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Relative binding affinities of fluorobenzene ligands in cationic rhodium bisphosphine $\eta^6$–fluorobenzene complexes probed using collision-induced dissociation

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**Abstract**

A range of cationic rhodium bisphosphine $\eta^6$-fluorobenzene ($\text{fluorobenzenes} = C_6H_6.F_{n}, n = 1–3$) and related complexes have been synthesized and characterized. These complexes act as useful organometallic precursors for catalysis or further synthetic elaboration. The relative binding affinity of the arene ligands has been investigated using Electrospray Ionisation Mass Spectrometry (ESI–MS) and two different collision-induced dissociation (CID) techniques. The influence of arene fluorination upon arene binding affinity is discussed as well as the comparison of different bis-phosphate ligands with regard to bite angle and phosphine substitution. We show that this simple technique allows fast and easy comparison of the binding affinity of arene ligands to cationic organometallic fragments.

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**Introduction**

The study and development of catalytic processes mediated by transition–metal complexes has been, and remains, an area of intense academic and industrial interest [1]. For systems that operate via inner–sphere processes, a catalyst typically requires available vacant sites for the substrate to bind. Often these are masked by a labile ligand, i.e. they are “operationally unsaturated” [2], and ideally this masking ligand does not interfere with the progress of the catalytic process. We have recently developed the use of fluorobenzene–ligated [Rh($\eta^6$-C$_6$H$_5$F)$_2$]$_2$[BArF$_4$] complexes [1$\text{L}_2$ = monodentate or bidentate phosphine, ArF$^+$ = 3,5-(CF$_3$)$_2$C$_6$H$_3$] as precatalysts for hydroacylation [3,4], silane reduction of C–H activation [5], Suzuki type C–C coupling via C–S activation [6], and the dehydrogenation of amine– and phosphine–boranes [7–11], as well as stoichiometric intramolecular C–H activation processes [12–14]. Some of these pre–catalysts have also been found to be bench–stable [3,4], while the bound arene can be substituted by solvents, such as acetone, to provide access to 16–electron [Rh($\text{L}_2$)(solvent)$_2$][BArF$_4$] complexes [4,6].

Many of these fluorobenzene complexes have been structurally characterized. The general synthetic route to their formation is hydrogenation of a strained bis–alkene ligand such as NBD (NBD = norbornadiene) in a precursor [Rh(NBD)(L)$_2$][BArF$_4$] complex in the appropriate solvent, i.e. fluorobenzene (Scheme 1).

Remarkably, given the now widespread use of fluorobenzene (and to a lesser extent ortho difluorobenzene) as a solvent in organometallic chemistry there are, outside of those listed above, relatively few examples of isolated fluorobenzene complexes [15,16]. In some examples coordination through the fluorine atoms can occur rather than coordination through the π–system e.g. A (Scheme 2) [17–19], while $\eta^6$–coordination of the arene is also possible given the appropriate electronic and steric environment is provided by the metal, e.g. B [20,21]. Fluorobenzene also acts as a ligand to main group species, e.g. [Ga($\eta^6$-C$_6$H$_5$F)$_3$]$^–$C [22] and post–transition metals, e.g. D, C–F activation of fluoroarenes has also been widely reported, and $\eta^6$–coordinated intermediates are suggested to be involved in the process that forms M–F and M–aryl bonds [23]. Closely related to these weakly–bound fluorobenzene complexes are zwitterionic species in which a [BArF$_4$]$^−$ anion coordinates with the metal through the arene ring, e.g. E [24–26].

Given the broad range of complexes of general formula [Rh($\eta^6$–fluoroarene)(L)$_2$][BArF$_4$] reported by our group and others, and the use of these complexes in both catalysis and synthesis, we...
were interested in a straightforward way of measuring the relative binding strength of fluorobenzene in a variety of complexes. For example, we have recently reported the strength of binding of fluorobenzene, relative to an alternative solvent complex, can be modified as a function of the bite angle [27,28] of the supporting chelating phosphine ligand in [Rh(\eta-C6H4F)]([L]2)[BARF 4] complexes where \( L = \text{chelating ligand, in which wider bite angle ligands promote equilibria that favor the solvent species, [Rh(\eta-C6H6)(acetone)2][BARF 4]} \) [4]. As fluorobenzenes are usually installed on metal centers to either stabilize a low-coordinate metal center or act as a masking ligand to reveal such a reactive center, a straightforward measure of the relative binding strengths of different fluorobenzenes with the same metal fragment, or different metal fragments with the same fluorobenzene would be useful. Of course, equilibrium studies in solution can provide such information, however we were interested in developing other techniques that might complement such methods, and turned to ESI–MS to do this. Fluorobenzene is quite polar enough to permit the acquisition of high quality ESI mass spectra [29].

Mass spectrometry techniques have been previously used to study the binding affinities of fluorobenzenes with metal cations. Klippenstein, Dunbar and co-workers reported the coordination of fluorobenzenes with \( \text{Cr}^+ \) ions probed by radiative association kinetics in the gas–phase using Fourier transform ion cyclotron resonance mass spectrometry [30]. The energetics of the arene binding in the \( [\text{Cr}(\text{fluorobenzene})]{}^+ \) fragment were determined and showed that increasing fluorination results in weaker binding affinity. Previous studies have suggested that coordination to the \( \pi \) system of arenes by transition metals has a significant electrostatic component [31,32], and that additional fluorine substituents reduce the negative charge located across the \( \pi \) region so that in the extreme case of hexafluorobenzene the \( \pi \) region has a partial positive charge.

Other, more accessible for the synthetic chemist, mass spectrometric techniques can be used for determining relative binding strengths, for example tandem electrospray ionization mass spectrometers (ESI-MS/MS) have the capability to selectively fragment ions in a collision cell and determine the energetics of their dissociation [33,34]. More generally, ESI–MS is a useful technique for characterizing charged complexes in polar solvents, as it is a “soft” ionization technique and allows the parent ion to be observed with little or no fragmentation [35]. This property is particularly useful for studying weakly–bound, or transient, organometallic complexes [36,37] and can be coupled with inert atmosphere glove-box techniques in order to study air-sensitive complexes [38]. In this contribution we utilize Collision Induced Dissociation (CID) techniques to establish comparative binding affinities of various fluorobenzene ligands in a range of complexes \([\text{Rh}(\eta-C6H5-F)\gamma\text{arene})]([L]_2)\) where the chelating phosphine (\( L \)) is also varied. We also correlate these results from ESI–MS with both ESI–MS/MS and solution–based equilibrium studies. In doing this we present ESI–MS as a simple and straightforward methodology for determining qualitative information on the relative binding strengths of the arenes. Quantification of ligand binding strength is a substantially more involved process that requires the use of energy-resolved threshold CID techniques that necessitate instrumentation that is not commercially available [39–41].

Results and discussion

Synthesis and characterization of \( \eta^5 \)-arene complexes

We start by comparing the relative binding strengths of a variety of fluorinated arenes ligated with the \([\text{Rh}(\text{Bu}_2\text{PCH}_2\text{CH}_2\text{Bu}_2)]\) fragment, a motif that we have previously used for the synthesis of a transition metal alkane complex in the solid–state [24]. Complexes 1, \([\text{Rh}(\text{Bu}_2\text{PCH}_2\text{CH}_2\text{Bu}_2)(\eta^5-C6H5-F)][\text{BARF 4}])\), 2, \([\text{Rh}(\text{Bu}_2\text{PCH}_2\text{CH}_2\text{Bu}_2)(\eta^5-C6H4F)][\text{BARF 4}]\), have been reported as precursors as part of this study. Hydrogenation of \([\text{Rh}(\text{Bu}_2\text{PCH}_2\text{CH}_2\text{Bu}_2)(\text{NBD})][\text{BARF 4}])\) (NBD = norbornadiene) in the presence of the desired arene (either as the solvent or as a reagent dissolved in non-coordinating \( \text{CH}_2\text{Cl}_2 \)) results in the formation of the corresponding arene complex (Scheme 1). In most cases the resulting product can be recrystallized, after removal of the hydrogen atmosphere, by layering the reaction mixture directly with pentane to yield the products as analytically pure material. Using this methodology the following species were synthesized \([\text{Rh}(\text{Bu}_2\text{PCH}_2\text{CH}_2\text{Bu}_2)(\eta^5-\text{arene})][\text{BARF 4}]\); arene = \( C6H5F \) (1), \( 1,2-C6H4F2 \) (2), \( 1,3-C6H4F2 \) (3), \( 1,4-C6H4F2 \) (4), \( 1,2,3-C6H3F3 \) (5), \( C6H5CF3 \) (6), \( C6H5Cl \) (7), & \( C6H4 \) (8). Complexes 1, 2 [24] and 7 [42] have been previously reported.

In solution all of the \([\text{Rh}(\text{Bu}_2\text{PCH}_2\text{CH}_2\text{Bu}_2)(\eta^5-\text{arene})][\text{BARF 4}]\) complexes exhibited similar \( 31P–^{10}R \) coupling constants in their \( 31P–^{1H} \) NMR spectra ranges from 199 to 202 Hz, consistent with similar examples reported for \([\text{Rh}(\text{PR}_3)_2]^{+} \) fragments coordinated to arenes that generally show large (greater than 170 Hz) coupling constants [4,7,43]. The \( ^{1H} \) NMR spectra of the arene complexes in \( \text{CD}_2\text{Cl}_2 \), or in the neat arene, show signals for the coordinated aromatics that are located upfield of signals for free ligand, indicative of \( \eta^5 \)-arene coordination [44]. In \( \text{CD}_2\text{Cl}_2 \) solvent these complexes are in equilibrium with the anion-coordinated zwitterionic complex 9 (vide infra) [24], and the ratio of these two species depends on the arene. No evidence of a \( \kappa^3-\text{fluoro-} \) coordination mode is observed in solution by NMR spectroscopy (including \( ^{19}F \) NMR spectroscopy) [17]. For many of these complexes the solid–state structures were determined, but unfortunately all show significant
disorder in both the phosphine and the fluoroarene. Although they could be modelled satisfactorily to give gross structures fully consistent with an η-coordinated arene ligand, due to the high number of necessary restraints in refinement, imposed by the disorder, discussion of the structural metrics is not appropriate (see Supporting materials). Nevertheless the spectroscopic, and micro-analytical data, are in full accord with the proposed structures.

All these complexes show the molecular ion in the ESI–MS spectrum, when the appropriate fluoroarene solvent is used as diluent, that also displays the correct isotope pattern. However for the most weakly bound arene, complex 5, at the required dilutions required for ESI–MS (1 × 10⁻⁵ mol dm⁻³) [38] trace amounts of arene impurities present in the solvent, such as benzene and fluoro benzene, displace a significant proportion of the weakly bound 1,2,3-C₆H₃F₃ ligand and so, although 5 is observed in the mass spectrum ([M⁺] m/z = 553.19, [M⁺] calc = 553.18, correct isotope pattern), it is only a minor peak (ca. 20%) with major peaks observed assigned to the cations of 1 and 8 Scheme 3. By contrast hydrogenation of [Rh(iBu₂PCH₂CH₂PiBu₂)(NBD)] [BARF₄] in 1,2,3,4-C₆H₄F₄, C₆HF₅ or C₆F₆ solvents forms zwitterionic 9 as the sole product (Scheme 4) to the detection limits of 3¹P NMR spectroscopy. In these cases the fluoro benzene now acts as a non-coordinating solvent.

Comparison of binding strength with the [BARF₄]⁻ anion

As the number of fluorine substituents on the arene is increased the [BARF₄]⁻ anion thus becomes a competitive ligand for coordination, to form zwitterionic 9, there being a tipping point in neat arene solvent with four fluorines in the arene. The position of the equilibrium between the arene complexes 1–8 and 9 can be measured using CH₂Cl₂ solutions and the relative integrals of each species in the 3¹P{¹H} NMR spectrum, allowing for the equilibrium constant at 298 K to be estimated (Table 1). Although 9 undergoes decomposition in neat CH₂Cl₂ over 1 h, equilibrium is established rapidly allowing for measurements to be taken upon freshly solvated samples [45]. The corresponding reverse reaction, i.e. addition of C₆H₅F to 9 in CH₂Cl₂ solution, quickly formed complex 1, demonstrating equilibrium conditions. These experiments show that by increasing the fluorine content of the arene the binding affinity of the arene with the [Rh(iBu₂PCH₂CH₂PiBu₂)]⁺ fragment decreases relative to [BARF₄]⁻. The resulting ΔG°/298 K values obtained can be plotted against the number of fluorine substituents to show a reasonably linear trend [Fig. 1]. Noteworthy is that C₆H₆ (complex 8) binds so strongly that complex 9 is not observed to the detection limits of ³¹P NMR spectroscopy. As reported previously, complex 7 does not undergo C–Cl bond activation unlike the C₆H₅Br analogue (thus precluding equilibrium measurements for the bromoarene) [42]. Interestingly, C₆H₅CF₃ binds less strongly than the [BARF₄]⁻ anion (which contains a bis–CF₃ substituted arene). We have previously reported that [BARF₄]⁻ coordination with a {Rh(L₉)}⁺ fragment is disfavoured entropically when compared with binding of [CB₁₁H₆Br₆]⁺ [25]. However, in this example, the favourable electrostatic interactions in the zwitterion 9 are presumably also important in determining the position of equilibrium.

Estimation of relative binding affinities of the arene in [Rh(iBu₂PCH₂CH₂PiBu₂)(η⁶-arene)]⁺ using ESI–MS techniques

The phosphine complexes [Rh(iBu₂PCH₂CH₂PiBu₂)(η⁶-arene)]⁺ are ideal for gas-phase ESI–MS fragmentation studies because the phosphine is not susceptible to C–H activation, unlike monodentate iBu₃P complexes [46]. Controlled fragmentation experiments were achieved by use of a glove–box interfaced with an ESI–MS [38], and variation of the capillery exit voltage to determine the degree of fragmentation by collision-induced dissociation processes in the source [34]. By such variation, the ratio of the arene–coordinated cation, [Rh(iBu₂PCH₂CH₂PiBu₂)(η⁶-arene)]⁺, to the nominally 12–electron, arene–free, rhodium phosphine fragment [Rh(iBu₂PCH₂CH₂PiBu₂)]⁺ can be controlled. In the gas phase it is likely that this arene–free fragment is stabilized by agostic interactions from the alkyl phosphine [46–48], but as the same species is being formed in each case then the experiment probes just the relative binding strength of the arene. The results are plotted as the percentage of arene–bound cations against exit voltage in Fig. 2 for selected species and tabulated for the full series in Table 1.

In each experiment the corresponding arene complex was diluted to a concentration of ~1 × 10⁻⁶ M, using the same arene as the coordinated ligand as the solvent (to avoid formation of 9), and the ESI–MS was recorded over a range of exit voltage values until less than 1% of the precursor ion remained. The spectra were analyzed by measuring the intensity of the largest isotope peak for the two signals [Rh(iBu₂PCH₂CH₂PiBu₂)(η⁶-arene)]⁺ and [Rh(iBu₂PCH₂CH₂PiBu₂)]⁺, and these intensities then normalized to account for differing isotopic distributions. Voltages were corrected to center-of-mass values with the assumption that the vast majority of collisions at this point in the source are with residual
Table 1  
Estimated equilibrium constants for arene complexes in equilibrium with 9 at 298 K in CH2Cl2.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Arene</th>
<th>(K) (298)</th>
<th>(\Delta G_{298}^\circ) (kJ mol(^{-1}))</th>
<th>Exit−voltage for 50% dissociation (V)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>C6H6</td>
<td>(&lt;1 \times 10^{-4})</td>
<td>&gt;25 (min value)</td>
<td>8.4</td>
</tr>
<tr>
<td>1</td>
<td>C6H5F</td>
<td>3 ((\pm 1.4) \times 10^{-3})</td>
<td>+14 ((\pm 1))</td>
<td>7.2</td>
</tr>
<tr>
<td>2</td>
<td>1,2-FC6H4</td>
<td>3.2 ((\pm 0.3))</td>
<td>-2.9 ((\pm 0.2))</td>
<td>6.3</td>
</tr>
<tr>
<td>3</td>
<td>1,3-FC6H4</td>
<td>12 ((\pm 0.2))</td>
<td>-6.1 ((\pm 0.3))</td>
<td>6.5</td>
</tr>
<tr>
<td>4</td>
<td>1,4-FC6H4</td>
<td>2.8 ((\pm 0.3))</td>
<td>-2.5 ((\pm 0.2))</td>
<td>6.6</td>
</tr>
<tr>
<td>5</td>
<td>1,2,3-FC6H3</td>
<td>260 ((\pm 125))</td>
<td>-14 ((\pm 1))</td>
<td>3.9</td>
</tr>
<tr>
<td>6</td>
<td>C6H5CF3</td>
<td>0.23 ((\pm 0.22))</td>
<td>+3.6 ((\pm 0.2))</td>
<td>6.4</td>
</tr>
<tr>
<td>7</td>
<td>C6H5Cl</td>
<td>6.1 ((\pm 6.4) \times 10^{-4})</td>
<td>+18 ((\pm 3))</td>
<td>7.1</td>
</tr>
</tbody>
</table>

\(\hat{a}\) Estimated value as ~15% of 1 present from impurities in the solvent (Fluorochem).

\(\hat{b}\) Exit−voltage at which 50% arene dissociation occurs from ESI−MS (mass corrected).

\(\hat{c}\) This species is present at small relative concentrations in the gas−phase due to the competitive formation of alternate cations such as 1 and 8 that arise from trace solvent impurities.

dinitrogen desolvation gas [34]. The point at which 50% fragmentation occurs was taken as a suitable and convenient value for comparison. The fragmentation profiles, shown in Fig. 2 and tabulated in Table 1, clearly show that as extra fluorine substituents are added to the arene the binding affinity of the arene drops, consistent with previous reports and calculations [30,49−52]. The fragmentation profile of 5, whilst broadly the same line-shape as for the other complexes, is distorted due to a large signal for the competitive formation of alternate cations such as 1 and 8 that arise from trace solvent impurities.

Fig. 2. Selected plots of fragmentation of [Rh(‘Bu2PCH2CH2PiBu2)(\(\eta^2\)-C6H6−nF\(_n\))].

Fig. 3. Comparison of the mass normalized 50% fragmentation point of [Rh(‘Bu2PCH2CH2PiBu2)(\(\eta^2\)-C6H6−nF\(_n\))] with number of fluorine substituents (n).

In Fig. 3 the three isomeric difluorobenzene complexes 2, 3, and 4 show very similar 50% fragmentation points [as well as \(K(298)\)] suggesting substituent positioning is not very influential on the overall binding affinity of these arenes. By contrast, in rhodium \(\eta^2\)-fluorobenzene complexes, Re(\(\eta^2\)-C5H5)(CO)\(_2\)(C6H6−xF\(_x\))
(x = 0−5), the binding affinities are highly dependent upon fluorine position, as coordination to the H−C=CH unit of the arene is favoured over FC−CH, so that 1,2,3-C6H3F3 binds more strongly than 1,3,5-C6H3F3 for example [21].

Estimation of binding affinities of [Rh(L2)(η5-C6H5F)][BAF24]
complexes (L2 = chelating phosphine) using ESI−MS techniques

Having established that variation of exit voltage in ESI−MS offers a qualitative measure of the strength of arene binding we then moved to probe the effect of phosphine ligand while keeping the arene fixed (C6H3F). The effect of phosphine substituent steric/electronic profile [53], and chelate bite angle [27,28] was probed by using a range of rhodium η5-C6H5F complexes. Scheme 5 presents the complexes studied. Many of these complexes have been previously reported, for example in hydroacylation [3,4] and C−S bond cleavage catalysis [6]. The complex [Rh(Pro)2PCH2CH2P {O(Pr)2}(η5-C6H5F)][BAF24], 16, is new and was prepared by hydrogenation of the NBD precursor. The solid−state structure of complex 16 is presented in Fig. 4, and the structural metrics are unremarkable.

Table 2 and Figs. 5 and 6 present the data collected, which show some interesting trends. Firstly when comparing the bite−angle of the chelating phosphine while keeping the P−functionality the same (i.e. PPr2) there is a clear trend for those ligands with methylene spacers that increasing the bite angle leads to a more labile arene ligand (12 < 15 < 17, Fig. 5). Whether this is a result of decreased Rh−arene bond strength or increased stability in the gas phase of the {Rh(L2)}+ fragment (possibility stabilized by agostic interactions) is currently not clear, although we have noted a similar trend in this series of complexes when dissolved in acetone solvent, in that the wider bite angle−ligands promote for equilibrium mixtures that favor the acetone adducts, i.e. [Rh(L2)2(acetone)]BAF24 [4]. Such bis−adducts are unlikely to have significant agostic interactions. We have also previously noted that wider−bite angle {Rh(L2)}+ fragments promote stronger binding with amine−boranes through Rh−H−B interactions [78], and qualitatively explained this by a better match between the frontier orbitals of the metal fragment with the B−H bonds on increasing bite angle [8].

Complex 11 lies a little below that of 12, even though the ligand has a smaller bite angle. This might reflect the electronic influence of the NMe over the CH2 group, in which delocalization of the nitrogen lone pair over the chelate has suggested to be significant in the improved performance of these ligands in ethene oligomerization catalysis. [55,56]

Comparison of differing phosphine functionalities while keeping the bite angle similar is also instructive, and this is facilitated by the range of small−bite angle methylene−backbone PCP−type ligands [57] that can be synthesised with 1Bu, Cy and 1Pr substituents (Fig. 6, Table 2). Interrogation of these species using variable−exit−voltage ESI−MS shows that the order of ease of dissociation of the fluoroarene ligand increases in the order 1Bu < 1Pr < 1Cy (Fig. 7) while the bite angles remain similar. This is counter−intuitive to the expected trend from simple steric arguments that would predict the bulky 1Bu−substituted phosphine to have the most labile fluoroarene ligand. The trend might, instead, reflect the ability for the {Rh(L2)}+ fragment to form stabilizing agostic bonds in the gas phase. This is perhaps demonstrated by that the fluoroarene complex 18 cannot be observed in the gas phase, even at very low exit voltages, with only the {Rh(PrBu3)2}+ fragment observed. It is likely that the lack of chelate backbone allows for more efficient agostic interactions from the phosphine, as we have shown for example, in the crystallographically−characterized [Rh(PrBu3)2(H2)][BAF24] [54], and suggested to occur in [Rh(PrBu3)2][BAF24]. By contrast, comparison of the quasi−isosteric phosphine complexes 1 (PrBu3) and 16 (P(O2Pr)2) which have ethylene backbones show that the arene is lost more readily in the former, suggesting stronger arene binding with the phosphite.

Comparisons with ESI−MS/MS data

In order to test the reliability of the variable exit−voltage ESI−MS technique a selection of the fluoroarene compounds were screened using ESI−MS/MS techniques, where the fragmentation of a selected mass species is controlled by altering the voltage across an argon−filled collision cell [33,34].

Fig. 7 shows these data, which when plotting the resulting 50% fragmentation voltages from these collision cell CID experiments against the in−source CID values shows a good, almost linear,
correlation (Fig. 8), thus demonstrating the validity of both approaches to produce a qualitative ordering.

The effect that steric factors have on the strength of binding can also be probed easily by the simple expedient of adding a drop of a more strongly binding arene (e.g. a non-fluorinated one) to a fluorobenzene solution of [Rh(iPr2PNMePiPr2)(C6H5F)][BArF4], 11. This experiment was conducted for the arenes benzene, toluene, xylene and mesitylene (Fig. 9). The arene complex formed was probed by ESI-MS in each case, and the new complex was selected for CID and fragmented progressively in the collision cell using Ar. These data show that the fluorobenzene complex is substantially easier to fragment using CID than any of the hydrocarbon-only arenes. While all four complexes [Rh(iPr2PNMePiPr2)(C6H6-nMen)]⁺ (n = 0–3) all dissociate their arene at about the same collision energy, there is a discernible trend towards it being more difficult to dissociate the more electron-rich arenes, despite steric effects acting to weaken the strength of the metal-ligand bonding.

### Table 2

<table>
<thead>
<tr>
<th>Complex</th>
<th>Backbone length, P–Rh–P (’ )</th>
<th>P–Substituents</th>
<th>Exit–voltage for 50% dissociation (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1, 74.57(5) [3]</td>
<td>1Bu</td>
<td>11.1</td>
</tr>
<tr>
<td>12</td>
<td>1, 72.64(5) [4]</td>
<td>1Pr</td>
<td>10.5</td>
</tr>
<tr>
<td>11</td>
<td>1 (N), 70.36(3) [4]</td>
<td>1Pr</td>
<td>10.4</td>
</tr>
<tr>
<td>15</td>
<td>2, 84.81(3) [4]</td>
<td>1Pr</td>
<td>9.7</td>
</tr>
<tr>
<td>13</td>
<td>1 (N), 70.49(4) [4]</td>
<td>Cy</td>
<td>8.8</td>
</tr>
<tr>
<td>14</td>
<td>1, 72.78(3) [3]</td>
<td>Cy</td>
<td>8.7</td>
</tr>
<tr>
<td>16</td>
<td>2, 82.83(4)</td>
<td>OPr</td>
<td>8.1</td>
</tr>
<tr>
<td>17</td>
<td>3, 93.78(3) [4]</td>
<td>1Bu</td>
<td>8.1</td>
</tr>
<tr>
<td>1</td>
<td>2, 84.21(6) [24]</td>
<td>1Bu</td>
<td>7.2</td>
</tr>
<tr>
<td>18</td>
<td>n/a, 95.31(3)[54]</td>
<td>1Bu</td>
<td>&lt;1.8</td>
</tr>
</tbody>
</table>

*a* Mass Corrected.

*b* Reported as the NBD adduct.

---

**Fig. 6.** Fragmentation of [Rh(iPr2PCH2PPr2)(η5–C6H5F)]⁺ (R = Pr, Cy or 1Bu) cations in ESI-MS over a range of exit voltage values.

**Fig. 7.** CID data from MS/MS experiments on 10, 11, 12, 15, 16, 17 and 1. Collision energy has been normalized to center of mass.

**Fig. 8.** Correlation between ESI-MS experiments and ESI-MS/MS experiments (mass corrected).
Agents were used as received from suppliers. NMR spectra were measured in CD$_2$Cl$_2$ solution, in which the [BArF$_4$] anion can displace the coordinated arene. The gas-phase binding affinity of C$_6$H$_5$F is also much greater in conjunction with smaller bite angle phosphine ligands, or with more electron withdrawing phosphines. The phosphate substituents also influence the gas-phase binding affinity of $\eta^6$-arene complexes of the type [Rh(L)$_2$(arene)][BArF$_4$]. These experiments show that increasing the number of electron withdrawing substituents reduces the binding affinity of the arene. The ordering of these results is in agreement with equilibrium measurements in CD$_2$Cl$_2$ solution, in which the [BArF$_4$] anion can displace the coordinated arene. The gas-phase binding affinity of C$_6$H$_5$F is also much greater in conjunction with smaller bite angle phosphine ligands, or with more electron withdrawing phosphines. The phosphate substituents also influence the gas-phase binding affinity of $\eta^6$-C$_6$H$_5$F, with tBu groups associated with the greatest binding affinities and cyclohexyl groups with the least, of those tested. Overall it is likely that these trends reflect a combination of arene binding strength and stabilization of the low-coordination [Rh(L)$_2$]$^+$ fragment in the gas-phase and computational studies are currently underway to delineate these factors.

These simple in-source and collision cell CID experiments can be performed quickly and without any extra modifications using standard ESI-MS/MS instruments, and are thus potentially useful processes for the qualitative comparison of the relative stabilities of various organometallic complexes.

Conclusions

A collection of CID experiments have been undertaken which probe the relative dissociation energy of an arene from a variety of $\eta^6$-arene complexes of the type [Rh(L)$_2$(arene)][BArF$_4$]. These experiments show that increasing the number of electron withdrawing substituents reduces the binding affinity of the arene. The ordering of these results is in agreement with equilibrium measurements in CD$_2$Cl$_2$ solution, in which the [BArF$_4$] anion can displace the coordinated arene. The gas-phase binding affinity of C$_6$H$_5$F is also much greater in conjunction with smaller bite angle phosphate ligands, or with more electron withdrawing phosphines. The phosphate substituents also influence the gas-phase binding affinity of $\eta^6$-C$_6$H$_5$F, with tBu groups associated with the greatest binding affinities and cyclohexyl groups with the least, of those tested. Overall it is likely that these trends reflect a combination of arene binding strength and stabilization of the low-coordination [Rh(L)$_2$]$^+$ fragment in the gas-phase and computational studies are currently underway to delineate these factors.

These simple in-source and collision cell CID experiments can be performed quickly and without any extra modifications using standard ESI-MS/MS instruments, and are thus potentially useful processes for the qualitative comparison of the relative stabilities of various organometallic complexes.

Experimental section

General details

All manipulations, unless otherwise stated, were performed under an atmosphere of argon, using standard Schlenk-line and glovebox techniques. Glassware was oven-dried at 403 K overnight and flame under vacuum prior to use. CH$_2$Cl$_2$, pentane and hexane were dried using a Grubbs-type solvent purification system (MBraun SPS-800) and degassed by successive freeze–pump–thaw cycles. CD$_2$Cl$_2$, and all fluoroarenes and trifluorotoluene solvents, were distilled under vacuum from CaH$_2$ and stored over 3 Å molecular sieves (diluorobenzene were also stirred over alumina prior to distillation). Na[BArF$_4$] [59], (OPr$_2$)$_2$PCH$_2$CH$_2$P(OPr$_2$)$_2$ [60,61], [(NBD)RhCl]$_2$ [62] and [Rh(Bu$_3$P)$_2$CH$_2$P$_2$Bu$_3$](NBD)[BArF$_4$] [24], were prepared by the literature procedures. Complexes 1 [22, 24], 7 [42], 10 [3], 11 [4], 12 [4], 13 [4], 14 [4], 15 [4], 17 [4], 18 [54] have been described previously. All other reagents were used as received from suppliers. NMR spectra were recorded on Varian Unity 500 MHz, Bruker AVD 500 MHz, or Varian Mercury 300 MHz spectrometers at room temperature unless otherwise stated. Non-Deuterated Solvents were locked to a standard C$_6$D$_6$ solution. Residual proto solvent was used as reference for $^1$H, $^13$C NMR spectra in deuterated solvent samples. In 1,2-C$_6$H$_4$F$_2$ and C$_6$H$_5$F $^1$H NMR spectra were referenced to the centre of the downfield solvent multiplet ($\delta$ 7.07 and 6.71 respectively). $^3$P NMR spectra were externally referenced to 85% H$_3$PO$_4$. All chemical shifts ($\delta$) are quoted in ppm and coupling constants in Hz. Elemental micro-analysis carried out upon crystalline samples dried under dynamic vacuum (1 × 10$^{-2}$ Torr) overnight, by Stephen Boyer at London Metropolitan University.

Electrospray Ionisation Mass Spectrometry (ESI–MS) experiments were recorded using a Bruker MicroOTOF instrument directly connected to a modified Innovative Technology glovebox [38]. Typical acquisition parameters were as follows: sample flow rate [4 µl/min], nebuliser gas pressure [0.4 bar], drying gas [argon at 333 K, flowing at 4 l/min], capillary voltage [4.5 kV], exit voltage [60 V (variable exit voltage studies 20–250 V)]. The spectrometer was calibrated using a mixture of tetralkyl ammonium bromides [N(C$_9$H$_{2n-1}$)]Br ($n = 2, 8, 12, 16$ & 18). Samples were diluted to a concentration of 1 × 10$^{-6}$ M in the appropriate solvent before running. Variable exit–voltage experiments were measured for $\pm$1 V per voltage step, and the intensity of the highest isotope peak of the fragmented and non-fragmented signals were measured. Subsequently the intensities were normalized to account for the varying isotopic distributions. In arene dissociation experiments where multiple fragmental products were formed (see Supporting materials) the intensities of the fragmented products were summed and compared to the non-fragmented intensity. None of the secondary fragments coordinate arene ligands and so are presumed to form after initial arene dissociation. ESI–MS/MS experiments were recorded using a Micromass Q-Tof micro instrument in positive ion mode using pneumatically assisted electrospray ionization. Typical experimental parameters were: capillary voltage, 2900 V; sample cone voltage, 15 V; extraction voltage, 0.5 V; source temperature, 84 °C; desolvation temperature, 184 °C; cone gas flow, 100 l/h; desolvation gas flow, 200 l/h; MCP voltage, 2400 V. Samples were prepared by dilution in fluoroarene to a concentration of 0.15 mM and introduced into the source at 10 ml/min via a syringe pump. Data collection was carried out in continuum mode and spectra were collected by selecting the parent ion of interest by the quadrupole. A scan time of 5 s per spectrum was used. The collision cell voltage was set to 0 V initially and increased by increments of 1 V per scan, up to a maximum of 60 V. Resultant data was corrected to the centre of mass according to the formula

$$E_0 = E_{lab}^s m_A/(m_A + m_I)$$

where $E_{lab}$ is the collision cell voltage, $m_A$ is the mass of the collision gas and $m_I$ is the mass of the target ion.

New complexes

$$[\text{Rh}^\text{II}(\text{Bu}_3\text{P})\text{PCH}_2\text{CH}_2\text{P}(_\text{Bu}_3)\eta^6-1,3-\text{C}_6\text{H}_4\text{F}_2)][\text{BArF}_4]$$ (3)

18 mg (0.013 mmol) of [Rh(Bu$_3$P)$_2$CH$_2$P$_2$Bu$_3$](NBD)][BArF$_4$] was dissolved in 1,3-C$_6$H$_4$F$_2$ in a high pressure NMR tube. The tube was charged with 1 atm H$_2$. A yellow solution of 3 forms upon shaking. The hydrogen gas was removed and pentane added to crystallise the product directly from the solution (Yield 9 mg, 49%). $^1$H NMR (500 MHz, 1,3-C$_6$H$_4$F$_2$ ref upfield solvent signal 57.16): $\delta$ 1.03 (d (iBu CH$_3$), 6 Hz, 12H), 1.11 (d (Bu CH$_3$), $J_{HH}$ = 6 Hz), 1.16 (m (Bu CH$_3$), 8H), 1.78 (d (PCH$_2$CH$_3$P), $J_{HH}$ = 17 Hz, 4H), 1.88 (m (Bu CH$_3$), 4H), 6.07 (s (1,3-C$_6$H$_4$F$_2$), 2H), 7.68 (s (BArF$_4$), 4H), 8.28 (s (BArF$_4$), 8H). Two aryl protons unaccounted for, likely to be

**Fig. 9.** Comparison of the 50% fragmentation point of [Rh(L)(C$_6$H$_5$F)]$^+$. L = benzene, toluene, xylene and mesitylene, and compared with that for complex 11 (fluorobenzene).
obscured by the solvent. ¹H NMR (500 MHz CDCl₃): (N.B. minor species (~20%) in CD₂Cl₂ solution as is in equilibrium with 9. 8. 103 (d (B'CH₃, J_HH = 7, 12H), 109 (d (B'CH₃, J_HH = 7, 12H), 1.2-1.9 (m (PCH₂CH₂P, Bu CH & B'CH₂), 16H), 6.19 (m (1,3-C₆H₄F₃), 2H), 7.01 (m (1,3-C₆H₄F₃), H), 7.56 (s (BARF₄), 4H), 7.72 (s (BARF₄), 8H). One arene resonance not located, it is likely coincident with another signal. ³¹P{¹H} NMR (202 MHz 1,3-C₆H₄F₃): 372.8 (d, J_{HH} = 200 Hz, 2P). ³¹F{¹H} NMR (169 MHz 1,3-C₆H₄F₃): δ = -123.4 (1,4-C₆H₄F₃), 2F). -62.9 (s (BARF₄), 24F). ESI−MS: [M⁺] m/z = 535.19. [M⁺] calc = 535.19 (correct isotope pattern). Elemental Micro−Analysis: C₅₆H₅₆FB₂₄PF₂₈Rh C. 479.7H, 3.84 found C, 48.09H, 4.04.

[¹H{¹³C} NMR (500 MHz 1,3-C₆H₄F₃): δ = 4.04 found C, 48.27; H, 3.94.]

8 mg (0.006 mmol) of [Rh{(OiPr₂)PCH₂CH₂P(OiPr₂)}(NBD)] showed an oily product after shaking for 2.5 h. The hydrogen gas was removed and pentane added to crystallise the product directly from the solution. (Yield = 11 mg, 68%). ¹H NMR (500 MHz CDCl₃): δ = 0.95 (d (B'CH₃, J_HH = 7, 12H), 1.03 (d (B'CH₃, J_HH = 7, 12H), 1.72 (m (PCH₂CH₂P, Bu CH & B'CH₂), 8H), 1.88 (m (PCH₂CH₂P and B'CH₂), 8H), 7.37 (s (BARF₄), 4H), 7.97 (s (BARF₄), 8H). The ¹H NMR resonances of the bound 1,2,3-C₆H₄F₃ are likely to be obscured by the free solvent resonances. ³¹P{¹H} NMR (202 MHz 1,2,3-C₆H₄F₃): δ = 75.05 (δ = 203 Hz, 2P). ³¹F{¹H} NMR (282 MHz 1,2,3-C₆H₄F₃): δ = -167.95 (C₆H₅F), 3F). J_{HH} = 30 Hz, F), -147.52 (d (C₆H₅F), J_{HH} = 30 Hz, F), -64.09 (s (BARF₄), 24F). ESI−MS: [M⁺] m/z = 535.19. [M⁺] calc = 535.19 (correct isotope pattern). No crystalline material suitable for micro-analysis was obtained.

11 mg (0.008 mmol) of [Rh{(OiPr₂)PCH₂CH₂P(OiPr₂)}(NBD)] was dissolved in C₆H₅CF₃ in a high pressure NMR tube. The tube was charged with 1 atm H₂. A yellow solution of 6 forms upon shaking. The hydrogen gas was removed and pentane added to crystallise the product directly from the solution. (Yield = 8 mg, 52%). ¹H NMR (500 MHz CDCl₃): δ = 1.00 (d (B'CH₃, J_HH = 7, 12H), 1.07 (d (B'CH₃, J_HH = 7, 12H), 1.63 (m (B'CH₃), 8H), 1.73 (d (PCH₂CH₂P), J_{HH} = 17 Hz, 4H), 1.85 (m (B'CH₃), 4H), 6.47 (s (C₆H₅F), 6H), 7.56 (s (BARF₄), 4H), 7.72 (s (BARF₄), 8H). ³¹P{¹H} NMR (202 MHz CDCl₃): δ = 73.4 (δ = 201 Hz). ESI−MS: [M⁺] m/z = 499.23. [M⁺] calc = 499.21 (correct isotope pattern). Elemental Micro−Analysis: C₄₆H₅₆FB₄₁PF₂₈Rh C. 41.36, 4.29 found C, 49.44H, 4.44.

25 mg (0.018 mmol) [Rh{(OiPr₂)PCH₂CH₂P(OiPr₂)}(NBD)] (16) was dissolved in C₆H₅F in a high pressure NMR tube. The tube was charged with 1 atm H₂. A pale yellow solution of 16 forms upon shaking. After 2.5 h the hydrogen was removed and pentane added to crystallise the product directly from the solution. (Yield = 8 mg, 32%). ¹H NMR (500 MHz CD₃F): δ = 1.13 (d (P'CH₃), J_{HH} = 4 Hz, 12H). 1.14 (d (P'CH₃), J_{HH} = 4 Hz, 12H), 1.55 (d (PCH₂CH₃P), J_{HH} = 24 Hz, 4H). 4.25 (m (OCh₃Me), 4H), 5.78 (t (C₆H₅F), J_{HH} = 6 Hz, H), 6.29 (m (C₆H₅F), 2H), 6.36 (t (C₆H₅F), J_{HH} = 6 Hz, 2H), 7.66 (s (BARF₄), 4H), 8.33 (s (BARF₄), 8H). ³¹P{¹H} NMR (202 MHz CD₃F): δ = 154.50 (C₆H₅F), F), -65.2 (s (BARF₄), 24F). ESI−MS: [M⁺] m/z = 525.12. [M⁺] calc = 525.12 (correct isotope pattern). Elemental Micro−Analysis: C₃₂H₂₉BF₂₅O⁻₅P⁺Rh C. 49.81H, 3.56 found C, 44.80H, 3.84.

90 mg (195 mmol) of [Rh{(OiPr₂)PCH₂CH₂P(OiPr₂)}(NBD)] was added to a Schlenk tube with a stirrer bar and dissolved in 5 mL of C₆H₄F₃. To this, 3 mL of a 0.131 M (393 mmol, 2 eq.) of a pentane solution of (O²Pr₂) PCH₂CH₂P(O²Pr₂) was added and the mixture stirred for 5 min, a slight darkening of the yellow solution is observed. This mixture was added to a Schlenk flask containing 3462 mg (391 mmol) Na [BARF₄] and a moving stirrer bar by cannula transfer to give an orange solution. The solvent was reduced by vacuum to 1 mL and 10 mL of pentane was added. A stream of argon bubbles was passed through the mixture to aid precipitation of the product. The product was dissolved in CH₂Cl₂ and NaCl removed by filter cannula methods. Finally recrystallisation was achieved by layering with pentane (N.B. an oily product is typical, although slow crystallisation occurs over time at 277 K). Yield = 220 mg (41%). ¹H NMR (300 MHz CDCl₃): δ = 1.29 (δ (P'CH₃), J_{HH} = 6 Hz, 12H), 1.33 (d (P'CH₃), J_{HH} = 6 Hz, 12H), 1.59 (d (PCH₂CH₃P), J_{HH} = 24 Hz, 4H). 1.88 (m (NBD CH₂), 2H), 4.17 (s (NBD bridgehead), 2H), 4.42 (m (OCh₃Me), 4H), 5.91 (s (NBD C=C), 4H), 7.65 (s (BARF₄), 4H), 7.72 (s (BARF₄), 8H). ³¹P{¹H} NMR (121 MHz CDCl₃): δ = 72.09 (δ = 200 Hz, 2P). ³¹F{¹H} NMR (282 MHz CDCl₃): δ = 561.36 or -61.01 (s (C₆H₅F), 3F), -62.84 (s (BARF₄), 24F) “ambiguous to which peak is 6 and which is 9. From the ESI−MS: [M⁺] m/z = 537.15. [M⁺] calc = 537.14 (correct isotope pattern). Elemental Micro−Analysis: C₄₃H₆₁FB₁₆₃PF₄₁Rh C. 45.97H, 3.79 found C, 45.95H, 3.81.

Single Crystal X−Ray Diffraction. Single crystal X-ray diffraction data for 16 were collected using an Agilent SuperNova (Cu Kα radiation, λ = 1.54180 Å) with the use of low temperature devices. Data were reduced using the instrument manufacturer software CrystAlisPro [63]. The structure was solved ab initio using SIR92 [64], and refined using CRYSTALS [65,66]. Refinement details for 16. On initial refinement disorder was located in two of the O²Pr groups;
both were modelled over two sites (one disorder model hinging at the O, the other at the P atom). Restrictions were used to maintain sensible geometries. The C\textsubscript{6}H\textsubscript{5}F ligand was also disordered with the fluorine atom located in 3 different positions around the ring. The carbons were, however, ordered and did not need further modelling. The fluorine/hydrogen occupancies were modelled appropriately over the three disorder positions. Several of the C\textsubscript{2}F groups upon the anion were modelled over two positions and restrained to maintain sensible geometries.

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Appendix A. Supplementary material

CCDC 1014324 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2014.08.012.

References