Sequential Arene Coordination and C–F Insertion in the Reactions of (η^5-Pentamethylcyclopentadienyl)rhodium Complexes with Hexafluorobenzene

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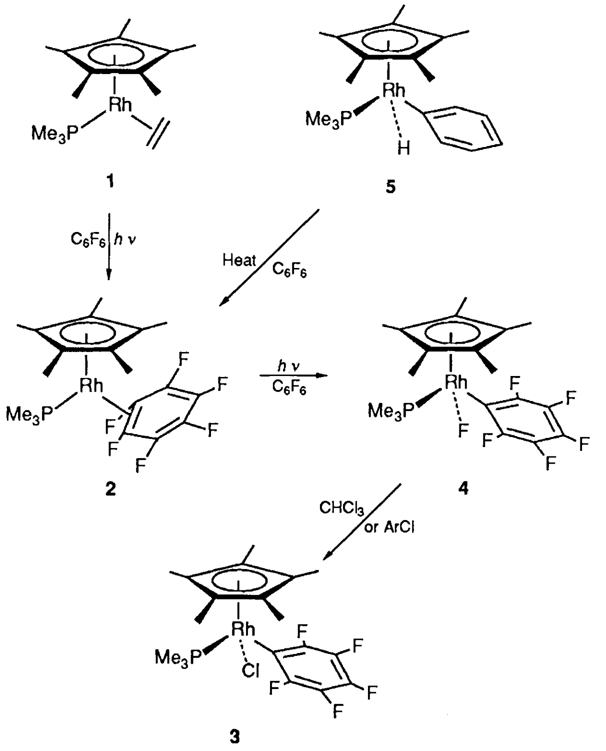
Hexafluorobenzene reacts with [(η^5-C_5Me_5)Rh(PMe_3)(C_2H_4)] in two sequential photochemical reactions to yield first the arene coordination product, [(η^5-C_5Me_5)Rh(PMe_3)(η^2-C_6F_6)], and then the C–F insertion product, [(η^5-C_5Me_5)Rh(PMe_3)(C_6F_5)F]; chlorination of the latter generates [(η^5-C_5Me_5)Rh(PMe_3)(C_6F_5)Cl], the structure of which has been determined crystallographically.

Reactive 16-electron transition-metal complexes interact with arenes to form either η^2-arene complexes or metal (aryl)hydrides.[1,2] There is strong evidence that the insertion products are formed *via* prior η^2-coordination.[1–4] We recently showed that the reaction could be arrested at the η^2-coordination stage by photochemical reaction of [(C_5H_5)Rh(PMe_3)(C_2H_4)] with C_6F_6 rather than with benzene.[4] Here we show that the reaction of the corresponding η^5-C_5Me_5 complex results in C–F activation *via* prior coordination of the C_6F_6 ligand.

Photolysis of a solution of [(C_5Me_5)Rh(PMe_3)(C_2H_4)] **1** in

C_6F_6 (λ > 285 nm, 14 h) generates $[(C_5Me_5)Rh(PMe_3)(\eta^2\text{-}C_6F_6)]$ **2** as an isolable product readily characterized by multinuclear NMR spectroscopy.† Unlike its C_5H_5 analogue,[4] prolonged photolysis (40 h) of the solution yields further products with ^{31}P NMR spectra characteristic of Rh^{III} species,[5] suggesting that the rhodium has inserted into a C–F bond (see below). Reaction of this solution with $CHCl_3$ simplifies the NMR spectra. In addition to **2** and $[(C_5Me_5)Rh(PMe_3)Cl_2]$ derived principally from residual **1**, there is one other Rh^{III} product with a ^{31}P NMR resonance coupled to a single fluorine. This product was isolated as small orange crystals and demonstrated by X-ray crystallography to be $[(C_5Me_5)Rh(PMe_3)(C_6F_5)Cl]$ **3**, thus establishing that a C–F bond has been cleaved (Fig. 1).‡ The structure shows a sterically crowded molecule with the C_6F_5 group lying in a plane at an angle of 20° to the plane of the C_5Me_5 ring. Comparison with the structure of $[(C_5H_5)(PMe_3)(\eta^2\text{-}C_6F_6)]$ shows that substantial reorganization of the C_6F_6 unit must have occurred prior to insertion into a C–F bond. The NMR spectra of **3** show that all fluorine nuclei are inequivalent even at 75 °C and the phosphorus is coupled to only one fluorine, presumably in an *ortho* position.† The barrier to internal rotation of the C_6F_5 unit about the Rh–C bond must, therefore, be very substantial.§

Examination of the products of prolonged photolysis of **1** with C_6F_6 before the addition of $CHCl_3$ showed the presence of $[(C_5Me_5)Rh(PMe_3)(C_6F_5)F]$ **4**, $[(C_5Me_5)Rh(PMe_3)(C_6F_5)Cl]$ **3** and a product tentatively identified as $[(C_5Me_5)Rh(PMe_3)F_2]$, in the ratio 8.3 : 1.2 : 1. The coordinated fluoride in **4** is evident from its ^{31}P NMR spectrum (Fig. 2), which shows a further doublet splitting compared to **3**, but this fluoride has not been located in the ^{19}F NMR spectrum, probably because of overlap with other resonances.† Despite careful purification of C_6F_6, we were unable to prevent formation of **3**, which probably arises from traces of chlorofluorobenzenes.¶



Scheme 1

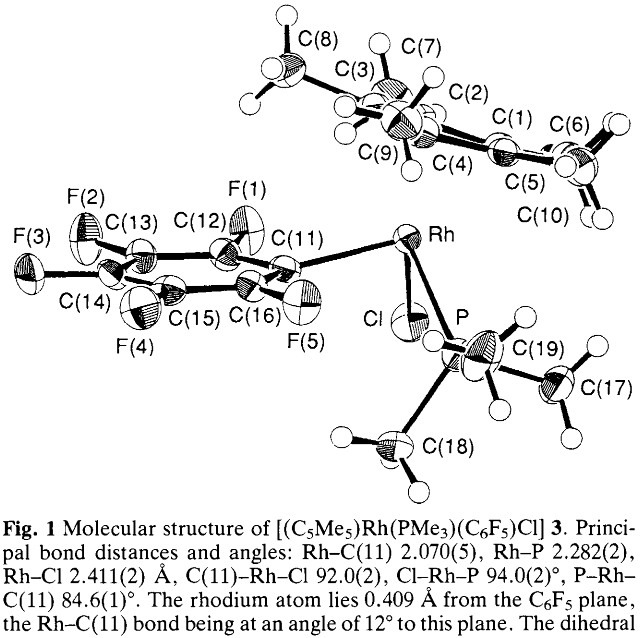


Fig. 1 Molecular structure of $[(C_5Me_5)Rh(PMe_3)(C_6F_5)Cl]$ **3**. Principal bond distances and angles: Rh–C(11) 2.070(5), Rh–P 2.282(2), Rh–Cl 2.411(2) Å, C(11)–Rh–Cl 92.0(2), Cl–Rh–P 94.0(2)°, P–Rh–C(11) 84.6(1)°. The rhodium atom lies 0.409 Å from the C_6F_5 plane, the Rh–C(11) bond being at an angle of 12° to this plane. The dihedral angle between the C_6F_5 plane and the C_5Me_5 plane is 20.4°.

The intermediacy of $\eta^2\text{-}C_6H_6$ complexes in the pathway to benzene C–H activation has been contrasted with the pathway to ethene coordination and insertion.[6] Ethene complexes may be converted photochemically to the (vinyl)hydride insertion products, but the latter regenerate ethene complexes thermally.[6,7] Intermolecular reaction with ethene generates either (vinyl)hydride or ethene complexes in two independent pathways.[6] The sequential growth of **2** and **4** implies that **4** is formed from **2**. The isolation of **2** gives a further opportunity

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† *Spectral data*: NMR in C_6D_6 at 300 MHz for ^{1}H unless otherwise stated; ^{1}H spectra relative to C_6D_5H at δ 7.13, ^{31}P spectra relative to external H_3PO_4, ^{19}F spectra relative to C_6F_6 at δ -162.9; coupling constants in Hz.

$[(C_5Me_5)Rh(PMe_3)(\eta^2\text{-}C_6F_6)]$ **2**, ^{1}H: δ 1.35 (d, 15H, J_{PH} 2.2, C_5Me_5) and 1.00 (dq, 9H, J_{PH} 9.8, $J_{RhH} = J_{FH} = 1.2$, PMe_3); ^{19}F: δ −147.4 (m, F^2, $F^{2'}$), −158.7 (m, F^1, $F^{1'}$, *i.e.* fluorines bound to coordinated carbons) and −177.5 (m, F^3, $F^{3'}$); $^{31}P\{^1H\}$: δ −0.43 (dt, J_{RhP} 195, J_{FP} 67).

$[(C_5Me_5)Rh(PMe_3)(C_6F_5)Cl]$ **3**, ^{1}H: δ 1.23 (d, 15H, J_{PH} 3.4, C_5Me_5) and 1.12 (dt, 9H, J_{PH} 10.8, $J_{RhH} = J_{FH} = 0.9$, PMe_3); ^{19}F: δ −107.2 (m, F_{ortho}), −112.9 (m, F_{ortho}), −161.4 (m, F_{para}), −162.5 (m, F_{meta} and −164.7 (m, F_{meta}) [assignments by COSY at 292.4 MHz; see also M. I. Bruce, *J. Chem. Soc. (A)*, 1968, 1459]; $^{31}P\{^1H\}$: δ 4.24 (dd, J_{RhP} 140, J_{FP} 22; *m/z* 516 (M^+) and 481 $(M\text{-}Cl)^+$.

$(C_5Me_5)Rh(PMe_3)(C_6F_5)F]$ **4**, ^{1}H: δ 1.10 (d, 15H, J_{PH} 2.3, C_5Me_5) and 0.91 (d, 9H, J_{PH} 11.2, PMe_3); ^{19}F: δ −114.2 (m, F_{ortho}), −115.4 (m, F_{ortho}) −160.3 (t, J_{FF} 20.3, F_{para}), −161.6 (m, F_{meta}) and −163.9 (m, F_{meta}); $^{31}P\{^1H\}$: δ 6.75 (ddd, J_{RhP} 145, J_{FP} 39, $J_{F'P}$ 17).

‡ *Crystal Data* for: **3**, $C_{19}H_{24}ClF_5PRh$, $M = 516.72$, monoclinic, space group *C2/c* (No. 15), $a = 14.129(4)$, $b = 9.610(7)$, $c = 30.320(5)$ Å, $\beta = 94.88(5)°$, $V = 4102(5)$ Å^3, $Z = 8$, $D_c = 1.67$ g cm^{-3}, λ(Mo-Kα) = 0.71069 Å, $\mu = 10.68$ cm^{-1}, $F(000) = 2080$, $T = 198$ K. Data were collected on an Enraf-Nonius CAD4 diffractometer for $2 < 2\theta < 50°$. The structure was solved by heavy-atom methods and refined by least-squares analysis to $R = 0.036$ and $R_w = 0.045$ for 2429 unique, observed absorption-corrected reflections $[I > 3\sigma(I)]$. The hydrogens were placed in idealized positions based on the difference Fourier map. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ We have also synthesized the C_5H_5 analogues of **3** and find that the C_6F_5 unit is freely rotating about the Rh–C bond on the NMR time-scale at ambient temperature. The free energy of activation for internal rotation of the Ph group of the related $[(C_5Me_5)Rh(PMe_3)(Ph)Br]$ is 59 kJ mol^{-1} (W. D. Jones and F. J. Feher, *Inorg. Chem.*, 1984, **23**, 2376).

¶ When the sample is heated, **4** is converted to **3**, implying that **4** scavenges chlorinated impurities in the C_6F_6 (nominal 99.9% and distilled prior to use).

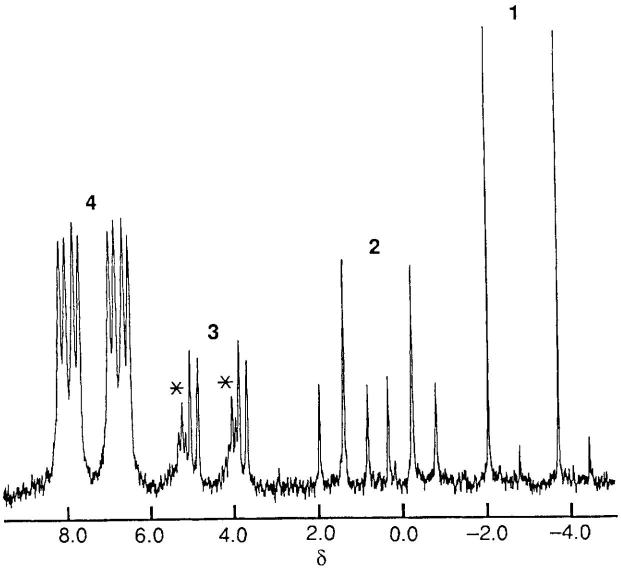

Fig. 2 $^{31}P\{^1H\}$ NMR spectrum in C_6F_6 solution of reaction mixture obtained by photolysis (40 h) of $[(C_5Me_5)Rh(PMe_3)(C_2H_4)]$ in C_6F_6. Each of the signals is coupled to ^{103}Rh giving a doublet ($J \approx 200$ Hz for Rh^I and ≈ 150 Hz for Rh^{III}). Additional couplings to two equivalent fluorines are observed for the η^2-C_6F_6 complex **2**, to one *ortho* fluorine in the C_6F_5 complex **3**, and to one *ortho* fluorine and the fluorine bound to rhodium in complex **4**. A trace of $[(C_5Me_5)Rh(PMe_3)F_2]$ (marked *) is also detected as a doublet of triplets. Note that the spectrum was recorded unlocked in C_6F_6, whereas the data in the footnote refer to spectra recorded in C_6D_6.

to test whether the η^2-C_6F_6 product is an intermediate *en route* to C–F activation. Accordingly, we purified **2** by sublimation (80 °C, 10^{-3} mbar), redissolved it in C_6F_6 and photolysed again. Once more the C–F insertion products were formed. It is also important to understand whether it is essential to carry these reactions out photochemically. $[(C_5Me_5)Rh(PMe_3)(Ph)H]$ **5** has been shown to be a good thermal source of $[(C_5Me_5)Rh(PMe_3)]$.[3] When **5** was heated in C_6F_6 to 65 °C, it reacted to form **2**, but no C–F insertion products were formed even on heating to 110 °C for 30 h. Thus, the C–F insertion step has only been achieved photochemically, and the relative stability of **2** and **4** remains unknown. The major reactions observed are summarised in Scheme 1.

Previous evidence has shown that intramolecular insertion into aryl C–F bonds is possible for complexes with ligands containing dangling C_6F_5 groups.[8–10] There are also reports of fluorine abstraction from C_6F_6 by organolanthanides to form organolanthanide fluorides.[11,12] The current experiments demonstrate the formation of $Rh(\eta^2\text{-}C_6F_6)$ and $Rh(C_6F_5)F$ complexes in *two sequential photochemical steps*. Thus, the extra strength of the C–F bonds $[D(F\text{–}C_6F_5) - D(H\text{–}C_6H_5) = 16 \text{ kJ mol}^{-1}]$,[13] coupled with substantial reorganization energy, create a barrier which is not overcome thermally even at 110 °C, but which may be surmounted photochemically. Although the intimate photochemical mechanism is unknown, this represents a graphic demonstration of the importance of precoordination of the arene. The ability of the C_5Me_5 complex **2**, but not its C_5H_5 analogue, to undergo C–F activation demonstrates the effect of the more electron-donating ligand in promoting insertion reactions. In the following Communication,[14] we exploit this effect to manipulate the outcome of reactions with arene towards either η^2-coordination or insertion, and put the ligand effect on a more quantitative basis.

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References

1 W. D. Harman and H. Taube, *J. Am. Chem. Soc.*, 1987, **109**, 1883.
2 W. D. Jones and F. J. Feher, *Acc. Chem. Res.*, 1989, **22**, 91.
3 W. D. Jones and F. J. Feher, *J. Am. Chem. Soc.*, 1984, **106**, 1650.
4 S. T. Belt, S. B. Duckett, M. Helliwell and R. N. Perutz, *J. Chem. Soc., Chem. Commun.*, 1989, 928.
5 B. Klingert and H. Werner, *Chem. Ber.*, 1983, **116**, 1450.
6 P. O. Stoutland and R. G. Bergman, *J. Am. Chem. Soc.*, 1988, **110**, 5732; M. V. Baker and L. D. Field, *J. Am. Chem. Soc.*, 1986, **108**, 7433, 7436.
7 D. M. Haddleton and R. N. Perutz, *J. Chem. Soc., Chem. Commun.*, 1986, 1734; T. W. Bell, D. M. Haddleton, A. McCamley, M. G. Partridge, R. N. Perutz and H. Willner, *J. Am. Chem. Soc.*, 1990, **112**, 9212.
8 T. G. Richmond, C. E. Osterberg and A. M. Arif, *J. Am. Chem. Soc.*, 1987, **109**, 8091.
9 N. M. Agh-Atabay, J. L. Davidson, G. Douglas and K. W. Muir, *J. Chem. Soc., Chem. Commun.*, 1989, 549.
10 C. M. Anderson, R. J. Puddephatt, G. Ferguson and A. J. Lough, *J. Chem. Soc., Chem. Commun.*, 1989, 1297.
11 C. J. Burns and R. A. Andersen, *J. Chem. Soc., Chem. Commun.*, 1989, 136.
12 P. L. Watson, T. H. Tulip and I. Williams, *Organometallics*, 1990, **9**, 1999.
13 *CRC Handbook of Chemistry and Physics*, 67th edn., CRC Press, Florida, 1986, p. F186.
14 S. T. Belt, L. Dong, S. B. Duckett, W. D. Jones, M. G. Partridge and R. N. Perutz, following communication.