Activation and η^2-Co-ordination of Arenes: Crystal and Molecular Structure of an (η^2-Hexafluorobenzene)rhodium Complex

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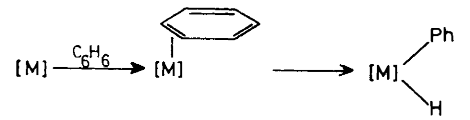
The photolytic reaction of (Cp)Rh(PMe$_3$)(C$_2$H$_4$), (**1**, Cp = η^5-C$_5$H$_5$) with benzene yields (Cp)Rh(PMe$_3$)(Ph)H *via* a transient η^2-C$_6$H$_6$ complex detected by laser flash photolysis; the corresponding reaction of (**1**) with C$_6$F$_6$ yields (Cp)Rh(PMe$_3$)(η^2-C$_6$F$_6$) which contains an almost planar C$_6$F$_4$ unit with the remaining fluorines bent out of the plane by 43°.

The activation of arenes by organometallics is usually considered to proceed *via* η^2-preco-ordination (Scheme 1). Strong evidence in favour of this mechanism comes from the study of aryl hydride rearrangement.[1] Here we show that (Cp)Rh(PMe$_3$)(C$_2$H$_4$) (**1**, Cp = η^5-C$_5$H$_5$) is an activator of the C–H bonds of benzene, but forms an isolable η^2-complex with C$_6$F$_6$, a solvent recently postulated to be inert for such reactions.[2] Moreover, laser flash photolysis of (**1**) allows the detection of the η^2-C$_6$H$_6$ complex and the determination of the activation parameters for isomerisation to the rhodium-(phenyl)hydride.

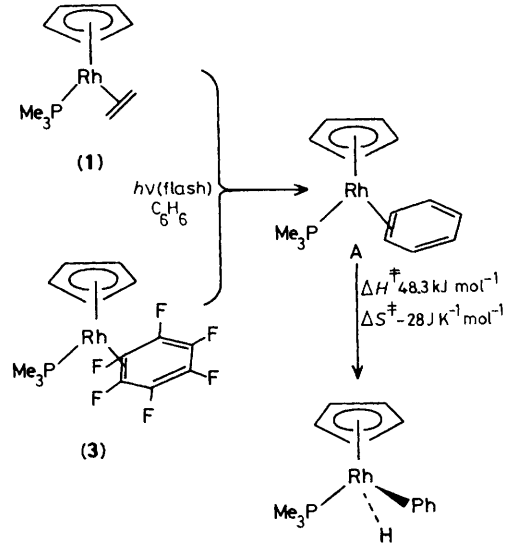
Photolysis of (**1**) (λ > 285 nm; 2 h) in C$_6$H$_6$/C$_6$D$_6$ (9:1) effects > 95% conversion to (Cp)Rh(PMe$_3$)(C$_6$H$_5$)H (**2**) and the corresponding deuteriated material.† Confirmation of the identification of (**2**) was obtained by conversion to (Cp)Rh(PMe$_3$)(Ph)Br *via* reaction with CHBr$_3$ at 195 K.[1]† When the hydridic resonance of (**2**) is decoupled, the intensities of the phenyl proton resonances are drastically reduced. However, (**2**) does not exchange with C$_6$D$_6$ at room temperature over a period of 10 hours. These experiments point to an intramolecular exchange process between hydride and aromatic protons *via* an η^2-arene intermediate, as has been thoroughly investigated for the C$_5$Me$_5$ analogue of (**2**).[1]



Scheme 1

When (**1**) was photolysed (λ > 285 nm; 6 h) in C$_6$F$_6$, the colour of the solution changed from yellow to red. Following removal of the solvent, the residue was dissolved in warm hexane. On cooling, orange crystals were obtained suitable for *X*-ray analysis (isolated yield 60%).‡ The crystal structure (Figure 1) demonstrates that the product is (Cp)Rh(PMe$_3$)(η^2-C$_6$F$_6$) (**3**). N.m.r. investigations show that (**3**) is stereochemically rigid over the temperature range 243—403 K.†

Although (η^2-arene) metal complexes are currently of intense interest,[3] crystal structures are sparse[3,4] and (η^2-C$_6$F$_6$)



Scheme 2. Laser flash photolysis of (**1**) and (**3**).

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† *Spectral data*, n.m.r. at 300 MHz for ^{1}H unless otherwise stated. ^{1}H spectra in CD$_3$CN relative to CD$_2$HCN at δ 2.0, ^{13}C spectra relative to CD$_3$CN at δ 0.3, ^{31}P spectra relative to external H$_3$PO$_4$, ^{19}F spectra relative to external CFCl$_3$. (Cp)Rh(PMe$_3$)(C$_6$H$_5$)H (**2**) ^{1}H (CD$_3$CN): δ 7.45 (m, 2H, H$_{ortho}$), 6.80 (m, 3H, H$_{para,meta}$), 5.29 (s, 5H, C$_5$H$_5$), 1.38 (dd, 9H, $J_{\rm PH}$ 10.9, $J_{\rm RhH}$ 1.3 Hz, PMe$_3$), −14.22 (dd, 1H, $J_{\rm PH}$ 41.0, $J_{\rm RhH}$ 29.6 Hz, RhH); ^{13}C (CD$_3$CN): δ 148.7 (dd, $J_{\rm RhC}$ 35, $J_{\rm PC}$ 17 Hz, Rh–C), 145.6 (s, C$_{ortho}$), 126.0 (s, C$_{meta}$), 121.0 (s, C$_{para}$), 87.7 (t, $J_{\rm PC} = J_{\rm RhC}$ = 3 Hz, C$_5$H$_5$), 21.0 (d, $J_{\rm PC}$ 36 Hz, Me), ^{31}P (90% C$_6$H$_6$, 10% C$_6$D$_6$): δ 13.62 (d, $J_{\rm RhP}$ 158 Hz, PMe$_3$).

(Cp)Rh(PMe$_3$)(C$_6$D$_5$)D, ^{31}P (C$_6$D$_6$): δ 13.72 (dt, $J_{\rm RhP}$ 158, $J_{\rm PD}$ 6.4 Hz, PMe$_3$).

(Cp)Rh(PMe$_3$)(C$_6$H$_5$)Br, ^{1}H (CDCl$_3$, 90 MHz): δ 7.65 (m, 2H, H$_{ortho}$), 6.95 (m, 3H, H$_{meta,para}$), 5.37 (t, 5H, $J_{\rm PH} = J_{\rm RhH}$ = 0.75 Hz, C$_5$H$_5$), 1.55 (dd, 9H, $J_{\rm PH}$ 11.4, $J_{\rm RhH}$ 0.9 Hz, Me); ^{13}C (CDCl$_3$): δ 144.1 (dd, $J_{\rm RhC}$ 31, $J_{\rm PC}$ 21 Hz, C$_{ipso}$), δ 141.7 (d, $J_{\rm PC}$ 3 Hz, C$_{ortho}$), 127.5 (s, C$_{meta}$), 122.9 (s, C$_{para}$), 90.8 (t, $J_{\rm PC} = J_{\rm RhC}$ = 4 Hz, C$_5$H$_5$), 18.6 (d, $J_{\rm PC}$ 36 Hz, Me); ^{31}P (CDCl$_3$): δ 13.2 (d, $J_{\rm RhP}$ 145 Hz); *m/z* 402, 400 (M^+), 321 (M − Br)$^+$. Satisfactory C, H, and Br analyses were obtained.

(Cp)Rh(PMe$_3$)(η^2-C$_6$F$_6$) (**3**), ^{1}H (CD$_3$CN): δ 5.05 (s, 5H, C$_5$H$_5$), 1.48 (dq, 9H, $J_{\rm PH}$ 10.7, $J_{\rm RhH} = J_{\rm FH}$ = 0.9 Hz, Me); ^{13}C (CD$_3$CN): δ 128—157 (m, C$_6$F$_6$), 90.2 (s, C$_5$H$_5$), 21.1 (d, $J_{\rm PC}$ 32 Hz, Me); ^{31}P (CD$_3$CN): δ 4.3 (dt, $J_{\rm RhP}$ 190, $J_{\rm FP}$ 55 Hz, PMe$_3$); ^{19}F (CD$_3$CN): δ (numbering as in Figure 1) −174 (m, F9F9′) −162 (m, $J_{\rm RhF}$ 15, $J_{\rm PF}$ 54 Hz, F7F7′), −147 (m, F8F8′), assignment by COSY and *J*-resolved spectra; mass spectrum, no molecular ion, *m/z* 244 [(Cp)Rh(PMe$_3$)]$^+$, 186 (C$_6$F$_6$$^+$). Satisfactory C, H, and F analyses were obtained.

‡ *Crystal data* for (Cp)Rh(PMe$_3$)(η^2-C$_6$F$_6$): C$_{14}$H$_{14}$PF$_6$Rh, M = 430.15, orthorhombic, space group *Pnma*, a = 10.533, b = 11.271, c = 13.074 Å, U = 1552.11 Å^3, F(000) = 847.99, μ = 11.29 cm^{-1}, Z = 4, D_c = 1.84 g cm^{-3}, R = 0.0375, R_w = 0.0497. 1685 unique reflections were collected with $2\theta \leq 54°$ in $\omega/2\theta$ mode with Mo-K_α radiation (λ = 0.7107 Å) and reduced to 1507 reflections with $I \geq 2\sigma(I)$. Number of parameters = 129. There is a crystallographically imposed mirror plane containing the Rh–P bond and perpendicular to the C$_6$F$_4$ plane. The PMe$_3$ group was disordered. The best model was obtained by refining two positions for each methyl carbon atom, each with an occupancy of 0.5. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

We also tried to refine the structure in the acentric space group *Pna*2$_1$ (with axes redefined appropriately) and reached a satisfactory R factor, but again experienced problems with disorder of the PMe$_3$ group. The geometry of the Rh(η^2-C$_6$F$_6$) group was similar to that in the centric space group, but correlations between the co-ordinates suggested the presence of a mirror plane. Since the two space groups could not be distinguished on the basis of E-statistics, we proceeded using the centric group.

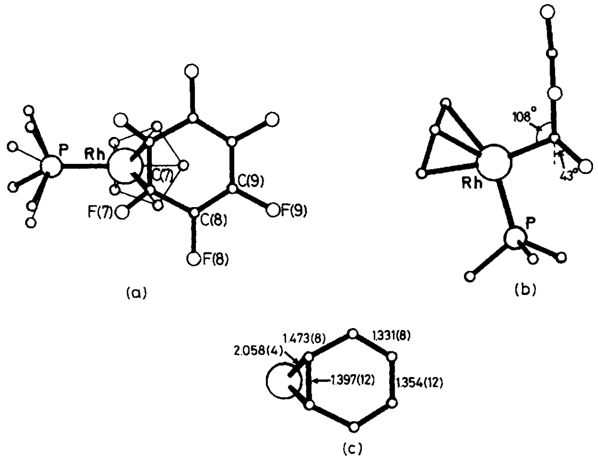

Figure 1. Molecular structure of (**3**). (a) View in the co-ordination plane of the rhodium; notice the two-fold disorder of the PMe_3 group. (b) Projection onto the crystallographic mirror plane, showing the principal interplane angles. The C_6F_4 unit C(7)C(7′)C(8)F(8)-C(8′)F(8′)C(9)F(9)C(9′)F(9′) is planar to within 0.05 Å. (c) The Rh(η^2-C_6) unit showing the principal bond lengths.

complexes unknown. The structure of (**3**) (Figure 1) retains an almost planar C_6F_4 unit, but the remaining two C–F bonds are bent out of the plane by 43°. Although the co-ordinated C=C bond is not significantly longer[5] than in free C_6F_6, the rest of the ring is distorted towards a diene structure. These features bear a close resemblance[4a,b] to $Pt(PEt_3)_2[\eta^2\text{-}C_6(CF_3)_6]$. The stereochemical rigidity of (**3**), its thermal stability, and the distortions of the co-ordinated C_6F_6 group demonstrate that this ligand is capable of strong interaction with a metal *via* the η^2-co-ordination mode. Despite the thermal stability of (**3**), the co-ordinated C_6F_6 group may be displaced by Pyrex-filtered photolysis of (**3**) in C_6D_6 which effects quantitative conversion to $[^2H_6]$-(**2**). This reaction suggests that (**3**) may be a useful precursor in C–H activation reactions.

Laser flash photolysis of (**1**) or (**3**) in benzene under argon {$\lambda_{ex.}$ 308 nm; flash duration *ca.* 20 ns; λ_{obs} 360 nm; [(**1**)] 10^{-3} mol dm^{-3}; 298 K} results in formation of transient A within 400 ns, the effective risetime of the apparatus at this wavelength. This species decays with first-order kinetics over *ca.* 1 ms to (**2**) (Figure 2). The lifetime is unaffected by replacement of the argon atmosphere by C_2H_4. Its spectrum shows no absorption maximum at $\lambda > 340$ nm, but a steadily decreasing absorbance at longer wavelengths. The corresponding transient in toluene has a lifetime 3.5 times longer, but no transients are observed in C_6F_6 or in cyclohexane. In mixed benzene/cyclohexane solutions ($[C_6H_6]/[C_6H_{12}] = 0.2$ to 1.0), the yield of A diminishes with increasing $[C_6H_{12}]$, but its lifetime is unchanged. The temperature dependence of the decay rate of A (Figure 2b) yields activation parameters $\Delta H^\ddagger$ 48.3 ± 3.8 kJ mol^{-1} and $\Delta S^\ddagger = -28 \pm 12$ J K^{-1} mol^{-1}. The formation of a common transient in benzene from two precursors, the effect of changing the arene from benzene to toluene, the independence of the lifetime of A on $[C_6H_6]$ and $[C_2H_4]$ and the absence of transients in alkanes, all support the assignment of A to (Cp)Rh(PMe_3)(η^2-C_6H_6). The activation parameters, the first recorded for the isomerisation of an η^2-arene complex to a metal(phenyl)hydride (Schemes 1 and 2) demonstrate the ordering of the transition state for this reaction.[1]

These experiments strongly support the pre-co-ordination mechanism of arene activation by the direct detection of the η^2-complex. It is also evident that the η^2-complex may be stabilised sufficiently for isolation by suitable choice of arene. Hexafluorobenzene is an ideal ligand for this purpose and also serves as a good leaving group for further studies of reactivity. The factors controlling whether fluoroaromatics co-ordinate as in (**3**) or whether C–F oxidative addition occurs,[6] have yet to be elucidated.

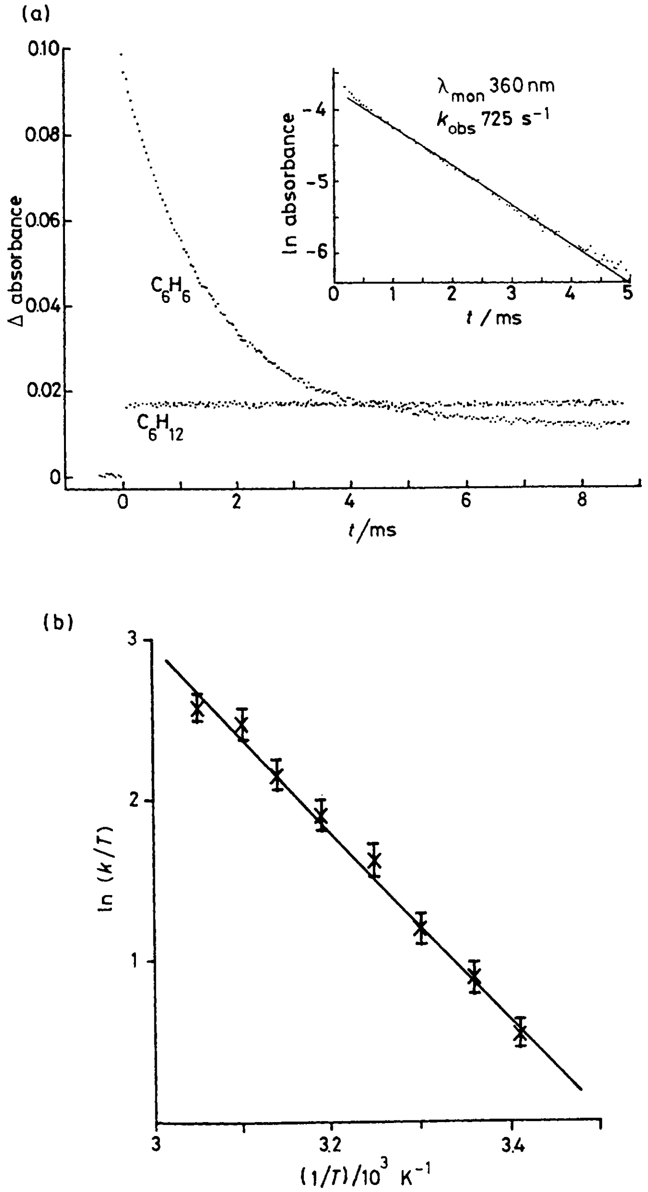

Figure 2. (a) Decay of transient observed on laser flash photolysis of (**1**) in benzene at 298 K monitored at 360 nm. The corresponding measurements in cyclohexane are also shown, but notice that no transient is observed. The insert shows the first-order kinetic plot for transient A which yields $k_{obs} = 725 \pm 70$ s^{-1}. Laser flash photolysis of (**3**) yields similar data to (**1**) and $k_{obs} = 770 \pm 60$ s^{-1}. (b) Eyring plots of kinetic data for the decay of transient A measured over the temperature range 293—328 K, yielding activation parameters.

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