Cleavage of Both Alkyl C–H Bonds and Aryl C–F Bonds and Concomitant C–C Bond Formation in a Pentamethylcyclopentadienylrhodium Phosphine Complex: X-Ray Structure of $[\{\eta^5\text{-}C_5Me_3[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}RhCl]^+BF_4^-$

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The reaction between bis(dipentafluorophenylphosphino)ethane, dfppe, and $[\{(\eta^5\text{-}C_5Me_5)RhCl(\mu\text{-}Cl)\}_2]$ proceeds with cleavage of two C–F bonds and two C–H bonds and formation of two C–C bonds to yield the ionic complex **1a**.

Activation of aryl C–F bonds, which are amongst the strongest known, has recently been observed in a number of systems.[1] However, activation of *ortho* C–F bonds in pentafluorophenylphosphine complexes has not yet been reported, except by nucleophilic substitution.[2] Here, we report the cleavage of *ortho* C–F bonds in bis(dipentafluorophenylphosphino)ethane, dfppe, and also of pentamethylcyclopentadienyl C–H bonds, with concomitant formation of C–C bonds to give a rhodium complex of a novel anionic 10-electron donor ligand, comprising a 13-membered heterocycle.

Treatment of $[\{(\eta^5\text{-}C_5Me_5)RhCl(\mu\text{-}Cl)\}_2]$ with the diphosphine dfppe, in refluxing benzene for 5 h, gave the complex $[\{\eta^5\text{-}C_5Me_3[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}RhCl]^+Cl^-$ **1a**, in high yield (*ca.* 90%). A single-crystal X-ray diffraction study of the tetrafluoroborate salt, **1b**, formed by anion metathesis, shows that one *ortho* C–F bond of one of the pentafluorophenyl rings bound to each phosphorus atom and one C–H bond of two of the methyl groups have been cleaved and C–C bonds between the respective *ortho* carbon atoms and the exocyclic carbons of the pentamethylcyclopentadienyl ring have been formed (Fig. 1).† The ^1H, ^{19}F and $^{31}P\{^1H\}$ NMR and mass spectra of **1a** and **1b** are virtually identical and entirely consistent with this structure.‡ The ^{19}F NMR spectrum of complex **1a** at 214 K exhibits nine multiplets, and at 333 K exhibits seven multiplets indicative of hindered rotation about the $P\text{–}C_6F_5$ bonds. From the variable-temperature ^{19}F NMR spectra of complex **1a** the value of $\Delta G^\ddagger$, the activation energy for rotation about the $P\text{–}C_6F_5$ bonds, is calculated to be 52.5 ± 2 kJ mol^{-1}. Presumably, rotation about the $P\text{–}C_6F_5$ bonds is hindered for steric reasons.

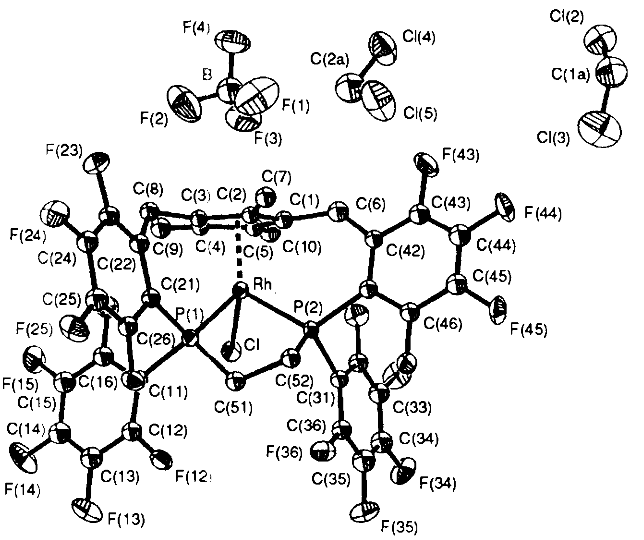

Fig. 1 Molecular structure of $\mathbf{1b}\cdot 2CH_2Cl_2$. Selected interatomic distances (Å) and angles (°): Rh–P(1) 2.283(3), Rh–P(2) 2.263(3), Rh–Cl 2.380(3), Rh–cp′ 1.837(1), P(1)–C(21) 1.817(11), C(21)–C(22) 1.400(14), C(22)–C(8) 1.540(15), C(8)–C(3) 1.497(15), P(2)–C(41) 1.848(10), C(41)–C(42) 1.381(15), C(42)–C(6) 1.538(16), C(6)–C(1) 1.469(16); P(1)–Rh–P(2) 87.9(1), P(1)–Rh–Cl 90.6(1), P(2)–Rh–Cl 93.0(1), cp′–Rh–P(1) 126.3(1), cp′–Rh–P(2) 122.2(1), cp′–Rh–Cl 126.1(1), Rh–P(1)–C(21) 113.6(3), P(1)–C(21)–C(22) 127.0(8), C(21)–C(22)–C(8) 125.6(9), C(22)–C(8)–C(3) 119.5(9), Rh–P(2)–C(41) 117.6(3), P(2)–C(41)–C(42) 125.3(8), C(41)–C(42)–C(6) 126.0(9), C(42)–C(6)–C(1) 120.1(10), Rh–P(1)–C(11) 120.6(3), Rh–P(1)–C(51) 105.4(4), Rh–P(2)–C(31) 117.3(3), Rh–P(2)–C(52) 105.3(4). cp′ Denotes the centroid of the cyclopentadienyl ring.

The reaction between $[\{(\eta^5\text{-}C_5Me_5)RhCl(\mu\text{-}Cl)\}_2]$ and dfppe in refluxing dichloromethane also proceeds to yield **1a**, but at a slower rate. The nett reaction may be considered as that shown in eqn. (1).

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

No evidence for the formation of HF has yet been obtained, but it seems likely that formation of the strong H–F bond (574 kJ mol^{-1})[3] provides a thermodynamic driving force for the reaction. A similar type of reaction has been observed previously, in which treatment of $[(C_5H_5)RuMe(PPh_3)_2]$ with $C_6F_5N{=}NC_6F_5$ yields $[(\eta^5C_5H_4C_6H_4PPh_2)Ru(C_6F_4N{=}NC_6F_5)]$, for which it was suggested that the electron-rich metal centre acted as a nucleophile.[4] It is not yet known what part the rhodium plays in this reaction. It seems unlikely, however, that a nucleophilic η^6-fulvene rhodium species is involved, since these are only formed in strong base.[5] The rhodium may act as a template holding the C–H and C–F bonds in close proximity. An electron transfer process may then occur between the pentamethylcyclopentadienyl ring and the electron-accepting pentafluorophenyl ring, similar to that proposed for the reaction between $[MeIr(PEt_3)_3]$ and C_6F_6,[6] with subsequent formation of C–C and H–F bonds. The bond angles and distances in the 13-membered ring show only minor perturbations from the other relevant angles and distances in **1b**, $[(\eta^5\text{-}C_5H_5)MoCl(CO)\{(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2\}]$,[7] $[Pt\{(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2\}_2]$,[8] $[RhCl(PPh_3)\{(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2\}]$[9] and $\{(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2\}$[9] itself. The angles C(41)–C(42)–C(6) and C(21)–C(22)–C(8) are *ca.* 2–4° greater than the $C_{ipso}\text{–}C_{ortho}\text{–}F$ angles, and, consequently, the angles C(43)–C(42)–C(6) and C(23)–C(22)–C(8) are *ca.* 2–4° less than those of $C_{meta}\text{–}C_{ortho}\text{–}F$. The two phosphorus atoms are chiral, but the steric requirements of the reaction lead to formation of only the *meso* stereoisomer.

All attempts to isolate the free ligand from the metal complex have been unsuccessful so far, but attempts to prepare the ligand bound to other metal centres are in progress.

We thank BNFL Fluorochemicals Ltd and the EPRSC for their support.

Received, 31st October 1994; Com. 4/06629D

Footnotes

† *Crystal data* for compound **1b**: $C_{36}H_{17}BClF_{22}P_2Rh\cdot 2CH_2Cl_2$, M = 1248.5, monoclinic, space group $P2_1/n$, a = 12.254(1), b = 13.316(1), c = 29.801(2) Å, β = 98.90(1)°, V = 4804(1) Å^3, Z = 4, D_c = 1.726 g cm^{-3}, $F(000)$ = 2448, μ(Mo-Kα) = 0.815 mm^{-1}, crystal dimensions

$0.45 \times 0.36 \times 0.36$ mm. Accurate unit-cell dimensions were determined by least-squares refinement of 55 centred reflections with $10 < 2\theta < 24°$. Data were measured on a Siemens P4 diffractometer with Mo-Kα radiation using ω-scans. 10556 reflections were measured with $2\theta < 50°$ and $-1 < h < 14$, $-1 < k < 15$, $-35 < l < 35$. The reflections were corrected for Lorentz and polarization effects and merged to give 8413 independent reflections (R_{int} = 0.033) with 5269 having $F > 4\sigma(F)$ regarded as observed. A semi-empirical absorption correction was applied to the data (max. and min. transmission factors 0.804 and 0.744). The structure was solved by direct methods using the program SHELXTL-PC.[10] All hydrogen atoms were included in calculated positions (C–H = 0.96 Å) with a single fixed isotropic thermal parameter (0.08 Å^2). The rhodium, phosphorus, chlorine and fluorine atoms were refined with anisotropic thermal parameters. All other atoms were refined with isotropic thermal parameters. Final cycles of refinement gave $R = 0.079$, $R_w = 0.122$ [$w^{-1} = \sigma^2F + 0.12F^2$], the maximum and minimum residual electron densities in the final ΔF map were 2.06 and -1.18 e Å^{-3} respectively. The mean and maximum shift/error in the final refinement cycle were 0.002 and 0.019 respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ *NMR data* for **1a**, MS (FAB): *m/z* 991 [(M–Cl)$^+$]. NMR: δ_H (300 MHz, CDCl$_3$) 4.44 (2H, m, CH$_2$), 3.88 (2H, m, CH$_2$), 3.80 (2H, m, CH$_2$), 3.68 (2H, dm, J = 19.0 Hz, CH$_2$), 2.05 (3H, s, CH$_3$), 2.03 (3H, s, CH$_3$), 1.36 (3H, s, CH$_3$); δ_P (121.50 MHz, CDCl$_3$) 71.28 [dm, ^1J(RhP) = 144.2 Hz]; δ_F (282.41 MHz, CDCl$_3$, 214 K) -116.17 (2F, m), -128.48 (2F, m, *ortho*-C$_6$F$_5$), -133.40 (2F, m, *ortho*-C$_6$F$_5$), -134.43 (2F, m), -142.50 (2F, m), -143.24 [2F, tm, J(FF) = 21.1 Hz], -150.43 [2F, tm, J(FF) = 21.1 Hz], -156.35 (2F, vt, J = 20.6 Hz, *meta*-C$_6$F$_5$), -157.51 (2F, vt, J = 23.1 Hz, *meta*-C$_6$F$_5$); (282.41 MHz, CDCl$_3$, 333 K) -117.60 (2F, m), -131.42 (4F, br s, *ortho*-C$_6$F$_5$), -135.24 (2F, m), -143.68 (2F, m), -144.71 [2F, tm, J(FF) = 20.1 Hz], -151.67 (2F, vt, J = 20.2 Hz), -158.44 (4F, vtm, J = 18.9 Hz, *meta*-C$_6$F$_5$).

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