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# Carbon–fluorine and –hydrogen bond activation and carbon–carbon bond formation in $\eta^5$-pentamethylcyclopentadienyl-rhodium and -iridium phosphine complexes; crystal structures of $[M(\eta^5\text{-}C_5Me_5)Cl\{(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2\}]^+BF_4^-$ (M = Rh or Ir)

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The reaction between $[\{M(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ (M = Rh or Ir) and $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ (dfppe) in refluxing benzene yielded the cationic species $[M\{\eta^5\text{-}C_5Me_3[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}Cl]^+$ in which two C–F and two C–H bonds have been cleaved and two C–C bonds formed; HF is also produced. The complexes $[M(\eta^5\text{-}C_5Me_5)Cl(dfppe)]^+BF_4^-$ (M = Rh or Ir), which have not undergone C–F bond activation, were formed by treatment of $[\{M(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ with $NH_4BF_4$ and dfppe, and have been structurally characterized by X-ray crystallography. Activation of the C–F bonds in these complexes is induced by thermolysis in refluxing ethanol. The reaction between $[\{M(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ (M = Rh or Ir) and dfppe in refluxing ethanol yielded a mixture of the cations $[M(\eta^5\text{-}C_5Me_5)Cl(dfppe)]^+$, $[M\{\eta^5\text{-}C_5Me_3[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}Cl]^+$ and, where M = Rh, the singly C–F bond-activated species $[Rh\{\eta^5\text{-}C_5Me_4CH_2C_6F_4P(C_6F_5)CH_2CH_2P(C_6F_5)_2\}Cl]^+$.

The activation of C–F bonds is of fundamental importance in the functionalization of fluorocarbons. Reactions in which the strong and generally unreactive C–F bond is cleaved are rare. The activation of C–F bonds by transition-metal complexes has been achieved,[1–4] but the reactions usually proceed in low yields and only under harsh conditions. There have been only a few reports of reactions of transition-metal species involving C–F bond activation which proceed under mild conditions and in high yield,[3,5,6] and one example of C–F bond activation in a catalytic cycle.[4]

Here we report our studies into the activation of the *ortho* C–F bonds of $(C_6F_5)_2PCH_2CH_2(C_6F_5)_2$ upon reaction with the rhodium and iridium species $[\{M(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ (M = Rh or Ir). Part of this work has been communicated.[7]

## Results and Discussion

Treatment of $[\{Rh(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ with the diphosphine $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ (dfppe), in refluxing benzene for 6 h, yielded a yellow solution from which a yellow solid was obtained on evaporation of the solvent. The solid was characterized by mass spectrometry, $^1H$, $^{19}F$ and $^{31}P\text{-}\{^1H\}$ NMR spectroscopies and single-crystal X-ray diffraction.[1] The product comprised the cationic rhodium diphosphine species $[Rh\{\eta^5\text{-}C_5Me_3[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}Cl]^+$ (Scheme 1) and was found to contain two anions, $Cl^-$ and $BF_4^-$. The presence of the latter was indicated by two resonances in the $^{19}F$ NMR spectrum at *ca.* $\delta$ −150, in 1:4 ratio, which accounted for *ca.* 3% of the total intensity of the peaks in the spectrum. The product was converted by anion metathesis in acetone–water into the $BF_4^-$ salt **1**, which was further characterized by elemental analysis. Analytical and spectroscopic data are given in Table 1. The two phosphorus atoms are chiral, but the steric requirements of the reaction lead to the exclusive formation of the *meso* stereoisomer. The $^{31}P\text{-}\{^1H\}$ NMR spectrum exhibits a doublet of multiplets indicating that the phosphorus atoms are equivalent. The $^1H$ NMR spectrum shows four multiplet resonances assigned to the $PCH_2$ and $CH_2C_6F_4$ methylene hydrogen atoms and three singlets assigned to the methyl hydrogen atoms.

The nett reaction is cleavage of two aryl C–F bonds and two C–H bonds and the formation of two C–C and two H–F bonds, equation (1). The formation of HF in C–F bond-activation

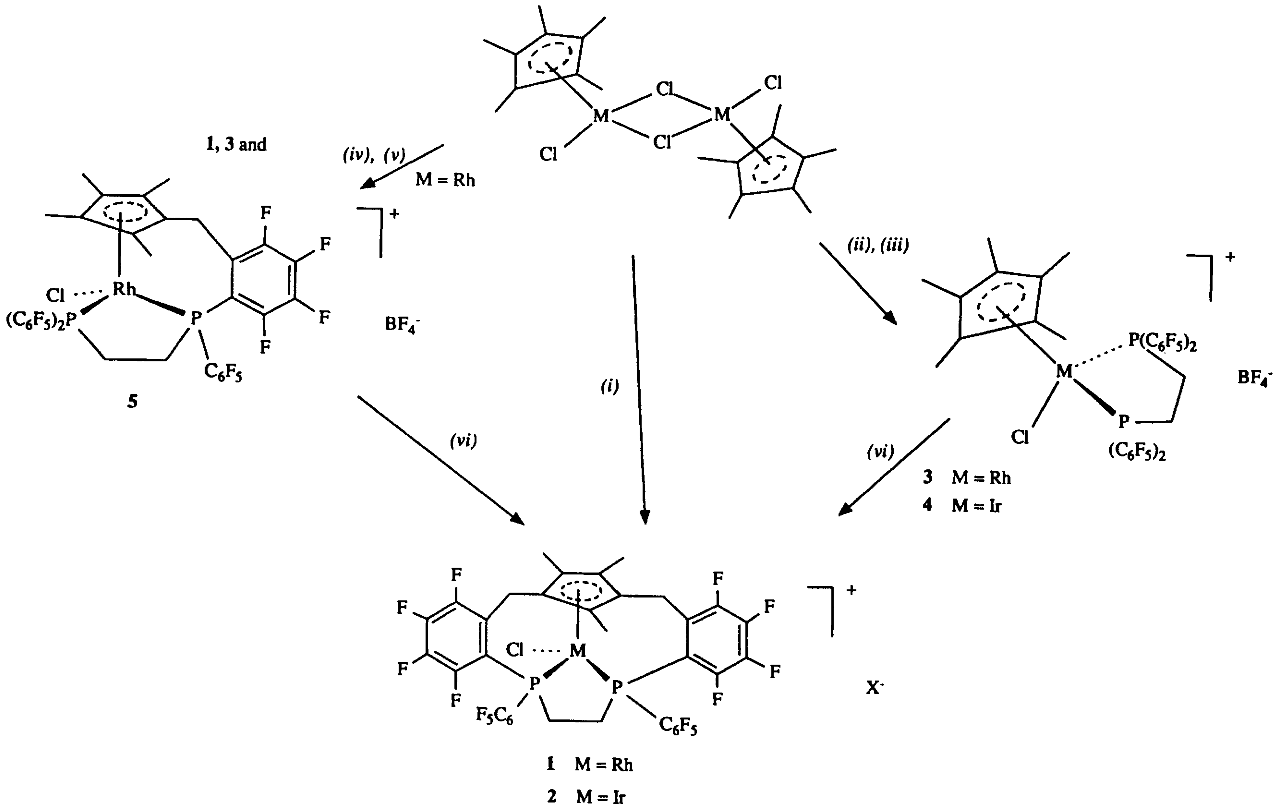
$$2\,C\text{–}F + 2\,C\text{–}H \longrightarrow 2\,C\text{–}C + 2HF \qquad (1)$$

processes has been proposed for a number of reactions,[8–12] but, except for a small number of examples where $SiF_4$, $SiF_5^-$ and $BF_4^-$ were formed by reaction with the glass reaction vessel,[13] there is no evidence for its presence. The presence of $BF_4^-$ in the product of the reaction between $[\{Rh(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ and dfppe carried out in borosilicate glass provides indirect evidence for the formation of HF, the bond energy of which $[D_0(H\text{–}F) = 570.3\ kJ\ mol^{-1}$ [14]$]$ is presumed to provide the driving force for the reaction.

The reaction is insensitive to air and moisture and may be carried out in other solvents, such as dichloromethane and toluene, and proceeds at room temperature, albeit at a far slower rate. Addition of either acid [HCl(aq)] or base ($NEt_3$) inhibits the reaction.

The reaction between $[\{Ir(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ and dfppe in refluxing benzene yielded a cream-coloured solid, which elemental analysis, mass spectrometry and $^1H$, $^{19}F$ and $^{31}P\text{-}\{^1H\}$ NMR spectroscopies (Table 1) indicate is $[Ir\{\eta^5\text{-}C_5Me_3[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}Cl]^+Cl^-$ **2**. Presumably HF, and thus $BF_4^-$, is formed, but only the chloride salt was isolated. The $^1H$ and $^{19}F$ NMR spectra of **2** are similar to those of **1** and, presumably, the structures of **1**[7] and **2** are similar.

Variable-temperature $^{19}F$ NMR spectroscopy of compounds **1**[7] and **2** in $CDCl_3$ shows seven resonances at the high-temperature limit and nine at the low-temperature limit (Table 1 and Fig. 1). This is indicative of hindered rotation about the $P\text{–}C_6F_5$ bonds. From the variable-temperature $^{19}F$ NMR spectra recorded in $CDCl_3$ values of $\Delta G^\ddagger$, the activation energy for rotation about the $P\text{–}C_6F_5$ bonds, are calculated[15] to be 52.5 ± 2 and 55 ± 2 kJ $mol^{-1}$ for **1** and **2** respectively.



Scheme 1 (*i*) dfppe, $C_6H_6$, heat; (*ii*) $NH_4BF_4$, MeOH; (*iii*) dfppe, $CH_2Cl_2$; (*iv*) dfppe, EtOH, heat; (*v*) $NH_4BF_4$; (*vi*) EtOH, heat

**Table 1** Analytical, mass spectral and NMR data for compounds **1**–**5**

| Analysis (%)[a] and $m/z$[b] Compound | NMR[c] |
|---|---|
| **1**[d] C, 40.8 (40.7); H, 1.6 (1.8); P, 5.1 (5.6)<br>991 ($M^+$) 955 ([$M$ − Cl]$^+$) | $^1$H 4.63 (2 H, m, $CH_2$), 4.08 [2 H, d, $J$ 18.6, $CH_2$], 3.95 (2 H, m, $CH_2$), 3.25 (2 H, m, $CH_2$), 2.14 (3 H, s, $CH_3$), 2.11 (3 H, s, $CH_3$), 1.17 (3 H, s, $CH_3$)[e]<br>$^{19}$F −117.93 (2 F, br m), −130.07 (4 F, br s, *o*), −135.70 (2 F, m), −146.83 (4 F, m), −151.02 and −151.08 (4 F, 2s, *ca.* 1:4, $BF_4^-$), −154.96 [2 F, t, $^3J$(FF) 21.5], −160.35 (4 F, m, *m*)[e]<br>$^{31}$P-{$^1$H}: 77.05 [dm, $^1J$(RhP) 144.5][e] |
| **2** C, 38.6 (38.7); H, 1.5 (1.5); P, 5.7 (5.55)<br>1081 ($M^+$), 1044 ([$M$ − Cl]$^+$) | $^1$H 4.33 [2 H, dt, $^3J$(HH) 17.9, $J$ 7.1, $PCH_2$], 4.03 [2 H, d, $^3J$(HH) 17.9, $PCH_2$], 3.85 (2 H, s, $C_6F_4CH_2$), 3.79 (2 H, s, $C_6F_4CH_2$), 2.15 (3 H, s, $CH_3$), 2.13 (3 H, s, $CH_3$), 1.47 (3 H, s, $CH_3$)[e]<br>$^{19}$F −117.93 (2 F, m), −131.36 (4 F, br s, *o*), −137.18 (2 F, m), −147.63 [2 F, t, $^3J$(FF) 20.2, *p*], −148.16 (2 F, m), −155.41 [2 F, t, $^3J$(FF) 21.6], −160.85 (4 F, vtd, $J$ 21.8, $J$ 6.8, *m*)[e]<br>$^{19}$F (225 K) −116.58 (2 F, m), −130.45 (2 F, m, *o*), −133.58 (2 F, m, *o*), −134.85 (2 F, m), −142.92 (2 F, m), −143.57 [2 F, t, $^3J$(FF) 21.4], −150.67 [2 F, t, $^3J$(FF) 22.3], −156.70 (2 F, m, *m*), −157.75 (2 F, vt, $J$ 21.8, *m*)[f]<br>$^{19}$F (333 K) −117.30 (2 F, m), −132.34 (4 F, m, *o*), −135.97 (m, 2 F), −143.95 (2 F, m), −145.19 (2 F, m), −151.46 (2 F, vt, $J$ 20.6), −158.80 (4 F, m, *m*)[f]<br>$^{31}$P-{$^1$H} 48.99 (m)[e] |
| **3** C, 38.3 (38.65); H, 1.6 (1.7); P, 4.3 (5.5)<br>1031 ($M^+$), 996 ([$M$ − Cl]$^+$) | $^1$H 3.43 (4 H, m, $CH_2$), 1.74 [15 H, t, $J$(PH) 4.9, $CH_3$][e]<br>$^{19}$F −124.48 (4 F, br s, *o*), −127.53 [4 F, d, $^3J(F_oF_m)$ 13.7, *o*], −144.88 [2 F, tm, $^3J(F_mF_p)$ 21.3, *p*], −146.15 [2 F, tm, $^3J(F_mF_p)$ 20.45, *p*], −150.94 and −150.99 (4 F, 2s, *ca.* 1:4, $BF_4^-$), −158.30 [4 F, dd, $^3J(F_oF_m)$ 20.5, $^3J(F_oF_m)$ 16.1, *m*], −160.30 (4 F, vtm, $J$ 18.7, *m*)[e]<br>$^{31}$P-{$^1$H} 35.09 [dm, $^1J$(RhP) 150.5][e] |
| **4** C, 35.7 (35.8); H, 1.4 (1.6); P, 5.3 (5.1)<br>1121 ($M^+$), 1087 ([$M$ − Cl]$^+$) | $^1$H 3.44 (4 H, m, $CH_2$), 1.75 [15 H, t, $J$(PH) 3.2, $CH_3$][e]<br>$^{19}$F −124.82 [4 F, dm, $^3J(F_oF_m)$ 14.7, *o*], −127.33 [4 F, dm, $^3J(F_oF_m)$ 13.2, *o*], −144.57 [2 F, tm, $^3J(F_mF_p)$ 20.9, *p*], −146.23, [2 F, tt, $^3J(F_mF_p)$ 20.5, $^4J(F_oF_p)$ 6.8, *p*], −150.60 and −150.65 (4 F, 2s, *ca.* 1:4, $BF_4^-$), −158.31 (4 F, vtm, $J$ 18.2, *m*), −160.31 (4 F, vtm, $J$ 19.4, *m*)[e]<br>$^{31}$P-{$^1$H} 9.79 (m)[e] |
| **5**<br>1011 ([$M$ + H]$^+$), 975 ([$M$ − Cl]$^+$) | $^1$H 4.57 (2 H, m, $CH_2$), 3.96 (2 H, m, $CH_2$), 3.04 (2 H, m, $CH_2$), 1.92 (6 H, m, $CH_3$), 1.16 (6 H, d, $J$ 2.5, $CH_3$)[e]<br>$^{19}$F −117.21 (1 F, br s), −127.13 [2 F, dm, $^3J$(FF) 19.9], −128.58 [2 F, dm, $^3J$(FF) 19.8], −136.44 (1 F, m), −144.12 (1 F, m), −145.80 (1 F, m), −146.84 (2 F, m), −150.89 and −150.94 (4 F, 2s, *ca.* 1:4, $BF_4^-$), −154.70 [1 F, t, $^3J$(FF) 21.4], −157.87 [2 F, dd, $^3J$(FF) 20.3, 17.8], −160.40 (2 F, m)[e,g]<br>$^{31}$P-{$^1$H} 83.86 [dm, $^1J$(RhP) 141.3, $P(C_6F_5)(C_6F_4)$], 49.14 [dm, $^1J$(RhP) 152.1, $P(C_6F_5)_2$][e] |

[a] Required values are given in parentheses. [b] Fast-atom bombardment with *m*-nitrobenzyl alcohol as matrix. [c] Unless otherwise stated recorded at 298 K. Data given as: chemical shift (δ) [relative intensity, multiplicity ($J$ Hz), assignment], s = singlet, d = doublet, t = triplet, vt = virtual triplet, m = multiplet, br denotes a signal broadened due to a fluxional process. [d] Crystallized with 0.5 $Me_2CO$. [e] Recorded in $(CD_3)_2CO$. [f] Recorded in $CDCl_3$. [g] Resonances assigned to two *o*- and two *m*-$C_6F_5$ fluorine atoms are not observed at 298 K due to coalescence.

Presumably, rotation about the P–$C_6F_5$ bonds is hindered for steric reasons.

Treatment of [{M($\eta^5$-$C_5Me_5$)Cl($\mu$-Cl)}$_2$] (M = Rh or Ir) with $NH_4BF_4$ in methanol and addition of dfppe in dichloromethane yielded the complexes [M($\eta^5$-$C_5Me_5$)Cl(dfppe)]$^+BF_4^-$ (M = Rh **3** or Ir **4**), in which C–F bonds have not been activated. These complexes were characterized by elemental analyses, mass spectrometry, and $^1H$, $^{19}F$ and $^{31}P$-{$^1H$} NMR spectroscopies (Table 1), and also by X-ray crystallography. Their structures are shown in Figs. 2 and 3 respectively. Selected distances and angles are given in Table 2. The structures of the complexes are virtually identical, both displaying three-legged piano-stool geometry about the metal atom. The P–M–P and P–M–Cl angles lie in the range 83.26–85.46°. The angles are essentially the same for the two complexes, but there are some differences in bond lengths about the metal atoms. The $C_5Me_5$–M distance is slightly longer and the M–P distances are significantly shorter for the iridium complex **4**. The variable-temperature $^{19}F$ NMR spectra of complexes **3** and **4** recorded in $(CD_3)_2CO$ indicate that there are two fluxional processes. These are due to hindered rotation about the P–$C_6F_5$ bonds. The activation energies, $\Delta G^‡$, for rotation about two pairs of P–$C_6F_5$ bonds, calculated from the spectra,[15] are 35 ± 4 and 46 ± 4 kJ mol$^{-1}$ for **3** and 41.5 ± 2 and 50 ± 2.5 kJ mol$^{-1}$ for **4**. Presumably, rotation about the P–$C_6F_5$ bonds is hindered for steric reasons. The larger values of $\Delta G^‡$ for complex **4** may be as a consequence of the shorter M–P bonds for M = Ir than for M = Rh, which increases the steric pressure in the former complex.

The structures of complexes **3** and **4** possess some short F $\cdots$ $H_3C$ distances. In particular, F(16) $\cdots$ C(6) are 3.139 and 3.154 Å and F(42) $\cdots$ C(9) are 3.137 and 3.103 Å for **3** and **4** respectively. There are also short $FBF_3 \cdots C$ distances. The plane formed by the atoms F(1), F(2) and F(4) is almost coplanar with the plane of the $C_5Me_5$ ring (5.1° deviation for **3** and 4.5° for **4**), and the distance between the two planes is *ca.* 3.19 Å for both structures. The $BF_4^-$ anion is displaced from the centroid of the $C_5Me_5$ ring towards C(1) and C(2) [Fig. 3(*b*)] such that there are a number of short F $\cdots$ C distances: F(1) $\cdots$ C(6) 3.194 and 3.164, F(1) $\cdots$ C(1) 3.285 and 3.279, F(2) $\cdots$ C(3) 3.253 and 3.240, F(2) $\cdots$ C(8) 3.296 and 3.283, F(4) $\cdots$ C(4) 3.142 and 3.160 and F(4) $\cdots$ C(5) 3.224 and 3.225

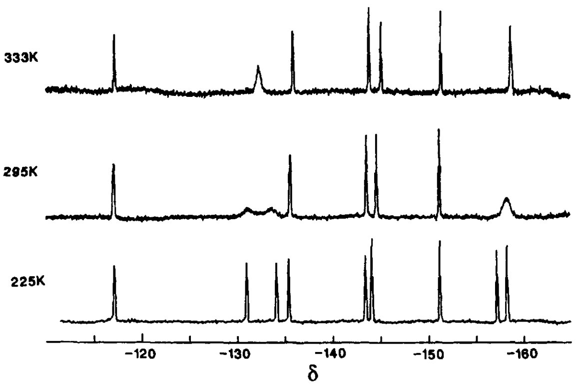


**Fig. 1** Variable-temperature $^{19}F$ NMR spectra of [Ir{($\eta^5$-$C_5Me_3$-[$CH_2C_6F_4P(C_6F_5)CH_2$]$_2$-1,3}Cl]$^+Cl^-$ **2** in $CDCl_3$ at 282.41 MHz

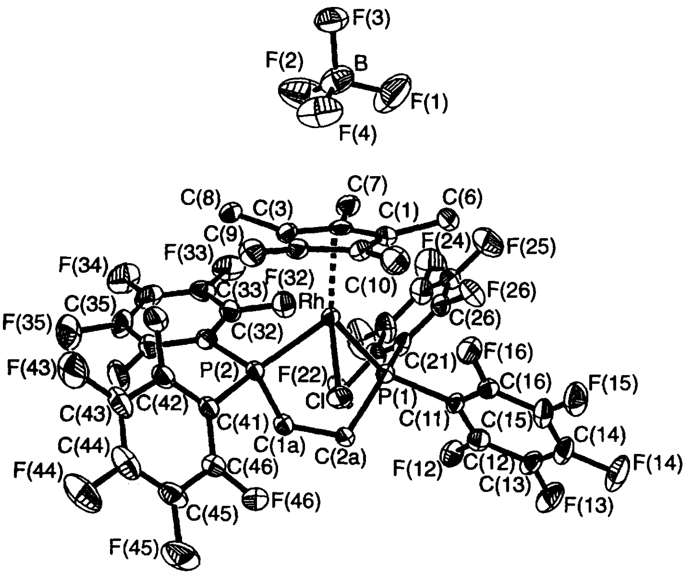


**Fig. 2** Molecular structure of [Rh($\eta^5$-$C_5Me_5$)Cl(dfppe)]$^+BF_4^-$ **3**. Displacement ellipsoids are shown at the 30% probability level. The hydrogen atoms are omitted for clarity

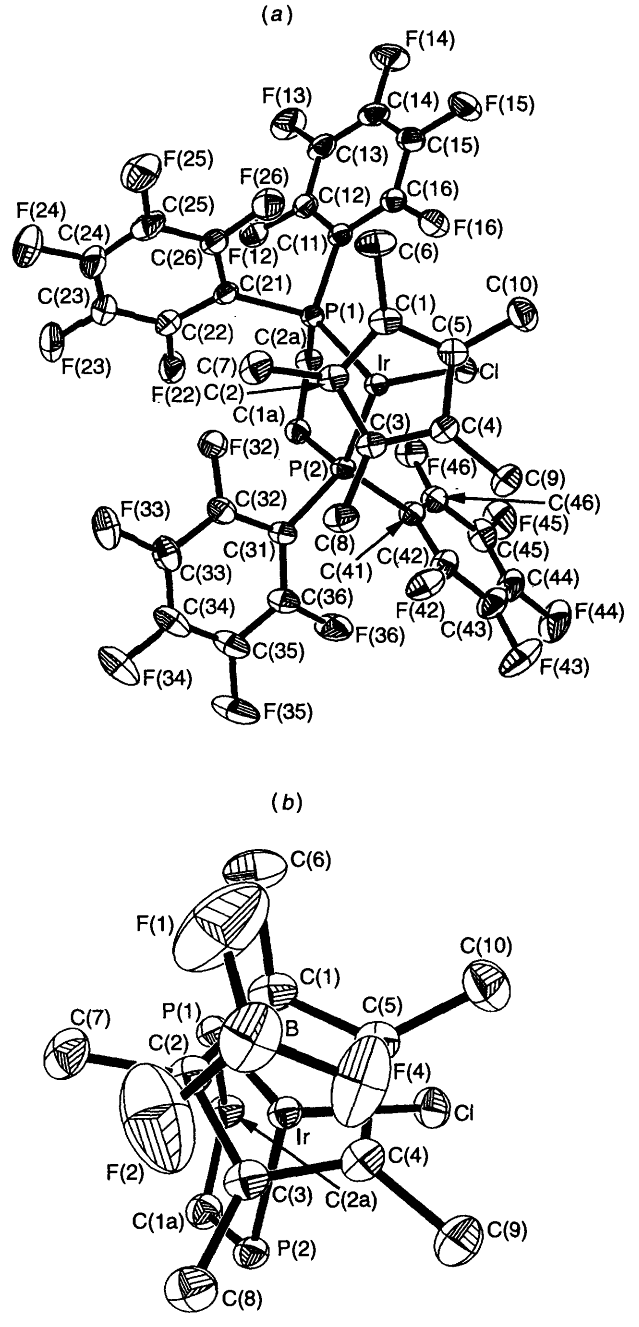


**Fig. 3** Molecular structure of [Ir($\eta^5$-$C_5Me_5$)Cl(dfppe)]$^+BF_4^-$ **4**. Displacement ellipsoids are shown at the 30% probability level. The hydrogen atoms are omitted for clarity. (*a*) View almost parallel to the cyclopentadienyl centroid–iridium axis. The $BF_4^-$ anion is omitted for clarity. (*b*) View parallel to the B–F(3) bond showing the arrangement of the $BF_4^-$ anion relative to the pentamethylcyclopentadienyl ring; F(3) and the $C_6F_5$ rings are omitted for clarity

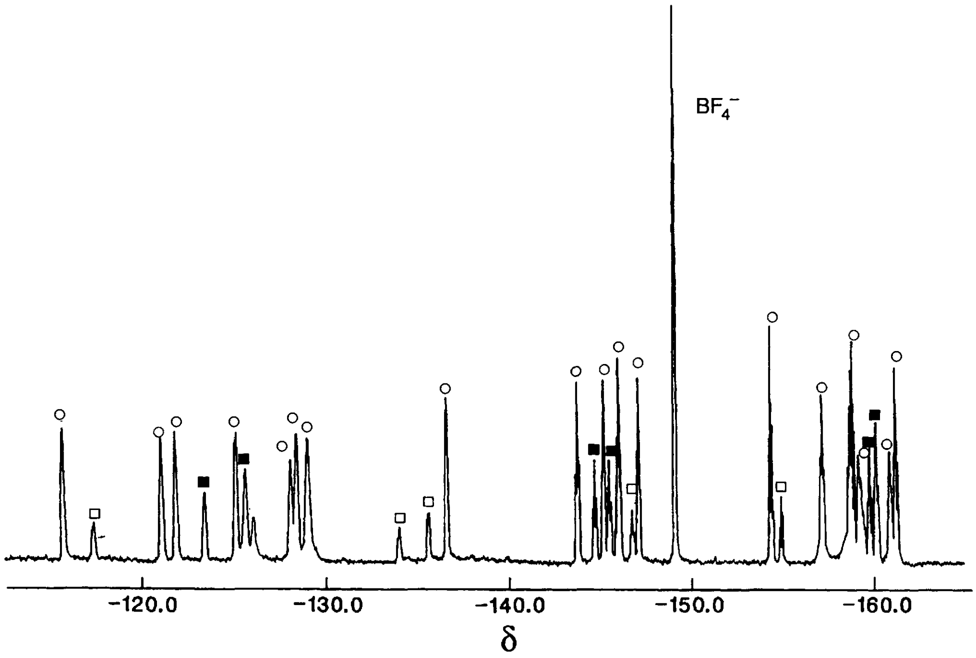


**Fig. 4** Fluorine-19 NMR spectrum recorded in $(CD_3)_2CO$ at 282.41 MHz and 189 K of the mixture of products formed by the reaction between $[\{Rh(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ and dfppe in refluxing ethanol: □, **1**; ■, **3**; ○, **5**. Three resonances of complex **1** and two *ortho* and two *meta* resonances of **3** are obscured. Two *meta* resonances of **5** are coincidental

**Table 2** Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for $[Rh(\eta^5\text{-}C_5Me_5)Cl(dfppe)]^+BF_4^-$ **3** and $[Ir(\eta^5\text{-}C_5Me_5)Cl(dfppe)]^+BF_4^-$ **4***

| | **3** (M = Rh) | **4** (M = Ir) |
|---|---|---|
| Cp*–M | 1.869(1) | 1.886(1) |
| M–P(1) | 2.362(2) | 2.3278(14) |
| M–P(2) | 2.342(2) | 2.311(2) |
| M–Cl | 2.380(2) | 2.3891(13) |
| P(1)–C(2a) | 1.825(6) | 1.833(5) |
| P(2)–C(1a) | 1.830(7) | 1.832(6) |
| C(1a)–C(2a) | 1.526(8) | 1.510(7) |
| P(1)–C(11) | 1.844(7) | 1.843(5) |
| P(1)–C(21) | 1.846(7) | 1.850(6) |
| P(2)–C(31) | 1.850(7) | 1.843(6) |
| P(2)–C(41) | 1.837(7) | 1.834(6) |
| Cp*–M–Cl | 121.89(6) | 121.10(4) |
| Cp*–M–P(1) | 134.24(6) | 133.97(4) |
| Cp*–M–P(2) | 130.98(5) | 131.36(3) |
| P(1)–M–Cl | 85.36(7) | 85.46(5) |
| P(2)–M–Cl | 83.26(7) | 83.96(5) |
| P(1)–M–P(2) | 84.05(8) | 84.32(5) |
| M–P(1)–C(2a) | 105.5(2) | 106.4(2) |
| M–P(1)–C(11) | 122.7(2) | 122.7(2) |
| M–P(1)–C(21) | 118.1(2) | 117.1(2) |
| C(2a)–P(1)–C(11) | 101.0(3) | 101.1(2) |
| C(2a)–P(1)–C(21) | 109.2(3) | 109.1(3) |
| C(11)–P(1)–C(21) | 98.8(3) | 99.1(2) |
| M–P(2)–C(1a) | 109.5(2) | 109.9(2) |
| M–P(2)–C(31) | 120.8(2) | 120.6(2) |
| M–P(2)–C(41) | 114.2(2) | 114.1(2) |
| C(1a)–P(2)–C(31) | 98.7(3) | 98.9(3) |
| C(1a)–P(2)–C(41) | 107.0(3) | 107.2(3) |
| C(31)–P(2)–C(41) | 105.0(3) | 104.5(3) |
| P(1)–C(2a)–C(1a) | 112.1(4) | 111.8(4) |
| P(2)–C(1a)–C(2a) | 112.7(5) | 112.6(4) |

* Cp* denotes the cyclopentadienyl centroid.

Å for complexes **3** and **4** respectively. The positions of the methyl hydrogen atoms were not determined, but simple molecular modelling indicates that there is a number of H ··· F distances which are significantly less than the sum of the van der Waals radii (2.55 Å) no matter how the methyl groups are orientated.

There are significant differences in the co-ordination about the rhodium atom between the doubly C–F bond-activated product **1**[7] and **3**. The Cp*–Rh distance is *ca.* 0.03 Å longer and the Rh–P distances are longer by *ca.* 0.08 Å in **3** than in **1**. The P–Rh–P angle of **1** is *ca.* 4° greater than that of **3**. The Rh–Cl distances, however, are identical.

Activation of two of the *ortho* aryl C–F bonds of complexes **3** and **4** to give **1** and **2** respectively proceeds quantitatively on thermolysis in refluxing ethanol for *ca.* 6 h. This reaction, however, does not occur in refluxing benzene (in which **3** and **4** are only sparingly soluble), dichloromethane or acetone, and only a small proportion of C–F activated product is obtained under the same conditions in refluxing acetonitrile.

Treatment of $[\{Rh(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ with dfppe in refluxing ethanol for 4.5 h, followed by addition of $NH_4BF_4$, yielded a yellow solid. Mass spectrometry and NMR spectroscopies indicate that the solid contains complexes **1** and **3**, and also another complex **5**. The low-temperature $^{19}F$ NMR spectrum of this mixture is shown in Fig. 4. It is not possible to separate these complexes, thus **5** could not be obtained pure. Complex **5** was identified by mass spectrometry and NMR spectroscopies (Table 1) as the singly C–F bond-activated species $[Rh\{(\eta^5\text{-}C_5Me_4CH_2C_6F_4P(C_6F_5)CH_2CH_2P(C_6F_5)_2\}Cl]^+BF_4^-$. The $^{31}P\text{-}\{^1H\}$ NMR spectrum exhibits two doublets at δ 83.86 and 49.14 with coupling constants, $^1J(RhP)$, of 141.3 and 152.1 Hz respectively. The former is assigned to the $CH_2P(C_6F_5)(C_6F_4)$ phosphorus atom and the latter to the $CH_2P(C_6F_5)_2$ phosphorus by analogy with the chemical shifts and coupling constants for complexes **1** and **3** respectively. Although the phosphorus atoms are non-equivalent, no phosphorus–phosphorus coupling can be resolved. This is consistent with low values of $^2J(PP)$ for metal complexes of $Ph_2PCH_2CH_2PPh_2$.[16] The $^{19}F$ NMR spectrum at 189 K shows the expected nineteen resonances, two of which are coincident (Fig. 4). Resonances at δ −115.87, −136.62 and −154.48 are assigned to three of the fluorine atoms of the $C_6F_4$ group by comparison with the spectrum of complex **1**. The six resonances between δ −120 and −130 are assigned to the six *o*-fluorine atoms of the three non-equivalent $C_6F_5$ groups. Three of the four resonances between δ −143 and −148 are assigned to the three *p*-fluorine atoms of the $C_6F_5$ groups and the fourth is assigned to the $C_6F_4$ group. There are six resonances, two of which are coincidental, between δ −156 and −162 which are assigned to the *m*-fluorine atoms of the $C_6F_5$ groups. There are two chiral centres in complex **5**: the rhodium atom and the $CH_2P(C_6F_5)(C_6F_4)$ phosphorus atom. The steric requirements of the molecule mean that only one pair of enantiomers exists. Presumably, under the reaction conditions a racemic mixture is formed. The proportions of **1**, **3** and **5** formed in this reaction may be altered by changing the reflux time. The mixture can be converted into complex **1** by thermolysis in refluxing ethanol for *ca.* 6 h.

## Conclusion

We have demonstrated that the activation of aryl C–F bonds occurs readily in the reactions between $[\{M(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ (M = Rh or Ir) and dfppe under mild conditions and in high yield, and that the reactions are insensitive to either air or moisture. The products of the reactions are dependent on the solvent. In refluxing benzene, dichloromethane or toluene the reaction proceeds with C–H activation and C–C and H–F bond formation to produce exclusively the cationic species $[M\{\eta^5\text{-}C_5Me_3[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}Cl]^+$. In refluxing ethanol the cations $[M(\eta^5\text{-}C_5Me_5)Cl(dfppe)]^+$ and $[Rh\{\eta^5\text{-}C_5Me_3[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}Cl]^+$ are also formed. Thermolysis of $[M(\eta^5\text{-}C_5Me_5)Cl(dfppe)]^+BF_4^-$ in refluxing ethanol induces C–F bond activation to give $[M\{\eta^5\text{-}C_5Me_3[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}Cl]^+\cdot BF_4^-$ in quantitative yield. Thermolysis of $[M(\eta^5\text{-}C_5Me_5)Cl(dfppe)]^+BF_4^-$ in refluxing benzene fails to induce C–F bond activation, which suggests that the cations $[M(\eta^5\text{-}C_5Me_5)Cl(dfppe)]^+$ are not intermediates in the reactions between $[\{M(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ and dfppe in benzene. However, the effect of the anion in determining the outcome of the reaction is not yet known, and the proximity of the $BF_4^-$ anions to the organometallic cations in the structures suggests that the anions exert a strong influence.

We are currently carrying out further investigations into these intriguing reactions to determine the mechanism of C–F bond activation.

## Experimental

### Physical measurements

Proton, $^{19}F$ and $^{31}P$ NMR spectra were recorded using a Bruker AM 300 spectrometer ($^1H$, 300.14; $^{19}F$, 282.41; $^{31}P$, 121.50 MHz), $^1H$ referenced internally using the residual protio solvent resonance relative to tetramethylsilane (δ 0), $^{19}F$ externally to $CFCl_3$ (δ 0) and $^{31}P$ externally to 85% $H_3PO_4$ (δ 0). The spectra of samples containing $BF_4^-$, the fluorine atoms of which exhibit a relatively long $T_1$, were recorded with a relaxation delay of 10 s. Infrared spectra were recorded as Nujol mulls between KBr plates on a Digilab FTS40 Fourier-transform spectrometer. Elemental analyses were performed by Butterworth Laboratories Ltd. and FAB mass spectra were recorded on a Kratos Concept 1 H mass spectrometer.

### Materials

The compounds $[\{M(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ (M = Rh or Ir) (Aldrich) and dfppe (Fluorochem) were used as supplied. Light petroleum (b.p. 40–60 °C) was used throughout.

### Preparations

**$[Rh\{(\eta^5\text{-}C_5Me_3[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}Cl]^+BF_4^-$ 1.** A slurry of $[\{Rh(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ (0.031 g, 0.050 mmol) and dfppe (0.106 g, 0.140 mmol) in benzene (15 $cm^3$) was heated at reflux under nitrogen for 6 h. The orange-yellow solution was concentrated to *ca.* 5 $cm^3$ by rotary evaporation and light petroleum (40 $cm^3$) added to precipitate a yellow solid, which was filtered off, washed with light petroleum (50 $cm^3$) and dried *in vacuo*. The solid was recrystallized from toluene–light petroleum. Yield 0.084 g, *ca.* 80%. The salt was dissolved in acetone and $KBF_4$ in water added to precipitate compound **1** which was filtered off, dissolved in dichloromethane and dried over $MgSO_4$. The solution was filtered and the solvent removed by rotary evaporation to afford **1** as a yellow solid, which was dried *in vacuo*. IR: 1644m, 1521s, 1480s, 1383m, 1344w, 1291m, 1180w, 1149w, 1114 (sh), 1094s, 1067s, 1034 (sh), 978s, 917w, 882w, 841w, 765w, 721m, 683w, 627w, 539w, 507w and 480w $cm^{-1}$.

**$[Ir\{(\eta^5\text{-}C_5Me_3[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}Cl]^+Cl^-$ 2.** A slurry of $[\{Ir(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ (0.036 g, 0.045 mmol) and dfppe (0.067 g, 0.088 mmol) in benzene (30 $cm^3$) was heated at reflux for 6 h. The yellow solution was allowed to cool and concentrated to yield a cream-coloured solid, which was filtered off and dried *in vacuo*. Yield 0.086 g, 86%. IR: 1645m, 1635m, 1519s, 1481s, 1423m, 1390m, 1346m, 1296m, 1167w, 1143w, 1117 (sh), 1093s, 1069s, 980s, 958m, 882w, 841w, 791w, 756w, 724m, 690w, 676w, 646w, 628m, 541m, 526w, 508w and 440m $cm^{-1}$.

**$[Rh(\eta^5\text{-}C_5Me_5)Cl(dfppe)]^+BF_4^-$ 3.** The salt $NH_4BF_4$ (0.26 g, 2.48 mmol) was added to $[\{Rh(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ (0.26 g, 0.42 mmol) in methanol (50 $cm^3$). After 10 min an orange solution had developed. The compound dfppe (0.66 g, 0.87 mmol) in dichloromethane (30 $cm^3$) was added, and the mixture stirred for 3.5 h. The solvents were removed by rotary evaporation to yield a yellow-orange solid which was extracted into dichloromethane (3 × 75 $cm^3$). The solution was filtered and concentrated to 30 $cm^3$ by rotary evaporation. Addition of light petroleum (50 $cm^3$) yielded the product as an orange crystalline solid, which was washed with light petroleum (100 $cm^3$) and dried. Yield 0.80 g, 86%. IR: 1647m, 1524s, 1482s, 1424w, 1393m, 1295m, 1148w, 1128m, 1092s, 1052s, 1012m, 981s, 886w, 843w, 813w, 759w, 725m, 676w, 655m, 628w, 590w, 526m and 477w $cm^{-1}$.

**$[Ir(\eta^5\text{-}C_5Me_5)Cl(dfppe)]^+BF_4^-$ 4.** The compounds $[\{Ir(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ (0.11 g, 0.14 mmol), $NH_4BF_4$ (0.119, 1.1 mmol) and dfppe (0.21 g, 0.28 mmol) were treated as for **3**. The product was obtained as a lemon-yellow crystalline solid. Yield 0.22 g, 64%. IR: 1647m, 1522s, 1477s, 1438m, 1391m, 1376m, 1292m, 1149m, 1128m, 1096s, 1053m, 1017m, 978s, 890w, 842w, 813w, 763w, 726m, 680w, 657w, 626w, 588w, 530m, 480w, 455w and 430m $cm^{-1}$.

**Reaction between $[\{Rh(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ and dfppe in ethanol.** A slurry of $[\{Rh(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ (0.21 g, 0.34 mmol) and dfppe (0.605 g, 0.80 mmol) in ethanol (150 $cm^3$) was heated at reflux for 4.5 h. The yellow solution was allowed to cool and $NH_4BF_4$ (1.00 g, mol) added. The solution was stirred for 2 h, filtered and the solvent removed by rotary evaporation. The solid was extracted into chloroform (150 $cm^3$) and filtered. Removal of the solvent by rotary evaporation gave *ca.* 0.4 g of a yellow solid comprising complexes **1**, **3** and **5**.

### Crystallography

Crystals of compounds **3** and **4**, suitable for diffraction, were grown from acetone. The crystal data and experimental parameters for both compounds are given in Table 3. Unit-cell parameters for **3** were determined from the optimized setting angles of 21 reflections in the range $9.32 < 2\theta < 24.27°$ and for **4** from 33 reflections in the range $9.94 < 2\theta < 25.04°$. A semiempirical absorption correction was applied to the data (based on ψ scans), and the data for both structures were corrected for Lorentz-polarization effects. Both structures were solved using the program SHELXTL-PC[17] and refined on $F^2$

**Table 3** X-Ray crystal data collection, solution and refinement details for $[Rh(\eta^5\text{-}C_5Me_5)Cl(dfppe)]^+BF_4^-$ **3** and $[Ir(\eta^5\text{-}C_5Me_5)Cl(dfppe)]^+BF_4^-$ **4**[a]

| Compound | **3** | **4** |
|---|---|---|
| Formula | $C_{36}H_{19}BClF_{24}P_2Rh$ | $C_{36}H_{19}BClF_{24}IrP_2$ |
| *M* | 1118.62 | 1207.91 |
| Crystal size/mm | 0.25 × 0.22 × 0.16 | 0.75 × 0.44 × 0.33 |
| *a*/Å | 12.647(7) | 12.675(4) |
| *b*/Å | 18.752(9) | 18.657(3) |
| *c*/Å | 16.942(7) | 16.998(2) |
| β/° | 99.24(3) | 99.52(2) |
| $U$/Å$^3$ | 3966(3) | 3964(2) |
| $D_c$/g cm$^{-3}$ | 1.874 | 2.024 |
| μ/cm$^{-1}$ | 7.22 | 36.59 |
| *F*(000) | 2192 | 2320 |
| 2θ Range/° | 5.34–48.02 | 5.32–52.00 |
| Scan width/° | ±0.6(ω)[b] | ±0.45(ω)[b] |
| Total data | 7648 | 8774 |
| Unique data, $R_{int}$ | 6216, 0.0456 | 7197, 0.0311 |
| $R1$, $wR2$ $[I > 2\sigma(I)]$[c] | 0.0570, 0.0898 | 0.0368, 0.0747 |
| (all data) | 0.1207, 0.1122 | 0.0627, 0.0845 |
| Goodness of fit on $F^2$[d] | 1.034 | 1.035 |
| Difference map features/e Å$^{-3}$ | 0.387, −0.368 | 0.851, −0.955 |

[a] Details in common: Siemens P4 diffractometer, $\lambda(\text{Mo-K}\alpha) = 0.710\,73$ Å; $T = 290$ K, monoclinic, space group $P2_1/n$; $Z = 4$, scan type ω, least-squares variables 586. [b] Around the $K\alpha_1$–$K\alpha_2$ angles. [c] $R1 = \Sigma||F_o| - |F_c||/|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$. [d] Goodness of fit, $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{\frac{1}{2}}$, where $n$ = number of reflections and $p$ = total number of parameters refined.

using SHELXL 93,[18] and crystal stability was monitored by the observation of the intensities of three standard reflections; for neither structure was there any significant loss of intensity.

The structures were solved by Patterson and Fourier methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were included in calculated positions (C–H 0.96 Å) with a fixed isotropic thermal parameter ($U_{iso} = 0.08$ Å$^2$).

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre, (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/106.

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