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Remarkable regioselectivity in the reaction between $[(\eta^5\text{-}C_5Me_4H)RhCl(\mu\text{-}Cl)]_2$ and $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$: synthesis of a chiral-at-metal rhodium complex cation via carbon–fluorine and –hydrogen bond activation and carbon–carbon bond formation[1]

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Abstract

The reaction between $[(\eta^5\text{-}C_5Me_4H)RhCl(\mu\text{-}Cl)]_2$ and $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ proceeds in refluxing benzene via activation of two C–F and C–H bonds and formation of two C–C bonds to yield the chiral cation $[\{\eta^5\text{-}C_5HMe_2\text{-}2,4\text{-}[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}RhCl]^+$, with $>90\%$ selectivity. © 1998 Elsevier Science S.A. All rights reserved.

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The activation of carbon–fluorine bonds of polyfluorinated compounds, which have formerly been considered as unreactive, is now being accomplished by an increasing number of reagents under remarkably mild conditions [1]. Recent advances have provided catalytic methods for the hydrogenolysis of perfluoroarenes [2] and the defluorination of perfluoroalkanes to perfluoroarenes [3] or perfluoroalkenes [4]. A small number of reactions involving the activation of carbon–fluorine bonds by transition metal complexes lead to carbon–carbon bond formation [5]. This type of reactivity could be of immense synthetic value if high yields and regioselectivity can be obtained under mild conditions. The reaction between $[(\eta^5\text{-}C_5Me_5)RhCl(\mu\text{-}Cl)]_2$ and $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ (dfppe) proceeds via the activation of two C–F and C–H bonds and formation of two C–C bonds to afford exclusively the complex $[\{\eta^5\text{-}C_5Me_3[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}RhCl]^+$ as a mixture of chloride (**1a**) and tetrafluoroborate (**1b**) salts in quantitative yield under mild aerobic conditions (Eq. (1)) [6,7].

$$1/2[(\eta^5-C_5Me_5)RhCl(\mu-Cl)]_2 + (C_6F_5)_2PCH_2CH_2P(C_6F_5)_2 \rightarrow [\{\eta^5-C_5Me_3[CH_2C_6F_4P(C_6F_5)CH_2]_2-1,3\}RhCl]^+ \cdot X^- + 2HF \quad (\mathbf{1a}\ X^- = Cl^-,\ \mathbf{1b}\ X^- = BF4^-) \qquad (1)$$

The reaction displays complete regiospecificity: only one *ortho* C–F bond of each $P(C_6F_5)_2$ moiety and C–H bonds of methyl groups exclusively in a 1,3 disposition are activated. Furthermore, of the two possible geometric isomers (Fig. 1) only isomer **I** is formed. This regiospecificity is presumably imposed by the geometric constraints of the reagents in the reaction. The regiospecificity, quantitative yield and mild conditions of reaction (1) suggest that the synthetic potential of C–F and C–H bond activation with concomitant C–C bond formation can be realised.

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[1] Dedicated to Prof. W.R. Roper FRS on the occasion of his 60th birthday.

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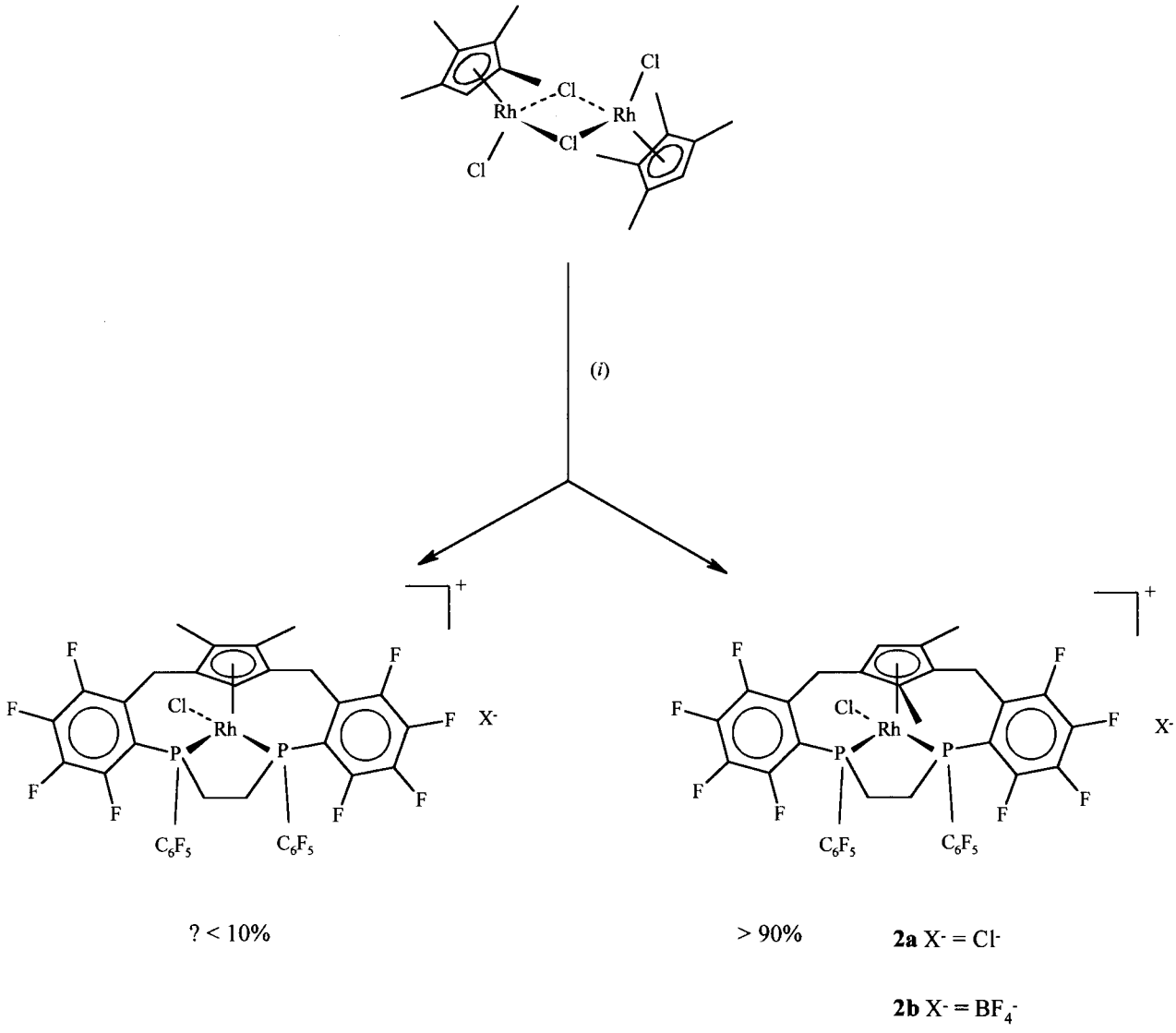

Scheme 1. C_6H_6, heat.

As part of our programme to understand the mechanism and extend the scope of reaction (1) we have found that the reaction between $[(\eta^5\text{-}C_5Me_4Et)RhCl(\mu\text{-}Cl)]_2$ and dfppe, which yields products similar to **1a**, shows no discernible selectivity as to which C–H bonds are activated [8]. Here we describe the remarkable regioselectivity displayed by the reaction between $[(\eta^5\text{-}C_5Me_4H)RhCl(\mu\text{-}Cl)]_2$ and dfppe to yield a chiral-at-metal complex. Such complexes are of current interest because of their possible applications in chiral synthesis and catalysis [9].

The reaction between $[(\eta^5\text{-}C_5Me_4H)RhCl(\mu\text{-}Cl)]_2$ and dfppe was expected to yield two isomers of the cation of formulation $[\{\eta^5\text{-}C_5HMe_2[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}RhCl]^+$, dependent on the positions of the two methyl groups. However, the reaction was found to yield the asymmetric isomer with $>90\%$ selectivity in high yield (Scheme 1). The chloride salt, **2a**[2], was precipitated in 50% yield on treatment of dfppe with $[(\eta^5\text{-}C_5Me_4H)RhCl(\mu\text{-}Cl)]_2$ in refluxing benzene, but could not be obtained analytically pure due to contamination by a small amount of tetrafluoroborate formed

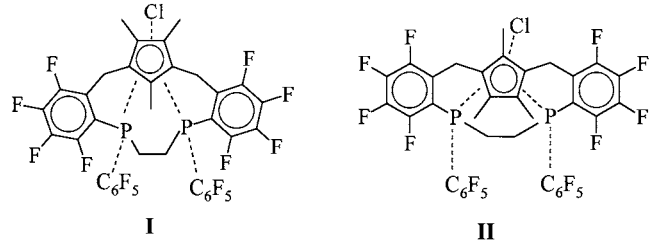

Fig. 1. Diagrammatic representation of the geometric isomers of the cation $[RhCl\{\eta^5\text{-}C_5Me_3[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}]^+$ viewed along the C_5(centroid)-Rh axis.

by the reaction between HF and the borosilicate glass reaction vessel. The tetrafluoroborate salt, **2b**[3], prepared by anion metathesis of **2a** with NH_4BF_4, was, however, obtained pure and satisfactory elemental analysis was obtained. The positive ion FAB mass spectra of **2a** and **2b** are identical and consistent with the parent cation and $[M-Cl-H]^+$. The $^{31}P-\{^1H\}$-NMR spectra exhibit two doublets of multiplets at ca. 70 ppm, with rhodium–phosphorus coupling constants, $^1J_{Rh-P}$, of ca. 140 Hz, consistent with the values of δ 71.3 and 144 Hz for **1a** [6]. The presence of two resonances is indicative of non-equivalent phosphorus atoms. The ^1H-NMR spectrum of **2a** possesses eight resonances in the region δ 3.5 to 5.0 indicating that all the methylene hydrogen atoms, PCH_2 and $C_5CH_2C_6F_4$, are unique. Each $C_5CH_2C_6F_4$ methylene group shows two mutually coupled resonances with a coupling, $^2J_{H-H}$, of ca. 18 Hz, one of which is further coupled to one phosphorus with a coupling, $^4J_{P-H}$, of ca. 10 Hz, which is confirmed by $^1H-\{^{31}P\}$-NMR spectroscopy. In contrast, the respective $C_5CH_2C_6F_4$ resonances of **2b** do not show coupling to phosphorus. Thus, the anion has a large effect on the spectroscopic properties of the cation. The ^1H-NMR spectra of **2a** and **2b** also differ in their methyl resonances. Those of **2a** occur as a doublet of doublets at δ 1.93, with couplings, $^4J_{P-H}$, of 14.2 and 1.9 Hz, and a doublet at δ 1.91 with $^4J_{P-H}$ 1.6 Hz, whereas those of **2b** occur as doublets at δ 1.98 and 1.89 with $^4J_{P-H}$ 8.7 and 2.7 Hz respectively. Although unequivocal assignment of these resonances cannot be made, we tentatively assign the resonances with the larger P–H couplings to the 4-methyl hydrogen atoms (since this methyl group may be considered as *trans* to one phosphorus atom) and the other resonances to the 2-methyl hydrogen atoms. Both spectra exhibit a doublet at ca. δ 5.5 with $^3J_{P-H}$ ca. 6.5 Hz which is assigned to the hydrogen atom of the cyclopentadienyl ring. The spectra are consistent with that of **1a**, which exhibits a doublet at δ 2.04 with a coupling, $^4J_{P-H}$, of ca. 6 Hz assigned to the equivalent 4- and 5-methyl groups. (Originally this was erroneously described by us as two singlets [6]). It is evident from the NMR data for **1a**, **2a** and **2b** that P–H coupling is small or negligible when the P–Rh–CMe angle is not close to 180° and the methyl and cyclopentadienyl hydrogen resonances show couplings of >5 Hz to only one phosphorus atom. The $^{13}C-\{^1H\}$-NMR and $^1H-^{13}C$ and $^1H-^{31}P$ correlation spectra of **2a** are also consistent with these observations. The ^{19}F-NMR spectra of **2a** and **2b** are similar and entirely consistent with a formulation in which both C_6F_4 and both C_6F_5 groups are non-equivalent. There are three chiral centres in the cations of **2a** and **2b**, the rhodium and both phosphorus atoms but, due to the geometric constraints of the reaction, only one pair of enantiomers can be formed. Presumably **2a** is formed as a racemic mixture.

Multinuclear NMR spectroscopic and mass spectrometric investigations indicate that **2a** is also the major species ($>50\%$) in the mother liquor. The data also provide evidence for the formation of $[(\eta^5\text{-}C_5Me_4H)RhCl(dfppe)]^+$ [m/z 1017 (M^+)], and one or more isomers of the singly C–F bond activated complex $[\{\eta^5\text{-}C_5HMe_3CH_2C_6F_4P(C_6F_5)CH_2CH_2P(C_6F_5)_2\}RhCl]^+$ [m/z 997 (M^+); δ_P 86.4 (dm, $^1J_{Rh-P}$ 123 Hz), 58.3 (dm, $^1J_{Rh-P}$ 141 Hz)], which are possible intermediates in the formation of **2a**, together with a trace amount of a complex with ^{31}P-NMR spectral data [δ_P ca. 68.5 (d, $^1J_{Rh-P}$ ca. 140 Hz)] similar to that of **1a**, which is tentatively assigned to the symmetric isomer of **2a**. The ratio of asymmetric to symmetric isomers of the doubly C–F bond activated product formed in the reaction was determined to be $>9{:}1$ from the ^{31}P-NMR spectra. Thus, the reaction between $[(\eta^5\text{-}C_5Me_4H)RhCl(\mu\text{-}Cl)]_2$ and dfppe not only displays the regiospecificity of reaction (1), but also a remarkably selective C–H bond activation.

In conclusion, the reaction demonstrates the synthetic potential that C–F and C–H bond activation with concomitant C–C bond formation can provide by

[2] Selected spectroscopic data for **2a**: MS (FAB): m/z 977 (M^+), 941 ($[M-Cl-H]^+$). ^1H-NMR ($CDCl_3$, 400.13 MHz): δ 5.45 (1H, d, $^3J_{P'-H}$ 6.9, C5H), 4.94 (1H, d, $^2J_{H-H'}$ 18.2, C*H*H′C_6F_4), 4.67 (1H, d, $^2J_{H''-H'''}$ 17.7, C*H*″H‴C_6F_4), 4.44 (1H, m, PCH_2), 4.18 (dd, $^2J_{H''-H'''}$ 17.7, $^4J_{P'-H'''}$ 9.8, CH″*H*‴C_6F_4), 4.08 (1H, dd, $^2J_{H-H'}$ 18.2, $^4J_{P''-H'}$ 9.8, CH*H*′C_6F_4), 3.88 (1H, m, PCH_2), 3.58 (2H, m, P′CH_2 and P″CH_2), 1.93 (3H, dd, $^4J_{P''-H}$ 14.2, $^4J_{P'-H}$ 1.6, 4-CH_3), 1.91 (3H, d, $^4J_{P-H}$ 1.9, 2-CH_3). $^{13}C-\{^1H\}$-NMR ($CDCl_3$, 100.62 MHz): δ 86.6 (d, J_{P-C} 7, *C*H of C_5 ring), 31.6 (dd, $^1J_{P-C}$ 34, $^2J_{P-C}$ 14, PCH_2), 29.5 (d, $^1J_{P-C}$ 41, PCH_2), 19.4 (d, $^3J_{P''-C}$ 6, *C*$H_2C_6F_4$), 18.4 (d, $^3J_{P'-C}$ 7, *C*$H_2C_6F_4$], 12.6 (s, 2-CH_3), 9.2 (d, $^3J_{P''-C}$ 4, 4-CH_3). ^{19}F-NMR ($CDCl_3$, 376.45 MHz): δ −120.54 (2F, m, C_6F_4), −129.82 (2F, br s, F_o of C_6F_5), −131.12 (2F, br s, F_o of C_6F_5), −135.30 (1F, m, C_6F_4), −135.61 (1F, m, C_6F_4), −143.52 (1F, ddd, J_{F-F} ca. 20.8, ca. 20.8, 9.3, C_6F_4), −143.68 (1F, ddd, J_{F-F} ca. 20.8, ca. 20.8, 9.1, C_6F_4), −144.91 (1F, m, F_p of C_6F_5), −145.06 (1F, m, F_p of C_6F_5), −153.08 (1F, dd, J_{F-F} ca. 21.7, ca. 21.7, C_6F_4), −153.38 (1F, dd, J_{F-F} ca. 21.8, ca. 21.8, C_6F_4), −158.39 (4F, m, F_m of C_6F_5). $^{31}P-\{^1H\}$-NMR ($CDCl_3$, 161.99 MHz): δ 78.8 (dm, $^1J_{Rh-P'}$ 141, P′), 73.2 (dm, $^1J_{Rh-P''}$ 141, P″].

[3] Selected spectroscopic data for **2b**: ^1H-NMR ($CDCl_3$, 400.13 MHz): δ 5.58 (1H, d, $^3J_{P-H}$ 6.5, C_5H), 4.09 (1H, d, $^2J_{H-H}$ 17.8, C*H*H′C_6F_4), 4.07 (1H, d, $^2J_{H-H}$ 18.6, C*H*″H‴C_6F_4), 3.87 (1H, d, $^2J_{H-H}$ 17.8, CH*H*′C_6F_4), 3.58 (2H, m, PCH_2), 3.33 (1H, d, $^2J_{H-H}$ 18.6, CH″*H*‴C_6F_4), 3.20 (1H, m, PCH_2), 2.90 (1H, m, PCH_2), 1.98 (3H, d, $^4J_{P-H}$ 8.7, 4-CH_3), 1.89 (3H, d, $^4J_{P-H}$ 2.7, 2-CH_3). ^{19}F-NMR ($CDCl_3$, 376.45 MHz): δ −120.50 (1F, m, C_6F_4), −120.68 (1F, m, C_6F_4), −129.14 (2F, d, $^3J_{F-F}$ 19.6, F_o of C_6F_5), −131.06 (2F, d, $^3J_{F-F}$ 18.6, F_o of C_6F_5), −134.27 (1F, m, C_6F_4), −134.65 (1F, m, C_6F_4), −143.67 (2F, m), −144.28 (2F, m), −152.87 (1F, dd, J_{F-F} ca. 20.6, ca. 20.6, C_6F_4), −153.07 (1F, dd, J_{F-F} ca. 23.0, ca. 23.0, C_6F_4), −153.70 and −153.76 (4F, 2s, 1:4, BF_4^-), −157.82 (2F, m, F_m of C_6F_5), −158.00 (2F, m, F_m of C_6F_5). $^{31}P-\{^1H\}$-NMR ($CDCl_3$, 161.99 MHz): δ 75.9 [dm, $^1J_{Rh-P}$ 140], 68.9 (dm, $^1J_{Rh-P}$ 138).

facilitating the selective high yield synthesis of a chiral-at-metal complex.

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