
N4	C22	1.485(3)	C32	C41	1.532(4)
N5	C21	1.338(3)	C33	C34	1.384(4)

N6	N7	1.330(3)	C34	C35	1.439(4)
N6	C25	1.354(3)	C35	C36	1.396(4)
N7	N8	1.312(3)	C35	C40	1.425(4)
N8	N9	1.331(3)	C36	C37	1.388(5)
N8	C26	1.483(3)	C37	C38	1.389(5)
N9	C25	1.340(3)	C37	C45	1.545(4)
N10	C29	1.392(3)	C38	C39	1.414(4)
N10	C40	1.393(3)	C39	C40	1.404(4)
N11	N12	1.334(3)	C39	C53	1.460(4)
N11	C49	1.353(3)	C41	C42	1.528(5)
N12	N13	1.308(3)	C41	C43	1.544(4)
N13	N14	1.329(3)	C41	C44	1.525(5)
N13	C50	1.477(3)	C45	C46	1.466(6)
N14	C49	1.338(3)	C45	C46B	1.573(11)
N15	N16	1.324(3)	C45	C47	1.574(7)
N15	C53	1.346(3)	C45	C47B	1.654(10)
N16	N17	1.311(3)	C45	C48	1.643(7)
N17	N18	1.328(4)	C45	C48B	1.291(10)
N17	C54	1.485(4)	C50	C51	1.515(4)
N18	C53	1.332(3)	C50	C52	1.515(4)
C1	C2	1.406(3)	C54	C55	1.586(9)
C1	C6	1.425(3)	C54	C55B	1.562(10)
C2	C3	1.404(3)	C54	C56	1.606(11)
C2	C21	1.458(3)	C54	C56B	1.342(10)
C3	C4	1.397(4)	C63	C64	1.401(7)
C4	C5	1.395(3)	C64	C65	1.446(8)
C4	C13	1.540(3)	C64	C69	1.365(7)
C5	C6	1.391(3)	C65	C66	1.378(9)
C6	C7	1.436(3)	C66	C67	1.390(9)
C7	C8	1.389(3)	C67	C68	1.402(8)
C7	C12	1.422(3)	C68	C69	1.340(7)

Table B-44 Bond Angles for **21**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Ce1	Si1	122.34(5)	C8	C9	C17	123.8(2)
N1	Ce1	N2	70.10(6)	C10	C9	C8	117.4(2)
N1	Ce1	N6	69.42(6)	C10	C9	C17	118.8(2)
N1	Ce1	N11	84.21(6)	C9	C10	C11	123.9(2)
N1	Ce1	N15	131.71(6)	C10	C11	C12	118.5(2)
N2	Ce1	Si1	90.79(5)	C10	C11	C25	117.6(2)
N2	Ce1	N6	118.23(6)	C12	C11	C25	124.0(2)
N2	Ce1	N15	70.52(6)	N1	C12	C7	112.3(2)
N6	Ce1	Si1	74.30(5)	N1	C12	C11	130.0(2)
N10	Ce1	Si1	153.70(5)	C11	C12	C7	117.7(2)

N10	Ce1	N1	80.36(6)	C14	C13	C4	108.9(2)
N10	Ce1	N2	84.76(7)	C15	C13	C4	109.9(2)
N10	Ce1	N6	130.25(6)	C15	C13	C14	109.1(3)
N10	Ce1	N11	69.73(7)	C15	C13	C16	107.8(2)
N10	Ce1	N15	69.28(7)	C16	C13	C4	112.4(2)
N11	Ce1	Si1	121.60(5)	C16	C13	C14	108.7(3)
N11	Ce1	N2	146.56(6)	C9	C17	C18	112.5(2)
N11	Ce1	N6	68.74(7)	C9	C17	C19	109.5(2)
N11	Ce1	N15	116.83(7)	C9	C17	C20	109.2(2)
N15	Ce1	Si1	84.78(5)	C19	C17	C18	108.8(2)
N15	Ce1	N6	157.05(6)	C20	C17	C18	108.1(2)
N19	Ce1	Si1	26.52(5)	C20	C17	C19	108.6(3)
N19	Ce1	N1	143.01(7)	N2	C21	C2	124.9(2)
N19	Ce1	N2	112.26(7)	N5	C21	N2	110.8(2)
N19	Ce1	N6	78.47(7)	N5	C21	C2	124.3(2)
N19	Ce1	N10	136.05(7)	N4	C22	C23	108.1(2)
N19	Ce1	N11	101.16(7)	N4	C22	C24	110.4(2)
N19	Ce1	N15	78.59(7)	C24	C22	C23	113.1(3)
N19	Si1	Ce1	38.09(7)	N6	C25	C11	125.4(2)
N19	Si1	C57	109.77(11)	N9	C25	N6	111.4(2)
N19	Si1	C58	112.30(14)	N9	C25	C11	123.2(2)
N19	Si1	C59	114.49(12)	N8	C26	C27	108.7(2)
C57	Si1	Ce1	73.06(9)	N8	C26	C28	109.7(2)
C58	Si1	Ce1	113.35(11)	C28	C26	C27	112.8(2)
C58	Si1	C57	104.66(14)	N10	C29	C30	129.4(2)
C59	Si1	Ce1	137.87(10)	N10	C29	C34	112.7(2)
C59	Si1	C57	107.98(13)	C30	C29	C34	117.9(2)
C59	Si1	C58	107.10(14)	C29	C30	C49	122.4(2)
N19	Si2	C60	110.57(12)	C31	C30	C29	119.2(2)
N19	Si2	C61	114.30(13)	C31	C30	C49	118.4(2)
N19	Si2	C62	112.06(13)	C30	C31	C32	123.1(3)
C61	Si2	C60	105.56(15)	C31	C32	C41	121.7(3)
C61	Si2	C62	106.44(15)	C33	C32	C31	117.5(3)
C62	Si2	C60	107.46(14)	C33	C32	C41	120.8(3)
C1	N1	Ce1	121.83(14)	C34	C33	C32	120.8(3)
C12	N1	Ce1	120.66(14)	C29	C34	C35	105.1(2)
C12	N1	C1	104.62(18)	C33	C34	C29	121.5(3)
N3	N2	Ce1	121.81(15)	C33	C34	C35	133.3(3)
N3	N2	C21	107.21(19)	C36	C35	C34	132.7(3)
C21	N2	Ce1	130.08(16)	C36	C35	C40	121.6(3)
N4	N3	N2	105.33(19)	C40	C35	C34	105.7(2)
N3	N4	N5	114.62(19)	C37	C36	C35	120.4(3)
N3	N4	C22	123.6(2)	C36	C37	C38	118.3(3)
N5	N4	C22	121.8(2)	C36	C37	C45	121.3(3)
N4	N5	C21	102.06(19)	C38	C37	C45	120.4(3)
N7	N6	Ce1	123.41(15)	C37	C38	C39	123.0(3)

N7	N6	C25	106.66(19)	C38	C39	C53	118.0(3)
C25	N6	Ce1	123.39(15)	C40	C39	C38	118.7(3)
N8	N7	N6	105.61(18)	C40	C39	C53	123.1(2)
N7	N8	N9	114.60(19)	N10	C40	C35	112.5(2)
N7	N8	C26	122.8(2)	N10	C40	C39	129.5(2)
N9	N8	C26	122.6(2)	C39	C40	C35	117.9(2)
N8	N9	C25	101.73(19)	C32	C41	C43	109.0(2)
C29	N10	Ce1	122.45(16)	C42	C41	C32	112.4(3)
C29	N10	C40	104.1(2)	C42	C41	C43	107.5(3)
C40	N10	Ce1	121.17(16)	C44	C41	C32	110.2(3)
N12	N11	Ce1	122.43(15)	C44	C41	C42	107.7(3)
N12	N11	C49	107.0(2)	C44	C41	C43	110.0(3)
C49	N11	Ce1	129.96(16)	C37	C45	C46B	104.9(4)
N13	N12	N11	105.2(2)	C37	C45	C47	111.5(3)
N12	N13	N14	114.9(2)	C37	C45	C47B	106.4(4)
N12	N13	C50	122.2(2)	C37	C45	C48	113.8(3)
N14	N13	C50	122.8(2)	C46	C45	C37	111.9(3)
N13	N14	C49	101.9(2)	C46	C45	C47	112.0(4)
N16	N15	Ce1	124.69(17)	C46	C45	C48	106.1(4)
N16	N15	C53	106.8(2)	C46B	C45	C47B	100.2(6)
C53	N15	Ce1	126.48(17)	C47	C45	C48	101.0(4)
N17	N16	N15	105.3(2)	C48B	C45	C37	107.9(5)
N16	N17	N18	114.7(2)	C48B	C45	C46B	123.1(8)
N16	N17	C54	122.1(3)	C48B	C45	C47B	113.0(8)
N18	N17	C54	123.2(3)	N11	C49	C30	125.2(2)
N17	N18	C53	101.5(2)	N14	C49	N11	111.0(2)
Si1	N19	Ce1	115.40(11)	N14	C49	C30	123.8(2)
Si1	N19	Si2	124.62(13)	N13	C50	C51	108.7(2)
Si2	N19	Ce1	119.98(11)	N13	C50	C52	108.7(2)
N1	C1	C2	130.2(2)	C51	C50	C52	114.2(3)
N1	C1	C6	111.9(2)	N15	C53	C39	125.1(2)
C2	C1	C6	117.9(2)	N18	C53	N15	111.7(3)
C1	C2	C21	122.5(2)	N18	C53	C39	123.1(2)
C3	C2	C1	119.0(2)	N17	C54	C55	107.4(4)
C3	C2	C21	118.5(2)	N17	C54	C55B	108.7(5)
C4	C3	C2	123.1(2)	N17	C54	C56	110.5(4)
C3	C4	C13	123.0(2)	C55	C54	C56	101.8(6)
C5	C4	C3	117.7(2)	C56B	C54	N17	112.8(5)
C5	C4	C13	119.3(2)	C56B	C54	C55B	122.0(6)
C6	C5	C4	120.6(2)	C63	C64	C65	114.2(6)
C1	C6	C7	105.8(2)	C69	C64	C63	128.7(6)
C5	C6	C1	121.6(2)	C69	C64	C65	117.1(6)
C5	C6	C7	132.5(2)	C66	C65	C64	119.2(6)
C8	C7	C6	132.5(2)	C65	C66	C67	118.4(7)
C8	C7	C12	122.1(2)	C66	C67	C68	123.9(7)
C12	C7	C6	105.4(2)	C69	C68	C67	114.9(6)

C7	C8	C9	120.3(2)	C68	C69	C64	126.4(6)

Table B-45 Summary of Crystallographic Data for **23**, **24** and **25**

	23•3.5 C₇H₈^a	24•C₆H₁₄^b	25^b
Emp. Formula	C _{80.5} H ₁₀₀ FeN ₁₈	C ₉₀ H ₁₁₀ FeN ₁₈	C ₅₆ H ₇₂ BF ₄ FeN ₁₈
Formula wgt. (g/mol)	1375.63	1499.80	1139.97
Temp. (K)	120.2	119.98	120.03
Crystal System	Triclinic	Monoclinic	Trigonal
Space Group	P-1	C2/c	P3 ₁ 21
a (Å)	16.1950(3)	19.0443(18)	20.4857(5)
b (Å)	16.8867(4)	16.0269(18)	20.4857(5)
c (Å)	17.1351(4)	26.878(3)	15.7808(4)
α (°)	64.8990(10)	90	90
β (°)	62.2780(10)	92.353(2)	90
γ (°)	87.5200(10)	90	120
Volume (Å³)	3686.43(15)	8196.9(15)	5735.4(3)
Z	2	4	3
Density (g/cm³)	1.239	1.215	0.990
Abs. coeff. μ (mm⁻¹)	2.084	0.241	0.248
F(000)	1470	3208	1803
Crystal Size (mm)	0.173 x 0.095 x 0.069	0.241 x 0.185 x 0.064	0.318 x 0.244 x 0.207
Colour and habit	Red block	Red-orange tablet	Green block
Theta range (°)	2.94° ≤ 2θ ≤ 71.92°	3.032° ≤ 2θ ≤ 52.778°	3.454° ≤ 2θ ≤ 56.556°
Refl. Collected	108561	67606	83494
Independent refl.	14038	8391	9501
GooF (F²)	1.034	1.040	1.041
Final R [I>2σ(I)]	0.0516	0.0451	0.0422
Final wR2	0.1308	0.1053	0.1127
R (all data)	0.0705	0.0660	0.0482
wR2 (all data)	0.1450	0.1156	0.1170
Max peak/hole (e/Å³)	0.525/-0.262	0.452/-0.420	0.580/-0.311

^a Data collected on a Bruker Kappa X8-Apex II diffractometer using Cu Kα radiation (λ = 1.54184 Å) at the University of Notre Dame. ^b Data collected on a Bruker Kappa X8-Apex II diffractometer using Mo Kα radiation (λ = 0.71073 Å) at the University of Notre Dame.

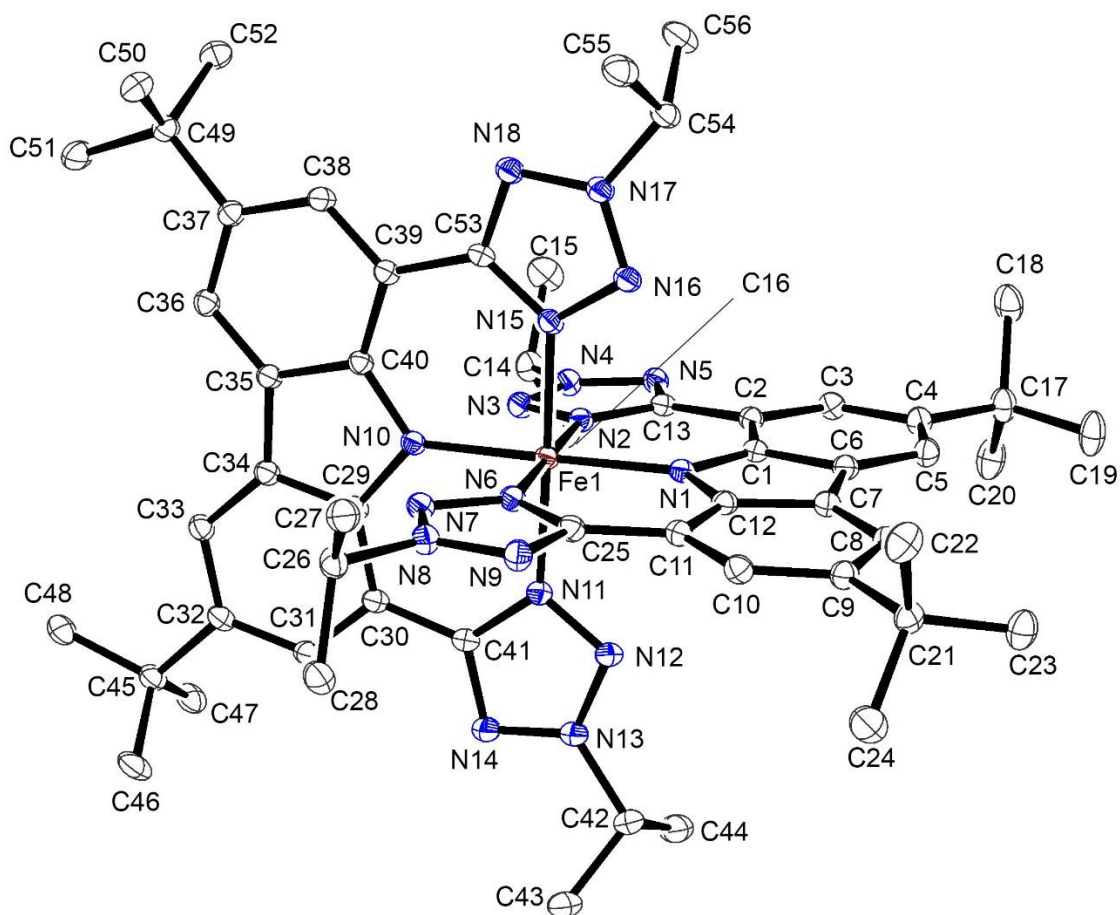


Figure B-13 Labeled ORTEP Drawing of **23**

H atoms not shown

Disordered toluenes of solvation not shown: C57-C84

Disordered tBu carbons C18A, C19A, C20A, C46A, C47A and C48A not shown

Table B-46 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **23**

Atom	x	y	z	U(eq)
Fe1	3398.4(2)	7305.1(2)	3255.4(3)	28.39(10)
N1	4328.6(13)	6953.5(12)	2267.6(14)	30.5(4)
N2	2636.8(13)	6065.1(13)	4074.3(14)	32.1(4)
N3	1861.0(14)	5784.0(14)	4962.7(15)	36.1(4)
N4	1565.3(14)	4946.8(14)	5242.8(15)	36.8(4)
N5	2093.5(14)	4643.0(14)	4600.3(15)	36.2(4)
N6	4171.0(13)	8528.1(13)	2433.9(14)	31.7(4)
N7	3931.0(14)	9183.1(13)	2684.5(15)	35.2(4)
N8	4621.9(14)	9871.2(14)	1979.2(15)	37.5(4)
N9	5315.8(14)	9719.2(14)	1273.2(16)	38.6(4)
N10	2450.9(13)	7652.8(12)	4243.2(14)	30.6(4)
N11	4145.7(13)	7017.2(13)	3975.3(15)	32.4(4)
N12	4996.1(14)	6784.9(14)	3649.8(16)	36.1(4)
N13	5269.2(14)	6720.7(15)	4283.6(16)	39.8(5)
N14	4656.8(15)	6892.5(15)	5017.5(17)	41.1(5)
N15	2665.6(13)	7642.5(13)	2526.1(14)	31.8(4)
N16	2949.5(14)	7621.2(14)	1671.3(15)	36.3(4)
N17	2293.9(14)	7912.4(15)	1428.7(15)	37.6(4)
N18	1586.4(14)	8124.4(14)	2067.0(15)	37.7(4)
C1	4280.5(15)	6143.7(15)	2274.0(17)	31.0(4)
C2	3575.1(16)	5369.9(16)	2983.2(17)	32.7(5)
C3	3684.7(17)	4607.5(16)	2847.3(18)	36.7(5)
C4	4463.1(18)	4580.4(17)	2024.7(19)	38.9(5)
C5	5155.0(17)	5348.2(16)	1324.9(18)	38.1(5)
C6	5072.1(16)	6121.6(16)	1440.3(17)	33.4(5)
C7	5661.1(16)	6990.3(16)	886.5(18)	33.5(5)
C8	6550.5(16)	7390.0(16)	32.8(18)	35.4(5)
C9	6948.0(16)	8267.6(17)	-321.0(18)	36.5(5)
C10	6423.8(17)	8738.3(16)	196.3(18)	36.2(5)
C11	5542.3(16)	8360.0(16)	1054.7(17)	33.4(5)
C12	5160.0(15)	7461.7(15)	1425.8(17)	31.5(4)
C13	2768.3(15)	5363.1(15)	3868.4(17)	31.5(4)
C14	740.8(18)	4367.4(18)	6225.4(19)	44.3(6)
C15	-42(2)	4056(3)	6110(2)	66.6(9)
C16	1075(2)	3583(2)	6790(2)	63.5(9)
C17	4532(2)	3712.4(18)	1926(2)	48.0(6)
C18	3689(3)	3482(3)	1807(3)	60.8(11)
C19	5453(3)	3776(3)	1058(3)	63.8(13)
C20	4444(3)	2946(2)	2885(3)	63.0(12)
C18A	5503(11)	3453(10)	1881(12)	49(4)
C19A	3782(10)	2997(10)	2632(11)	46(3)
C20A	4699(11)	3970(11)	850(12)	52(4)

C21	7916.3(17)	8750.4(17)	-1270.7(19)	40.0(5)
C22	7765(2)	9480(2)	-2078(2)	53.3(7)
C23	8437(2)	8113(2)	-1665(2)	52.0(7)
C24	8555(2)	9174(3)	-1058(2)	63.8(9)
C25	5015.8(16)	8866.0(15)	1576.3(17)	33.4(5)
C26	4647.5(18)	10736.4(17)	1995(2)	40.9(5)
C27	4878(2)	11473.6(17)	985(2)	45.1(6)
C28	5365(2)	10834(2)	2300(2)	50.7(7)
C29	2438.6(16)	7622.1(15)	5057.7(17)	32.2(5)
C30	3109.7(16)	7349.8(16)	5379.8(18)	34.6(5)
C31	2947.2(17)	7358.9(17)	6249.4(19)	38.0(5)
C32	2149.8(17)	7619.8(17)	6819.7(18)	38.0(5)
C33	1491.4(17)	7890.5(17)	6494.7(18)	36.5(5)
C34	1634.3(16)	7891.6(15)	5628.2(17)	33.5(5)
C35	1095.7(16)	8107.7(15)	5113.2(17)	32.6(5)
C36	233.1(16)	8391.6(16)	5286.6(18)	35.8(5)
C37	-118.1(16)	8519.6(16)	4650.8(18)	35.2(5)
C38	421.8(16)	8363.4(16)	3827.3(18)	34.9(5)
C39	1291.0(16)	8084.7(15)	3628.3(17)	31.9(4)
C40	1637.0(15)	7947.7(15)	4279.4(16)	30.3(4)
C41	3954.6(16)	7086.3(16)	4799.5(18)	34.3(5)
C42	6195.0(19)	6471(2)	4193(2)	46.8(6)
C43	6556(2)	6940(2)	4587(3)	55.0(7)
C44	6085(2)	5466(2)	4747(3)	56.5(7)
C45	2000.6(18)	7587.1(19)	7789.8(19)	41.1(5)
C46	2868(3)	8138(3)	7579(3)	57.8(11)
C47	1859(3)	6625(3)	8526(3)	51.1(9)
C48	1123(3)	7966(3)	8264(3)	50.8(9)
C46A	1088(11)	6923(10)	8660(12)	55(4)
C47A	1999(11)	8504(10)	7709(12)	56(4)
C48A	2845(11)	7250(10)	8002(12)	54(4)
C49	-1077.4(16)	8808.4(18)	4818.1(19)	38.8(5)
C50	-901.0(19)	9733.8(19)	3980(2)	48.4(6)
C51	-1617(2)	8853(2)	5802(2)	56.3(8)
C52	-1696.9(18)	8141(2)	4830(2)	50.1(7)
C53	1842.5(15)	7950.5(15)	2749.4(17)	31.7(5)
C54	2331.7(18)	8003.1(19)	517.2(19)	42.9(6)
C55	2330(2)	8971(2)	-100(2)	52.6(7)
C56	1495(2)	7376(2)	791(2)	55.4(7)
C57	8554(2)	9039(2)	1820(3)	61.1(8)
C58	8010(3)	9466(2)	2368(3)	66.5(9)
C59	7040(3)	9378(2)	2713(3)	66.1(9)
C60	6601(3)	8864(2)	2519(3)	66.9(9)
C61	7132(3)	8443(2)	1971(3)	63.9(8)
C62	8093(3)	8527(2)	1631(3)	63.6(8)
C63	9611(3)	9132(3)	1441(4)	91.3(13)

C64	7491(2)	5548(2)	2129(3)	60.3(8)
C65	8034(3)	4970(2)	2427(3)	64.9(9)
C66	9018(3)	5214(4)	1935(4)	93.9(15)
C67	9456(3)	6057(4)	1143(4)	98.7(16)
C68	8917(4)	6635(3)	872(3)	88.0(12)
C69	7957(3)	6398(3)	1347(3)	75.3(10)
C70	6454(3)	5270(4)	2584(3)	87.7(13)
C71	1351(3)	4406(3)	1362(3)	67.9(9)
C72	756(3)	3846(2)	2349(3)	65.5(9)
C73	845(2)	3930(2)	3078(3)	64.2(8)
C74	1531(3)	4557(3)	2829(3)	69.5(9)
C75	2138(3)	5119(3)	1847(3)	81.7(11)
C76	2056(3)	5050(3)	1114(3)	76.9(11)
C77	1242(5)	4348(3)	575(4)	109.5(18)
C78	4577(5)	10160(8)	5010(5)	86(3)
C79	5310(30)	10630(20)	4990(20)	87(9)
C80	5977(7)	10379(6)	5109(6)	74(2)
C81	6119(10)	9511(11)	5211(11)	77(3)
C82	5539(8)	9073(6)	5199(6)	81(2)
C83	4860(20)	9270(17)	5057(19)	60(4)
C84	3700(15)	10300(20)	4930(17)	249(19)

Table B-47 Anisotropic Displacement Parameters (U_{ij} , Å² x10³) for **23**

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Fe1	26.74(17)	32.02(18)	28.57(18)	-	-	3.91(13)
				14.80(14)	14.23(14)	
N1	28.9(9)	33.2(9)	31.2(10)	-14.4(8)	-16.3(8)	3.8(7)
N2	29.1(9)	37.0(10)	29.4(9)	-15.0(8)	-14.0(8)	4.1(7)
N3	32.8(10)	39.1(11)	32.7(10)	-15.6(8)	-13.9(8)	2.3(8)
N4	34.5(10)	37.7(11)	33.3(10)	-15.7(8)	-13.1(8)	2.1(8)
N5	33.7(10)	40.6(11)	32.7(10)	-17.6(9)	-14.1(8)	4.1(8)
N6	33.7(9)	32.0(9)	34.0(10)	-16.4(8)	-18.9(8)	7.0(7)
N7	36.4(10)	35.7(10)	37.0(11)	-18.0(8)	-19.5(9)	6.6(8)
N8	37.9(10)	35.9(10)	37.2(11)	-17.7(9)	-16.7(9)	6.5(8)
N9	36.3(10)	37.3(11)	39.7(11)	-19.6(9)	-15.1(9)	6.0(8)
N10	29.7(9)	33.5(9)	31.0(9)	-15.7(8)	-15.7(8)	4.1(7)
N11	30.9(9)	33.9(10)	35.2(10)	-16.6(8)	-17.7(8)	5.9(7)
N12	33.5(10)	40.3(11)	41.0(11)	-19.5(9)	-22.4(9)	8.5(8)
N13	37.5(11)	49.0(12)	43.2(12)	-24.0(10)	-25.1(9)	11.2(9)
N14	37.7(11)	53.0(13)	42.0(12)	-24.9(10)	-24.0(9)	11.6(9)
N15	31.1(9)	36.9(10)	29.3(9)	-17.0(8)	-14.3(8)	3.4(7)
N16	33.7(10)	46.1(11)	33.6(10)	-20.9(9)	-17.5(8)	5.9(8)
N17	34.4(10)	49.6(12)	33.5(10)	-21.5(9)	-17.9(8)	8.3(8)
N18	34.0(10)	49.3(12)	33.5(10)	-20.8(9)	-17.4(8)	6.2(8)

C1	31.9(11)	34.7(11)	31.7(11)	-16.0(9)	-18.8(9)	7.4(9)
C2	31.1(11)	37.4(12)	31.3(11)	-16.3(9)	-16.2(9)	5.9(9)
C3	37.2(12)	33.2(12)	35.5(12)	-14.1(10)	-15.9(10)	1.8(9)
C4	39.7(13)	38.3(13)	38.4(13)	-19.6(10)	-17.2(10)	6.8(10)
C5	35.8(12)	39.6(13)	36.8(13)	-19.9(10)	-14.2(10)	7.3(10)
C6	30.9(11)	37.4(12)	31.1(11)	-15.0(9)	-15.3(9)	5.1(9)
C7	34.5(11)	35.3(12)	33.7(12)	-16.4(9)	-18.6(10)	8.5(9)
C8	34.3(11)	39.2(12)	33.3(12)	-18.0(10)	-16.0(10)	7.8(9)
C9	32.4(11)	41.1(13)	31.9(12)	-15.4(10)	-13.9(10)	4.9(9)
C10	36.0(12)	34.0(12)	36.4(12)	-15.3(10)	-16.7(10)	2.8(9)
C11	33.0(11)	36.2(12)	34.0(12)	-17.0(9)	-17.8(10)	6.3(9)
C12	30.6(11)	35.7(11)	30.0(11)	-14.5(9)	-16.8(9)	6.2(9)
C13	30.4(11)	34.9(11)	30.0(11)	-13.2(9)	-16.8(9)	3.4(9)
C14	37.5(13)	44.4(14)	33.8(13)	-14.7(11)	-6.9(10)	-1.8(10)
C15	50.2(17)	76(2)	50.5(18)	-23.1(16)	-11.1(14)	-16.0(15)
C16	56.7(18)	55.5(18)	41.0(16)	-9.7(13)	-7.4(13)	7.9(14)
C17	49.4(15)	38.7(14)	48.0(15)	-23.9(12)	-14.3(12)	4.6(11)
C18	57(2)	55(2)	68(3)	-40(2)	-16.9(19)	-1.9(17)
C19	56(2)	43(2)	68(3)	-35.5(19)	-2.4(19)	-0.7(16)
C20	65(2)	36.9(18)	62(2)	-22.4(17)	-12.8(19)	10.0(17)
C21	32.8(12)	42.8(13)	35.2(12)	-17.1(10)	-10.4(10)	2.2(10)
C22	44.0(15)	48.4(16)	39.3(14)	-9.3(12)	-9.2(12)	4.6(12)
C23	41.0(14)	50.6(16)	46.4(15)	-22.6(13)	-7.7(12)	5.3(12)
C24	38.1(15)	91(2)	52.0(18)	-38.5(17)	-7.1(13)	-10.0(15)
C25	31.7(11)	34.6(11)	33.1(12)	-15.2(9)	-15.4(9)	2.2(9)
C26	43.9(13)	37.5(13)	45.5(14)	-23.2(11)	-21.6(11)	9.8(10)
C27	48.3(14)	37.9(13)	52.0(16)	-20.6(12)	-27.0(12)	9.2(11)
C28	61.0(17)	49.2(15)	61.5(18)	-33.8(14)	-37.5(15)	16.5(13)
C29	32.3(11)	35.5(11)	30.4(11)	-15.5(9)	-15.8(9)	2.1(9)
C30	34.4(11)	38.6(12)	35.2(12)	-17.0(10)	-20.2(10)	5.6(9)
C31	38.4(12)	44.4(13)	38.5(13)	-19.7(11)	-23.8(10)	8.1(10)
C32	40.9(13)	43.8(13)	34.0(12)	-19.5(10)	-19.9(10)	2.9(10)
C33	35.4(12)	41.9(13)	33.9(12)	-20.3(10)	-15.5(10)	5.5(9)
C34	32.3(11)	36.2(12)	33.1(12)	-16.6(9)	-16.0(9)	4.0(9)
C35	31.0(11)	37.1(12)	31.0(11)	-16.2(9)	-15.5(9)	4.3(9)
C36	32.1(11)	41.0(12)	32.8(12)	-18.8(10)	-13.0(9)	4.9(9)
C37	29.8(11)	38.3(12)	35.8(12)	-16.9(10)	-14.9(9)	4.9(9)
C38	31.1(11)	42.1(12)	32.3(12)	-15.7(10)	-17.2(9)	4.7(9)
C39	31.6(11)	34.3(11)	31.0(11)	-15.1(9)	-16.0(9)	3.3(9)
C40	28.2(10)	33.1(11)	29.5(11)	-14.4(9)	-13.8(9)	2.7(8)
C41	34.1(11)	36.8(12)	36.4(12)	-16.0(10)	-21.2(10)	5.2(9)
C42	38.0(13)	60.3(17)	54.9(17)	-30.6(14)	-29.2(12)	15.9(12)
C43	49.0(16)	65.7(19)	70(2)	-34.4(16)	-41.7(15)	19.1(14)
C44	53.1(17)	60.4(18)	69(2)	-30.7(16)	-39.4(16)	16.2(14)
C45	40.5(13)	52.9(15)	35.3(13)	-24.0(11)	-18.9(11)	5.2(11)
C46	51(2)	87(3)	46(2)	-41(2)	-21.8(17)	-2.1(19)

C47	65(2)	60(2)	38.4(18)	-24.8(16)	-30.9(17)	12.4(18)
C48	58(2)	68(2)	39.8(18)	-32.6(17)	-26.6(16)	14.3(17)
C49	30.9(11)	50.0(14)	37.9(13)	-22.5(11)	-16.8(10)	9.9(10)
C50	39.5(13)	52.9(16)	52.1(16)	-22.7(13)	-23.7(12)	15.1(12)
C51	39.8(14)	90(2)	49.0(17)	-40.6(16)	-22.2(13)	24.9(15)
C52	31.3(12)	62.0(17)	58.9(17)	-30.4(14)	-21.1(12)	6.7(12)
C53	33.0(11)	33.7(11)	33.2(12)	-15.5(9)	-19.5(9)	2.9(9)
C54	37.5(13)	60.6(16)	34.5(13)	-25.3(12)	-17.1(10)	5.4(11)
C55	51.4(16)	66.3(19)	38.9(14)	-21.1(13)	-23.6(12)	6.1(13)
C56	55.7(17)	73(2)	44.6(16)	-29.9(15)	-26.0(13)	-1.2(14)
C57	59.4(19)	64(2)	65(2)	-25.2(16)	-38.8(16)	11.1(15)
C58	85(2)	58.3(19)	77(2)	-31.3(17)	-56(2)	15.5(17)
C59	76(2)	65(2)	65(2)	-28.7(17)	-41.4(18)	24.3(17)
C60	60.8(19)	65(2)	69(2)	-16.5(17)	-39.6(18)	10.2(16)
C61	71(2)	68(2)	64(2)	-24.1(17)	-46.4(18)	8.7(16)
C62	70(2)	70(2)	61(2)	-34.0(17)	-36.4(17)	13.6(17)
C63	66(2)	101(3)	107(4)	-40(3)	-50(2)	13(2)
C64	65.6(19)	74(2)	62(2)	-40.6(17)	-39.3(17)	18.6(16)
C65	78(2)	55.3(18)	81(2)	-32.8(17)	-52(2)	17.9(16)
C66	91(3)	115(4)	148(5)	-94(4)	-84(3)	51(3)
C67	67(3)	131(4)	111(4)	-84(4)	-24(3)	-2(3)
C68	93(3)	90(3)	70(3)	-41(2)	-27(2)	3(3)
C69	107(3)	64(2)	56(2)	-25.8(17)	-43(2)	14(2)
C70	71(2)	132(4)	87(3)	-65(3)	-45(2)	23(2)
C71	82(2)	66(2)	73(2)	-35.8(18)	-49(2)	28.9(19)
C72	75(2)	49.2(17)	77(2)	-21.3(16)	-47.5(19)	4.6(15)
C73	59.2(19)	59.1(19)	73(2)	-26.5(17)	-35.1(17)	13.5(15)
C74	71(2)	79(2)	79(3)	-41(2)	-48(2)	18.3(18)
C75	71(2)	80(3)	90(3)	-23(2)	-49(2)	-2(2)
C76	58(2)	85(3)	65(2)	-20.0(19)	-27.4(18)	16.1(18)
C77	184(6)	87(3)	109(4)	-58(3)	-100(4)	47(4)
C78	42(4)	119(8)	37(3)	0(4)	-9(3)	24(5)
C79	76(11)	63(12)	76(11)	-6(8)	-27(7)	8(8)
C80	66(5)	88(6)	50(4)	-20(4)	-23(4)	-9(4)
C81	45(5)	111(8)	54(6)	-31(6)	-16(4)	18(5)
C82	117(8)	70(5)	54(4)	-28(4)	-43(5)	42(5)
C83	79(12)	38(6)	45(6)	-6(4)	-29(6)	8(6)
C84	63(10)	390(40)	77(10)	53(14)	-19(8)	64(16)

Table B-48 Bond Lengths for **23**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe1	N1	1.9723(19)	C21	C24	1.532(4)
Fe1	N2	1.999(2)	C26	C27	1.515(4)
Fe1	N6	1.9826(19)	C26	C28	1.519(4)
Fe1	N10	1.9781(18)	C29	C30	1.413(3)
Fe1	N11	2.0128(19)	C29	C34	1.415(3)
Fe1	N15	2.0030(19)	C30	C31	1.394(3)
N1	C1	1.368(3)	C30	C41	1.455(3)
N1	C12	1.369(3)	C31	C32	1.399(3)
N2	N3	1.334(3)	C32	C33	1.397(3)
N2	C13	1.356(3)	C32	C45	1.541(3)
N3	N4	1.314(3)	C33	C34	1.391(3)
N4	N5	1.331(3)	C34	C35	1.445(3)
N4	C14	1.483(3)	C35	C36	1.395(3)
N5	C13	1.339(3)	C35	C40	1.423(3)
N6	N7	1.330(3)	C36	C37	1.387(3)
N6	C25	1.357(3)	C37	C38	1.405(3)
N7	N8	1.314(3)	C37	C49	1.540(3)
N8	N9	1.329(3)	C38	C39	1.397(3)
N8	C26	1.475(3)	C39	C40	1.401(3)
N9	C25	1.331(3)	C39	C53	1.462(3)
N10	C29	1.365(3)	C42	C43	1.511(4)
N10	C40	1.372(3)	C42	C44	1.521(4)
N11	N12	1.337(3)	C45	C46	1.525(4)
N11	C41	1.354(3)	C45	C47	1.519(5)
N12	N13	1.315(3)	C45	C48	1.541(4)
N13	N14	1.332(3)	C45	C46A	1.529(15)
N13	C42	1.495(3)	C45	C47A	1.494(15)
N14	C41	1.341(3)	C45	C48A	1.596(15)
N15	N16	1.332(3)	C49	C50	1.529(4)
N15	C53	1.352(3)	C49	C51	1.531(3)
N16	N17	1.317(3)	C49	C52	1.529(4)
N17	N18	1.330(3)	C54	C55	1.525(4)
N17	C54	1.475(3)	C54	C56	1.513(4)
N18	C53	1.332(3)	C57	C58	1.387(5)
C1	C2	1.407(3)	C57	C62	1.389(5)
C1	C6	1.422(3)	C57	C63	1.510(5)
C2	C3	1.393(3)	C58	C59	1.387(5)
C2	C13	1.466(3)	C59	C60	1.374(5)
C3	C4	1.405(3)	C60	C61	1.374(5)
C4	C5	1.390(3)	C61	C62	1.375(5)
C4	C17	1.539(3)	C64	C65	1.381(5)
C5	C6	1.394(3)	C64	C69	1.395(5)
C6	C7	1.435(3)	C64	C70	1.479(5)

C7	C8	1.399(3)	C65	C66	1.390(6)
C7	C12	1.420(3)	C66	C67	1.388(7)
C8	C9	1.391(3)	C67	C68	1.359(7)
C9	C10	1.406(3)	C68	C69	1.357(6)
C9	C21	1.544(3)	C71	C72	1.375(5)
C10	C11	1.392(3)	C71	C76	1.390(5)
C11	C12	1.409(3)	C71	C77	1.481(5)
C11	C25	1.460(3)	C72	C73	1.386(5)
C14	C15	1.517(4)	C73	C74	1.347(5)
C14	C16	1.524(4)	C74	C75	1.373(6)
C17	C18	1.558(5)	C75	C76	1.374(6)
C17	C19	1.504(4)	C78	C79	1.44(3)
C17	C20	1.546(5)	C78	C83	1.53(3)
C17	C18A	1.589(15)	C78	C84	1.49(2)
C17	C19A	1.384(15)	C79	C80	1.21(4)
C17	C20A	1.588(16)	C80	C81	1.42(2)
C21	C22	1.528(4)	C81	C82	1.233(18)
C21	C23	1.528(4)	C82	C83	1.24(3)

Table B-49 Bond Angles for **23**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Fe1	N2	89.85(8)	C22	C21	C24	109.0(3)
N1	Fe1	N6	89.36(8)	C23	C21	C9	111.9(2)
N1	Fe1	N10	179.17(7)	C23	C21	C24	107.9(2)
N1	Fe1	N11	91.28(8)	C24	C21	C9	110.1(2)
N1	Fe1	N15	89.69(7)	N6	C25	C11	124.7(2)
N2	Fe1	N11	91.85(8)	N9	C25	N6	111.4(2)
N2	Fe1	N15	90.20(8)	N9	C25	C11	123.9(2)
N6	Fe1	N2	179.14(8)	N8	C26	C27	109.0(2)
N6	Fe1	N11	87.82(8)	N8	C26	C28	108.9(2)
N6	Fe1	N15	90.14(8)	C27	C26	C28	112.8(2)
N10	Fe1	N2	89.72(8)	N10	C29	C30	128.0(2)
N10	Fe1	N6	91.07(8)	N10	C29	C34	113.26(19)
N10	Fe1	N11	89.44(8)	C30	C29	C34	118.8(2)
N10	Fe1	N15	89.60(8)	C29	C30	C41	120.2(2)
N15	Fe1	N11	177.73(8)	C31	C30	C29	118.3(2)
C1	N1	Fe1	127.35(15)	C31	C30	C41	121.5(2)
C1	N1	C12	104.75(18)	C30	C31	C32	123.1(2)
C12	N1	Fe1	127.89(15)	C31	C32	C45	120.4(2)
N3	N2	Fe1	123.98(15)	C33	C32	C31	118.2(2)
N3	N2	C13	106.68(18)	C33	C32	C45	121.4(2)
C13	N2	Fe1	129.33(15)	C34	C33	C32	120.1(2)
N4	N3	N2	105.24(18)	C29	C34	C35	104.76(19)
N3	N4	N5	114.93(19)	C33	C34	C29	121.5(2)

N3	N4	C14	122.6(2)	C33	C34	C35	133.7(2)
N5	N4	C14	122.3(2)	C36	C35	C34	134.4(2)
N4	N5	C13	101.61(19)	C36	C35	C40	120.9(2)
N7	N6	Fe1	123.06(15)	C40	C35	C34	104.69(19)
N7	N6	C25	106.82(18)	C37	C36	C35	120.6(2)
C25	N6	Fe1	130.08(15)	C36	C37	C38	118.2(2)
N8	N7	N6	104.99(19)	C36	C37	C49	123.0(2)
N7	N8	N9	115.05(19)	C38	C37	C49	118.8(2)
N7	N8	C26	122.4(2)	C39	C38	C37	122.7(2)
N9	N8	C26	122.5(2)	C38	C39	C40	118.8(2)
N8	N9	C25	101.70(19)	C38	C39	C53	121.0(2)
C29	N10	Fe1	128.04(15)	C40	C39	C53	120.2(2)
C29	N10	C40	104.64(18)	N10	C40	C35	112.65(19)
C40	N10	Fe1	127.28(15)	N10	C40	C39	128.5(2)
N12	N11	Fe1	124.05(15)	C39	C40	C35	118.8(2)
N12	N11	C41	106.86(18)	N11	C41	C30	125.4(2)
C41	N11	Fe1	128.87(15)	N14	C41	N11	111.4(2)
N13	N12	N11	105.10(18)	N14	C41	C30	123.2(2)
N12	N13	N14	114.98(19)	N13	C42	C43	109.0(2)
N12	N13	C42	122.8(2)	N13	C42	C44	110.9(2)
N14	N13	C42	122.3(2)	C43	C42	C44	111.0(2)
N13	N14	C41	101.63(19)	C32	C45	C48	112.2(2)
N16	N15	Fe1	123.79(15)	C32	C45	C48A	111.8(6)
N16	N15	C53	106.72(18)	C46	C45	C32	109.6(2)
C53	N15	Fe1	129.45(15)	C46	C45	C48	107.8(3)
N17	N16	N15	104.86(18)	C47	C45	C32	109.1(2)
N16	N17	N18	115.13(19)	C47	C45	C46	109.8(3)
N16	N17	C54	123.1(2)	C47	C45	C48	108.3(3)
N18	N17	C54	121.8(2)	C46A	C45	C32	109.2(6)
N17	N18	C53	101.34(19)	C46A	C45	C48A	106.8(8)
N1	C1	C2	128.6(2)	C47A	C45	C32	109.7(6)
N1	C1	C6	112.6(2)	C47A	C45	C46A	113.2(9)
C2	C1	C6	118.9(2)	C47A	C45	C48A	106.1(8)
C1	C2	C13	120.1(2)	C50	C49	C37	109.2(2)
C3	C2	C1	118.7(2)	C50	C49	C51	108.2(2)
C3	C2	C13	121.2(2)	C51	C49	C37	111.9(2)
C2	C3	C4	122.9(2)	C52	C49	C37	109.5(2)
C3	C4	C17	119.8(2)	C52	C49	C50	109.6(2)
C5	C4	C3	118.2(2)	C52	C49	C51	108.3(2)
C5	C4	C17	122.1(2)	N15	C53	C39	124.8(2)
C4	C5	C6	120.5(2)	N18	C53	N15	111.9(2)
C1	C6	C7	105.04(19)	N18	C53	C39	123.3(2)
C5	C6	C1	120.9(2)	N17	C54	C55	108.9(2)
C5	C6	C7	134.0(2)	N17	C54	C56	109.4(2)
C8	C7	C6	134.4(2)	C56	C54	C55	111.7(2)
C8	C7	C12	120.7(2)	C58	C57	C62	117.7(3)

C12	C7	C6	104.8(2)	C58	C57	C63	121.0(3)
C9	C8	C7	120.5(2)	C62	C57	C63	121.3(4)
C8	C9	C10	118.0(2)	C59	C58	C57	120.7(3)
C8	C9	C21	122.9(2)	C60	C59	C58	120.4(3)
C10	C9	C21	119.1(2)	C61	C60	C59	119.6(3)
C11	C10	C9	123.1(2)	C60	C61	C62	120.1(3)
C10	C11	C12	118.4(2)	C61	C62	C57	121.5(3)
C10	C11	C25	121.8(2)	C65	C64	C69	117.9(4)
C12	C11	C25	119.8(2)	C65	C64	C70	121.7(4)
N1	C12	C7	112.8(2)	C69	C64	C70	120.4(4)
N1	C12	C11	128.1(2)	C64	C65	C66	121.1(4)
C11	C12	C7	119.1(2)	C67	C66	C65	119.2(4)
N2	C13	C2	124.6(2)	C68	C67	C66	119.6(4)
N5	C13	N2	111.5(2)	C69	C68	C67	121.4(5)
N5	C13	C2	123.8(2)	C68	C69	C64	120.8(4)
N4	C14	C15	110.7(2)	C72	C71	C76	118.1(4)
N4	C14	C16	108.9(2)	C72	C71	C77	121.7(4)
C15	C14	C16	111.5(3)	C76	C71	C77	120.2(4)
C4	C17	C18	109.2(2)	C71	C72	C73	121.0(3)
C4	C17	C20	109.0(2)	C74	C73	C72	120.4(4)
C4	C17	C18A	106.1(6)	C73	C74	C75	119.6(4)
C4	C17	C20A	106.3(6)	C74	C75	C76	120.9(4)
C19	C17	C4	112.6(2)	C75	C76	C71	120.1(4)
C19	C17	C18	109.1(3)	C79	C78	C83	107(2)
C19	C17	C20	108.8(3)	C79	C78	C84	140(2)
C20	C17	C18	108.1(3)	C84	C78	C83	114(2)
C19A	C17	C4	117.8(6)	C80	C79	C78	130(3)
C19A	C17	C18A	111.0(9)	C79	C80	C81	117.0(18)
C19A	C17	C20A	110.3(9)	C82	C81	C80	117.1(14)
C20A	C17	C18A	104.4(8)	C81	C82	C83	131.2(15)
C22	C21	C9	109.7(2)	C82	C83	C78	117.2(17)
C22	C21	C23	108.2(2)				

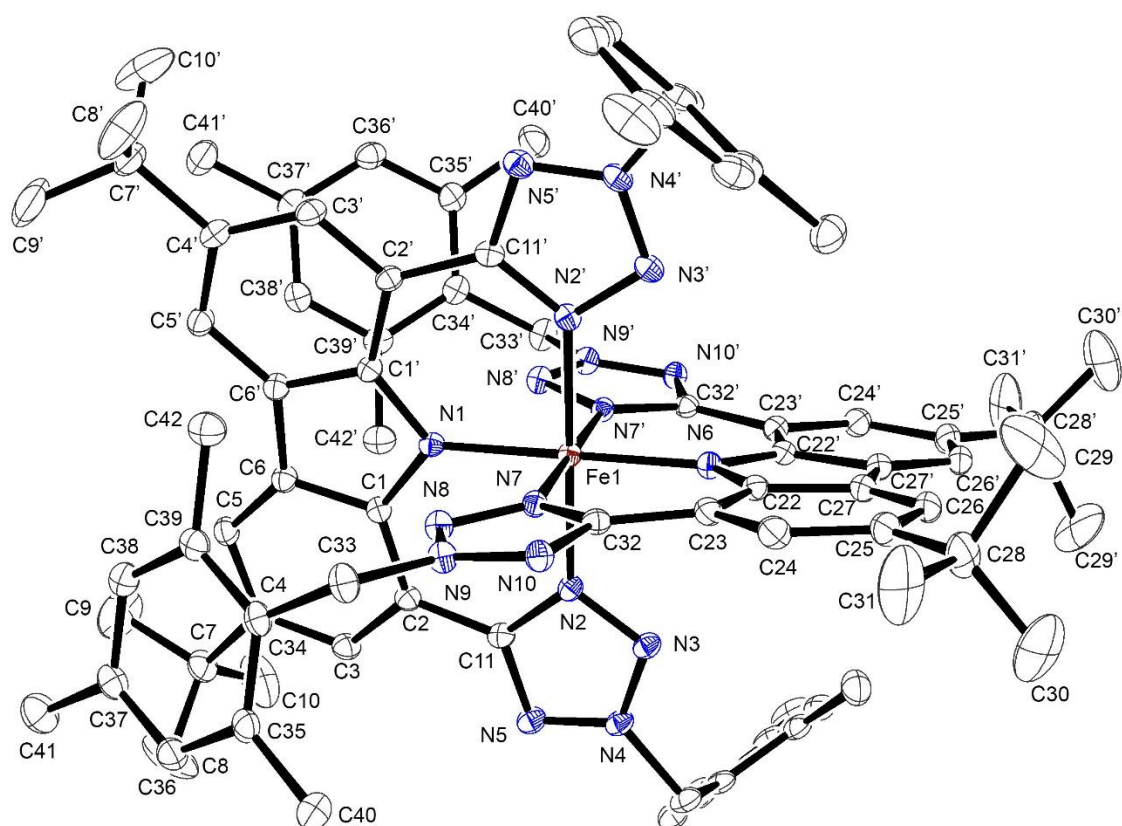


Figure B-14 Labelled ORTEP Drawing of **24**

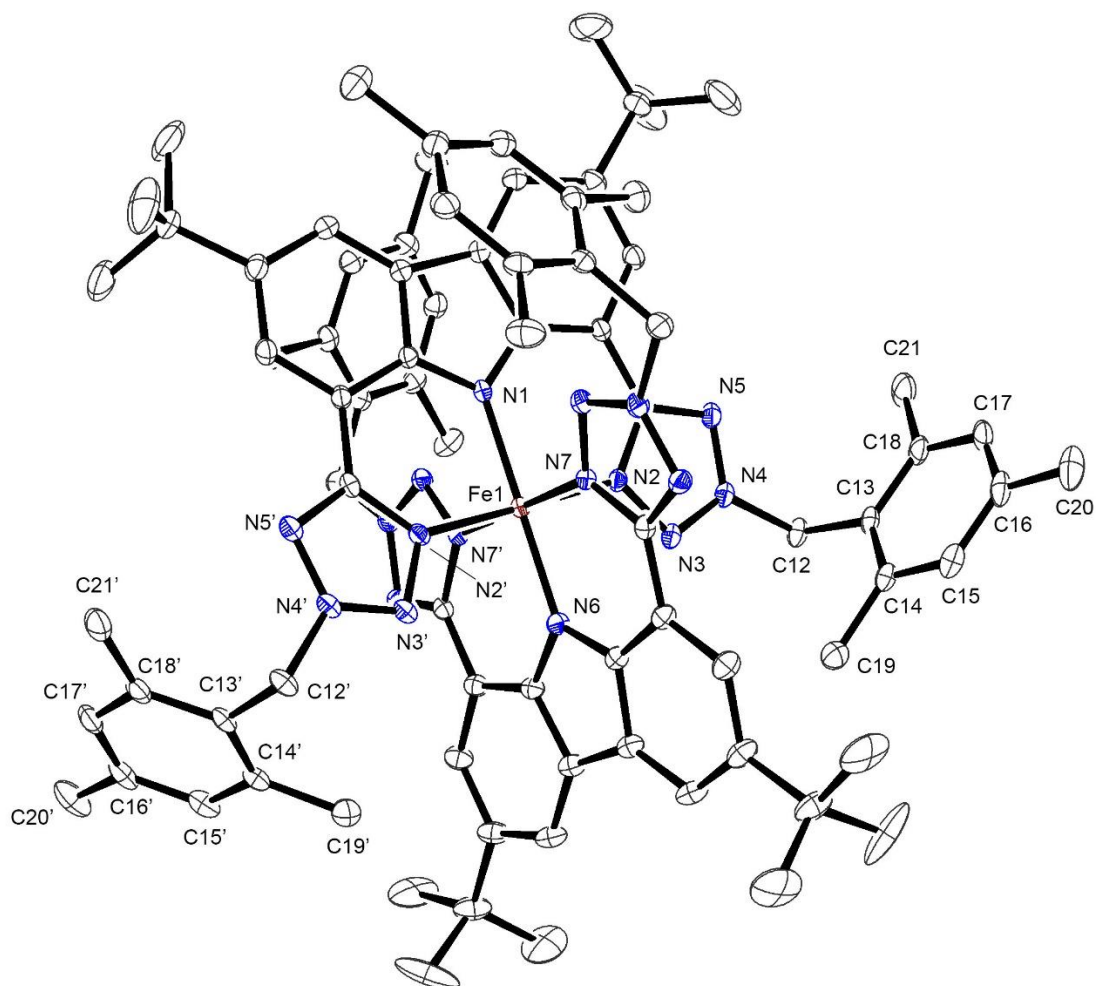


Figure B-15 Labelled ORTEP Drawing of **24** Alternate Perspective

H atoms not shown

Disordered hexane of solvation not shown: C43, C44, C45, C43', C44' and C45'

Disordered tBu carbons C29A, C30A and C31A not shown

Table B-50 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **24**

Atom	x	y	z	U(eq)
Fe1	5000	5405.8(2)	2500	18.38(10)
N1	5000	6627.7(13)	2500	19.1(5)
N7	5747.6(8)	5400.4(9)	2020.3(5)	20.1(3)
N4	6420.3(8)	4976.8(10)	3610.8(6)	24.0(4)
N3	6000.9(8)	4720.1(10)	3244.0(6)	23.4(4)
N2	5706.1(8)	5409.8(10)	3057.5(5)	20.4(3)
N8	6071.1(8)	6089.6(10)	1881.8(6)	23.2(3)
N6	5000	4188.7(14)	2500	21.6(5)
N5	6423.5(9)	5795.4(11)	3685.1(6)	25.8(4)
N9	6518.7(8)	5840.2(10)	1553.9(6)	23.0(3)
N10	6513.1(8)	5025.6(10)	1461.4(6)	23.7(4)
C1	5344.2(9)	7145.7(11)	2830.1(7)	20.5(4)
C6	5220.5(10)	7999.6(12)	2724.0(7)	23.8(4)
C27	5235.7(10)	2812.4(12)	2296.5(8)	26.0(4)
C2	5785.0(10)	6924.4(12)	3240.6(7)	22.2(4)
C32	6022.0(9)	4756.3(12)	1762.9(7)	21.3(4)
C22	5363.5(9)	3670.7(12)	2201.0(7)	22.4(4)
C11	5968.8(10)	6059.4(12)	3329.3(7)	21.7(4)
C13	6377.6(10)	4254.3(13)	4409.5(7)	25.5(4)
C34	7084.0(10)	7222.5(12)	1562.1(7)	25.7(4)
C26	5542.4(10)	2199.1(13)	2014.3(8)	31.1(5)
C14	5861.4(10)	3636.5(13)	4405.8(7)	28.2(4)
C23	5830.5(10)	3892.1(12)	1833.4(7)	24.5(4)
C35	7689.5(10)	7295.5(13)	1868.4(8)	28.9(4)
C33	6947.5(11)	6431.7(13)	1275.5(8)	29.7(5)
C18	6478.9(11)	4781.8(14)	4822.4(8)	32.1(5)
C25	5993.4(11)	2412.0(13)	1638.4(9)	33.1(5)
C5	5481.0(10)	8612.8(13)	3046.3(7)	27.2(4)
C3	6036.4(10)	7555.3(13)	3554.6(7)	27.4(4)
C39	6593.0(10)	7877.8(13)	1532.2(7)	27.4(4)
C37	7316.8(11)	8667.1(13)	2127.9(8)	31.1(5)
C36	7798.6(11)	8017.9(13)	2143.6(8)	32.6(5)
C38	6722.3(11)	8585.1(13)	1815.7(8)	29.5(4)
C4	5876.9(11)	8393.3(13)	3474.8(7)	28.8(4)
C24	6135.7(10)	3253.9(13)	1560.0(8)	30.3(5)
C15	5441.4(11)	3574.3(15)	4816.3(8)	34.5(5)
C12	6796.6(10)	4390.5(13)	3950.3(7)	28.4(4)
C16	5520.0(12)	4101.6(15)	5220.6(8)	37.1(5)
C17	6047.5(12)	4691.1(15)	5219.8(8)	37.4(5)
C42	5922.8(11)	7815.9(15)	1224.5(8)	36.8(5)
C28	6346.3(12)	1736.4(14)	1327.8(10)	43.5(6)
C19	5746.8(13)	3050.2(15)	3972.1(9)	40.4(5)

C7	6127.3(12)	9042.0(14)	3865.7(8)	36.8(5)
C40	8226.7(12)	6604.2(15)	1909.9(10)	43.1(6)
C21	7028.3(15)	5459.5(17)	4844.2(9)	50.1(7)
C43	7185.5(14)	7703.2(17)	113.3(9)	48.3(6)
C41	7434.8(14)	9441.6(15)	2437.3(10)	45.2(6)
C44	6905.8(17)	8446.2(19)	-175.5(11)	62.4(8)
C20	5037.4(14)	4053.7(19)	5648.2(9)	53.4(7)
C8	5907(2)	8777(2)	4380.0(10)	73.4(10)
C10	6902.4(17)	9133(3)	3868.6(13)	83.5(12)
C9	5812(2)	9890.0(19)	3755.3(14)	100.4(16)
C45	6284(2)	8857(3)	65.3(15)	98.3(14)
C31	3151(5)	2073(4)	4059(3)	82(3)
C30	3247(4)	1139(4)	3354(3)	81(3)
C29	4233(4)	1261(6)	3994(4)	101(4)
C30A	2880(4)	1743(6)	3480(4)	81(4)
C31A	3694(8)	1963(6)	4190(3)	94(5)
C29A	3927(6)	885(4)	3554(5)	91(5)

Table B-51 Anisotropic Displacement Parameters (U_{ij} , Å² x10³) for **24**

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Fe1	21.21(19)	18.51(19)	15.46(18)	0	1.11(14)	0
N1	21.4(11)	22.4(11)	13.6(10)	0	0.1(8)	0
N7	24.0(8)	18.4(8)	17.7(7)	-0.5(6)	-1.3(6)	-0.6(6)
N4	24.3(8)	27.6(9)	20.0(8)	5.5(7)	0.8(7)	3.5(7)
N3	24.3(8)	26.3(9)	19.6(8)	5.1(7)	1.3(6)	3.0(7)
N2	23.3(8)	21.6(8)	16.5(7)	3.2(6)	2.2(6)	0.9(6)
N8	27.3(8)	24.1(8)	18.5(8)	-0.1(7)	4.8(6)	-0.8(7)
N6	21.7(11)	20.6(11)	22.5(11)	0	2.7(9)	0
N5	28.4(9)	29.5(9)	19.3(8)	3.4(7)	-0.5(7)	2.3(7)
N9	25.6(8)	24.8(9)	19.1(8)	-0.6(7)	6.5(6)	-1.1(7)
N10	26.1(8)	21.7(9)	23.3(8)	-2.4(7)	2.7(7)	0.4(7)
C1	23.6(9)	21.8(9)	16.4(9)	-0.8(7)	2.2(7)	-1.3(8)
C6	27.1(10)	22.9(10)	21.4(9)	0.2(8)	0.8(8)	0.1(8)
C27	21.7(9)	21.5(10)	34.5(11)	-0.8(8)	-1.3(8)	0.1(8)
C2	24.2(9)	24.8(10)	17.4(9)	-0.9(8)	-0.3(7)	-1.3(8)
C32	20.2(9)	24.5(10)	19.2(9)	-1.9(8)	-0.4(7)	1.3(7)
C22	19.5(9)	21.8(9)	25.7(10)	-2.0(8)	-1.0(7)	1.5(7)
C11	22.5(9)	27.9(10)	14.9(9)	2.2(8)	1.9(7)	-0.1(8)
C13	24.3(10)	31.6(11)	20.2(9)	8.5(8)	-2.9(8)	5.6(8)
C34	29.4(10)	25.9(10)	22.4(10)	2.9(8)	9.1(8)	-6.0(8)
C26	24.9(10)	19.8(10)	48.4(13)	-2.5(9)	-1.5(9)	0.6(8)
C14	27.8(10)	30.2(11)	26.3(10)	9.8(9)	-2.6(8)	4.7(9)
C23	22.4(9)	23.4(10)	27.4(10)	-3.0(8)	-0.4(8)	0.3(8)
C35	28.6(10)	26.3(11)	32.4(11)	5.9(9)	6.3(9)	-4.0(8)

C33	34.7(11)	29.3(11)	26.1(10)	0.5(9)	12.6(9)	-5.2(9)
C18	36.6(11)	35.1(12)	23.8(10)	10.0(9)	-8.3(9)	0.6(9)
C25	27.4(10)	26.0(11)	46.0(13)	-9.8(10)	1.9(9)	3.3(9)
C5	30.7(10)	22.2(10)	28.6(11)	-0.8(8)	-0.1(8)	-2.6(8)
C3	29.4(10)	30.8(11)	21.5(10)	-1.0(8)	-4.0(8)	-2.7(9)
C39	27.0(10)	32.4(11)	23.3(10)	3.7(8)	5.7(8)	-4.6(9)
C37	33.5(11)	31.5(11)	28.8(11)	-1.8(9)	6.3(9)	-8.0(9)
C36	32.6(11)	33.1(12)	31.7(11)	5.1(9)	-3.1(9)	-6.9(9)
C38	30.6(11)	28.4(11)	30.1(11)	2.1(9)	7.3(9)	1.9(9)
C4	29.4(10)	30.1(11)	26.6(10)	-4.6(9)	-0.9(8)	-5.8(8)
C24	25.2(10)	29.8(11)	35.9(12)	-6.2(9)	3.6(9)	1.5(8)
C15	26.0(10)	41.9(13)	35.6(12)	16.3(10)	0.0(9)	-0.3(9)
C12	24.1(10)	35.6(12)	25.5(10)	10.2(9)	-0.3(8)	6.2(8)
C16	36.3(12)	51.7(15)	23.6(11)	14.5(10)	2.5(9)	15.9(11)
C17	50.4(14)	42.4(14)	19.0(10)	6.4(9)	-4.7(9)	9.5(11)
C42	33.8(11)	42.9(13)	33.5(12)	0.0(10)	0.4(9)	-0.8(10)
C28	38.1(12)	28.7(12)	64.9(17)	-12.5(11)	16.0(12)	3.7(10)
C19	50.5(14)	33.3(12)	37.1(13)	3.4(10)	-3.3(11)	-6.8(11)
C7	45.3(13)	31.5(12)	32.9(12)	-7.3(9)	-6.7(10)	-7.2(10)
C40	39.2(13)	34.2(13)	55.5(15)	9.8(11)	-2.3(11)	2.6(10)
C21	65.1(17)	51.0(15)	32.3(12)	8.7(11)	-20.1(12)	-18.2(13)
C43	56.9(16)	55.7(16)	32.4(13)	-1.3(11)	3.7(11)	-23.7(13)
C41	48.6(14)	39.2(14)	47.7(14)	-12.1(11)	1.9(12)	-6.6(11)
C44	77(2)	63.5(19)	47.3(16)	8.0(14)	14.3(15)	-15.3(16)
C20	47.9(15)	78(2)	35.8(13)	22.5(13)	14.1(11)	24.1(14)
C8	116(3)	66(2)	39.3(15)	-23.4(14)	17.2(17)	-36.9(19)
C10	63(2)	120(3)	67(2)	-39(2)	0.7(16)	-43(2)
C9	165(4)	37.6(17)	92(3)	-26.6(17)	-73(3)	8(2)
C45	115(3)	90(3)	93(3)	44(2)	46(3)	22(2)
C31	106(6)	44(3)	101(7)	18(4)	70(6)	-16(4)
C30	92(6)	56(5)	101(5)	1(4)	44(4)	-42(5)
C29	66(4)	95(7)	142(9)	97(7)	17(5)	2(4)
C30A	54(4)	68(6)	121(8)	36(5)	15(4)	-27(4)
C31A	144(11)	84(7)	56(5)	28(4)	14(6)	-70(8)
C29A	103(9)	30(4)	145(10)	41(5)	76(8)	13(4)

Table B-52 Bond Lengths for **24**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe1	N1	1.958(2)	C34	C35	1.394(3)
Fe1	N7 ¹	1.9597(15)	C34	C33	1.500(3)
Fe1	N7	1.9596(15)	C34	C39	1.406(3)
Fe1	N2	1.9719(15)	C26	C25	1.395(3)
Fe1	N2 ¹	1.9719(15)	C14	C15	1.393(3)
Fe1	N6	1.951(2)	C14	C19	1.506(3)

N1	C1	1.363(2)	C23	C24	1.400(3)
N1	C1 ¹	1.363(2)	C35	C36	1.385(3)
N7	N8	1.325(2)	C35	C40	1.509(3)
N7	C32	1.359(2)	C18	C17	1.382(3)
N4	N3	1.309(2)	C18	C21	1.508(3)
N4	N5	1.327(2)	C25	C24	1.394(3)
N4	C12	1.475(2)	C25	C28	1.539(3)
N3	N2	1.329(2)	C5	C4	1.396(3)
N2	C11	1.356(2)	C3	C4	1.392(3)
N8	N9	1.313(2)	C39	C38	1.382(3)
N6	C22 ¹	1.364(2)	C39	C42	1.495(3)
N6	C22	1.364(2)	C37	C36	1.387(3)
N5	C11	1.332(2)	C37	C38	1.388(3)
N9	N10	1.329(2)	C37	C41	1.506(3)
N9	C33	1.475(2)	C4	C7	1.540(3)
N10	C32	1.334(2)	C15	C16	1.380(3)
C1	C6	1.416(3)	C16	C17	1.379(3)
C1	C2	1.404(3)	C16	C20	1.503(3)
C6	C6 ¹	1.439(4)	C28	C31 ¹	1.541(7)
C6	C5	1.388(3)	C28	C30 ¹	1.481(7)
C27	C27 ¹	1.443(4)	C28	C29 ¹	1.571(7)
C27	C22	1.422(3)	C28	C30A ¹	1.540(8)
C27	C26	1.385(3)	C28	C31A ¹	1.437(9)
C2	C11	1.447(3)	C28	C29A ¹	1.498(7)
C2	C3	1.390(3)	C7	C8	1.522(4)
C32	C23	1.447(3)	C7	C10	1.483(4)
C22	C23	1.402(3)	C7	C9	1.510(4)
C13	C14	1.395(3)	C43	C43 ²	1.513(5)
C13	C18	1.402(3)	C43	C44	1.507(4)
C13	C12	1.513(3)	C44	C45	1.522(5)

Table B-53 Bond Angles for **24**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Fe1	N7	90.25(5)	C35	C34	C33	119.72(19)
N1	Fe1	N7 ¹	90.25(5)	C35	C34	C39	120.20(19)
N1	Fe1	N2	89.81(5)	C39	C34	C33	120.05(18)
N1	Fe1	N2 ¹	89.82(5)	C27	C26	C25	120.60(19)
N7	Fe1	N7 ¹	179.50(9)	C13	C14	C19	121.87(19)
N7 ¹	Fe1	N2	89.50(6)	C15	C14	C13	118.2(2)
N7	Fe1	N2 ¹	89.50(6)	C15	C14	C19	119.9(2)
N7 ¹	Fe1	N2 ¹	90.50(6)	C22	C23	C32	120.35(17)
N7	Fe1	N2	90.50(6)	C24	C23	C32	121.22(18)
N2 ¹	Fe1	N2	179.63(9)	C24	C23	C22	118.31(18)
N6	Fe1	N1	180.0	C34	C35	C40	121.59(19)

N6	Fe1	N7	89.75(5)	C36	C35	C34	119.21(19)
N6	Fe1	N7 ¹	89.75(5)	C36	C35	C40	119.2(2)
N6	Fe1	N2 ¹	90.18(5)	N9	C33	C34	111.73(15)
N6	Fe1	N2	90.19(5)	C13	C18	C21	122.5(2)
C1 ¹	N1	Fe1	127.51(11)	C17	C18	C13	118.8(2)
C1	N1	Fe1	127.52(11)	C17	C18	C21	118.7(2)
C1	N1	C1 ¹	105.0(2)	C26	C25	C28	121.1(2)
N8	N7	Fe1	122.67(12)	C24	C25	C26	118.40(19)
N8	N7	C32	107.28(14)	C24	C25	C28	120.5(2)
C32	N7	Fe1	130.02(13)	C6	C5	C4	120.25(19)
N3	N4	N5	115.01(15)	C2	C3	C4	122.75(18)
N3	N4	C12	122.11(16)	C34	C39	C42	122.17(19)
N5	N4	C12	122.52(16)	C38	C39	C34	118.55(19)
N4	N3	N2	104.95(15)	C38	C39	C42	119.20(19)
N3	N2	Fe1	123.26(12)	C36	C37	C38	118.02(19)
N3	N2	C11	107.15(15)	C36	C37	C41	121.2(2)
C11	N2	Fe1	129.57(13)	C38	C37	C41	120.8(2)
N9	N8	N7	104.89(15)	C35	C36	C37	121.8(2)
C22	N6	Fe1	127.49(11)	C39	C38	C37	122.2(2)
C22 ¹	N6	Fe1	127.49(11)	C5	C4	C7	122.32(19)
C22 ¹	N6	C22	105.0(2)	C3	C4	C5	118.53(18)
N4	N5	C11	101.96(16)	C3	C4	C7	119.13(18)
N8	N9	N10	115.09(15)	C25	C24	C23	122.7(2)
N8	N9	C33	122.21(16)	C16	C15	C14	122.2(2)
N10	N9	C33	122.46(15)	N4	C12	C13	109.73(15)
N9	N10	C32	101.81(15)	C15	C16	C20	121.4(2)
N1	C1	C6	112.70(16)	C17	C16	C15	118.3(2)
N1	C1	C2	127.85(18)	C17	C16	C20	120.3(2)
C2	C1	C6	119.46(17)	C16	C17	C18	122.0(2)
C1	C6	C6 ¹	104.78(11)	C25	C28	C31 ¹	114.7(3)
C5	C6	C1	120.42(17)	C25	C28	C29 ¹	109.1(3)
C5	C6	C6 ¹	134.69(12)	C25	C28	C30A ¹	104.3(3)
C22	C27	C27 ¹	104.67(11)	C31 ¹	C28	C29 ¹	103.8(5)
C26	C27	C27 ¹	134.78(12)	C30 ¹	C28	C25	111.8(3)
C26	C27	C22	120.55(18)	C30 ¹	C28	C31 ¹	106.9(5)
C1	C2	C11	120.27(17)	C30 ¹	C28	C29 ¹	110.1(5)
C3	C2	C1	118.26(18)	C30 ¹	C28	C30A ¹	48.7(4)
C3	C2	C11	121.47(17)	C30 ¹	C28	C29A ¹	57.8(5)
N7	C32	C23	123.80(16)	C31A ¹	C28	C25	109.9(3)
N10	C32	N7	110.93(16)	C31A ¹	C28	C29A ¹	115.4(7)
N10	C32	C23	125.18(17)	C29A ¹	C28	C25	111.3(3)
N6	C22	C27	112.80(17)	C8	C7	C4	110.02(19)
N6	C22	C23	127.83(18)	C10	C7	C4	110.5(2)
C23	C22	C27	119.36(17)	C10	C7	C8	109.5(3)
N2	C11	C2	124.44(16)	C10	C7	C9	107.5(3)
N5	C11	N2	110.94(17)	C9	C7	C4	111.4(2)

N5	C11	C2	124.61(17)	C9	C7	C8	107.9(3)
C14	C13	C18	120.51(19)	C44	C43	C43 ²	113.7(3)
C14	C13	C12	119.45(18)	C43	C44	C45	112.8(2)
C18	C13	C12	119.91(19)				

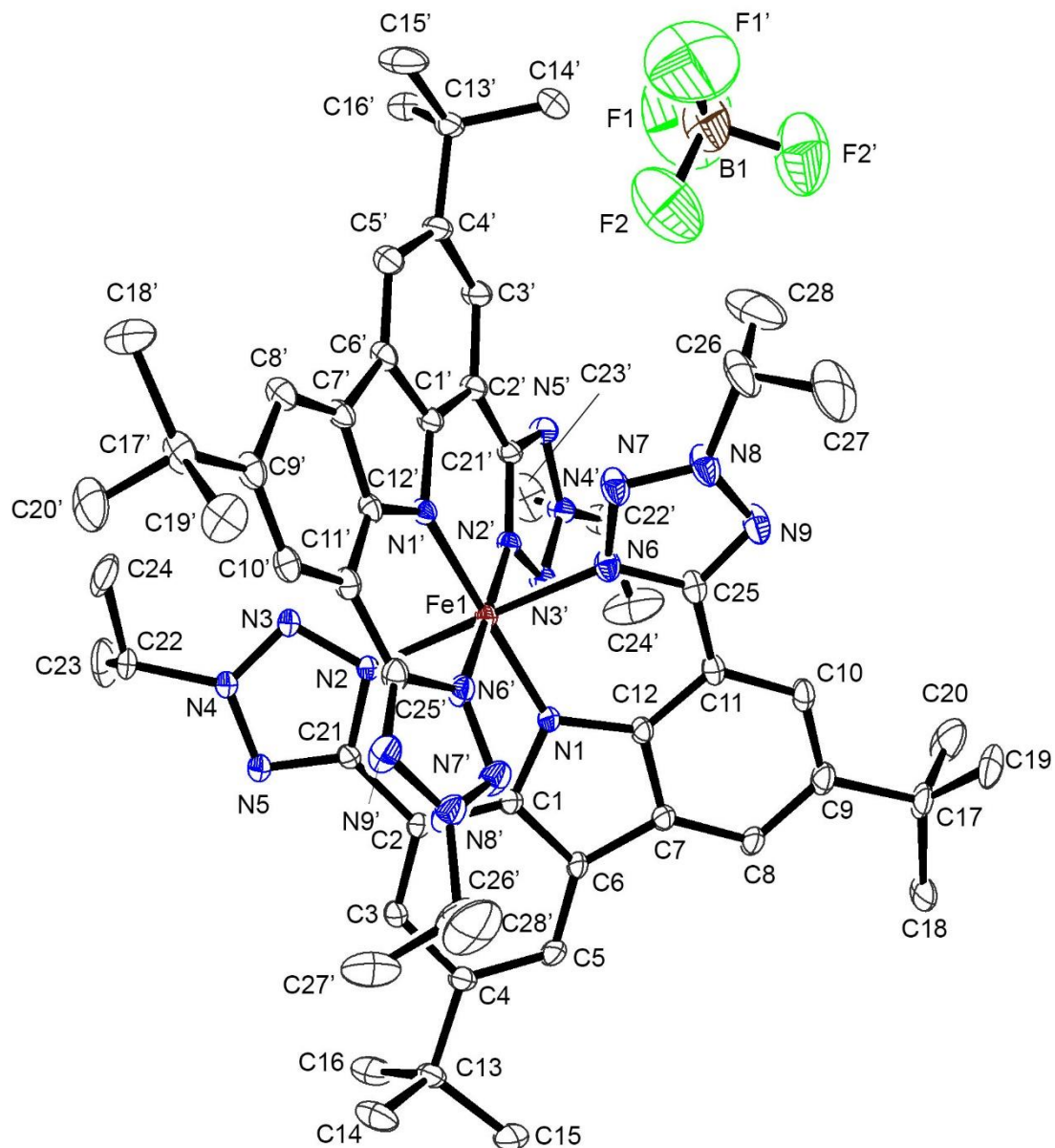


Figure B-16 Labelled ORTEP Drawing of 25

H atoms not shown

Disordered tBu carbons C18A, C19A and C20A not shown

Disordered iPr carbons C23A and C24A not shown

Table B-54 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **25**

Atom	x	y	z	U(eq)
Fe1	0	6128.2(2)	6666.67	20.93(11)
F1	-3823(7)	5614(4)	4719(5)	264(5)
F2	-3336(3)	6541(3)	5650(3)	151(2)
N1	1003.7(11)	6640.9(12)	6232.0(11)	22.7(4)
N2	312.9(11)	5634.6(12)	7524.8(12)	21.8(4)
N3	-170.4(12)	5091.1(12)	8032.9(13)	24.9(4)
N4	253.8(13)	5011.4(13)	8602.8(13)	28.1(5)
N5	990.0(12)	5469.5(13)	8503.5(13)	28.9(5)
N6	-294.7(14)	6629.6(13)	5800.4(13)	28.9(5)
N7	-979.7(15)	6548.4(16)	5771.5(15)	38.1(6)
N8	-1007.7(17)	6833.7(19)	5039.3(16)	45.2(7)
N9	-389.6(17)	7093.6(17)	4570.5(15)	40.1(6)
C1	1647.8(14)	6746.6(15)	6635.9(15)	25.3(5)
C2	1698.9(14)	6426.0(15)	7398.1(15)	26.4(5)
C3	2411.9(15)	6644.7(17)	7721.8(16)	31.6(6)
C4	3071.6(15)	7168.4(18)	7300.2(17)	33.4(6)
C5	3010.0(16)	7446.7(17)	6516.8(16)	33.5(6)
C6	2306.7(14)	7230.3(15)	6182.3(14)	27.7(5)
C7	2047.2(15)	7422.4(15)	5416.6(15)	27.6(5)
C8	2409.9(17)	7856.9(16)	4708.1(16)	33.3(6)
C9	1987.3(16)	7949.7(17)	4070.8(16)	34.2(6)
C10	1216.2(16)	7632.4(16)	4181.0(15)	30.6(6)
C11	838.6(16)	7195.7(15)	4889.8(15)	28.3(5)
C12	1255.5(15)	7061.4(14)	5498.6(15)	24.1(5)
C13	3836.1(15)	7413.1(19)	7732.3(17)	34.8(6)
C14	3840(2)	7756(2)	8599(2)	50.3(9)
C15	4493.7(19)	7994(3)	7202(2)	64.6(13)
C16	3933(2)	6735(2)	7852(2)	50.6(9)
C17	2364(2)	8410.8(18)	3260.5(17)	41.3(7)
C18	3259(7)	8591(13)	3193(8)	64(4)
C18A	3146(6)	8887(10)	3329(8)	59(4)
C19	2402(14)	9112(6)	3285(7)	58(5)
C19A	1986(9)	8946(7)	3078(8)	52(3)
C20	2000(12)	7903(13)	2455(14)	31(3)
C20A	2095(15)	7933(15)	2553(16)	67(7)
C21	1018.9(14)	5860.2(15)	7816.1(15)	23.9(5)
C22	-64.4(18)	4472(2)	9319.3(19)	42.3(8)
C23	106(6)	3808(4)	9088(4)	62(2)
C23A	-478(14)	3731(7)	9083(8)	72(8)
C24	-865(4)	4171(6)	9413(5)	85(4)
C24A	-526(17)	4835(15)	9861(11)	109(10)
C25	61.9(15)	6968.1(17)	5064.6(15)	29.7(5)

C26	-1718(3)	6776(3)	4724(3)	67.3(13)
C27	-2055(3)	6157(4)	4082(4)	103(2)
C28	-1556(4)	7526(4)	4373(4)	98(2)
B1	-3838(5)	6162(5)	5000	74(2)

Table B-55 Anisotropic Displacement Parameters (U_{ij} , Å² x10³) for **25**

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Fe1	22.9(2)	24.36(18)	15.05(19)	0.66(9)	1.32(17)	11.45(12)
F1	450(14)	155(5)	254(8)	-81(6)	-50(9)	200(8)
F2	202(5)	205(5)	89(3)	-48(3)	-37(3)	135(5)
N1	23.3(10)	24.2(10)	16.8(8)	1.7(7)	0.1(7)	9.1(8)
N2	21.0(10)	24.7(10)	16.8(8)	1.6(7)	0.9(7)	9.3(9)
N3	26.0(11)	27.0(10)	19.5(9)	4.6(8)	2.2(8)	11.6(9)
N4	25.4(11)	32.7(11)	20.1(10)	6.2(8)	0.8(8)	9.9(9)
N5	26.2(11)	34.4(12)	22.2(10)	6.9(8)	2.1(8)	12.2(10)
N6	34.4(12)	36.3(13)	22.2(10)	3.4(8)	4.9(8)	22.3(11)
N7	44.2(13)	53.0(16)	32.7(12)	11.0(11)	6.5(10)	36.1(12)
N8	51.8(17)	75(2)	33.2(12)	14.1(12)	8.2(11)	49.9(17)
N9	50.7(16)	58.0(16)	28.3(11)	11.8(11)	6.8(10)	39.8(14)
C1	22.6(11)	28.1(12)	18.0(10)	1.4(9)	0.8(8)	7.2(10)
C2	22.4(11)	30.4(12)	18.6(11)	3.2(9)	1.0(8)	7.4(10)
C3	25.2(13)	42.8(15)	18.4(11)	6.1(10)	0.0(9)	10.6(12)
C4	21.8(12)	45.5(16)	23.1(12)	0.4(11)	-1.3(9)	9.5(11)
C5	25.5(13)	36.2(15)	22.1(12)	3.7(10)	4.3(9)	2.9(11)
C6	28.3(12)	30.0(13)	14.6(10)	5.0(9)	2.6(8)	6.9(11)
C7	28.1(13)	25.3(12)	19.4(11)	1.3(9)	-1.4(9)	5.8(10)
C8	33.1(14)	30.7(13)	20.1(12)	5.2(10)	2.0(10)	4.0(11)
C9	42.7(15)	30.0(14)	20.2(11)	3.4(10)	3.6(10)	11.0(13)
C10	42.6(14)	30.6(14)	17.6(10)	3.8(9)	1.5(10)	17.5(12)
C11	36.6(14)	32.3(14)	17.7(10)	2.8(9)	0.7(9)	18.4(12)
C12	28.7(13)	24.8(12)	15.3(10)	0.1(8)	0.3(9)	10.8(10)
C13	22.6(12)	49.6(17)	22.3(12)	-1.8(11)	-2.5(9)	10.5(12)
C14	40.3(17)	71(2)	38.4(17)	-22.0(16)	-15.0(14)	27.4(17)
C15	24.7(15)	85(3)	48(2)	16.8(19)	-3.6(14)	-0.3(17)
C16	31.5(16)	65(2)	55(2)	-14.3(17)	-10.5(14)	23.4(16)
C17	53.2(19)	35.9(15)	19.5(12)	10.3(11)	6.4(12)	10.8(14)
C18	33(4)	107(11)	35(5)	41(6)	12(3)	21(6)
C18A	32(4)	88(9)	44(5)	44(5)	13(3)	21(4)
C19	96(12)	38(5)	33(4)	14(3)	20(5)	27(6)
C19A	64(7)	40(5)	52(5)	26(4)	15(5)	27(5)
C20	37(4)	42(6)	12(4)	-9(4)	-2(3)	18(4)
C20A	76(13)	61(9)	34(9)	6(7)	24(8)	12(9)
C21	21.9(12)	29.7(13)	17.5(10)	0.7(9)	-1.5(8)	10.8(10)
C22	34.3(15)	50.2(18)	25.6(13)	20.1(12)	2.1(11)	8.6(14)

C23	100(6)	42(3)	45(3)	18(2)	0(3)	35(4)
C23A	124(19)	33(6)	29(5)	11(4)	-8(7)	17(8)
C24	41(3)	114(8)	84(5)	75(6)	26(3)	25(4)
C24A	180(20)	115(18)	55(10)	56(11)	80(13)	90(19)
C25	39.6(14)	34.4(14)	21.2(11)	2.5(11)	1.6(9)	23.2(13)
C26	64(3)	126(4)	49(2)	26(2)	8.6(18)	75(3)
C27	64(3)	149(6)	110(4)	-14(4)	-32(3)	64(4)
C28	113(5)	142(6)	97(4)	37(4)	12(3)	109(5)
B1	107(5)	107(5)	35(3)	-12.3(15)	12.3(15)	72(6)

Table B-56 Bond Lengths for 25

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe1	N1 ¹	1.908(2)	C4	C5	1.393(4)
Fe1	N1	1.908(2)	C4	C13	1.544(4)
Fe1	N2 ¹	1.979(2)	C5	C6	1.383(4)
Fe1	N2	1.979(2)	C6	C7	1.451(3)
Fe1	N6 ¹	1.977(2)	C7	C8	1.390(3)
Fe1	N6	1.977(2)	C7	C12	1.412(4)
F1	B1	1.221(7)	C8	C9	1.401(4)
F2	B1	1.384(8)	C9	C10	1.386(4)
N1	C1	1.381(3)	C9	C17	1.547(4)
N1	C12	1.380(3)	C10	C11	1.399(3)
N2	N3	1.327(3)	C11	C12	1.401(4)
N2	C21	1.360(3)	C11	C25	1.443(4)
N3	N4	1.316(3)	C13	C14	1.536(4)
N4	N5	1.328(3)	C13	C15	1.525(4)
N4	C22	1.484(3)	C13	C16	1.511(5)
N5	C21	1.332(3)	C17	C18	1.685(16)
N6	N7	1.329(3)	C17	C18A	1.403(12)
N6	C25	1.362(3)	C17	C19	1.399(11)
N7	N8	1.309(3)	C17	C19A	1.652(11)
N8	N9	1.327(4)	C17	C20	1.573(19)
N8	C26	1.485(4)	C17	C20A	1.40(2)
N9	C25	1.329(4)	C22	C23	1.607(8)
C1	C2	1.399(3)	C22	C23A	1.370(14)
C1	C6	1.407(3)	C22	C24	1.443(7)
C2	C3	1.393(4)	C22	C24A	1.697(19)
C2	C21	1.451(3)	C26	C27	1.495(8)
C3	C4	1.404(4)	C26	C28	1.507(8)

Table B-57 Bond Angles for **25**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1 ¹	Fe1	N1	178.68(13)	C7	C8	C9	119.7(3)
N1	Fe1	N2	89.54(8)	C8	C9	C17	121.6(3)
N1 ¹	Fe1	N2 ¹	89.54(8)	C10	C9	C8	118.9(2)
N1 ¹	Fe1	N2	91.35(9)	C10	C9	C17	119.5(3)
N1	Fe1	N2 ¹	91.35(9)	C9	C10	C11	122.4(3)
N1 ¹	Fe1	N6 ¹	89.45(9)	C10	C11	C12	118.5(3)
N1 ¹	Fe1	N6	89.66(9)	C10	C11	C25	121.8(2)
N1	Fe1	N6	89.46(9)	C12	C11	C25	119.2(2)
N1	Fe1	N6 ¹	89.66(9)	N1	C12	C7	112.1(2)
N2 ¹	Fe1	N2	95.40(12)	N1	C12	C11	128.6(2)
N6 ¹	Fe1	N2	84.54(8)	C11	C12	C7	119.2(2)
N6	Fe1	N2 ¹	84.55(8)	C14	C13	C4	108.3(2)
N6 ¹	Fe1	N2 ¹	178.99(10)	C15	C13	C4	111.6(3)
N6	Fe1	N2	178.99(9)	C15	C13	C14	109.4(3)
N6 ¹	Fe1	N6	95.53(13)	C16	C13	C4	109.6(3)
C1	N1	Fe1	127.04(16)	C16	C13	C14	109.7(3)
C12	N1	Fe1	127.49(17)	C16	C13	C15	108.4(3)
C12	N1	C1	105.0(2)	C9	C17	C18	110.0(5)
N3	N2	Fe1	123.10(16)	C9	C17	C19A	107.1(4)
N3	N2	C21	107.54(19)	C9	C17	C20	109.7(10)
C21	N2	Fe1	128.25(17)	C18A	C17	C9	114.1(5)
N4	N3	N2	104.8(2)	C18A	C17	C19A	107.6(7)
N3	N4	N5	114.7(2)	C19	C17	C9	111.1(5)
N3	N4	C22	122.8(2)	C19	C17	C18	106.3(9)
N5	N4	C22	122.5(2)	C19	C17	C20	117.7(11)
N4	N5	C21	102.4(2)	C20	C17	C18	101.4(10)
N7	N6	Fe1	122.44(18)	C20A	C17	C9	109.2(12)
N7	N6	C25	107.4(2)	C20A	C17	C18A	117.3(13)
C25	N6	Fe1	128.94(19)	C20A	C17	C19A	100.1(11)
N8	N7	N6	104.7(2)	N2	C21	C2	123.4(2)
N7	N8	N9	115.2(2)	N5	C21	N2	110.6(2)
N7	N8	C26	121.3(3)	N5	C21	C2	125.9(2)
N9	N8	C26	123.1(3)	N4	C22	C23	104.9(3)
N8	N9	C25	102.2(2)	N4	C22	C24A	101.0(6)
N1	C1	C2	127.8(2)	C23A	C22	N4	114.6(5)
N1	C1	C6	112.4(2)	C23A	C22	C24A	116.8(14)
C2	C1	C6	119.8(2)	C24	C22	N4	112.2(3)
C1	C2	C21	119.9(2)	C24	C22	C23	110.1(6)
C3	C2	C1	118.5(2)	N6	C25	C11	123.5(2)
C3	C2	C21	121.6(2)	N9	C25	N6	110.5(2)
C2	C3	C4	121.7(2)	N9	C25	C11	125.9(2)
C3	C4	C13	118.1(2)	N8	C26	C27	108.3(4)
C5	C4	C3	118.9(2)	N8	C26	C28	109.6(4)

C5	C4	C13	122.9(3)	C27	C26	C28	112.8(5)
C6	C5	C4	120.0(2)	F1	B1	F1 ²	127.0(14)
C1	C6	C7	105.2(2)	F1 ²	B1	F2 ²	115.5(6)
C5	C6	C1	120.7(2)	F1 ²	B1	F2	98.7(5)
C5	C6	C7	134.0(2)	F1	B1	F2	115.5(6)
C8	C7	C6	133.8(3)	F1	B1	F2 ²	98.7(5)
C8	C7	C12	121.0(2)	F2 ²	B1	F2	98.6(8)
C12	C7	C6	105.2(2)				

Table B-58 Summary of Crystallographic Data for **9**, **26** and **27**

	9•3.5 C₇H₈^a	26^b	27•3 C₇H₈^c
Emp. Formula	C _{80.50} H ₁₀₀ N ₁₈ Zn	C ₁₆₈ H ₂₁₆ N ₅₄ Ni ₃	C ₇₇ H ₉₆ CoN ₁₈
Formula wgt. (g/mol)	1385.15	3168.06	1332.64
Temp. (K)	120(2)	273.15	149.95
Crystal System	Triclinic	Monoclinic	Triclinic
Space Group	P-1	P2 ₁ /n	P-1
a (Å)	16.1420(17)	17.3530(17)	16.2886(8)
b (Å)	16.9313(18)	60.854(6)	16.9760(8)
c (Å)	17.2417(18)	18.6444(18)	17.3350(8)
α (°)	65.170(6)	90	64.869(3)
β (°)	63.122(5)	117.380(2)	62.804(3)
γ (°)	87.932(6)	90	87.482(3)
Volume (Å³)	3745.2(7)	17483(3)	3792.2(3)
Z	2	4	2
Density (g/cm³)	1.228	1.204	1.167
Abs. coeff. μ (mm⁻¹)	0.892	0.481	0.280
F(000)	1478	6744	1422
Crystal Size (mm)	0.230 x 0.141 x 0.086	0.12 x 0.05 x 0.01	0.3 x 0.12 x 0.1
Colour and habit	Colourless block	Yellow block	Orange rod
Theta range (°)	2.929° ≤ 2Θ ≤ 72.485°	2.972° ≤ 2Θ ≤ 51.052°	2.698° ≤ 2Θ ≤ 52.828°
Refl. Collected	86549	211744	98761
Independent refl.	14173	25096	15485
GooF (F²)	1.037	1.027	1.007
Final R [I>2σ(I)]	0.0582	0.0497	0.0484
Final wR2	0.1665	0.1188	0.1190
R (all data)	0.0696	0.0659	0.0934
wR2 (all data)	0.1805	0.1261	0.1400
Max peak/hole (e/Å³)	1.142/-0.481	0.531/-0.448	0.712/-0.351

^a Data collected on a Bruker Kappa X8-Apex II diffractometer using Cu Kα radiation (λ = 1.54184 Å) at the University of Notre Dame. ^b Data collected at the Advanced Light Source (ALS) synchrotron facility (λ = 0.7749 Å), Lawrence Berkeley National Laboratory, Berkeley, CA. ^c Data collected on a Bruker Kappa X8-Apex II diffractometer using Mo Kα radiation (λ = 0.71073 Å) at McMaster University.

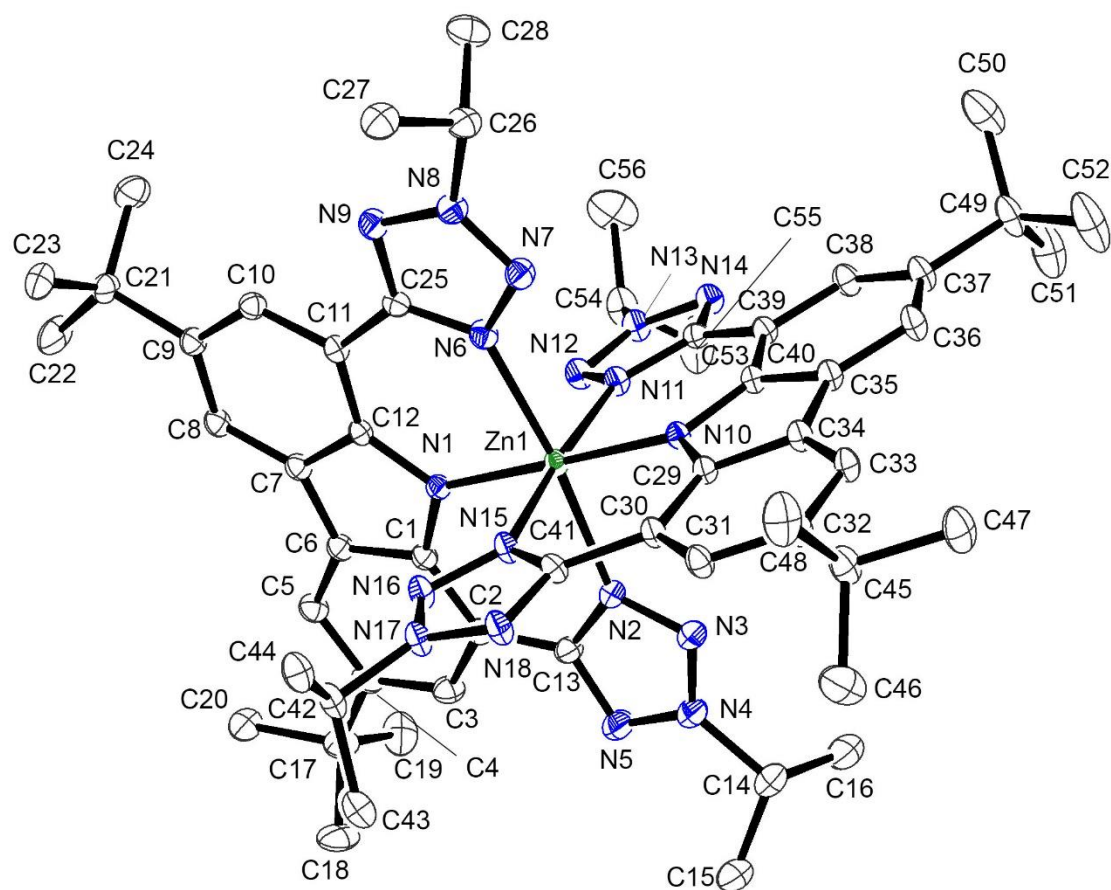


Figure B-17 Labelled ORTEP Drawing of **9**

H atoms not shown

Disordered toluenes of solvation not shown: C57-C84

Disordered tBu carbons C18A, C19A and C20A

Table B-59 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **9**

Atom	x	y	z	U(eq)
Zn1	3344.5(2)	7328.6(2)	3245.5(2)	22.70(11)
N1	2380.5(13)	7695.3(13)	4243.5(14)	22.2(4)
N2	4118.2(14)	6994.9(14)	4096.3(16)	28.3(4)
N3	4960.8(16)	6766.8(17)	3825.6(18)	35.3(5)
N4	5191.0(17)	6716.7(18)	4483.3(19)	39.2(5)
N5	4549.9(17)	6900.7(18)	5178.1(19)	40.0(6)
N6	2511.0(15)	7761.5(14)	2455.1(14)	27.0(4)
N7	2742.1(15)	7756.3(16)	1615.1(15)	31.0(5)
N8	2091.7(15)	8089.3(15)	1393.6(15)	29.6(5)
N9	1436.3(15)	8316.7(15)	2037.5(15)	29.2(4)
N10	4288.0(13)	6948.0(13)	2250.9(14)	22.0(4)
N11	2526.2(14)	5958.3(14)	4082.3(15)	26.1(4)
N12	1769.9(15)	5639.6(15)	4958.7(16)	30.7(5)
N13	1530.5(15)	4803.0(15)	5199.9(16)	31.7(5)
N14	2080.9(15)	4543.2(14)	4535.8(15)	29.6(4)
N15	4260.9(14)	8640.6(14)	2331.1(15)	26.5(4)
N16	4079.1(15)	9327.4(14)	2526.6(16)	29.0(4)
N17	4798.0(15)	9968.7(14)	1822.5(16)	29.5(4)
N18	5455.1(15)	9753.3(14)	1166.6(16)	30.2(5)
C1	2360.0(16)	7621.3(16)	5080.5(17)	24.7(5)
C2	3009.2(18)	7344.7(18)	5433.2(19)	29.2(5)
C3	2814(2)	7334.8(19)	6316(2)	35.0(6)
C4	2014(2)	7584.1(19)	6867.9(19)	33.8(6)
C5	1374.9(18)	7858.7(18)	6523.1(18)	31.5(5)
C6	1545.3(17)	7879.6(17)	5643.0(17)	26.8(5)
C7	1027.5(17)	8128.1(17)	5111.8(17)	25.8(5)
C8	170.2(17)	8417.7(17)	5298.1(17)	27.8(5)
C9	-174.7(17)	8600.2(17)	4650.4(18)	27.7(5)
C10	365.8(17)	8488.1(17)	3811.5(18)	26.7(5)
C11	1225.8(16)	8196.1(15)	3600.2(16)	23.3(5)
C12	1571.3(15)	8001.3(15)	4267.5(16)	21.7(4)
C13	3878.9(18)	7079.4(18)	4909.4(19)	30.2(5)
C14	6112(2)	6482(2)	4429(3)	47.4(7)
C15	6414(2)	6923(3)	4872(3)	52.3(8)
C16	6049(3)	5504(3)	4873(3)	58.6(9)
C17	1844(2)	7542(2)	7845(2)	42.4(7)
C18	2678(4)	8124(5)	7657(4)	57.6(19)
C19	1671(5)	6616(5)	8570(4)	58.8(18)
C20	953(4)	7956(4)	8280(3)	43.7(14)
C18A	1004(8)	6860(9)	8635(6)	71(4)
C19A	1870(10)	8424(8)	7767(8)	74(4)
C20A	2705(7)	7181(8)	8059(7)	59(3)

C21	-1119.9(18)	8911.7(19)	4814(2)	32.7(6)
C22	-1625(2)	8962(3)	5782(2)	53.7(9)
C23	-941(2)	9833(2)	3990(2)	43.2(7)
C24	-1762(2)	8258(2)	4826(3)	46.1(7)
C25	1722.5(17)	8097.3(16)	2704.3(17)	23.9(5)
C26	2083.5(19)	8194(2)	499.3(18)	34.3(6)
C27	2096(2)	9156(2)	-103(2)	40.3(6)
C28	1241(2)	7562(2)	783(2)	45.0(7)
C29	5128.3(16)	7447.7(16)	1430.7(17)	23.0(5)
C30	5548.7(17)	8336.2(16)	1051.1(17)	25.5(5)
C31	6425.6(17)	8686.3(17)	207.0(19)	29.1(5)
C32	6917.9(17)	8195.8(18)	-290.7(18)	29.6(5)
C33	6495.0(17)	7331.1(17)	69.5(18)	28.2(5)
C34	5611.8(17)	6960.6(16)	913.5(18)	26.2(5)
C35	5013.3(17)	6103.4(17)	1450.5(18)	27.0(5)
C36	5101.5(19)	5340.4(18)	1313.5(19)	32.3(6)
C37	4401(2)	4579.8(18)	1978(2)	34.4(6)
C38	3632.5(19)	4608.1(17)	2774.8(19)	30.9(5)
C39	3520.9(17)	5354.8(16)	2941.9(18)	25.7(5)
C40	4225.5(16)	6133.7(16)	2258.7(17)	23.4(5)
C41	5094.7(17)	8906.5(16)	1507.7(17)	25.3(5)
C42	4874.9(19)	10859.7(18)	1771(2)	33.7(6)
C43	5595(2)	10970(2)	2066(2)	41.6(7)
C44	5096(2)	11549.5(19)	757(2)	40.8(6)
C45	7869.8(18)	8657.6(19)	-1230(2)	34.7(6)
C46	8544(2)	9051(3)	-1024(3)	56.7(10)
C47	8342(2)	8011(2)	-1627(2)	43.5(7)
C48	7714(2)	9399(2)	-2013(2)	50.9(8)
C49	4465(2)	3727(2)	1850(2)	43.7(7)
C50	3638(3)	3521(3)	1716(3)	69.6(12)
C51	4404(3)	2952(3)	2749(3)	69.4(12)
C52	5390(3)	3816(3)	971(3)	78.0(14)
C53	2711.2(16)	5291.0(16)	3833.9(17)	24.3(5)
C54	738(2)	4187(2)	6161(2)	43.4(7)
C55	1115(3)	3439(3)	6689(3)	71.1(13)
C56	-19(3)	3860(3)	6033(3)	74.6(13)
C57	7455(3)	5599(3)	2196(3)	60.2(9)
C58	8038(4)	6383(4)	1371(3)	85.3(15)
C59	8989(5)	6487(5)	1003(4)	109(2)
C60	9398(4)	5813(5)	1450(5)	105(2)
C61	8804(4)	5067(4)	2295(5)	89.3(17)
C62	7870(3)	4984(3)	2637(4)	67.8(11)
C63	6423(4)	5469(4)	2559(4)	93.8(17)
C64	8394(3)	9065(3)	1951(3)	53.8(8)
C65	7951(3)	8542(3)	1759(3)	62.0(10)
C66	6974(3)	8407(3)	2145(3)	64.9(10)

C67	6439(3)	8795(3)	2732(3)	63.5(10)
C68	6873(3)	9308(3)	2931(3)	59.6(9)
C69	7840(3)	9439(3)	2547(3)	54.9(8)
C70	9448(3)	9231(4)	1530(4)	84.6(14)
C71	1440(5)	4519(5)	1193(4)	102(2)
C72	2081(4)	5268(5)	1032(6)	128(3)
C73	1964(4)	5255(4)	1886(6)	95.5(18)
C74	1402(5)	4695(5)	2755(6)	110(2)
C75	857(4)	4065(4)	2895(5)	91.8(16)
C76	846(3)	3943(3)	2157(4)	70.0(11)
C77	1500(9)	4509(7)	400(8)	192(5)
C78	4483(5)	9879(6)	4879(6)	93(3)
C79	4833(5)	9111(5)	5183(5)	70(2)
C80	5578(6)	9122(7)	5378(5)	98(3)
C81	5972(5)	9903(9)	5269(7)	128(5)
C82	5622(7)	10672(7)	4965(7)	144(5)
C83	4877(7)	10660(5)	4770(7)	124(5)
C84	3693(8)	9712(8)	4677(9)	109(4)

Table B-60 Anisotropic Displacement Parameters (U_{ij} , Å² x10³) for **9**

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Zn1	21.61(17)	22.89(19)	22.12(17)	-12.39(14)	-7.43(13)	4.77(12)
N1	22.8(9)	23.5(11)	21.5(9)	-11.5(8)	-10.5(8)	5.3(7)
N2	25.8(10)	30.4(12)	33.2(11)	-16.6(9)	-15.9(9)	9.1(8)
N3	30.9(11)	43.5(14)	43.0(13)	-25.1(11)	-21.9(10)	13.9(10)
N4	35.5(12)	49.5(16)	47.9(14)	-28.7(12)	-26.4(11)	16.9(11)
N5	37.4(12)	52.1(16)	45.3(13)	-28.2(12)	-26.4(11)	17.2(11)
N6	28.8(10)	31.2(12)	20.5(9)	-13.4(9)	-9.9(8)	6.0(8)
N7	29.5(11)	39.9(13)	25.7(10)	-18.5(10)	-12.1(9)	10.9(9)
N8	28.7(10)	38.3(13)	22.3(10)	-15.7(9)	-10.8(8)	7.2(9)
N9	29.2(10)	35.8(13)	23.4(10)	-16.3(9)	-10.8(8)	9.0(9)
N10	22.7(9)	18.9(10)	22.0(9)	-9.5(8)	-8.7(8)	3.5(7)
N11	23.5(10)	24.8(11)	22.6(9)	-9.7(8)	-6.0(8)	1.8(8)
N12	26.1(10)	27.5(12)	29.1(10)	-12.9(9)	-5.5(9)	0.2(8)
N13	28.0(10)	26.5(12)	29.1(11)	-11.0(9)	-6.1(9)	0.1(8)
N14	27.9(10)	25.6(12)	27.9(10)	-11.3(9)	-8.3(8)	1.5(8)
N15	27.8(10)	21.8(11)	27.5(10)	-14.4(9)	-8.6(8)	5.2(8)
N16	29.8(10)	21.9(11)	29.7(10)	-13.9(9)	-8.0(9)	5.0(8)
N17	31.0(11)	22.5(12)	29.3(10)	-14.5(9)	-7.7(9)	4.8(8)
N18	30.3(11)	24.3(12)	30.4(10)	-16.0(9)	-6.9(9)	3.7(8)
C1	25.5(11)	25.1(13)	23.1(11)	-11.9(10)	-10.4(9)	3.8(9)
C2	30.0(12)	31.9(14)	29.8(12)	-16.0(11)	-15.8(10)	7.3(10)
C3	37.3(14)	40.8(16)	32.2(13)	-16.6(12)	-20.8(11)	7.3(11)
C4	40.5(14)	38.4(16)	25.3(12)	-16.2(11)	-16.1(11)	4.4(11)

C5	31.5(13)	37.0(15)	25.9(12)	-17.7(11)	-10.6(10)	5.3(10)
C6	27.8(12)	28.4(13)	23.9(11)	-13.4(10)	-10.9(9)	4.9(9)
C7	25.4(11)	27.1(13)	24.0(11)	-13.6(10)	-9.4(9)	3.7(9)
C8	26.2(12)	32.2(14)	23.5(11)	-16.5(10)	-7.4(9)	5.7(9)
C9	22.5(11)	30.2(14)	28.3(12)	-15.5(11)	-8.6(9)	4.7(9)
C10	26.3(11)	28.4(13)	25.9(11)	-12.7(10)	-12.4(10)	4.6(9)
C11	23.3(11)	21.5(12)	21.0(10)	-9.6(9)	-7.5(9)	2.8(8)
C12	21.4(10)	20.2(12)	19.6(10)	-9.6(9)	-6.2(8)	2.2(8)
C13	29.8(12)	30.7(14)	34.6(13)	-14.2(11)	-19.5(11)	7.2(10)
C14	40.7(16)	56(2)	60.6(19)	-30.7(17)	-33.1(15)	21.0(14)
C15	47.7(18)	56(2)	72(2)	-31.7(18)	-41.3(18)	18.1(15)
C16	52(2)	58(2)	83(3)	-34(2)	-45(2)	20.1(16)
C17	46.3(16)	61(2)	31.5(14)	-27.0(14)	-22.2(13)	11.3(14)
C18	43(3)	106(5)	56(3)	-61(4)	-26(3)	15(3)
C19	84(5)	69(4)	33(3)	-27(3)	-33(3)	34(3)
C20	45(3)	69(4)	29(2)	-32(2)	-20(2)	20(2)
C18A	65(6)	111(10)	29(4)	-29(5)	-18(4)	2(6)
C19A	120(10)	83(8)	60(6)	-50(6)	-61(7)	44(7)
C20A	72(6)	83(7)	49(5)	-40(5)	-43(5)	27(5)
C21	25.0(12)	43.6(16)	33.6(13)	-22.8(12)	-12.7(10)	11.9(11)
C22	39.2(16)	92(3)	45.4(17)	-45.5(19)	-20.7(14)	34.9(17)
C23	36.6(15)	45.6(18)	52.5(17)	-25.2(15)	-23.3(14)	18.6(13)
C24	27.1(13)	58(2)	53.1(18)	-27.8(16)	-16.3(13)	7.0(13)
C25	28.6(12)	21.2(12)	21.5(10)	-7.8(9)	-13.4(9)	2.5(9)
C26	33.6(13)	47.7(17)	23.7(12)	-19.1(12)	-12.9(10)	8.5(11)
C27	41.8(15)	47.3(18)	28.4(13)	-14.7(13)	-16.5(12)	7.9(12)
C28	48.2(17)	55(2)	34.0(14)	-22.6(14)	-18.9(13)	0.4(14)
C29	23.1(11)	21.6(12)	23.3(11)	-11.6(10)	-9.3(9)	5.0(8)
C30	25.5(11)	22.1(13)	26.0(11)	-13.0(10)	-8.4(9)	4.7(9)
C31	27.9(12)	22.7(13)	30.2(12)	-13.5(11)	-7.3(10)	1.1(9)
C32	25.6(12)	29.1(14)	28.3(12)	-15.4(11)	-6.0(10)	3.5(9)
C33	28.1(12)	26.4(13)	26.3(12)	-15.2(10)	-7.3(10)	7.4(9)
C34	26.5(12)	22.3(13)	26.3(11)	-12.1(10)	-9.0(10)	4.9(9)
C35	26.2(12)	23.0(13)	27.7(12)	-12.5(10)	-8.8(10)	4.3(9)
C36	32.6(13)	27.0(14)	31.1(13)	-17.8(11)	-6.4(10)	5.6(10)
C37	40.2(14)	24.6(14)	35.1(13)	-17.4(12)	-12.1(12)	5.5(10)
C38	34.6(13)	21.6(13)	29.9(12)	-11.1(11)	-10.7(11)	1.4(10)
C39	26.5(11)	23.1(13)	26.5(11)	-12.4(10)	-11.0(10)	4.3(9)
C40	25.0(11)	21.6(12)	23.2(11)	-11.4(10)	-10.2(9)	5.9(9)
C41	28.7(12)	20.7(13)	24.3(11)	-10.8(10)	-10.2(9)	2.2(9)
C42	37.3(14)	24.1(14)	36.5(14)	-18.7(12)	-10.7(11)	5.9(10)
C43	49.6(17)	37.3(17)	44.4(16)	-25.9(14)	-21.0(14)	10.5(12)
C44	49.6(17)	25.2(15)	45.0(16)	-16.0(13)	-20.6(14)	8.0(12)
C45	27.3(12)	33.1(15)	30.6(13)	-17.6(12)	-0.7(10)	-0.1(10)
C46	29.7(15)	77(3)	54.1(19)	-43.3(19)	1.0(14)	-9.7(15)
C47	33.3(14)	39.7(17)	36.6(14)	-20.1(13)	2.1(12)	2.9(11)

C48	42.7(17)	39.7(19)	35.4(15)	-10.1(14)	2.0(13)	4.2(13)
C49	50.2(17)	25.9(16)	43.4(16)	-21.0(13)	-8.5(13)	2.4(12)
C50	80(3)	57(3)	73(3)	-45(2)	-24(2)	2(2)
C51	78(3)	41(2)	66(2)	-27.3(19)	-14(2)	15.0(18)
C52	82(3)	44(2)	72(3)	-39(2)	3(2)	-1.3(19)
C53	24.3(11)	21.3(12)	24.3(11)	-7.7(9)	-11.6(9)	1.1(9)
C54	37.4(15)	32.1(16)	32.3(14)	-9.3(13)	1.0(12)	-1.9(11)
C55	73(3)	44(2)	35.0(17)	0.7(15)	4.4(17)	13.6(18)
C56	53(2)	70(3)	64(2)	-23(2)	-4.0(19)	-29.6(19)
C57	61(2)	69(3)	63(2)	-37(2)	-33.2(19)	19.2(18)
C58	118(4)	75(3)	55(2)	-17(2)	-45(3)	8(3)
C59	95(4)	127(6)	64(3)	-38(3)	-10(3)	-25(4)
C60	58(3)	151(6)	129(5)	-103(5)	-27(3)	13(3)
C61	81(3)	84(4)	151(5)	-77(4)	-72(4)	37(3)
C62	74(3)	46(2)	89(3)	-25(2)	-48(2)	11.4(18)
C63	77(3)	135(5)	105(4)	-72(4)	-56(3)	39(3)
C64	52.3(19)	53(2)	55(2)	-17.8(17)	-31.3(17)	12.1(15)
C65	75(3)	65(3)	58(2)	-29(2)	-40(2)	22(2)
C66	77(3)	56(2)	73(3)	-20(2)	-54(2)	6.1(19)
C67	51(2)	59(3)	63(2)	-10.2(19)	-30.5(18)	5.0(17)
C68	63(2)	59(2)	48.2(19)	-17.2(17)	-27.2(17)	17.3(18)
C69	61(2)	54(2)	53.6(19)	-18.9(17)	-35.7(17)	11.1(16)
C70	53(2)	95(4)	91(3)	-30(3)	-34(2)	19(2)
C71	112(5)	110(5)	77(3)	-38(3)	-49(3)	67(4)
C72	61(3)	89(5)	117(5)	15(4)	-12(3)	32(3)
C73	78(3)	82(4)	117(5)	-23(4)	-60(4)	16(3)
C74	113(5)	111(6)	143(6)	-67(5)	-85(5)	49(4)
C75	85(3)	94(4)	139(5)	-72(4)	-71(4)	45(3)
C76	72(3)	59(3)	87(3)	-35(2)	-43(2)	16(2)
C77	328(16)	148(9)	169(9)	-99(8)	-154(10)	123(10)
C78	86(6)	91(6)	48(5)	-19(5)	-4(4)	46(5)
C79	72(5)	70(5)	50(5)	-30(4)	-12(4)	7(4)
C80	93(7)	127(9)	53(5)	-47(6)	-15(5)	43(6)
C81	108(10)	190(11)	51(6)	-57(8)	-6(6)	-16(8)
C82	148(12)	131(11)	67(8)	-31(8)	4(7)	-16(8)
C83	150(11)	89(8)	75(8)	-49(7)	2(7)	25(7)
C84	101(7)	104(9)	66(6)	-21(6)	-12(5)	18(6)

Table B-61 Bond Lengths for **9**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn1	N1	2.0431(19)	C21	C23	1.529(4)
Zn1	N2	2.223(2)	C21	C24	1.530(4)
Zn1	N6	2.225(2)	C26	C27	1.515(4)
Zn1	N10	2.0423(19)	C26	C28	1.516(4)
Zn1	N11	2.213(2)	C29	C30	1.413(3)
Zn1	N15	2.190(2)	C29	C34	1.424(3)
N1	C1	1.380(3)	C30	C31	1.395(3)
N1	C12	1.377(3)	C30	C41	1.468(3)
N2	N3	1.325(3)	C31	C32	1.411(3)
N2	C13	1.345(3)	C32	C33	1.386(4)
N3	N4	1.315(3)	C32	C45	1.539(3)
N4	N5	1.331(3)	C33	C34	1.402(3)
N4	C14	1.496(4)	C34	C35	1.436(3)
N5	C13	1.339(3)	C35	C36	1.399(3)
N6	N7	1.326(3)	C35	C40	1.419(3)
N6	C25	1.336(3)	C36	C37	1.394(4)
N7	N8	1.306(3)	C37	C38	1.392(4)
N8	N9	1.330(3)	C37	C49	1.543(4)
N8	C26	1.482(3)	C38	C39	1.399(3)
N9	C25	1.335(3)	C39	C40	1.419(3)
N10	C29	1.378(3)	C39	C53	1.462(3)
N10	C40	1.380(3)	C42	C43	1.509(4)
N11	N12	1.327(3)	C42	C44	1.515(4)
N11	C53	1.347(3)	C45	C46	1.536(4)
N12	N13	1.315(3)	C45	C47	1.531(4)
N13	N14	1.330(3)	C45	C48	1.523(5)
N13	C54	1.483(3)	C49	C50	1.530(5)
N14	C53	1.340(3)	C49	C51	1.515(5)
N15	N16	1.329(3)	C49	C52	1.525(5)
N15	C41	1.345(3)	C54	C55	1.510(5)
N16	N17	1.308(3)	C54	C56	1.497(5)
N17	N18	1.331(3)	C57	C58	1.402(6)
N17	C42	1.480(3)	C57	C62	1.364(6)
N18	C41	1.335(3)	C57	C63	1.477(6)
C1	C2	1.410(3)	C58	C59	1.354(8)
C1	C6	1.422(3)	C59	C60	1.413(10)
C2	C3	1.400(4)	C60	C61	1.384(9)
C2	C13	1.462(4)	C61	C62	1.335(7)
C3	C4	1.392(4)	C64	C65	1.384(6)
C4	C5	1.387(4)	C64	C69	1.389(5)
C4	C17	1.550(3)	C64	C70	1.498(5)
C5	C6	1.399(3)	C65	C66	1.389(6)
C6	C7	1.434(3)	C66	C67	1.389(6)

C7	C8	1.393(3)	C67	C68	1.369(6)
C7	C12	1.425(3)	C68	C69	1.376(5)
C8	C9	1.383(4)	C71	C72	1.515(11)
C9	C10	1.402(3)	C71	C76	1.378(8)
C9	C21	1.537(3)	C71	C77	1.333(10)
C10	C11	1.396(3)	C72	C73	1.388(10)
C11	C12	1.411(3)	C73	C74	1.268(9)
C11	C25	1.464(3)	C74	C75	1.277(9)
C14	C15	1.490(5)	C75	C76	1.379(7)
C14	C16	1.489(5)	C78	C79	1.3900
C17	C18	1.523(6)	C78	C83	1.3900
C17	C19	1.473(7)	C78	C84	1.528(8)
C17	C20	1.586(6)	C79	C80	1.3900
C17	C18A	1.466(11)	C80	C81	1.3900
C17	C19A	1.443(12)	C81	C82	1.3900
C17	C20A	1.628(10)	C82	C83	1.3900
C21	C22	1.531(4)			

Table B-62 Bond Angles for **9**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Zn1	N2	87.43(8)	C19A	C17	C20A	105.8(7)
N1	Zn1	N6	87.24(8)	C22	C21	C9	111.5(2)
N1	Zn1	N11	91.83(8)	C23	C21	C9	109.6(2)
N1	Zn1	N15	93.50(8)	C23	C21	C22	108.3(3)
N2	Zn1	N6	174.07(8)	C23	C21	C24	109.6(2)
N10	Zn1	N1	178.93(8)	C24	C21	C9	109.1(2)
N10	Zn1	N2	93.26(8)	C24	C21	C22	108.7(3)
N10	Zn1	N6	92.11(8)	N6	C25	C11	124.5(2)
N10	Zn1	N11	87.34(8)	N9	C25	N6	111.1(2)
N10	Zn1	N15	87.34(8)	N9	C25	C11	124.3(2)
N11	Zn1	N2	91.55(8)	N8	C26	C27	109.5(2)
N11	Zn1	N6	91.21(8)	N8	C26	C28	109.2(2)
N15	Zn1	N2	87.85(8)	C27	C26	C28	113.4(3)
N15	Zn1	N6	89.90(8)	N10	C29	C30	130.0(2)
N15	Zn1	N11	174.60(7)	N10	C29	C34	111.9(2)
C1	N1	Zn1	127.29(16)	C30	C29	C34	118.1(2)
C12	N1	Zn1	127.34(15)	C29	C30	C41	122.5(2)
C12	N1	C1	105.18(18)	C31	C30	C29	118.8(2)
N3	N2	Zn1	125.21(17)	C31	C30	C41	118.8(2)
N3	N2	C13	107.4(2)	C30	C31	C32	123.2(2)
C13	N2	Zn1	126.98(16)	C31	C32	C45	118.7(2)
N4	N3	N2	105.0(2)	C33	C32	C31	118.0(2)
N3	N4	N5	114.7(2)	C33	C32	C45	123.2(2)
N3	N4	C14	121.6(2)	C32	C33	C34	120.2(2)

N5	N4	C14	123.7(2)	C29	C34	C35	105.4(2)
N4	N5	C13	101.6(2)	C33	C34	C29	121.7(2)
N7	N6	Zn1	124.83(16)	C33	C34	C35	132.8(2)
N7	N6	C25	107.6(2)	C36	C35	C34	132.6(2)
C25	N6	Zn1	127.54(16)	C36	C35	C40	122.0(2)
N8	N7	N6	104.92(19)	C40	C35	C34	105.3(2)
N7	N8	N9	114.7(2)	C37	C36	C35	120.1(2)
N7	N8	C26	122.4(2)	C36	C37	C49	121.9(2)
N9	N8	C26	123.0(2)	C38	C37	C36	117.8(2)
N8	N9	C25	101.7(2)	C38	C37	C49	120.3(2)
C29	N10	Zn1	127.38(16)	C37	C38	C39	123.8(2)
C29	N10	C40	105.14(18)	C38	C39	C40	118.4(2)
C40	N10	Zn1	127.48(15)	C38	C39	C53	119.0(2)
N12	N11	Zn1	124.80(16)	C40	C39	C53	122.5(2)
N12	N11	C53	107.5(2)	N10	C40	C35	112.1(2)
C53	N11	Zn1	127.65(16)	N10	C40	C39	130.1(2)
N13	N12	N11	104.9(2)	C39	C40	C35	117.8(2)
N12	N13	N14	114.9(2)	N15	C41	C30	124.3(2)
N12	N13	C54	122.4(2)	N18	C41	N15	111.1(2)
N14	N13	C54	122.7(2)	N18	C41	C30	124.7(2)
N13	N14	C53	101.6(2)	N17	C42	C43	109.4(2)
N16	N15	Zn1	124.17(15)	N17	C42	C44	108.8(2)
N16	N15	C41	107.4(2)	C43	C42	C44	114.0(2)
C41	N15	Zn1	128.42(16)	C46	C45	C32	109.7(2)
N17	N16	N15	104.96(19)	C47	C45	C32	111.7(2)
N16	N17	N18	114.8(2)	C47	C45	C46	108.2(3)
N16	N17	C42	122.3(2)	C48	C45	C32	109.8(2)
N18	N17	C42	122.9(2)	C48	C45	C46	109.2(3)
N17	N18	C41	101.8(2)	C48	C45	C47	108.2(2)
N1	C1	C2	130.2(2)	C50	C49	C37	109.3(3)
N1	C1	C6	112.0(2)	C51	C49	C37	110.2(3)
C2	C1	C6	117.8(2)	C51	C49	C50	108.4(3)
C1	C2	C13	122.7(2)	C51	C49	C52	108.2(3)
C3	C2	C1	118.4(2)	C52	C49	C37	111.9(3)
C3	C2	C13	119.0(2)	C52	C49	C50	108.9(3)
C4	C3	C2	123.8(2)	N11	C53	C39	124.8(2)
C3	C4	C17	120.6(2)	N14	C53	N11	111.1(2)
C5	C4	C3	118.1(2)	N14	C53	C39	124.0(2)
C5	C4	C17	121.4(2)	N13	C54	C55	109.2(3)
C4	C5	C6	119.9(2)	N13	C54	C56	110.3(3)
C1	C6	C7	105.4(2)	C56	C54	C55	112.3(4)
C5	C6	C1	122.1(2)	C58	C57	C63	119.6(5)
C5	C6	C7	132.5(2)	C62	C57	C58	118.0(4)
C8	C7	C6	132.6(2)	C62	C57	C63	122.5(4)
C8	C7	C12	122.0(2)	C59	C58	C57	119.9(5)
C12	C7	C6	105.4(2)	C58	C59	C60	120.5(6)

C9	C8	C7	120.1(2)	C61	C60	C59	118.6(5)
C8	C9	C10	118.0(2)	C62	C61	C60	119.4(5)
C8	C9	C21	123.0(2)	C61	C62	C57	123.5(5)
C10	C9	C21	119.0(2)	C65	C64	C69	118.5(4)
C11	C10	C9	123.6(2)	C65	C64	C70	121.3(4)
C10	C11	C12	118.3(2)	C69	C64	C70	120.2(4)
C10	C11	C25	118.7(2)	C64	C65	C66	120.4(4)
C12	C11	C25	123.0(2)	C67	C66	C65	119.9(4)
N1	C12	C7	112.0(2)	C68	C67	C66	120.0(4)
N1	C12	C11	130.0(2)	C67	C68	C69	119.8(4)
C11	C12	C7	117.9(2)	C68	C69	C64	121.4(4)
N2	C13	C2	125.1(2)	C76	C71	C72	114.8(6)
N5	C13	N2	111.3(2)	C77	C71	C72	117.0(8)
N5	C13	C2	123.7(2)	C77	C71	C76	128.2(9)
C15	C14	N4	109.0(3)	C73	C72	C71	114.1(5)
C16	C14	N4	111.2(3)	C74	C73	C72	127.6(7)
C16	C14	C15	113.7(3)	C73	C74	C75	118.5(8)
C4	C17	C20	111.2(3)	C74	C75	C76	124.2(7)
C4	C17	C20A	109.8(4)	C71	C76	C75	120.8(6)
C18	C17	C4	109.1(3)	C79	C78	C83	120.0
C18	C17	C20	104.9(4)	C79	C78	C84	110.5(7)
C19	C17	C4	110.4(3)	C83	C78	C84	129.4(7)
C19	C17	C18	113.1(5)	C78	C79	C80	120.0
C19	C17	C20	107.9(4)	C81	C80	C79	120.0
C18A	C17	C4	108.1(4)	C82	C81	C80	120.0
C18A	C17	C20A	104.7(7)	C81	C82	C83	120.0
C19A	C17	C4	109.6(4)	C82	C83	C78	120.0
C19A	C17	C18A	118.6(8)				

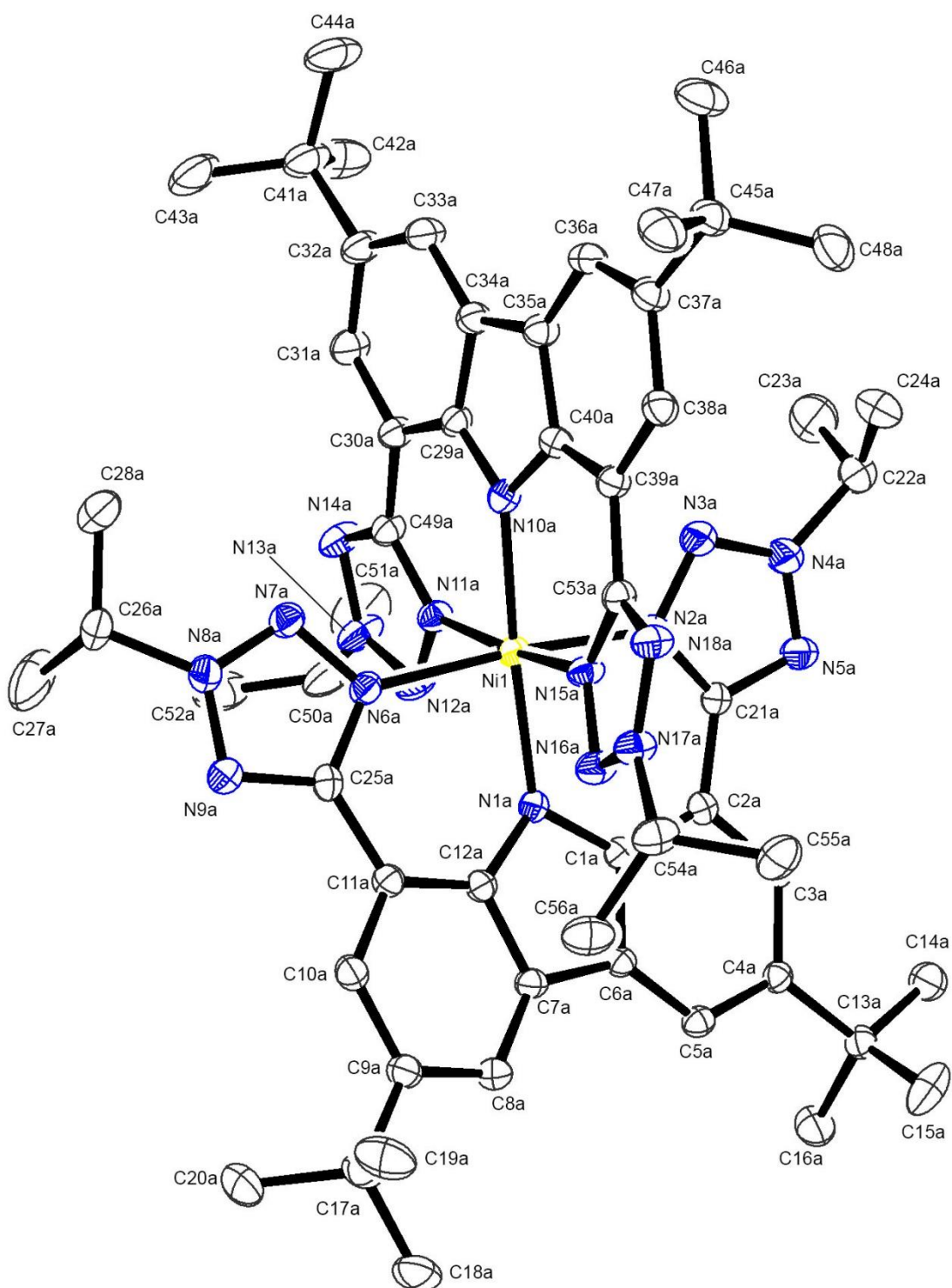


Figure B-18 Labelled ORTEP Drawing of **26** Molecule A

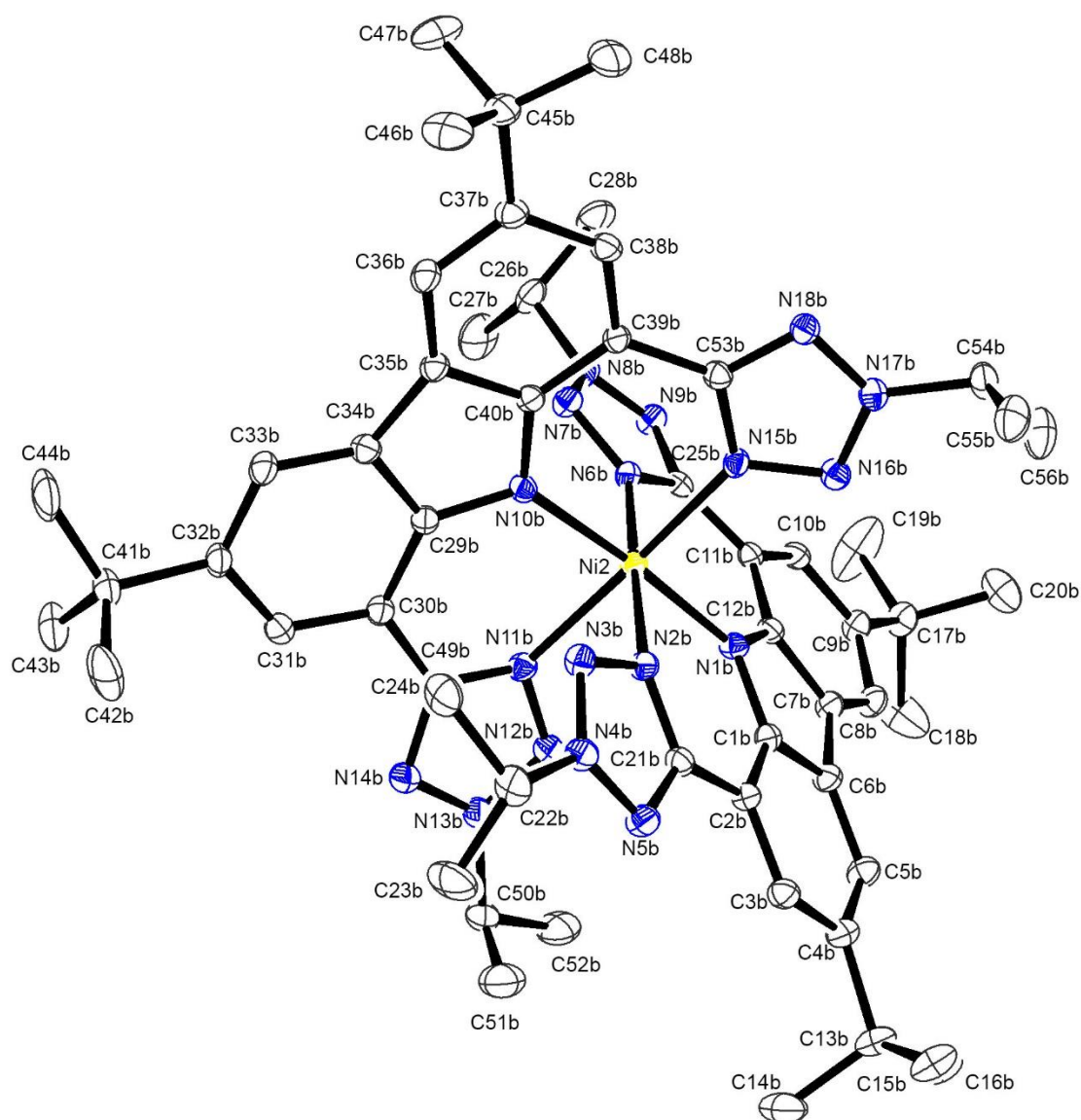


Figure B-19 Labelled ORTEP Drawing of **26** Molecule B

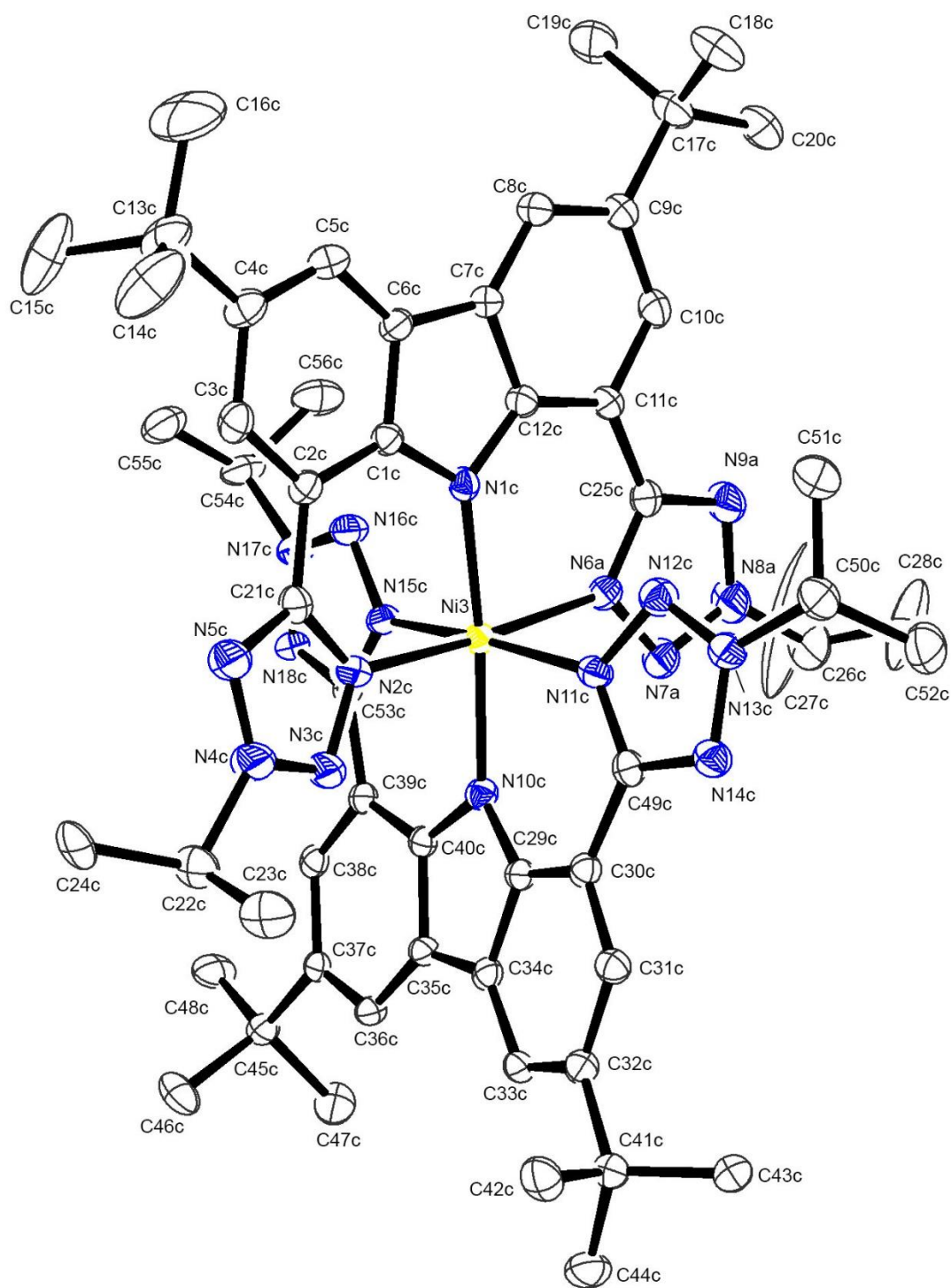


Figure B-20 Labelled ORTEP Drawing of **26** Molecule C

H atoms not shown

Disordered tBu carbons C1-C12 not shown

Disordered iPr carbons C13 and C14 not shown

Table B-63 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **26**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
Ni1	2628.6(3)	6479.2(2)	6332.7(2)	27.50(11)
N1A	2221.6(16)	6225.2(4)	5528.0(14)	26.8(6)
N2A	3865.5(18)	6429.0(4)	6452.8(16)	34.4(7)
N3A	4555(2)	6535.5(5)	6995(2)	49.0(8)
N4A	5217(2)	6452.9(5)	6926(2)	49.1(8)
N5A	5004.6(19)	6299.7(5)	6346.1(18)	44.6(8)
N6A	1330.2(18)	6524.1(4)	6052.4(15)	31.7(6)
N7A	1012.1(19)	6712.1(5)	6170.3(16)	36.4(7)
N8A	176.1(19)	6676.9(5)	5890.6(17)	39.2(7)
N9A	-86.3(19)	6475.6(5)	5586.6(17)	40.5(7)
N10A	3083.5(17)	6708.4(4)	7234.3(15)	29.5(6)
N11A	2417.9(18)	6743.2(4)	5507.4(15)	33.0(7)
N12A	2133(2)	6719.7(5)	4716.2(16)	42.8(8)
N13A	2008(2)	6921.8(5)	4429.4(17)	51.6(9)
N14A	2188(2)	7079.7(5)	4977.0(16)	44.3(8)
N15A	2813.8(18)	6245.9(4)	7253.7(15)	31.3(6)
N16A	2451.6(19)	6045.5(4)	7091.2(16)	36.4(7)
N17A	2632.6(19)	5961.7(4)	7800.6(16)	37.0(7)
N18A	3097.0(19)	6091.7(4)	8426.1(16)	37.2(7)
C1A	2740(2)	6090.1(5)	5332.1(17)	26.9(7)
C2A	3610(2)	6115.1(5)	5516.4(18)	28.1(7)
C3A	3993(2)	5955.8(5)	5240.7(18)	29.0(7)
C4A	3552(2)	5770.9(5)	4797.4(18)	29.0(7)
C5A	2695(2)	5741.3(5)	4662.4(18)	29.9(8)
C6A	2293(2)	5894.8(5)	4929.1(17)	26.8(7)
C7A	1464(2)	5905.6(5)	4928.1(18)	28.9(7)
C8A	781(2)	5758.2(6)	4702.7(19)	34.4(8)
C9A	69(2)	5808.7(5)	4815.7(19)	34.5(8)
C10A	53(2)	6014.9(5)	5153.9(19)	34.1(8)
C11A	727(2)	6166.1(5)	5384.3(18)	30.2(8)
C12A	1458(2)	6109.7(5)	5290.2(18)	28.3(7)
C13A	3988(2)	5599.8(6)	4505.3(19)	33.5(8)
C14A	4870(2)	5678.2(7)	4610(3)	57.2(11)
C15A	4132(3)	5387.8(7)	4993(3)	64.3(13)
C16A	3422(3)	5550.4(7)	3612(2)	52.8(11)
C17A	-681(2)	5645.0(6)	4625(2)	40.7(9)

C18A	-636(3)	5449.8(6)	4137(3)	54.7(11)
C19A	-604(3)	5557.2(8)	5427(3)	65.3(13)
C20A	-1554(3)	5756.3(7)	4139(3)	68.0(13)
C21A	4143(2)	6284.7(5)	6065.0(19)	31.1(8)
C22A	6119(3)	6527.7(7)	7446(3)	56.4(11)
C23A	6206(3)	6744.3(8)	7129(3)	74.2(14)
C24A	6307(3)	6528.5(8)	8320(3)	71.2(14)
C25A	655(2)	6383.0(5)	5689.1(19)	31.2(8)
C26A	-444(3)	6851.0(7)	5852(2)	49.0(10)
C27A	-1012(4)	6905.6(10)	5006(3)	118(3)
C28A	27(3)	7045.5(8)	6344(3)	97(2)
C29A	3122(2)	6932.0(5)	7160.9(18)	29.4(8)
C30A	2789(2)	7060.9(5)	6456.8(19)	33.6(8)
C31A	2843(2)	7288.4(6)	6539(2)	42.8(9)
C32A	3235(3)	7396.8(6)	7290(2)	43.8(9)
C33A	3601(2)	7267.3(6)	7977(2)	40.9(9)
C34A	3561(2)	7040.0(5)	7921.0(19)	33.2(8)
C35A	3832(2)	6866.5(5)	8508.6(19)	33.0(8)
C36A	4285(2)	6863.1(6)	9350(2)	37.9(9)
C37A	4425(2)	6667.3(6)	9767.8(19)	35.2(8)
C38A	4065(2)	6475.2(6)	9319.8(19)	35.1(8)
C39A	3614(2)	6472.4(5)	8475.7(19)	30.1(8)
C40A	3515(2)	6669.6(5)	8056.3(18)	29.6(8)
C41A	3253(3)	7649.3(6)	7310(2)	60.2(12)
C42A	3693(4)	7736.8(7)	6815(3)	85.2(18)
C43A	2337(4)	7732.5(8)	6967(3)	101(2)
C44A	3754(4)	7736.5(7)	8177(3)	77.9(16)
C45A	4940(2)	6649.6(6)	10687(2)	40.2(9)
C46A	5366(3)	6867.1(7)	11073(2)	58.7(12)
C47A	4334(3)	6575.9(7)	11035(2)	52.0(11)
C48A	5660(3)	6479.2(7)	10899(2)	53.0(11)
C49A	2448(2)	6961.9(5)	5656(2)	34.8(8)
C50A	1734(4)	6971.3(7)	3571(2)	68.9(15)
C51A	2375(4)	7123.8(9)	3485(3)	95.7(19)
C52A	831(4)	7059.1(8)	3205(3)	84.1(17)
C53A	3197(2)	6270.8(5)	8060.6(18)	30.3(8)
C54A	2315(2)	5741.7(5)	7899(2)	41.0(9)
C55A	3060(3)	5581.4(6)	8187(2)	49.5(10)
C56A	1543(3)	5676.9(6)	7129(2)	51.6(10)
Ni2	-1803.4(2)	5095.4(2)	11341.6(2)	22.31(10)
N1B	-2621.7(16)	5354.4(4)	10981.7(14)	23.8(6)
N2B	-1665.5(16)	5135.3(4)	10279.3(14)	25.5(6)
N3B	-1233.6(17)	4989.5(4)	10070.8(15)	28.4(6)
N4B	-1524.9(18)	5017.3(4)	9289.2(15)	30.2(6)
N5B	-2129.3(18)	5172.4(4)	8959.6(15)	31.8(6)
N6B	-2029.4(16)	5068.6(4)	12352.7(14)	24.9(6)

N7B	-1711.6(17)	4908.5(4)	12900.4(15)	28.5(6)
N8B	-2030.3(17)	4946.4(4)	13404.6(15)	29.2(6)
N9B	-2547.1(17)	5120.3(4)	13233.8(15)	29.8(6)
N10B	-1046.2(16)	4822.9(4)	11623.2(14)	23.9(6)
N11B	-2874.3(16)	4888.0(4)	10545.7(15)	26.9(6)
N12B	-3626.4(17)	4977.6(4)	10027.8(15)	31.6(6)
N13B	-3962.4(17)	4839.6(4)	9411.7(16)	33.0(7)
N14B	-3473.2(18)	4663.4(4)	9486.1(16)	34.8(7)
N15B	-668.8(16)	5277.1(4)	12045.8(14)	24.3(6)
N16B	-629.2(17)	5496.3(4)	12065.4(15)	27.9(6)
N17B	180.2(17)	5542.9(4)	12576.2(15)	28.0(6)
N18B	688.2(16)	5368.4(4)	12900.3(15)	28.0(6)
C1B	-2976(2)	5455.9(5)	10235.3(17)	25.5(7)
C2B	-2827(2)	5411.3(5)	9569.7(17)	25.6(7)
C3B	-3317(2)	5522.9(5)	8849.3(18)	30.8(8)
C4	2738(12)	4393(3)	13787(14)	91(9)
C4B	-3949(2)	5680.1(5)	8752.7(19)	31.9(8)
C5	3082(9)	4765(4)	13371(10)	72(7)
C5B	-4083(2)	5726.0(5)	9419.5(19)	32.4(8)
C6	2871(9)	4738(3)	14578(9)	54(5)
C6B	-3606(2)	5616.2(5)	10149.9(18)	28.6(7)
C7	-4116(7)	6032(2)	12607(8)	53(4)
C7B	-3644(2)	5614.1(5)	10904.5(18)	27.7(7)
C8	-5484(8)	5852(3)	11638(10)	86(7)
C8B	-4127(2)	5730.4(5)	11200.9(19)	32.5(8)
C9	-4589(15)	5694(2)	13036(12)	100(9)
C9B	-4059(2)	5682.4(5)	11957.7(19)	29.8(8)
C10B	-3507(2)	5510.2(5)	12397.2(18)	27.7(7)
C11B	-3017(2)	5388.8(5)	12118.0(17)	24.3(7)
C12B	-3052(2)	5447.7(5)	11369.9(17)	24.8(7)
C13B	-4483(2)	5784.9(6)	7922(2)	39.9(9)
C14B	-5026(3)	5604.5(7)	7319(2)	57.7(11)
C15B	-3877(3)	5891.3(7)	7631(2)	50.2(10)
C16B	-5117(3)	5956.0(7)	7934(2)	51.7(11)
C17B	-4572(2)	5810.3(6)	12312(2)	36.1(8)
C18B	-5100(9)	5995(2)	11766(7)	98(5)
C19B	-3956(5)	5905.9(14)	13132(6)	54(3)
C20B	-5194(5)	5652.3(12)	12433(5)	45(2)
C21B	-2210(2)	5243.6(5)	9600.5(17)	26.6(7)
C22B	-1237(2)	4877.0(6)	8806(2)	39.1(9)
C23B	-2022(3)	4782.2(7)	8114(2)	64.0(13)
C24B	-616(2)	4704.2(6)	9329(2)	42.7(9)
C25B	-2531.0(19)	5197.7(5)	12566.4(17)	24.2(7)
C26B	-1868(2)	4797.9(6)	14087.4(19)	38.3(9)
C27B	-2715(3)	4694.2(7)	13951(3)	63.9(12)
C28B	-1426(3)	4923.4(6)	14872(2)	54.5(11)

C29B	-1268(2)	4620.3(5)	11248.3(17)	24.4(7)
C30B	-2044(2)	4553.4(5)	10585.3(18)	25.9(7)
C31B	-2083(2)	4341.1(5)	10275.0(18)	28.9(7)
C32B	-1401(2)	4191.0(5)	10596.2(19)	29.8(8)
C33B	-637(2)	4258.8(5)	11256.5(19)	31.2(8)
C34B	-563(2)	4469.8(5)	11573.0(18)	27.2(7)
C35B	150(2)	4590.4(5)	12187.2(18)	26.7(7)
C36B	1012(2)	4542.0(5)	12689.2(19)	30.9(8)
C37B	1581(2)	4702.1(5)	13183.3(18)	30.0(8)
C38B	1255(2)	4913.6(5)	13146.1(18)	28.6(7)
C39B	389(2)	4970.6(5)	12648.4(17)	24.3(7)
C40B	-188(2)	4806.5(5)	12169.7(17)	23.5(7)
C41B	-1495(2)	3964.3(5)	10197(2)	35.2(8)
C42B	-1495(3)	3996.1(7)	9388(3)	64.7(13)
C43B	-2335(3)	3853.2(6)	10057(3)	50.8(10)
C44B	-742(3)	3811.9(6)	10716(3)	69.0(14)
C45B	2546(2)	4647.0(6)	13718(2)	34.3(8)
C46B	2918(3)	4540.3(11)	13203(3)	49.7(18)
C47B	2631(3)	4488.5(10)	14385(3)	51.8(18)
C48B	3095(3)	4851.1(9)	14120(3)	49.1(17)
C49B	-2789(2)	4697.4(5)	10209.8(18)	26.6(7)
C50B	-4767(2)	4886.3(6)	8657(2)	41.3(9)
C51B	-4527(3)	4942.7(7)	7998(2)	60.6(12)
C52B	-5268(2)	5068.1(7)	8797(2)	54.9(11)
C53B	135(2)	5201.6(5)	12551.9(17)	25.3(7)
C54B	530(2)	5769.9(5)	12724(2)	36.1(8)
C55B	944(3)	5814.8(6)	12176(2)	49.7(10)
C56B	-178(3)	5929.4(6)	12604(3)	56.8(11)
Ni3	-716.8(3)	6836.0(2)	9564.2(2)	29.33(11)
N1C	-1272.0(17)	6891.1(4)	8345.6(15)	30.3(6)
N2C	-1055.4(19)	6501.0(4)	9274.8(16)	35.6(7)
N3C	-981(2)	6354.5(5)	9827.8(19)	54.8(9)
N4C	-1346(3)	6175.5(5)	9424(2)	68.4(12)
N5C	-1665(2)	6191.4(5)	8627.2(19)	53.0(9)
N6C	-499.9(18)	7178.9(5)	9727.6(15)	34.6(7)
N7C	-156(2)	7277.1(5)	10446.0(17)	44.0(8)
N8C	-185(2)	7488.8(5)	10280.9(19)	55.2(9)
N9C	-526(2)	7537.8(5)	9498.8(19)	51.6(9)
N10C	-170.1(17)	6747.6(4)	10756.0(15)	29.6(6)
N11C	-1874.8(18)	6895.7(4)	9641.2(15)	32.8(7)
N12C	-2532.6(19)	7017.4(5)	9105.7(17)	39.6(7)
N13C	-3094.8(19)	7028.3(5)	9395.7(16)	38.8(7)
N14C	-2851.5(19)	6922.0(5)	10093.8(17)	39.3(7)
N15C	517.6(17)	6802.2(4)	9640.3(15)	31.0(6)
N16C	682.8(19)	6842.1(5)	9025.3(16)	38.3(7)
N17C	1516.7(18)	6806.3(5)	9306.1(16)	36.0(7)

N18C	1928.3(17)	6745.2(4)	10075.9(15)	31.1(6)
C1	3421(7)	6227.7(18)	12596(6)	62(4)
C1C	-1593(2)	6736.7(5)	7736.4(18)	29.5(8)
C2	3199(7)	6351(2)	13751(6)	61(4)
C2C	-1690(2)	6508.8(5)	7779.1(19)	31.3(8)
C3	3827(6)	6607.0(19)	13149(6)	62(4)
C3C	-2068(2)	6387.6(6)	7061(2)	39.6(9)
C4C	-2362(2)	6482.8(6)	6297(2)	42.9(9)
C5C	-2275(2)	6707.9(6)	6256(2)	40.8(9)
C6C	-1885(2)	6833.9(5)	6957.2(19)	32.9(8)
C7C	-1739(2)	7065.4(5)	7102.0(19)	31.7(8)
C8C	-1893(2)	7246.2(6)	6603(2)	39.3(9)
C9C	-1681(3)	7456.9(6)	6921(2)	42.4(9)
C10	-2457(8)	6396(2)	4960(7)	48(3)
C10C	-1309(2)	7479.1(6)	7760(2)	41.8(9)
C11	-2816(13)	6107(2)	5672(7)	80(6)
C11C	-1137(2)	7300.8(5)	8288.8(19)	33.5(8)
C12	-3836(7)	6419(2)	5090(6)	54(4)
C12C	-1360(2)	7088.9(5)	7957.9(19)	31.7(8)
C13	-1790(17)	6050(3)	10464(13)	139(11)
C13C	-2799(3)	6340.2(7)	5526(2)	60.3(12)
C14	-1025(16)	5822(4)	9910(20)	112(10)
C14C	-3459(7)	6187(2)	5555(6)	94(4)
C15	-1732(16)	5979.8(19)	9699(10)	52(4)
C15C	-2021(6)	6178.7(16)	5569(6)	102(4)
C16C	-3090(10)	6465(2)	4758(5)	121(6)
C17C	-1861(3)	7655.7(6)	6350(2)	51.9(11)
C18C	-2831(3)	7672.4(8)	5770(3)	74.3(14)
C19C	-1373(3)	7623.4(7)	5853(3)	72.2(14)
C20C	-1578(3)	7872.9(7)	6799(3)	69.4(13)
C21C	-1466(2)	6399.8(5)	8546(2)	35.3(8)
C22C	-1208(13)	5976.7(18)	9949(9)	48(3)
C23C	-1963(8)	5989(2)	10120(10)	59(4)
C24C	-1162(10)	5768(2)	9504(8)	48(3)
C25C	-732(2)	7338.3(5)	9157(2)	36.9(8)
C26C	124(3)	7660.5(7)	10923(3)	73.6(15)
C27C	894(5)	7754(2)	11021(8)	321(10)
C28C	-570(4)	7802.5(11)	10812(4)	128(3)
C29C	-620(2)	6692.0(5)	11181.2(18)	28.4(7)
C30C	-1498(2)	6722.8(5)	10969.7(19)	30.8(8)
C31C	-1802(2)	6645.8(5)	11493.1(19)	33.6(8)
C32C	-1273(2)	6546.0(5)	12237(2)	34.0(8)
C33C	-399(2)	6520.9(5)	12444.8(19)	31.5(8)
C34C	-74(2)	6587.4(5)	11926.4(18)	29.3(8)
C35C	763(2)	6575.0(5)	11956.5(18)	29.4(8)
C36C	1565(2)	6491.1(5)	12515.4(18)	30.8(8)

C37C	2287(2)	6502.8(5)	12375.9(18)	30.0(8)
C38C	2165(2)	6592.5(5)	11639.3(18)	29.8(8)
C39C	1373(2)	6674.2(5)	11058.0(18)	27.4(7)
C40C	663(2)	6673.1(5)	11223.6(18)	27.8(7)
C41C	-1676(2)	6454.6(6)	12752(2)	39.2(9)
C42C	-2205(3)	6248.0(6)	12340(2)	49.0(10)
C43C	-2267(3)	6625.6(6)	12855(2)	45.0(9)
C44C	-986(3)	6391.6(7)	13596(2)	52.7(11)
C45C	3174(2)	6415.4(6)	12991(2)	36.0(8)
C46C	3113(5)	6163.6(11)	13114(4)	55(2)
C47C	3468(5)	6524.5(16)	13836(4)	52(2)
C48C	3897(4)	6445.8(14)	12762(4)	51(2)
C49C	-2077(2)	6842.1(5)	10238.1(19)	31.8(8)
C50C	-3923(2)	7154.4(7)	9003(2)	47.7(10)
C51C	-4015(3)	7259.3(8)	8245(2)	71.8(14)
C52C	-3949(3)	7321.0(7)	9588(3)	66.5(13)
C53C	1283(2)	6744.2(5)	10277.8(18)	28.2(7)
C54C	1937(2)	6824.4(7)	8777(2)	46.1(10)
C55C	1539(3)	6654.8(7)	8115(2)	58.7(12)
C56C	1857(3)	7058.1(7)	8485(2)	62.4(12)

Table B-64 Anisotropic Displacement Parameters (U_{ij} , Å² x10³) for **26**

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Ni1	30.5(2)	25.1(2)	26.3(2)	-0.69(17)	12.48(19)	0.03(18)
N1A	27.6(15)	27.1(15)	26.6(14)	1.7(11)	13.3(12)	1.9(12)
N2A	30.8(16)	31.3(16)	34.9(16)	-6.3(13)	9.9(14)	-2.7(13)
N3A	36.1(19)	46(2)	62(2)	-17.3(16)	20.6(17)	-2.1(16)
N4A	33.3(18)	50(2)	61(2)	-15.7(17)	19.3(16)	-4.8(16)
N5A	37.9(19)	40.9(19)	54.4(19)	-14.6(15)	20.7(16)	-5.6(15)
N6A	34.1(17)	29.7(16)	31.3(15)	-1.7(12)	15.1(13)	3.9(13)
N7A	39.2(19)	35.3(18)	33.9(16)	-3.2(13)	16.1(14)	3.9(14)
N8A	33.2(18)	43.5(19)	38.3(17)	-4.5(14)	14.3(14)	5.6(14)
N9A	36.7(18)	40.4(19)	44.0(18)	-8.5(14)	18.3(15)	2.4(15)
N10A	32.6(16)	26.7(16)	30.5(15)	3.8(12)	15.7(13)	1.3(12)
N11A	39.5(17)	31.1(17)	28.9(15)	-2.5(12)	16.3(13)	0.8(13)
N12A	68(2)	29.4(17)	32.3(17)	2.6(13)	23.8(16)	7.5(15)
N13A	90(3)	31.9(18)	30.2(16)	3.0(14)	25.6(17)	14.2(17)
N14A	73(2)	29.2(17)	30.2(16)	2.0(13)	23.4(16)	9.1(15)
N15A	39.7(17)	24.0(16)	29.0(15)	-1.0(12)	14.8(13)	-3.0(13)
N16A	48.5(19)	28.2(17)	29.0(16)	1.1(12)	14.8(14)	-2.3(14)
N17A	50.4(19)	29.2(16)	29.5(16)	1.6(13)	16.6(14)	-2.5(14)
N18A	47.5(19)	30.2(16)	30.9(16)	-1.9(13)	15.5(14)	-4.3(14)
C1A	31.5(19)	27.7(18)	21.3(16)	3.4(13)	12.0(14)	2.1(15)
C2A	29.4(19)	29.8(19)	24.9(16)	5.5(14)	12.4(15)	1.3(15)

C3A	27.0(18)	31.9(19)	26.4(17)	2.3(14)	10.8(15)	4.9(15)
C4A	30.2(19)	29.4(19)	25.4(17)	1.3(14)	11.2(15)	4.1(15)
C5A	35(2)	27.5(18)	27.5(17)	-0.1(14)	14.4(15)	0.3(15)
C6A	29.3(19)	27.6(18)	22.2(16)	-1.0(13)	10.7(14)	0.7(15)
C7A	31.5(19)	26.3(18)	25.9(17)	-0.8(14)	10.6(15)	-1.7(15)
C8A	35(2)	32(2)	33.2(19)	-4.8(15)	13.6(16)	-1.1(16)
C9A	33(2)	33(2)	34.5(19)	-1.5(15)	12.6(16)	-3.2(16)
C10A	27.8(19)	38(2)	34.7(19)	-1.1(15)	12.6(16)	-0.2(16)
C11A	30.1(19)	30.5(19)	28.5(17)	-0.2(14)	12.2(15)	0.2(15)
C12A	29.2(19)	28.5(19)	24.2(16)	1.3(14)	9.7(14)	1.8(15)
C13A	34(2)	37(2)	29.5(18)	-3.0(15)	14.1(15)	4.7(16)
C14A	39(2)	65(3)	67(3)	-26(2)	24(2)	3(2)
C15A	95(4)	48(3)	62(3)	11(2)	48(3)	31(2)
C16A	46(2)	72(3)	39(2)	-18(2)	18.4(19)	4(2)
C17A	32(2)	43(2)	44(2)	-7.6(17)	14.2(17)	-10.9(17)
C18A	48(3)	48(3)	69(3)	-13(2)	26(2)	-21(2)
C19A	65(3)	73(3)	65(3)	-13(2)	36(2)	-36(2)
C20A	34(2)	56(3)	96(4)	-8(2)	15(2)	-10(2)
C21A	28(2)	31.9(19)	33.4(18)	-1.5(15)	14.2(16)	1.6(15)
C22A	38(2)	50(3)	76(3)	-13(2)	21(2)	-2(2)
C23A	57(3)	69(3)	103(4)	-5(3)	42(3)	-13(3)
C24A	54(3)	67(3)	64(3)	-17(2)	3(2)	-6(2)
C25A	27.0(19)	36(2)	32.4(18)	2.7(15)	15.0(15)	4.2(16)
C26A	40(2)	48(2)	54(2)	-4.6(19)	18(2)	14.8(19)
C27A	124(5)	118(5)	56(3)	-15(3)	-6(3)	82(4)
C28A	78(4)	74(4)	96(4)	-41(3)	2(3)	32(3)
C29A	32.1(19)	25.1(19)	30.7(18)	0.4(14)	14.1(15)	1.6(15)
C30A	41(2)	27.5(19)	32.4(19)	-1.0(15)	16.4(16)	0.0(16)
C31A	56(3)	32(2)	33(2)	5.0(16)	14.0(18)	5.2(18)
C32A	59(3)	26(2)	40(2)	-1.4(16)	17.8(19)	3.0(18)
C33A	51(2)	32(2)	34(2)	-4.8(16)	15.2(18)	-1.8(17)
C34A	36(2)	29(2)	31.6(18)	-0.6(15)	13.0(16)	-0.4(16)
C35A	37(2)	30.2(19)	30.6(19)	-0.2(15)	14.5(16)	-1.9(16)
C36A	40(2)	32(2)	34(2)	-7.9(16)	11.1(17)	-3.3(16)
C37A	36(2)	36(2)	28.8(18)	0.0(15)	10.8(16)	-2.2(16)
C38A	34(2)	34(2)	32.2(19)	1.7(15)	11.3(16)	0.2(16)
C39A	31.7(19)	28.2(19)	28.9(18)	0.9(14)	12.6(15)	-1.0(15)
C40A	29.5(19)	31.8(19)	26.5(17)	-1.8(14)	12.0(15)	-2.5(15)
C41A	87(3)	32(2)	43(2)	-2.5(18)	14(2)	9(2)
C42A	140(5)	38(3)	58(3)	4(2)	28(3)	-21(3)
C43A	122(5)	49(3)	81(4)	-20(3)	3(3)	40(3)
C44A	118(4)	30(2)	56(3)	-9(2)	16(3)	4(3)
C45A	41(2)	40(2)	31.1(19)	-0.3(16)	9.1(17)	-2.7(17)
C46A	67(3)	53(3)	32(2)	-3.3(18)	3(2)	-11(2)
C47A	52(3)	69(3)	31(2)	-5.2(19)	15.1(19)	-2(2)
C48A	43(2)	58(3)	42(2)	6.1(19)	5.9(19)	3(2)

C49A	41(2)	29(2)	34.1(19)	0.8(15)	17.5(17)	2.6(16)
C50A	123(4)	43(3)	28(2)	1.7(18)	23(2)	25(3)
C51A	159(6)	90(4)	71(3)	33(3)	81(4)	26(4)
C52A	120(5)	57(3)	39(2)	-4(2)	5(3)	9(3)
C53A	33.9(19)	27.1(19)	28.1(18)	3.4(14)	12.8(15)	1.8(15)
C54A	60(3)	29(2)	37(2)	3.7(15)	24.5(19)	-4.9(18)
C55A	61(3)	32(2)	62(3)	6.1(18)	33(2)	1.9(19)
C56A	65(3)	38(2)	53(2)	-1.9(18)	29(2)	-15(2)
Ni2	23.9(2)	22.6(2)	20.2(2)	-0.96(16)	10.03(17)	2.90(17)
N1B	24.4(14)	28.0(15)	20.4(13)	-0.7(11)	11.4(11)	2.6(11)
N2B	25.9(15)	25.8(15)	24.8(14)	-0.8(11)	11.6(12)	4.0(12)
N3B	31.9(16)	27.8(15)	30.4(15)	-1.6(12)	18.5(13)	1.9(12)
N4B	36.5(17)	32.5(16)	26.5(15)	-1.4(12)	18.6(13)	1.4(13)
N5B	37.7(17)	32.7(16)	27.5(15)	0.8(12)	17.1(13)	6.4(14)
N6B	26.9(15)	21.5(14)	25.2(14)	-0.6(11)	11.1(12)	2.0(12)
N7B	35.7(16)	27.9(15)	26.3(14)	2.6(12)	18.1(13)	5.0(13)
N8B	38.0(17)	25.8(15)	26.8(14)	3.1(11)	17.3(13)	4.2(13)
N9B	34.4(16)	29.8(16)	29.1(15)	2.4(12)	18.0(13)	4.2(13)
N10B	27.2(15)	23.9(14)	21.8(13)	-2.7(11)	12.3(12)	-0.1(11)
N11B	24.1(15)	27.9(15)	27.5(14)	1.1(12)	10.8(12)	3.8(12)
N12B	30.1(16)	30.4(16)	31.1(15)	-1.2(13)	11.3(13)	-1.4(13)
N13B	28.8(16)	29.0(16)	33.4(16)	-0.6(13)	7.6(13)	0.6(13)
N14B	32.5(16)	31.1(17)	31.9(16)	-2.5(12)	7.3(13)	2.4(13)
N15B	28.7(16)	19.5(15)	25.4(14)	0.4(11)	13.0(12)	3.1(11)
N16B	27.4(16)	27.7(16)	29.4(15)	-3.0(11)	13.8(13)	2.1(12)
N17B	29.9(16)	25.1(15)	30.6(15)	-2.1(12)	15.3(13)	-0.1(13)
N18B	27.2(15)	24.5(15)	30.0(14)	-2.1(12)	11.1(12)	3.9(13)
C1B	27.6(18)	23.7(17)	25.6(17)	-2.0(13)	12.4(14)	0.9(14)
C2B	25.3(18)	26.1(18)	24.4(16)	1.1(13)	10.6(14)	0.9(14)
C3B	35(2)	32.6(19)	25.5(17)	-0.7(14)	14.3(15)	2.5(16)
C4	47(11)	66(13)	111(19)	-11(12)	-5(12)	20(10)
C4B	29.3(19)	34(2)	29.5(18)	5.6(14)	11.2(15)	3.4(15)
C5	24(9)	110(18)	67(12)	-2(11)	9(8)	31(10)
C5B	32.2(19)	33(2)	33.6(19)	4.3(15)	16.3(16)	8.3(15)
C6	25(8)	70(12)	46(9)	9(8)	-1(7)	14(8)
C6B	28.9(18)	27.4(18)	27.7(17)	0.7(14)	11.6(15)	4.5(15)
C7	47(7)	59(8)	64(9)	-28(7)	35(7)	-1(6)
C7B	31.3(19)	26.7(18)	27.2(17)	0.2(14)	15.4(15)	3.5(15)
C8	29(7)	124(16)	100(11)	-64(12)	25(7)	18(8)
C8B	35(2)	28.4(19)	36.2(19)	2.0(15)	18.4(16)	8.6(15)
C9	170(20)	78(11)	129(16)	40(11)	138(17)	58(13)
C9B	33.0(19)	28.2(19)	33.7(18)	-0.6(14)	20.1(16)	4.7(15)
C10B	30.3(19)	30.3(19)	22.7(16)	-3.1(14)	12.4(14)	-1.5(15)
C11B	26.4(18)	22.9(17)	22.5(16)	-3.8(13)	10.2(14)	-0.3(14)
C12B	24.7(17)	24.8(17)	22.9(16)	-3.0(13)	9.1(14)	0.2(14)
C13B	39(2)	48(2)	30.5(19)	13.8(16)	14.2(17)	14.2(18)

C14B	50(3)	74(3)	32(2)	3(2)	4.1(19)	8(2)
C15B	51(2)	57(3)	46(2)	24.3(19)	25(2)	20(2)
C16B	48(2)	65(3)	42(2)	21.0(19)	19.7(19)	22(2)
C17B	40(2)	34(2)	43(2)	-0.8(16)	26.6(18)	9.4(16)
C18B	147(13)	101(9)	88(8)	49(7)	89(9)	97(9)
C19B	49(4)	58(6)	71(6)	-38(5)	40(4)	-12(4)
C20B	38(4)	53(4)	52(5)	-16(4)	28(4)	-3(3)
C21B	29.7(18)	26.7(18)	23.7(17)	-2.9(14)	12.6(15)	-1.5(15)
C22B	54(2)	39(2)	37(2)	-7.4(16)	31.9(18)	4.0(18)
C23B	65(3)	72(3)	39(2)	-23(2)	11(2)	18(2)
C24B	42(2)	41(2)	48(2)	-13.1(17)	23.2(18)	6.0(18)
C25B	24.1(17)	27.8(18)	20.5(16)	-5.8(13)	10.1(14)	-3.8(14)
C26B	57(2)	29(2)	35.1(19)	10.0(15)	26.9(18)	10.6(17)
C27B	81(3)	54(3)	70(3)	16(2)	47(3)	-9(2)
C28B	83(3)	49(3)	29(2)	10.4(17)	24(2)	15(2)
C29B	29.7(18)	23.5(17)	22.6(16)	0.0(13)	14.2(14)	-0.5(14)
C30B	27.5(18)	23.5(18)	26.8(17)	0.0(13)	12.5(15)	0.7(14)
C31B	30.8(19)	28.6(19)	27.7(17)	-2.9(14)	13.8(15)	-2.6(15)
C32B	37(2)	20.6(17)	33.0(18)	-2.9(14)	16.9(16)	0.7(15)
C33B	35(2)	23.6(18)	35.6(19)	0.1(14)	16.6(16)	5.8(15)
C34B	25.7(18)	28.5(18)	26.5(17)	-1.2(14)	11.3(14)	2.9(14)
C35B	28.5(19)	25.0(18)	25.7(16)	0.1(13)	11.8(15)	6.1(14)
C36B	34(2)	25.0(18)	33.5(18)	-0.1(14)	15.4(16)	6.9(15)
C37B	25.7(18)	33(2)	28.5(17)	-0.1(14)	10.0(15)	5.2(15)
C38B	29.0(19)	30.5(19)	23.0(16)	-3.5(14)	9.2(14)	1.3(15)
C39B	27.3(18)	23.2(17)	22.3(16)	-0.8(13)	11.4(14)	4.3(14)
C40B	27.0(18)	24.6(17)	19.9(15)	-0.8(13)	11.6(14)	3.6(14)
C41B	38(2)	24.7(19)	44(2)	-8.6(15)	19.6(17)	-1.2(16)
C42B	102(4)	46(3)	66(3)	-28(2)	57(3)	-17(2)
C43B	50(3)	29(2)	75(3)	-12.2(19)	31(2)	-5.5(18)
C44B	54(3)	29(2)	98(4)	-27(2)	14(3)	6(2)
C45B	24.4(19)	38(2)	35.7(19)	0.6(15)	9.9(16)	6.7(16)
C46B	31(3)	72(5)	44(3)	-7(3)	15(2)	18(3)
C47B	31(3)	69(4)	48(3)	23(3)	12(3)	16(3)
C48B	28(3)	52(4)	53(4)	-6(3)	6(3)	4(2)
C49B	28.9(19)	24.4(18)	27.0(17)	-2.2(14)	13.4(15)	-3.3(14)
C50B	28(2)	39(2)	38(2)	-2.4(16)	-1.2(16)	0.2(17)
C51B	58(3)	67(3)	41(2)	3(2)	9(2)	14(2)
C52B	34(2)	66(3)	48(2)	6(2)	4.4(19)	11(2)
C53B	26.3(18)	26.5(18)	23.6(16)	-3.3(14)	11.8(14)	0.5(15)
C54B	39(2)	24.1(19)	42(2)	-4.0(15)	16.3(17)	-3.7(16)
C55B	50(2)	37(2)	66(3)	3.9(19)	31(2)	-5.1(19)
C56B	64(3)	29(2)	85(3)	-7(2)	40(2)	3(2)
Ni3	33.0(2)	27.9(2)	25.8(2)	-0.42(17)	12.43(19)	0.05(19)
N1C	33.7(16)	24.1(15)	32.1(15)	-2.1(12)	14.2(13)	0.4(12)
N2C	45.9(18)	31.6(16)	30.3(16)	5.3(13)	18.4(14)	3.5(14)

N3C	98(3)	27.1(18)	43.8(19)	2.9(15)	36.7(19)	2.9(18)
N4C	139(4)	26.7(19)	55(2)	1.7(16)	57(2)	-9(2)
N5C	86(3)	29.4(18)	51(2)	-1.7(15)	37.7(19)	-11.9(17)
N6C	37.2(17)	35.0(17)	28.4(15)	-5.4(13)	12.3(13)	-2.0(13)
N7C	48(2)	38.6(19)	37.5(17)	-8.8(14)	12.6(15)	-1.7(15)
N8C	67(2)	37(2)	44(2)	-12.5(15)	10.9(17)	-0.5(17)
N9C	68(2)	30.6(18)	45(2)	-6.0(15)	16.6(17)	-2.2(16)
N10C	32.1(16)	29.1(15)	26.7(14)	-2.1(12)	12.7(13)	-1.8(12)
N11C	34.5(17)	31.2(16)	28.6(15)	3.7(12)	11.1(13)	1.4(13)
N12C	37.6(18)	41.2(18)	36.8(17)	0.5(14)	14.4(15)	0.4(15)
N13C	35.8(18)	42.4(18)	34.3(16)	3.5(14)	13.0(14)	5.5(14)
N14C	37.1(18)	41.0(18)	37.7(17)	3.8(14)	15.4(14)	3.9(14)
N15C	35.2(17)	32.8(16)	26.0(15)	0.6(12)	14.9(13)	-0.4(13)
N16C	37.0(19)	49.3(19)	28.7(15)	6.6(13)	15.3(14)	4.4(15)
N17C	31.5(17)	48.6(19)	29.0(16)	4.3(13)	14.9(13)	1.3(14)
N18C	33.5(16)	36.0(16)	23.7(15)	0.7(12)	13.3(13)	-1.5(13)
C1	67(7)	79(8)	45(6)	10(5)	30(5)	42(6)
C1C	29.1(19)	30.9(19)	27.8(17)	-1.6(14)	12.4(15)	1.0(15)
C2	58(7)	91(10)	38(6)	24(6)	27(5)	37(7)
C2C	33(2)	31(2)	31.2(18)	-3.3(15)	16.6(16)	-3.3(15)
C3	41(6)	64(8)	50(6)	14(6)	-4(5)	-5(5)
C3C	45(2)	32(2)	43(2)	-9.4(16)	21.3(18)	-6.1(17)
C4C	46(2)	47(2)	34(2)	-9.1(17)	17.0(18)	-9.7(19)
C5C	44(2)	48(2)	28.5(19)	0.0(16)	14.9(17)	-0.9(18)
C6C	35(2)	37(2)	28.3(18)	-1.6(15)	15.5(16)	1.6(16)
C7C	35(2)	32(2)	28.6(18)	1.8(15)	14.8(15)	3.2(15)
C8C	43(2)	42(2)	34.4(19)	6.8(17)	19.1(17)	6.4(18)
C9C	54(2)	33(2)	44(2)	6.7(17)	26.2(19)	7.6(18)
C10	46(7)	58(8)	28(6)	-26(5)	6(6)	0(6)
C10C	54(2)	27(2)	49(2)	1.4(16)	27.5(19)	4.4(17)
C11	124(16)	40(8)	38(7)	-21(5)	4(9)	-24(9)
C11C	40(2)	25.6(19)	35.1(19)	2.4(15)	17.9(16)	0.8(16)
C12	41(7)	73(9)	36(6)	-21(6)	9(5)	-11(6)
C12C	34(2)	30(2)	32.6(18)	3.0(15)	17.0(16)	1.4(15)
C13	260(30)	92(13)	65(12)	-20(10)	77(14)	-120(15)
C13C	79(3)	60(3)	41(2)	-21(2)	27(2)	-23(2)
C14	90(14)	64(18)	160(30)	36(19)	42(17)	-11(12)
C14C	84(8)	130(11)	75(7)	-63(7)	41(6)	-60(8)
C15	51(10)	37(6)	47(9)	13(5)	4(8)	-23(7)
C15C	104(8)	102(8)	132(9)	-83(7)	83(7)	-50(6)
C16C	177(15)	115(10)	42(6)	-23(6)	24(8)	-38(10)
C17C	65(3)	40(2)	54(2)	17.3(19)	30(2)	11(2)
C18C	79(4)	59(3)	71(3)	31(2)	22(3)	18(3)
C19C	108(4)	55(3)	79(3)	26(2)	64(3)	11(3)
C20C	102(4)	37(2)	73(3)	18(2)	42(3)	13(2)
C21C	41(2)	25.6(19)	39(2)	-2.3(15)	18.0(17)	-1.9(16)

C22C	55(9)	35(6)	48(6)	-2(5)	19(6)	-14(6)
C23C	64(7)	51(7)	58(9)	-4(6)	24(6)	-26(5)
C24C	54(6)	20(5)	74(8)	5(5)	32(6)	-7(4)
C25C	43(2)	28(2)	40(2)	-3.4(16)	19.2(17)	-0.6(16)
C26C	92(4)	46(3)	54(3)	-28(2)	9(3)	-2(3)
C27C	94(6)	371(15)	510(20)	-399(16)	144(9)	-111(8)
C28C	68(4)	154(6)	159(6)	-120(5)	50(4)	-17(4)
C29C	35(2)	22.7(18)	25.8(17)	-2.3(13)	13.1(15)	-2.5(15)
C30C	34(2)	28.0(19)	32.5(18)	-2.5(14)	17.1(16)	-1.4(15)
C31C	35(2)	31.3(19)	34.5(19)	1.0(15)	15.7(16)	-0.7(16)
C32C	41(2)	29.2(19)	35.9(19)	0.6(15)	21.4(17)	-0.7(16)
C33C	42(2)	22.6(18)	30.9(18)	1.8(14)	17.5(16)	1.2(15)
C34C	34(2)	25.0(18)	30.6(18)	-3.6(14)	16.5(16)	-2.8(15)
C35C	38(2)	25.2(18)	25.4(17)	-0.2(14)	14.4(15)	-0.4(15)
C36C	39(2)	28.9(19)	24.7(17)	0.5(14)	14.9(16)	0.3(16)
C37C	40(2)	23.2(18)	26.1(17)	-2.7(13)	14.1(16)	3.3(15)
C38C	34(2)	25.0(18)	31.8(18)	-6.0(14)	15.9(16)	-3.5(15)
C39C	31.3(19)	23.0(17)	26.8(17)	-4.7(13)	12.5(15)	-3.3(14)
C40C	33(2)	21.8(17)	26.2(17)	-2.7(13)	11.9(15)	-0.7(14)
C41C	45(2)	39(2)	40(2)	7.6(16)	24.2(18)	8.4(18)
C42C	50(2)	39(2)	67(3)	8.6(19)	35(2)	-1.2(19)
C43C	53(2)	46(2)	46(2)	6.9(18)	32(2)	7.3(19)
C44C	53(3)	65(3)	50(2)	17(2)	33(2)	9(2)
C45C	38(2)	40(2)	33.6(19)	4.3(15)	19.3(17)	7.2(17)
C46C	50(5)	44(4)	57(5)	14(3)	12(4)	15(3)
C47C	37(4)	65(6)	35(4)	-6(4)	1(3)	7(4)
C48C	37(4)	71(6)	40(4)	18(4)	14(3)	16(4)
C49C	30(2)	28.0(19)	36.0(19)	-1.5(15)	14.2(16)	-1.0(15)
C50C	36(2)	54(3)	46(2)	4.9(19)	12.4(18)	9.4(19)
C51C	80(3)	77(3)	48(3)	13(2)	20(2)	32(3)
C52C	62(3)	70(3)	60(3)	0(2)	22(2)	25(2)
C53C	34(2)	23.5(18)	26.2(17)	-2.2(13)	13.1(16)	-2.3(15)
C54C	39(2)	74(3)	30.0(19)	8.6(19)	19.9(17)	4(2)
C55C	59(3)	85(3)	39(2)	3(2)	29(2)	14(2)
C56C	65(3)	80(3)	53(3)	15(2)	36(2)	-7(2)

Table B-65 Bond Lengths for **26**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ni1	N1A	2.041(3)	C9B	C10B	1.402(4)
Ni1	N2A	2.076(3)	C9B	C17B	1.542(4)
Ni1	N6A	2.084(3)	C10B	C11B	1.395(4)
Ni1	N10A	2.043(3)	C11B	C12B	1.414(4)
Ni1	N11A	2.137(3)	C11B	C25B	1.454(4)
Ni1	N15A	2.135(3)	C13B	C14B	1.543(5)

N1A	C1A	1.385(4)	C13B	C15B	1.533(5)
N1A	C12A	1.381(4)	C13B	C16B	1.521(5)
N2A	N3A	1.327(4)	C17B	C18B	1.509(9)
N2A	C21A	1.358(4)	C17B	C19B	1.523(8)
N3A	N4A	1.313(4)	C17B	C20B	1.538(7)
N4A	N5A	1.344(4)	C22B	C23B	1.496(5)
N4A	C22A	1.484(5)	C22B	C24B	1.500(5)
N5A	C21A	1.341(4)	C26B	C27B	1.511(5)
N6A	N7A	1.331(4)	C26B	C28B	1.510(5)
N6A	C25A	1.356(4)	C29B	C30B	1.406(4)
N7A	N8A	1.314(4)	C29B	C34B	1.422(4)
N8A	N9A	1.339(4)	C30B	C31B	1.404(4)
N8A	C26A	1.488(5)	C30B	C49B	1.448(4)
N9A	C25A	1.336(4)	C31B	C32B	1.394(4)
N10A	C29A	1.372(4)	C32B	C33B	1.394(5)
N10A	C40A	1.382(4)	C32B	C41B	1.540(4)
N11A	N12A	1.330(4)	C33B	C34B	1.394(4)
N11A	C49A	1.356(4)	C34B	C35B	1.441(4)
N12A	N13A	1.319(4)	C35B	C36B	1.382(4)
N13A	N14A	1.330(4)	C35B	C40B	1.434(4)
N13A	C50A	1.476(5)	C36B	C37B	1.392(4)
N14A	C49A	1.340(4)	C37B	C38B	1.395(4)
N15A	N16A	1.341(4)	C37B	C45B	1.541(4)
N15A	C53A	1.345(4)	C38B	C39B	1.399(4)
N16A	N17A	1.314(4)	C39B	C40B	1.405(4)
N17A	N18A	1.331(4)	C39B	C53B	1.460(4)
N17A	C54A	1.490(4)	C41B	C42B	1.520(5)
N18A	C53A	1.338(4)	C41B	C43B	1.516(5)
C1A	C2A	1.396(4)	C41B	C44B	1.530(5)
C1A	C6A	1.429(4)	C45B	C46B	1.527(6)
C2A	C3A	1.400(4)	C45B	C47B	1.526(6)
C2A	C21A	1.448(4)	C45B	C48B	1.534(6)
C3A	C4A	1.397(4)	C50B	C51B	1.507(5)
C4A	C5A	1.401(5)	C50B	C52B	1.502(5)
C4A	C13A	1.526(4)	C54B	C55B	1.520(5)
C5A	C6A	1.388(4)	C54B	C56B	1.499(5)
C6A	C7A	1.438(4)	Ni3	N1C	2.047(3)
C7A	C8A	1.389(5)	Ni3	N2C	2.122(3)
C7A	C12A	1.416(4)	Ni3	N6C	2.117(3)
C8A	C9A	1.380(5)	Ni3	N10C	2.046(3)
C9A	C10A	1.410(5)	Ni3	N11C	2.111(3)
C9A	C17A	1.545(5)	Ni3	N15C	2.091(3)
C10A	C11A	1.392(5)	N1C	C1C	1.379(4)
C11A	C12A	1.400(5)	N1C	C12C	1.376(4)
C11A	C25A	1.465(5)	N2C	N3C	1.324(4)
C13A	C14A	1.528(5)	N2C	C21C	1.358(4)

C13A	C15A	1.531(5)	N3C	N4C	1.309(4)
C13A	C16A	1.524(5)	N4C	N5C	1.330(4)
C17A	C18A	1.520(5)	N4C	C15	1.564(14)
C17A	C19A	1.535(5)	N4C	C22C	1.503(12)
C17A	C20A	1.520(5)	N5C	C21C	1.341(4)
C22A	C23A	1.481(6)	N6C	N7C	1.331(4)
C22A	C24A	1.507(6)	N6C	C25C	1.357(4)
C26A	C27A	1.462(6)	N7C	N8C	1.320(4)
C26A	C28A	1.491(6)	N8C	N9C	1.331(4)
C29A	C30A	1.405(4)	N8C	C26C	1.491(5)
C29A	C34A	1.424(4)	N9C	C25C	1.341(4)
C30A	C31A	1.391(5)	N10C	C29C	1.386(4)
C30A	C49A	1.459(4)	N10C	C40C	1.377(4)
C31A	C32A	1.408(5)	N11C	N12C	1.341(4)
C32A	C33A	1.384(5)	N11C	C49C	1.351(4)
C32A	C41A	1.537(5)	N12C	N13C	1.317(4)
C33A	C34A	1.387(5)	N13C	N14C	1.336(4)
C34A	C35A	1.436(4)	N13C	C50C	1.491(5)
C35A	C36A	1.394(5)	N14C	C49C	1.336(4)
C35A	C40A	1.423(4)	N15C	N16C	1.326(4)
C36A	C37A	1.383(5)	N15C	C53C	1.360(4)
C37A	C38A	1.405(5)	N16C	N17C	1.311(4)
C37A	C45A	1.529(5)	N17C	N18C	1.329(4)
C38A	C39A	1.399(4)	N17C	C54C	1.476(4)
C39A	C40A	1.399(4)	N18C	C53C	1.335(4)
C39A	C53A	1.453(4)	C1	C45C	1.523(10)
C41A	C42A	1.539(7)	C1C	C2C	1.404(4)
C41A	C43A	1.501(7)	C1C	C6C	1.428(4)
C41A	C44A	1.536(5)	C2	C45C	1.452(10)
C45A	C46A	1.526(5)	C2C	C3C	1.400(5)
C45A	C47A	1.535(5)	C2C	C21C	1.457(5)
C45A	C48A	1.530(5)	C3	C45C	1.556(10)
C50A	C51A	1.513(7)	C3C	C4C	1.398(5)
C50A	C52A	1.490(7)	C4C	C5C	1.384(5)
C54A	C55A	1.507(5)	C4C	C13C	1.547(5)
C54A	C56A	1.498(5)	C5C	C6C	1.393(5)
Ni2	N1B	2.019(2)	C6C	C7C	1.435(5)
Ni2	N2B	2.115(2)	C7C	C8C	1.385(5)
Ni2	N6B	2.101(2)	C7C	C12C	1.426(4)
Ni2	N10B	2.029(2)	C8C	C9C	1.389(5)
Ni2	N11B	2.170(3)	C9C	C10C	1.398(5)
Ni2	N15B	2.108(3)	C9C	C17C	1.546(5)
N1B	C1B	1.382(4)	C10	C13C	1.469(13)
N1B	C12B	1.379(4)	C10C	C11C	1.403(5)
N2B	N3B	1.330(3)	C11	C13C	1.450(13)
N2B	C21B	1.352(4)	C11C	C12C	1.405(5)

N3B	N4B	1.315(3)	C11C	C25C	1.455(5)
N4B	N5B	1.333(4)	C12	C13C	1.667(11)
N4B	C22B	1.485(4)	C13	C15	1.53(3)
N5B	C21B	1.337(4)	C13C	C14C	1.497(10)
N6B	N7B	1.334(3)	C13C	C15C	1.643(10)
N6B	C25B	1.361(4)	C13C	C16C	1.488(11)
N7B	N8B	1.312(3)	C14	C15	1.46(3)
N8B	N9B	1.327(4)	C17C	C18C	1.529(6)
N8B	C26B	1.479(4)	C17C	C19C	1.528(6)
N9B	C25B	1.343(4)	C17C	C20C	1.520(6)
N10B	C29B	1.382(4)	C22C	C23C	1.49(2)
N10B	C40B	1.367(4)	C22C	C24C	1.537(18)
N11B	N12B	1.332(4)	C26C	C27C	1.384(10)
N11B	C49B	1.359(4)	C26C	C28C	1.418(7)
N12B	N13B	1.322(4)	C29C	C30C	1.401(5)
N13B	N14B	1.335(4)	C29C	C34C	1.422(4)
N13B	C50B	1.484(4)	C30C	C31C	1.386(4)
N14B	C49B	1.342(4)	C30C	C49C	1.462(5)
N15B	N16B	1.335(3)	C31C	C32C	1.401(5)
N15B	C53B	1.355(4)	C32C	C33C	1.390(5)
N16B	N17B	1.315(4)	C32C	C41C	1.529(5)
N17B	N18B	1.334(3)	C33C	C34C	1.384(4)
N17B	C54B	1.483(4)	C34C	C35C	1.430(5)
N18B	C53B	1.342(4)	C35C	C36C	1.396(4)
C1B	C2B	1.406(4)	C35C	C40C	1.427(4)
C1B	C6B	1.419(4)	C36C	C37C	1.395(5)
C2B	C3B	1.392(4)	C37C	C38C	1.400(4)
C2B	C21B	1.461(4)	C37C	C45C	1.531(5)
C3B	C4B	1.403(4)	C38C	C39C	1.393(4)
C4	C45B	1.571(19)	C39C	C40C	1.402(5)
C4B	C5B	1.394(4)	C39C	C53C	1.454(4)
C4B	C13B	1.530(4)	C41C	C42C	1.537(5)
C5	C45B	1.536(19)	C41C	C43C	1.535(5)
C5B	C6B	1.396(4)	C41C	C44C	1.524(5)
C6	C45B	1.538(15)	C45C	C46C	1.561(7)
C6B	C7B	1.438(4)	C45C	C47C	1.564(8)
C7	C17B	1.535(12)	C45C	C48C	1.510(8)
C7B	C8B	1.391(4)	C50C	C51C	1.491(6)
C7B	C12B	1.419(4)	C50C	C52C	1.506(5)
C8	C17B	1.522(14)	C54C	C55C	1.511(5)
C8B	C9B	1.392(4)	C54C	C56C	1.506(6)
C9	C17B	1.538(13)			

Table B-66 Bond Angles for **26**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1A	Ni1	N2A	87.64(10)	C18B	C17B	C9B	112.3(4)
N1A	Ni1	N6A	86.92(10)	C18B	C17B	C19B	108.7(6)
N1A	Ni1	N10A	173.82(10)	C18B	C17B	C20B	108.3(6)
N1A	Ni1	N11A	98.82(10)	C19B	C17B	C9B	110.2(3)
N1A	Ni1	N15A	87.75(10)	C19B	C17B	C20B	107.9(5)
N2A	Ni1	N6A	172.58(10)	C20B	C17B	C9B	109.3(3)
N2A	Ni1	N11A	90.82(11)	N2B	C21B	C2B	124.1(3)
N2A	Ni1	N15A	92.84(11)	N5B	C21B	N2B	111.3(3)
N6A	Ni1	N11A	85.04(10)	N5B	C21B	C2B	124.5(3)
N6A	Ni1	N15A	91.98(11)	N4B	C22B	C23B	108.5(3)
N10A	Ni1	N2A	91.30(11)	N4B	C22B	C24B	110.5(3)
N10A	Ni1	N6A	94.64(10)	C23B	C22B	C24B	112.8(3)
N10A	Ni1	N11A	87.27(10)	N6B	C25B	C11B	125.0(3)
N10A	Ni1	N15A	86.23(10)	N9B	C25B	N6B	110.9(3)
N15A	Ni1	N11A	172.61(10)	N9B	C25B	C11B	124.0(3)
C1A	N1A	Ni1	126.6(2)	N8B	C26B	C27B	109.0(3)
C12A	N1A	Ni1	125.3(2)	N8B	C26B	C28B	109.6(3)
C12A	N1A	C1A	104.9(3)	C28B	C26B	C27B	113.3(3)
N3A	N2A	Ni1	122.4(2)	N10B	C29B	C30B	129.4(3)
N3A	N2A	C21A	107.8(3)	N10B	C29B	C34B	112.0(3)
C21A	N2A	Ni1	129.8(2)	C30B	C29B	C34B	118.5(3)
N4A	N3A	N2A	105.1(3)	C29B	C30B	C49B	122.1(3)
N3A	N4A	N5A	114.6(3)	C31B	C30B	C29B	118.3(3)
N3A	N4A	C22A	121.7(3)	C31B	C30B	C49B	119.6(3)
N5A	N4A	C22A	123.7(3)	C32B	C31B	C30B	123.7(3)
C21A	N5A	N4A	101.9(3)	C31B	C32B	C41B	119.9(3)
N7A	N6A	Ni1	123.6(2)	C33B	C32B	C31B	117.4(3)
N7A	N6A	C25A	107.3(3)	C33B	C32B	C41B	122.6(3)
C25A	N6A	Ni1	128.9(2)	C32B	C33B	C34B	120.8(3)
N8A	N7A	N6A	105.1(3)	C29B	C34B	C35B	105.5(3)
N7A	N8A	N9A	114.5(3)	C33B	C34B	C29B	121.3(3)
N7A	N8A	C26A	123.0(3)	C33B	C34B	C35B	133.1(3)
N9A	N8A	C26A	122.2(3)	C36B	C35B	C34B	134.1(3)
C25A	N9A	N8A	102.0(3)	C36B	C35B	C40B	121.0(3)
C29A	N10A	Ni1	127.8(2)	C40B	C35B	C34B	104.8(3)
C29A	N10A	C40A	104.7(3)	C35B	C36B	C37B	121.1(3)
C40A	N10A	Ni1	127.1(2)	C36B	C37B	C38B	117.7(3)
N12A	N11A	Ni1	124.8(2)	C36B	C37B	C45B	120.4(3)
N12A	N11A	C49A	107.0(3)	C38B	C37B	C45B	121.9(3)
C49A	N11A	Ni1	127.8(2)	C37B	C38B	C39B	123.3(3)
N13A	N12A	N11A	104.9(3)	C38B	C39B	C40B	118.7(3)
N12A	N13A	N14A	115.2(3)	C38B	C39B	C53B	119.5(3)
N12A	N13A	C50A	122.8(3)	C40B	C39B	C53B	121.3(3)

N14A	N13A	C50A	122.0(3)	N10B	C40B	C35B	112.2(3)
N13A	N14A	C49A	101.4(3)	N10B	C40B	C39B	129.4(3)
N16A	N15A	Ni1	122.78(19)	C39B	C40B	C35B	118.2(3)
N16A	N15A	C53A	107.1(2)	C42B	C41B	C32B	108.5(3)
C53A	N15A	Ni1	129.7(2)	C42B	C41B	C44B	108.3(3)
N17A	N16A	N15A	104.8(2)	C43B	C41B	C32B	111.3(3)
N16A	N17A	N18A	114.8(3)	C43B	C41B	C42B	108.9(3)
N16A	N17A	C54A	122.8(3)	C43B	C41B	C44B	108.2(3)
N18A	N17A	C54A	122.4(3)	C44B	C41B	C32B	111.5(3)
N17A	N18A	C53A	101.9(3)	C5	C45B	C4	110.4(12)
N1A	C1A	C2A	129.1(3)	C5	C45B	C6	105.5(10)
N1A	C1A	C6A	111.8(3)	C5	C45B	C37B	108.3(6)
C2A	C1A	C6A	119.0(3)	C6	C45B	C4	107.9(11)
C1A	C2A	C3A	118.5(3)	C6	C45B	C37B	111.4(6)
C1A	C2A	C21A	121.3(3)	C37B	C45B	C4	113.1(7)
C3A	C2A	C21A	119.8(3)	C46B	C45B	C37B	109.5(3)
C4A	C3A	C2A	123.5(3)	C46B	C45B	C48B	107.7(4)
C3A	C4A	C5A	117.2(3)	C47B	C45B	C37B	109.5(3)
C3A	C4A	C13A	122.3(3)	C47B	C45B	C46B	109.5(4)
C5A	C4A	C13A	120.5(3)	C47B	C45B	C48B	108.0(4)
C6A	C5A	C4A	121.1(3)	C48B	C45B	C37B	112.7(3)
C1A	C6A	C7A	105.3(3)	N11B	C49B	C30B	123.8(3)
C5A	C6A	C1A	120.4(3)	N14B	C49B	N11B	111.2(3)
C5A	C6A	C7A	134.3(3)	N14B	C49B	C30B	125.0(3)
C8A	C7A	C6A	133.2(3)	N13B	C50B	C51B	109.0(3)
C8A	C7A	C12A	121.2(3)	N13B	C50B	C52B	110.1(3)
C12A	C7A	C6A	105.5(3)	C52B	C50B	C51B	111.9(3)
C9A	C8A	C7A	120.6(3)	N15B	C53B	C39B	124.6(3)
C8A	C9A	C10A	118.0(3)	N18B	C53B	N15B	111.0(3)
C8A	C9A	C17A	122.6(3)	N18B	C53B	C39B	124.1(3)
C10A	C9A	C17A	119.3(3)	N17B	C54B	C55B	108.8(3)
C11A	C10A	C9A	122.7(3)	N17B	C54B	C56B	109.8(3)
C10A	C11A	C12A	118.7(3)	C56B	C54B	C55B	113.0(3)
C10A	C11A	C25A	120.4(3)	N1C	Ni3	N2C	86.63(10)
C12A	C11A	C25A	120.9(3)	N1C	Ni3	N6C	87.71(10)
N1A	C12A	C7A	112.5(3)	N1C	Ni3	N11C	94.04(10)
N1A	C12A	C11A	128.8(3)	N1C	Ni3	N15C	92.06(10)
C11A	C12A	C7A	118.7(3)	N6C	Ni3	N2C	173.58(10)
C4A	C13A	C14A	111.9(3)	N10C	Ni3	N1C	174.18(10)
C4A	C13A	C15A	109.6(3)	N10C	Ni3	N2C	87.67(10)
C14A	C13A	C15A	107.8(3)	N10C	Ni3	N6C	98.05(10)
C16A	C13A	C4A	110.4(3)	N10C	Ni3	N11C	87.25(10)
C16A	C13A	C14A	107.7(3)	N10C	Ni3	N15C	87.22(10)
C16A	C13A	C15A	109.3(3)	N11C	Ni3	N2C	91.24(11)
C18A	C17A	C9A	111.9(3)	N11C	Ni3	N6C	86.13(11)
C18A	C17A	C19A	107.8(3)	N15C	Ni3	N2C	94.46(11)

C18A	C17A	C20A	107.6(3)	N15C	Ni3	N6C	88.76(11)
C19A	C17A	C9A	108.3(3)	N15C	Ni3	N11C	171.88(10)
C20A	C17A	C9A	110.7(3)	C1C	N1C	Ni3	127.5(2)
C20A	C17A	C19A	110.6(4)	C12C	N1C	Ni3	127.5(2)
N2A	C21A	C2A	124.7(3)	C12C	N1C	C1C	105.0(3)
N5A	C21A	N2A	110.6(3)	N3C	N2C	Ni3	122.2(2)
N5A	C21A	C2A	124.0(3)	N3C	N2C	C21C	107.0(3)
N4A	C22A	C24A	110.3(4)	C21C	N2C	Ni3	130.3(2)
C23A	C22A	N4A	106.4(4)	N4C	N3C	N2C	105.4(3)
C23A	C22A	C24A	114.7(4)	N3C	N4C	N5C	115.1(3)
N6A	C25A	C11A	123.8(3)	N3C	N4C	C15	127.8(7)
N9A	C25A	N6A	111.0(3)	N3C	N4C	C22C	113.9(6)
N9A	C25A	C11A	125.0(3)	N5C	N4C	C15	113.6(7)
N8A	C26A	C28A	110.9(3)	N5C	N4C	C22C	130.2(6)
C27A	C26A	N8A	109.1(3)	N4C	N5C	C21C	101.5(3)
C27A	C26A	C28A	113.0(4)	N7C	N6C	Ni3	123.7(2)
N10A	C29A	C30A	129.0(3)	N7C	N6C	C25C	107.6(3)
N10A	C29A	C34A	112.7(3)	C25C	N6C	Ni3	128.5(2)
C30A	C29A	C34A	118.3(3)	N8C	N7C	N6C	104.6(3)
C29A	C30A	C49A	121.6(3)	N7C	N8C	N9C	115.1(3)
C31A	C30A	C29A	118.4(3)	N7C	N8C	C26C	122.4(3)
C31A	C30A	C49A	119.9(3)	N9C	N8C	C26C	122.5(3)
C30A	C31A	C32A	123.5(3)	N8C	N9C	C25C	101.8(3)
C31A	C32A	C41A	119.2(3)	C29C	N10C	Ni3	125.7(2)
C33A	C32A	C31A	117.4(3)	C40C	N10C	Ni3	127.0(2)
C33A	C32A	C41A	123.4(3)	C40C	N10C	C29C	105.1(3)
C32A	C33A	C34A	120.8(3)	N12C	N11C	Ni3	123.7(2)
C29A	C34A	C35A	104.9(3)	N12C	N11C	C49C	107.0(3)
C33A	C34A	C29A	121.4(3)	C49C	N11C	Ni3	129.0(2)
C33A	C34A	C35A	133.5(3)	N13C	N12C	N11C	105.1(3)
C36A	C35A	C34A	133.4(3)	N12C	N13C	N14C	114.4(3)
C36A	C35A	C40A	121.2(3)	N12C	N13C	C50C	123.6(3)
C40A	C35A	C34A	105.4(3)	N14C	N13C	C50C	122.0(3)
C37A	C36A	C35A	120.6(3)	C49C	N14C	N13C	102.1(3)
C36A	C37A	C38A	117.8(3)	N16C	N15C	Ni3	123.1(2)
C36A	C37A	C45A	123.6(3)	N16C	N15C	C53C	106.9(3)
C38A	C37A	C45A	118.6(3)	C53C	N15C	Ni3	130.0(2)
C39A	C38A	C37A	123.0(3)	N17C	N16C	N15C	105.2(2)
C38A	C39A	C40A	118.6(3)	N16C	N17C	N18C	115.1(3)
C38A	C39A	C53A	119.6(3)	N16C	N17C	C54C	121.0(3)
C40A	C39A	C53A	121.6(3)	N18C	N17C	C54C	123.8(3)
N10A	C40A	C35A	112.2(3)	N17C	N18C	C53C	101.6(3)
N10A	C40A	C39A	129.1(3)	N1C	C1C	C2C	129.8(3)
C39A	C40A	C35A	118.5(3)	N1C	C1C	C6C	112.0(3)
C32A	C41A	C42A	110.0(4)	C2C	C1C	C6C	118.1(3)
C43A	C41A	C32A	108.7(4)	C1C	C2C	C21C	121.4(3)

C43A	C41A	C42A	110.4(4)	C3C	C2C	C1C	118.8(3)
C43A	C41A	C44A	107.9(4)	C3C	C2C	C21C	119.7(3)
C44A	C41A	C32A	111.5(3)	C4C	C3C	C2C	123.2(3)
C44A	C41A	C42A	108.3(4)	C3C	C4C	C13C	120.5(3)
C37A	C45A	C47A	109.5(3)	C5C	C4C	C3C	117.9(3)
C37A	C45A	C48A	108.9(3)	C5C	C4C	C13C	121.5(3)
C46A	C45A	C37A	112.0(3)	C4C	C5C	C6C	120.7(3)
C46A	C45A	C47A	109.4(3)	C1C	C6C	C7C	105.4(3)
C46A	C45A	C48A	107.8(3)	C5C	C6C	C1C	121.2(3)
C48A	C45A	C47A	109.2(3)	C5C	C6C	C7C	133.2(3)
N11A	C49A	C30A	125.0(3)	C8C	C7C	C6C	133.7(3)
N14A	C49A	N11A	111.6(3)	C8C	C7C	C12C	121.3(3)
N14A	C49A	C30A	123.2(3)	C12C	C7C	C6C	105.0(3)
N13A	C50A	C51A	110.7(4)	C7C	C8C	C9C	121.0(3)
N13A	C50A	C52A	108.5(4)	C8C	C9C	C10C	117.5(3)
C52A	C50A	C51A	113.6(4)	C8C	C9C	C17C	119.9(3)
N15A	C53A	C39A	124.1(3)	C10C	C9C	C17C	122.6(3)
N18A	C53A	N15A	111.4(3)	C9C	C10C	C11C	123.5(3)
N18A	C53A	C39A	124.4(3)	C10C	C11C	C12C	118.3(3)
N17A	C54A	C55A	108.7(3)	C10C	C11C	C25C	119.9(3)
N17A	C54A	C56A	109.7(3)	C12C	C11C	C25C	121.8(3)
C56A	C54A	C55A	114.4(3)	N1C	C12C	C7C	112.5(3)
N1B	Ni2	N2B	87.95(9)	N1C	C12C	C11C	129.1(3)
N1B	Ni2	N6B	88.04(9)	C11C	C12C	C7C	118.4(3)
N1B	Ni2	N10B	175.53(10)	C4C	C13C	C12	104.5(5)
N1B	Ni2	N11B	88.66(10)	C4C	C13C	C15C	104.4(4)
N1B	Ni2	N15B	96.32(10)	C10	C13C	C4C	110.5(5)
N2B	Ni2	N11B	81.76(10)	C10	C13C	C12	106.6(7)
N6B	Ni2	N2B	175.68(10)	C11	C13C	C4C	114.7(6)
N6B	Ni2	N11B	96.54(10)	C11	C13C	C10	114.3(10)
N6B	Ni2	N15B	89.32(9)	C11	C13C	C12	105.3(9)
N10B	Ni2	N2B	89.86(9)	C14C	C13C	C4C	111.8(4)
N10B	Ni2	N6B	94.03(9)	C14C	C13C	C15C	104.6(7)
N10B	Ni2	N11B	87.17(10)	C16C	C13C	C4C	114.4(5)
N10B	Ni2	N15B	87.67(10)	C16C	C13C	C14C	115.2(8)
N15B	Ni2	N2B	92.72(10)	C16C	C13C	C15C	105.0(8)
N15B	Ni2	N11B	172.45(10)	C13	C15	N4C	108.3(11)
C1B	N1B	Ni2	127.07(19)	C14	C15	N4C	99.1(16)
C12B	N1B	Ni2	127.95(19)	C14	C15	C13	110(3)
C12B	N1B	C1B	104.3(2)	C18C	C17C	C9C	110.3(3)
N3B	N2B	Ni2	121.24(19)	C19C	C17C	C9C	108.9(3)
N3B	N2B	C21B	107.3(2)	C19C	C17C	C18C	108.4(4)
C21B	N2B	Ni2	127.0(2)	C20C	C17C	C9C	112.9(3)
N4B	N3B	N2B	104.9(2)	C20C	C17C	C18C	107.7(4)
N3B	N4B	N5B	115.0(2)	C20C	C17C	C19C	108.5(4)
N3B	N4B	C22B	122.2(3)	N2C	C21C	C2C	123.8(3)

N5B	N4B	C22B	122.7(3)	N5C	C21C	N2C	111.1(3)
N4B	N5B	C21B	101.6(2)	N5C	C21C	C2C	125.1(3)
N7B	N6B	Ni2	124.17(19)	N4C	C22C	C24C	110.2(8)
N7B	N6B	C25B	107.0(2)	C23C	C22C	N4C	101.9(12)
C25B	N6B	Ni2	128.8(2)	C23C	C22C	C24C	115.3(15)
N8B	N7B	N6B	104.9(2)	N6C	C25C	C11C	125.3(3)
N7B	N8B	N9B	115.4(2)	N9C	C25C	N6C	110.8(3)
N7B	N8B	C26B	122.2(3)	N9C	C25C	C11C	123.9(3)
N9B	N8B	C26B	122.3(3)	C27C	C26C	N8C	111.2(5)
N8B	N9B	C25B	101.7(2)	C27C	C26C	C28C	118.3(6)
C29B	N10B	Ni2	127.0(2)	C28C	C26C	N8C	110.1(4)
C40B	N10B	Ni2	127.3(2)	N10C	C29C	C30C	129.2(3)
C40B	N10B	C29B	105.4(2)	N10C	C29C	C34C	111.8(3)
N12B	N11B	Ni2	120.22(19)	C30C	C29C	C34C	118.9(3)
N12B	N11B	C49B	107.1(2)	C29C	C30C	C49C	121.4(3)
C49B	N11B	Ni2	124.8(2)	C31C	C30C	C29C	118.3(3)
N13B	N12B	N11B	105.3(2)	C31C	C30C	C49C	120.3(3)
N12B	N13B	N14B	114.5(2)	C30C	C31C	C32C	123.7(3)
N12B	N13B	C50B	123.3(3)	C31C	C32C	C41C	119.9(3)
N14B	N13B	C50B	121.9(3)	C33C	C32C	C31C	117.3(3)
N13B	N14B	C49B	102.0(2)	C33C	C32C	C41C	122.7(3)
N16B	N15B	Ni2	124.23(19)	C34C	C33C	C32C	121.0(3)
N16B	N15B	C53B	107.2(2)	C29C	C34C	C35C	105.7(3)
C53B	N15B	Ni2	128.6(2)	C33C	C34C	C29C	120.8(3)
N17B	N16B	N15B	105.1(2)	C33C	C34C	C35C	133.6(3)
N16B	N17B	N18B	114.8(2)	C36C	C35C	C34C	134.0(3)
N16B	N17B	C54B	123.0(3)	C36C	C35C	C40C	120.6(3)
N18B	N17B	C54B	121.9(3)	C40C	C35C	C34C	105.4(3)
N17B	N18B	C53B	101.9(2)	C37C	C36C	C35C	121.0(3)
N1B	C1B	C2B	128.7(3)	C36C	C37C	C38C	117.3(3)
N1B	C1B	C6B	112.5(3)	C36C	C37C	C45C	121.5(3)
C2B	C1B	C6B	118.6(3)	C38C	C37C	C45C	121.1(3)
C1B	C2B	C21B	122.0(3)	C39C	C38C	C37C	123.6(3)
C3B	C2B	C1B	118.6(3)	C38C	C39C	C40C	118.7(3)
C3B	C2B	C21B	119.4(3)	C38C	C39C	C53C	119.8(3)
C2B	C3B	C4B	123.5(3)	C40C	C39C	C53C	121.4(3)
C3B	C4B	C13B	119.2(3)	N10C	C40C	C35C	112.0(3)
C5B	C4B	C3B	117.6(3)	N10C	C40C	C39C	129.2(3)
C5B	C4B	C13B	123.1(3)	C39C	C40C	C35C	118.7(3)
C4B	C5B	C6B	120.4(3)	C32C	C41C	C42C	108.9(3)
C1B	C6B	C7B	105.3(3)	C32C	C41C	C43C	111.0(3)
C5B	C6B	C1B	121.3(3)	C43C	C41C	C42C	109.7(3)
C5B	C6B	C7B	133.2(3)	C44C	C41C	C32C	111.8(3)
C8B	C7B	C6B	133.7(3)	C44C	C41C	C42C	108.4(3)
C8B	C7B	C12B	121.3(3)	C44C	C41C	C43C	107.1(3)
C12B	C7B	C6B	105.0(3)	C1	C45C	C3	108.2(7)

C7B	C8B	C9B	120.7(3)	C1	C45C	C37C	107.9(4)
C8B	C9B	C10B	117.8(3)	C2	C45C	C1	112.4(7)
C8B	C9B	C17B	122.1(3)	C2	C45C	C3	109.0(7)
C10B	C9B	C17B	120.1(3)	C2	C45C	C37C	113.1(5)
C11B	C10B	C9B	123.2(3)	C37C	C45C	C3	106.0(4)
C10B	C11B	C12B	118.5(3)	C37C	C45C	C46C	109.8(4)
C10B	C11B	C25B	120.1(3)	C37C	C45C	C47C	110.9(4)
C12B	C11B	C25B	121.4(3)	C46C	C45C	C47C	106.3(5)
N1B	C12B	C7B	112.8(3)	C48C	C45C	C37C	115.2(3)
N1B	C12B	C11B	128.7(3)	C48C	C45C	C46C	106.6(5)
C11B	C12B	C7B	118.3(3)	C48C	C45C	C47C	107.7(5)
C4B	C13B	C14B	108.9(3)	N11C	C49C	C30C	124.2(3)
C4B	C13B	C15B	109.9(3)	N14C	C49C	N11C	111.4(3)
C15B	C13B	C14B	109.3(3)	N14C	C49C	C30C	124.4(3)
C16B	C13B	C4B	112.1(3)	N13C	C50C	C51C	110.2(3)
C16B	C13B	C14B	107.1(3)	N13C	C50C	C52C	109.5(3)
C16B	C13B	C15B	109.5(3)	C51C	C50C	C52C	111.9(4)
C7	C17B	C9	107.8(9)	N15C	C53C	C39C	124.3(3)
C7	C17B	C9B	107.1(4)	N18C	C53C	N15C	111.2(3)
C8	C17B	C7	108.5(8)	N18C	C53C	C39C	124.4(3)
C8	C17B	C9	111.7(11)	N17C	C54C	C55C	108.3(3)
C8	C17B	C9B	108.5(6)	N17C	C54C	C56C	108.7(3)
C9	C17B	C9B	113.0(5)	C56C	C54C	C55C	114.7(3)

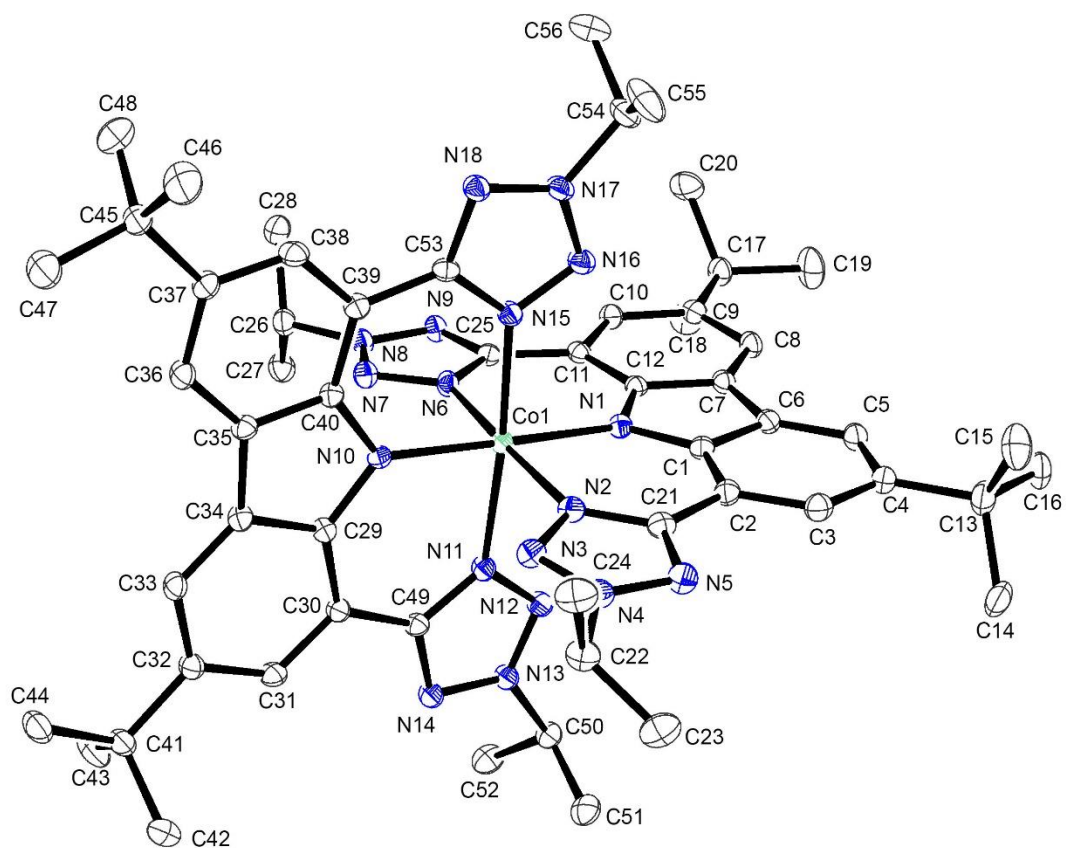


Figure B-21 Labelled ORTEP Drawing of 27

H atoms not shown

Disordered toluenes of solvation not shown: C57-C77

Disordered tBu carbons C14A, C15A and C16A not shown

Table B-67 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **27**

Atom	x	y	z	U(eq)
Co1	3363.2(2)	7315.8(2)	3251.5(2)	22.34(10)
N1	2397.9(13)	7683.2(12)	4250.4(14)	22.9(4)
N2	4125.6(14)	7001.8(13)	4072.7(15)	26.2(5)
N3	4969.6(14)	6775.5(14)	3793.9(15)	28.7(5)
N4	5207.8(14)	6724.3(14)	4442.6(15)	29.3(5)
N5	4573.5(15)	6908.2(14)	5141.2(16)	32.8(5)
N6	2546.2(14)	7729.8(13)	2487.8(14)	25.3(5)
N7	2782.5(14)	7730.1(14)	1644.5(15)	29.2(5)
N8	2132.6(14)	8054.6(14)	1420.6(14)	26.6(5)
N9	1467.3(14)	8272.8(14)	2065.6(15)	28.0(5)
N10	4311.8(13)	6939.7(12)	2249.4(14)	21.9(4)
N11	4253.2(14)	8603.7(13)	2349.6(14)	24.9(4)
N12	4058.9(14)	9288.5(13)	2546.7(15)	27.7(5)
N13	4770.6(14)	9937.5(13)	1844.2(15)	27.0(5)
N14	5437.1(14)	9732.6(13)	1184.7(15)	28.0(5)
N15	2569.3(14)	5977.4(12)	4067.3(14)	24.6(4)
N16	1810.2(14)	5661.7(13)	4945.9(15)	29.0(5)
N17	1558.1(14)	4827.1(13)	5190.3(15)	29.2(5)
N18	2102.8(14)	4564.4(13)	4526.0(15)	27.9(5)
C1	2376.8(17)	7621.6(15)	5082.1(17)	24.5(5)
C2	3033.5(17)	7353.1(16)	5419.5(18)	26.7(5)
C3	2848.4(19)	7346.6(17)	6297.0(19)	31.3(6)
C4	2048.2(18)	7597.2(17)	6855.6(18)	30.9(6)
C5	1407.0(18)	7862.6(17)	6516.8(18)	30.4(6)
C6	1562.6(17)	7879.7(16)	5647.8(18)	25.6(5)
C7	1040.7(17)	8117.5(15)	5123.9(17)	25.1(5)
C8	186.0(17)	8404.5(16)	5308.0(18)	29.1(6)
C9	-160.0(17)	8573.4(16)	4665.1(18)	27.8(6)
C10	377.5(17)	8452.2(16)	3833.9(18)	27.4(5)
C11	1235.5(16)	8162.9(15)	3624.8(17)	23.6(5)
C12	1582.2(16)	7980.5(15)	4286.3(17)	22.6(5)
C13	1894(2)	7563(2)	7818(2)	39.0(7)
C14	2732(3)	8155(4)	7613(4)	52.3(16)
C14A	1868(11)	8418(8)	7768(9)	71(4)
C15	1751(5)	6636(3)	8543(4)	54.4(16)
C15A	2733(8)	7186(9)	8044(8)	64(4)
C16	1004(3)	7964(3)	8267(3)	40.7(13)
C16A	1047(9)	6842(9)	8640(7)	72(4)
C17	-1108.0(18)	8877.2(18)	4833(2)	33.6(6)
C18	-936(2)	9802.3(19)	4002(2)	44.7(7)
C19	-1621(2)	8931(3)	5799(2)	56.0(9)
C20	-1741(2)	8226(2)	4841(2)	48.0(8)

C21	3896.2(17)	7085.2(16)	4888.3(18)	27.3(5)
C22	6122.9(19)	6491.3(18)	4386(2)	34.9(6)
C23	6420(2)	6932(2)	4838(2)	44.1(7)
C24	6055(2)	5498.3(19)	4851(2)	44.1(7)
C25	1743.3(16)	8060.0(15)	2734.7(17)	23.6(5)
C26	2136.4(18)	8162.3(18)	524.7(18)	31.3(6)
C27	2144(2)	9125.3(18)	-76(2)	37.8(7)
C28	1298(2)	7537.7(19)	799(2)	40.3(7)
C29	5149.5(16)	7438.6(15)	1426.6(17)	22.4(5)
C30	5561.8(16)	8326.7(15)	1055.2(17)	23.9(5)
C31	6432.6(17)	8677.0(16)	214.1(18)	28.2(6)
C32	6930.5(17)	8199.0(16)	-293.2(18)	28.0(6)
C33	6510.9(17)	7335.1(16)	58.2(18)	27.4(5)
C34	5633.3(17)	6960.2(15)	897.5(17)	24.7(5)
C35	5029.7(17)	6102.9(15)	1435.3(18)	24.8(5)
C36	5115.6(18)	5342.7(16)	1302.5(18)	28.9(6)
C37	4421.7(18)	4584.6(16)	1965.2(19)	29.7(6)
C38	3654.8(18)	4612.0(16)	2765.6(19)	29.6(6)
C39	3542.7(17)	5358.6(15)	2931.9(17)	24.8(5)
C40	4247.9(16)	6130.6(15)	2248.3(17)	22.5(5)
C41	7881.4(18)	8668.0(17)	-1235.1(19)	33.2(6)
C42	8549(2)	9053(2)	-1026(2)	55.3(9)
C43	7724(2)	9414(2)	-2014(2)	50.3(8)
C44	8362(2)	8030.1(19)	-1637(2)	43.5(7)
C45	4478(2)	3726.8(17)	1849(2)	37.6(7)
C46	4410(3)	2951.8(19)	2754(2)	57.8(9)
C47	5392(2)	3813(2)	965(3)	63.3(11)
C48	3647(3)	3534(2)	1715(3)	60.2(10)
C49	5096.3(16)	8880.1(15)	1519.7(17)	23.5(5)
C50	4830.0(19)	10828.4(16)	1797.3(19)	30.7(6)
C51	5545(2)	10938.9(18)	2094(2)	39.0(7)
C52	5051(2)	11520.2(17)	787(2)	39.5(7)
C53	2745.5(16)	5303.4(15)	3818.8(17)	23.7(5)
C54	765.1(19)	4219.1(18)	6150(2)	39.0(7)
C55	1138(2)	3480(2)	6706(2)	59.7(10)
C56	25(2)	3873(2)	6022(3)	64.8(10)
C57	7475(2)	5602(2)	2172(2)	50.3(8)
C58	8043(3)	6389(3)	1363(3)	70.9(11)
C59	8999(4)	6519(4)	979(3)	94.3(16)
C60	9418(3)	5854(4)	1404(4)	98.9(18)
C61	8850(3)	5096(3)	2222(4)	89.5(15)
C62	7899(3)	4975(2)	2596(3)	60.2(9)
C63	6438(3)	5439(3)	2558(3)	80.5(13)
C64	8448(2)	9069(2)	1917(2)	48.1(8)
C65	8010(3)	8562(2)	1714(2)	54.0(9)
C66	7046(3)	8431(2)	2082(3)	59.9(10)

C67	6502(3)	8815(2)	2667(3)	58.5(9)
C68	6926(3)	9317(2)	2870(2)	54.7(9)
C69	7886(2)	9438(2)	2505(2)	49.6(8)
C70	9500(3)	9218(3)	1512(3)	80.5(12)
C71	1421(3)	4507(3)	1252(3)	78.5(12)
C72	831(3)	3926(2)	2209(3)	64.3(10)
C73	842(3)	4025(3)	2959(4)	80.8(13)
C74	1409(4)	4667(3)	2792(4)	90.8(14)
C75	2003(3)	5256(3)	1867(5)	87.4(15)
C76	2054(3)	5222(3)	1066(4)	93.6(16)
C77	1436(6)	4468(4)	442(5)	160(3)

Table B-68 Anisotropic Displacement Parameters (U_{ij} , Å² x10³) for **27**

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Co1	22.69(18)	19.03(17)	22.97(18)	- 10.13(14)	-8.82(14)	4.33(13)
N1	24.9(11)	20.3(10)	23.3(11)	-9.9(9)	-11.6(9)	5.3(8)
N2	24.3(11)	24.4(11)	30.3(12)	-13.4(9)	-12.7(10)	6.3(9)
N3	28.6(12)	29.0(11)	32.3(12)	-14.6(10)	-17.3(10)	8.3(9)
N4	26.6(12)	30.6(12)	32.5(12)	-14.5(10)	-15.6(10)	7.6(9)
N5	31.5(12)	36.0(13)	35.0(13)	-17.9(11)	-18.0(11)	10.5(10)
N6	26.4(11)	26.1(11)	23.8(11)	-14.4(9)	-9.9(9)	6.9(9)
N7	28.7(12)	31.3(12)	27.9(12)	-15.4(10)	-12.5(10)	8.3(9)
N8	23.4(11)	33.0(12)	22.9(11)	-14.8(10)	-9.2(9)	7.0(9)
N9	26.7(11)	32.0(12)	24.5(11)	-14.3(10)	-10.7(10)	7.4(9)
N10	23.7(11)	18.1(10)	23.4(11)	-9.5(9)	-10.9(9)	2.6(8)
N11	26.4(11)	21.3(10)	26.5(11)	-13.1(9)	-10.5(10)	7.0(9)
N12	26.6(11)	21.4(10)	29.9(12)	-12.6(9)	-8.9(10)	4.4(9)
N13	26.5(11)	21.5(11)	29.1(12)	-14.2(9)	-8.2(10)	4.8(9)
N14	28.5(11)	21.2(11)	28.9(12)	-13.5(9)	-7.7(10)	3.8(9)
N15	24.5(11)	21.3(10)	23.7(11)	-9.9(9)	-8.6(9)	3.9(9)
N16	27.6(12)	23.9(11)	28.5(12)	-11.3(9)	-8.6(10)	1.4(9)
N17	27.0(11)	22.6(11)	26.2(11)	-9.1(9)	-5.3(10)	-1.4(9)
N18	27.4(11)	22.8(11)	27.0(11)	-11.0(9)	-8.4(10)	2.7(9)
C1	28.8(13)	17.7(12)	24.5(13)	-8.5(10)	-11.6(11)	1.4(10)
C2	30.1(14)	22.6(12)	26.6(13)	-11.1(11)	-13.1(11)	4.3(10)
C3	33.9(15)	30.5(14)	30.0(14)	-11.3(12)	-17.8(12)	4.1(11)
C4	33.2(15)	32.8(14)	26.3(14)	-14.4(12)	-12.9(12)	2.4(12)
C5	31.5(14)	31.0(14)	26.0(14)	-14.6(12)	-10.2(12)	3.9(11)
C6	25.4(13)	23.5(12)	25.4(13)	-11.6(11)	-9.9(11)	3.5(10)
C7	26.1(13)	21.9(12)	23.2(13)	-10.0(10)	-8.9(11)	2.9(10)
C8	27.8(14)	29.0(13)	26.2(13)	-16.0(11)	-7.0(11)	6.3(11)
C9	26.1(13)	24.0(13)	29.9(14)	-12.8(11)	-10.6(11)	5.5(10)
C10	28.1(13)	27.9(13)	26.5(13)	-12.3(11)	-13.5(11)	5.7(11)

C11	22.5(12)	19.6(12)	23.8(13)	-8.3(10)	-8.8(11)	2.3(10)
C12	21.7(12)	18.6(12)	22.7(12)	-9.4(10)	-6.9(10)	1.0(10)
C13	41.1(17)	52.7(18)	30.9(15)	-24.2(14)	-18.8(14)	11.3(14)
C14	43(3)	88(4)	51(3)	-51(3)	-24(2)	11(3)
C14A	122(13)	74(8)	61(7)	-47(7)	-64(9)	45(8)
C15	75(4)	55(3)	36(3)	-21(2)	-29(3)	24(3)
C15A	78(8)	99(10)	46(6)	-45(7)	-44(6)	39(7)
C16	41(3)	58(3)	30(2)	-28(2)	-16(2)	17(2)
C16A	65(8)	109(11)	30(6)	-28(6)	-15(6)	-6(8)
C17	27.5(14)	42.6(16)	33.9(15)	-22.7(13)	-13.0(12)	12.8(12)
C18	39.6(17)	42.3(17)	54.8(19)	-23.7(15)	-24.5(15)	19.8(14)
C19	39.1(18)	92(3)	50(2)	-45(2)	-22.5(16)	36.6(18)
C20	27.0(15)	55(2)	58(2)	-27.5(17)	-16.6(15)	8.7(14)
C21	29.9(14)	21.8(12)	27.9(14)	-7.8(11)	-15.5(12)	3.7(10)
C22	28.9(14)	36.7(15)	41.1(16)	-17.3(13)	-19.2(13)	11.4(12)
C23	41.8(17)	45.3(17)	63(2)	-27.8(16)	-36.6(16)	16.8(14)
C24	37.4(16)	40.7(17)	61(2)	-22.9(16)	-29.5(16)	14.3(13)
C25	24.6(13)	20.4(12)	22.2(13)	-8.0(10)	-10.0(11)	1.5(10)
C26	30.5(14)	38.8(15)	25.7(14)	-16.6(12)	-12.8(12)	7.0(12)
C27	40.0(16)	39.8(16)	29.2(15)	-12.6(13)	-16.3(13)	5.2(13)
C28	46.5(18)	43.5(17)	32.9(16)	-18.9(14)	-18.7(14)	1.7(14)
C29	23.2(12)	20.6(12)	21.9(12)	-8.8(10)	-10.6(11)	5.5(10)
C30	23.2(12)	21.0(12)	26.5(13)	-12.3(11)	-10.1(11)	5.4(10)
C31	29.1(14)	20.0(12)	31.7(14)	-11.3(11)	-11.9(12)	1.6(10)
C32	25.6(13)	26.1(13)	29.9(14)	-14.9(11)	-9.7(11)	5.5(11)
C33	29.3(14)	25.4(13)	27.2(13)	-15.8(11)	-10.3(11)	8.2(11)
C34	28.6(13)	19.4(12)	25.2(13)	-10.3(10)	-12.4(11)	7.1(10)
C35	26.6(13)	20.5(12)	27.0(13)	-10.8(11)	-12.8(11)	4.4(10)
C36	30.5(14)	24.7(13)	28.7(14)	-14.7(11)	-10.0(12)	7.4(11)
C37	34.5(15)	21.5(13)	32.3(14)	-15.5(11)	-12.8(12)	7.0(11)
C38	30.6(14)	20.9(12)	30.8(14)	-8.3(11)	-12.7(12)	0.4(11)
C39	26.7(13)	21.2(12)	25.6(13)	-10.0(11)	-12.7(11)	5.9(10)
C40	25.0(13)	19.6(12)	23.1(12)	-9.8(10)	-11.9(11)	5.8(10)
C41	27.0(14)	27.8(14)	33.6(15)	-15.9(12)	-4.1(12)	1.1(11)
C42	31.7(17)	67(2)	56(2)	-37.1(19)	-2.9(15)	-10.2(15)
C43	42.5(18)	39.6(17)	34.8(17)	-8.0(14)	-1.0(14)	6.7(14)
C44	31.9(16)	39.2(16)	40.8(17)	-21.0(14)	-0.7(13)	2.5(13)
C45	44.0(17)	20.6(13)	36.9(16)	-16.2(12)	-7.9(13)	2.4(12)
C46	75(2)	27.9(16)	55(2)	-20.7(15)	-18.8(19)	13.4(16)
C47	67(2)	34.9(17)	61(2)	-31.3(17)	-0.7(18)	-0.9(16)
C48	70(2)	46.4(19)	68(2)	-37.9(18)	-25(2)	3.3(17)
C49	24.3(13)	18.6(12)	25.9(13)	-9.6(10)	-11.4(11)	3.8(10)
C50	33.7(14)	20.8(12)	36.9(15)	-18.4(12)	-11.8(12)	6.7(11)
C51	44.3(17)	33.1(15)	47.2(17)	-25.6(14)	-21.6(15)	11.3(13)
C52	50.5(18)	22.4(13)	48.3(18)	-16.2(13)	-26.1(15)	8.1(12)
C53	23.9(13)	18.9(12)	25.5(13)	-7.0(10)	-12.5(11)	2.6(10)

C54	34.7(16)	28.6(14)	30.3(15)	-9.9(12)	-0.6(13)	-1.7(12)
C55	58(2)	40.9(18)	31.7(17)	-1.3(14)	1.4(16)	6.4(16)
C56	47(2)	61(2)	56(2)	-18.8(19)	-6.2(17)	-23.5(17)
C57	56(2)	51(2)	49(2)	-26.1(17)	-26.7(17)	13.4(16)
C58	101(3)	55(2)	46(2)	-15.9(19)	-34(2)	7(2)
C59	86(4)	100(4)	60(3)	-36(3)	-5(3)	-27(3)
C60	51(3)	136(5)	127(5)	-97(4)	-21(3)	4(3)
C61	84(3)	87(3)	161(5)	-87(4)	-82(4)	48(3)
C62	66(2)	35.1(18)	82(3)	-18.8(18)	-44(2)	7.5(16)
C63	60(3)	121(4)	79(3)	-56(3)	-40(2)	29(2)
C64	48.3(19)	42.5(18)	51(2)	-14.8(16)	-28.5(17)	10.2(15)
C65	71(2)	46.8(19)	53(2)	-23.4(17)	-36.4(19)	20.2(17)
C66	78(3)	41.3(19)	72(2)	-14.3(18)	-55(2)	4.5(18)
C67	48(2)	49(2)	57(2)	-3.2(17)	-27.3(18)	4.3(16)
C68	59(2)	49(2)	49(2)	-16.3(17)	-26.3(18)	15.3(17)
C69	60(2)	41.9(18)	57(2)	-20.7(16)	-37.6(18)	9.9(16)
C70	49(2)	84(3)	99(3)	-34(3)	-36(2)	17(2)
C71	97(3)	74(3)	80(3)	-39(3)	-54(3)	48(3)
C72	72(3)	43(2)	84(3)	-27(2)	-45(2)	12.9(18)
C73	70(3)	75(3)	119(4)	-54(3)	-54(3)	30(2)
C74	103(4)	90(4)	119(4)	-58(3)	-77(4)	43(3)
C75	78(3)	59(3)	126(4)	-23(3)	-68(3)	16(2)
C76	60(3)	75(3)	89(4)	-2(3)	-27(3)	28(2)
C77	278(10)	114(5)	145(6)	-85(5)	-127(6)	99(6)

Table B-69 Bond Lengths for **27**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Co1	N1	2.0499(19)	C13	C16A	1.517(12)
Co1	N2	2.183(2)	C17	C18	1.539(4)
Co1	N6	2.181(2)	C17	C19	1.534(4)
Co1	N10	2.0530(19)	C17	C20	1.536(4)
Co1	N11	2.152(2)	C22	C23	1.510(4)
Co1	N15	2.1661(19)	C22	C24	1.511(4)
N1	C1	1.385(3)	C26	C27	1.517(4)
N1	C12	1.384(3)	C26	C28	1.524(4)
N2	N3	1.332(3)	C29	C30	1.417(3)
N2	C21	1.357(3)	C29	C34	1.427(3)
N3	N4	1.317(3)	C30	C31	1.392(3)
N4	N5	1.335(3)	C30	C49	1.459(3)
N4	C22	1.495(3)	C31	C32	1.409(3)
N5	C21	1.342(3)	C32	C33	1.392(3)
N6	N7	1.331(3)	C32	C41	1.546(3)
N6	C25	1.355(3)	C33	C34	1.399(3)
N7	N8	1.311(3)	C34	C35	1.446(3)

N8	N9	1.331(3)	C35	C36	1.395(3)
N8	C26	1.482(3)	C35	C40	1.422(3)
N9	C25	1.336(3)	C36	C37	1.392(4)
N10	C29	1.382(3)	C37	C38	1.398(3)
N10	C40	1.383(3)	C37	C45	1.546(3)
N11	N12	1.332(3)	C38	C39	1.402(3)
N11	C49	1.361(3)	C39	C40	1.418(3)
N12	N13	1.313(3)	C39	C53	1.457(3)
N13	N14	1.333(3)	C41	C42	1.537(4)
N13	C50	1.485(3)	C41	C43	1.526(4)
N14	C49	1.342(3)	C41	C44	1.529(4)
N15	N16	1.334(3)	C45	C46	1.518(4)
N15	C53	1.362(3)	C45	C47	1.527(4)
N16	N17	1.318(3)	C45	C48	1.544(4)
N17	N18	1.334(3)	C50	C51	1.517(4)
N17	C54	1.482(3)	C50	C52	1.513(4)
N18	C53	1.345(3)	C54	C55	1.521(4)
C1	C2	1.413(4)	C54	C56	1.506(4)
C1	C6	1.427(3)	C57	C58	1.392(5)
C2	C3	1.404(3)	C57	C62	1.373(5)
C2	C21	1.465(3)	C57	C63	1.494(5)
C3	C4	1.402(4)	C58	C59	1.368(6)
C4	C5	1.390(4)	C59	C60	1.404(7)
C4	C13	1.545(4)	C60	C61	1.371(7)
C5	C6	1.396(3)	C61	C62	1.363(6)
C6	C7	1.440(3)	C64	C65	1.383(4)
C7	C8	1.394(3)	C64	C69	1.383(4)
C7	C12	1.428(3)	C64	C70	1.511(5)
C8	C9	1.389(4)	C65	C66	1.385(5)
C9	C10	1.403(3)	C66	C67	1.388(5)
C9	C17	1.543(3)	C67	C68	1.364(5)
C10	C11	1.398(3)	C68	C69	1.378(5)
C11	C12	1.416(3)	C71	C72	1.373(6)
C11	C25	1.465(3)	C71	C76	1.454(7)
C13	C14	1.541(5)	C71	C77	1.423(7)
C13	C14A	1.418(11)	C72	C73	1.388(6)
C13	C15	1.482(6)	C73	C74	1.305(6)
C13	C15A	1.622(11)	C74	C75	1.346(7)
C13	C16	1.582(5)	C75	C76	1.378(7)

Table B-70 Bond Angles for **27**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Co1	N2	87.50(7)	C19	C17	C9	112.0(2)
N1	Co1	N6	87.21(7)	C19	C17	C18	108.1(2)

N1	Co1	N10	179.02(8)	C19	C17	C20	108.8(2)
N1	Co1	N11	93.51(7)	C20	C17	C9	109.7(2)
N1	Co1	N15	91.93(7)	C20	C17	C18	108.8(2)
N6	Co1	N2	174.04(7)	N2	C21	C2	124.9(2)
N10	Co1	N2	93.30(8)	N5	C21	N2	111.3(2)
N10	Co1	N6	92.02(7)	N5	C21	C2	123.8(2)
N10	Co1	N11	87.10(7)	N4	C22	C23	109.1(2)
N10	Co1	N15	87.47(7)	N4	C22	C24	110.8(2)
N11	Co1	N2	87.24(8)	C23	C22	C24	112.9(2)
N11	Co1	N6	90.34(8)	N6	C25	C11	124.5(2)
N11	Co1	N15	174.54(7)	N9	C25	N6	111.3(2)
N15	Co1	N2	92.51(7)	N9	C25	C11	124.2(2)
N15	Co1	N6	90.41(8)	N8	C26	C27	109.4(2)
C1	N1	Co1	127.62(16)	N8	C26	C28	109.5(2)
C12	N1	Co1	127.62(15)	C27	C26	C28	112.7(2)
C12	N1	C1	104.57(19)	N10	C29	C30	129.4(2)
N3	N2	Co1	125.00(16)	N10	C29	C34	112.4(2)
N3	N2	C21	106.9(2)	C30	C29	C34	118.2(2)
C21	N2	Co1	127.77(16)	C29	C30	C49	122.0(2)
N4	N3	N2	105.42(19)	C31	C30	C29	118.4(2)
N3	N4	N5	114.6(2)	C31	C30	C49	119.6(2)
N3	N4	C22	122.3(2)	C30	C31	C32	123.8(2)
N5	N4	C22	123.1(2)	C31	C32	C41	119.0(2)
N4	N5	C21	101.8(2)	C33	C32	C31	117.7(2)
N7	N6	Co1	124.78(15)	C33	C32	C41	123.3(2)
N7	N6	C25	106.71(19)	C32	C33	C34	120.4(2)
C25	N6	Co1	128.47(16)	C29	C34	C35	104.9(2)
N8	N7	N6	105.51(18)	C33	C34	C29	121.6(2)
N7	N8	N9	114.59(19)	C33	C34	C35	133.5(2)
N7	N8	C26	122.57(19)	C36	C35	C34	132.7(2)
N9	N8	C26	122.8(2)	C36	C35	C40	121.8(2)
N8	N9	C25	101.90(19)	C40	C35	C34	105.5(2)
C29	N10	Co1	127.72(15)	C37	C36	C35	120.4(2)
C29	N10	C40	104.89(18)	C36	C37	C38	117.8(2)
C40	N10	Co1	127.39(15)	C36	C37	C45	122.5(2)
N12	N11	Co1	123.70(15)	C38	C37	C45	119.7(2)
N12	N11	C49	107.21(19)	C37	C38	C39	123.8(2)
C49	N11	Co1	129.07(15)	C38	C39	C40	118.1(2)
N13	N12	N11	105.17(18)	C38	C39	C53	119.5(2)
N12	N13	N14	114.93(19)	C40	C39	C53	122.3(2)
N12	N13	C50	122.32(19)	N10	C40	C35	112.3(2)
N14	N13	C50	122.7(2)	N10	C40	C39	129.5(2)
N13	N14	C49	101.98(19)	C39	C40	C35	118.2(2)
N16	N15	Co1	124.42(14)	C42	C41	C32	109.9(2)
N16	N15	C53	107.34(18)	C43	C41	C32	109.7(2)
C53	N15	Co1	128.21(15)	C43	C41	C42	109.4(3)

N17	N16	N15	105.19(18)	C43	C41	C44	108.3(2)
N16	N17	N18	114.64(19)	C44	C41	C32	111.8(2)
N16	N17	C54	122.4(2)	C44	C41	C42	107.7(2)
N18	N17	C54	122.8(2)	C46	C45	C37	110.2(2)
N17	N18	C53	102.23(18)	C46	C45	C47	108.9(3)
N1	C1	C2	129.3(2)	C46	C45	C48	108.7(3)
N1	C1	C6	112.4(2)	C47	C45	C37	111.7(2)
C2	C1	C6	118.2(2)	C47	C45	C48	108.4(3)
C1	C2	C21	122.5(2)	C48	C45	C37	108.9(2)
C3	C2	C1	118.4(2)	N11	C49	C30	124.6(2)
C3	C2	C21	119.1(2)	N14	C49	N11	110.7(2)
C4	C3	C2	123.5(2)	N14	C49	C30	124.7(2)
C3	C4	C13	120.2(2)	N13	C50	C51	109.1(2)
C5	C4	C3	117.7(2)	N13	C50	C52	108.8(2)
C5	C4	C13	122.1(2)	C52	C50	C51	113.8(2)
C4	C5	C6	120.7(2)	N15	C53	C39	125.0(2)
C1	C6	C7	105.3(2)	N18	C53	N15	110.6(2)
C5	C6	C1	121.4(2)	N18	C53	C39	124.4(2)
C5	C6	C7	133.3(2)	N17	C54	C55	109.2(2)
C8	C7	C6	132.9(2)	N17	C54	C56	110.4(2)
C8	C7	C12	121.9(2)	C56	C54	C55	112.4(3)
C12	C7	C6	105.2(2)	C58	C57	C63	121.0(4)
C9	C8	C7	120.2(2)	C62	C57	C58	118.0(3)
C8	C9	C10	118.1(2)	C62	C57	C63	121.0(3)
C8	C9	C17	122.9(2)	C59	C58	C57	121.0(4)
C10	C9	C17	119.1(2)	C58	C59	C60	119.9(4)
C11	C10	C9	123.5(2)	C61	C60	C59	118.6(4)
C10	C11	C12	118.4(2)	C62	C61	C60	120.8(5)
C10	C11	C25	119.2(2)	C61	C62	C57	121.7(4)
C12	C11	C25	122.4(2)	C65	C64	C70	121.6(3)
N1	C12	C7	112.5(2)	C69	C64	C65	117.5(3)
N1	C12	C11	129.5(2)	C69	C64	C70	120.9(3)
C11	C12	C7	118.0(2)	C64	C65	C66	121.3(3)
C4	C13	C15A	110.7(4)	C65	C66	C67	119.7(3)
C4	C13	C16	111.3(3)	C68	C67	C66	119.4(3)
C14	C13	C4	109.5(3)	C67	C68	C69	120.4(3)
C14	C13	C16	105.3(3)	C68	C69	C64	121.6(3)
C14A	C13	C4	110.7(5)	C72	C71	C76	117.0(4)
C14A	C13	C15A	108.5(7)	C72	C71	C77	124.6(5)
C14A	C13	C16A	117.0(8)	C77	C71	C76	118.4(5)
C15	C13	C4	110.4(3)	C71	C72	C73	121.0(4)
C15	C13	C14	111.9(4)	C74	C73	C72	122.0(5)
C15	C13	C16	108.3(3)	C73	C74	C75	119.5(5)
C16A	C13	C4	107.3(4)	C74	C75	C76	123.6(5)
C16A	C13	C15A	102.4(7)	C75	C76	C71	117.0(4)
C18	C17	C9	109.4(2)				

Table B-71 Summary of Crystallographic Data for **30**, **31**, **32** and **33**

	30^a	31^b	32^a	33^a
Emp. Formula	C ₄₇ H ₆₇ FeN ₉ O ₂	C ₄₃ H ₅₉ FeN ₉ O	C ₄₈ H ₆₈ FeN ₁₀ O	C ₆₁ H ₇₄ FeN ₉ O ₂ P
Formula wgt. (g/mol)	846.02	773.84	856.97	1052.11
Temp. (K)	120.02	120.04	296.15	273.15
Crystal System	Monoclinic	tetragonal	monoclinic	monoclinic
Space Group	P2 ₁ /m	I4 ₁ /a	P2 ₁ /m	P2 ₁ /c
a (Å)	11.1325(12)	37.8079(16)	11.3536(3)	15.6888(14)
b (Å)	17.7239(19)	37.8079(16)	17.8789(5)	16.0720(14)
c (Å)	11.6559(13)	12.5725(6)	11.6217(4)	21.9928(19)
α (°)	90	90	90	90
β (°)	98.339(2)	90	98.8730(10)	92.664(2)
γ (°)	90	90	90	90
Volume (Å³)	2275.5(4)	17971.6(17)	2330.86(12)	5539.5(8)
Z	2	16	2	4
Density (g/cm³)	1.235	1.144	1.221	1.262
Abs. coeff. μ (mm⁻¹)	0.379	3.006	0.370	0.353
F(000)	908	6624	920	2240
Crystal Size (mm)	0.233 x 0.142 x 0.132	0.255 x 0.236 x 0.201	0.259 x 0.24 x 0.208	0.214 x 0.165 x 0.14
Colour and habit	Yellow block	Dark green block	Yellow block	Yellow rods
Theta range (°)	3.532° ≤ 2Θ ≤ 56.858°	4.674° ≤ 2Θ ≤ 141.524°	3.63° ≤ 2Θ ≤ 56.562°	3.14° ≤ 2Θ ≤ 54.332°
Refl. Collected	53612	180409	83364	96654
Independent refl.	5892	8624	5969	12244
GooF (F²)	1.026	1.047	1.060	1.052
Final R [I > 2σ(I)]	0.0348	0.0547	0.0387	0.0467
Final wR2	0.0818	0.1486	0.0960	0.0957
R (all data)	0.0490	0.0578	0.0467	0.0705
wR2 (all data)	0.0882	0.1515	0.1010	0.1053
Max peak/hole (e/Å³)	0.428/-0.302	0.606/-0.484	0.372/-0.281	1.245/-0.378

^a Data collected on a Bruker Kappa X8-Apex II diffractometer using Mo Kα radiation (λ = 0.71073 Å) at the University of Notre Dame. ^b Data collected on a Bruker PHOTON-II diffractometer using Cu Kα radiation (λ = 1.54178 Å) at the University of Notre Dame.

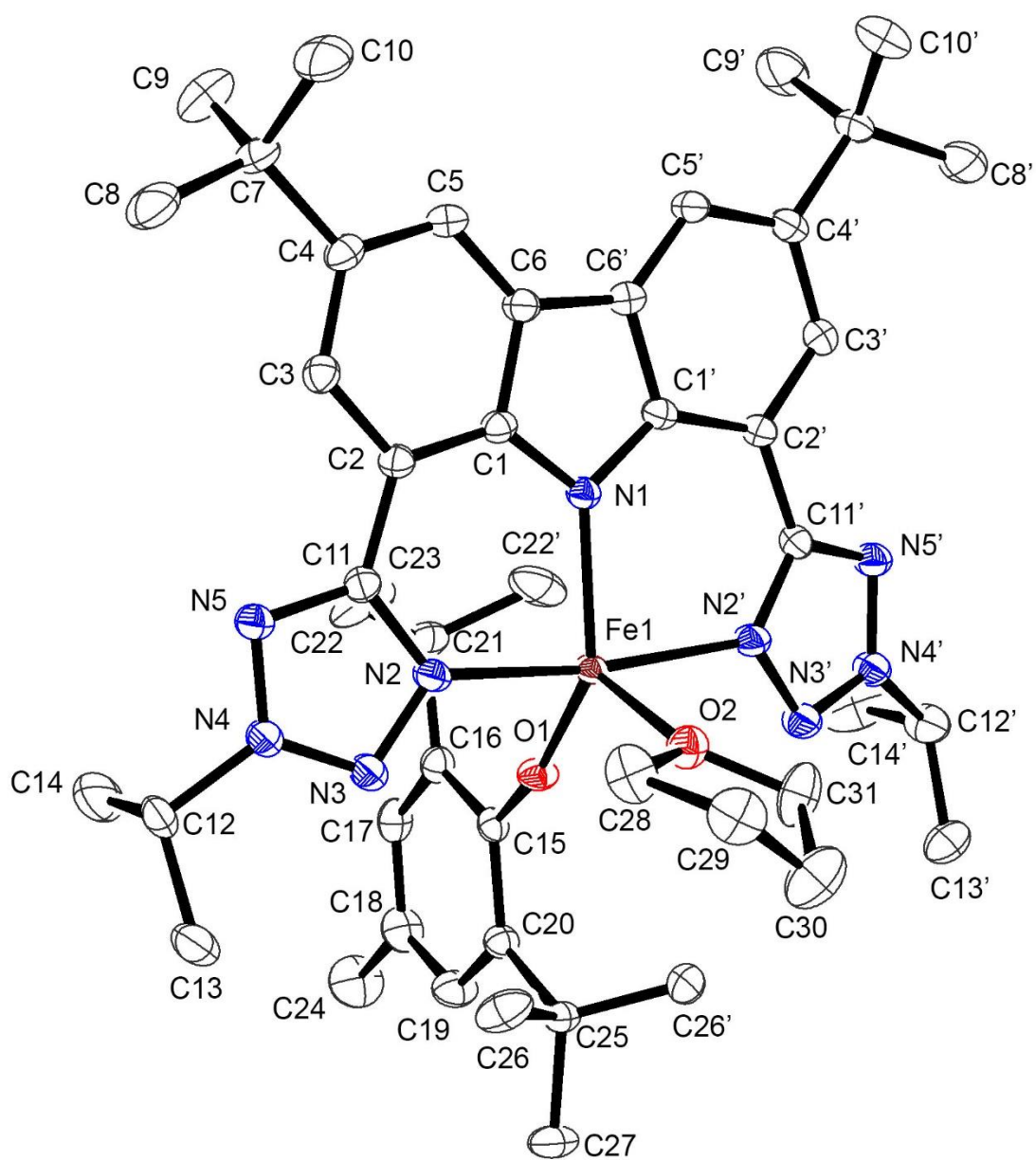


Figure B-22 Labelled ORTEP Drawing of **30**

H atoms not shown

Table B-72 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **30**

Atom	x	y	z	U(eq)
Fe1	5305.8(2)	2500	3479.7(2)	15.24(8)
O1	5052.3(12)	2500	1834.1(11)	19.7(3)
O2	3660.1(13)	2500	4242.6(12)	24.0(3)
N1	6806.2(14)	2500	4749.0(13)	16.5(3)
N2	5362.6(10)	3737.0(7)	3624.4(10)	20.1(2)
N3	4698.9(11)	4183.0(7)	2860.6(10)	22.8(3)
N4	5178.3(11)	4857.6(7)	3032.8(10)	21.2(2)
N5	6133.4(11)	4893.2(7)	3862.9(10)	21.6(2)
C1	7423.3(12)	3120.6(8)	5273.5(11)	16.9(3)
C2	7199.6(12)	3897.6(8)	5097.2(11)	17.3(3)
C3	7961.7(12)	4417.5(8)	5751.2(11)	19.1(3)
C4	8943.0(12)	4205.3(8)	6574.2(11)	19.9(3)
C5	9161.8(12)	3435.5(8)	6745.6(11)	20.1(3)
C6	8420.8(12)	2904.9(8)	6114.7(11)	18.8(3)
C7	9793.7(13)	4784.5(8)	7254.0(12)	23.2(3)
C8	9325.6(16)	5590.6(10)	7065.7(17)	39.5(4)
C9	11036.9(15)	4730.7(11)	6852.4(16)	39.4(4)
C10	9938.7(17)	4616.7(11)	8556.1(14)	37.6(4)
C11	6235.1(12)	4176.8(8)	4222.1(11)	17.7(3)
C12	4852.8(15)	5497.9(9)	2224.9(13)	29.2(3)
C13	3554.0(14)	5430.8(9)	1657.3(14)	30.4(3)
C14	5746.9(17)	5501.7(13)	1351.9(18)	50.4(5)
C15	5143.6(17)	2500	713.2(15)	16.3(4)
C16	6304.4(18)	2500	315.4(17)	19.6(4)
C17	6342.8(19)	2500	-871.9(18)	23.3(4)
C18	5316(2)	2500	-1689.9(17)	27.6(5)
C19	4199(2)	2500	-1293.4(17)	26.1(4)
C20	4072.7(17)	2500	-119.4(16)	18.0(4)
C21	7498.1(19)	2500	1157.5(19)	29.0(5)
C22	7583.2(15)	3216.6(11)	1911.9(15)	39.6(4)
C23	8631(2)	2500	539(2)	44.4(7)
C24	5422(3)	2500	-2966.0(19)	41.1(6)
C25	2791.6(17)	2500	235.8(16)	17.8(4)
C26	2598.3(14)	3209.8(10)	934.3(15)	32.6(4)
C27	1788(2)	2550(30)	-816(2)	29(3)
C28	2854(6)	1917(3)	4299(5)	34.4(12)
C29	1662(3)	2262(2)	4550(4)	43.5(11)
C30	2101(3)	2946(2)	5270(3)	35.1(9)
C31	3133(6)	3222(3)	4689(5)	32.0(11)

Table B-73 Anisotropic Displacement Parameters (U_{ij} , Å² x10³) for **30**

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Fe1	17.14(14)	15.68(14)	11.85(12)	0	-1.49(9)	0
O1	17.3(6)	28.8(8)	12.7(6)	0	1.7(5)	0
O2	22.7(7)	25.8(8)	23.9(7)	0	5.3(6)	0
N1	17.9(8)	15.6(8)	15.1(7)	0	-0.3(6)	0
N2	21.6(6)	18.0(6)	18.8(5)	1.0(4)	-4.2(4)	1.0(5)
N3	26.0(6)	17.2(6)	22.8(6)	1.9(5)	-4.5(5)	0.1(5)
N4	24.5(6)	17.1(6)	20.4(5)	1.6(4)	-2.6(4)	-0.4(5)
N5	22.7(6)	19.2(6)	21.1(6)	0.8(4)	-3.0(4)	-0.4(5)
C1	16.3(6)	19.7(7)	14.4(6)	-1.0(5)	1.0(5)	-1.3(5)
C2	17.8(6)	18.6(6)	15.0(6)	-0.5(5)	0.8(5)	-0.7(5)
C3	20.5(7)	17.5(6)	19.2(6)	-1.6(5)	2.7(5)	-1.1(5)
C4	19.0(6)	22.8(7)	17.6(6)	-3.7(5)	1.6(5)	-3.6(5)
C5	17.3(6)	23.8(7)	18.0(6)	-1.4(5)	-1.7(5)	-0.1(5)
C6	17.2(6)	20.7(7)	17.8(6)	0.7(5)	0.3(5)	0.3(5)
C7	19.8(7)	24.8(7)	23.3(7)	-6.4(6)	-2.4(5)	-3.6(6)
C8	34.8(9)	27.4(9)	51.2(11)	-9.8(8)	-11.5(8)	-5.0(7)
C9	27.3(8)	45.7(11)	45.6(10)	-12.8(8)	6.4(7)	-12.9(8)
C10	41.1(10)	44.0(10)	25.0(8)	-8.6(7)	-3.9(7)	-8.0(8)
C11	19.2(6)	17.6(6)	16.1(6)	-1.6(5)	1.9(5)	-0.7(5)
C12	37.9(9)	17.3(7)	28.7(7)	7.6(6)	-7.7(6)	-1.5(6)
C13	28.9(8)	31.9(9)	29.5(8)	9.6(6)	0.9(6)	7.2(7)
C14	33.0(10)	62.6(13)	54.4(12)	35.5(10)	1.6(8)	-5.4(9)
C15	20.2(9)	14.6(9)	14.4(8)	0	3.0(7)	0
C16	19.1(9)	18.3(9)	22.0(9)	0	4.8(7)	0
C17	24.5(10)	21.2(10)	26.7(10)	0	12.3(8)	0
C18	34.8(12)	31.7(12)	18.0(9)	0	9.2(8)	0
C19	25.2(10)	37.8(12)	15.0(9)	0	1.7(8)	0
C20	18.2(9)	20.1(9)	15.7(8)	0	2.2(7)	0
C21	15.1(10)	41.8(13)	30.4(11)	0	4.3(8)	0
C22	24.6(8)	56.7(12)	37.5(9)	-12.8(8)	4.2(7)	-17.3(8)
C23	18.5(11)	72(2)	45.1(14)	0	12.0(10)	0
C24	46.1(15)	59.3(17)	20.5(10)	0	13.7(10)	0
C25	15.3(9)	21.7(10)	15.9(8)	0	0.3(7)	0
C26	19.4(7)	35.2(9)	42.6(9)	-15.6(7)	2.6(6)	3.4(6)
C27	19.0(10)	43(9)	23.1(10)	1(4)	-3.3(8)	1(3)
C28	39(3)	29(3)	40(3)	-10(2)	23(2)	-10(2)
C29	30.2(18)	52(3)	52(2)	-12.3(17)	18.1(16)	-6.0(15)
C30	33.9(19)	39(2)	35.0(18)	-5.2(15)	13.7(15)	9.1(15)
C31	42(3)	23(2)	34(3)	-6.5(19)	14(2)	9.2(18)

Table B-74 Bond Lengths for **30**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe1	O1	1.8977(13)	C6	C6 ¹	1.435(3)
Fe1	O2	2.1494(14)	C7	C8	1.526(2)
Fe1	N1	2.0645(15)	C7	C9	1.527(2)
Fe1	N2 ¹	2.1992(12)	C7	C10	1.532(2)
Fe1	N2	2.1991(12)	C12	C13	1.505(2)
O1	C15	1.325(2)	C12	C14	1.523(3)
O2	C28	1.377(6)	C15	C16	1.435(3)
O2	C31	1.530(6)	C15	C20	1.424(3)
N1	C1	1.3906(16)	C16	C17	1.391(3)
N1	C1 ¹	1.3906(16)	C16	C21	1.533(3)
N2	N3	1.3315(15)	C17	C18	1.378(3)
N2	C11	1.3565(17)	C18	C19	1.388(3)
N3	N4	1.3129(17)	C18	C24	1.509(3)
N4	N5	1.3313(16)	C19	C20	1.396(3)
N4	C12	1.4855(18)	C20	C25	1.542(3)
N5	C11	1.3367(18)	C21	C22	1.540(2)
C1	C2	1.4092(19)	C21	C22 ¹	1.540(2)
C1	C6	1.4230(18)	C21	C23	1.541(3)
C2	C3	1.4008(18)	C25	C26	1.5307(18)
C2	C11	1.4562(18)	C25	C26 ¹	1.5307(18)
C3	C4	1.3968(19)	C25	C27	1.537(4)
C4	C5	1.395(2)	C28	C29	1.528(7)
C4	C7	1.5366(19)	C29	C30	1.514(5)
C5	C6	1.3892(19)	C30	C31	1.498(8)

Table B-75 Bond Angles for **30**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Fe1	O2	114.04(6)	C8	C7	C10	108.00(14)
O1	Fe1	N1	135.28(6)	C9	C7	C4	108.57(12)
O1	Fe1	N2 ¹	94.36(3)	C9	C7	C10	108.76(13)
O1	Fe1	N2	94.36(3)	C10	C7	C4	110.47(12)
O2	Fe1	N2	89.14(3)	N2	C11	C2	124.39(12)
O2	Fe1	N2 ¹	89.14(3)	N5	C11	N2	111.30(11)
N1	Fe1	O2	110.67(6)	N5	C11	C2	124.23(12)
N1	Fe1	N2 ¹	86.20(3)	N4	C12	C13	110.41(12)
N1	Fe1	N2	86.20(3)	N4	C12	C14	107.70(13)
N2	Fe1	N2 ¹	171.06(6)	C13	C12	C14	112.70(14)
C15	O1	Fe1	167.18(12)	O1	C15	C16	121.34(16)
C28	O2	Fe1	128.3(2)	O1	C15	C20	119.71(16)
C28	O2	C31	109.1(2)	C20	C15	C16	118.94(16)
C31	O2	Fe1	122.2(3)	C15	C16	C21	122.05(17)
C1 ¹	N1	Fe1	127.72(7)	C17	C16	C15	118.73(18)

C1	N1	Fe1	127.72(7)	C17	C16	C21	119.22(18)
C1 ¹	N1	C1	104.56(15)	C18	C17	C16	123.11(19)
N3	N2	Fe1	122.25(9)	C17	C18	C19	117.58(18)
N3	N2	C11	106.79(11)	C17	C18	C24	120.4(2)
C11	N2	Fe1	128.52(9)	C19	C18	C24	122.0(2)
N4	N3	N2	105.35(11)	C18	C19	C20	123.28(19)
N3	N4	N5	114.73(11)	C15	C20	C25	122.18(16)
N3	N4	C12	122.85(11)	C19	C20	C15	118.36(17)
N5	N4	C12	121.35(12)	C19	C20	C25	119.46(17)
N4	N5	C11	101.84(11)	C16	C21	C22 ¹	109.96(12)
N1	C1	C2	130.04(12)	C16	C21	C22	109.96(12)
N1	C1	C6	112.13(12)	C16	C21	C23	113.14(19)
C2	C1	C6	117.83(12)	C22	C21	C22 ¹	111.1(2)
C1	C2	C11	122.07(12)	C22	C21	C23	106.28(12)
C3	C2	C1	118.89(12)	C22 ¹	C21	C23	106.28(12)
C3	C2	C11	118.98(12)	C26	C25	C20	110.47(10)
C4	C3	C2	123.25(13)	C26 ¹	C25	C20	110.47(10)
C3	C4	C7	122.44(13)	C26	C25	C26 ¹	110.56(18)
C5	C4	C3	117.68(12)	C26	C25	C27	103.7(16)
C5	C4	C7	119.85(12)	C26 ¹	C25	C27	109.1(16)
C6	C5	C4	120.55(12)	C27	C25	C20	112.31(17)
C1	C6	C6 ¹	105.59(8)	O2	C28	C29	107.4(4)
C5	C6	C1	121.80(13)	C30	C29	C28	101.9(3)
C5	C6	C6 ¹	132.61(8)	C31	C30	C29	102.6(3)
C8	C7	C4	112.29(12)	C30	C31	O2	103.7(4)
C8	C7	C9	108.68(14)				

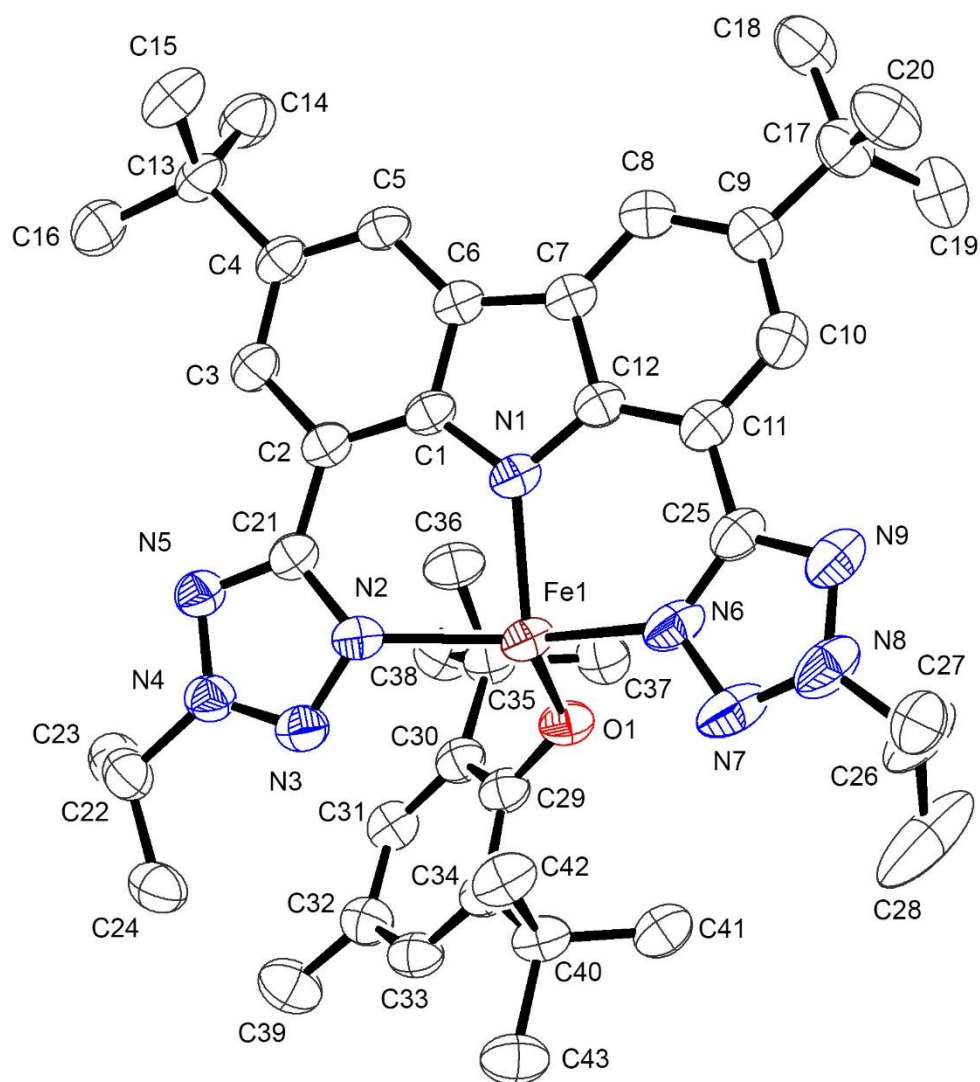


Figure B-23 Labelled ORTEP Drawing of **31**

H atoms not shown

Table B-76 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **31**

Atom	x	y	z	U(eq)
Fe1	5371.8(2)	5046.6(2)	3463.4(3)	37.08(12)
O1	5690.7(4)	5297.5(4)	2580.6(13)	39.7(4)
N1	5380.3(5)	4538.6(5)	3999.4(15)	35.5(4)
N2	5529.7(5)	5184.9(5)	5017.0(16)	38.6(4)
N3	5578.3(5)	5520.7(5)	5298.7(16)	41.7(4)
N4	5776.5(6)	5508.8(5)	6150.3(16)	41.0(4)
N5	5865.7(6)	5184.2(5)	6466.9(16)	40.9(4)
N6	4970.2(5)	4873.8(6)	2404.9(18)	46.6(5)
N7	4768.5(6)	5086.2(7)	1806(2)	57.7(6)
N8	4593.6(6)	4872.8(7)	1173(2)	58.2(6)
N9	4657.9(6)	4533.4(6)	1303.8(18)	50.1(5)
C1	5569.4(6)	4407.4(6)	4858.0(17)	34.6(4)
C2	5727.0(6)	4597.9(6)	5688.5(18)	36.0(5)
C3	5905.5(6)	4407.8(6)	6482.6(18)	37.8(5)
C4	5930.4(6)	4039.9(6)	6485.8(18)	38.9(5)
C5	5769.9(6)	3854.5(6)	5655.0(19)	37.7(5)
C6	5593.8(6)	4033.0(6)	4842.2(18)	34.7(4)
C7	5404.2(6)	3925.2(6)	3897.7(18)	35.9(5)
C8	5342.0(6)	3600.4(6)	3405.0(19)	39.9(5)
C9	5153.7(6)	3581.9(7)	2452(2)	42.7(5)
C10	5012.6(6)	3895.2(7)	2041(2)	42.3(5)
C11	5066.8(6)	4223.3(6)	2517.0(19)	38.9(5)
C12	5276.6(6)	4242.4(6)	3436.9(17)	34.3(4)
C13	6116.6(7)	3838.1(7)	7392.3(19)	43.0(5)
C14	6400.2(8)	3594.3(8)	6921(2)	54.6(7)
C15	5846.4(8)	3619.7(9)	8004(2)	58.5(7)
C16	6306.6(9)	4084.1(8)	8177(2)	58.7(7)
C17	5091.0(7)	3235.3(7)	1845(2)	50.3(6)
C18	5307.1(8)	2931.4(8)	2310(3)	61.1(7)
C19	5196.4(9)	3279.7(9)	671(3)	63.1(8)
C20	4695.2(8)	3141.0(8)	1904(3)	63.5(8)
C21	5708.0(6)	4981.8(6)	5737.1(18)	37.2(5)
C22	5913.3(8)	5830.5(7)	6684(2)	47.5(6)
C23	6315.7(8)	5828.5(8)	6599(2)	54.3(7)
C24	5747.0(8)	6157.5(7)	6197(2)	51.9(6)
C25	4900.8(6)	4537.9(7)	2080.7(19)	41.1(5)
C26	4330.0(8)	5004.3(11)	382(3)	69.9(10)
C27	3967.5(7)	4952.4(8)	817(2)	49.4(6)
C28	4438.0(11)	5318.2(16)	-62(4)	123(2)
C29	5886.7(6)	5581.2(6)	2867.1(18)	37.8(5)
C30	6250.1(6)	5539.1(6)	3109.4(18)	38.8(5)
C31	6435.0(6)	5830.3(7)	3493.5(19)	41.9(5)

C32	6281.4(7)	6161.4(7)	3619(2)	44.2(5)
C33	5932.6(7)	6200.4(6)	3297(2)	42.7(5)
C34	5728.1(6)	5923.6(6)	2912.9(18)	38.7(5)
C35	6447.9(6)	5186.5(6)	2923(2)	42.1(5)
C36	6313.8(7)	4893.0(7)	3659(2)	50.9(6)
C37	6403.0(7)	5076.6(8)	1762(2)	49.7(6)
C38	6848.0(7)	5221.0(8)	3121(3)	53.3(6)
C39	6485.1(8)	6465.0(8)	4092(3)	60.0(7)
C40	5342.3(6)	5991.2(6)	2564(2)	42.2(5)
C41	5282.2(7)	5867.5(7)	1422(2)	48.1(6)
C42	5078.2(6)	5807.1(7)	3311(2)	47.1(6)
C43	5247.9(7)	6387.2(7)	2598(3)	54.6(7)

Table B-77 Anisotropic Displacement Parameters (U_{ij} , Å² x10³) for **31**

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Fe1	34.4(2)	35.5(2)	41.4(2)	11.10(14)	-1.65(14)	0.46(13)
O1	34.8(8)	35.8(8)	48.3(9)	8.3(7)	2.0(7)	-0.9(6)
N1	32.7(9)	35.0(9)	38.9(10)	8.7(7)	-0.8(7)	0.2(7)
N2	41.0(10)	32.0(9)	42.9(10)	4.8(8)	-0.4(8)	1.5(7)
N3	45.5(11)	36.0(10)	43.7(10)	4.8(8)	2.4(9)	0.9(8)
N4	45.7(11)	36.2(10)	41.1(10)	2.3(8)	4.9(8)	-1.8(8)
N5	45.2(11)	37.9(10)	39.5(10)	4.7(8)	1.7(8)	-1.0(8)
N6	35.0(10)	50.0(12)	54.7(12)	20.9(10)	-7.9(9)	-1.5(8)
N7	43.2(12)	58.6(14)	71.3(15)	32.2(12)	-9.2(11)	-0.6(10)
N8	38.1(11)	72.2(16)	64.4(14)	30.4(13)	-16.8(10)	-12.7(11)
N9	38.3(11)	62.9(14)	49.2(12)	21.3(10)	-6.8(9)	-8.1(9)
C1	31.3(10)	36.4(11)	36.2(11)	8.2(8)	4.3(8)	2.4(8)
C2	33.9(10)	37.4(11)	36.6(11)	5.9(9)	2.7(9)	2.3(8)
C3	34.8(11)	42.6(12)	36.1(11)	4.8(9)	0.2(9)	3.9(9)
C4	35.1(11)	44.0(12)	37.5(11)	8.1(9)	1.7(9)	8.3(9)
C5	36.9(11)	34.7(11)	41.5(12)	7.5(9)	4.5(9)	7.5(9)
C6	31.6(10)	35.2(11)	37.4(11)	5.5(9)	4.1(8)	3.2(8)
C7	30.9(10)	37.1(11)	39.5(11)	5.9(9)	3.2(8)	1.8(8)
C8	34.4(11)	38.1(12)	47.0(13)	4.0(9)	5.2(9)	0.4(9)
C9	32.0(11)	47.6(13)	48.6(13)	-1.0(10)	3.6(9)	-5.0(9)
C10	32.3(11)	52.7(14)	41.9(12)	2.5(10)	-1.1(9)	-7.7(9)
C11	30.6(10)	46.0(12)	40.2(11)	8.6(10)	1.8(9)	-2.2(9)
C12	29.2(10)	36.1(11)	37.7(11)	6.2(8)	2.2(8)	-1.0(8)
C13	44.7(13)	45.7(13)	38.7(12)	9.9(10)	-2.1(10)	9.7(10)
C14	55.3(15)	57.4(16)	51.1(14)	9.8(12)	-4.3(12)	17.4(12)
C15	53.7(15)	71.4(19)	50.4(15)	23.8(14)	-1.0(12)	8.2(13)
C16	66.0(18)	58.1(16)	51.9(15)	6.4(13)	-18.2(13)	14.5(13)
C17	39.1(13)	51.1(14)	60.5(16)	-6.1(12)	-1.6(11)	-4.1(11)
C18	58.7(17)	48.7(15)	76(2)	-14.6(14)	-7.9(15)	2.4(12)

C19	57.1(17)	73(2)	58.8(17)	-18.3(15)	-2.5(14)	-4.5(14)
C20	44.3(15)	56.0(16)	90(2)	-12.3(16)	-2.0(15)	-10.5(12)
C21	35.8(11)	39.1(11)	36.6(11)	4.7(9)	1.7(9)	1.4(9)
C22	59.3(15)	41.1(13)	42.1(12)	-4.0(10)	6.9(11)	-8.5(11)
C23	55.9(16)	50.9(15)	56.2(16)	-3.7(12)	1.2(12)	-10.4(12)
C24	63.6(16)	37.6(12)	54.6(15)	-2.3(11)	15.0(13)	-5.0(11)
C25	31.7(10)	49.6(13)	42.1(12)	14.8(10)	-2.1(9)	-5.7(9)
C26	45.0(15)	101(3)	63.4(18)	40.1(18)	-12.1(13)	2.3(15)
C27	43.3(13)	59.5(16)	45.5(13)	3.2(11)	-8.0(10)	2.5(11)
C28	62(2)	187(5)	119(4)	108(4)	-38(2)	-36(3)
C29	37.4(11)	37.8(11)	38.2(11)	7.3(9)	6.6(9)	-0.3(9)
C30	37.0(11)	40.6(12)	38.7(11)	5.9(9)	4.7(9)	1.6(9)
C31	34.6(11)	46.8(13)	44.4(12)	4.8(10)	4.0(9)	0.1(9)
C32	43.3(13)	41.8(12)	47.6(13)	1.8(10)	7.8(10)	-1.8(10)
C33	42.5(12)	36.8(12)	48.7(13)	6.4(10)	10.6(10)	2.7(9)
C34	36.5(11)	39.4(11)	40.2(11)	8.1(9)	8.6(9)	2.0(9)
C35	36.1(11)	42.0(12)	48.1(13)	2.0(10)	2.3(10)	5.3(9)
C36	43.3(13)	45.5(14)	63.9(16)	11.6(12)	0.4(12)	10.4(11)
C37	42.3(13)	52.4(14)	54.3(14)	-5.0(12)	3.3(11)	8.4(11)
C38	39.3(13)	51.4(15)	69.1(17)	-2.3(13)	0.3(12)	6.4(11)
C39	49.9(15)	49.3(15)	81(2)	-7.1(14)	2.1(14)	-4.2(12)
C40	37.6(12)	39.5(12)	49.4(13)	10.0(10)	7.2(10)	4.5(9)
C41	40.4(13)	53.8(15)	50.1(14)	12.3(11)	1.0(10)	4.5(11)
C42	35.1(12)	52.7(14)	53.6(14)	14.6(11)	8.3(10)	7.6(10)
C43	42.9(13)	44.3(14)	76.6(19)	7.5(13)	1.3(13)	8.0(11)

Table B-78 Bond Lengths for **31**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe1	O1	1.8936(16)	C9	C10	1.398(4)
Fe1	N1	2.0359(18)	C9	C17	1.535(4)
Fe1	N2	2.108(2)	C10	C11	1.392(4)
Fe1	N6	2.122(2)	C11	C12	1.404(3)
O1	C29	1.353(3)	C11	C25	1.452(3)
N1	C1	1.386(3)	C13	C14	1.533(4)
N1	C12	1.381(3)	C13	C15	1.522(4)
N2	N3	1.331(3)	C13	C16	1.535(4)
N2	C21	1.365(3)	C17	C18	1.526(4)
N3	N4	1.308(3)	C17	C19	1.539(4)
N4	N5	1.334(3)	C17	C20	1.540(4)
N4	C22	1.482(3)	C22	C23	1.525(4)
N5	C21	1.335(3)	C22	C24	1.517(4)
N6	N7	1.340(3)	C26	C27	1.489(4)
N6	C25	1.359(3)	C26	C28	1.374(5)
N7	N8	1.312(4)	C29	C30	1.416(3)

N8	N9	1.316(4)	C29	C34	1.428(3)
N8	C26	1.493(3)	C30	C31	1.391(4)
N9	C25	1.341(3)	C30	C35	1.547(3)
C1	C2	1.401(3)	C31	C32	1.389(4)
C1	C6	1.419(3)	C32	C33	1.387(4)
C2	C3	1.403(3)	C32	C39	1.505(4)
C2	C21	1.455(3)	C33	C34	1.388(4)
C3	C4	1.394(3)	C34	C40	1.544(3)
C4	C5	1.397(4)	C35	C36	1.531(4)
C4	C13	1.542(3)	C35	C37	1.528(4)
C5	C6	1.394(3)	C35	C38	1.538(3)
C6	C7	1.446(3)	C40	C41	1.527(4)
C7	C8	1.395(3)	C40	C42	1.537(3)
C7	C12	1.417(3)	C40	C43	1.540(3)
C8	C9	1.395(4)			

Table B-79 Bond Angles for **31**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Fe1	N1	131.04(7)	N1	C12	C11	128.6(2)
O1	Fe1	N2	103.80(8)	C11	C12	C7	119.1(2)
O1	Fe1	N6	104.03(8)	C14	C13	C4	109.3(2)
N1	Fe1	N2	85.57(8)	C14	C13	C16	106.6(2)
N1	Fe1	N6	85.89(8)	C15	C13	C4	109.6(2)
N2	Fe1	N6	149.30(8)	C15	C13	C14	109.8(2)
C29	O1	Fe1	126.16(15)	C15	C13	C16	108.5(2)
C1	N1	Fe1	127.12(15)	C16	C13	C4	112.9(2)
C12	N1	Fe1	126.23(15)	C9	C17	C19	110.1(2)
C12	N1	C1	104.76(18)	C9	C17	C20	108.9(2)
N3	N2	Fe1	121.48(15)	C18	C17	C9	111.7(2)
N3	N2	C21	106.97(19)	C18	C17	C19	108.1(3)
C21	N2	Fe1	127.94(16)	C18	C17	C20	109.1(2)
N4	N3	N2	105.33(18)	C19	C17	C20	108.9(3)
N3	N4	N5	114.9(2)	N2	C21	C2	123.9(2)
N3	N4	C22	122.9(2)	N5	C21	N2	110.7(2)
N5	N4	C22	122.1(2)	N5	C21	C2	125.4(2)
N4	N5	C21	102.08(19)	N4	C22	C23	108.2(2)
N7	N6	Fe1	125.13(18)	N4	C22	C24	109.9(2)
N7	N6	C25	106.4(2)	C24	C22	C23	112.9(2)
C25	N6	Fe1	127.86(16)	N6	C25	C11	124.6(2)
N8	N7	N6	105.0(2)	N9	C25	N6	111.2(2)
N7	N8	N9	115.5(2)	N9	C25	C11	124.1(2)
N7	N8	C26	122.4(3)	C27	C26	N8	109.0(2)
N9	N8	C26	122.1(3)	C28	C26	N8	111.1(3)
N8	N9	C25	101.8(2)	C28	C26	C27	122.5(4)

N1	C1	C2	128.0(2)	O1	C29	C30	120.0(2)
N1	C1	C6	112.3(2)	O1	C29	C34	120.0(2)
C2	C1	C6	119.7(2)	C30	C29	C34	120.1(2)
C1	C2	C3	118.1(2)	C29	C30	C35	122.3(2)
C1	C2	C21	121.5(2)	C31	C30	C29	118.3(2)
C3	C2	C21	120.3(2)	C31	C30	C35	119.4(2)
C4	C3	C2	123.1(2)	C32	C31	C30	122.8(2)
C3	C4	C5	118.0(2)	C31	C32	C39	121.2(2)
C3	C4	C13	121.8(2)	C33	C32	C31	117.4(2)
C5	C4	C13	120.2(2)	C33	C32	C39	121.4(2)
C6	C5	C4	120.9(2)	C32	C33	C34	123.4(2)
C1	C6	C7	105.11(19)	C29	C34	C40	122.4(2)
C5	C6	C1	120.3(2)	C33	C34	C29	117.6(2)
C5	C6	C7	134.6(2)	C33	C34	C40	120.0(2)
C8	C7	C6	134.1(2)	C36	C35	C30	111.9(2)
C8	C7	C12	120.4(2)	C36	C35	C38	106.8(2)
C12	C7	C6	105.4(2)	C37	C35	C30	109.0(2)
C7	C8	C9	120.7(2)	C37	C35	C36	110.1(2)
C8	C9	C10	118.0(2)	C37	C35	C38	106.7(2)
C8	C9	C17	123.2(2)	C38	C35	C30	112.2(2)
C10	C9	C17	118.7(2)	C41	C40	C34	110.9(2)
C11	C10	C9	122.7(2)	C41	C40	C42	109.8(2)
C10	C11	C12	118.9(2)	C41	C40	C43	106.8(2)
C10	C11	C25	120.2(2)	C42	C40	C34	111.44(19)
C12	C11	C25	120.9(2)	C42	C40	C43	105.8(2)
N1	C12	C7	112.35(19)	C43	C40	C34	111.8(2)

Table B-80 Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **31**

Atom	x	y	z	U(eq)
H3	6014.57	4535.73	7044.18	45
H5	5780.91	3603.54	5643.63	45
H8	5428.91	3389.45	3721.77	48
H10	4874.05	3883.75	1411.84	51
H14A	6287.48	3417.31	6463.65	82
H14B	6527.16	3475.02	7498.37	82
H14C	6567.19	3734.77	6500.59	82
H15A	5671.54	3777.47	8329.5	88
H15B	5966.82	3484.18	8561.62	88
H15C	5727.06	3456.72	7515.88	88
H16A	6483.23	4225	7795.26	88
H16B	6424.11	3942.31	8725.83	88
H16C	6133.82	4242.04	8511.87	88
H18A	5556.61	3000.62	2348.72	92

H18B	5283.16	2722.52	1854.1	92
H18C	5220.45	2875.95	3025.33	92
H19A	5051.23	3465.22	345.53	95
H19B	5158.64	3056.17	292.73	95
H19C	5446.57	3346.03	625.51	95
H20A	4625.76	3110.8	2649.91	95
H20B	4652.39	2920.38	1515.94	95
H20C	4555.55	3331.79	1585	95
H22	5846.82	5820.14	7453.73	57
H23A	6408.68	5610.66	6915.26	82
H23B	6412.18	6033.41	6978.08	82
H23C	6384.7	5840.29	5848.41	82
H24A	5808.68	6170.19	5440.76	78
H24B	5835.47	6368.69	6562.11	78
H24C	5489.3	6144.94	6272.63	78
H26	4345.42	4830.79	-216.39	84
H27A	3918.53	4698.76	881.59	74
H27B	3794.4	5060.59	336.67	74
H27C	3950.88	5063.65	1519.33	74
H28A	4441.45	5502.74	485.14	184
H28B	4273.57	5386.02	-629.39	184
H28C	4675.91	5289.89	-359.51	184
H31	6676.98	5801.45	3678.3	50
H33	5828.27	6428.49	3342.15	51
H36A	6333.86	4970.22	4400.81	76
H36B	6456.02	4679.2	3552.67	76
H36C	6065.64	4841.68	3495.14	76
H37A	6150.81	5049.86	1600.88	74
H37B	6524.32	4851.15	1640.19	74
H37C	6505.14	5258.45	1298.61	74
H38A	6946.33	5401.25	2645.38	80
H38B	6963.1	4993.36	2981.83	80
H38C	6889.41	5290.22	3861.72	80
H39A	6381.01	6529.78	4778.87	90
H39B	6474.85	6668.37	3609.72	90
H39C	6732.17	6394.59	4195.94	90
H41A	5431.84	6005.44	939.69	72
H41B	5033.2	5901.28	1231.35	72
H41C	5343.06	5616.28	1363.29	72
H42A	5099.16	5550.17	3229.94	71
H42B	4837.11	5880.88	3129.12	71
H42C	5129.8	5872.91	4048.33	71
H43A	5263.16	6472.79	3332.61	82
H43B	5006.58	6421.06	2332.29	82
H43C	5413.75	6519.85	2151.45	82

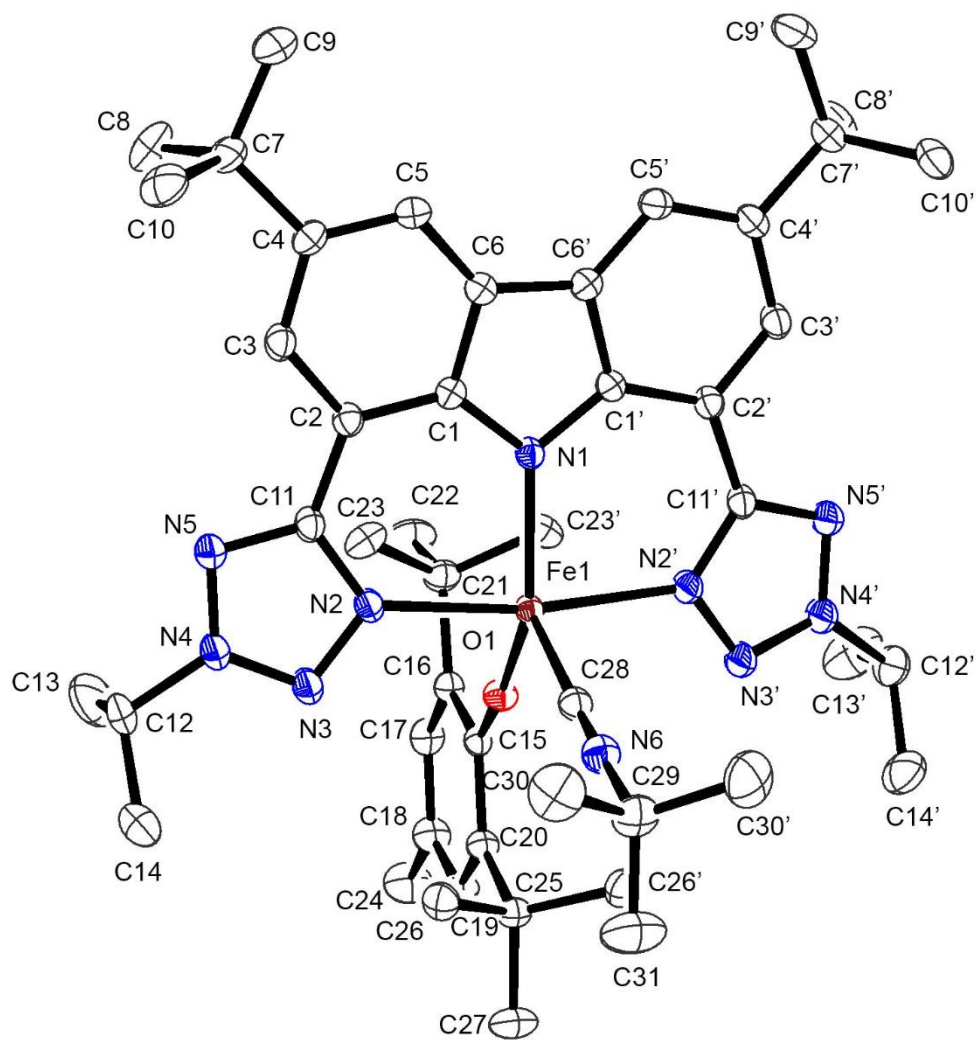


Figure B-24 Labelled ORTEP Drawing of 32

H atoms not shown

Disordered tBu carbons C8A, C9A and C10A not shown

Table B-81 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **32**

Atom	x	y	z	U(eq)
Fe1	5585.4(3)	2500	3431.5(2)	15.10(8)
O1	5328.3(13)	2500	1780.6(12)	18.6(3)
N1	7023.5(15)	2500	4780.9(14)	16.2(3)
N2	5706.4(11)	3730.6(7)	3550.7(10)	20.5(3)
N3	5052.9(12)	4179.2(7)	2793.2(11)	24.9(3)
N4	5479.6(12)	4853.0(7)	3036.5(12)	25.0(3)
N5	6384.8(12)	4885.4(7)	3907.4(12)	24.6(3)
N6	2984.9(17)	2500	4317.1(16)	24.0(4)
C1	7583.1(12)	3114.9(8)	5365.5(12)	16.4(3)
C2	7402.7(13)	3886.7(8)	5153.9(12)	18.2(3)
C3	8114.5(13)	4397.1(8)	5856.5(13)	21.3(3)
C4	8990.8(13)	4187.6(8)	6784.9(13)	21.0(3)
C5	9148.3(13)	3425.8(8)	7010.6(12)	19.6(3)
C6	8467.9(12)	2902.2(8)	6311.0(12)	17.7(3)
C7	9773.9(14)	4786.4(9)	7477.9(14)	26.0(3)
C8	10555(2)	5152.8(14)	6640(2)	35.1(6)
C8A	10993(8)	4728(5)	7254(10)	45(3)
C9	10615(2)	4465.7(14)	8499(2)	40.9(7)
C9A	9768(9)	4586(5)	8848(7)	39(2)
C10	9026(2)	5397.8(15)	7920(3)	33.5(6)
C10A	9243(11)	5557(5)	7314(11)	46(3)
C11	6508.7(13)	4166.1(8)	4220.7(12)	19.1(3)
C12	5119.3(16)	5505.1(9)	2271.3(16)	32.6(4)
C13	5891(2)	5515.7(14)	1319(2)	53.9(6)
C14	3813.0(17)	5470.5(11)	1809.0(18)	38.3(4)
C15	5329.1(18)	2500	641.6(16)	16.2(4)
C16	6424.4(18)	2500	171.3(17)	17.8(4)
C17	6378.6(19)	2500	-1033.5(18)	22.4(4)
C18	5315(2)	2500	-1801.1(18)	24.7(4)
C19	4263(2)	2500	-1334.0(18)	24.0(4)
C20	4230.0(18)	2500	-140.9(17)	18.8(4)
C21	7644.5(19)	2500	954.8(19)	23.0(4)
C22	8689(2)	2500	255(2)	36.4(6)
C23	7780.7(15)	3205.6(10)	1714.4(15)	30.4(4)
C24	5317(2)	2500	-3103(2)	35.7(6)
C25	3010.1(18)	2500	295.5(17)	19.5(4)
C26	2870.4(14)	3203.5(9)	1021.9(14)	24.6(3)
C27	1966(2)	2500	-714(2)	31.1(5)
C28	3882.1(19)	2500	3994.1(17)	19.6(4)
C29	1861(2)	2500	4787(2)	30.0(5)
C30	1849.7(19)	3200.7(12)	5521.6(19)	45.0(5)
C31	851(3)	2500	3766(3)	50.6(8)

Table B-82 Anisotropic Displacement Parameters (U_{ij} , Å² x10³) for **32**

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Fe1	18.25(14)	14.37(14)	12.34(13)	0	1.33(10)	0
O1	20.0(7)	22.8(7)	12.9(6)	0	2.8(5)	0
N1	20.2(8)	14.0(7)	14.3(7)	0	2.5(6)	0
N2	25.8(6)	15.0(6)	19.2(6)	1.6(4)	-1.3(5)	0.2(5)
N3	31.5(7)	15.9(6)	24.7(6)	1.7(5)	-3.7(5)	0.2(5)
N4	30.3(7)	15.5(6)	27.0(6)	2.8(5)	-3.1(5)	0.2(5)
N5	27.4(7)	16.7(6)	27.4(7)	1.4(5)	-3.2(5)	-0.6(5)
N6	25.9(10)	25.2(9)	21.2(9)	0	4.0(7)	0
C1	17.1(6)	16.9(6)	15.5(6)	-1.0(5)	4.1(5)	-0.7(5)
C2	21.5(7)	16.4(6)	16.7(6)	-0.8(5)	3.2(5)	-0.1(5)
C3	26.9(7)	15.8(6)	20.9(7)	-1.1(5)	2.8(6)	-1.0(5)
C4	21.8(7)	20.4(7)	20.4(7)	-4.6(5)	2.5(5)	-3.1(5)
C5	17.9(6)	22.6(7)	18.0(6)	-1.2(5)	1.3(5)	-0.1(5)
C6	17.9(6)	18.9(7)	16.7(6)	0.4(5)	3.7(5)	0.8(5)
C7	27.1(8)	22.4(7)	26.5(8)	-6.9(6)	-2.2(6)	-2.3(6)
C8	33.2(12)	31.2(13)	42.4(14)	-14.3(11)	10.4(10)	-14.0(10)
C8A	42(5)	31(5)	62(6)	-21(5)	13(5)	-19(4)
C9	41.5(15)	31.5(12)	42.6(14)	-5.6(10)	-16.6(12)	-6.0(10)
C9A	55(6)	35(4)	25(4)	-10(3)	-5(4)	-9(4)
C10	32.7(12)	32.4(13)	34.0(14)	-15.1(11)	0.5(11)	-0.4(10)
C10A	59(7)	27(5)	44(6)	-14(4)	-21(5)	-9(4)
C11	23.9(7)	14.8(6)	18.5(6)	-0.6(5)	3.2(5)	0.3(5)
C12	38.5(9)	17.4(7)	38.7(9)	8.9(7)	-3.7(7)	1.0(6)
C13	44.7(12)	53.8(13)	64.4(14)	35.0(12)	12.4(10)	1.5(10)
C14	36.5(10)	31.0(9)	45.4(11)	10.0(8)	0.0(8)	6.0(8)
C15	19.8(9)	14.3(8)	14.6(9)	0	2.6(7)	0
C16	18.1(9)	17.6(9)	18.1(9)	0	3.6(7)	0
C17	24.4(10)	24.4(10)	20.4(10)	0	9.9(8)	0
C18	28.8(11)	30.2(11)	15.9(9)	0	5.6(8)	0
C19	22.0(10)	32.6(11)	16.3(9)	0	-0.4(8)	0
C20	19.0(9)	20.6(9)	16.7(9)	0	3.0(7)	0
C21	16.9(9)	27.8(11)	24.5(10)	0	4.0(8)	0
C22	18.0(11)	54.9(16)	37.4(13)	0	7.9(10)	0
C23	23.7(8)	34.9(9)	31.9(8)	-4.7(7)	1.8(6)	-8.3(7)
C24	37.6(14)	52.8(16)	17.9(10)	0	7.7(9)	0
C25	17.3(9)	23.8(10)	17.1(9)	0	2.1(7)	0
C26	22.8(7)	23.6(7)	28.4(8)	-0.9(6)	6.9(6)	3.1(6)
C27	18.0(10)	47.4(15)	26.6(11)	0	-0.3(9)	0
C28	22.7(10)	19.6(9)	15.9(9)	0	1.4(7)	0
C29	21.4(11)	38.7(13)	31.9(12)	0	10.5(9)	0
C30	41.0(11)	47.3(12)	50.4(12)	-8.6(9)	19.3(9)	6.3(9)
C31	27.0(13)	76(2)	46.9(17)	0	0.8(12)	0

Table B-83 Bond Lengths for **32**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe1	O1	1.8956(14)	C7	C8A	1.451(9)
Fe1	N1	2.0822(17)	C7	C9	1.516(3)
Fe1	N2 ¹	2.2076(12)	C7	C9A	1.633(8)
Fe1	N2	2.2075(12)	C7	C10	1.521(3)
Fe1	C28	2.135(2)	C7	C10A	1.504(10)
O1	C15	1.324(2)	C12	C13	1.514(3)
N1	C1	1.3931(16)	C12	C14	1.499(3)
N1	C1 ¹	1.3931(16)	C15	C16	1.433(3)
N2	N3	1.3294(17)	C15	C20	1.426(3)
N2	C11	1.3503(18)	C16	C17	1.393(3)
N3	N4	1.3128(18)	C16	C21	1.536(3)
N4	N5	1.3279(18)	C17	C18	1.386(3)
N4	C12	1.485(2)	C18	C19	1.386(3)
N5	C11	1.3380(19)	C18	C24	1.513(3)
N6	C28	1.139(3)	C19	C20	1.393(3)
N6	C29	1.463(3)	C20	C25	1.547(3)
C1	C2	1.4110(19)	C21	C22	1.538(3)
C1	C6	1.4215(19)	C21	C23	1.534(2)
C2	C3	1.396(2)	C21	C23 ¹	1.534(2)
C2	C11	1.4548(19)	C25	C26	1.5366(19)
C3	C4	1.401(2)	C25	C26 ¹	1.5366(19)
C4	C5	1.393(2)	C25	C27	1.534(3)
C4	C7	1.538(2)	C29	C30	1.517(2)
C5	C6	1.3930(19)	C29	C30 ¹	1.517(2)
C6	C6 ¹	1.438(3)	C29	C31	1.517(4)
C7	C8	1.559(3)			

Table B-84 Bond Angles for **32**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Fe1	N1	137.96(6)	C9	C7	C10	108.93(18)
O1	Fe1	N2 ¹	93.55(3)	C10	C7	C4	111.68(15)
O1	Fe1	N2	93.55(3)	C10	C7	C8	108.05(18)
O1	Fe1	C28	107.74(7)	C10A	C7	C4	112.5(4)
N1	Fe1	N2 ¹	85.34(3)	C10A	C7	C9A	105.3(6)
N1	Fe1	N2	85.34(3)	N2	C11	C2	124.25(13)
N1	Fe1	C28	114.30(7)	N5	C11	N2	111.35(13)
N2	Fe1	N2 ¹	170.67(6)	N5	C11	C2	124.39(13)
C28	Fe1	N2 ¹	91.80(3)	N4	C12	C13	108.08(15)
C28	Fe1	N2	91.80(3)	N4	C12	C14	110.38(14)
C15	O1	Fe1	171.21(13)	C14	C12	C13	113.02(17)
C1 ¹	N1	Fe1	127.80(8)	O1	C15	C16	121.05(17)
C1	N1	Fe1	127.81(8)	O1	C15	C20	120.14(17)

C1	N1	C1 ¹	104.21(15)	C20	C15	C16	118.82(17)
N3	N2	Fe1	122.46(9)	C15	C16	C21	122.01(17)
N3	N2	C11	106.98(12)	C17	C16	C15	118.89(18)
C11	N2	Fe1	129.85(10)	C17	C16	C21	119.10(18)
N4	N3	N2	105.14(12)	C18	C17	C16	122.73(19)
N3	N4	N5	114.89(12)	C17	C18	C19	117.76(19)
N3	N4	C12	122.21(13)	C17	C18	C24	120.5(2)
N5	N4	C12	122.10(13)	C19	C18	C24	121.7(2)
N4	N5	C11	101.65(12)	C18	C19	C20	123.1(2)
C28	N6	C29	177.4(2)	C15	C20	C25	122.04(17)
N1	C1	C2	130.07(13)	C19	C20	C15	118.67(19)
N1	C1	C6	112.38(12)	C19	C20	C25	119.29(18)
C2	C1	C6	117.56(12)	C16	C21	C22	112.66(18)
C1	C2	C11	122.11(13)	C23	C21	C16	110.06(12)
C3	C2	C1	118.81(13)	C23 ¹	C21	C16	110.06(12)
C3	C2	C11	119.07(13)	C23	C21	C22	106.66(12)
C2	C3	C4	123.63(13)	C23 ¹	C21	C22	106.66(12)
C3	C4	C7	120.11(13)	C23 ¹	C21	C23	110.67(19)
C5	C4	C3	117.49(13)	C26 ¹	C25	C20	110.71(11)
C5	C4	C7	122.34(13)	C26	C25	C20	110.71(11)
C6	C5	C4	120.23(13)	C26 ¹	C25	C26	109.88(17)
C1	C6	C6 ¹	105.52(8)	C27	C25	C20	112.01(17)
C5	C6	C1	122.25(13)	C27	C25	C26 ¹	106.68(11)
C5	C6	C6 ¹	132.22(8)	C27	C25	C26	106.68(11)
C4	C7	C8	107.69(14)	N6	C28	Fe1	178.60(18)
C4	C7	C9A	105.6(3)	N6	C29	C30	107.08(14)
C8A	C7	C4	110.2(3)	N6	C29	C30 ¹	107.08(13)
C8A	C7	C9A	107.8(6)	N6	C29	C31	107.8(2)
C8A	C7	C10A	114.7(7)	C30 ¹	C29	C30	111.3(2)
C9	C7	C4	112.96(15)	C30 ¹	C29	C31	111.65(14)
C9	C7	C8	107.32(18)	C30	C29	C31	111.65(14)

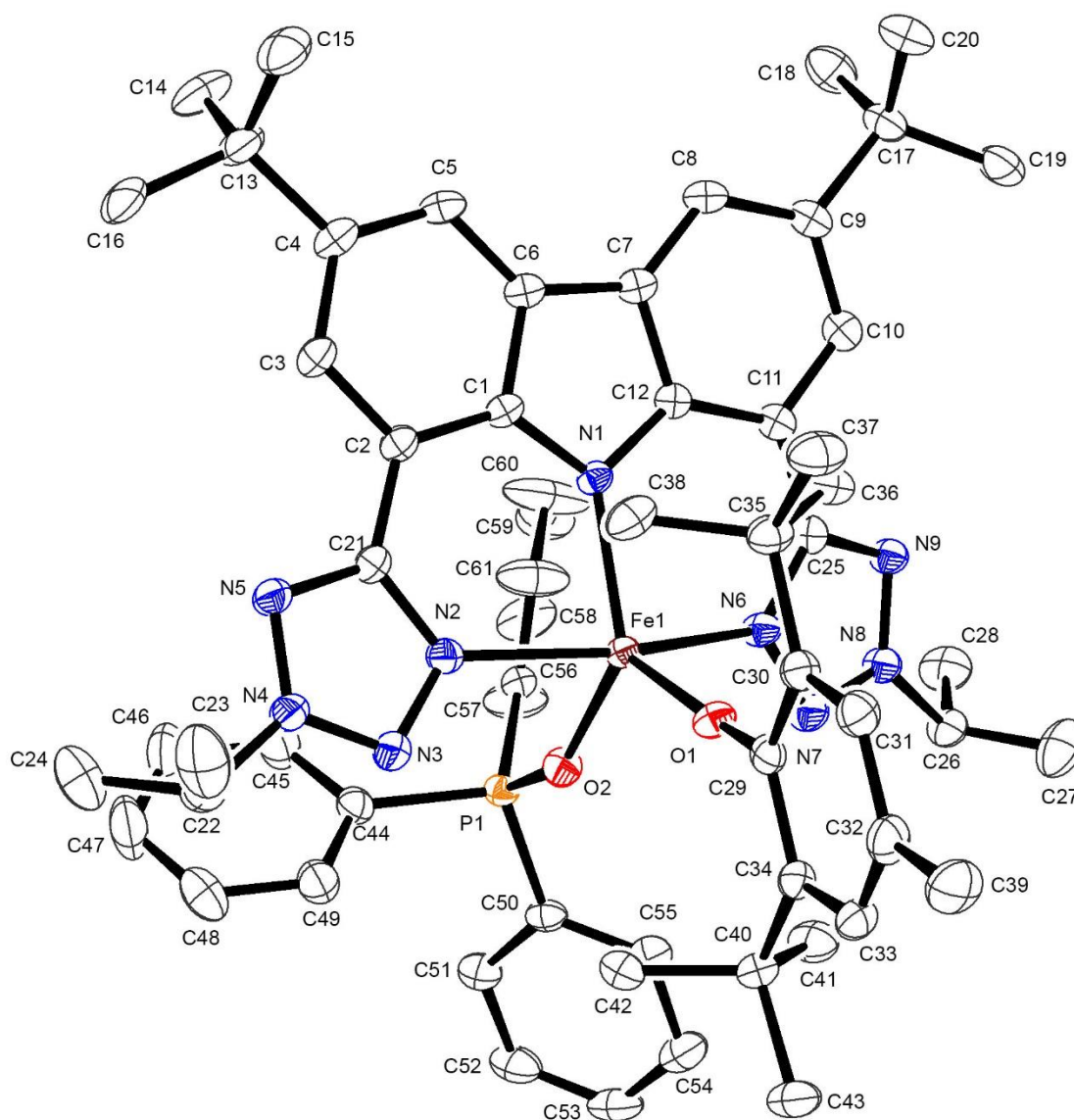


Figure B-25 Labelled ORTEP Drawing of **33**

H atoms not shown

Disordered tBu carbons C14A, C15A, C16A, C18A, C19A and C20A not shown

Table B-85 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **33**

Atom	x	y	z	U(eq)
Fe1	7959.4(2)	2400.7(2)	3623.1(2)	15.16(7)
P1	7570.3(3)	760.7(3)	2628.0(2)	17.49(11)
O1	8965.6(9)	2581.7(9)	4112.0(6)	21.9(3)
O2	7979.1(9)	1328.2(9)	3090.1(6)	21.9(3)
N1	6924.6(10)	3208.3(10)	3530.2(7)	16.4(3)
N2	7165.5(11)	1675.0(11)	4239.4(8)	19.6(4)
N3	7417.6(11)	989.8(11)	4532.6(8)	23.4(4)
N4	6789.4(11)	811.0(11)	4889.5(8)	23.9(4)
N5	6140.5(11)	1336.5(11)	4856.2(8)	23.0(4)
N6	8399.0(11)	3023.5(11)	2812.8(7)	19.7(4)
N7	8983.2(11)	2713.2(11)	2456.5(8)	22.8(4)
N8	9065.1(11)	3270.2(11)	2030.8(8)	21.4(4)
N9	8573.4(11)	3938.4(11)	2075.0(8)	21.2(4)
C1	6196.0(12)	3213.3(13)	3861.0(9)	17.0(4)
C2	5906.2(13)	2617.7(13)	4268.7(9)	18.9(4)
C3	5134.9(13)	2759.3(14)	4545.7(9)	20.7(4)
C4	4646.8(13)	3473.6(14)	4448.7(9)	23.1(5)
C5	4943.5(13)	4070.0(14)	4055.0(9)	22.7(5)
C6	5705.6(13)	3950.9(13)	3766.3(9)	19.0(4)
C7	6177.2(13)	4446.6(13)	3352.2(9)	18.6(4)
C8	6058.8(14)	5240.1(13)	3108.4(9)	21.5(4)
C9	6644.4(14)	5570.5(13)	2715.9(9)	22.0(4)
C10	7332.2(14)	5072.6(13)	2566.4(9)	21.7(4)
C11	7468.1(13)	4269.9(13)	2799.0(9)	19.2(4)
C12	6898.9(13)	3957.9(12)	3218.2(9)	16.5(4)
C13	3805.2(14)	3588.3(15)	4767.1(11)	29.2(5)
C14	3052(3)	3591(4)	4267(3)	38.5(14)
C14A	3154(6)	3184(8)	4474(5)	45(3)
C15	3811(4)	4356(4)	5120(3)	36.4(14)
C15A	3602(8)	4574(8)	4824(9)	70(5)
C16	3593(3)	2837(3)	5184(3)	44.8(18)
C16A	3980(7)	3366(12)	5458(4)	79(6)
C17	6522.0(15)	6452.2(14)	2450.2(10)	25.9(5)
C18	5753(2)	6465(2)	2012.8(15)	34.6(9)
C18A	5631(8)	6874(6)	2671(6)	43(3)
C19	7312(2)	6735(2)	2099.0(18)	37.9(9)
C19A	6353(9)	6410(7)	1765(5)	49(4)
C20	6416(2)	7076.5(19)	2960.5(15)	34.0(9)
C20A	7210(8)	6990(7)	2636(7)	55(4)
C21	6392.3(13)	1879.3(13)	4442.2(9)	18.4(4)
C22	6846.4(15)	127.5(15)	5337.0(11)	31.5(5)
C23	6966.4(19)	497.1(19)	5963.4(12)	46.5(7)

C24	6056.4(19)	-412.3(17)	5281.8(12)	43.1(7)
C25	8153.3(13)	3762.6(13)	2574.5(9)	18.2(4)
C26	9639.3(14)	3140.1(14)	1522.8(9)	24.1(5)
C27	10454.2(16)	3611.9(19)	1646.3(12)	41.4(7)
C28	9171.7(17)	3370.6(17)	934.0(10)	35.4(6)
C29	9551.7(13)	2744.4(13)	4534.0(9)	19.2(4)
C30	9468.2(13)	3419.3(13)	4948.0(9)	21.0(4)
C31	10102.9(14)	3548.0(14)	5400.3(10)	24.6(5)
C32	10830.1(14)	3057.2(14)	5463.1(10)	26.1(5)
C33	10914.4(13)	2414.2(14)	5054.6(10)	24.7(5)
C34	10301.0(13)	2230.1(13)	4595.6(9)	20.7(4)
C35	8678.0(14)	3982.8(14)	4909.3(10)	23.5(5)
C36	8578.1(15)	4404.4(14)	4284.7(10)	26.6(5)
C37	8728.9(16)	4685.4(15)	5383.5(11)	32.5(6)
C38	7882.6(14)	3469.0(15)	5039.2(10)	27.7(5)
C39	11491.4(16)	3222.3(17)	5968.5(12)	36.3(6)
C40	10397.2(13)	1462.3(14)	4190.9(10)	23.3(5)
C41	10406.7(16)	1705.9(15)	3517.1(10)	29.5(5)
C42	9668.2(15)	844.2(14)	4286.8(12)	30.7(5)
C43	11230.4(15)	993.7(15)	4342.0(12)	33.2(6)
C44	6874.4(14)	23.3(13)	2968.7(10)	22.5(4)
C45	6025.4(16)	-74.9(16)	2784.0(12)	37.4(6)
C46	5509.5(19)	-614.3(19)	3093.4(15)	51.5(8)
C47	5842.3(19)	-1063.8(18)	3577.1(14)	48.2(7)
C48	6695.8(18)	-988.0(16)	3753.7(12)	38.3(6)
C49	7208.2(15)	-440.1(14)	3457.6(10)	28.3(5)
C50	8354.0(13)	156.7(13)	2254.9(9)	20.5(4)
C51	8145.9(15)	-606.5(14)	1988.0(10)	27.5(5)
C52	8759.3(17)	-1059.5(15)	1700.9(11)	33.7(6)
C53	9582.8(16)	-769.8(16)	1692.1(10)	33.4(6)
C54	9796.7(15)	-14.8(16)	1960.6(10)	31.6(5)
C55	9183.2(14)	456.2(15)	2238.7(10)	25.4(5)
C56	6933.5(13)	1322.5(13)	2062.7(9)	19.9(4)
C57	6791.8(17)	1047.5(18)	1473.2(11)	39.3(6)
C58	6282.5(17)	1495.8(18)	1061.7(11)	40.8(7)
C59	5942.1(18)	2238.8(18)	1230.8(13)	43.7(7)
C60	6060(2)	2506.3(19)	1816.7(16)	64.6(11)
C61	6550.9(18)	2050.0(17)	2233.0(13)	44.9(7)

Table B-86 Anisotropic Displacement Parameters (U_{ij} , Å² x10³) for **33**

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Fe1	14.11(14)	17.13(15)	14.27(13)	0.67(11)	0.91(10)	1.67(12)
P1	18.9(3)	16.2(3)	17.4(2)	-0.9(2)	1.7(2)	1.7(2)
O1	17.1(7)	24.8(8)	23.6(7)	0.9(6)	-1.4(6)	4.1(6)
O2	22.3(8)	22.8(8)	20.7(7)	-3.1(6)	1.6(6)	-0.5(6)
N1	16.2(8)	19.3(9)	13.9(8)	0.7(7)	2.3(6)	1.8(7)
N2	20.2(9)	18.3(9)	20.6(9)	1.6(7)	3.7(7)	2.2(7)
N3	20.7(9)	23.1(10)	26.8(10)	4.1(8)	5.9(7)	1.4(8)
N4	19.8(9)	25.4(10)	26.9(10)	8.0(8)	6.2(7)	4.7(8)
N5	18.2(9)	25.1(10)	25.9(9)	7.5(8)	4.2(7)	4.5(8)
N6	21.6(9)	21.9(9)	16.0(8)	2.3(7)	4.3(7)	5.0(7)
N7	23.9(9)	25.4(10)	19.8(9)	4.1(8)	7.3(7)	4.3(8)
N8	24.3(9)	22.2(9)	18.2(9)	3.1(7)	7.1(7)	3.6(8)
N9	23.4(9)	21.3(9)	19.2(9)	2.0(7)	5.1(7)	3.5(7)
C1	14.9(10)	21.7(10)	14.2(9)	-2.4(8)	-0.7(7)	2.4(8)
C2	17.2(10)	22.7(11)	16.8(9)	-0.5(8)	1.9(8)	1.6(8)
C3	16.4(10)	28.6(12)	17.2(10)	1.5(9)	2.0(8)	1.2(9)
C4	16.9(10)	33.5(13)	18.9(10)	-1.3(9)	1.9(8)	4.4(9)
C5	19.7(11)	26.5(12)	21.8(11)	-0.1(9)	-0.8(8)	9.3(9)
C6	18.9(10)	21.3(11)	16.6(10)	-1.7(8)	-0.7(8)	3.4(8)
C7	18.5(10)	21.5(11)	15.6(10)	-1.7(8)	-1.3(8)	2.8(8)
C8	22.8(11)	21.6(11)	20.0(10)	-1.9(8)	-0.9(8)	7.1(9)
C9	29.3(12)	18.3(11)	18.1(10)	-0.7(8)	-2.6(9)	2.1(9)
C10	26.7(11)	22.2(11)	16.5(10)	-0.5(8)	1.5(8)	-0.5(9)
C11	23.1(11)	18.9(10)	15.5(10)	-0.6(8)	0.0(8)	1.0(8)
C12	18.1(10)	18.4(10)	12.9(9)	-1.2(8)	-1.9(7)	0.6(8)
C13	20.6(11)	36.8(14)	31.0(12)	4.4(10)	9.6(10)	9.0(10)
C14	17(2)	55(4)	43(3)	-15(2)	0(2)	9(2)
C14A	23(4)	60(7)	52(6)	-8(5)	11(4)	1(5)
C15	31(3)	41(3)	38(3)	-13(2)	12(2)	2(2)
C15A	30(6)	51(8)	131(14)	-38(9)	43(8)	0(5)
C16	32(3)	48(3)	57(4)	22(2)	30(3)	14(2)
C16A	34(5)	173(16)	31(5)	10(7)	18(4)	44(8)
C17	34.0(13)	17.9(11)	26.0(11)	2.2(9)	2.5(9)	3.3(9)
C18	45(2)	27.4(18)	30.9(18)	6.3(14)	-6.1(16)	2.7(15)
C18A	53(7)	17(5)	59(8)	13(5)	17(6)	8(5)
C19	44(2)	20.5(17)	50(2)	10.3(15)	14.9(17)	5.8(14)
C19A	72(9)	33(6)	43(7)	18(5)	11(6)	15(6)
C20	45(2)	20.7(16)	36.3(18)	-3.5(14)	-0.1(15)	7.4(14)
C20A	47(7)	27(6)	91(11)	17(7)	10(7)	-5(5)
C21	16.7(10)	21.8(11)	16.9(10)	-0.8(8)	1.4(8)	-0.3(8)
C22	25.8(12)	32.9(13)	36.3(13)	15.2(11)	6.5(10)	8.3(10)
C23	48.8(17)	53.1(18)	36.0(15)	17.7(13)	-13.6(13)	-15.4(14)
C24	60.6(19)	32.8(14)	35.8(14)	9.1(12)	2.3(13)	-9.7(13)

C25	19.3(10)	20.7(11)	14.6(9)	0.6(8)	0.4(8)	-2.0(8)
C26	26.8(12)	26.8(12)	19.6(10)	-0.3(9)	9.8(9)	3.0(9)
C27	32.5(14)	57.1(18)	35.4(14)	-11.4(13)	11.4(11)	-6.7(13)
C28	42.5(15)	40.0(15)	24.4(12)	-4.2(11)	9.3(11)	6.9(12)
C29	21.6(10)	18.4(10)	18.1(10)	1.5(8)	6.0(8)	-1.1(8)
C30	20.8(11)	21.2(11)	21.3(10)	2.4(8)	2.8(8)	0.1(9)
C31	24.3(11)	23.4(11)	26.0(11)	-3.1(9)	0.0(9)	-2.4(9)
C32	21.3(11)	28.5(12)	28.2(12)	0.9(10)	-3.7(9)	-4.6(9)
C33	17.4(10)	26.5(12)	30.1(12)	4.7(10)	0.3(9)	1.5(9)
C34	18.1(10)	21.0(11)	23.2(11)	3.8(9)	4.0(8)	0.5(8)
C35	22.2(11)	23.8(11)	24.2(11)	-5.0(9)	-0.4(9)	3.2(9)
C36	28.5(12)	22.2(12)	28.8(12)	-2.4(9)	-2.7(9)	5.4(9)
C37	31.9(13)	31.5(13)	33.9(13)	-10.2(11)	-2.7(10)	7.3(11)
C38	21.4(11)	35.6(13)	26.4(12)	-6.4(10)	3.7(9)	4.2(10)
C39	26.2(13)	38.5(15)	43.2(15)	-4.6(12)	-10.1(11)	-0.2(11)
C40	18.3(10)	22.5(11)	29.3(12)	1.0(9)	1.9(9)	4.0(9)
C41	32.8(13)	28.0(13)	28.1(12)	-4.2(10)	5.7(10)	6.4(10)
C42	28.4(12)	18.5(11)	45.3(14)	0.9(10)	3.1(11)	2.5(9)
C43	26.6(12)	28.6(13)	44.1(14)	-0.2(11)	0.3(11)	10.5(10)
C44	25.1(11)	17.9(11)	24.8(11)	-1.6(9)	4.0(9)	-0.2(9)
C45	32.5(14)	35.8(14)	43.5(15)	12.9(12)	-3.3(11)	-5.6(11)
C46	34.4(15)	49.5(18)	70(2)	19.0(16)	-3.8(14)	-16.0(13)
C47	47.4(17)	41.5(16)	56.2(18)	13.3(14)	7.7(14)	-18.2(13)
C48	52.4(17)	27.9(13)	34.5(14)	9.3(11)	2.0(12)	-3.7(12)
C49	29.9(12)	25.9(12)	29.3(12)	1.5(10)	2.7(10)	-1.1(10)
C50	22.4(11)	22.5(11)	16.5(10)	2.0(8)	0.1(8)	6.6(9)
C51	30.0(12)	23.0(12)	29.7(12)	-2.4(9)	2.3(10)	4.0(10)
C52	44.4(15)	24.6(12)	32.6(13)	-2.7(10)	5.6(11)	10.9(11)
C53	39.4(14)	37.1(14)	24.3(12)	6.1(11)	8.6(10)	21.5(12)
C54	24.5(12)	44.2(15)	26.4(12)	7.0(11)	4.3(9)	9.0(11)
C55	25.8(12)	30.7(12)	19.6(10)	0.5(9)	0.2(9)	3.6(10)
C56	17.5(10)	19.7(11)	22.6(10)	1.4(8)	1.0(8)	1.5(8)
C57	49.4(16)	45.2(16)	23.2(12)	-4.5(11)	1.6(11)	24.5(13)
C58	40.7(15)	60.2(18)	21.6(12)	0.3(12)	3.6(11)	17.9(13)
C59	41.7(16)	41.3(16)	46.5(16)	6.7(13)	-14.2(13)	13.7(13)
C60	77(2)	39.4(17)	73(2)	-23.9(16)	-44.0(19)	36.5(16)
C61	52.0(17)	39.5(15)	40.7(15)	-19.4(12)	-22.8(13)	23.1(13)

Table B-87 Bond Lengths for 33

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe1	O1	1.8907(14)	C13	C16	1.561(5)
Fe1	O2	2.0857(14)	C13	C16A	1.574(9)
Fe1	N1	2.0812(17)	C17	C18	1.508(4)
Fe1	N2	2.2149(17)	C17	C18A	1.647(11)

Fe1	N6	2.1835(17)	C17	C19	1.558(4)
P1	O2	1.4884(15)	C17	C19A	1.519(12)
P1	C44	1.798(2)	C17	C20	1.520(4)
P1	C50	1.795(2)	C17	C20A	1.427(13)
P1	C56	1.801(2)	C22	C23	1.504(4)
O1	C29	1.302(3)	C22	C24	1.513(4)
N1	C1	1.383(2)	C26	C27	1.500(3)
N1	C12	1.386(3)	C26	C28	1.505(3)
N2	N3	1.327(2)	C29	C30	1.426(3)
N2	C21	1.352(3)	C29	C34	1.438(3)
N3	N4	1.320(2)	C30	C31	1.390(3)
N4	N5	1.322(2)	C30	C35	1.534(3)
N4	C22	1.475(3)	C31	C32	1.389(3)
N5	C21	1.334(3)	C32	C33	1.380(3)
N6	N7	1.330(2)	C32	C39	1.508(3)
N6	C25	1.347(3)	C33	C34	1.394(3)
N7	N8	1.306(2)	C34	C40	1.533(3)
N8	N9	1.328(2)	C35	C36	1.533(3)
N8	C26	1.482(2)	C35	C37	1.537(3)
N9	C25	1.337(3)	C35	C38	1.534(3)
C1	C2	1.402(3)	C40	C41	1.534(3)
C1	C6	1.423(3)	C40	C42	1.537(3)
C2	C3	1.398(3)	C40	C43	1.532(3)
C2	C21	1.452(3)	C44	C45	1.384(3)
C3	C4	1.391(3)	C44	C49	1.390(3)
C4	C5	1.387(3)	C45	C46	1.386(4)
C4	C13	1.534(3)	C46	C47	1.369(4)
C5	C6	1.393(3)	C47	C48	1.382(4)
C6	C7	1.440(3)	C48	C49	1.376(3)
C7	C8	1.393(3)	C50	C51	1.392(3)
C7	C12	1.420(3)	C50	C55	1.389(3)
C8	C9	1.394(3)	C51	C52	1.383(3)
C9	C10	1.395(3)	C52	C53	1.374(4)
C9	C17	1.541(3)	C53	C54	1.384(4)
C10	C11	1.400(3)	C54	C55	1.389(3)
C11	C12	1.406(3)	C56	C57	1.378(3)
C11	C25	1.454(3)	C56	C61	1.374(3)
C13	C14	1.576(6)	C57	C58	1.382(3)
C13	C14A	1.349(10)	C58	C59	1.367(4)
C13	C15	1.457(7)	C59	C60	1.363(4)
C13	C15A	1.622(13)	C60	C61	1.379(4)

Table B-88 Bond Angles for **33**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Fe1	O2	114.39(6)	C16A	C13	C15A	100.0(8)
O1	Fe1	N1	125.93(6)	C9	C17	C18A	111.1(4)
O1	Fe1	N2	102.21(6)	C9	C17	C19	111.6(2)
O1	Fe1	N6	96.12(6)	C18	C17	C9	109.7(2)
O2	Fe1	N2	86.11(6)	C18	C17	C19	108.1(2)
O2	Fe1	N6	84.64(6)	C18	C17	C20	110.5(2)
N1	Fe1	O2	119.48(6)	C19A	C17	C9	110.3(5)
N1	Fe1	N2	86.00(6)	C19A	C17	C18A	101.5(7)
N1	Fe1	N6	84.75(6)	C20	C17	C9	110.1(2)
N6	Fe1	N2	161.58(7)	C20	C17	C19	106.9(2)
O2	P1	C44	111.72(9)	C20A	C17	C9	111.6(5)
O2	P1	C50	111.16(9)	C20A	C17	C18A	107.9(7)
O2	P1	C56	111.83(9)	C20A	C17	C19A	113.9(8)
C44	P1	C56	106.86(10)	N2	C21	C2	125.45(18)
C50	P1	C44	106.03(10)	N5	C21	N2	111.41(18)
C50	P1	C56	108.99(9)	N5	C21	C2	123.04(18)
C29	O1	Fe1	168.34(13)	N4	C22	C23	108.6(2)
P1	O2	Fe1	150.81(9)	N4	C22	C24	110.5(2)
C1	N1	Fe1	127.73(13)	C23	C22	C24	111.5(2)
C1	N1	C12	104.45(16)	N6	C25	C11	124.40(18)
C12	N1	Fe1	126.53(13)	N9	C25	N6	111.28(18)
N3	N2	Fe1	124.82(13)	N9	C25	C11	124.11(18)
N3	N2	C21	107.03(16)	N8	C26	C27	109.56(18)
C21	N2	Fe1	127.78(14)	N8	C26	C28	108.96(18)
N4	N3	N2	104.82(16)	C27	C26	C28	114.1(2)
N3	N4	N5	114.98(17)	O1	C29	C30	121.66(19)
N3	N4	C22	122.36(17)	O1	C29	C34	119.92(18)
N5	N4	C22	122.37(17)	C30	C29	C34	118.42(19)
N4	N5	C21	101.76(16)	C29	C30	C35	120.76(19)
N7	N6	Fe1	124.15(13)	C31	C30	C29	119.09(19)
N7	N6	C25	107.09(16)	C31	C30	C35	120.13(19)
C25	N6	Fe1	128.77(13)	C32	C31	C30	123.0(2)
N8	N7	N6	105.00(16)	C31	C32	C39	120.5(2)
N7	N8	N9	115.14(16)	C33	C32	C31	117.6(2)
N7	N8	C26	121.81(17)	C33	C32	C39	121.9(2)
N9	N8	C26	123.00(17)	C32	C33	C34	123.1(2)
N8	N9	C25	101.50(16)	C29	C34	C40	120.66(18)
N1	C1	C2	129.27(18)	C33	C34	C29	118.69(19)
N1	C1	C6	112.47(18)	C33	C34	C40	120.54(19)
C2	C1	C6	118.25(18)	C30	C35	C37	112.31(18)
C1	C2	C21	122.98(18)	C36	C35	C30	111.05(17)
C3	C2	C1	118.71(19)	C36	C35	C37	106.46(19)
C3	C2	C21	118.23(18)	C36	C35	C38	110.77(18)

C4	C3	C2	123.3(2)	C38	C35	C30	109.51(18)
C3	C4	C13	120.6(2)	C38	C35	C37	106.62(18)
C5	C4	C3	117.89(19)	C34	C40	C41	111.17(18)
C5	C4	C13	121.5(2)	C34	C40	C42	110.29(17)
C4	C5	C6	120.7(2)	C41	C40	C42	109.77(19)
C1	C6	C7	105.26(17)	C43	C40	C34	112.08(19)
C5	C6	C1	121.16(19)	C43	C40	C41	106.77(18)
C5	C6	C7	133.6(2)	C43	C40	C42	106.59(19)
C8	C7	C6	133.39(19)	C45	C44	P1	123.22(18)
C8	C7	C12	121.33(19)	C45	C44	C49	119.3(2)
C12	C7	C6	105.26(17)	C49	C44	P1	117.46(17)
C7	C8	C9	120.48(19)	C44	C45	C46	120.2(2)
C8	C9	C10	117.81(19)	C47	C46	C45	120.1(3)
C8	C9	C17	120.71(19)	C46	C47	C48	120.1(2)
C10	C9	C17	121.48(19)	C49	C48	C47	120.2(2)
C9	C10	C11	123.3(2)	C48	C49	C44	120.1(2)
C10	C11	C12	118.54(19)	C51	C50	P1	121.13(17)
C10	C11	C25	119.67(18)	C55	C50	P1	119.12(17)
C12	C11	C25	121.67(18)	C55	C50	C51	119.7(2)
N1	C12	C7	112.53(17)	C52	C51	C50	120.1(2)
N1	C12	C11	129.06(18)	C53	C52	C51	120.2(2)
C11	C12	C7	118.41(18)	C52	C53	C54	120.0(2)
C4	C13	C14	108.4(2)	C53	C54	C55	120.4(2)
C4	C13	C15A	109.2(5)	C54	C55	C50	119.4(2)
C4	C13	C16	112.7(2)	C57	C56	P1	123.28(17)
C4	C13	C16A	107.4(3)	C61	C56	P1	118.27(17)
C14A	C13	C4	111.9(4)	C61	C56	C57	118.4(2)
C14A	C13	C15A	111.1(7)	C56	C57	C58	120.8(2)
C14A	C13	C16A	116.5(7)	C59	C58	C57	119.9(2)
C15	C13	C4	111.1(3)	C60	C59	C58	119.7(2)
C15	C13	C14	110.8(3)	C59	C60	C61	120.5(3)
C15	C13	C16	109.8(3)	C56	C61	C60	120.6(2)
C16	C13	C14	103.8(3)				

Table B-89 Summary of Crystallographic Data for **35^a**

Emp. Formula	C₇₁H₉₅Cl₃Fe₂N₁₈O
Formula wgt.(g/mol)	1434.69
Temp. (K)	119.98
Crystal System	Triclinic
Space Group	P-1
a (Å)	13.4707(11)
b (Å)	14.4407(12)
c (Å)	20.1411(16)
α (°)	92.296(3)
β (°)	99.465(3)
γ (°)	92.199(3)
Volume (Å³)	3857.5(5)
Z	2
Density (g/cm³)	1.235
Abs. coeff. μ (mm⁻¹)	0.533
F(000)	1516
Crystal Size (mm)	0.295 x 0.22 x 0.126
Colour and habit	Red block
Theta range (°)	$2.826^\circ \leq 2\theta \leq 54.362^\circ$
Refl. Collected	57336
Independent refl.	17060
GooF (F²)	1.088
Final R [$I > 2\sigma(I)$]	0.0652
Final wR2	0.1682
R (all data)	0.0869
wR2 (all data)	0.1795
Max peak/hole (e/Å³)	0.880/-0.573

^a Data collected on a Bruker PHOTON-II diffractometer using Mo K α radiation (λ = 0.71073 Å) at the University of Notre Dame.

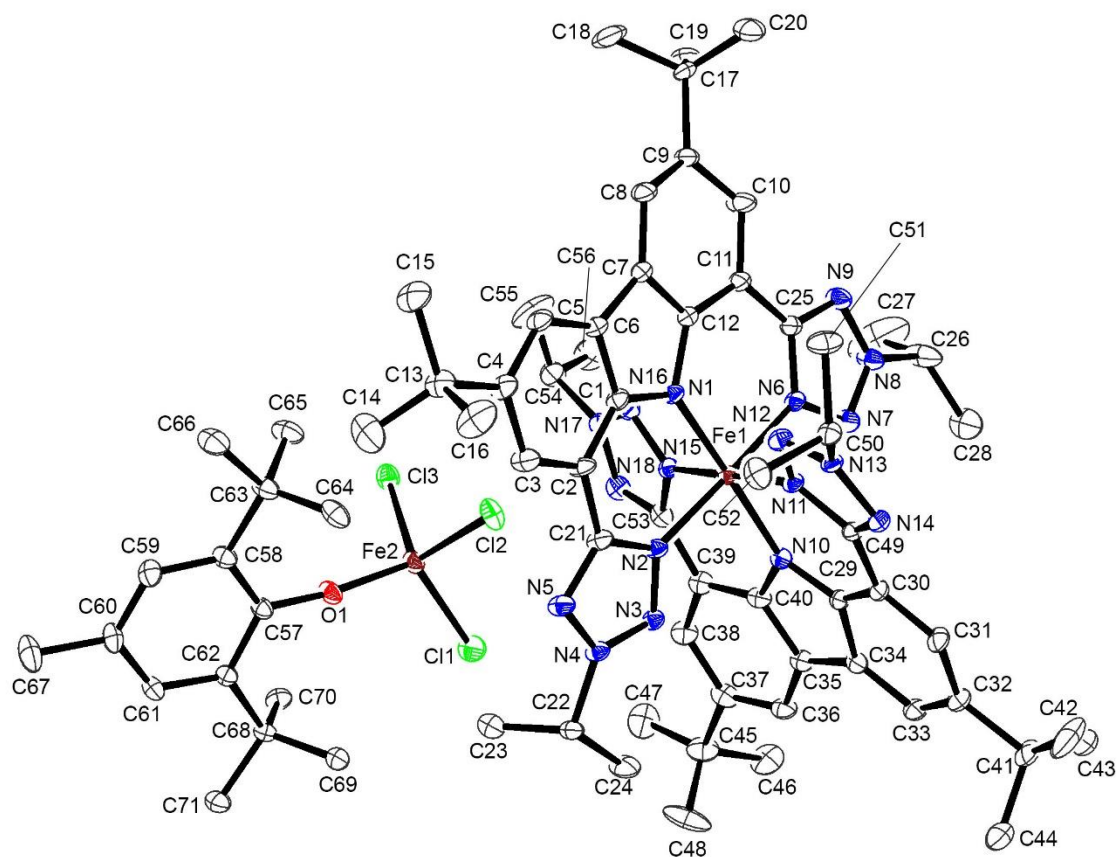


Figure B-26 Labelled ORTEP Drawing of **35**

H atoms not shown

Disordered tBu carbons C9A, C17A, C18A, C19A, C20A, C46A, C47A and C48A not shown

Table B-90 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **35**

Atom	x	y	z	U(eq)
Fe1	5872.9(3)	7748.0(3)	3196.5(2)	20.99(12)
Fe2	5709.5(4)	3467.9(4)	2179.7(3)	28.82(13)
Cl1	4087.0(8)	3427.8(9)	2252.5(5)	46.1(3)
Cl2	6259.0(9)	4936.4(7)	2350.9(5)	40.8(2)
Cl3	6490.5(8)	2672.4(7)	3029.7(5)	35.1(2)
O1	5982.6(19)	3010.7(19)	1381.8(12)	30.6(6)
N1	7284(2)	7687(2)	3151.2(14)	21.4(6)
N2	5554(2)	7240(2)	2257.5(14)	23.5(6)
N3	4631(2)	6928(2)	1978.5(14)	23.7(6)
N4	4716(2)	6627(2)	1371.0(14)	25.7(6)
N5	5638(2)	6716(2)	1220.3(15)	30.7(7)
N6	6215(2)	8191(2)	4153.4(14)	23.4(6)
N7	5513(2)	8343(2)	4535.8(15)	32.0(7)
N8	6023(2)	8499(3)	5146.3(15)	34.5(7)
N9	7013(2)	8460(3)	5199.6(16)	36.9(8)
N10	4440(2)	7824(2)	3191.0(14)	23.4(6)
N11	5920(2)	9011(2)	2875.9(14)	21.7(6)
N12	6748(2)	9384(2)	2704.6(15)	25.4(6)
N13	6500(2)	10189(2)	2472.8(14)	22.2(6)
N14	5532(2)	10383(2)	2474.8(15)	25.7(6)
N15	5807(2)	6498(2)	3530.1(14)	23.4(6)
N16	6629(2)	6081(2)	3796.7(14)	26.6(6)
N17	6298(2)	5280(2)	3972.9(15)	28.9(6)
N18	5301(3)	5132(2)	3849.6(16)	32.3(7)
C1	7718(3)	7551(3)	2579.0(17)	25.4(7)
C2	7231(2)	7308(3)	1921.6(18)	29.6(8)
C3	7821(3)	7228(3)	1412.2(19)	34.4(9)
C4	8865(3)	7382(3)	1534.9(19)	31.9(8)
C5	9332(3)	7602(3)	2191.1(19)	30.4(8)
C6	8773(2)	7686(2)	2710.4(18)	25.7(7)
C7	9026(3)	7907(3)	3425.8(19)	29.4(8)
C8	9925(3)	8059(4)	3869(2)	47.2(12)
C9	9892(7)	8070(7)	4613(5)	28(2)
C9A	9948(8)	8457(9)	4488(6)	26(2)
C10	8990(3)	8305(4)	4773(2)	59.3(16)
C11	8077(3)	8157(3)	4334.7(19)	32.9(8)
C12	8097(3)	7919(2)	3660.0(18)	26.0(7)
C13	9456(3)	7310(3)	941(2)	38.2(9)
C14	9152(4)	6425(4)	520(3)	67.6(17)
C15	10589(3)	7348(4)	1190(2)	51.0(12)
C16	9209(4)	8132(4)	497(3)	60.9(15)
C17	10882(6)	8146(10)	5122(5)	37(2)

C17A	10956(7)	8674(10)	4966(6)	36(2)
C18	11726(8)	7674(11)	4833(6)	61(3)
C18A	11649(8)	9298(9)	4644(5)	55(3)
C19	10724(6)	7567(6)	5728(4)	47(2)
C19A	11391(16)	7779(12)	5134(10)	80(6)
C20	10826(10)	9205(11)	5582(7)	71(4)
C20A	11206(10)	9129(9)	5336(8)	48(3)
C21	6158(3)	7101(3)	1789.8(17)	28.5(8)
C22	3866(3)	6164(3)	897.0(18)	27.4(7)
C23	4144(4)	5180(3)	746(3)	53.9(13)
C24	2911(3)	6213(4)	1193(2)	48.3(12)
C25	7122(3)	8268(3)	4567.2(18)	27.6(7)
C26	5533(3)	8615(5)	5755(2)	60.8(16)
C27	5629(6)	7711(8)	6107(4)	132(4)
C28	4469(4)	8908(5)	5573(3)	65.0(16)
C29	3851(2)	8564(2)	2999.3(17)	24.0(7)
C30	4137(2)	9439(2)	2809.0(18)	25.4(7)
C31	3410(3)	10088(3)	2641(2)	32.0(8)
C32	2383(3)	9891(3)	2648(2)	34.7(9)
C33	2100(3)	8994(3)	2801(2)	32.6(8)
C34	2804(3)	8329(3)	2964.4(18)	27.4(7)
C35	2755(3)	7353(3)	3103.8(18)	28.5(8)
C36	1962(3)	6686(3)	3073.8(19)	33.0(8)
C37	2152(3)	5759(3)	3169(2)	35.8(9)
C38	3164(3)	5510(3)	3320(2)	34.6(8)
C39	3968(3)	6169(3)	3370.2(18)	29.7(8)
C40	3762(3)	7089(3)	3239.7(17)	26.6(7)
C41	1580(3)	10619(3)	2490(2)	42.1(10)
C42	2013(4)	11532(4)	2291(4)	78(2)
C43	1099(3)	10803(4)	3119(3)	54.5(13)
C44	766(4)	10236(4)	1912(3)	54.5(13)
C45	1285(3)	5013(3)	3075(2)	46.0(11)
C46	556(7)	5293(7)	3571(6)	55(3)
C46A	227(9)	5391(9)	2991(9)	69(5)
C47	1664(9)	4065(8)	3267(8)	63(4)
C47A	1362(15)	4322(19)	3589(13)	117(11)
C48	737(10)	5043(10)	2373(5)	78(5)
C48A	1285(10)	4433(10)	2368(7)	60(4)
C49	5186(2)	9630(2)	2731.6(17)	22.6(7)
C50	7206(3)	10759(2)	2148.4(18)	26.1(7)
C51	8218(3)	10849(3)	2607(2)	44.1(10)
C52	7254(3)	10306(3)	1461(2)	38.1(9)
C53	5000(3)	5915(3)	3571.2(18)	28.3(7)
C54	6969(3)	4580(3)	4298(2)	38.5(9)
C55	8045(4)	4875(5)	4277(4)	75.7(19)
C56	6735(5)	4476(5)	5002(3)	68.1(16)

C57	6270(3)	2573(3)	844.3(17)	26.4(7)
C58	7272(3)	2713(3)	715.2(18)	28.5(7)
C59	7549(3)	2193(3)	185(2)	32.5(8)
C60	6896(3)	1582(3)	-237(2)	34.0(8)
C61	5911(3)	1503(3)	-128.6(18)	30.2(8)
C62	5566(3)	1977(2)	400.6(17)	24.7(7)
C63	8009(3)	3460(3)	1113.4(19)	34.1(9)
C64	7556(3)	4415(3)	1034(2)	39.0(9)
C65	8287(3)	3230(3)	1864(2)	42.5(10)
C66	9022(3)	3524(4)	845(2)	45.2(11)
C67	7237(4)	1031(3)	-813(3)	52.7(13)
C68	4462(3)	1843(2)	492.5(18)	26.6(7)
C69	3954(3)	2781(3)	478.5(19)	31.5(8)
C70	4406(3)	1361(3)	1150(2)	32.4(8)
C71	3833(3)	1217(3)	-80(2)	36.3(9)

Table B-91 Anisotropic Displacement Parameters (U_{ij} , Å² x10³) for **35**

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Fe1	16.4(2)	28.2(3)	19.3(2)	1.83(18)	5.37(17)	0.88(18)
Fe2	29.9(3)	35.7(3)	21.2(3)	-4.3(2)	7.4(2)	-1.8(2)
Cl1	33.1(5)	71.3(8)	35.9(5)	-5.7(5)	13.6(4)	0.7(5)
Cl2	61.1(7)	32.9(5)	29.6(5)	-4.6(4)	13.4(4)	-1.6(4)
Cl3	42.8(5)	37.3(5)	26.7(4)	0.4(4)	10.6(4)	3.0(4)
O1	28.8(13)	40.3(15)	22.9(12)	-6.3(11)	8.5(10)	-7.1(11)
N1	16.3(13)	28.9(15)	19.8(13)	2.4(11)	4.4(10)	3.6(11)
N2	17.4(13)	32.8(16)	20.4(14)	2.8(12)	3.5(11)	0.8(11)
N3	19.6(13)	30.8(15)	21.6(14)	3.2(12)	5.3(11)	2.4(11)
N4	18.4(13)	38.3(17)	21.2(14)	4.0(12)	5.0(11)	2.3(12)
N5	20.4(14)	51(2)	21.1(14)	2.7(13)	5.2(11)	1.6(13)
N6	17.4(13)	30.5(15)	23.4(14)	0.2(12)	7.2(11)	1.4(11)
N7	25.4(15)	49(2)	22.5(15)	-2.7(14)	9.2(12)	-1.8(14)
N8	25.6(16)	55(2)	22.9(15)	-5.9(14)	6.4(12)	-6.6(14)
N9	27.5(16)	57(2)	25.4(16)	-10.3(15)	4.4(13)	0.1(15)
N10	20.3(13)	29.4(15)	21.6(14)	0.3(11)	7.8(11)	-1.5(11)
N11	15.3(12)	29.7(15)	21.1(13)	1.0(11)	5.7(10)	1.6(11)
N12	18.6(13)	31.5(16)	27.3(15)	4.4(12)	6.7(11)	0.8(12)
N13	14.8(12)	28.4(15)	23.2(14)	0.3(11)	2.8(11)	1.6(11)
N14	18.9(13)	29.0(15)	29.8(15)	-1.5(12)	6.0(12)	2.1(11)
N15	21.5(14)	30.4(15)	19.3(13)	-0.1(11)	6.1(11)	3.5(12)
N16	27.4(15)	32.2(16)	20.0(14)	0.8(12)	2.5(12)	3.9(12)
N17	32.9(16)	29.6(16)	23.5(15)	2.5(12)	1.9(12)	3.3(13)
N18	38.4(18)	33.4(17)	25.9(16)	4.5(13)	7.4(13)	-0.6(14)
C1	20.7(16)	32.9(19)	24.2(17)	4.1(14)	7.2(13)	3.5(14)
C2	14.1(15)	51(2)	24.0(17)	5.1(16)	4.5(13)	1.8(15)

C3	25.3(18)	58(3)	20.7(17)	5.0(17)	6.1(14)	2.1(17)
C4	22.5(17)	46(2)	30.4(19)	6.5(16)	12.5(15)	2.2(16)
C5	17.3(16)	42(2)	33.3(19)	2.8(16)	7.2(14)	2.1(15)
C6	17.5(15)	29.9(18)	29.7(18)	2.3(14)	3.2(13)	1.6(13)
C7	19.2(16)	36(2)	32.3(19)	-6.3(15)	3.7(14)	4.2(14)
C8	17.4(17)	79(3)	42(2)	-27(2)	0.3(16)	8.5(19)
C9	21(4)	35(5)	26(4)	0(4)	-2(3)	0(4)
C9A	14(4)	34(6)	29(5)	1(5)	4(3)	-2(5)
C10	25(2)	114(5)	34(2)	-35(3)	-2.6(17)	13(2)
C11	20.0(17)	48(2)	29.1(19)	-11.6(16)	1.9(14)	6.0(15)
C12	20.9(16)	28.8(18)	27.1(18)	-2.5(14)	0.8(13)	4.9(14)
C13	27.4(19)	60(3)	30(2)	4.6(18)	14.5(16)	0.6(18)
C14	51(3)	91(4)	67(3)	-29(3)	44(3)	-26(3)
C15	32(2)	86(4)	40(2)	4(2)	17.8(19)	7(2)
C16	49(3)	95(4)	48(3)	27(3)	27(2)	17(3)
C17	21(4)	51(7)	37(5)	-12(4)	-8(3)	16(4)
C17A	29(5)	33(6)	41(6)	3(5)	-9(4)	4(5)
C18	24(5)	106(10)	49(7)	-6(6)	-6(4)	22(5)
C18A	43(6)	80(8)	37(5)	-5(5)	-4(4)	-24(5)
C19	37(4)	54(5)	44(5)	3(4)	-14(4)	8(4)
C19A	60(12)	77(11)	85(14)	-9(10)	-35(10)	6(10)
C20	34(6)	121(11)	48(7)	-13(6)	-14(5)	-12(6)
C20A	31(6)	43(6)	65(9)	-3(6)	-6(6)	-9(5)
C21	19.9(16)	47(2)	20.2(16)	6.3(15)	5.2(13)	3.8(15)
C22	21.1(16)	37(2)	22.8(17)	0.7(14)	-0.2(13)	-0.7(14)
C23	50(3)	52(3)	52(3)	-17(2)	-13(2)	11(2)
C24	18.1(18)	81(3)	44(2)	-15(2)	6.7(17)	-8.2(19)
C25	22.8(17)	33.6(19)	25.5(17)	-3.3(14)	2.3(14)	1.6(14)
C26	31(2)	127(5)	24(2)	-16(3)	10.3(17)	-16(3)
C27	76(5)	255(12)	88(5)	104(7)	49(4)	38(6)
C28	42(3)	108(5)	49(3)	-23(3)	26(2)	0(3)
C29	17.4(15)	33.7(19)	21.7(16)	-6.4(14)	7.2(12)	1.7(13)
C30	18.3(16)	29.4(18)	29.1(18)	-5.0(14)	7.7(13)	1.3(13)
C31	20.0(17)	30.4(19)	47(2)	-4.6(16)	12.7(16)	1.2(14)
C32	17.8(17)	42(2)	45(2)	-6.6(18)	7.1(15)	5.6(15)
C33	14.5(15)	46(2)	38(2)	-9.1(17)	8.2(14)	-0.5(15)
C34	20.6(16)	37(2)	25.4(17)	-6.2(15)	10.1(13)	-3.2(14)
C35	22.4(17)	42(2)	22.5(17)	-1.4(15)	9.2(13)	-3.0(15)
C36	19.6(17)	49(2)	30.6(19)	-2.2(17)	7.4(14)	-3.5(16)
C37	31(2)	45(2)	32(2)	0.4(17)	11.5(16)	-14.5(17)
C38	31(2)	37(2)	37(2)	6.0(17)	8.9(16)	-5.9(16)
C39	26.1(18)	38(2)	26.7(18)	4.0(15)	10.9(14)	-3.9(15)
C40	22.2(16)	38(2)	20.4(16)	2.1(14)	7.3(13)	-5.0(14)
C41	19.7(18)	45(2)	63(3)	-5(2)	11.3(18)	8.5(17)
C42	34(3)	49(3)	157(7)	21(4)	24(3)	18(2)
C43	28(2)	70(3)	63(3)	-22(3)	4(2)	17(2)

C44	42(3)	66(3)	53(3)	-6(2)	1(2)	23(2)
C45	31(2)	52(3)	54(3)	7(2)	6.2(19)	-15.6(19)
C46	32(4)	60(6)	77(8)	13(5)	22(5)	-12(4)
C46A	33(6)	67(8)	106(14)	-25(8)	24(7)	-24(5)
C47	42(6)	41(5)	110(12)	-3(6)	29(6)	-24(4)
C47A	64(13)	150(20)	124(19)	74(17)	-39(12)	-70(14)
C48	68(8)	103(10)	50(6)	2(6)	-13(5)	-60(8)
C48A	41(6)	58(8)	75(9)	-24(6)	-1(6)	-12(6)
C49	17.1(15)	27.4(17)	22.7(16)	-3.8(13)	2.9(12)	0.9(13)
C50	21.5(16)	26.8(18)	31.2(18)	2.4(14)	8.5(14)	-1.5(13)
C51	23.5(19)	53(3)	53(3)	7(2)	-0.7(18)	-9.7(18)
C52	45(2)	41(2)	31(2)	0.5(17)	16.0(18)	-1.2(18)
C53	32.4(19)	29.9(19)	23.7(17)	1.7(14)	9.3(14)	-2.9(15)
C54	44(2)	33(2)	36(2)	6.1(17)	-1.9(18)	6.9(18)
C55	40(3)	79(4)	111(5)	49(4)	8(3)	22(3)
C56	76(4)	85(4)	46(3)	29(3)	6(3)	24(3)
C57	28.5(18)	30.3(18)	20.3(16)	-1.2(14)	5.8(14)	-3.0(14)
C58	30.4(18)	32.6(19)	22.4(17)	1.8(14)	4.4(14)	-3.2(15)
C59	31.8(19)	34(2)	35(2)	0.9(16)	15.3(16)	-1.6(16)
C60	43(2)	29.9(19)	33(2)	-4.1(16)	18.6(17)	0.0(16)
C61	36(2)	27.9(18)	25.6(18)	-5.4(14)	5.6(15)	-4.4(15)
C62	25.9(17)	25.8(17)	22.1(16)	2.0(13)	3.8(13)	-1.0(14)
C63	30.4(19)	48(2)	23.8(18)	-3.9(16)	7.2(15)	-11.8(17)
C64	46(2)	39(2)	31(2)	-5.8(17)	10.2(18)	-16.7(18)
C65	36(2)	64(3)	26(2)	-0.9(19)	3.8(16)	-13(2)
C66	33(2)	64(3)	39(2)	-8(2)	12.5(18)	-19(2)
C67	62(3)	46(3)	55(3)	-20(2)	33(2)	-11(2)
C68	23.9(17)	28.4(18)	25.1(17)	-1.3(14)	-1.1(14)	-3.1(14)
C69	32.3(19)	32(2)	28.9(19)	-0.7(15)	2.1(15)	1.6(15)
C70	24.0(17)	37(2)	36(2)	6.6(16)	5.9(15)	-3.3(15)
C71	32(2)	36(2)	37(2)	-4.4(17)	-2.7(16)	-3.6(16)

Table B-92 Bond Lengths for **35**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe1	N1	1.923(3)	C13	C16	1.528(7)
Fe1	N2	1.974(3)	C17	C17A	0.845(12)
Fe1	N6	1.981(3)	C17	C18	1.530(12)
Fe1	N10	1.936(3)	C17	C19	1.545(16)
Fe1	N11	1.961(3)	C17	C19A	0.880(19)
Fe1	N15	1.956(3)	C17	C20	1.766(18)
Fe2	Cl1	2.2132(12)	C17	C20A	1.494(16)
Fe2	Cl2	2.2138(12)	C17A	C18	1.847(16)
Fe2	Cl3	2.2395(11)	C17A	C18A	1.512(17)
Fe2	O1	1.812(2)	C17A	C19A	1.469(19)

O1	C57	1.350(4)	C17A	C20	1.471(17)
N1	C1	1.386(4)	C17A	C20A	0.980(16)
N1	C12	1.391(4)	C18	C19A	0.83(2)
N2	N3	1.331(4)	C19	C19A	1.64(3)
N2	C21	1.357(4)	C20	C20A	0.777(14)
N3	N4	1.306(4)	C22	C23	1.515(6)
N4	N5	1.330(4)	C22	C24	1.507(5)
N4	C22	1.483(4)	C26	C27	1.511(10)
N5	C21	1.330(5)	C26	C28	1.501(7)
N6	N7	1.333(4)	C29	C30	1.393(5)
N6	C25	1.358(4)	C29	C34	1.428(5)
N7	N8	1.312(4)	C30	C31	1.392(5)
N8	N9	1.324(4)	C30	C49	1.464(4)
N8	C26	1.492(5)	C31	C32	1.404(5)
N9	C25	1.325(5)	C32	C33	1.397(6)
N10	C29	1.386(5)	C32	C41	1.543(5)
N10	C40	1.391(4)	C33	C34	1.386(5)
N11	N12	1.323(4)	C34	C35	1.448(5)
N11	C49	1.363(4)	C35	C36	1.403(5)
N12	N13	1.304(4)	C35	C40	1.410(5)
N13	N14	1.345(4)	C36	C37	1.388(6)
N13	C50	1.481(4)	C37	C38	1.411(6)
N14	C49	1.323(5)	C37	C45	1.540(5)
N15	N16	1.326(4)	C38	C39	1.402(5)
N15	C53	1.364(5)	C39	C40	1.393(5)
N16	N17	1.308(4)	C39	C53	1.448(5)
N17	N18	1.332(5)	C41	C42	1.516(7)
N17	C54	1.482(5)	C41	C43	1.533(6)
N18	C53	1.330(5)	C41	C44	1.532(7)
C1	C2	1.402(5)	C45	C46	1.564(11)
C1	C6	1.407(5)	C45	C46A	1.533(14)
C2	C3	1.400(5)	C45	C47	1.521(14)
C2	C21	1.444(5)	C45	C47A	1.461(19)
C3	C4	1.396(5)	C45	C48	1.486(11)
C4	C5	1.386(5)	C45	C48A	1.621(13)
C4	C13	1.544(5)	C50	C51	1.514(5)
C5	C6	1.389(5)	C50	C52	1.519(5)
C6	C7	1.445(5)	C54	C55	1.503(7)
C7	C8	1.385(5)	C54	C56	1.513(7)
C7	C12	1.410(5)	C57	C58	1.425(5)
C8	C9	1.506(11)	C57	C62	1.427(5)
C8	C9A	1.347(13)	C58	C59	1.389(5)
C9	C9A	0.629(9)	C58	C63	1.542(5)
C9	C10	1.359(11)	C59	C60	1.383(6)
C9	C17	1.540(13)	C60	C61	1.381(5)
C9	C17A	1.685(15)	C60	C67	1.522(5)

C9A	C10	1.508(12)	C61	C62	1.397(5)
C9A	C17	1.725(16)	C62	C68	1.534(5)
C9A	C17A	1.543(15)	C63	C64	1.533(6)
C10	C11	1.394(5)	C63	C65	1.549(5)
C11	C12	1.393(5)	C63	C66	1.549(5)
C11	C25	1.453(5)	C68	C69	1.540(5)
C13	C14	1.510(7)	C68	C70	1.532(5)
C13	C15	1.524(6)	C68	C71	1.550(5)

Table B-93 Bond Angles for **35**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Fe1	N2	89.28(12)	C20A	C17	C20	25.9(6)
N1	Fe1	N6	89.81(11)	C9	C17A	C18	91.3(8)
N1	Fe1	N10	176.91(12)	C9A	C17A	C9	21.9(4)
N1	Fe1	N11	88.58(12)	C9A	C17A	C18	104.5(9)
N1	Fe1	N15	92.36(12)	C17	C17A	C9	65.5(11)
N2	Fe1	N6	176.95(12)	C17	C17A	C9A	87.4(12)
N10	Fe1	N2	88.13(12)	C17	C17A	C18	55.2(10)
N10	Fe1	N6	92.86(11)	C17	C17A	C18A	144.7(14)
N10	Fe1	N11	89.73(12)	C17	C17A	C19A	32.4(12)
N10	Fe1	N15	89.36(12)	C17	C17A	C20	95.6(13)
N11	Fe1	N2	90.27(12)	C17	C17A	C20A	109.6(15)
N11	Fe1	N6	92.62(12)	C18A	C17A	C9	129.6(9)
N15	Fe1	N2	90.56(12)	C18A	C17A	C9A	111.1(9)
N15	Fe1	N6	86.57(12)	C18A	C17A	C18	90.4(9)
N15	Fe1	N11	178.75(12)	C19A	C17A	C9	87.2(11)
Cl1	Fe2	Cl2	106.80(5)	C19A	C17A	C9A	106.7(12)
Cl1	Fe2	Cl3	107.32(5)	C19A	C17A	C18	25.8(10)
Cl2	Fe2	Cl3	107.82(4)	C19A	C17A	C18A	112.4(13)
O1	Fe2	Cl1	114.18(9)	C19A	C17A	C20	110.4(14)
O1	Fe2	Cl2	110.02(9)	C20	C17A	C9	111.9(9)
O1	Fe2	Cl3	110.45(9)	C20	C17A	C9A	112.4(9)
C57	O1	Fe2	171.1(3)	C20	C17A	C18	131.5(10)
C1	N1	Fe1	127.2(2)	C20	C17A	C18A	103.8(12)
C1	N1	C12	104.3(3)	C20A	C17A	C9	140.7(13)
C12	N1	Fe1	127.7(2)	C20A	C17A	C9A	136.0(13)
N3	N2	Fe1	122.4(2)	C20A	C17A	C18	118.7(12)
N3	N2	C21	107.0(3)	C20A	C17A	C18A	78.3(13)
C21	N2	Fe1	130.6(2)	C20A	C17A	C19A	108.6(14)
N4	N3	N2	105.1(3)	C20A	C17A	C20	29.0(9)
N3	N4	N5	115.0(3)	C17	C18	C17A	26.9(5)
N3	N4	C22	122.8(3)	C19A	C18	C17	27.2(14)
N5	N4	C22	122.0(3)	C19A	C18	C17A	50.6(17)
N4	N5	C21	101.9(3)	C17	C19	C19A	31.9(6)

N7	N6	Fe1	122.4(2)	C17	C19A	C17A	30.9(11)
N7	N6	C25	107.0(3)	C17	C19A	C19	68(2)
C25	N6	Fe1	130.0(2)	C17A	C19A	C19	95.6(15)
N8	N7	N6	104.4(3)	C18	C19A	C17	127(3)
N7	N8	N9	115.4(3)	C18	C19A	C17A	104(2)
N7	N8	C26	123.1(3)	C18	C19A	C19	159(2)
N9	N8	C26	121.2(3)	C17A	C20	C17	28.4(5)
N8	N9	C25	101.9(3)	C20A	C20	C17	57.1(15)
C29	N10	Fe1	127.0(2)	C20A	C20	C17A	37.8(13)
C29	N10	C40	105.3(3)	C17A	C20A	C17	32.2(8)
C40	N10	Fe1	126.5(2)	C20	C20A	C17	97.0(18)
N12	N11	Fe1	121.6(2)	C20	C20A	C17A	113.2(19)
N12	N11	C49	106.8(3)	N2	C21	C2	123.1(3)
C49	N11	Fe1	131.4(2)	N5	C21	N2	111.1(3)
N13	N12	N11	105.7(3)	N5	C21	C2	125.7(3)
N12	N13	N14	114.4(3)	N4	C22	C23	108.1(3)
N12	N13	C50	121.0(3)	N4	C22	C24	109.7(3)
N14	N13	C50	124.0(3)	C24	C22	C23	113.2(4)
C49	N14	N13	101.7(3)	N6	C25	C11	123.6(3)
N16	N15	Fe1	121.7(2)	N9	C25	N6	111.2(3)
N16	N15	C53	107.5(3)	N9	C25	C11	125.2(3)
C53	N15	Fe1	130.8(2)	N8	C26	C27	106.5(5)
N17	N16	N15	104.7(3)	N8	C26	C28	111.4(4)
N16	N17	N18	115.4(3)	C28	C26	C27	114.1(5)
N16	N17	C54	123.2(3)	N10	C29	C30	129.4(3)
N18	N17	C54	121.4(3)	N10	C29	C34	111.6(3)
C53	N18	N17	101.8(3)	C30	C29	C34	118.8(3)
N1	C1	C2	127.9(3)	C29	C30	C49	119.1(3)
N1	C1	C6	112.6(3)	C31	C30	C29	119.7(3)
C2	C1	C6	119.6(3)	C31	C30	C49	121.0(3)
C1	C2	C21	120.0(3)	C30	C31	C32	122.2(4)
C3	C2	C1	118.2(3)	C31	C32	C41	122.4(4)
C3	C2	C21	121.6(3)	C33	C32	C31	117.4(3)
C4	C3	C2	122.6(4)	C33	C32	C41	120.1(3)
C3	C4	C13	119.4(3)	C34	C33	C32	121.7(3)
C5	C4	C3	118.2(3)	C29	C34	C35	105.1(3)
C5	C4	C13	122.5(3)	C33	C34	C29	119.8(3)
C4	C5	C6	120.9(3)	C33	C34	C35	135.0(3)
C1	C6	C7	105.5(3)	C36	C35	C34	133.8(4)
C5	C6	C1	120.5(3)	C36	C35	C40	120.1(4)
C5	C6	C7	134.1(3)	C40	C35	C34	105.9(3)
C8	C7	C6	134.0(3)	C37	C36	C35	121.0(4)
C8	C7	C12	120.7(4)	C36	C37	C38	118.2(3)
C12	C7	C6	105.3(3)	C36	C37	C45	121.0(4)
C7	C8	C9	118.1(5)	C38	C37	C45	120.7(4)
C9A	C8	C7	121.2(6)	C39	C38	C37	121.8(4)

C9A	C8	C9	24.7(4)	C38	C39	C53	121.2(4)
C8	C9	C17	119.7(8)	C40	C39	C38	119.1(3)
C8	C9	C17A	104.0(7)	C40	C39	C53	119.7(3)
C9A	C9	C8	63.3(17)	N10	C40	C35	111.9(3)
C9A	C9	C10	91.1(18)	N10	C40	C39	128.2(3)
C9A	C9	C17	96.2(19)	C39	C40	C35	119.8(3)
C9A	C9	C17A	66.2(17)	C42	C41	C32	112.8(3)
C10	C9	C8	113.7(7)	C42	C41	C43	108.4(4)
C10	C9	C17	123.3(8)	C42	C41	C44	108.7(5)
C10	C9	C17A	120.1(8)	C43	C41	C32	108.6(4)
C17	C9	C17A	29.9(5)	C44	C41	C32	109.1(4)
C8	C9A	C10	114.3(8)	C44	C41	C43	109.2(4)
C8	C9A	C17	117.6(8)	C37	C45	C46	107.0(5)
C8	C9A	C17A	121.0(9)	C37	C45	C48A	108.5(5)
C9	C9A	C8	92.0(19)	C46A	C45	C37	114.9(6)
C9	C9A	C10	64.3(16)	C46A	C45	C48A	103.2(8)
C9	C9A	C17	62.6(17)	C47	C45	C37	111.6(6)
C9	C9A	C17A	91.9(19)	C47	C45	C46	107.1(6)
C10	C9A	C17	104.1(8)	C47A	C45	C37	115.2(7)
C10	C9A	C17A	120.1(9)	C47A	C45	C46A	108.5(12)
C17A	C9A	C17	29.3(5)	C47A	C45	C48A	105.5(14)
C9	C10	C9A	24.6(4)	C48	C45	C37	107.8(5)
C9	C10	C11	123.5(5)	C48	C45	C46	108.6(8)
C11	C10	C9A	119.4(6)	C48	C45	C47	114.4(9)
C10	C11	C25	121.2(3)	N11	C49	C30	123.2(3)
C12	C11	C10	118.6(3)	N14	C49	N11	111.3(3)
C12	C11	C25	120.2(3)	N14	C49	C30	125.3(3)
N1	C12	C7	112.4(3)	N13	C50	C51	108.9(3)
N1	C12	C11	128.0(3)	N13	C50	C52	108.2(3)
C11	C12	C7	119.6(3)	C51	C50	C52	113.3(3)
C14	C13	C4	110.7(3)	N15	C53	C39	122.9(3)
C14	C13	C15	109.6(4)	N18	C53	N15	110.6(3)
C14	C13	C16	108.5(4)	N18	C53	C39	126.4(3)
C15	C13	C4	111.3(3)	N17	C54	C55	109.2(4)
C15	C13	C16	108.3(4)	N17	C54	C56	107.5(4)
C16	C13	C4	108.5(4)	C55	C54	C56	114.2(5)
C9	C17	C9A	21.2(4)	O1	C57	C58	120.1(3)
C9	C17	C19	107.5(8)	O1	C57	C62	120.0(3)
C9	C17	C20	104.5(8)	C58	C57	C62	119.9(3)
C9A	C17	C20	91.7(8)	C57	C58	C63	121.7(3)
C17A	C17	C9	84.5(12)	C59	C58	C57	117.7(3)
C17A	C17	C9A	63.3(11)	C59	C58	C63	120.5(3)
C17A	C17	C18	97.9(13)	C60	C59	C58	123.7(4)
C17A	C17	C19	148.4(12)	C59	C60	C67	121.6(4)
C17A	C17	C19A	117(2)	C61	C60	C59	117.5(3)
C17A	C17	C20	56.0(10)	C61	C60	C67	120.9(4)

C17A	C17	C20A	38.2(10)	C60	C61	C62	123.1(3)
C18	C17	C9	110.9(8)	C57	C62	C68	122.1(3)
C18	C17	C9A	111.1(8)	C61	C62	C57	117.9(3)
C18	C17	C19	104.4(10)	C61	C62	C68	120.0(3)
C18	C17	C20	133.4(10)	C58	C63	C65	111.4(3)
C19	C17	C9A	125.8(7)	C58	C63	C66	111.9(3)
C19	C17	C20	92.5(7)	C64	C63	C58	109.7(3)
C19A	C17	C9	126.4(13)	C64	C63	C65	111.7(3)
C19A	C17	C9A	133.6(15)	C64	C63	C66	106.5(3)
C19A	C17	C18	25.4(17)	C66	C63	C65	105.5(3)
C19A	C17	C19	80(2)	C62	C68	C69	110.5(3)
C19A	C17	C20	128.5(13)	C62	C68	C71	112.4(3)
C19A	C17	C20A	113.1(14)	C69	C68	C71	106.1(3)
C20A	C17	C9	112.4(10)	C70	C68	C62	109.7(3)
C20A	C17	C9A	93.4(10)	C70	C68	C69	111.5(3)
C20A	C17	C18	109.7(11)	C70	C68	C71	106.4(3)
C20A	C17	C19	111.8(9)				