SYNTHESIS AND REACTIONS OF PALLADIUM AND PLATINUM COMPLEXES OF THE TYPE $[M_2X_2(PR_3)_4][BF_4]_2$

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ABSTRACT

Studies of the methods available for synthesis of complexes of the type $[M_2X_2(PR_3)_4][BF_4]_2$, where M = Pd or Pt; X = Cl, Br or I; and R = ethyl or phenyl, are reported: including the synthesis and characterisation of the new complexes $[Pd_2Br_2(PEt_3)_4][BF_4]_2$ and $[Pd_2I_2(PPh_3)_4][BF_4]_2$.

Mass spectral studies of nine triethylphosphine complexes of nickel (II), palladium (II) and platinum (II) are described.

Reactions of the cations $[M_2X_2(PR_3)_4]^{2+}$ with aldehydes, acetone, acetyl chloride, carboxylic acids, formate esters, olefins and pyridine are described, and the results compared with reactions of related rhodium (I) and iridium (I) complexes.

The reaction of $[Pt_2Cl_2(PR_3)_4]^{2+}$, where R = ethyl or phenyl, with formic acid leads to catalytic decomposition of the acid to hydrogen and carbon dioxide, and a possible reaction cycle is proposed.

Supervisor: Dr. Keith R. Dixon

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CHAPTER I

INTRODUCTION

The following group VIII transition metal ions show the common electronic configuration $ns^2np^6nd^8$

period	d^8 ions			orbital
4	Fe(0)	Co(I)	Ni(II)	3d
5	Ru(0)	Rh(I)	Pd(II)	4d
6	Os(0)	Ir(I)	Pt(II)	5d

A characteristic feature of transition metals is their ability to form complexes with a variety of neutral ligands which tend to stabilize metal ions, such as d^8, in low oxidation states.

Stabilization is associated with the fact that the donor atoms of these ligands possess vacant orbitals in addition to lone pairs of electrons. The vacant orbitals accept electron density from filled metal orbitals forming a π bond, supplementing the σ bonding arising from lone pair donation. Such ligands are often referred to as π-acceptor (or π-acid) ligands.

Two such ligand types, of present interest, are carbon monoxide and tertiary phosphines. The bonding scheme of a tertiary phosphine is diagramatically represented in figure 1.

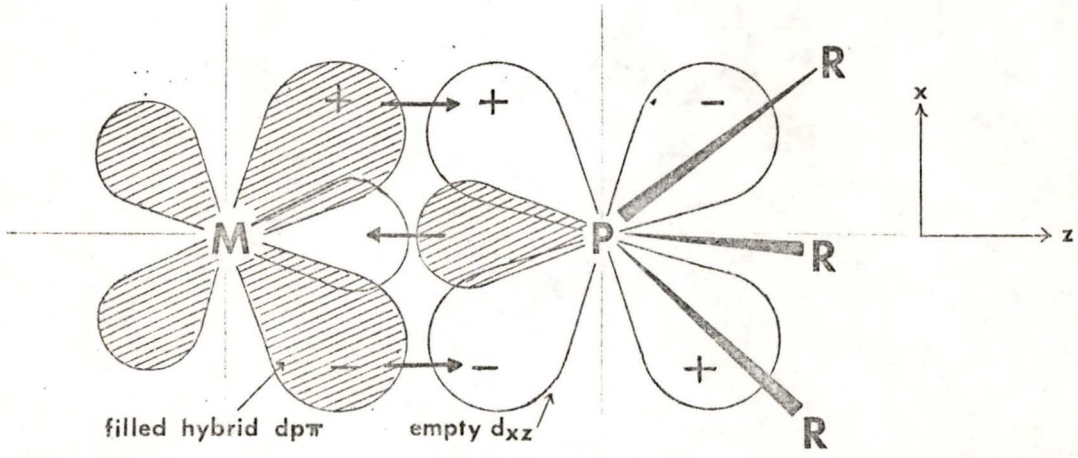


fig. 1. A conventional representation of the bonding in M-PR_3 system. Only the π bonding in the xz plane is shown. A similar interaction is present in the yz plane.

Careful differentiation must be made between a π-acceptor ligand and the so-called π-bonding ligand -- of which an example is the ethylene molecule.

The metal-ethylene bonding may be described as follows:- combination of two carbon p_z orbitals give a π-bonding and a π-antibonding molecular orbital. The vacant anti-bonding molecular orbital accepts electron density from the filled metal orbitals forming a π-bond, which supplements the σ bonding arising from overlap of the filled π-bonding molecular orbital with a vacant metal hybrid orbital.

There is no σ bonding as a result of lone pair donation.

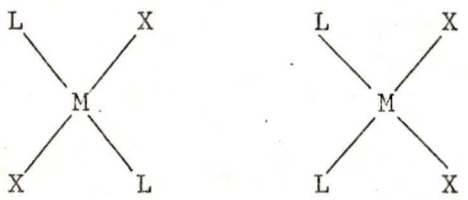
Configuration of d^8 complexes

The transition metal ion shows a coordination number of four (square planar* complexes) or five (trigonal bipyramidal complexes). Tendancy to five coordination increases on (i) ascending a triad (ii) passing right to left in group VIII.

Since the basis of this dissertation is founded on the reactions of complexes of nickel (II), palladium (II) and platinum (II); and of rhodium (I) and iridium (I), square planar configurations are predominant.

Isomerism in Square Planar Complexes

Both cis and trans configurations are known: e.g.



trans cis

L = tertiary phosphine
X = halide
M = metal (II)

* A few complexes, particularly those of nickel (II) e.g., $[NiX_2(PPh_3)_2]$, where X = Cl or I, are thought to possess tetrahedral structures.[1]

Interconversion of isomeric forms is often facile, stability being governed by thermodynamic principles. Well documented criteria for the characterisation of each structural type have been established (see characterisation).

Complexes of d^8 metal ions containing Tertiary Phosphine Ligands

With the possible exception of Fe(0), all group VIII elements belong to Ahrland's class (b) type[2], where the coordinating affinities of donor atom (group V A) for the metal (group VIII) lie in the sequence:

$$N < P > As > Sb > Bi$$

ie. the phosphorus atom coordinates most strongly -- all these metals forming stable phosphine complexes. The high ligand field strength of tertiary phosphines ensures a large energy difference between the low energy and high energy d orbitals of the metal; and generally the most stable complexes occur where the metal has its low energy (bonding) orbitals completely occupied by electrons and its high energy (anti-bonding) orbitals vacant.

The stabilizing effect of phosphine ligands has been utilized in the preparation of a wide range of stable hydrido [3] and organometallic[4] compounds.

The following table illustrates several types of mononuclear tertiary phosphine complexes of d^8 ions.

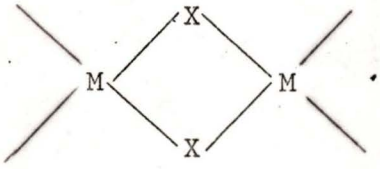
TABLE I. SOME MONONUCLEAR TERTIARY PHOSPHINE d^8 COMPLEXES

M (I)	M (II)
$[MX(PPh_3)_3]$	<u>cis</u> and <u>trans</u>- $[MX_2(PR_3)_2]$ $[MX(PPh_3)_3]^+$ $[Pt(PEt_3)_4]^{2+}$ <u>trans</u>- $[MHX(PPh_3)_2]$ <u>trans</u>- $[MXR(PEt_3)_2]$ <u>trans</u>- $[MR_2(PEt_3)_2]$
<u>trans</u>- $[MCl(CO)(PPh_3)_2]$	<u>trans</u>- $[MCl(CO)(PPh_3)_2]^+$

Where M (I) is rhodium (I) or iridium (I)
M(II) is palladium (II) or platinum (II)
X is Cl, Br or I
R is alkyl or aryl.

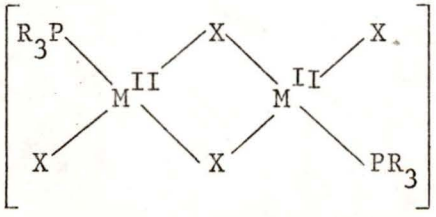
<u>Bridged Binuclear Complexes</u>

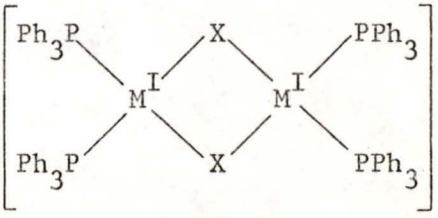
Palladium (II) and platinum (II) chemistry in particular, and also that of rhodium (I), is characterised by the formation of planar binuclear bridge networks:



The bridging species may be halide (most common), azide[5], thiocyanate[6], RS^-,[7] R_2P^-[8] etc.

The following halogen bridged species containing tertiary phosphine ligands:

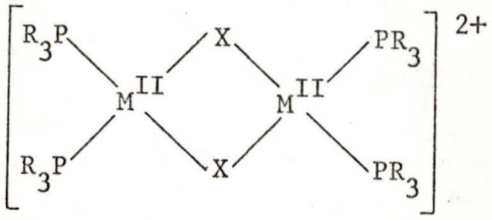




M^{II} is Pt (II) or Pd (II)
X is Cl, Br or I
R_3P is tertiary phosphine

M^{I} is Rh (I)
X is Cl or Br

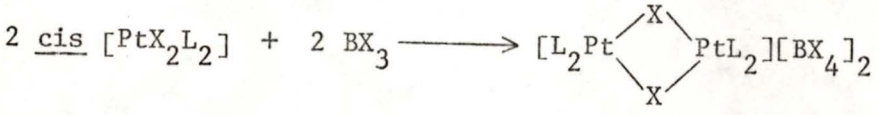
are well known.[9,10,11] However, the cationic species:



M^{II} is Pt (II) or Pd (II)
X is Cl, Br, I
R_3P is tertiary phosphine

have been described only recently.

The first synthesis was reported by Druce et al.,[12] (1967), when the following reaction scheme was used:



where L = $(n\text{-Bu})_3P$; X = Cl or Br.

Since then, Clark et al.,[13,14] (L = PEt_3 and PPh_3) and also Goggin, Goodfellow et al.,[15] (L = PMe_3), have synthesised a number of platinum (II) derivatives.

Both groups also prepared tertiary arsine[15,16] and Clark[16] some stibine analogues. Synthesis of analogous palladium (II) derivatives proved less facile.[17] Results are summarized in Tables IIA and IIB.

TABLE IIA. OCCURENCE OF $[Pt_2X_2L_4]^{2+}$ SPECIES

Halogen = X			PR_3	AsR_3	SbR_3	= L
Cl	Br	I	PMe_3	$AsMe_3$		
Cl	Br	I	PPh_3			
Cl	Br		PEt_3			
Cl				$AsPh_3$	$SbPh_3$	
Cl				$AsEt_3$	$SbEt_3$	

TABLE IIB. OCCURENCE OF $[Pd_2X_2L_4]^{2+}$ SPECIES

Halogen = X			PR_3	AsR_3	SbR_3	= L
Cl	Br	I	PMe_3	$AsMe_3$		
Cl	Br		PPh_3			
Cl			PEt_3			

Characterisation of Tertiary Phosphine Complexes of Platinum (II) and Palladium (II)

(a) Infrared Spectroscopy

A large amount of data has been obtained by several workers,[15,18,19] and a brief summary of the essential vibrational modes will be attempted.

Metal-halogen vibrations

Only metal-chlorine vibrational modes will be discussed, since metal-bromine and metal-iodine modes lie below 250 cm^{-1} and, therefore, beyond the range of the routine spectrophotometric equipment used in this laboratory (see experimental, chapter IV).

Metal-chlorine bonds may be terminal ($[MCl_2(PR_3)_2]$), or bridging ($[M_2Cl_2(PR_3)_4]^{2+}$). The spectral region in which vibrations occur depends in particular on the nature of the transition metal, and on the ligand(s) *trans* to the chlorine.

Some data are summarised in Table III.

Metal-phosphorus vibrations

Until recently, the ν(M-P) stretching frequencies were assigned to bands in the 400-450 cm^{-1} region. However, recent studies[19] of isotopic shifts using, for example, $^{104}PdCl_2(PPh_3)_2$ and $^{110}PdCl_2(PPh_3)_2$, suggest that these assignments are incorrect. It was observed that the bands in the region 400-450 cm^{-1} are not sensitive to metal isotope substitution. Two bands at 360 and 191 cm^{-1} do show large isotopic shifts -- the former being assigned to the Pd-Cl stretching mode, the latter consequently to the Pd-P stretching mode.

(Pd-P) stretching bands were assigned at ca. 235-232 cm^{-1} for *trans*-$[PdX_2(PEt_3)_2]$ and at ca. 190 cm^{-1} for *trans*-$[PdCl_2(PPh_3)_2]$.

TABLE III. METAL-CHLORINE STRETCHING FREQUENCIES (NUJOL MULLS) FOR SOME METAL (II) COMPLEXES[13,15,17,18]

	trans-$[MCl_2(PR_3)_2]$		cis-$[MCl_2(PR_3)_2]$		$[M_2Cl_4(PR_3)_2]$		$[M_2Cl_2(PMe_3)_4]^{2+}$	
	Pd	Pt	* Pd	Pt	Pd	Pt	Pd	Pt
ν(M-Cl)t, asym.	355-60	340	270	277-80	346-56	347-51		
ν(M-Cl)t, sym.			284	300-10		340-4		
ν(M-Cl)b trans to PR_3					256-60	260-5		
ν(M-Cl)b trans to Cl					294-301	327-30 315-22		
ν(M-Cl)b							300 272	308 273

t terminal b bridging * cis $[PdCl_2(PMe_3)_2]$

TABLE IV. PHOSPHINE STRETCHING FREQUENCIES (NUJOL MULLS) FOR SOME METAL (II) COMPLEXES[13,15,17,18]

	trans- $[MX_2(PEt_3)_2]$	trans- $[PdX_2(PPh_3)_2]$	cis- $[MX_2(PR_3)_2]$	$[Pd_2X_4(PR_3)_2]$	$[M_2X_2(PR_3)_4]^{2+}$
"phosphine" vibration	408-15	430-40	415-27 440-45	423-35	415-25 435-445

The bands at 400-450 cm^{-1} may be assignable to internal vibrations of the tertiary phosphine ligand[19]. Their occurrence - a single band for trans isomers, two bands for cis isomers, is still valuable in characterisation[13].

Some data are summarised in Table IV.

Other Stretching Modes

Certain stretching modes, important in later discussion, appear in Table V.

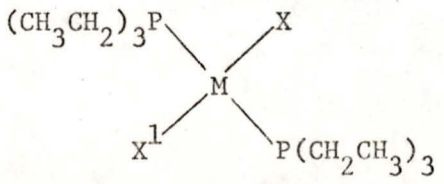
TABLE V. STRETCHING MODES OF SOME NEUTRAL AND CATIONIC PLATINUM (II) SPECIES WITH THEIR COUNTERANIONS[13,14,17]

Compound	Vibration	Assignment and wavenumber (cm^{-1})
trans- $[PtHCl(PEt_3)_2]$	Pt-H	ν(Pt-H) 2210; δ(Pt-H) 820;346
trans- $[PtCl(CO)(PEt_3)_2]^+$	Pt-CO	ν_{CO} 2110; δ(Pt-CO) 540,520,500,460
trans- $[PtH(CO)(PEt_3)_2]^+$	Pt-H	ν(Pt-H) 2162
	Pt-CO	ν_{CO} 2043
trans- $[PtCl(COOEt)(PPh_3)_2]$	Pt-$\overset{|}{C}$=O	ν(Pt-$\overset{|}{C}$=O) 1640-5
	BF_4^-	ν_3(B-F) sym.1090;1050
		ν_4(B-F) asym.515
	SiF_5^-	875,775,475,440
	SiF_6^{2-}	740,480

(b) Proton Nuclear Magnetic Resonance Spectroscopy

This technique provides a facile, qualitative distinction between cis and trans configurations for triethylphosphine complexes.[13]

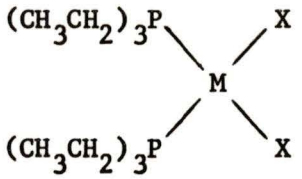
Trans-



Where X = halide; X^1 = halide or hydrido

The methyl proton resonances of trans-$[PtX_2(PEt_3)_2]$, trans-$[PtHX(PEt_3)_2]$ where X = Cl or Br, and analogous palladium (II) complexes, are interpreted as approximately 1:4:6:4:1 quintets centred about -1.2 parts per million (p.p.m.).* These result from overlapping triplets arising from coupling with two methylene protons (J_{H-H} = 8 Hz.) and virtual coupling with two phosphorus nuclei (J_{P-H} = 7.8 Hz.) in a trans configuration. The methylene proton resonances are broad with complex, poorly resolved fine structure -- centred about -1.9 p.p.m.

Cis-



X = halide

The methyl proton resonances of cis-$[PtX_2(PEt_3)_2]$ where X = Cl or Br, are interpreted as approximately 1:2:2:2:1 quintets, centred about -1.2 p.p.m. These result from overlapping triplets arising from coupling with phosphorus (J_{P-H} = 16 Hz.), further split by coupling with two methylene protons (J_{H-H} = 8 Hz.). Virtual coupling with two phosphorus nuclei does not occur. The methylene proton resonances approximate to septets -- centred about -2.1 p.p.m.

The ethyl proton resonances in $[M_2Cl_2(PEt_3)_4][BF_4]_2$ are similar.[13,20] The above interpretations are approximate since they omit, for example, any consideration of coupling with ^{195}Pt. However, as shown in figure 2, they do present a method for configurational analysis.

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* The minus sign indicates that the resonance was downfield from the reference tetramethylsilane resonance.

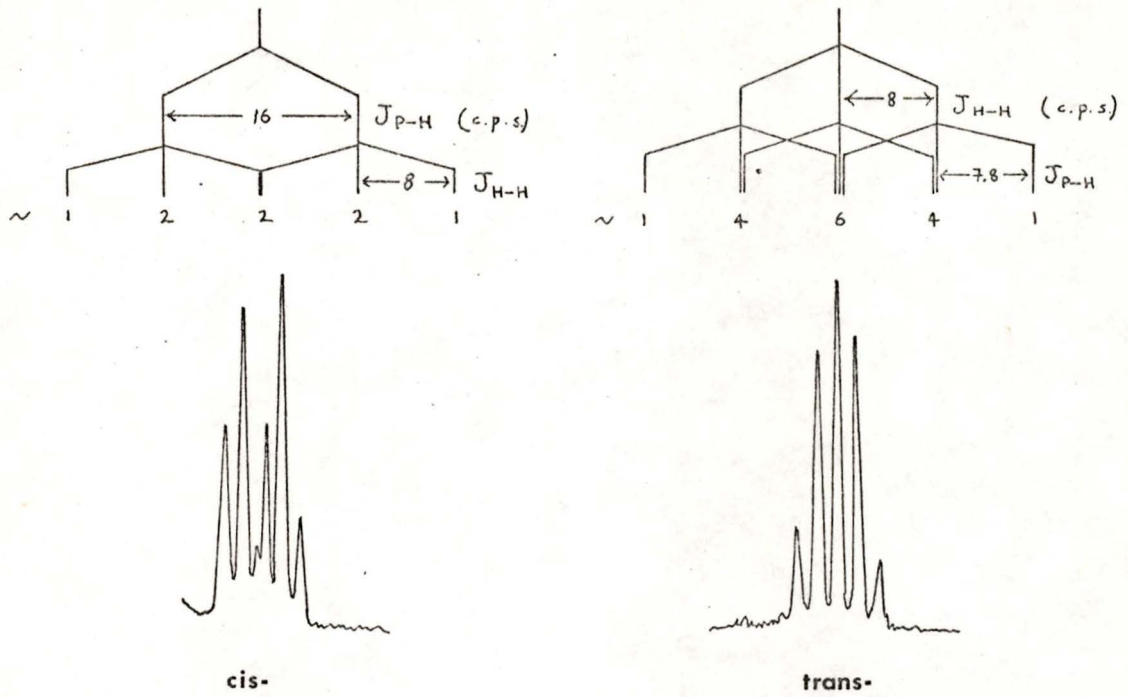
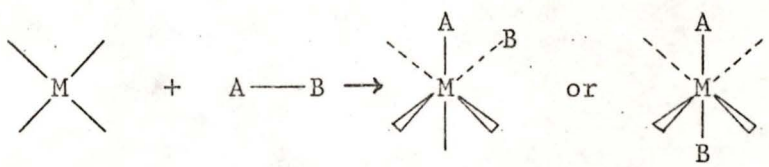


fig. 2. Interpretation of methyl proton Resonances of Triethylphosphine Complexes of Platinum (II) and Palladium (II).

Reactivity of Tertiary Phosphine Complexes of d^8 Ions

An important class of reaction in transition metal chemistry is that involving OXIDATIVE-ADDITIONS of a covalent molecule to, for example, a d^8 complex.[21]



The formal oxidation state of M is raised two units. AB can be oxygen, hydrogen, olefins, hydrogen halides, etc.

(i) Tendency to form oxidative-addition products increases upon descending the group VIII triad, or on passing right to left within it.

Ease of oxidation: Pt(II) > Pd(II) > Ni(II)

Os(0) > Ir(I) > Pt(II)

(ii) ligands which increase electron density at the central metal enhance the tendency of the metal to undergo oxidative-addition.

Predicted ease of oxidation $PEt_3 > PPh_3 > P(C_6F_5)_3$

Oxidative-Addition of Hydrogen & Catalysis

Hydrogenation is of great practical significance. Many transition metal complexes, expecially d^8 complexes, catalyse the hydrogenation of unsaturated hydrocarbons under homogeneous conditions. $[RhCl(PPh_3)_3]$ and trans- $[IrCl(CO)(PPh_3)_2]$ are particularly active. It has been suggested [10,21] that hydride complexes are initially formed, $[RhH_2Cl(PPh_3)_2]$ and $[IrH_2Cl(CO)(PPh_3)_2]$, followed by addition of the olefin -- which is then reduced and eliminated as the parent hydrocarbon.

$$RCH = CH_2 \xrightarrow[\text{catalyst}]{H_2} RCH_2CH_3$$

Hydroformylation is also considered to occur through initial hydrogenation.[21]

$$RCH = CH_2 \xrightarrow[\text{catalyst}]{H_2/CO} RCH_2CH_2 \cdot CHO$$

The most common catalyst is $Co_2(CO)_8$, although several tertiary phosphine complexes, including $[RhCl(PPh_3)_3]$ and $[RhH(CO)(PPh_3)_3]$, are also effective.

Reactivity of Tertiary Phosphine Complexes of Platinum (II) and Palladium (II)

Synthesis of $[PtX(CO)(PR_3)_2]^+$ X = Cl, Br or I; R = ethyl or phenyl prompted its examination for similar activity to $[IrCl(CO)(PPh_3)_2]$. Similar catalytic character was not observed.[14]

There have been only a few, isolated instances of parallel reactivity of platinum (II) complexes with iridium (I) and rhodium (I) complexes. These are:

(i) Catalytic dehydrogenation of formic acid by $[PtCl_2(PBu^t_3)_2]$.[22]

(ii) Several oxidative-addition reactions of $[PtXY(PEt_3)_2]$[21]

e.g. $[PtHCl(PEt_3)_2] + HCl \longrightarrow [PtH_2Cl_2(PEt_3)_2]$

$[PtI_2(PEt_3)_2] + Cl_2 \longrightarrow [PtCl_2I_2(PEt_3)_2]$

It was our intention, therefore:

A: To attempt the synthesis of further members of the series $[Pd_2X_2(PR_3)_4][BF_4]_2$, where complexes with X = Cl, R = ethyl and phenyl; and X = Br, R = phenyl were already known.

B: To carry out a detailed investigation into the chemical nature of $[Pt_2X_2(PR_3)_4]^{2+}$ and $[Pd_2X_2(PR_3)_4]^{2+}$, in order to determine whether any parallels in activity could be drawn with $[RhCl(PPh_3)_3]$ and <u>trans</u>-$[IrCl(CO)(PPh_3)_2]$.

CHAPTER II

SYNTHESIS AND CHARACTERISATION OF

$[M_2X_2(PR_3)_4][BF_4]_2$

II A: SYNTHESIS

Introduction

The synthetic methods will be considered in chronological order and accordingly, in addition to our current results, will include a review of synthetic routes employed

(a) prior to this thesis, and

(b) by other workers concurrent to this thesis.

The author feels that such coverage will lead to a fuller appreciation of the synthetic work as a whole.

Scheme 1: Gaseous Boron Trifluoride (1967-9)

This is an extension of the original synthesis proposed by Druce, Lappert and Riley:[12]

$$2\ \underline{cis}\text{-}\ [PtX_2L_2] + 2\ BX_3 \xrightarrow[\text{anhydrous solvent}]{\text{inert atmosphere}} \left[L_2Pt\begin{smallmatrix} X \\ \diagup\diagdown \\ X \end{smallmatrix}PtL_2 \right] [BX_4]_2$$

where $L = n\text{-}Bu_3P$; X = Cl or Br.

Clark, Dixon and Jacobs[13,14] employed gaseous boron trifluoride $BF_3(g)$ in an inert solvent (anhydrous chloroform), and besides synthesising a number of platinum derivatives were able also to partially extend their method to palladium (II) chemistry[17], viz:

$$2\ \underline{cis}\text{-}\ [PtX_2(PR_3)_2] + 4\ BF_3 \xrightarrow{CHCl_3} [Pt_2X_2(PR_3)_4][BF_4]_2 + 2[BF_2X]$$

$$2\ \underline{trans}\text{-}\ [PdCl_2(PR_3)_2] + 4\ BF_3 \xrightarrow{CHCl_3} [Pd_2Cl_2(PR_3)_4][BF_4]_2 + 2[BF_2Cl]$$

where X = Cl, Br or I; R = ethyl or phenyl.

The results are summarised in Tables VI A and VI B.

TABLE VI A: REACTION OF cis- $[PtX_2(PR_3)_2]$ WITH $BF_3(g)$ IN ANHYDROUS $CHCl_3$[13,14]

Pt	X = Cl	Br	I
$PR_3 = PEt_3$	25°/15 hr ⟶ 88% C	50°/12 hr ⟶ 75% C	70°/28 hr ⟶ $[PtI(PEt_3)_3][BF_4]$ + N
PPh_3	25°/12 hr ⟶ 85% C	70°/12 hr ⟶ 76% C	130°/48 hr ⟶ 35% C

TABLE VI B: REACTION OF trans- $[PdX_2(PR_3)_2]$ WITH $BF_3(g)$ IN ANHYDROUS $CHCl_3$[17]

Pd	X = Cl	Br	I
$PR_3 = PEt_3$	75°/20 hr ⟶ 38% C, 6% N	120°/60 hr ⟶ NO REACTION	120°/60 hr ⟶ 35% N (60% M)
PPh_3	120°/24 hr ⟶ 36% C (25% M)	COMPLEX REACTIONS - INCOMPLETE CHARACTERISATION	

where C is $[M_2X_2(PR_3)_4][BF_4]_2$
N is $[M_2X_4(PR_3)_2]$
M is $[MX_2(PR_3)_2]$ starting compound

It was shown that:

1. Yield of $[M_2X_2(PR_3)_4]^{2+}$ species increases markedly in the order

$$I < Br < Cl$$

2. The formation of neutral (N) dimeric species $[M_2X_4(PR_3)_2]$ is in accordance with the following equation[17]:

$$2\ \underline{\text{trans}}\text{-}\ [PdI_2(PEt_3)_2] + 2\ BF_3 \xrightarrow[120°]{CHCl_3} [Pd_2I_4(PEt_3)_2] + 2[F_3B{\leftarrow}PEt_3]$$

3. It may be noted that the reaction of <u>cis</u>- $[PtI_2(PEt_3)_2]$ with BF_3 is entirely anomalous. Clark et al. proposed the following equation[14] to explain the formation of observed products:

$$3\ \underline{\text{cis}}\text{-}\ [PtI_2(PEt_3)_2] + 3\ BF_3 \xrightarrow[70°]{CHCl_3} [Pt_2I_4(PEt_3)_2]$$

$$+ [PtI(PEt_3)_3][BF_4] + [F_3B{\leftarrow}PEt_3] + [BF_2I]$$

<u>Mechanism</u>

These reactions are thought to proceed via halide abstraction[12,13] by boron trifluoride according to reactions of the type:

$$2\ L_nM\text{-}X + 2\ BF_3 \longrightarrow 2\ L_nM^+ + 2\ BF_3X^-$$

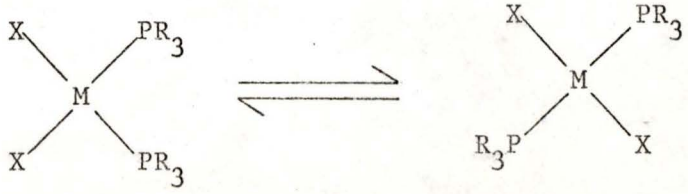
$$2\ L_nM^+ \xrightarrow{\text{dimerisation}} (L_nM)_2^{2+}$$

$$2\ BF_3X^- + 2\ BF_3 \longrightarrow 2\ BF_4^- + 2\ BF_2X$$

where $L_n = [X(PR_3)_2]$

Why the difference in reactivity between the platinum (II) and palladium (II) monomers to boron trifluoride?

The answer likely rests in the case of <u>cis</u> to <u>trans</u> isomerism



<u>cis</u> <u>trans</u>

of these monomers.

In the case of the cis isomer, the strong trans effect of the phosphine results in labilisation, and thence abstraction, of a halide X^- ion. For the trans isomer, however, labilisation and abstraction of a phosphine ligand would be expected to occur. The occurrence of neutral dimers, such as $[Pd_2I_4(PEt_3)_2]$, is consistent with this reasoning:

$$2\ \underline{\text{trans}}\ \ L_nPd\text{-}PEt_3 \ +\ 2\ BF_3 \longrightarrow 2\ L_nPd \ +\ F_3B{\leftarrow}PEt_3$$

$$\downarrow \text{dimerisation}$$

where $L_n = [I_2(PEt_3)]$

Summarising, monomers reacting in cis configuration give rise to cationic $[M_2X_2(PR_3)_4]^{2+}$ species, while those reacting in trans yield neutral $[M_2X_4(PR_3)_2]$ species.

Further it is known[23] that the equilibrium percentage of cis isomer for the complexes $[PtX_2(PEt_3)_2]$ increases in the order:

$$I < Br < Cl$$

which is consistent with yields obtained for cationic species.

While the preferred configuration of platinum (II) monomers is cis, only trans isomers of the analogous palladium (II) monomers have been reported in the literature, although cis $[PdCl_2(PEt_3)_2]$ has been observed as a metastable form.[24]

That both neutral and cationic dimeric species result from the reaction between $[PdCl_2(PEt_3)_2]$ and $BF_3(g)$ may be explained by the occurrence of cis $\rightleftharpoons$ trans equilibrium for $[PdCl_2(PEt_3)_2]$.

Scheme 2: Boron Trifluoride Diethyl Etherate

Coordination compounds of boron trifluoride with ethers are weakly associated substances, containing one mole ether per mole boron trifluoride. Vapour density measurements[25] and high values for Trouton Constant, indicate some dissociation at and below the boiling point (125.7°). The equilibria:[25]

$$BF_3 \cdot Et_2O\ (l) \rightleftharpoons BF_3 \cdot Et_2O\ (g)$$

$$BF_3 \cdot Et_2O\ (g) \rightleftharpoons BF_3\ (g) + Et_2O\ (g)$$

suggest that some free gaseous boron trifluoride is always present. The advantage of digesting $[MX_2(PR_3)_2]$ species in an excess of the etherate at the boiling point lies in attaining complete homogeneity, whereas complete solubility in the BF_3 (g) / $CHCl_3$ systems is rarely achieved.

Therefore, $[PdX_2(PR_3)_2]$ was digested in an excess of $BF_3 \cdot Et_2O$ at its boiling point, and the results summarised in Table VII.

TABLE VII. REACTION OF trans $[PdX_2(PR_3)_2]$ WITH $BF_3 \cdot Et_2O$ UNDER REFLUX

Pd	X = Cl	Br	I
$PR_3 = PEt_3$	125-30°/30 min ⟶ 65% C 28% N	130°/30 min ⟶ 71% N (15% M)	125-30°/30 min ⟶ 45% N (20% M) Pd metal
PPh_3	125-30°/30 min ⟶ 91% C	*0→135°/180 min ⟶ 52% C	130°/30 min COMPLEX some free PPh_3

* system gradually heated until homogeneity was achieved[35]

C, N, M as in table VI.

It has been shown that:

1. Yield of $[Pd_2X_2(PR_3)_4]^{2+}$ species again increases in the order

$$(I <) \quad Br < Cl$$

2. The new species $[Pd_2Br_2(PPh_3)_4][BF_4]_2$ was synthesised.

3. The occurence of the neutral $[Pd_2X_4(PEt_3)_2]$ species is more marked than in scheme 1. The hitherto unreactive[17] trans-$[PdBr_2(PEt_3)_2]$ gives a high yield of $[Pd_2Br_4(PEt_3)_2]$, as expected from its trans configuration. Yield of $[Pd_2X_4(PEt_3)_2]$ increases in the order

$$Cl < I < Br$$

The occurence of elemental palladium in the iodo- system (reduction of Pd(II) to Pd(0)) may have caused transposition of I and Br.

4. Species of the type $[Pd_2X_4(PPh_3)_2]$ are not observed. One infers that the lability of the PPh_3 ligand is rather less than that of the PEt_3 ligand in this system.

Scheme 3: Silver Tetrafluoroborate

The reaction between silver tetrafluoroborate $AgBF_4$ and trans-$[PdX_2(PR_3)_2]$ in equimolar ratio in anhydrous acetone (or anhydrous methylene chloride) yields insoluble silver halide and a filtrate from which $[Pd_2X_2(PR_3)_4][BF_4]_2$ can be isolated:

$$2 \text{ trans-}[PdX_2(PR_3)_2] + 2\ AgBF_4 \xrightarrow[25]{\text{acetone}} [Pd_2X_2(PR_3)_4][BF_4]_2 + 2\ AgX\downarrow$$

The results are summarised in Table VIII:

TABLE VIII. REACTION OF Trans-$[PdX_2(PR_3)_2]$ WITH $AgBF_4$ IN ANHYDROUS ACETONE AT 25°

Pd	X = Cl	Br	I
PR_3 = PEt_3		76% C (trace M)	ionic -OH compound suggests hydrolysis
PPh_3	90% C	97% C	87% C

C and M as in Table VI.

$[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ was also synthesised in 89% yield.

It has been shown that:

1. The new species $[Pd_2Br_2(PEt_3)_4][BF_4]_2$ and $[Pd_2I_2(PPh_3)_4][BF_4]_2$ were synthesised.

2. Yields are almost quantitative: the method, rapid and facile.

3. It is not possible to synthesise the species $[Pd_2I_2(PEt_3)_4][BF_4]_2$, the reaction being characterised by the formation of an ionic compound containing an -OH group, which may be hydroxo on the palladium. This system seems to be prone to hydrolysis.

It may be noted that the analogous platinum (II) derivative has also eluded synthesis.[14]

Mechanism.

Reaction is thought to proceed via halide abstraction by the cationic silver Ag^+ species according to the following reactions:

$$2\ L_nM\text{-}X\ +\ 2\ Ag^+ \longrightarrow 2\ L_nM^+\ +\ 2\ AgX\downarrow$$

$$2\ L_nM^+ \xrightarrow{\text{dimerisation}} (L_nM)_2^{2+}$$

where L_n = $[X(PR_3)_2]$

The facility of the reaction is unaffected by the configuration of the starting monomer.

Silver (I) Complexes

From one experiment between trans-$[PdI_2(PPh_3)_2]$ and $AgBF_4$ (where some decomposition of the latter was suspected), tetrakis (triphenyl phosphine) silver (I) tetrafluoroborate was isolated in 85% yield according to the equation:

$$AgBF_4 + 2\ [PdI_2(PPh_3)_2] \longrightarrow [Ag(PPh_3)_4][BF_4] + 2\ PdI_2$$

Further investigations with carefully controlled equimolar ratios gave the required product according to:

$$2\ AgBF_4 + 2\ [PdI_2(PPh_3)_2] \longrightarrow [Pd_2I_2(PPh_3)_4][BF_4]_2 + 2\ AgI\downarrow$$

the latter reaction showing no temperature dependance over the range -10° to +25°.

Obviously very careful control over molar ratios and purity of reactants is necessary.

Other work

Using silver tetrafluoroborate, Goggin, Goodfellow et al.[15] recently synthesised a series of dimers of the type

$[M_2X_2(YMe_3)_4][BF_4]_2$ where M = Pd(II) or Pt(II)
X = Cl, Br or I
Y = P or As

Scheme 4: Aqueous Fluoroboric Acid

It is interesting to note that on reacting cis-$[PtCl_2(PEt_3)_2]$ with an excess of aqueous 48% HBF_4 the following reaction occurs:

$$2\ \underline{cis}\text{-}[PtCl_2(PEt_3)_2] + 2\ HBF_4 \xrightarrow[\text{reflux}]{\text{acetone}} [Pt_2Cl_2(PEt_3)_4][BF_4]_2 + 2\ HCl$$

46%

Although the reaction is slow and incomplete after 6½ hours at reflux, nevertheless it is a feasible method of synthesis and of at least academic interest.

Summary of Synthetic Routes.

Without doubt, the scheme using silver tetrafluoroborate possesses all of the major advantages. It is (i) quantitative (ii) specific; in terms of non-formation of $[M_2X_4(PR_3)_2]$ species (iii) rapid and (iv) facile; requiring no specialised vacuum line techniques.

II B: CHARACTERISATION

Physical Properties

The salts of the dimeric cations $[M_2X_2(PR_3)_4]^{2+}$ are air-stable, non-hygroscopic crystalline solids, whose colours vary from white (chloride bridge) through orange (iodide bridge).

They have conductances in nitromethane of the order expected for 2:1 electrolytes[27] (ca. 170-230 ohm^{-1} cm^2 $mole^{-1}$).

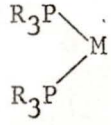
They show appreciable solubility only in polar solvents -- dichloromethane, nitromethane, ethanol -- the triethylphosphine derivatives being decidedly more soluble than those of triphenylphosphine.

The following techniques are commonly used for purposes of characterisation:

(i) Infrared spectroscopy* (ii) proton nuclear magnetic resonance spectroscopy (iii) conductance measurements (iv) elemental analysis, whilst a fifth (v) mass spectrometry receives discussion in section II C.

Discussion will centre on species (a) previously unreported and (b) commonly occurring in reactions in Chapter IV.

(i) Infra red Spectra

The main features (Table IX) require little comment except to note that the spectra of the new compounds are entirely consistent with those reported hitherto[13,15] (see introduction, Chapter I). The doublet appearing in the region 415-450 cm^{-1} is characteristic of cis coordinated phosphines  and therefore of this dimeric bridged system.

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* Goggin, Goodfellow et al.[15] have used Raman techniques also.

TABLE IX. CHARACTERISATION DATA OF $[M_2X_2(PR_3)_4][BF_4]_2$ SPECIES

compound	colour	mp°	conductance $ohm^{-1}\ cm^2$	%C calcd (found)	%H calcd (found)	IR (nujol mull) cm^{-1} ν(M-X)	^{d} ligand
$[Pd_2Cl_2(PEt_3)_4][BF_4]_2$ [a]	yellow	~ 200d	190[c]	a		290 (w,b)	435 (w) 420 (m)
$[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ [a]	colourless	~ 250d	170	a		280 (w,b)	440 (w) 425 (m)
$[Pt_2Cl_2(PPh_3)_4][BF_4]_2$ [a]	colourless	~ 300d	174	a		300 (w,b)	445 (w) 415 (w)
$[Pd_2Br_2(PEt_3)_4][BF_4]_2$	yellow	~ 140-5d	197	28.3 (28.9)	5.9 (6.1)	< 250	435 (w) 420 (w)
$[Pd_2Br_2(PPh_3)_4][BF_4]_2$	yellow	~ 250d	-	54.2 (53.9)	3.8 (3.7)	< 250	445 (w) 415 (w)
$[Pd_2I_2(PPh_3)_4][BF_4]_2$	orange yellow	215-20d[b]	176	51.2 (51.5)	3.6 (3.8)	< 250	455 (w) 420 (w)
$[Ag(PPh_3)_4][BF_4]$	colourless	285-8	85	69.5 (69.1)	4.9 (4.8)	-	435 (m)

ν(B-F) all compounds
ν_3 1090 (s), 1050 (vs)
ν_4 515 (w)

[a] previously reported[13,14] [b] darkens at ~ 185°

[c] previously reported at 177 $ohm^{-1}\ cm^2$ [17]

[d] previously assigned to ν(M-P) (see introduction)

(The tetrahedral $[Ag(PPh_3)_4]^+$ ion gives rise to a single band at 435 cm^{-1}).

Preliminary studies in the region below 250 cm^{-1} proved somewhat inconclusive and await further investigation.[26]

(ii) Proton NMR Spectra

Of the new compounds, only $[Pd_2Br_2(PEt_3)_4][BF_4]_2$ proved amenable to analysis. The methyl proton resonance is interpreted as a crude quintet (1:2:2:2:1), arising from overlap of a doublet of 1:2:1 triplets, and centred about 8.75 τ. The methylene proton resonance approximates to a crude quintet centred about 8.0 τ. The relative integrated intensities of methyl to methylene protons are approximately 3:2.

The data is consistent with a cis configuration of the phosphorus nuclei about each palladium nucleus, and with earlier data for $[M_2X_2(PEt_3)_4]^{2+}$ species[13] (introduction).

TABLE X. PROTON NMR PARAMETERS FOR $[M_2X_2(PR_3)_4][BF_4]_2$[13]

compound	solvent	chemical shift (τ) CH_3	CH_2	coupling constants J_{P-H}	J_{H-H} (cps)
$[Pt_2Cl_2(PEt_3)_4][BF_4]_2$	CH_2Cl_2	8.8(q)	8.0(s)	19 ~ 24	7.25 7.25
$[Pt_2Br_2(PEt_3)_4][BF_4]_2$	CH_2Cl_2				
$[Pd_2Cl_2(PEt_3)_4][BF_4]_2$	CH_2Cl_2	8.7(q)	8.0(q)	19.5 17	7.5 7.5
$[Pd_2Br_2(PEt_3)_4][BF_4]_2$	CH_2Cl_2	8.75(q)	8.0(q)	19.5 17	7.5 7.5

(q) crude quintet (s) crude septet

II C: MASS SPECTROMETRY OF TERTIARY PHOSPHINE COMPLEXES OF NICKEL (II), PALLADIUM (II) AND PLATINUM (II)

Introduction

The fragmentation patterns of a number of metal complexes containing tertiary phosphine and carbonyl ligands have been reported.

Lewis et al.[28] investigated a series of derivatives of molybdenum, tungsten and manganese of the type: $[Ph_3PM(CO)_5]$ and [diphos $M(CO)_4$] where M = W or Mo, diphos is $Ph_2P\text{-}CH_2\text{-}CH_2\text{-}PPh_2$; [diphos $W(CO)_5]_2$; cis $Et_3PMn(CO)_4Cl$ and $[R_3PMn(CO)_4]_2$ where R = ethyl or phenyl, for example. It was concluded that: (i) Carbonyl groups are lost prior to loss of phosphine ligands (ii) Carbonyl groups and halogen atoms tend to break away from a monometallic ion at about the same rate. (iii) Spectra of phosphine complexes do not commonly show metallic ions containing partially dissociated ligands. When such ions do occur they are usually of low intensity. (iv) Ions containing two metal atoms are of very low intensity (< 0.5%).

Lewis pointed out that fragmentation in the mass spectrometer is in marked contrast to the thermal behaviour of such complexes, where the phosphine is initially lost to give a metal carbonyl residue.

Mass spectral studies of the complexes $[Re(CO)_x(PMe_2Ph)_{5-x}X]$ where X = Br or Cl[29]; species of the type $Fe(CO)_3[P(NMe_2)_3]_2$ and $Cr(CO)_5[P(NMe_2)_3]$[30]; and of $(CO)_3Fe\begin{smallmatrix}\diagup PPh_2 \diagdown \\ \diagdown PPh_2 \diagup\end{smallmatrix}Fe(CO)_3$[31], are consistent with Lewis' observations that loss of CO occurs before loss of phosphine ligands.

Despite considerable interest in the mass spectra of metal carbonyls and metal carbonyl phosphines, there is no literature on transition metal phosphine complexes where carbonyl is absent.

It was decided, therefore, to select a number of well characterised triethylphosphine complexes and investigate them by mass spectrometry.

These included:

(a) trans- $[PdX_2(PEt_3)_2]$ where X = Cl, Br and I

(b) trans- $[NiCl_2(PEt_3)_2]$

(c) cis- $[PtCl_2(PEt_3)_2]$

(d) $[Pd_2X_4(PEt_3)_2]$ where X = Cl, Br and I

(e) $[M_2X_2(PEt_3)_4][BF_4]_2$ where M = Pd(II) and Pt(II)
X = Cl and Br

Results and Discussion

The fragmentation patterns were dominated without exception by fragments derived from the triethylphosphine ligands. However, the low intensity metal containing ions provide the greater interest, since their fragmentation patterns may be compared with the known chemical behaviour of the parent complexes.

Molecular Ions

These were observed for the monomeric species: trans- $[PdCl_2(PEt_3)_2]$ at m/e 410-20; trans- $[PdBr_2(PEt_3)_2]$, m/e 498-508; trans- $[PdI_2(PEt_3)_2]$, m/e 594-600; and cis- $[PtCl_2(PEt_3)_2]$, m/e 498-506.

Trans- $[NiCl_2(PEt_3)_2]$ did not yield a molecular ion, and nor did the dimeric species (d) and (e). The highest intensity was obtained for trans- $[PdI_2(PEt_3)_2]$ due to its relatively high volatility compared to other monomers.

Comparison of observed peak intensities with calculated isotopic ratios was used to confirm the molecular ion assignments.

An example is shown in Table XI.

TABLE XI. INTENSITY DISTRIBUTION IN MOLECULAR ION REGION OF trans- $[PdI_2(PEt_3)_2]$

m/e	% of total peak intensities	
	Found	Calculated[a]
592	1	1
593		
594	11	10
595	19.5	21
596	26	26
597	3	3.5
598	24	23
599	3	3.5
600	11	11
601	1.5	1
total	100	100

[a] based on 1.11% natural abundance of ^{13}C. ^{31}P and ^{127}I both occur in 100% natural abundance.

Primary Fragmentation Process

(a) Monomeric $[MX_2(PEt_3)_2]$

Primary fragmentation process for complexes $[MX_2(PEt_3)_2]$ (where M = Pd(II), X = Cl, Br and I; M = Pt(II), X = Cl) was as follows:

$$[MX_2(PEt_3)_2]^+ \xrightarrow{-X\cdot} [MX(PEt_3)_2]^+ \xrightarrow{-X\cdot} [M(PEt_3)_2]^+$$

This is consistent with Lewis' observation[28] that halogens are lost prior to loss of phosphines.

One can draw a comparison here with the reaction of $[MX_2(PEt_3)_2]$ species with BF_3, where both halogen abstraction (to form BF_3X^-) and phosphine abstraction (to form $Et_3P \rightarrow BF_3$) are known (see experimental and synthesis). The former reaction is favoured for cis and the latter for trans isomers. However, both cis and trans isomers lose halogen as first step in the mass spectra.

(b) Dimeric species

The ion of highest mass in the spectra of $[Pd_2Br_4(PEt_3)_2]$ and $[Pd_2Br_2(PEt_3)_4][BF_4]_2$ was $[PdBr_2(PEt_3)_2]^+$, m/e 496-504. $[PdBr(PEt_3)_2]^+$ and $[Pd(PEt_3)_2]^+$ were also observed.

The formation of the bromine containing fragments probably occurs by asymmetric cleavage of the bromine bridge.

No metal-chlorine fragments were observed in the spectra of the complexes $[M_2Cl_2(PEt_3)_4][BF_4]_2$: where M = Pt(II) the ion of highest mass was $[Pt(PEt_3)_2]^+$, and for M = Pd(II) it was $Pd(PEt_3)^+$.

Complexes $[Pd_2X_4(PEt_3)_2]$ where X = Cl and I, proved too involatile for analysis. Finally there was no evidence for the formation of ions of the type $\left[\begin{smallmatrix} M & M \\ & X \end{smallmatrix}\right]^+$ similar to those observed by Lupin and Cais.[32]

Further Fragmentation

Fragmentation of the ion $[M(PEt_3)_2]^+$ gave a series of metal ions containing partially dissociated PEt_3 ligands, which resulted from successive loss of C_2H_4 and/or $C_2H_5\cdot$ radicals. This is consistent with Bruce's suggestions that there are three main fragmentations of coordinated phosphines[33] which are (modified to our system):

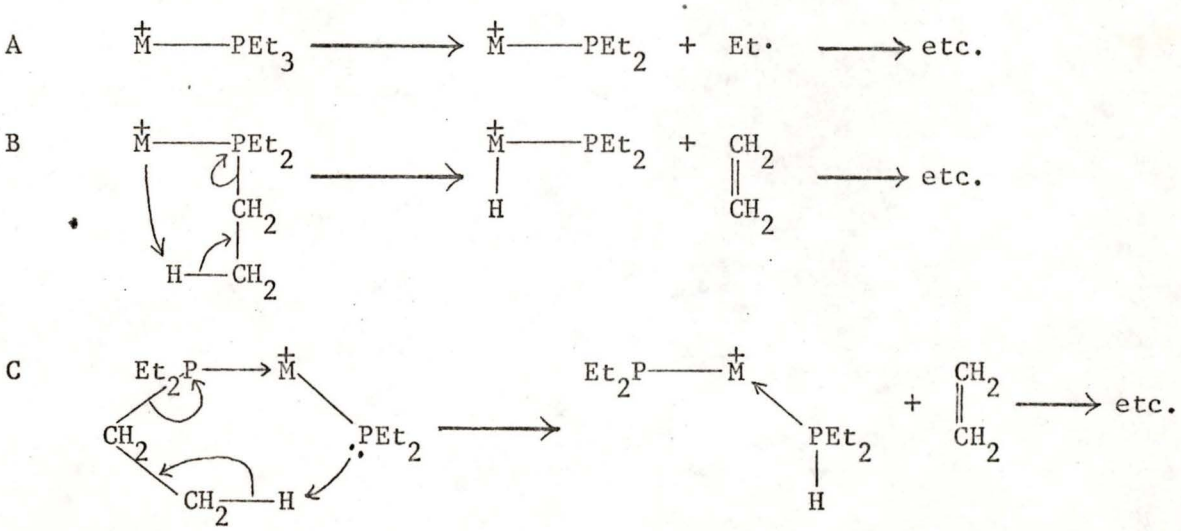

fig. 3. Fragmentations of Coordinated Phosphines

Since the H mass is only one unit, one cannot differentiate between, for example, $MPEt_2^+$ and $HMPEt_2^+$, and accurate mass measurements would be necessary for definitive analysis of these fragments.

The occurrence of the ion PEt_3X^+ was general, and is considered to result from fragmentation of $[MX_2(PEt_3)_2]^+$ or $[MX(PEt_3)_2]^+$. PEt_3Cl^+ was the highest fragment in the spectrum of trans-$[NiCl_2(PEt_3)_2]$.

All spectra were dominated by ions arising from fragmentation of PEt_3^+. The following were of particularly high intensity: PH_2Et^+, m/e 62 (Base Peak) > $PHEt_2^+$, m/e 90 > PEt_3^+, m/e 118. In the spectrum of $[Pd_2Br_4(PEt_3)_2]$ there was also evidence for the bimolecular species: $EtHP\text{-}PH_2^+$, m/e 94; $EtHP\text{-}PHEt^+$, m/e 122; and $Et_2P\text{-}PHEt^+$, m/e 150 (cf. mass spectrum of pure PEt_3, page 34).

Fragments due to Impurities

The spectra of $[MX_2(PEt_3)_2]$, M = Pd or Pt, showed evidence of iodide impurities where X = Br, and bromide and iodide impurities where X = Cl. The preparation of these complexes involved the use of sodium halides which normally contain ca. 0.005% of heavier halogen impurities*. Since it is known[34] that equilibria such as:

$$PtX_4^{2-} + 4\,\overset{*}{X}^- \rightleftharpoons Pt\overset{*}{X}_4^{2-} + 4X^-$$

strongly favour the heavier halogens it is likely that similar exchange reactions, occurring during the preparations, may be responsible for the high impurity levels observed.

For example: the mass spectrum of trans-$[PdCl_2(PEt_3)_2]$ showed a molecular ion due to $[PdBrCl(PEt_3)_2]^+$. Intensity measurements showed

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* ANALAR reagents

$$\text{ratio of total intensity} = \frac{[PdBrCl(PEt_3)_2]^+}{[PdCl_2(PEt_3)_2]^+} = \frac{69}{290} = 22\%.$$

Consider the equilibrium,

$$PdCl_2(PEt_3)_2 + Br^- \rightleftharpoons PdBrCl(PEt_3)_2 + Cl^- \quad .....(1)$$

It is known that ANALAR sodium chloride contains ca. 0.005% (I^- + Br^-). Assuming that all impurities are due to Br^- ion,

$$\text{then} \quad K_{equ.} \simeq \frac{22}{100} \cdot \frac{100}{0.005} \simeq 4400$$

Thus equilibrium in (1) lies very much to the right. Initial bromide impurities are concentrated by a factor of 10^3 - 10^4.

It should be stressed that although this example provided the best spectrum for computation, it was the worst in terms of impurity concentration. The normal impurity level was in the region of 2 - 3%, representing a concentration factor of 10^2 - 10^3.

Dunning and Martin[34] found the equilibrium constant for the reaction

$$[PtCl_4]^{2-} + 4\ Br^- \rightleftharpoons [PtBr_4]^{2-} + 4\ Cl^-$$

to be ca. 400, or a factor of 10 lower than the figure from mass spectral data. It should be noted, however, that fragment intensity is not a true indication of concentration in a neutral sample.[28] Also volatility of halide complexes follows the order

$$I > Br > Cl$$

i.e. species containing impurities will show the higher volatilities.

Some data appear in Table XII, and three spectra are diagramatically represented in fig. 4(a), 4(b) and 5.

TABLE XII. MASS SPECTRAL DATA FOR SOME COMPLEXES OF TRIETHYLPHOSPHINE

m/e	RELATIVE ABUNDANCE (%) OF PEAKS							assignment
	A	B	C	D	E	F	PEt_3	
14	a			2				
15				2	1	3		
18		4				15		
19				2				
20				1	6	9		
25		1			1			
26	6	5	2	4	4	11	1	
27	16	17	18	18	17	22	10	
28		12		1	8	19	4	
29	10	11	16	14	20	23	7	Et^+
30		1		4	1			
31				40		5		P^+
34	5	4	5	4	4	4	2	
35		3		2	1	2		
36	3	18	4	10	5	14		
38		6		3	2	4	1	
39		2		2	2	2	8	
41	5	8	10	9	8	10	9	
42		1		2		1		
43		5	4	8	4	13	5	
44		2		2	1	2	1	
45	10	9	13	15	7	7	9	
46	2	2		6	2		2	
47	5	4	6	6	4	6	5	
48		1			6	6		
49		1		2	20	26	1	
53		1		2			1	
55	6	10	10	11	9	10	9	
56		1		2	1	2	2	
57	16	20	24	17	14	9	21	
58	7	8	10	9	8	12	10	
59	23	25	29	26	23	24	27	
60	7	7	7	8	6	7	8	
61	51	54	58	54	52	54	57	$HPEt^+$
62	100	100	100	100	100	100	98	H_2PEt^+
63	3	3	3	4	3	3	7	
64		1					1	
65	a	3			1		9	
68					2	2		
69		2		3	2	4	2	
71		2			1	3	1	
73	2	4	4	4	3	4	3	
75	13	15	16	15	13	14	16	
76		1			1	2		
80		1			4	4		
88		2		2	2			
89	7	8	7	8	6	8	11	
90	75	84	73	82	94	85	100	$HPEt_2^+$
91	4	5	4	4	4	4	76	

TABLE XII CONT'D.

m/e	RELATIVE ABUNDANCE (%) OF PEAKS A	B	C	D	E	F	PEt_3	assignment
92		1					58	
94		12	4	4	4	2	.1	
103	17	18	16	15	15	18	25	
104	2	2			1	2	2	
105		1		2	1	25		
106					0	29		
108					4	2		
116		2			1			
117	4	7	8	6	4	7	8	
118	40	52	40	57	40	45	71	PEt_3^+
119	3	7		6	4	9	4	
121		2						
122		5		2	2			
125		1			2			
127					3			
128					2			
150		5		2	1			
153	3	43	4	7		3		PEt_3Cl^{35+}
155	1	14		2		1		PEt_3Cl^{37+}
156		2			1			
181					1			
197		7	78	2				PEt_3Br^{79+}
198								
199		7	78	2				PEt_3Br^{81+}
200								
165-173		t	t					
194-203		t	t					
222-231		t	t		t			
243-264		t	t	t				
280-289		t	t	t		t		
308-319		t	t	t		t		metal-phosphine ions
337-347		t	t	t		t		
365-379				t		t		
394-406				t		t		e.g.
425-433				t		t		$Pt(PEt_3)_2^+$
373-385		t						$PdCl(PEt_3)_2^+$
409-417		t						$PdCl_2(PEt_3)_2^+$

TABLE XII CONT'D.

m/e	RELATIVE ABUNDANCE (%) OF PEAKS A	B	C	D	E	F	assignment
416-424			t				$PdBr(PEt_3)_2^+$
454-466		t	t				$PdBrCl(PEt_3)_2^+$
464-471				t			$PtCl(PEt_3)_2^+$
495-502		t	t				$PdBr_2(PEt_3)_2^+$
499-506				t			$PtCl_2(PEt_3)_2^+$
545-552				t			$PtBrCl(PEt_3)_2^+$
502-512		t					$PdICl(PEt_3)_2^+$
546-556			t				$PdIBr(PEt_3)_2^+$

a indicates absent, or less than 1% relative abundance
t (trace) indicates that each band in a group of ions is present in less than 1% relative abundance (RA).
ΣRA for a group is estimated to be 2-10%.

COMPLEXES:

A $\underline{trans}$-$[NiCl_2(PEt_3)_2]$

B $\underline{trans}$-$[PdCl_2(PEt_3)_2]$

C $\underline{trans}$-$[PdBr_2(PEt_3)_2]$

D $\underline{cis}$-$[PtCl_2(PEt_3)_2]$

E $[Pd_2Cl_2(PEt_3)_4][BF_4]_2$

F $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$

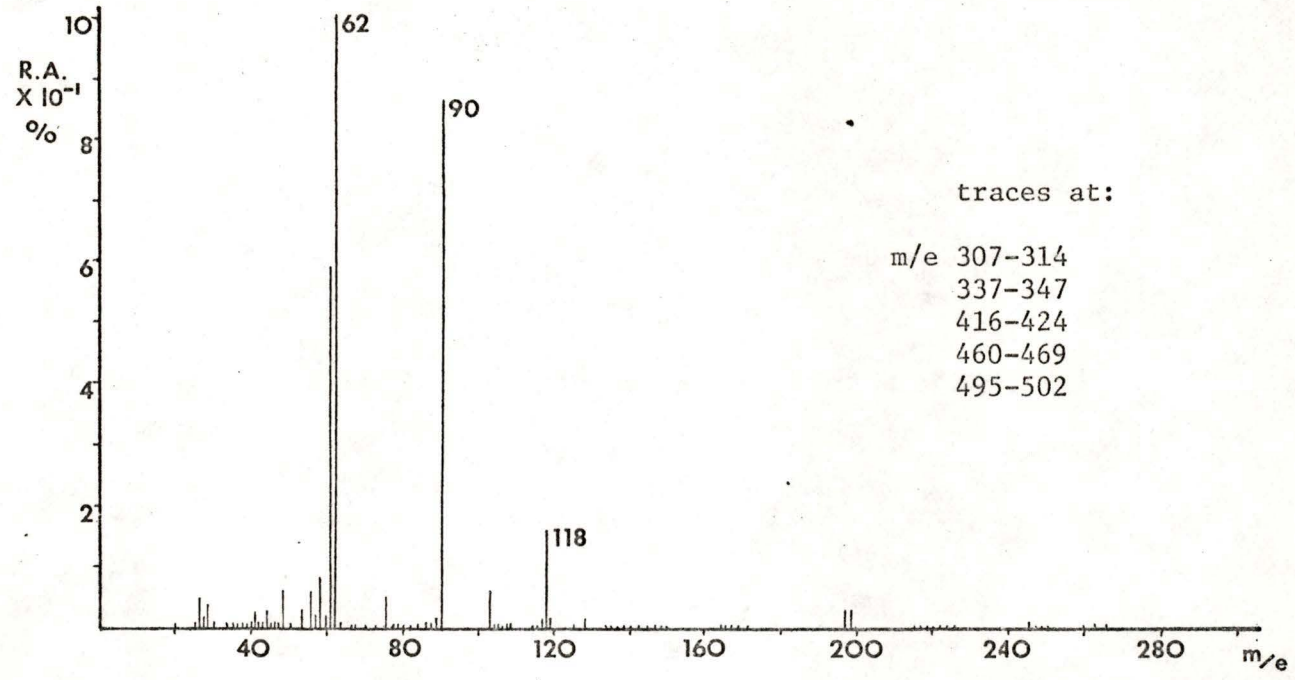


fig. 4(a): mass spectrum of $[Pd_2Br_2(PEt_3)_4][BF_4]_2$

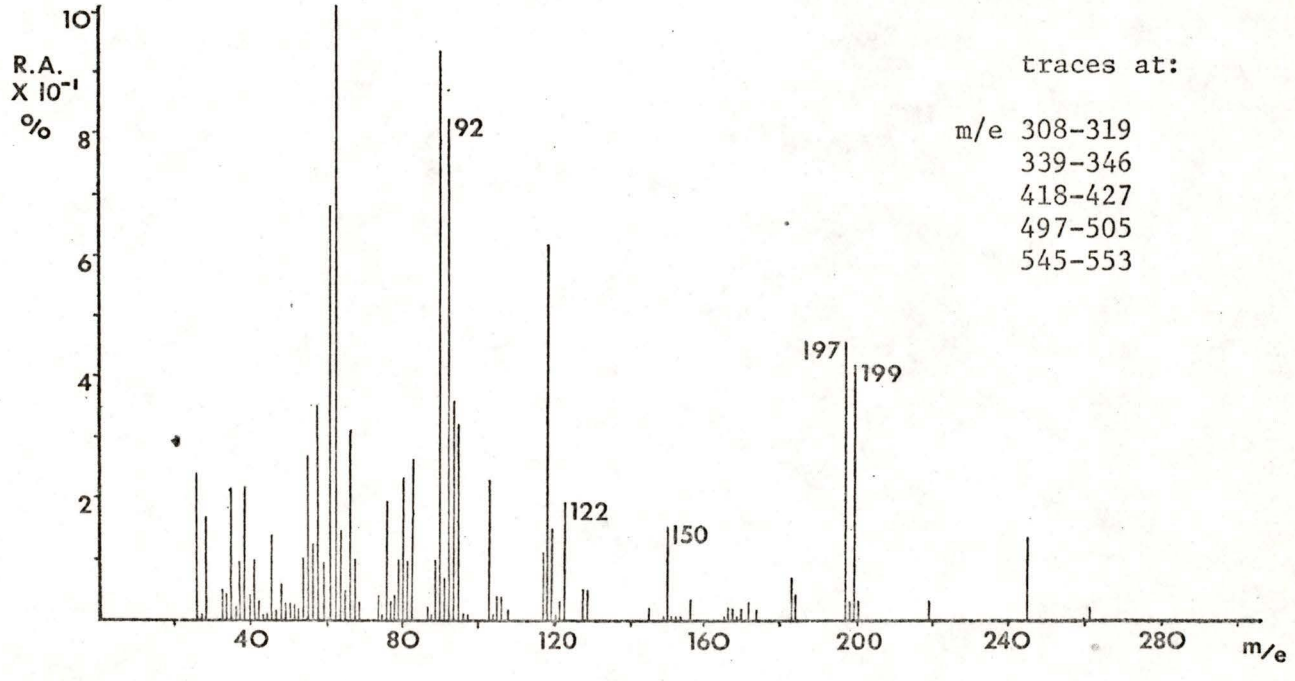


fig. 4(b): mass spectrum of $[Pd_2Br_4(PEt_3)_2]$

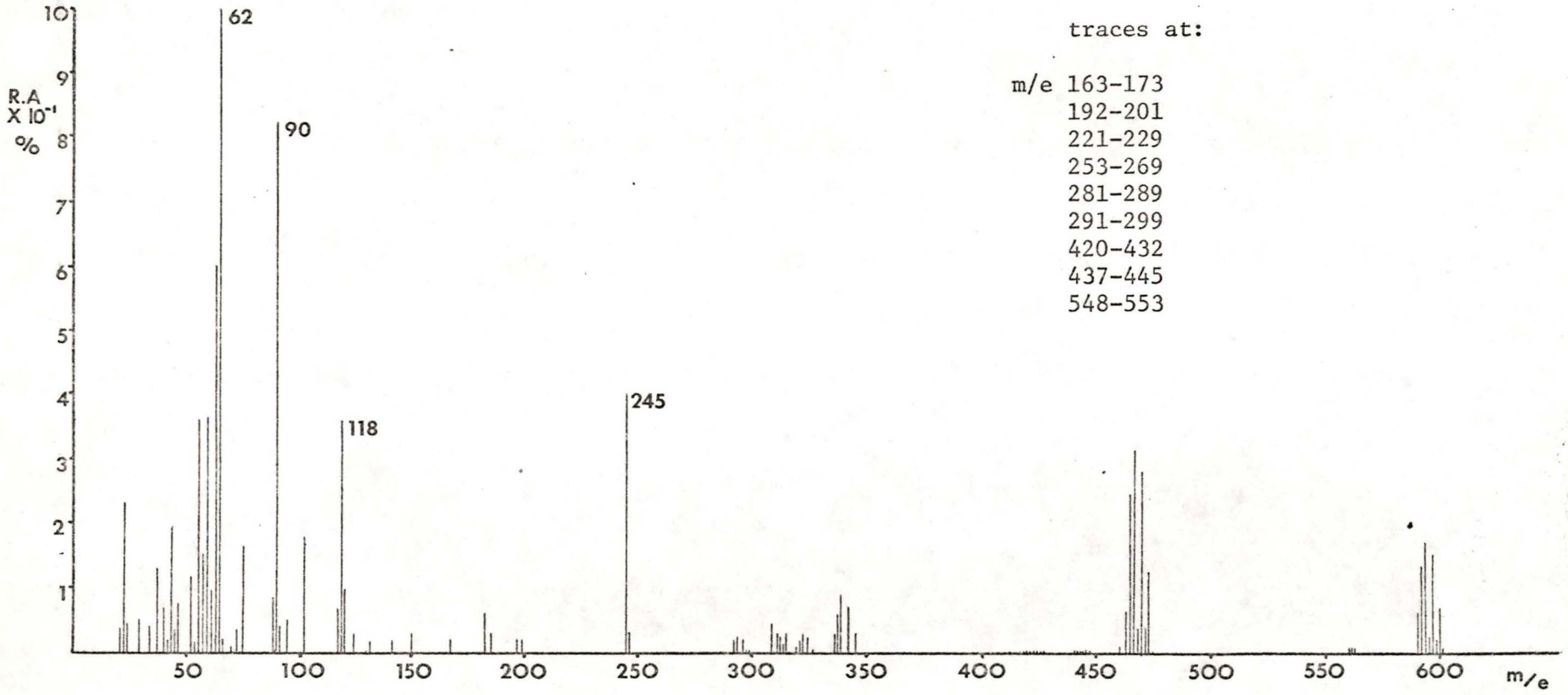


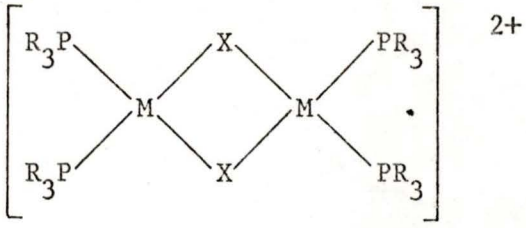
fig. 5: mass spectrum of <u>trans</u>- $[PdI_2(PEt_3)_2]$

CHAPTER III

REACTIONS OF

$[M_2X_2(PR_3)_4]^{2+}$

Reactions of the cation



probably proceed by symmetrical cleavage of the halogen bridge by ligands which have Lewis base character.

The following equilibrium may be set up:

$$[M_2X_2(PR_3)_4][BF_4]_2 \quad + \quad 2\ Z: \rightleftharpoons 2\ [MXZ(PR_3)_2][BF_4]$$

Lewis base

and in cases where the right hand side is favoured, a monomeric derivative may be isolated. For Z = CO, the following reactions have been described:[14,17]

$$[M_2X_2(PR_3)_4][BF_4]_2 \quad + \quad 2\ CO \longrightarrow 2\ \underline{trans}\text{-}\ [MX(CO)(PR_3)_2][BF_4]$$

where M = Pt; X = Cl, Br or I; R = ethyl or phenyl
M = Pd, X = Cl; R = ethyl.

The reaction is essentially instantaneous in chloroform solution under 1 atmosphere pressure of CO. The palladium derivative may be isolated, but it is unstable -- readily losing CO on standing.[17] This instability, together with the non-occurrence of analogous bromo- and iodo- derivatives, is consistent with previous observations that palladium carbonyl species are generally much less stable than their platinum counterparts.

A recent paper[16] also describes the synthesis and carbonylation of the complexes $[Pt_2X_2(YR_3)_4][BF_4]_2$, where X = Cl, Br or I; Y = As or Sb.

Similar cleavage reactions are known where Z = PR_3 (R = ethyl or phenyl)[35], but no other bridge cleavage ligands had been studied prior to this dissertation.

At this point parallels can be drawn with the isoelectronic species $[Rh_2Cl_2(PPh_3)_4]$ and also $[RhCl(PPh_3)_3]$ since the following equilibria prevail in solution:

$$[RhCl(PPh_3)_3] \rightleftharpoons [RhCl(PPh_3)_2] + PPh_3 \rightleftharpoons \tfrac{1}{2}[Rh_2Cl_2(PPh_3)_4]$$

$[RhCl(PPh_3)_2]$ is considered to exist as a solvated species $[RhCl(PPh_3)_2 \cdot$ solvent], where four coordination is maintained, and may be the active intermediate during many of the reactions of $[RhCl(PPh_3)_3]$[10] (see section III E). It may be noted that recent studies by Shriver et al.[36] suggest that dissociation of $[RhCl(PPh_3)_3]$ does not occur in the absence of free oxygen.

These rhodium (I) species[10] and also $[IrCl(PPh_3)_3]$[37] react with CO in an analogous manner to $[Pt_2X_2(PR_3)_4]^{2+}$ -- e.g.

$$[Rh_2Cl_2(PPh_3)_4] \rightleftharpoons 2\,[RhCl(PPh_3)_3] + 2\,CO \longrightarrow 2\ \underline{trans}\text{-}\ [RhCl(CO)(PPh_3)_2]$$

III A: PYRIDINE

Cleavage of chloride bridges by monoamines (am) is well known[38] for complexes of the type $[M_2Cl_4L_2]$, where M = Pt or Pd; L = e.g. C_2H_4, PR_3, amine, according to:

$$[M_2Cl_4L_2] + 2\ am \rightleftharpoons 2\ [MCl_2L(am)]$$

We have found that reaction of the complexes $[M_2Cl_2(PEt_3)_4][BF_4]_2$, where M = Pt or Pd, with pyridine (py) proceeds according to the following reaction:

$$[M_2Cl_2(PEt_3)_4][BF_4]_2 + 2\ py \longrightarrow 2\ \underline{cis}\text{-}\ [MCl(PEt_3)_2(py)][BF_4]$$

Proton NMR of the products show s a methyl proton resonance which approximates to a 1:2:2:2:1 quintet, consistent with coupling to two phosphorus nuclei in a cis- configuration.[13] Relative intensity of heterocyclic protons to aliphatic protons is approximately 1:6.

These NMR data, together with the data in Table XIII, are consistent with the formulation:

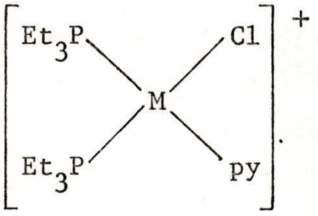


TABLE XIII: CHARACTERISATION DATA FOR COMPLEXES cis- $[MCl(PEt_3)_2(py)][BF_4]$

complex M=	colour	mp°	% C calcd (found)	% H calcd (found)	IR (nujol) cm^{-1} ν(M-Cl)	phosphine	pyridine
Pt	colourless	203-5[a]	37.5 (37.5	6.5 (6.4)	315(s)	435 (w) 415 (w)	3100 (w) 3070 (w) 3025 (w) 1605 (s)
Pd	colourless	212-15	32.3 (32.6)	5.6 (5.6)	305(s)	440 (w) 425 (w)	1450 (s) 1215 (s) 1155 (w) 705 (s)

a yellowing at 135°

III B: MOLECULES CONTAINING A CARBONYL GROUP

Wilkinson's complex $[RhCl(PPh_3)_3]$ has such a high affinity for CO that it abstracts this molecule from several organic systems, notably aldehydes.[10,39,40] Decarbonylation of aldehydes occurs according to the following reactions:

$$[RhCl(PPh_3)_3] \rightleftharpoons [RhCl(PPh_3)_2] + PPh_3$$

$$[RhCl(PPh_3)_2] + R'CHO \xrightarrow{\text{e.g. toluene}} \underline{\text{trans}}\text{-}[RhCl(CO)(PPh_3)_2] + R'H$$

R' = alkyl or aryl

Often decarbonylation occurs over a period of hours in the cold, otherwise in minutes at reflux. Aliphatic aldehydes often yield some olefin by-product. Tsuji and Ohno[40] observed that at high temperatures, e.g. in boiling toluene, the dimeric $[Rh_2Cl_2(PPh_3)_4]$ tended to precipitate and was not an effective decarbonylating agent.

Abstraction of carbon monoxide from allyl alcohol[41], acetate ion[41], DMF[10], dioxan (in presence of excess PPh_3)[10], and acyl and aroyl halides[42] have also been described.

It was decided to make a comparative study of the reactivity of $[M_2X_2(PR_3)_4]^{2+}$ ions with several classes of carbonyl compounds, including (i) aldehydes (ii) a ketone (iii) carboxylic acids (iv) an acyl halide and (v) esters.

(i) ALDEHYDES

A number of aldehydes were selected and heated with the complex $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ in a Carius tube. In certain systems, decarbonylation of the aldehyde does occur, according to the equation:

$$[Pt_2Cl_2(PEt_3)_4][BF_4]_2 \quad (I) \quad + \quad 2\ R'CHO \longrightarrow 2\ \underline{trans}\text{-}\ [PtCl(CO)(PEt_3)_2][BF_4] + 2\ R'H$$

The reaction was extended in the case of benzaldehyde to further platinum and palladium species. The results are summarised in Table XIV A and B.

TABLE XIV A: REACTION OF ALDEHYDES WITH $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$

aldehyde R'	solvent[a]	temp °C	time hr	products
C_6H_5	acetone	reflux	14	(I) recovered (72%)
"	none	80	48	$[PtCl(CO)(PEt_3)_2][BF_4]$ (65%); C_6H_6[b]
"	none	97-100	3	(I) recovered (89%)
$n\text{-}C_6H_{13}$	none	110	20	(I) recovered (79%); aldehyde recovered (10-15%); CO_2; $n\text{-}C_6H_{14}$[b]
"	acetone	110	20	(I) recovered
CH_3	none	80	48	(I) recovered, and $[PtCl(CO)(PEt_3)_2][BF_4]$ (10-30%)
CCl_3	none	97-100	3	cis- $[PtCl_2(PEt_3)_2]$ (71%) $[PtCl(CO)(PEt_3)_2][BF_4]$ (ca. 10%)
CF_3	none	70	2½	(I) recovered (89%)
"	none	80	4	(I) recovered (85-90%) ↓ increasing yield of $(CF_3CHO)_n$
"	none	80	12	
"	none	80	48	
"	acetone	80	48	

a where no solvent is mentioned, reaction was carried out in excess aldehyde

b detected by Gas-Liquid Chromatography (G.L.C.).

TABLE XIV B: REACTION OF BENZALDEHYDE[a] WITH $[M_2X_2(PR_3)_4][BF_4]_2$

dimer	T°	time hr	products
$[Pt_2Cl_2(PEt_3)_4]^{2+}$	80	48	$[PtCl(CO)(PEt_3)_2][BF_4]$ (65%); C_6H_6
$[Pt_2Cl_2(PPh_3)_4]^{2+}$	80	48	dimer recovered (82%)
$[Pd_2Cl_2(PEt_3)_4]^{2+}$	80	48	degradation to palladium
$[Pd_2I_2(PPh_3)_4]^{2+}$	80	2½	

a acting as solvent also

1. High yields of carbonyl are obtained only from benzaldehyde.

2. In the absence of kinetic date, the yields are used as a guide to aldehyde reactivity:

   Reactivity R': CCl_3 > C_6H_5 > CH_3 > n-C_6H_{13}

   PR_3: PEt_3 > PPh_3

   Decarbonylation of CCl_3CHO occurs under the mildest conditions (3 hr @ 100°). However, the major product is not trans-$[PtCl(CO)(PEt_3)_2][BF_4]$, but cis- $[PtCl_2(PEt_3)_2]$. Trichloral is apparently acting as both carbonylating and chlorinating agent.

3. Palladium systems do not yield stable carbonyl species but are rapidly degraded to elemental palladium. This is consistent with the known instability of palladium carbonyls.[17]

4. There is no evidence for decarbonylation of n-heptanal, and the dimeric starting compound is recovered in high yield. However in the absence of solvent (acetone), extensive oxidation of the aldehyde to carbon dioxide and n-hexane occurs. No decomposition occurs on heating the aldehyde alone. These products could result from decarboxylation of n-heptanoic acid:

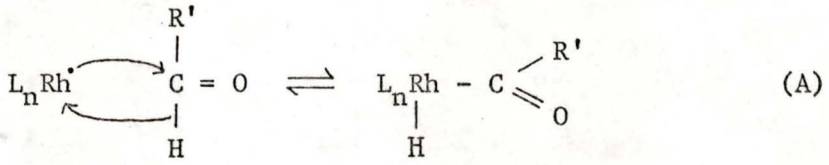
$$n\text{-}C_6H_{13}CO_2H \xrightarrow{\Delta} n\text{-}C_6H_{14} + CO_2$$

   Further work is required to resolve the question of whether the acid is formed, and if so, how it is formed. The only source of oxygen is in the aldehyde itself.

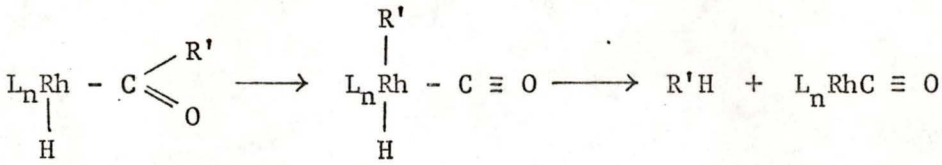
Mechanism of Decarbonylation

Decarbonylation of aldehydes by $[RhCl(PPh_3)_3]$ has been extensively studied by Wilkinson and coworkers[10]. They propose the following reaction scheme (figure 6) whereby initial nucleophilic attack by the

rhodium atom upon the carbon atom of the carbonyl group ensues -- with cleavage of the aldehydic C-H bond, and hydrogen transfer to the metal. The acyl intermediate (A) is considered to undergo decarbonylation by alkyl migration, followed by hydrogen transfer to the alkyl group:



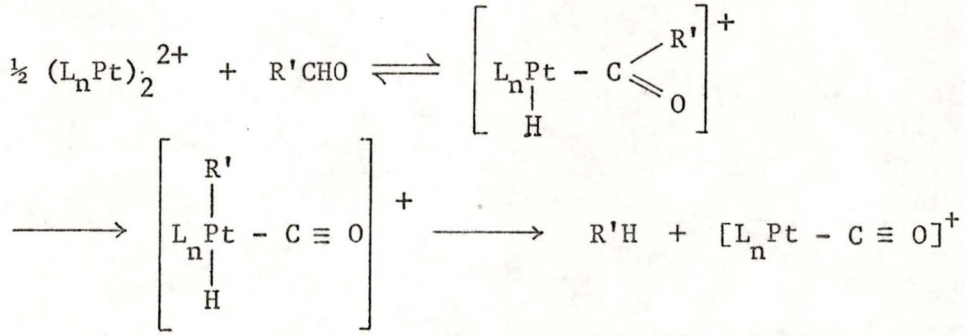
(A)



where $L_n = (PPh_3)_2Cl \cdot solvent$

fig. 6: Proposed Mechanism for Decarbonylation of Aldehydes by $[RhCl(PPh_3)_3]$ (Wilkinson)

We propose for the platinum (II) system an analogous reaction scheme:



where $L_n = (PEt_3)_2Cl$.

fig. 7: Proposed Mechanism for Decarbonylation of Aldehydes by $[Pt_2Cl_2(PEt_3)_4]^{2+}$

Factors making the aldehyde a better electrophile, e.g. the presence of electron withdrawing R' groups, or alternatively making the metal atom more nucleophilic, e.g. presence of electron donating R groups on the phosphine ligands, would favour the formation of a carbonyl

species. The results (Table XIV) are consistent with this hypothesis.

Other Aldehyde

Attempts to decarbonylate trifluoral, CF_3CHO, were unsuccessful, although the above reasoning suggests that CF_3CHO should be more easily decarbonylated than CCl_3CHO.

Unfortunately, trifluoral tends to associate:

$$n(CF_3CHO) \longrightarrow (CF_3CHO)_n$$

even at room temperature, with an accompanying loss of reactivity. Husted and Ahlbrecht[43] reported that perfluoroaldehydes polymerise very easily to give viscous or solid polymers which are chemically and thermally quite stable. Both types are observed in our system. A mass spectrum of a liquid specimen shows intense bands at m/e 127 and m/e 69 which may be assigned to $CF_3CH(OH)CO^+$ and CF_3^+ from fragmentation of $CF_3.CH(OH).CO.CF_3$ or some larger polymer.

Comparative Rates of Decarbonylation

The following data (Table XV) illustrate how much slower is the rate of decarbonylation of benzaldehyde by our platinum (II) system, compared to a rhodium (I) system.

TABLE XV. COMPARATIVE RATES OF DECARBONYLATION OF BENZALDEHYDE

$[RhCl(PPh_3)_3]$[10,39]			$[Pt_2Cl_2(PEt_3)_4]^{2+}$		
solvent	T°	time (yield %)	solvent	T°	time (yield %)
none	180[a]	5 min (80)	none	95-100	3 hr (0)
toluene	110[a]	2 hr (92)	none	80	48 hr (65)
none	25	24 hr (77)	acetone	65[a]	14 hr (0)

a reflux

This is consistent with Wilkinson's proposed mechanism[10] (fig. 6), in that the rhodium atom is more nucleophilic than the positively charged platinum ion.

Conclusions

We have shown that $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ decarbonylates aldehydes in a manner analogous to $[RhCl(PPh_3)_3]$, except that the platinum complex is considerably less reactive.

(ii) OTHER CARBONYL SPECIES

1. Acetone

On heating acetone with the complex $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ in order to assess the former's reactivity when used as a solvent, there is no reaction. A similar system involving $[Pd_2Cl_2(PEt_3)_4][BF_4]_2$ undergoes slight degradation to palladium.

2. Carboxylic Acids

On heating the three acids: benzoic, acetic and formic acid with the complex $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ in a Carius tube, there is no evidence for carbonyl formation. The reaction with acetic acid results in some anion exchange, CH_3COO^- for BF_4^-, but no cleavage of the cation.

Formic acid, however, is catalytically dehydrogenated to hydrogen and carbon dioxide. This significant reaction is discussed in section III D, together with reactions of some formate esters.

3. Acetyl Chloride

On heating acetyl chloride with the complex $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ in a Carius tube, decarbonylation occurs to give trans- $[PtCl(CO)(PEt_3)_2][BF_4]$ (~ 5% yield). However, cis- $[PtCl_2(PEt_3)_2]$ is isolated in

about 90% yield. CH_3COCl is apparently acting primarily as a chlorinating agent (assisted, perhaps by slight hydrolysis to HCl), and in a secondary role as a carbonylating agent.

III C: OLEFINS

(i) TETRAFLUOROETHYLENE C_2F_4

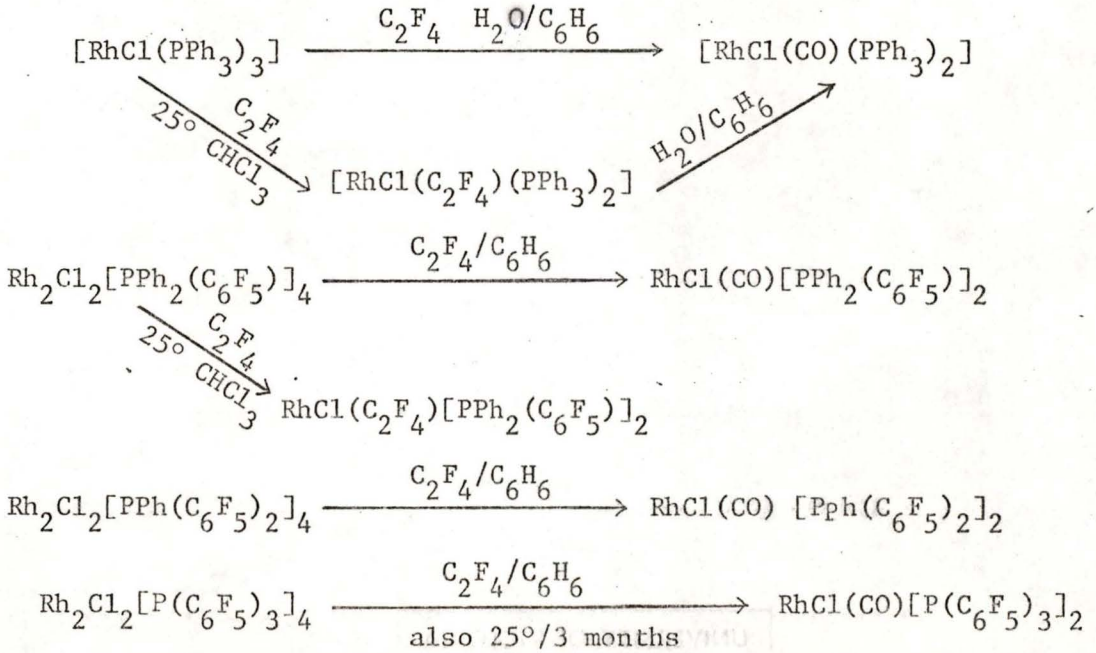
Both ethylene[10] and tetrafluoroethylene[44,45] displace PPh_3 from $[RhCl(PPh_3)_3]$ at room temperature according to the following reaction:

$$[RhCl(PPh_3)_3] + C_2X_4 \longrightarrow PPh_3 + \underline{trans}\text{-}[RhCl(C_2X_4)(PPh_3)_2]$$

X = F or H

The fluoroolefin derivative differs from its ethylene analogue and from $[RhCl(PPh_3)_3]$ in that it does not dissociate in benzene at 37°, and the C_2F_4 ligand is not displaced by an excess of C_2H_4 or PPh_3.

Under certain conditions, hydrolysis of coordinated C_2F_4 in $\underline{trans}$-$[RhCl(C_2F_4)(PPh_3)_2]$ and in several related systems gives almost quantitative yields of carbonyl complexes.[45] Some data are summarised in figure 8.



T = 120° (unless indicated); C_6H_6 indicates "anhydrous" benzene.

Fig. 8: Some Reactions of Rhodium (I) Complexes with C_2F_4

The following results were obtained by Kemmitt and Nichols[45]:

1. Formation of carbonyl complexes involves the hydrolysis of an intermediate π-bonded olefin complex. There is sufficient water in reagent grade benzene for hydrolysis to occur.

2. It was not possible to isolate fluoroolefin intermediates in every case despite the use of "anhydrous" benzene. e.g. where $PR_3 = P(C_6F_5)_3$ or $PPh(C_6F_5)_2$, only carbonyls were isolated.

3. The gaseous fluorocarbon products varied according to the surface of the reaction vessel. From the hydrolysis of $[RhCl(C_2F_4)(PPh_3)_2]$ the main gaseous products were (i) $CF_2H.CF_2H$, using a glass tube (ii) $CF_2H.CF_2H$ and CF_2H_2, using a steel bomb.

4. The reaction was extended to other fluoroolefins and it was shown that (a) carbonyl complexes are formed by non-terminal as well as terminal olefins and (b) chloroolefins do not give carbonyl complexes as easily as fluoroolefins.

An analogous but more limited study of the $[IrCl(PPh_3)_3]/C_2F_4$ system has been made by Clarke, Green and Stone[46] whose results are summarised in figure 9.

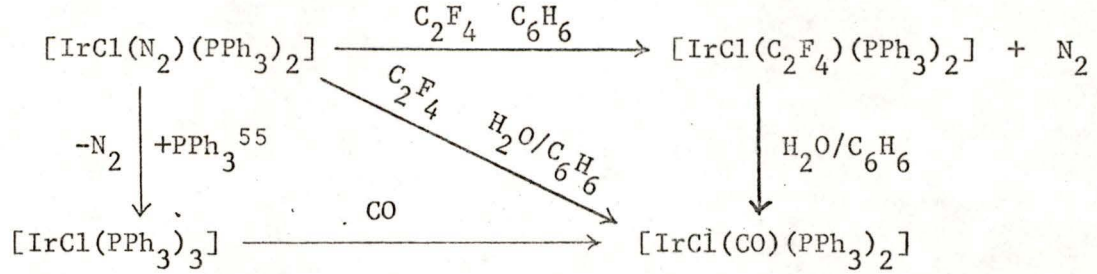


fig. 9: Some Reactions of Iridium (I) Complexes with C_2F_4.

Again it was found that reactions in reagent grade benzene yielded trans- $[IrCl(CO)(PPh_3)_2]$ in high yield.

Clark, Dixon and Jacobs[13] investigating the reaction between trans-$[PtHCl(PR_3)_2]$, where R = ethyl or phenyl, and C_2F_4 in reagent grade benzene, obtained fluorovinyl complexes of the type $[PtCl(PR_3)_2(CF=CF_2)]$ and $[PtCl(PR_3)_2(C(CF_2H)=CF_2)]$; and also trans-$[PtCl(CO)(PR_3)_2][BF_4]$.

This work is relevant since Clark proposed a series of reactions which were consistent with his data; his scheme being later modified to explain the formation of products from the rhodium (I)[45] and iridium (I)[46] systems described above. Mechanistic details will be discussed following presentation of our results for the platinum (II) system, $[Pt_2Cl_2(PEt_3)_4]^{2+}$.

Results and Discussion

C_2F_4 was heated with the complexes $[M_2Cl_2(PEt_3)_4][BF_4]_2$, where M = Pt or Pd, in acetone or THF in a Carius tube. The results are summarised in Table XVI.

TABLE XVI: REACTION OF C_2F_4 WITH $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ (I) AND $[Pd_2Cl_2(PEt_3)_4][BF_4]_2$ (II)

M	solvent[a]	T°	t hr	products[c]
Pt	acetone	25	138	$[Pt_2Cl_2(PEt_3)_4][BF_4]_x[SiF_5]_{2-x}$
	acetone	45-50	15	
	acetone	80	210	$[PtCl(CO)(PEt_3)_2][BF_4]$ (84%); $NaBF_4$; Na_2SiF_6
	acetone	110	20	$[PtCl(CO)(PEt_3)_2][BF_4]$ (91%)
	[b] acetone	110.	20	$[PtCl(CO)(PEt_3)_2][BF_4]$ + (I) [d]
	THF	110	20	(I) + $[PtCl(CO)(PEt_3)_2][BF_4]$ [d]
Pd	acetone	25	22	no reaction; (II) recovered (74%)
		80	82	
	THF	110	90	rather intractable; product contained (II) + some Pd metal

a dried by repeated condensations on to molecular sieves (see Chapter IV).
b steel bomb
c CO_2 was a product of every reaction
d first mentioned was major constituent (~ 70%)

1. There is no evidence for the formation of a fluoroolefin intermediate.

2. Under mild conditions (< 50°) the dimeric structure is retained; however, some substitution by SiF_5^- for BF_4^- is apparent in the platinum system. Also small quantities of water soluble white powders are formed, which show infrared absorptions characteristic of SiF_6^{2-} and BF_4^-. These ions probably arise from etching of the glass, indicating the formation of HF, since it is known that

$$HF + \text{glass} \longrightarrow H_2O,\ BF_3,\ SiF_4,\ BF_4^-,\ SiF_6^{2-}$$

(BF_4^- is originally present as counteranion to the platinum complex cation) In this case the powders are sodium salts.

3. At higher temperatures (> 80°), the bridge is cleaved and <u>trans</u>-$[PtCl(CO)(PEt_3)_2][BF_4]$ formed. In the palladium (II) system, degradation to the metal occurs, consistent with the known instability of <u>trans</u>- $[PdCl(CO)(PEt_3)_2][BF_4]_2$[17].

4. Infrared investigation of the gaseous products indicates the presence of CO_2 and cyclo-C_4F_8 (the latter being a normal product of heating C_2F_4).*

<u>Mechanism of hydrolysis</u>

If it is assumed that carbonyl formation involves the hydrolysis of an intermediate fluoroolefin complex by analogy with Kemmitt's rhodium (I) system, then mechanistic possibilities can now be considered. Kemmitt and Nichols, adopting Clark's original scheme, proposed[45] the following series of reactions (fig. 10):

---

* Recent mass spectral studies show that fluorocarbons are not present in the gaseous products [49]

$$Rh + C_2F_4 \longrightarrow Rh(\pi C_2F_4) \quad (1)$$

$$Rh(\pi C_2F_4) + H^+ \longrightarrow RhCF_2CF_2H^+ \quad (2)$$

$$RhCF_2CF_2H^+ \longrightarrow RhCF = CF_2^+ + HF \quad (3)$$

$$RhCF = CF_2^+ + H_2O \longrightarrow RhCF(OH)CF_2H^+ \quad (4)$$

$$RhCF(OH)CF_2H^+ \longrightarrow RhCO.CF_2H^+ + HF \quad (5)$$

$$RhCO.CF_2H^+ \longrightarrow Rh(CO)CF_2H^+ \quad (6)$$

$$Rh(CO)CF_2H^+ \longrightarrow RhCO + \tfrac{1}{2}(CF_2H.CF_2H) \quad (7)$$

overall reaction:

$$Rh(\pi C_2F_4) + H^+ + H_2O \longrightarrow RhCO + 2HF + \tfrac{1}{2}(CF_2H.CF_2H)$$

fig. 10: Proposed Hydrolysis of Coordinated Fluoroolefin (Kemmitt & Nichols)

Step (7) contains a fundamental error in that charge is not balanced.

Kemmitt and Nichols proposed an alternative reaction:

$$Rh(CO)CF_2H^+ + F^- \longrightarrow RhCO + CF_3H$$

While this overcomes the problem of charge balance, the fact is that CF_3H is not observed in the reaction. The other gaseous product besides CF_2HCF_2H is CF_2H_2. As a possible explanation for the occurrence of CF_2H_2 and the absence of CF_3H, Kemmitt and Nichols draw an analogy with their hydrolysis of $[RhCl_2(COCH_3)(PPh_3)_2]$ which yields trans-$[RhCl(CO)(PPh_3)_2]$ and CH_4 -- no CH_3Cl being observed[45].

To support the protonation envisaged in step (2), Kemmitt and Nichols draw an analogy with their reactions:[47]

$$[RhCl(C_2F_3X)(PPh_3)_2] \xrightarrow[CH_2Cl_2]{HCl} [RhCl_2(CFX.CF_2H)(PPh_3)_2]$$

X = F, Cl or H

(A)

$$\downarrow H_2O$$

$$[RhCl(CO)(PPh_3)_2]$$

Where X = F, hydrolysis of (A) only occurs in the presence of glass, no carbonyl being formed when hydrolysis is attempted in a steel bomb. Therefore, Kemmitt and Nichols suggested that the hydrolysis of $[RhCl(C_2F_4)(PPh_3)_2]$ to $[RhCl(CO)(PPh_3)_2]$ in a steel bomb goes via another mechanism.

Clarke, Green and Stone[46] put forward the following scheme (fig. 11) for the hydrolysis of $[IrCl(CF_3C{\equiv}CCF_3)(PPh_3)_2]$:

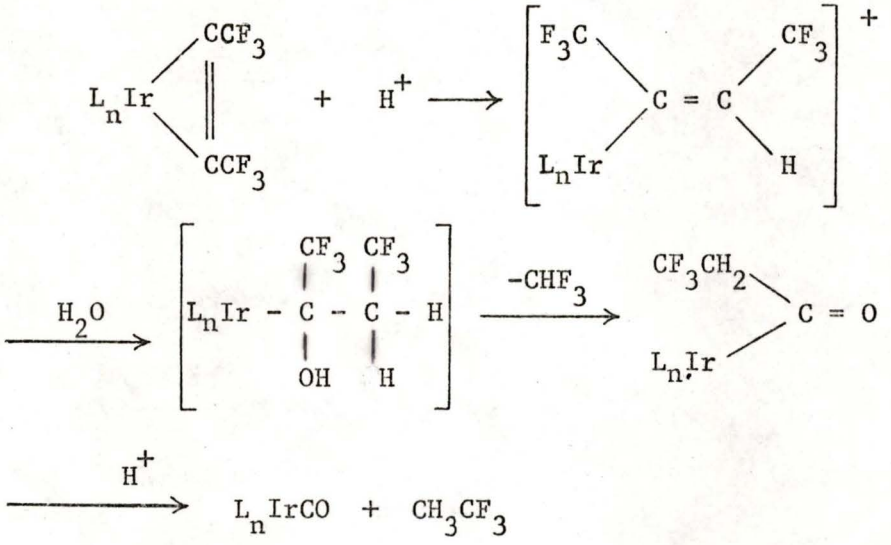


fig. 11: Proposed Hydrolysis of Coordinated Fluoroacetylene (Clark, Green and Stone)

Again, this scheme is unsound, since it contrives to lose positive charge.

Obviously in the absence of kinetic data, and without the isolation of intermediates, it is impossible to discuss mechanisms in detail for the platinum (II) system. However, some possibilities may be outlined. Assuming the formation of a fluoroolefin intermediate, the overall reaction might be:

$$\tfrac{1}{2}(L_nPt)_2^{2+} + C_2F_4 \longrightarrow [L_nPt(\pi C_2F_4)]^+ \xrightarrow{H_2O} [L_nPtCO]^+$$

where $L_n = (PEt_3)_2Cl$

Possible hydrolysis schemes are:

1. Carbon is bonded to the platinum throughout (per Kemmitt and Nichols).

2. Catalytic hydrolysis of the C_2F_4 to free CO[56], which then reacts by bridge cleavage.

e.g. $$C_2F_4 \xrightarrow[\text{catalyst}]{H_2O/\text{acetone}} 2\ CO + 4\ HF$$

$$\tfrac{1}{2}(L_nPt)_2^{2+} + CO \longrightarrow [L_nPtCO]^+$$

The catalyst may be the starting dimer, or perhaps the fluoroolefin intermediate.

3. Oxidation of the olefin (C_2F_4) to an aldehyde (CF_3CFO), followed by decarbonylation (cf. Wacker Process[48]).

Wacker Process $$C_2H_4 + PdCl_2 + H_2O \longrightarrow CH_3CHO + Pd + 2\ HCl$$

Conclusions

Despite the rigorous drying of solvents it is conceivable that they contained residual water in the low concentrations (~ 0.3 mole per cent) required for hydrolysis. Alternatively etching processes could produce water. For further work, one might suggest that a kinetic study be made of these three systems: rhodium (I), iridium (I) and platinum (II).

(ii) ETHYLENE

C_2H_4 was heated with the complex $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ in acetone in a Carius tube or steel bomb. The results are summarised in Table XVII.

TABLE XVII: REACTION OF C_2H_4 WITH $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ (I) IN ACETONE

vessel	$P_{C_2H_4}$ atmos.	T°	t hr	products
glass tube	5	80	20	No reaction; (I) recovered (83%)
glass tube	5	80	39	(I) recovered (54%);
		110	25	trace cis-$[PtCl_2(PEt_3)_2]$
glass tube	5	25	240	No reaction; (I) recovered.
steel bomb	15	110	20	No reaction; (I) recovered (65%)

Also an NMR study of the complex $[Pt_2Cl_2(PPh_3)_4][BF_4]_2$ in methylene chloride under 1 atmosphere pressure of C_2H_4 revealed no evidence for a coordinated ethylene ligand.[49]

Conclusions

There is no evidence for reaction under these conditions.

IIID: FORMIC ACID

Introduction

While the decomposition of formic acid on heterogeneous catalysts has been studied for a number of years[50], the study of similar homogeneous activity is quite recent. Several papers have described the decarbonylation of formic acid by transition metal complexes[50], the reaction being stoichiometric with respect to the metal. Oxidation of formic acid to CO_2 and H_2O, catalysed by both main group and transition metal complexes, has also been described.[50]

More recently, Coffey[22] has described the homogeneous dehydrogenation of formic acid by several phosphine-stabilised complexes of transition metals, particularly iridium and ruthenium, but also rhodium, nickel, palladium and platinum. The solvent was acetic acid under reflux

(or sometimes esters with the more active catalysts). Coffey's findings were:

1. Decomposition of formic acid to H_2 and CO_2 occurred (approx. 1:1), and the system could be used to reduce functional groups.
2. The reactivity of the complexes studied decreased in the order:

   Complexes of general formula $MCl_2(PR_3)_2$: Pt(II) > Pd(II) ≃ Ni(II)

   where R = ethyl

   Complexes of general formula $[MHBr(CO)(PR_3)_3]$ and $[MHCl(diphos)_2]$

   Ru (II) > Os(II)

   Complexes of general formula $[MH_xCl_{3-x}(PR_3)_3]$

   where x = 0, 1, 2 or 3; R = alkyl or aryl, and $[MCl(CO)(PR_3)_2]$ where R = aryl

   Ir (III) > Rh (III); Ir (I) > Rh(I)
3. Some loss of catalyst occurred, by conversion to complexes containing phosphine, carbonyl, hydride and acetate ligands,

   e.g. $[IrH_2Cl(CO)(PPh_3)_2]$ from $[IrCl(CO)(PPh_3)_2]$[51]
4. No free carbon monoxide was detected.

Marangoni et al.[50] have also described the catalytic dehydrogenation of formic acid by cobalt (I) complexes of the type $[CoH(CO)_x(PBu^n_3)_{4-x}]$, where x = 1, 2 or 3.

Results and Discussion

Complexes $[M_2Cl_2(PR_3)_4][BF_4]_2$, where M = Pt, R = ethyl and phenyl; M = Pd, R = ethyl, were heated with excess HCOOH in acetone in a steel bomb or Carius tube. The results are summarised in Table XVIII.

TABLE XVIII: REACTION OF HCOOH WITH $[M_2Cl_2(PR_3)_4][BF_4]_2$ IN ACETONE

	dimer 0.10 mmole	HCOOH mmole	T°	time hr	products
1	I	~ 130	80	17	I recovered + $[PtCl(CO)(PEt_3)_2][BF_4]$ IR band at 2160 cm^{-1} (Pt-H) in I Tube fractured.
2	I	2	110	20	I recovered (68%); IR bands at 2200 and 2160 cm^{-1} (Pt-H) and 2110 cm^{-1} (Pt-CO) CO_2 detected.
3	I	43.6	110	20	I recovered (ca. 30%); IR as for 2. H_2 (26.6 mmole); CO_2 (34.6 mmole)
4	III	43.6	110	20	IR bands at 2110 cm^{-1} (Pt-C≡O) and 1640-50 cm^{-1} (Pt-$\overset{\shortmid}{C}$=O) H_2 (ca. 3.5 mmole); CO_2 (ca. 3.5 mmole)
5	II	43.6	110	20	III recovered. Trace of H_2 (ca. 0.1 mmole); CO_2 (ca. 0.1 mmole)

I $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ III $[Pt_2Cl_2(PPh_3)_4][BF_4]_2$

II $[Pd_2Cl_2(PEt_3)_4][BF_4]_2$

expts: 1 and 2 in Carius tube; expts: 3, 4 and 5 in steel bomb.

1. The complexes $[Pt_2Cl_2(PR_3)_4][BF_4]_2$ cause catalytic dehydrogenation of HCOOH to H_2 and CO_2 (approx. 1:1).
   Rate of dehydrogenation where R = Et is ~10 times that where R = Ph
2. Degradation of the catalyst is quite rapid being more rapid in the steel bomb than in the glass tubes.
3. Trans- $[PtCl(CO)(PEt_3)_2][BF_4]$ and trans- $[PtHCl(PEt_3)_2]$ are minor products, where R = ethyl. The major product where R = phenyl shows infrared absorptions at 2110 cm^{-1}, characteristic of the Pt-C≡O linkage; at 1645-50 cm^{-1}, characteristic of the Pt-$\overset{\shortmid}{C}$=O linkage,

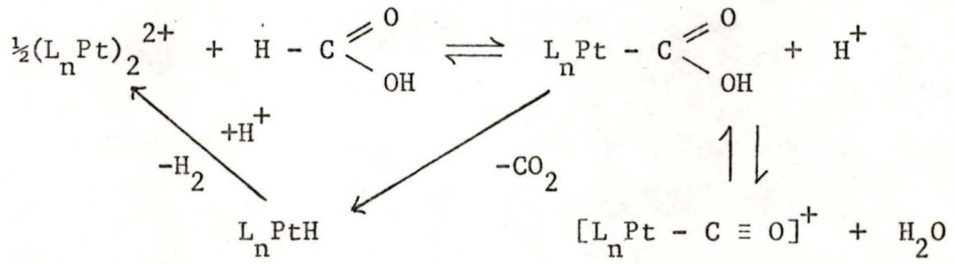
and at 3450-3550 (vb) cm^{-1}, characteristic of -OH.

4. No free CO is detected.

5. $[Pd_2Cl_2(PEt_3)_4][BF_4]_2$ does not act as a catalyst.

Mechanism of Dehydrogenation

The above observations, together with the known chemical nature of the several products, suggest that catalysis by $[Pt_2Cl_2(PR_3)_4][BF_4]_2$ may proceed according to the following scheme:



where $L_n = (PR_3)_2Cl$.

overall reaction $\quad HCOOH \xrightarrow{\text{catalyst}} H_2 + CO_2$

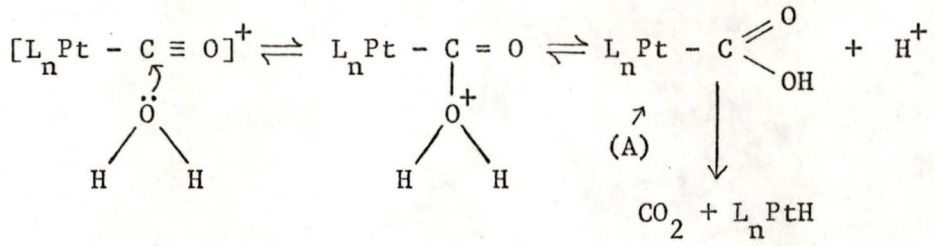
fig. 12: Proposed Catalytic Cycle for Dehydrogenation of Formic Acid

1. The initial step is similar to that proposed for the decarbonylation of aldehydic systems. Factors enhancing the nucleophilic character of the platinum would be expected to favour formation of the carboxylate intermediate. Our findings that (i) rate of dehydrogenation for PEt_3 complex : PPh_3 complex was ca. 10:1 and (ii) the more electropositive palladium complex was not an active catalyst, are consistent with this premise.

2. The following reaction is known:[14,53]

trans-$[PtCl(CO)(PEt_3)_2]^+ + H_2O \longrightarrow$ trans-$[PtHCl(PEt_3)_2] + CO_2 + H^+$

A kinetic study by Clark and Jacobs[52] led them to suggest that since the carbonyl carbon will be somewhat positive in nature because of removal of electron density by the positively charged metal, attack by H_2O or OH^- ion at the acyl carbon might yield (A) as an intermediate



No direct experimental evidence for (A) could be obtained, but the closely analogous alcoholysis:[14,53]

$$\underline{\text{trans}}\text{-}[PtCl(CO)(PPh_3)_2][BF_4] + R'OH \rightleftharpoons [PtCl(COOR')(PPh_3)_2] + HBF_4$$

can be stressed.

In our system R = Ph, infrared evidence indicates the presence of both [Pt - C ≡ O] and [Pt-C = O] linkages, which is consistent with the presence of the equilibrium:

$$L_nPt - C \equiv O^+ + H_2O \rightleftharpoons L_nPt - \overset{OH}{\underset{|}{C}} = O + H^+$$

The formation of a stable compound at this point in the cycle suggests that a lower number of cycles will be achieved (i.e. less decomposition of formic acid).

Carboxylate species have certainly been isolated e.g. an Ir(III) derivative may be prepared according to the following reaction:[54]

$$[IrCl_2(CO)_2(PMe_2Ph)_2]^+ + H_2O \rightleftharpoons [IrCl_2(CO)(COOH)(PMe_2Ph)_2] + H^+$$

This product undergoes thermal decomposition to give $[IrHCl_2(CO)(PMe_2Ph)_2]$ and CO_2.[54]

3. We have shown that reaction between trans-$[PtHCl(PEt_3)_2]$ and HBF_4 occurs under similar conditions according to the following equation:

$$2\ [PtHCl(PEt_3)_2] + 2\ HBF_4 \longrightarrow [Pt_2Cl_2(PEt_3)_4][BF_4]_2 + H_2$$

thus demonstrating the feasibility of the last step in the cycle, (fig. 12).

(ii) Formate Esters

Since the complexes $PtCl(COOH)(PR_3)_2$ were not isolable intermediates in our system, attempts were made to generate an alkoxycarbonyl species, using formate esters in place of formic acid, according to the following reaction:

$$\tfrac{1}{2}(L_nPt)_2^{2+} + H-C(=O)-OR' \underset{}{\overset{K_2CO_3}{\rightleftharpoons}} L_nPt-C(=O)-OR' + H^+$$

R' = Et or Me

After unsuccessful early experiments, anhydrous potassium carbonate was added to neutralize the acidic products and drive the reaction.

The anticipated products were already well characterised.[14] The results are summarised in Table XIX.

The results were disappointing, since the anticipated complexes $[PtCl(COOR')(PR_3)_2]$ were not isolated.

However, products from several of the reactions did show infrared absorptions at 1645-50 cm^{-1}, which is characteristic of the Pt - $\overset{|}{C}$ = O linkage. The appearance of bands at ca. 2200 cm^{-1}, characteristic of Pt - H, and at 3560 cm^{-1}, characteristic of PtO - H suggests that hydrolysis products were present.

TABLE XIX. REACTION OF HCOOR' WITH $[Pt_2Cl_2(PR_3)_4][BF_4]_2$ IN ACETONE UNDER REFLUX

dimer	ester R'=	T°	time hr	products
I[a,b]	Et	80	22	I recovered; IR bands in region 1600-50 cm^{-1} (e.g. Pt - $\overset{\vert}{C}$ = O)
I[a,b]	Et	110	20	
I	Et	reflux	4½	Product showed IR bands at 1645-50 cm^{-1} (Pt - $\overset{\vert}{C}$ = O), and 2220 and 2180 cm^{-1} (Pt-H)
I[a]	Et	80	20	intractable.
III	Et	reflux	3	non-ionic species: IR band at 1645-50 cm^{-1} (Pt - $\overset{\vert}{C}$ = O): Proton NMR inconsistent with formula $[PtCl(COOEt)(PPh_3)_2]$
III	Et	"	3	cis- $[PtCl_2(PPh_3)_2]$
III	Et	"	12	Product with IR band at 3560 cm^{-1} (PtO - H)
III[c]	Et	"	3	II recovered (93%)
III	Me	"	21	II recovered (36%); (PtO-H) band
III[c]	Me	"	21	II recovered -- no reaction

I $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ III $[Pt_2Cl_2(PPh_3)_4][BF_4]_2$

a glass tube

b K_2CO_3 absent

c no solvent

Conclusions

The results obtained are consistent with the proposed cycle for dehydrogenation of formic acid. Further work is required: with particular effort directed to isolating the carboxylate complexes $[PtCl(COOH)(PR_3)_2]$.

Finally we suggest that similar reactions may be involved in Coffey's ruthenium, rhodium and iridium systems.[22]

IIIE: NATURE OF THE ACTIVE SPECIES IN REACTIONS OF $[Pt_2Cl_2(PR_3)_4][BF_4]_2$

The active species in reactions of $[Pt_2Cl_2(PR_3)_4]^{2+}$ may be $[PtCl(PR_3)_2.solvent]^+$ according to:

$$[Pt_2Cl_2(PR_3)_4]^{2+} + 2\ solvent \rightleftharpoons 2[PtCl(PR_3)_2.solvent]^+$$

by analogy with the system:

$$[RhCl(PPh_3)_3] + solvent \rightleftharpoons [RhCl(PPh_3)_2.solvent] + PPh_3$$

$$2\ [RhCl(PPh_3)_2.solvent] \rightleftharpoons [Rh_2Cl_2(PPh_3)_4] + 2\ solvent$$

proposed by Wilkinson.[10]

CHAPTER IV

EXPERIMENTAL

Standard high-vacuum techniques were used for most reactions where $[M_2X_2(PR_3)_4][BF_4]_2$ complexes were reactants. Reactions were performed in thick-walled pyrex glass tubes having volumes of about 50 ml, or in a stainless steel bomb having a volume of 60 ml. All other reactions were conducted under an atmosphere of nitrogen.

Infrared spectra were recorded with a Beckman IR 20 spectrophotometer. Solid samples were examined as Nujol mulls between caesium iodide plates. Spectra were recorded from 4000-250 cm^{-1} with an accuracy of ±5 cm^{-1}, and were calibrated against polystyrene film or water vapor.

Proton NMR spectra were recorded on a Varian A-60 spectrometer, and the chemical shift data measured relative to the solvent, methylene chloride. The mass spectra were obtained with a Perkin-Elmer-Hitachi RMU 7 mass spectrometer, using direct insertion technique with an ionising energy of 70 eV. Mass spectra are plotted or tabulated in terms of relative peak heights.

Conductance measurements were made with a dip-type cell connected to a conductivity bridge, Model RC 16 B2 of Industrial Instruments Inc.

Gas chromatograms were recorded in a Microtek MT 220 gas chromatograph with a flame ionisation detector. Separations were made on a SE 30 column (5% on chromoport XXX 80/90) using helium as carrier gas.

Melting points were determined on a Kofler hot stage microscope (corrected) or by capillary methods (uncorrected).

Microanalysis were by Schwarzkopf Microanalytical Laboratory, New York, N.Y.

The complexes <u>trans</u>- $[PdX_2(PR_3)_2]$, where X= Cl, Br or I; R = ethyl or phenyl[17], <u>cis</u>- $[PtCl_2(PEt_3)_2]$[57], and <u>trans</u>- $[PtHCl(PEt_3)_2]$[3] and <u>trans</u>- $[NiCl_2(PEt_3)_2]$[3] were prepared as previously described.

C_2F_4 was prepared and purified as previously described[58], with SiF_4 being removed by several condensations on to moist KF. Pyridine, ethyl formate and benzaldehyde were distilled (the last under N_2) and condensed onto molecular sieves (type 4A) before use. Other reagents were used as received, or as prepared. Solvents were of reagent grade and used as received, except where dry solvents are specified below. Diethyl ether, acetone and methylene chloride were dried by fractional distillation from drierite onto molecular sieves (type 4A). Tetrahydrofuran (THF) was dried as previously described[17]. Acetone and THF were rigorously dried for use in experiments involving olefins, by several condensations onto dry molecular sieves under vacuum.

Where solvent pairs are indicated for recrystallisations e.g. A/B, the second solvent (B) was added dropwise to a concentrated solution of the complex in the first (A), until crystallisation began.

The infrared spectra of all products described below were recorded, and where additional characterisation is not given these served to identify the products.

A: SYNTHESIS

1. Reactions of complexes trans- $[PdX_2(PR_3)_2]$ with $BF_3.Et_2O$

(a) trans- $[PdCl_2(PPh_3)_2]$ (1.945 g; 2.77 mmole) in excess $BF_3.Et_2O$ (50 ml) was heated to 125° under reflux until the mixture was homogeneous and red-brown in colour (2 hours). The mixture was heated at this temperature for a further 30 minutes. Volatile materials were removed under vacuum at 30°, and the yellow-brown residue extracted with nitromethane (50 ml). Addition of 250 ml ether* to the extract gave

* diethyl ether: this abbreviation is used throughout.

$[Pd_2Cl_2(PPh_3)_4][BF_4]_2$ (0.72 g; 0.77 mmole; 35%*) as a yellow precipitate, whose molar conductivity in 10^{-3} M solution in nitromethane was 170.7 ohm^{-1} cm^2 (lit: . 167 ohm^{-1} cm^2 [17]).

(b) <u>trans</u>- $[PdI_2(PPh_3)_2]$ (0.442 g; 0.50 mmole) in excess $BF_3.Et_2O$ (8 ml) was heated to 130° under reflux, and maintained at this temperature for 30 minutes. Homogeneity was not achieved, a brown solid being present. The products proved rather intractable; except for a small quantity of PPh_3, no pure products were isolated.

(c) <u>trans</u>- $[PdCl_2(PEt_3)_2]$ (0.827 g; 2.00 mmoles) in excess $BF_3.Et_2O$ (20 ml) was heated to 120° under reflux until homogeneous, and maintained at this temperature for 30 minutes. Volatile products were removed under vacuum, and the residue extracted with nitromethane (25 ml). An insoluble orange-yellow powder was filtered off, washed with nitromethane and dried. Recrystallisation from 100% EtOH gave orange-red crystals of $[Pd_2Cl_4(PEt_3)_2]$ (0.165 g; 0.28 mmole; 28%), m.p. 230-1° (lit: 231-3° [17]). The nitromethane filtrate was evaporated to a small volume and an excess of ether added, giving $[Pd_2Cl_2(PEt_3)_4][BF_4]_2$ (0.598 g; 0.65 mmole, 65%) as a yellow precipitate. Recrystallisation from acetone/ether gave yellow needles, m.p. 185-90d (lit: ~200d[17]), characterised by NMR, and whose molar conductivity in 10^{-3} M solution in nitromethane was 189.5 ohm^{-1} cm^2 (lit: 177 ohm^{-1} cm^2 [17])

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* obtained previously in 91% yield: K. R. Dixon, unpublished result.

(d) trans- $[PdBr_2(PEt_3)_2]$ (1.004 g; 2.00 mmoles) in excess $BF_3.Et_2O$ (20 ml) was heated to 130° under reflux until homogeneous, and maintained at this temperature for 30 minutes. A similar work up to (c) gave $[Pd_2Br_4(PEt_3)_2]$ (0.543 g; 0.71 mmole; 71%), which was recrystallised from acetone as orange-red crystals, m.p. 215° (lit: 212-13° [59]), and characterised by proton NMR. Anal. calcd. for $C_{12}H_{30}Br_4P_2Pd_2$: C, 18.8; H, 3.9%. Found: C, 19.0; H, 4.0%. Addition of excess ether to the nitromethane extract gave a sticky brown solid (o.21 g), insoluble in ether and smelling of PEt_3. Evaporation of the ethereal filtrate gave trans- $[PdBr_2(PEt_3)_2]$ (0.15 g; 15%).

(e) trans- $[PdI_2(PEt_3)_2]$ (0.299 g; 0.50 mmole) in excess $BF_3.Et_2O$ (6 ml) was heated to 120° under reflux until homogeneous, and maintained at this temperature for 30 minutes. A similar work up to (c) gave $[Pd_2I_4(PEt_3)_2]$ (0.106 g; 0.112 mmole; 45%), which was recrystallised from acetone as violet crystals, m.p. 195-6° (lit: 194.5-196[17]) and characterised by NMR. Evaporation of the nitromethane extract gave orange crystals of trans- $[PdI_2(PEt_3)_2]$ (0.06 g; 0.10 mmole; 20%).

2. Reactions of complexes trans- $[PdX_2(PR_3)_2]$ with $AgBF_4$

Generally a solution or suspension of trans- $[PdX_2(PR_3)_2]$ in dry acetone was added dropwise, while stirring, to a solution of $AgBF_4$ in dry acetone. Immediate precipitation of silver halide occurred; however, the suspension was stirred at 25° for 30-60 minutes to ensure complete reaction.

The silver halide was filtered off, well washed with dry acetone and dried under vacuum. Its identity was confirmed by its featureless IR spectrum and by qualitative solubility tests in dilute ammonia. The acetone filtrate, varying from yellow to pale-brown in colour, was evaporated to a small volume and added to an excess of dry ether. This gave a crude yellow or orange precipitate of $[Pd_2X_2(PR_3)_4][BF_4]_2$, which was filtered off, washed with dry ether and dried under vacuum. Recrystallisation was from: CH_3NO_2/Et_2O or CH_2Cl_2/Et_2O where R = Ph; $(CH_3)_2CO/Et_2O$ where R = Et. Any variations or modifications are discussed as required.

Procedures 2 (a), 2 (c) (i), 2 (d), and 3 used $AgBF_4$ which was synthesised in situ as follows: An excess of $BF_3.Et_2O$ was added dropwise, while stirring to anhydrous AgF. The reaction flask was sheathed in aluminium foil to minimise photochemical decomposition. Stirring was continued for about 15 minutes at 25°, then volatile material was removed under vacuum at this temperature. A suitable volume of dry acetone was condensed on to the residue under vacuum.

The resulting pale-brown solution was used for subsequent operations.

Procedures 2 (b), 2 (c) (ii - v), 2 (e) and 2 (f) employed $AgBF_4$, purchased from Alpha Inorganics.

(a) <u>trans</u>- $[PdCl_2(PPh_3)_2]$ (0.700 g; 1.00 mmole) and $AgBF_4$ (0.197 g; 1.00 mmole) gave AgCl (0.165 g) and a yellow precipitate of $[Pd_2Cl_2(PPh_3)_4][BF_4]_2$ (0.681 g; 0.90 mmole; 90%), which was recrystallised from $CH_2Cl_2/CHCl_3$.

(b) <u>trans</u>- $[PdBr_2(PPh_3)_2]$ (0.200 g; 0.025 mmole) and $AgBF_4$ (0.056 g; 0.028 mmole) gave AgBr (0.046 g; 0.025 mmole) and a yellow precipitate of $[Pd_2Br_2(PPh_3)_4][BF_4]_2$ (0.193 g; 0.012 mmole;

97%), which was recrystallised from CH_3NO_2/Et_2O.

(c) (i) trans- $[PdI_2(PPh_3)_2]$ (1.770 g; 2.00 mmoles) was stirred with $AgBF_4$ (0.392 g; 2.00 mmole) in dry acetone solution. Trans- $[PdI_2(PPh_3)_2]$ (0.218 g; 0.25 mmole) was filtered off, and the filtrate evaporated to dryness. Extraction of the yellow residue with methanol (20 ml), followed by filtration, gave a white powder which was well washed with MeOH and dried under vacuum. Recrystallisation from MeOH gave colourless crystals of $[Ag(PPh_3)_4][BF_4]$ (1.058 g; 0.85 mmole; 85%) m.p. 285-8° , and characterised by mixed m.p. with a pure, independently prepared sample (see 3).

The methanolic filtrate was evaporated to a small volume, during which time a trace of black solid was deposited (elemental palladium or silver) and removed by filtration. Addition of the filtrate to excess ether gave an off-white precipitate (0.061 g), and evaporation of the ethereal filtrate gave a crude sand-coloured solid (0.729 g). Neither solid was characterised. However, their IR spectra both showed absorptions at 1090 (s) and 1050 (vs, b) cm^{-1}, characteristic of BF_4^-, and at 1170-80 (vs, b), 1120 (s) and 720 (vs) cm^{-1}, characteristic of $OPPh_3$.

(ii) $AgBF_4$ (0.059 g; 0.30 mmole) in dry acetone (10 ml) was added dropwise while stirring to trans- $[PdI_2(PPh_3)_2]$ (0.267 g; 0.30 mmole) in dry acetone (20 ml) at -10°. Stirring was continued for 2 hours. The brown precipitate formed (0.087 g) was filtered off and digested in boiling toluene (20 ml). A yellow residue of AgI (0.064 g; 0.27 mmole) was filtered off, and evaporation

of the toluene filtrate gave trans- $[PdI_2(PPh_3)_2]$ (0.020 g; 0.022 mmole; ~7%).

Addition of the acetone filtrate to excess dry ether gave an orange-yellow precipitate of the new $[Pd_2I_2(PPh_3)_4][BF_4]_2$ (0.222g; 0.13 mmole; 87%). This was recrystallised from CH_3NO_2/Et_2O as a bright orange microcrystalline solid m.p. 215-20 d. Anal. calcd. for $C_{72}H_{60}B_2F_8I_2P_4Pd_2$: C, 51.2; H, 3.6%. Found: C, 51.5; H, 3.8%.

(iii) a repeat of (i) but at -10° and

(iv) a repeat of (ii) but at 25° and

(v) a repeat of (i)

All gave AgI and $[Pd_2I_2(PPh_3)_4][BF_4]_2$ (80-90%).

(d) trans- $[PdBr_2(PEt_3)_2]$ (0.502 g; 1.00 mmole) and $AgBF_4$ (0.196 g; 1.00 mmole) gave AgBr (0.170 g; 0.90 mmole) and a yellow precipitate of the new $[Pd_2Br_2(PEt_3)_4][BF_4]_2$ (0.388 g; 0.38 mmole; 76%). This was recrystallised from CH_3OH/Et_2O as yellow needles, m.p. 140-5 d, and characterised by proton NMR. Anal. calcd. for $C_{24}H_{60}B_2Br_2F_8P_4Pd_2$: C, 28.3; H, 5.9%. Found: C, 28.9; H, 6.1%. Molar conductivity in 10^{-3} M solution in nitromethane was 197.2 ohm^{-1} cm^2.

(e) trans- $[PdI_2(PEt_3)_2]$ (0.442 g; 0.75 mmole) and $AgBF_4$ (0.144 g; 0.75 mmole) gave AgI (0.157 g; 0.67 mmole) and an ether-insoluble dull-green powder (yield undetermined), whose IR spectrum showed strong absorption in the region 1040-1100 cm^{-1} characteristic of BF_4^-, and also a band at 3490 (s) cm^{-1}, characteristic of a non-hydrogen bonded -OH (possibly PdO-H).

(f) cis- $[PtCl_2(PEt_3)_2]$ (1.728 g; 3.44 mmoles) and $AgBF_4$ (0.734 g;

3.77 mmoles) gave AgCl (0.518 g; 3.58 mmoles) and a white precipitate of $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ (1.688 g; 1.53 mmole; 89%).

3. Preparation of $[Ag(PPh_3)_4][BF_4]$

PPh_3 (1.049 g; 4.00 mmoles) was stirred with $AgBF_4$ (0.196 g; 1.00 mmole) in a dry acetone solution. The resulting white precipitate was filtered off, and to it added the white precipitate produced by adding the acetone filtrate to excess ether. This was the new $[Ag(PPh_3)_4][BF_4]$ (0.92 g; 0.75 mmole; 75%), and it was recrystallised from methanol as colourless crystals, m.p. 285-8°. Anal. calcd. for $C_{72}H_{60}AgBF_4P$: C, 69.5; H, 4.9%. Found: C, 69.1; H, 4.8%. Molar conductance in 10^{-3} M solution in nitromethane was 84.9 ohm^{-1} cm^2. A qualitative analysis for silver was achieved by decomposition of a sample of the product with HNO_3 in a porcelain crucible, leaching with HNO_3, adjusting the pH and precipitating as AgCl by addition of dil. HCl.

4. Reaction of cis- $[PtCl_2(PEt_3)_2]$ with aqueous HBF_4

cis- $[PtCl_2(PEt_3)_2]$ (0.100 g; 0.20 mmole) and aqueous 48% HBF_4 (0.10 ml) in acetone (20 ml) were heated under reflux for 6½ hours. The orange-brown solution, originally colourless, was added to excess ether giving cis- $[PtCl_2(PEt_3)_2]$ (0.057 g; 0.11 mmoles; 57%) as a white precipitate.

Evaporation of the filtrate to a small volume, followed by addition of further ether gave a white precipitate of $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ (0.046 g; 0.04 mmole; 46%).

B: REACTIONS

1. Pyridine

(i) $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ (0.1107 g; 0.10 mmole) was heated under reflux with pyridine (0.055 g; 0.70 mmole) in dry acetone (5 ml) for 8 hr. Addition to excess ether gave a white flocculent precipitate of the new cis-$[PtCl(PEt_3)_2(py)][BF_4]$ (0.126 g; 0.198 mmole, 99%). This was recrystallised from acetone/ether as colourless crystals, m.p. 212-5°. Anal. calcd. for $C_{17}H_{35}BClF_4NP_2Pt$: C, 32.3; H, 5.6%. Found: C, 32.6; H, 5.6%.

The IR spectrum showed absorptions at 3100 (w), 3080 (w), 3030 (w), 1610 (s), 1450 (s), 1215 (s), 1155 (w) and 705 (s) cm^{-1} characteristic of the pyridine ligand. The proton NMR spectrum showed a methyl proton resonance which approximated to a 1:2:2:2:1 quintet, consistent with coupling with two phosphorus nuclei in a cis configuration, and the relative intensity of heterocyclic protons to aliphatic protons was approx. 1:6. The mass spectrum showed a base peak at m/e 79 ($C_5H_5N^+$).

(ii) A similar reaction between $[Pd_2Cl_2(PEt_3)_4][BF_4]_2$ (0.0932 g; 0.10 mmole) and pyridine (0.055 g; 0.70 mmole) gave the new cis-$[PdCl(PEt_3)_2(py)][BF_4]$ (0.095 g; 0.175 mmole, 87%). This was recrystallised from acetone/ether as colourless crystals m.p. 203-5° (turning yellow at 135°). Anal. calcd. for $C_{17}H_{35}BClF_4NP_2Pd$: C, 37.5; H, 6.5%. Found: C, 37.5; H, 6.4%. The IR, proton NMR and mass spectra are similar to those of the platinum alalogue.

2. Aldehydes

(a) Benzaldehyde

(i) $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ (I) (0.055 g; 0.05 mmole) was heated

under reflux with C_6H_5CHO (0.011 g; 0.10 mmole) in dry acetone (20 ml) for 14 hours. Addition of the product to excess ether gave a white precipitate of (I) (0.040 g; 0.036 mmole; 72%).

(ii) (I) (0.179 g; 0.162 mmole) dissolved in C_6H_5CHO (4.0 ml; 39 mmole) was heated at 80° for 48 hr. in a glass tube. The initially pale yellow solution was now brown in colour (some degradation was a normal feature of 'tube' reactions and will be assumed henceforth). A semi-quantitative analysis of the product by G.L.C. showed the presence of C_6H_6 (~0.15 mmole) in the excess C_6H_5CHO. The latter was removed under vacuum. The residue was taken up in the minimum of acetone and added to excess ether giving a white precipitate of trans-$[PtCl(CO)(PEt_3)_2][BF_4]$ (0.123 g; 0.212 mmole; 65%). This was recrystallised from benzene as a colourless crystalline solid, m.p. 168-9° (lit: 168-171° [13,14]). The ethereal filtrate was evaporated to dryness, the residue containing a further amount of carbonyl.

(iii) (I) (0.080 g; 0.072 mmole) dissolved in C_6H_5CHO (3.0 ml) was stirred at 97-100° for 3 hours. A similar work up to (ii) gave (I) (0.071g;0.064 mmole; 89%).

(iv) $[Pt_2Cl_2(PPh_3)_4][BF_4]_2$ (0.150 g; 0.089 mmole) dissolved in C_6H_5CHO (4.0 ml) was heated at 80° for 48 hr. in a glass tube. A similar workup to (ii) gave $[Pt_2Cl_2(PPh_3)_4][BF_4]_2$ (0.123 g; 0.073 mmole; 82%). There was no IR evidence for carbonyl formation.

(v) $[Pd_2Cl_2(PEt_3)_4][BF_4]_2$ (0.093 g; 0.10 mmole) was dissolved in benzaldehyde (4.0 ml) and stirred at 80° for 48 hrs.

Elemental palladium was filtered from the reaction mixture (0.049 g). A similar work up to (ii) gave $[Pd_2Cl_2(PEt_3)_4][BF_4]_2$ (~ 0.020 g; 0.022 mmole; 22%).

(vi) A similar reaction to (v) but using $[Pd_2I_2(PPh_3)_4][BF_4]_2$ showed almost complete degradation to palladium after 2½ hours at 80°.

(b) n-heptanal $C_6H_{13}CHO$

(i) (I) (0.2214 g; 0.20 mmole) suspended in n-heptanal (4.0 ml) was heated at 110° for 20 hr. in a glass tube. IR analysis showed the presence of CO_2 in the gaseous products. Semi-quantitative analysis of the liquid by G.L.C. demonstrated that (a) n-hexane was a reaction product and (b) extensive decomposition of the n-heptanal had occurred, the peak showing only 10-15% of its intensity before reaction. Addition of the product to excess ether gave crude (I) (0.174 g; 0.157 mmole; 79%). An IR spectrum of the evaporated ether extract showed no evidence for carbonyl formation.

(ii) n-heptanal (4 ml) was heated at 110° for 20 hr in a glass tube. IR analysis of the gaseous products showed that CO_2 was absent.

(iii) (I) (0.1107 g; 0.10 mmole) was heated with n-heptanal (0.50 ml) in dry acetone (5 ml) at 110° for 20 hr. in a glass tube. No CO_2 was detected in the gaseous products, and (I) was regained in almost quantitative yield.

(c) acetaldehyde

(I) (0.1107 g; 0.10 mmole) dissolved in CH_3CHO (2.0 ml) was heated

at 80° for 48 hr. in a glass tube. Volatile products were removed under vacuum. The residue was taken up in dry acetone and added to excess ether giving a white precipitate (0.080 g). An IR spectrum of this product indicated that it was mainly (I) together with trans- $[PtCl(CO)(PEt_3)_2][BF_4]$ (~10-30%).

(d) trichloral CCl_3CHO

Preparation: Conc. H_2SO_4 (25 ml) and chloral hydrate (25 g) were refluxed under N_2 and then fractionally distilled, that fraction distilling at 96-8° being condensed onto molecular sieves (~15 ml)

(I) (0.080 g; 0.072 mmole) was heated under reflux in CCl_3CHO (3.0 ml) for 3 hr. Addition of the product to excess ether gave cis- $[PtCl_2(PEt_3)_2]$ (0.055 g; 0.11 mmole; 76%). The ethereal filtrate was evaporated to dryness, and an IR spectrum indicated that this was trans-$[PtCl(CO)(PEt_3)_2][BF_4]$ (~10%) together with unreacted (I).

(e) trifluoral CF_3CHO

Preparation: for example, conc. H_2SO_4 (2 ml) and fluoral hydrate (2.32 g; 1.58 ml) were mixed at ~-180°. The reactants were allowed to warm to room temperature and the aldehyde (bp -18°) allowed to vaporize into an evacuated bulb and manometer system. The vapor exerted a pressure of 21 cm (theory 55 cm). (some of the vapor had condensed to a colourless liquid. Its IR spectrum differed from that of CF_3CHO (g) in having bands at 3620 (s), 2990, 1135, 1100 and 1070 cm^{-1}. Its mass spectrum showed intense peaks at m/e 127 and 69 which might result from cleavage of $CF_3.CHOH.CO.CF_3$. There was no evidence for the ion $(CF_3CHO)_2^+$).

(i) The CF_3CHO (g) (~6.7 mmole) was condensed onto (I) (0.1107 g; 0.10 mmole) in a glass tube, and heated at 70° for 150 min. The gaseous product was CF_3CHO (~1 mmole). Addition of the product to excess ether gave (I) (0.099 g; 0.089 mmole; 89%). There was no evidence for carbonyl formation.

Using the same reactant ratios, the tube and contents were heated at 80° for (ii) 4 hr. (iii) 12 hr. and (iv) 48 hr. In each case (I) was regained in 85-90% yield. There was no evidence for carbonyl formation. The longer the heating time, the greater was the yield of a rather intractible glassy solid, which was insoluble in most solvents except EtOH. Its mass spectrum showed fragments > m/e 500 but no obvious molecular ion due to $(CF_3CHO)_n$, where n = 2, 3, 4, etc.

3. Acetone

(i) (I) (0.1107 g; 0.10 mmole) dissolved in dry acetone (15 ml) was heated at 80° for 210 hr. in a glass tube. Addition of the products to excess dry ether gave $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ (0.064 g; 0.058 mmole; 58%) as a white precipitate. The ethereal filtrate contained further dimer, but no evidence for carbonyl formation.

(ii) A similar reaction using $[Pd_2Cl_2(PEt_3)_4][BF_4]_2$ gave comparable results. However, degradation was more marked in this system -- the acetone solution being rather red in colour before workup.

4. Carboxylic Acids

(a) benzoic acid

(I) (0.2214 g; 0.20 mmole) was heated with $C_6H_5CO_2H$ (0.050 g; 0.41 mmole) in dry acetone (4 ml) at 110° for 20 hr. in a glass tube. Addition of the product to excess ether gave (I) (0.171 g;

0.155 mmole; 78%) as a white precipitate. There was no evidence for carbonyl formation, and qualitative tests for phenol (using methanolic $FeCl_3$) proved negative.

(b) acetic acid

(I) (0.1107 g; 0.10 mmole) dissolved in glacial CH_3CO_2H (3.0 ml) was heated at 110° for 20 hr. in a glass tube. The solution remained colourless throughout. A similar workup to (a) gave a white solid (0.101 g), insoluble in ether. This was recrystallised from acetone/ether as off-white crystals m.p. 165-70 d, whose IR spectrum showed strong absorption at 1020-1100 cm^{-1} characteristic of BF_4^-, and also at 3440-20 (b), 1555-25 (b), 1450-1400 (vb) and 700 (s) cm^{-1}, characteristic of the CH_3COO^- ion. A mass spectrum showed a strong band at m/e 43 (CH_3CO^+). It was considered that some anionic substitution had occurred, giving $[Pt_2Cl_2(PEt_3)_4][BF_4]_x[CH_3COO]_{2-x}$ where $2 > x > 0$

5. Acetyl chloride

(I) (0.1107 g; 0.10 mmole) dissolved in CH_3COCl (0.50 ml) was heated at 80° for 48 hr. in a glass tube. Addition of the product to excess dry light petrol (b.p t. 30-60°) gave a white precipitate of cis-$[PtCl_2(PEt_3)_2]$ (0.091 g; 0.182 mmole; 91%). Evaporation of the pet. ether filtrate gave a residue whose IR spectrum showed that trans-$[PtCl(CO)(PEt_3)_2][BF_4]$ and (I) were present.

6. Olefins

(a) Ethylene

(i) (I) (0.1107 g; 0.10 mmole) was heated with C_2H_4 (5 atmospheres; ~10 mmoles) in dry acetone at 80° for 20 hr. in a glass tube.

The gaseous components were C_2H_4 and acetone vapor. Addition of the product to excess dry ether gave (I) (0.092 g; 0.083 mmole; 83%). Evaporation of the ethereal filtrate gave a residue whose IR spectrum showed further (I), but no evidence for olefinic absorption modes.

(ii) This was a repeat of (i) except that the reactants were heated at 80° for 39 hr., and then at 110° for 25 hr. A similar workup to (i) gave (I) (0.060 g; 0.054 mmole; 54%) and also cis- $[PtCl_2(PEt_3)_2]$ (0.010 g; 0.02 mmole). Further amounts of the latter were present in the ethereal filtrate.

(iii) (I) (0.1107 g; 0.10 mmole) was heated with C_2H_4 (15 atmospheres; ~37 mmoles) in dry acetone (~5 ml) at 110° for 20 hr. in a steel bomb. A similar workup to (i) gave (I) (0.072 g; 0.065 mmole; 65%) and further (I) was present in the ethereal filtrate.

(iv) This was a repeat of (i) except that the reactants were shaken at 25° for 10 days in a glass tube. Acetone was allowed to evaporate from the product under 1 atmosphere pressure of C_2H_4. The residue was (I) (0.110 g; 0.099 mmole; 99%).

(b) Tetrafluoroethylene

(i) (I) (0.162 g; 0.147 mmole) was heated with C_2F_4 (5 atmospheres; ~10 mmoles) in dry acetone (~3 ml) at 110° for 20 hr. in a glass tube. A small amount of CO_2 and cyclo-C_4F_8 were present in the gaseous products. Addition of the product to an excess of dry ether gave a white precipitate of trans- $[PtCl(CO)(PEt_3)_2][BF_4]$ (0.155 g; 0.266 mmole; 91%). This was recrystallised from benzene as a colourless crystalline solid, m.p. 168-170° (lit: 168-71°[13,14]). There was no evidence for olefinic absorption modes.

(ii) (I) (0.221 g; 0.20 mmole) was heated with C_2F_4 (5 atmospheres) in dry acetone (~20 ml) at 80° for 210 hr. in a glass tube. CO_2 and cyclo-C_4F_8 were again present in the gaseous products. A similar workup to (i) gave $[PtCl(CO)(PEt_3)_4][BF_4]$ (0.196 g; 0.34 mmole; 84%). A water soluble white powder (0.005 g) was also isolated -- whose IR spectrum showed absorptions characteristic of SiF_6^{2-} (740 and 480 cm^{-1}) and BF_4^- (1040-1100 cm^{-1}). It probably consisted of sodium salts resulting from etching the glass.

(iii) (I) (0.221 g; 0.20 mmole) was shaken with C_2F_4 (5 atmospheres) in dry acetone (5 ml) at 25° for 138 hr. in a glass tube. A trace of CO_2, but no cyclo-C_4F_8, was present in the gaseous products. A similar workup to (i) gave a white solid (0.148 g) whose IR spectrum showed strong absorptions at 875 (vs, b), 775 (vs, b), 475 (w) and 445 (w) cm^{-1}, characteristic of the SiF_5^- ion, in addition to absorptions characteristic of BF_4^-. It was considered that some anionic substitution had occurred giving $[Pt_2Cl_2(PEt_3)_4][BF_4]_x[SiF_5]_{2-x}$ where $2 > x > 0$.

(iv) This was similar to (iii) but at 45-50¼ for 15 hr. The same products were obtained.

(v) (I) (0.1500 g; 0.136 mmole) was heated with C_2F_4 (5 atmospheres) while suspended in dry THF (3 ml) at 110° for 20 hr. in a glass tube. CO_2 and cyclo-C_4F_8 were present in the gaseous products. A similar work up to (i) gave a white solid (0.130 g) which was predominately (I) containing a trace of <u>trans</u>- $[PtCl(CO)(PEt_3)_2][BF_4]$.

(vi) $[Pd_2Cl_2(PEt_3)_4][BF_4]_2$ (II) (0.186 g; 0.20 mmole) was heated with C_2F_4 (5 atmospheres) in dry THF (20 ml) at 110° for 90 hr. in a glass tube. A trace of CO_2 was detected in the gaseous products. Elemental palladium (0.026 g; 0.024 mmole) was filtered from the solution, and a similar work up to (i) gave a rather intractable oily yellow precipitate (~0.2 g) whose IR spectrum closely resembled that of (II). Attempts to purify this product by column chromatography (6 cm Florisil column) proved ineffectual.

(vii) This was a repeat of (vi) except that the reactants were shaken at 25° for 22 hr., and then at 80° for 82 hr. A similar workup to (i) gave (II) (0.137 g; 0.147 mmole; 74%).

(c) Cyclohexene

C_6H_{10} (~0.05 g; 0.60 mmole) was added to (II) (0.094 g; 0.10 mmole) in a mixture of dry THF (16 ml) and dry acetone (8 ml), and the mixture heated under reflux for 2½ hr. Addition of the orange-brown solution to excess ether gave (II) (0.070 g; 0.074 mmole; 74%). Evaporation of the ethereal filtrate gave a residue whose IR spectrum showed no evidence for olefinic absorption modes.

7. Formic Acid

(i) (I) (0.055 g; 0.05 mmole) was heated under reflux with HCOOH (0.015 g; 0.30 mmole) in dry acetone (10 ml) for 9 hr. Addition of the product to an excess of ether gave (I) (0.034 g; 0.031 mmole), with further (I) being present in the ethereal filtrate.

(ii) (I) (0.1107 g; 0.10 mmole) was heated with HCOOH (0.10 g; 2.00 mmole) in dry acetone (5 ml) at 110° for 20 hr. in a glass

tube. CO_2 was present in large quantity in the gaseous products. A similar workup to (i) gave (I) (0.074 g; 0.068 mmole; 68%). The ethereal filtrate was evaporated to dryness and an IR spectrum of the residue showed absorptions at 2110 (s) and 540 (w) cm^{-1} characteristic of Pt-C≡O, and at 2200 (w) and 2160 (w) cm^{-1} characteristic of Pt-H stretching modes.

(iii) (I) (0.1107 g; 0.10 mmole) was heated with HCOOH (2.00 g; 43.6 mmole) in dry acetone (~4 ml) at 110° for 20 hr. in a steel bomb. The bomb was cooled in liquid nitrogen and a quantitative measurement made of the non-condensible hydrogen (26.6 mmoles). The bomb was now placed in an acetone/dry ice bath (~-80°) and the gaseous material pumped into a trap cooled in liquid nitrogen, via a U tube cooled in a slurry of CS_2/liquid nitrogen at -112° (which condensed traces of acetone vapor). The contents of the trap were allowed to warm to room temperature and a quantitative measurement made of the carbon dioxide (34.6 mmoles). Products were checked for purity by mass spectrometry. Workup of the reaction solution gave (I) (0.030-0.040 g; ~0.03 mmole; ~30%), whose IR spectrum showed the presence of some Pt-C≡O.

(iv) (II) (0.093 g; 0.10 mmole) was heated with HCOOH (2.00 g; 43.6 mmole) as in (iii). H_2 (~0.10 mmole) and CO_2 (~0.10 mmole) were detected by mass spectrometry. A similar workup to (iii) gave (II) (0.090 g) contaminated with formate ion.

(v) $[Pt_2Cl_2(PPh_3)_4][BF_4]_2$ (III) (0.1263 g; 0.075 mmole) was heated with HCOOH (2.00 g; 43.6 mmole) as in (iii). H_2 (~3.5 mmoles) and CO_2 (~3.5 mmoles) were detected by mass spectrometry. A similar workup to (iii) gave a white solid (0.124 g) whose

IR spectrum showed absorptions at 2110 (s) cm^{-1} characteristic of Pt-C≡O, and at 1645-50 (s, b) cm^{-1} characteristic of Pt-$\overset{|}{C}$=O. Attempts to further separate this mixed product were unsuccessful.

8. Esters

(a) ethyl formate

(i) (I) (0.1107 g; 0.10 mmole) was heated with HCOOEt (0.09 g; 1.2 mmoles) in dry acetone (~4 ml) at 80° for 22 hr. in a glass tube. Addition of the products to excess ether gave a white precipitate of (I) (0.106 g), whose IR spectrum showed weak impurity bands at 1645-50, 1570 and 1530 cm^{-1}.

(ii) A similar reaction at 110° for 20 hr. gave the same result as (i).

(iii) (I) (0.050 g; 0.05 mmole) was heated with HCOOEt (0.09 g; 1.2 mmoles) and anhydrous K_2CO_3 (0.050 g; 0.05 mmole) in dry acetone (4 ml) at 80° for 20 hr. in a glass tube. A similar workup to (i) gave a sticky, brown intractable solid.

(iv) A similar reaction to (iii) but under reflux for 4½ hrs. gave a yellow product. The crude K_2CO_3 (0.051 g) was removed by filtration, and the yellow filtrate evaporated to dryness. The IR spectrum of the residue showed a doublet at 2230 and 2180 cm^{-1} characteristic of Pt-H, and a band at 1645-50 (b) cm^{-1} characteristic of Pt-$\overset{|}{C}$=O.

(v) (III) (0.168 g; 0.10 mmole) was heated at reflux with HCOOEt (0.09 g; 1.2 mmoles) in the presence of anhydrous K_2CO_3 (0.050 g; 0.05 mmole) in dry acetone (10 ml) for 3 hrs. After removal of the crude K_2CO_3 (0.058 g) by filtration, the filtrate was evaporated to dryness and the residue extracted with 100% EtOH.

Part dissolved, while the remainder was present as an insoluble white solid. The latter was filtered off (0.087 g) and recrystallised from EtOH as a white powder, m.p. 212-16°, whose molar conductivity in ~10^{-3} M solution in nitromethane was 11 ohm^{-1} cm^2. Its IR spectrum showed bands at 1645-50 (s) cm^{-1} characteristic of Pt-$\overset{|}{C}$=O, and at 1225 (m) cm^{-1} characteristic of ν(C-O). There were no bands at 1090 and 1050 cm^{-1} characteristic of BF_4^-. The proton NMR spectrum showed a triplet centred about 7.9 τ and a crude quintet about 8.75 τ. The relative intensity of aromatic protons to aliphatic protons was 4.5:1. (For $[PtCl(COOEt)(PPh_3)_2]$: the methyl proton resonance is a triplet, centred about 9.5 τ; the methylene proton resonance is a multiplet, centred about 7.3 τ. Relative intensity of aromatic protons to aliphatic protons is 6:1)[14].

The yellow ethanolic extract was evaporated to dryness and an IR spectrum of the residue showed a band at 1645-50 cm^{-1}, characteristic of Pt-$\overset{|}{C}$=O.

(vi) This was a repeat of (v) except that the weight of K_2CO_3 was reduced to 0.030 g from 0.050 g. A similar workup gave <u>cis</u>-$[PtCl_2(PPh_3)_2]$ (0.046 g; 0.058 mmole; 30%) and (III) (0.101 g; 0.06 mmole; 60%).

(vii) This was a repeat of (vi) except that the reactants were heated under reflux for 12 hours. A similar workup gave a white solid (0.052 g) insoluble in EtOH, whose IR spectrum showed a band at 3560 cm^{-1} characteristic of a non-hydrogen bonded -OH (perhaps PtO-H) and the band at 300 cm^{-1} characteristic of Pt-Cl, much diminished in intensity relative to its intensity in starting

compound (III).

(viii) There was no reaction on heating (III) under reflux in HCOOEt for 3 hr.

(b) methyl formate

(i) (III) (0.502 g; 0.30 mmole) was heated under reflux with HCOOMe (0.050 g; 8 mmoles) in the presence of anhydrous K_2CO_3 (0.050 g; 0.05 mmole) in dry acetone (20 ml) for 21 hr. After removal of the crude K_2CO_3 by filtration, a similar workup to that in 8 (a) (v) gave (III) (0.490 g; 0.293 mmole; 98%), whose IR spectrum showed the presence of an -OH group (perhaps PtO-H) at 3460 (w) cm^{-1}.

(ii) There was no reaction on heating (III) under reflux in HCOOMe for 21 hr.

9. Reaction of trans-$[PtHCl(PEt_3)_2]$ with HBF_4

Trans- $[PtHCl(PEt_3)_2]$ (0.1872 g; 0.40 mmole) was heated with aq. 48% HBF_4 (0.10 ml) in acetone (5 ml) at 70° for 90 min. in a glass tube. H_2 was detected in the gaseous products by mass spectrometry. Addition of the product to excess ether gave a white precipitate of (I) (0.075 g; 0.068 mmole; 34%). $PtHCl(PEt_3)_2$ was recovered from the ethereal filtrate.

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