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Synthesis of rhodium complexes of an asymmetric η^5,η^1,η^1-*cyclo*-pentadienyl-bis(phosphine) ligand by regioselective intramolecular dehydrofluorinative C–C coupling

Ronan M. Bellabarba, Mark Nieuwenhuyzen, Graham C. Saunders *

School of Chemistry, The Queen's University of Belfast, David Keir Building, Belfast, Northern Ireland BT9 5AG, UK

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Abstract

The reaction between $[\{(\eta^5\text{-}C_5Me_4H)RhX_2\}_2]$ and $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ (dfppe) proceeds in refluxing benzene via cleavage of two C–F bonds and C–H bonds of adjacent methyl groups and formation of two C–C bonds to yield selectively the asymmetric cation $[\{\eta^5,\eta^1,\eta^1\text{-}C_5HMe_2\text{-}3,4\text{-}[CH_2\text{-}2\text{-}C_6F_4P(C_6F_5)CH_2]_2\text{-}1,2\}RhX]^+$. The selectivity for X = Cl was determined to be >90%. Treatment of $[(\eta^5\text{-}C_5Me_4H)RhCl(dfppe)]BF_4$ with proton sponge afforded $[\{\eta^5,\eta^1,\eta^1\text{-}C_5HMe_2\text{-}3,4\text{-}[CH_2\text{-}2\text{-}C_6F_4P(C_6F_5)CH_2]_2\text{-}1,2\}RhCl]BF_4$ exclusively. The regioselectivity displayed by these reactions is in stark contrast to that in the reaction between $[(Cp^*RhX_2)_2]$ and dfppe, and that between $[Cp^*RhCl(dfppe)]^+$ and proton sponge, in which C–H bonds of methyl groups in a 1,3 disposition are cleaved to yield the cation $[\{\eta^5,\eta^1,\eta^1\text{-}C_5Me_3[CH_2\text{-}2\text{-}C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}RhX]^+$ exclusively. The structure of $[\{(\eta^5\text{-}C_5Me_4H)RhCl_2\}_2]$ has been determined by single-crystal X-ray diffraction.

Keywords: Rhodium; η^5-*Cyclo*-pentadienide; Phosphine; C–C coupling

1. Introduction

Chelating bi- or tri-functional chelating ligands containing both *cyclo*-pentadienide and phosphine moieties are expected to exert dramatically different effects on metals than the separated ligands. This has been confirmed for a number of complexes [1]. For example, these ligands have allowed the isolation of zirconium complexes, the unlinked *cyclo*-pentadienide phosphine analogues of which are either unknown or unstable [2–4], the hybrid ligand complex $[\{\eta^5,\eta^1\text{-}(indenyl)CH_2CH_2\text{-}PPh_2\}RhMe(CO)]BF_4$ reacts with 1-phenylpropyne at room temperature to form the alkenyl complex $[\{\eta^5,\eta^1\text{-}(indenyl)CH_2CH_2PPh_2\}RhMe\{O{=}CMeC(Me){=}CPh\}]\text{-}BF_4$, whereas under the same conditions $[(\eta^5\text{-}indenyl)RhMe(CO)(PPh_3)]BF_4$ does not react [5], and $[\{\eta^5,\eta^1\text{-}C_5H_2(CO_2CH_2CH_2PPh_2)MeR\text{-}2,4\}Ru\text{-}(NCMe)_2]PF_6$ shows a high diastereoselectivity in ligand substitution reactions with phosphines, in contrast to the low diastereoselectivity shown by $[\{\eta^5\text{-}C_5H_2(CO_2Et)MeR\text{-}2,4\}Ru(NCMe)_2\{P(OMe)_3\}]PF_6$ [6]. The development of the chemistry of complexes of chelating hybrid *cyclo*-pentadienide–phosphine ligands has been severely hindered by the lack of convenient ligand syntheses [1]. However, recently we reported that intramolecular dehydrofluorinative C–C coupling provides a convenient method of synthesizing complexes of hybrid *cyclo*-pentadienide–phosphine ligands [7,8]. The reaction is particularly well suited to the coupling of pentamethyl-*cyclo*-pentadienide and chelating diphosphine ligands. We have reported that the coupling of Cp* and $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ (dfppe) in a rhodium(III) complex can be accomplished either by the one-pot reaction between $[(Cp^*RhCl_2)_2]$ and dfppe in refluxing benzene or ethanol (reaction 1) [9,10] or by treatment of the tetrafluoroborate salt, the isolated intermediate cation $[Cp^*RhCl(dfppe)]^+$ with proton sponge [7]. In both cases, the product $[\{\eta^5,\eta^1,\eta^1\text{-}C_5Me_3[CH_2\text{-}2\text{-}C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}RhCl]^+$ was obtained in virtually quantitative yield, as a mixture of chloride **1a** and tetrafluoroborate **1b** salts in the former and as **1b** in the latter.

* Corresponding author. Tel.: +44-28-9027 4682; fax: +44-28-9038 2117.

E-mail address: g.saunders@qub.ac.uk (G.C. Saunders).

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$$1/2[(Cp^*RhCl_2)_2] + (C_6F_5)_2PCH_2CH_2P(C_6F_5)_2 \rightarrow [\{\eta^5\eta^1\eta^1\text{-}C_5Me_3[CH_2\text{-}2\text{-}C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}RhCl]X + 2HF \quad (\mathbf{1a}\ X = Cl^-, \mathbf{1b}\ X = BF_4^-) \quad (1)$$

The reaction displays complete regiospecificity in that C–H bonds of methyl groups exclusively in a 1,3 disposition are activated and, of the two possible geometric isomers (Fig. 1), only isomer **I** is formed. The regio- and stereo-specificity are presumably imposed by the geometric constraints of the reagents and product of the reaction.

As part of a programme to extend the scope of reaction (1) it was found that similar reactions occur for the iridium complex $[(Cp^*IrCl_2)_2]$ [10], the rhodium bromide complex $[(Cp^*RhBr_2)_2]$ [11] and the diphosphine $(C_6H_3F_2\text{-}2,6)_2PCH_2CH_2P(C_6H_3F_2\text{-}2,6)_2$ [12]. We have also investigated the reaction between dfppe and $[\{(\eta^5\text{-}C_5Me_4Et)RhCl_2\}_2]$, which contains four different types of C–H bond, in order to establish any additional regioselectivity in the C–H bond activation. This reaction produced a range of products similar to **1a** but showed no discernible selectivity as to which C–H bonds are activated [13]. As a further attempt to investigate any selectivity in the C–H bond activation, it was decided to study the reactions between dfppe and $[\{(\eta^5\text{-}C_5Me_4H)RhX_2\}_2]$ (X = Cl or Br), which contains two different types of methyl C–H bond. Herein is reported the results of this investigation, part of which has been communicated [14,15].

2. Experimental

2.1. Physical measurements

The ^1H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded using Bruker DPX300, DRX400 or DRX500 spectrometers. ^1H NMR (300.01, 400.13 or 500.13 MHz) were referenced internally using the residual protio solvent resonance relative to $SiMe_4$ (δ 0), ^{13}C NMR (75.45 or 100.62 MHz) externally to $SiMe_4$ (δ 0), ^{19}F NMR (282.26 or 376.50 MHz) externally to $CFCl_3$ (δ 0) and ^{31}P NMR (121.45 or 161.98 MHz) externally to 85% H_3PO_4 (δ 0). All chemical shifts are quoted in δ (ppm), using the high-frequency positive convention, and coupling constants in Hz. Positive ion FAB mass spectra were recorded on a Kratos Concept 1H mass spectrometer. Elemental analyses were carried out by ASEP, The School of Chemistry, The Queen's University of Belfast or by Butterworths Ltd.

2.2. Materials

The compounds $NaBF_4$ (Aldrich) and dfppe (Fluorochem) were used as supplied. $[\{(\eta^5\text{-}C_5Me_4H)RhCl_2\}_2]$ was prepared from tetramethyl-*cyclo*-pentadiene and $RhCl_3{\cdot}3H_2O$ as described for $[(Cp^*RhCl_2)_2]$ [16].

2.3. Preparations

2.3.1. *$[\{\eta^5,\eta^1,\eta^1\text{-}C_5HMe_2\text{-}3,4\text{-}[CH_2\text{-}2\text{-}C_6F_4P(C_6F_5)\text{-}CH_2]_2\text{-}1,2\}RhCl]X$ (**2a**, $X = Cl^-$ and **2b**, $X = BF_4^-$)*

A slurry of $[\{(\eta^5\text{-}C_5Me_4H)RhCl_2\}_2]$ (0.062 g, 0.105 mmol) and dfppe (0.165 g, 0.218 mmol) in benzene (40 cm^3) was refluxed under nitrogen for 10.5 h, during which time a lemon yellow precipitate of the chloride salt **2a** contaminated with a small amount of **2b**, was formed. The solid was filtered off and washed with hexane. Concentration of the filtrate and addition of hexane yielded a further quantity of **2a**. Yield 0.127 g (60%). FAB MS: 977 ($[M–Cl]^+$), 941 ($[M–2Cl–H]^+$). ^1H NMR ($CDCl_3$): δ 5.45 [d, $^3J(P_A–H_a) = 6.9$ Hz, 1H, H_a], 4.94 [d, $^2J(H_d–H_{d'}) = 18.2$ Hz, 1H, H_d or $H_{d'}$], 4.67 [d, $^2J(H_e–H_{e'}) = 17.7$ Hz, 1H, H_e or $H_{e'}$], 4.44 (m, 1H, PCH_2), 4.18 [dd, $^2J(H_e–H_{e'}) = 17.7$ Hz, $^4J(P_A–H) = 9.8$ Hz, 1H, H_e or $H_{e'}$], 4.08 [dd, $^2J(H_d–H_{d'}) = 18.2$ Hz, $^4J(P_B–H) = 9.8$ Hz, 1H, H_d or $H_{d'}$], 3.88 (m, 1H, PCH_2), 3.58 (m, 2H, P_ACH_2 and P_BCH_2), 1.93 [dd, $^4J(P_B–H_b) = 14.2$ Hz, $^4J(P_A–H_b) = 1.6$ Hz, 3H, H_b], 1.91 [d, $^4J(P_B–H_c) = 1.9$ Hz, 3H, H_c]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 149.6 [dm, $^1J(C–F) = 249$ Hz, CF], 149.2 [dm, $^1J(C–F) = 228$ Hz, CF], 146.8 [dm, $^1J(C–F) = 242$ Hz, CF], 144.4 [dm, $^1J(C–F) = 249$ Hz, CF], 144.2 [dm, $^1J(C–F) = 291$ Hz, CF], 139.7 [dm, $^1J(C–F) = 263$ Hz, CF], 138.1 [dm, $^1J(C–F) = 257$ Hz, CF], 128.5–132 (m),

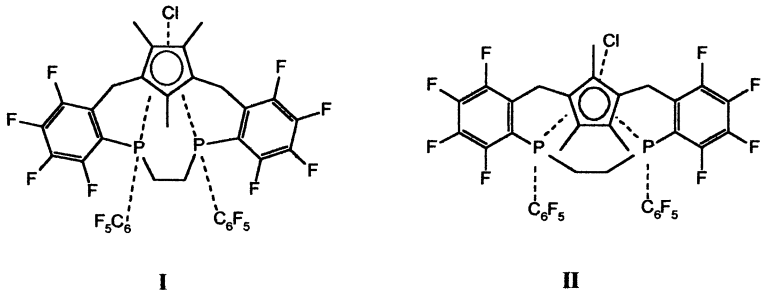


Fig. 1. Diagrammatic representation of the geometric isomers of the cation $[RhCl\{\eta^5,\eta^1,\eta^1\text{-}C_5Me_3[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}]^+$ (**1**) viewed along the C_5 (centroid)–Rh axis.

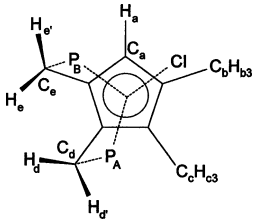


Fig. 2. Atom labels for **2a** viewed along the C_5 (centroid)–Rh axis. The aryl rings are omitted for clarity.

104.5–107.0 (m), 104.1 [dm, ^2J(P–C) = 16 Hz, CMe], 99.7 [dm, ^2J(P–C) = 6 Hz, CMe], 92.9 [dm, ^2J(P–C) = 7 Hz, CMe], 86.6 [d, J(P–C_a) = 7 Hz, C_a], 31.6 [dd, ^1J(P–C) = 34 Hz, ^2J(P–C) = 14 Hz, PCH_2], 29.5 [d, ^1J(P–C) = 41 Hz, PCH_2], 19.4 [d, $^3J(P_B–C_d)$ = 6 Hz, C_d], 18.4 [d, $^3J(P_A–C_e)$ = 7 Hz, C_e], 12.6 (s, C_c), 9.2 [d, $^3J(P_B–C_b)$ = 4 Hz, C_b]. ^{19}F NMR ($CDCl_3$): δ −120.54 (m, 2F, C_6F_4), −129.82 (br s, 2F, F_o of C_6F_5), −131.12 (br s, 2F, F_o of C_6F_5), −135.30 (m, 1F, C_6F_4), −135.61 (m, 1F, C_6F_4), −143.52 [ddd, ^3J(F–F) ≈ 20.8 Hz, ≈ 20.8 Hz, ^4J(F–F) = 9.3 Hz, 1F, C_6F_4], −143.68 [ddd, ^3J(F–F) ≈ 20.8 Hz, ≈ 20.8 Hz, ^4J(F–F) = 9.1 Hz, 1F, C_6F_4], −144.91 (m, 1F, F_p of C_6F_5), −145.06 (m, 1F, F_p of C_6F_5), −153.08 [dd, ^3J(F–F) ≈ 21.7 Hz, ≈ 21.7 Hz, 1F, C_6F_4], −153.38 [dd, ^3J(F–F) ≈ 21.8 Hz, ≈ 21.8 Hz, 1F, C_6F_4], −158.39 (m, 4F, F_m of C_6F_5). ^{19}F NMR ($CDCl_3$, 213 K): −119.43 (m, 1F, C_6F_4), −119.92 (m, 1F, C_6F_4), −127.69 (m, 2F, F_o of C_6F_5 and C_6F_5'), −130.32 (m, 1F, F_o of C_6F_5), −131.46 (m, 1F, C_6F_4), −134.91 (m, 2F, C_6F_4 and F_o of C_6F_5'), −142.24 (m, 1F, C_6F_4), −142.43 (m, 1F, C_6F_4), −143.52 [t, ^3J(F–F) = 20.7 Hz, 1F, F_p of C_6F_5], −143.79 [t, ^3J(F–F) = 20.7 Hz, 1F, F_p of C_6F_5], −152.11 (m, 1F, C_6F_4), −152.21 (m, 1F, C_6F_4), −157.15 (m, 4F, F_m of C_6F_5). ^{31}P{^{1}H} NMR: δ 78.8 [dm, $^1J(Rh–P_A)$ = 141 Hz, P_A], 73.2 [dm, $^1J(Rh–P_B)$ = 141 Hz, P_B]. The atom labels are shown in Fig. 2. Satisfactory analysis could not be obtained due to contamination by **2b**, which could not be separated. The salt **2b** was prepared from **2a**, which was slurried in acetone (30 cm^3) and NH_4BF_4 (1.0 g, 9.5 mmol) added. After 16 h, the solvent was removed by rotary evaporation and the solid extracted into dichloromethane. The extract was filtered and the solvent removed by rotary evaporation to afford **2b** as a yellow solid, which was dried in vacuo. *Anal.* Calc. for $C_{35}H_{15}BClF_{22}P_2Rh$: C, 39.5; H, 1.4; P, 5.8. Found: C, 39.7; H, 1.3; P, 5.5%. FAB MS: 977 ([M–BF_4]$^+$), 941 ([M–BF_4–Cl–H]$^+$). ^{1}H NMR ($CDCl_3$): δ 5.58 [d, ^3J(P–H) = 6.5 Hz, 1H, C_5H], 4.09 [d, ^2J(H–H) = 17.8 Hz, 1H, CHH′C_6F_4], 4.07 [d, ^2J(H–H) = 18.6 Hz, 1H, CH''H′′′C_6F_4], 3.87 [d, ^2J(H–H) = 17.8 Hz, 1H, CH$H'$$C_6F_4$], 3.58 (m, 2H, PCH_2), 3.33 [d, ^2J(H–H) = 18.6 Hz, 1H, CH′′$H'''$$C_6F_4$], 3.20 (m, 1H, PCH_2), 2.90 (m, 1H, PCH_2), 1.98 [d, ^4J(P–H) = 8.7 Hz, 3H, CH_3], 1.89 [d, ^4J(P–H) = 2.7 Hz, 3H, CH_3]. ^{19}F NMR ($CDCl_3$): δ −120.50 (m, 1F, C_6F_4), −120.68 (m, 1F, C_6F_4), −129.14 [d, ^3J(F–F) = 19.6 Hz, 2F, F_o of C_6F_5], −131.06 [d, ^3J(F–F) = 18.6 Hz, 2F, F_o of C_6F_5], −134.27 (m, 1F, C_6F_4), −134.65 (m, 1F, C_6F_4), −143.67 (m, 2F), −144.28 (m, 2F), −152.87 [dd, ^3J(F–F) ≈ 20.6 Hz, ≈ 20.6 Hz, 1F, C_6F_4], −153.07 [dd, ^3J(F–F) ≈ 23.0 Hz, ≈ 23.0 Hz, 1F, C_6F_4], −153.70 and −153.76 (2s, 1:4, 4F, BF_4^-), −157.82 (m, 2F, F_m of C_6F_5), −158.00 (m, 2F, F_m of C_6F_5). ^{31}P{^{1}H} NMR ($CDCl_3$): 75.9 [dm, ^1J(Rh–P) = 140 Hz], 68.9 [dm, ^1J(Rh–P) = 138 Hz].

2.3.2. [{(η^5-C_5Me_4H)$RhBr_2$}$_2$] (**3**)

A slurry of [{(η^5-C_5Me_4H)$RhCl_2$}$_2$] (0.295 g, 0.50 mmol) and NaBr (3.00 g, 0.029 mol) in methanol (70 cm^3) was heated at reflux under nitrogen for 37 h. The solvent was removed by rotary evaporation and the product extracted into dichloromethane (2 × 80 cm^3). The insoluble salts were filtered off and the solvent concentrated by rotary evaporation. Addition of petroleum ether (b.p. 100–120 °C) yielded the product **3** as a red solid, which was washed with hexane (2 × 30 cm^3) and dried in vacuo. Yield 0.205 g (53%). *Anal.* Calc. for $C_{18}H_{26}Br_4Rh_2$: C, 28.2; H, 3.4. Found: C, 28.3; H, 3.1%. FAB MS: 687 ([M–Br]$^+$), 607 ([M–2Br]$^+$). ^{1}H NMR ($CDCl_3$): δ 5.05 (s, 1H, C_5H), 1.81 (s, 6H, Me), 1.76 (s, 6H, Me). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 97.6 [d, ^1J(Rh–C) = 9 Hz, C_5], 96.5 [d, ^1J(Rh–C) = 8 Hz, C_5], 79.1 [d, ^1J(Rh–C) = 9 Hz, C_5], 11.6 (s, Me), 9.9 (s, Me).

2.3.3. [{η^5,η^1-C_5HMe_2-3,4-[CH_2-2-$C_6F_4P(C_6F_5)$-CH_2]$_2$-1,2}$RhBr$]Br (**4a**)

A slurry of [{(η^5-C_5Me_4H)$RhBr_2$}$_2$] (0.071 g, 0.093 mmol) and dfppe (0.145 g, 0.191 mmol) in benzene (70 cm^3) was refluxed under nitrogen for 38 h, during which time a lemon yellow precipitate of **4a** was formed. The solid was filtered off, washed with petroleum ether (b.p. 100–120 °C) and hexane, and dried in vacuo. Yield 0.109 g (53%). *Anal.* Calc. for $C_{35}H_{15}Br_2F_{22}P_2Rh$: C, 38.1; H, 1.4. Found: C, 38.25; H, 1.45%. MS FAB: 1023, 1021 ([M–Br]$^+$), 941 ([M–2Br]$^+$). ^{1}H NMR ($CDCl_3$): δ 5.48 [d, ^3J(P–H) = 6.6 Hz, 1H, C_5H], 4.75 [d, ^2J(H–H′) = 18.3 Hz, 1H, CHH′C_6F_4], 4.59 [d, ^2J(H′′–H′′′) = 17.5 Hz, 1H, CH''H′′′C_6F_4], 4.24 (m, 1H, PCH_2), 4.09 (m, 2H, CH$H'$$C_6F_4$ and CH′′$H'''$$C_6F_4$), 3.68 (m, 3H, PCH_2), 2.13 [dd, ^4J(P–H) = 3.3 Hz, ^4J(P–H) = 1.5 Hz, 3H, CH_3], 1.94 [dd, ^4J(P–H) = 9.1 Hz, ^4J(P–H) = 1.3 Hz, 3H, CH_3]. ^{19}F NMR ($CDCl_3$): δ −120.26 [d, ^3J(F–F) = 11.4 Hz, 1F, C_6F_4], −120.53 [dd, ^3J(F–F) = 20.9 Hz, ^4J(F–F) = 9.8 Hz, 1F, C_6F_4], −129.25 (s, 2F, F_o of C_6F_5), −131.53 (br s, 2F, F_o of C_6F_5), −134.34 (m, 1F, C_6F_4), −135.17 (m, 1F, C_6F_4), −143.19 (m, 1F, C_6F_4), −143.48 (m, 1F, C_6F_4), −144.76 [t, ^3J(F–F) = 20.4 Hz, 1F, F_p of C_6F_5], −145.05 [t, ^3J(F–F) = 20.4 Hz, 1F, F_p of C_6F_5], −152.63

[dd, ^3J(F–F) ≈22.0 Hz, ≈22.0 Hz, 1F, C_6F_4], −153.11 [dd, ^3J(F–F) ≈22.0 Hz, ≈22.0 Hz, 1F, C_6F_4], −158.20 (m, 4F, F_m of C_6F_5). ^{19}F NMR ($CDCl_3$, 213 K): δ −119.19 (m, 1F, C_6F_4), −120.01 (m, 1F, C_6F_4), −128.18 (m, 2F, F_o of C_6F_5 and C_6F_5'), −128.53 (m, 1F, F_o of C_6F_5), −133.58 (m, 1F, C_6F_4), −134.48 (m, 1F, C_6F_4), −135.43 (m, 1F, F_o of C_6F_5'), −141.98 (m, 1F, C_6F_4), −142.42 (m, 1F, C_6F_4), −143.32 (m, 1F, F_p of C_6F_5), −143.86 (m, 1F, F_p of C_6F_5), −151.69 (m, 1F, C_6F_4), −152.27 (m, 1F, C_6F_4), −157.08 (m, 4F, F_m of C_6F_5). ^{31}P{^{1}H} NMR ($CDCl_3$): 73.8 [dm, ^1J(Rh–P) = 144 Hz], 68.3 [dm, ^1J(Rh–P) = 138 Hz]. The tetrafluoroborate salt **4b** was prepared from **4a** by treatment with an appropriate anion source as described for **2b**. ^{1}H NMR ($CDCl_3$): δ 5.53 [d, ^3J(P–H) = 6.0 Hz, 1H, C_5H], 4.20 [d, ^2J(H–H′) = 17.6 Hz, 1H, C*H*H′C_6F_4], 4.04 [dd, ^2J(H″–H‴) = 18.6 Hz, ^4J(P–H″) = 9.3 Hz, 1H, C*H*″H‴C_6F_4], 3.95 [dd, ^2J(H″–H‴) = 17.6 Hz, ^4J(P–H′) = 6.0 Hz, 1H, C*H*′HC_6F_4], 3.62 (m, 2H, PCH_2 and CH″*H*‴C_6F_4), 3.45 (m, 2H, PCH_2), 3.32 (m, 1H, PCH_2), 2.03 [dd, ^4J(P–H) = 3.9 Hz, 3H, CH_3], 1.91 [d, ^4J(P–H) = 9.0 Hz, 3H, CH_3]. ^{19}F NMR ($CDCl_3$): δ −120.63 (m, 2F, C_6F_4), −128.86 (m, 2F, F_o of C_6F_5), −131.30 (m, 2F, F_o of C_6F_5), −134.27 (m, 1F, C_6F_4), −134.81 (m, 1F, C_6F_4), −144.29 (m, 2F), −144.78 (m, 2F), −153.24 [dd, ^3J(F–F) ≈20.0 Hz, ≈20.0 Hz, 1F, C_6F_4], −153.66 (m, 1F, C_6F_4), −153.98 and −154.04 (2s, 1:4, 4F, BF_4^-), −158.00 (m, 2F, F_m of C_6F_5), −158.23 (m, 2F, F_m of C_6F_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 72.0 [dm, ^1J(Rh–P) = 143 Hz], 65.2 [dm, ^1J(Rh–P) = 136 Hz].

Table 1
Crystal data and summary of data collection for [{(η^5-C_5Me_4H)$RhCl_2$}$_2$]

Empirical formula	$C_{18}H_{26}Cl_4Rh_2$
Formula weight	590.00
Temperature (K)	153(2)
Wavelength (Mo Kα) (Å)	0.71073
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	15.768(7)
b (Å)	8.123(4)
c (Å)	16.766(8)
β (°)	102.003(8)
V (Å^3)	2100.4(16)
Z	8
D_{calc} (g cm^{-3})	1.866
μ (mm^{-1})	2.079
F(0 0 0)	1168
Reflections collected	10 751
Independent reflections	4218 (R_{int} = 0.1012)
Parameters refined	225
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0487, wR_2 = 0.0899
R indices (all data)	R_1 = 0.0775, wR_2 = 0.0996
Largest difference peak and hole (e Å^{-3})	0.691 and −0.840
Goodness-of-fit on F^2	0.886

2.3.4. [(η^5-C_5Me_4H)RhCl(dfppe)]BF_4 (**5**)

The salt $NaBF_4$ (approximately 0.4 g, 3.7 mmol) was added to [{(η^5-C_5Me_4H)$RhCl_2$}$_2$] (0.037 g, 0.063 mmol) and dfppe (0.100 g, 0.132 mmol) in methanol (40 cm^3) and dichloromethane (10 cm^3) with vigorous stirring. After 30 min, the solvent was removed by rotary evaporation and the orange solid extracted into dichloromethane (70 cm^3) and filtered. Concentration of the solution by rotary evaporation and addition of hexane yielded yellow crystals of **5**, which were washed with hexane and dried in vacuo. Yield 0.093 g (67%). *Anal.* Calc. for $C_{35}H_{17}BClF_{24}P_2Rh$: C, 38.1; H, 1.55. Found: C, 38.2; H, 1.7%. ^{1}H NMR [$(CD_3)_2CO$]: δ 6.40 (s, 1H, C_5H), 3.67 (m, 2H, PCH_2), 3.45 (m, 2H, PCH_2), 1.82 [dd, ^4J(P–H) = 7.9 Hz, ^4J(P–H) = 2.4 Hz, 6H, CH_3], 1.58 [d, ^4J(P–H) = 5.0 Hz, 6H, CH_3]. ^{19}F NMR [$(CD_3)_2CO$]: −125.30 [d, ^3J(F_o–F_m) = 17 Hz, 4F, F_o], −128.27 [d, ^3J(F_o–F_m) = 8 Hz, 4F, F_o], −144.89 [t, ^3J(F_p–F_m) = 21 Hz, 1F, F_p], −146.05 (m, 2F, F_p), −151.04 and −151.09 (2s, 1:4, 4F, BF_4^-), −158.42 [dd, ^3J(F–F) ≈ 19 Hz, ≈19 Hz, 4F, F_m], −160.31 (m, 4F, F_m). ^{19}F NMR [$(CD_3)_2CO$, 193 K]: δ −124.47 (m, 1F, F_o), −126.72 (m, 1F, F_o), −128.68 (br s, 2F, F_o), −144.47 (m, 2F, F_p), −145.33 (m, 2F, F_p), −149.40 and −149.46 (2s, 1:4, 4F, BF_4^-), −158.10 (m, 4F, F_m), −160.19 (4F, m, F_m). ^{31}P{^{1}H} NMR [$(CD_3)_2CO$]: 32.9 [dm, ^1J(Rh–P) = 149 Hz].

2.4. Crystal structure determination of compound [{(η^5-C_5Me_4H)$RhCl_2$}$_2$]

A crystal of [{(η^5-C_5Me_4H)$RhCl_2$}$_2$] with approximate dimensions 0.34 × 0.23 × 0.17 mm was grown from acetone. Crystal data and a summary of data collection and refinement parameters are given in Table 1. The molecular structure is shown in Fig. 4. Selected bond distances and angles are listed in Table 2. Data were collected on a Bruker SMART diffractometer using the SAINT-NT software with Mo Kα radiation. Lattice parameters were determined from a least-squares refinement of 2184 reflections. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in calculated positions (C–H 0.96 Å), assigned fixed isotropic thermal parameters at 1.2 times for C–H the equivalent isotropic U_{ij} (1.5 for methyl) of the atoms to which they are attached and allowed to ride on their respective parent atoms. All calculations were performed using SHELXTL version 5.0.

3. Results and discussion

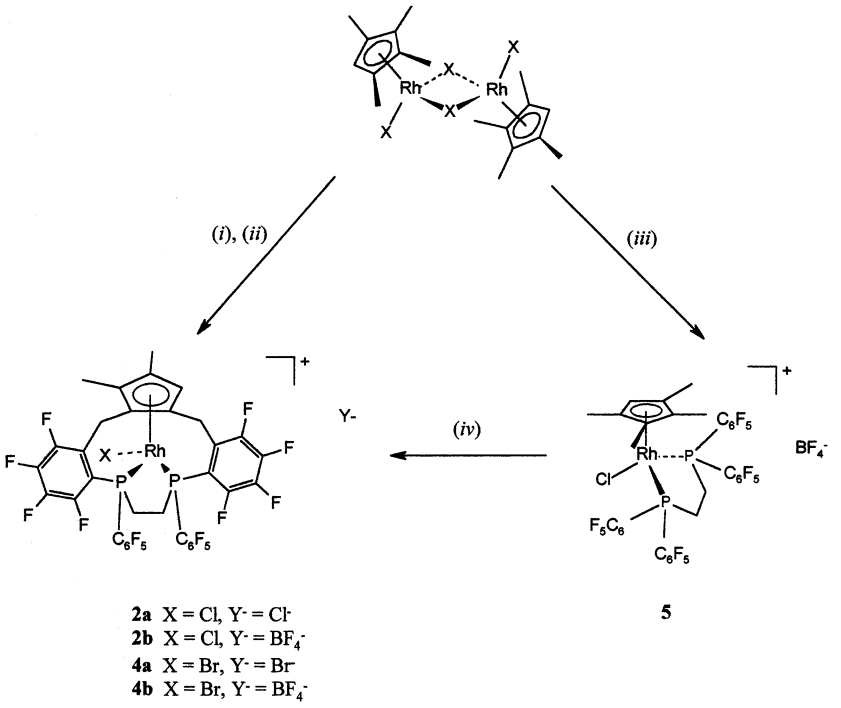
Treatment of the rhodium chloride complex [{(η^5-C_5Me_4H)$RhCl_2$}$_2$] with dfppe in refluxing benzene

Table 2
Selected bond lengths (Å) and angles (°) with e.s.d. values in parentheses for $[\{(\eta^5\text{-}C_5Me_4H)RhCl_2\}_2]$

Cp†(1)–Rh(1)	1.759	Cp†(2)–Rh(2)	1.755
Rh(1)–Cl(1)	2.402(2)	Rh(2)–Cl(4)	2.3919(19)
Rh(1)–Cl(2)	2.434(2)	Rh(2)–Cl(2)	2.4575(18)
Rh(1)–Cl(3)	2.4551(19)	Rh(2)–Cl(3)	2.457(2)
Rh(1)–C(1A)	2.125(6)	Rh(2)–C(1B)	2.115(6)
Rh(1)–C(2A)	2.136(6)	Rh(2)–C(2B)	2.133(6)
Rh(1)–C(3A)	2.136(6)	Rh(2)–C(3B)	2.123(5)
Rh(1)–C(4A)	2.139(6)	Rh(2)–C(4B)	2.152(5)
Rh(1)–C(5A)	2.149(6)	Rh(2)–C(5B)	2.147(6)
C(1A)–C(2A)	1.417(10)	C(1B)–C(2B)	1.428(8)
C(2A)–C(3A)	1.429(8)	C(2B)–C(3B)	1.410(8)
C(3A)–C(4A)	1.445(8)	C(3B)–C(4B)	1.450(8)
C(4A)–C(5A)	1.425(8)	C(4B)–C(5B)	1.417(8)
C(5A)–C(1A)	1.417(10)	C(5B)–C(1B)	1.431(8)
Cp†(1)–Rh(1)–Cl(1)	125.4	Cp†(2)–Rh(2)–Cl(4)	128.4
Cp†(1)–Rh(1)–Cl(2)	126.8	Cp†(2)–Rh(2)–Cl(2)	127.1
Cp†(1)–Rh(1)–Cl(3)	126.8	Cp†(2)–Rh(2)–Cl(3)	125.6
Cl(1)–Rh(1)–Cl(2)	90.55(6)	Cl(4)–Rh(2)–Cl(2)	89.40(6)
Cl(1)–Rh(1)–Cl(3)	91.40(6)	Cl(4)–Rh(2)–Cl(3)	89.71(7)
Cl(2)–Rh(1)–Cl(3)	83.32(5)	Cl(2)–Rh(2)–Cl(3)	82.78(5)
Rh(1)–Cl(2)–Rh(2)	97.09(6)	Rh(1)–Cl(3)–Rh(2)	96.53(6)

Cp†(1) and Cp†(2) are the centroids of the *cyclo*-pentadienyl rings defined by C(1A), C(2A), C(3A), C(4A), C(5A) and C(1B), C(2B), C(3B), C(4B), C(5B), respectively.

yielded the salt $[\{\eta^5,\eta^1,\eta^1\text{-}C_5HMe_2\text{-}3,4\text{-}[CH_2\text{-}2\text{-}C_6F_4P(C_6F_5)CH_2]_2\text{-}1,2\}RhCl]Cl$ (**2a**) as a yellow precipitate in 60% yield (Scheme 1). Similarly, treatment of the bromide complex $[\{(\eta^5\text{-}C_5Me_4H)RhBr_2\}_2]$ (**3**) with dfppe yielded $[\{\eta^5,\eta^1,\eta^1\text{-}C_5HMe_2\text{-}3,4\text{-}[CH_2\text{-}2\text{-}C_6F_4P(C_6F_5)CH_2]_2\text{-}1,2\}RhBr]Br$ (**4a**) in 53% yield. Salts **2a** and **4a** were characterized by mass spectrometry, which showed the parent cations, and multinuclear NMR spectroscopies. The former was contaminated by a small amount of the tetrafluoroborate salt, formed by the reaction of the by-product HF with the borosilicate glass vessel [10], and satisfactory analysis could not be obtained. However, the latter was obtained pure and satisfactory elemental analysis was obtained. The structure of **4a** was determined by single-crystal X-ray diffraction [15], which clearly established the formulation. The similarity of the NMR spectroscopic data of **2a** and **4a** indicates the same formulation for **2a**. The tetrafluoroborate salts **2b** and **4b** were prepared by anion metathesis and characterized by multinuclear NMR spectroscopies. Salt **2b** was further characterized by elemental analysis. The $^{31}P\{^1H\}$ NMR spectra of **2a**, **2b**, **4a** and **4b** exhibit two doublets of multiplets at approximately δ 70, with rhodium–phosphorus coupling constants $|^1J(Rh\text{–}P)|$ of approximately 140 Hz, consistent with the values of δ 71.3 and 144 Hz for **1a** [9,10] and δ 68.5 and 142 Hz for the bromide analogue of **1b** [11]. The presence of two resonances is indicative of non-equivalent phosphorus atoms and the asymmetry within the cations **2** and **4**. The ^1H NMR spectrum of **2a** possesses eight resonances in the region δ 3.5–5.0 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 $|^2J(H\text{–}H)|$ of approximately 18



Scheme 1. (i) C_6H_6, heat; (ii) NH_4BF_4, acetone; (iii) X = Cl; $NaBF_4$, dfppe, CH_2Cl_2/MeOH; (iv) EtOH, heat or proton sponge, CD_2Cl_2.

Hz, one of which is further coupled to one phosphorus, as confirmed by the $^1H\{^{31}P\}$ NMR spectrum, with a coupling $|^4J(P–H)|$ of approximately 10 Hz. In contrast, the respective $C_5CH_2C_6F_4$ resonances of **2b** do not show coupling to phosphorus. Thus, the anion exerts a large effect on the NMR spectroscopic properties of the cation. There are also differences between the methyl resonances of **2a** and **2b**. 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. Both spectra exhibit a doublet at approximately δ 5.5 with $|^3J(P–H)|$ approximately 6.5 Hz which is assigned to the hydrogen atom of the *cyclo*-pentadienyl ring. The ^1H spectra of **4a** and **4b** are similar to those of **2a** and **2b**, respectively, but show some differences. Namely, both methyl resonances of **4a** appear as doublet of doublets and one resonance of each $C_5CH_2C_6F_4$ methylene hydrogen atom pair of **4b** shows coupling to one phosphorus. Although unequivocal assignment of the resonances cannot be made, the $^{13}C\{^1H\}$ NMR and $^1H–^{13}C$ and $^1H–^{31}P$ correlation spectra of **2a** and comparison of the ^1H NMR data with the structure of **4a** [15] does allow the tentative assignment of most of the resonances of **2a** (the labelling scheme is shown in Fig. 2). These assignments are based on the assumption that for a large P–H coupling (>5 Hz) to be observed, the P–Rh–CR angle must be significantly greater than 90°. Where the P–Rh–C angle is close to 90°, the P–H coupling is small or negligible. For example, $J(P_A–H_a)$ is 6.9 Hz and the corresponding P–Rh–CH angles are 147.9(9) and 155.3(9)° for the two independent ion pairs in the structure of **4a**, whereas $J(P_B–H_a)$ is not observed for the corresponding angles of 107.3(8) and 93.1(10)°. The ^{19}F NMR spectra of **2a**, **2b**, **4a** and **4b** are similar and entirely consistent with a formulation in which both C_6F_4 and both C_6F_5 groups are non-equivalent. The two *ortho*-C_6F_5 fluorine resonances of these salts are broadened slightly due to hindered rotation about the P–C_6F_5 bonds. Values of the activation energy, $\Delta G^‡$, of 42.5 ± 2.5 and 47 ± 2 kJ mol^{-1} for rotation about the two different P–C_6F_5 bonds of **2a** were calculated from variable temperature ^{19}F NMR spectra [17]. Values of $\Delta G^‡$ of 45 ± 2 and 47 ± 2 kJ mol^{-1} were calculated for **4a**. In comparison, the value of $\Delta G^‡$ for rotation about the pair of P–C_6F_5 bonds in **1a** was determined to be 52.5 ± 2 kJ mol^{-1} [9,10].

The cations of **2** and **4** contain three chiral centres: the rhodium and both phosphorus atoms. However, due to the geometric constraints of the reaction, only one pair of enantiomers can be formed. Addition of the chiral shift reagent praseodymium tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate] to the NMR sample of **2a** confirms that the cation is formed as a racemic mixture. The most noticeable change occurred in the $^1H\{^{31}P\}$ NMR spectrum where the doublets at δ 4.94 and 4.67, assigned to two of the $C_5CH_2C_6F_4$ hydrogen atoms were shifted to lower frequency and appear as two doublets with a ratio of integrals of 1.5:0.5 at δ 4.09 and 4.03. The former consists of coincidental signals. Other small shifts are noted in the ^1H NMR spectrum, but little change is observed in either the ^{19}F or ^{31}P NMR spectra.

On the basis of the relative position of C–H bond cleavage in reaction 1, the reaction between $[\{(\eta^5\text{-}C_5Me_4H)RhX_2\}_2]$ and dfppe was expected to yield two isomers of the cation of formulation $[\{\eta^5,\eta^1,\eta^1\text{-}C_5HMe_2[CH_2\text{-}2\text{-}C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}RhX]^+$ (**III**) and (**IV**) dependent on the positions of the two methyl groups (Fig. 3). Neither of these two isomers could be unambiguously identified in the crude products. Instead only products resulting from cleavage of C–H bonds of adjacent methyl groups could be positively identified. The asymmetric cation **V** is that precipitated in the reaction as **2a** or **4a**. The symmetric cation **VI** was not observed in the precipitate. The reaction has been repeated a number of times, and the result is entirely reproducible. Further, for the reaction involving $[\{(\eta^5\text{-}C_5Me_4H)RhCl_2\}_2]$ multinuclear NMR spectroscopic and mass spectrometric investigations indicated that **2a** is also the major species in the mother liquor. The mass spectral data of the solid derived from removal of solvent from the mother liquor provided evidence for the formation of $[(\eta^5\text{-}C_5Me_4H)RhCl(dfppe)]^+$ and at least one isomer of the singly C–F bond activated complex $[\{\eta^5,\eta^1,\eta^1\text{-}C_5HMe_3CH_2\text{-}2\text{-}C_6F_4P(C_6F_5)CH_2\text{-}CH_2P(C_6F_5)_2\}RhCl]^+$. These two cations are intermediates in the formation of **2a**. On one occasion the $^{31}P\{^1H\}$ NMR spectrum of the solid also comprised a low intensity doublet of multiplet resonance at approximately δ 68.5 with $|^1J(Rh–P)|$ approximately 140 Hz, which, by comparison with the spectral data of **1a**, is tentatively assigned to one of the symmetric isomers **IV** or **VI**. The ratio of asymmetric to symmetric isomers of the product formed was determined from the NMR spectral data to be greater than 9:1, although typically resonances which could be ascribed to a symmetric isomer were not observed. Thus, the reaction between $[\{(\eta^5\text{-}C_5Me_4H)RhX_2\}_2]$ and dfppe displays regioselectivity in the activation of C–H bond activation in contrast to that of reaction (1).

The intermediate cation $[(\eta^5\text{-}C_5Me_4H)RhCl(dfppe)]^+$ was prepared independently as the tetrafluoroborate salt **5** by addition of $NaBF_4$ and dfppe to $[\{(\eta^5\text{-}C_5Me_4H)RhCl_2\}_2]$ (Scheme 1). Salt **5** was characterized by elemental analysis, mass spectrometry and multinuclear NMR spectroscopies. The ^{19}F and ^{31}P NMR spectroscopic data are similar to those of the pentamethyl-*cyclo*-pentadienyl analogue [10]. In particular, the ^{31}P NMR resonance is a doublet of multiplets at δ 32.9 with $|^1J(Rh–P)|$ of 149 Hz, which are comparable

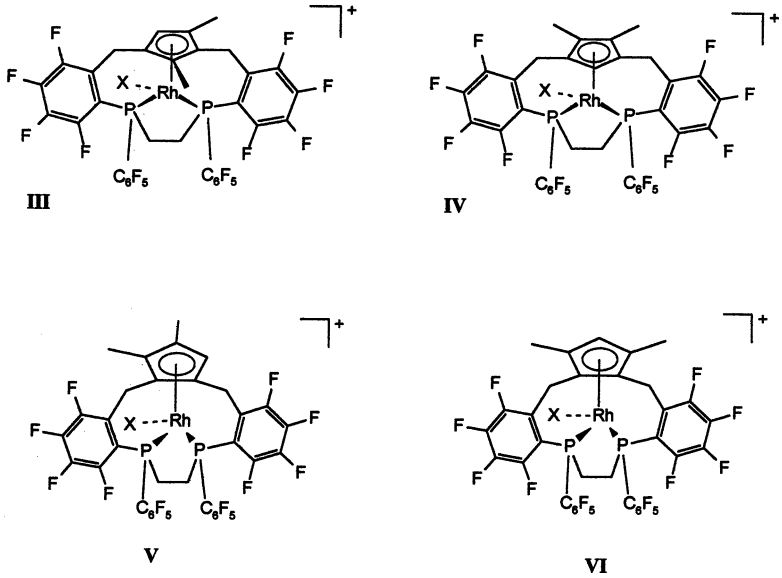


Fig. 3. Asymmetric and symmetric isomers of the cations $[RhCl\{\eta^5,\eta^1,\eta^1\text{-}C_5Me_2H\text{-}2,4\text{-}[CH_2\text{-}2\text{-}C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}]^+$ and $[RhCl\{\eta^5,\eta^1,\eta^1\text{-}C_5Me_2H\text{-}3,4\text{-}[CH_2\text{-}2\text{-}C_6F_4P(C_6F_5)CH_2]_2\text{-}1,2\}]^+$ viewed along the C_5 (centroid)–Rh axis.

to the values of δ 35.1 and $|^1J(Rh–P)|$ 150.5 Hz for [Cp*RhCl(dfppe)]BF_4. There is hindered rotation about the P–C_6F_5 bonds of **5** as indicated by broad resonances in the ^{19}F NMR spectrum recorded at 293 K. The value of $\Delta G^{\ddagger}$ for rotation about one pair of P–C_6F_5 bonds, calculated from variable temperature ^{19}F NMR spectra in acetone [17], is 43.5 ± 2 kJ mol^{-1}. This value is consistent with the values of 46 ± 4 and 43 ± 2 kJ mol^{-1} for the higher activation energies for rotation about one pair of P–C bonds in [Cp*RhCl-(dfppe)]BF_4 [10] and [Cp*RhCl{$(C_6H_3F_2\text{-}2,6)_2PCH_2$-$CH_2P(C_6H_3F_2\text{-}2,6)_2$}]$BF_4$ [12], respectively. The value of $\Delta G^{\ddagger}$ for rotation about the other pair of P–C_6F_5 bonds could not be found since the fluxional process could not be frozen out at a spectrometer frequency of 282 MHz. The methyl hydrogen resonances in the ^1H NMR spectrum appear as a doublet of doublets at δ 1.82 with couplings $|^4J(P–H)|$ of 7.9 and 2.4 Hz and a doublet at δ 1.58 with $|^4J(P–H)|$ 5.0 Hz, each integrating for six hydrogen atoms. The coupling to phosphorus is confirmed by the $^1H\{^{31}P\}$ NMR spectrum. It is not clear why the P–H couplings should be so different, but it is noted that the resonances are temperature independent and thus not determined by hindered rotation about the Rh–C_5 (centroid) axis.

In situ NMR experiments in CD_2Cl_2 confirmed that **5** is converted to **2b** rapidly and almost quantitatively on addition of 2 equiv. of proton sponge. On a preparative scale **2b** was isolated in only approximately 50% yield from treatment of **5** with proton sponge in dichloromethane. The low yield is ascribed to difficulties in separating the product from protonated proton sponge, presumably present as one or more of the tetrafluoroborate, fluoride and bifluoride salts. Thus, the reaction between $[\{(\eta^5\text{-}C_5Me_4H)RhCl_2\}_2]$ and dfppe in benzene provides a more convenient route to **2b**, giving a higher isolated yield. Thermolysis of **5** in ethanol for 5 h also afforded **2b** as evidenced by multinuclear NMR spectroscopy (Scheme 1), but the reaction is not clean, the NMR spectra showing the presence of other unidentified compounds.

The difference in regioselectivity between reaction (1) and that between $[\{(\eta^5\text{-}C_5Me_4H)RhX_2\}_2]$ and dfppe is striking. We have reported differences between the geometries of tetramethyl- and pentamethyl-*cyclo*-pentadienyl complexes $[(\eta^5\text{-}C_5Me_4R)RhCl_2P]$ (P = phosphine) [18]. In particular, for the pentamethyl-*cyclo*-pentadienyl complex, the Rh–C_5 moiety possesses C_5 symmetry with identical distances, within experimental error, for the Rh–C and C–C bonds. In contrast, the ring of similar tetramethyl-*cyclo*-pentadienyl complexes is distorted to give two longer and two shorter Rh–CMe distances and a short Rh–CH distance. The C–C ring distances also vary significantly suggesting that there is a degree of localization in the carbon–carbon bonding within the ring and could be tentatively described as 'ene-enyl' [19–22] rather than pentadienyl, with the CH the centre of the allylic group. In order to ascertain whether a similar ring distortion was the cause of the difference in regioselectivity, we endeavoured to perform a structural study of complexes **2**–**5**. Unfortunately crystals of salts **2a**, **2b**, **4b** and **5** were unsuitable for single-crystal X-ray diffraction, and the large estimated standard deviations (e.s.d. values) of the structural data of **4a** [15] do not permit a detailed comparison with the structure of **1b**. However, the structure of $[\{(\eta^5\text{-}C_5Me_4H)RhCl_2\}_2]$ has been determined (Fig. 4). Selected distances and angles are pre-

sented in Table 2. Unlike the pentamethyl-*cyclo*-pentadienyl analogue [(Cp*$RhCl_2$)$_2$] [23], the centre of the $RhCl_2Rh$ core of [{(η^5-C_5Me_4H)$RhCl_2$}$_2$] does not lie on a crystallographic centre of symmetry. The Rh–C distances range from 2.115(6) to 2.152(5) Å and the ring C–C distances from 1.410(8) to 1.450(8) Å. Although the longest and shortest Rh–C distances differ significantly, the C–C distances are the same within experimental error. Thus, the ring cannot be described as 'ene-enyl'. The distortion from C_5 symmetry along the Rh–C_5 (centroid) axis can be compared with that in [(Cp*$RhCl_2$)$_2$], in which the Rh–C distances vary from 2.116(4) to 2.140(3) Å, but the ring C–C distances range from 1.370(5) to 1.452(7) Å. The distances and angles of the $Cl_2Rh_2(\mu\text{-}Cl)_2$ unit are similar for the two structures, although that of [{(η^5-C_5Me_4H)$RhCl_2$}$_2$] does possess one anomalously short Rh–Cl (bridging) distance of 2.434(2) Å and the Rh–Cl–Rh and Cl–Rh–Cl angles are 1–1.5° more acute and obtuse, respectively, than those of [(Cp*$RhCl_2$)$_2$]. Thus, the regioselectivity differences between the two reactions does not arise from an inherent distortion from C_5 symmetry of the Rh–C_5 moiety of the starting material. However, differences arising from ring distortion in the intermediate [(η^5-C_5Me_4R)RhCl(dfppe)]$^+$ cations cannot be ruled out as a possible source of the difference in regioselectivity.

A possible mechanism to account for the high selectivity in the reactions between [(η^5-C_5Me_4H)RhX_2]$_2$ and dfppe is shown in Scheme 2. Deprotonation of the intermediate cation [(η^5-C_5Me_4H)RhX(dfppe)]$^+$ forms an η^4-fulvene complex, the methylene carbon of which carries out S_NAr attack at an *ortho* C–F bond to form a C–C bond [7]. Since the hydrogen atoms of the methyl groups of the 1- and 4-methyl groups of the cation are the more acidic, the first C–C coupling occurs at the 1-position to give cation **A** or **B**. Both these intermediates are chiral and would exist as a pair of enantiomers. The product cation **V** is obtained by deprotonation, and subsequent C–C coupling, occurring at the 2-methyl group. The hydrogen atoms of the 4-methyl group are expected to be more acidic than those of the 2- and 3-methyl groups, but deprotonation at this methyl group gives an η^4-fulvene complex which cannot carry out an intramolecular nucleophilic attack at a pentafluorophenyl ring for geometric reasons. The acidities of the hydrogen atoms of the 2- and 3-methyl groups are expected to be similar and presumably the high selectivity for reaction at the 2-position is geometric. The methyl and pentafluorophenyl groups of cation **B** are not disposed to give the product **V**. Deprotonation of the 4-methyl group, which comprises the most acidic hydrogen atoms, and C–C coupling would give **IV**, which is presumably not formed for geometric reasons. Since the yields of **2a** and **4a** are over 50%, and **2b** is formed virtually quantitatively by the reaction of **5** with proton sponge at room temperature, either **B** can isomerize to **A** or **A** is formed preferentially to **B**. The former explanation requires either dissociation of both phosphine moieties, inversion at the chiral phosphorus atom and recoordination of the two phosphorus atoms as shown in Scheme 2 or dissociation of the *cyclo*-pentadienide, rotation about the C_5–CH_2 bond and recoordination. Although *cyclo*-pentadieneide ligands can be displaced from rhodium by phosphorus(III) ligands [24], or in other ways [25], subsequent recoordination is without precedent, and for this reason the latter possibility may be discounted. Dissociation and recoordination of chelating phosphines from rhodium is known. For example, cleavage of Rh–P bonds has been proposed to explain the epimerization of the chiral cation of (R_{Rh},R_C)-[Cp*RhCl($Ph_2PCH_2CHMePPh_2$)]BF_4 on heating in polar solvents, a process accelerated by the presence of chloride ions [26]. Furthermore, treatment of the diastereoisomer of [Cp*RhCl{$Ph_2PCH_2CH_2PPh$-(C_5F_4N-4)}]$^+$ in which the tetrafluoropyridyl group is distant to the Cp* ring with proton sponge does give the coupled product [{η^5,η^1,η^1-$C_5Me_4CH_2$(-2-C_5F_3N-

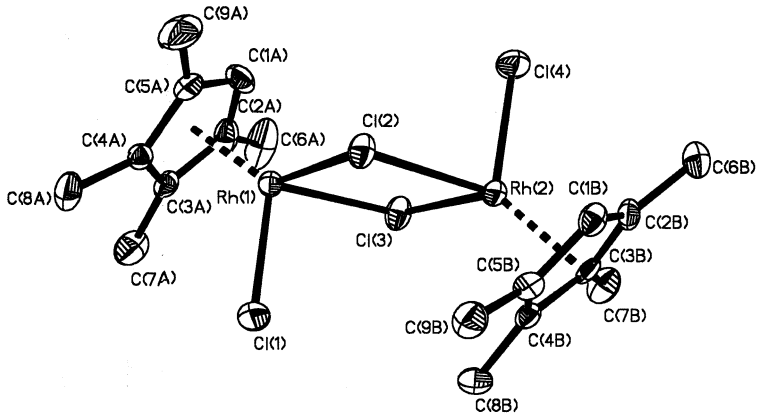
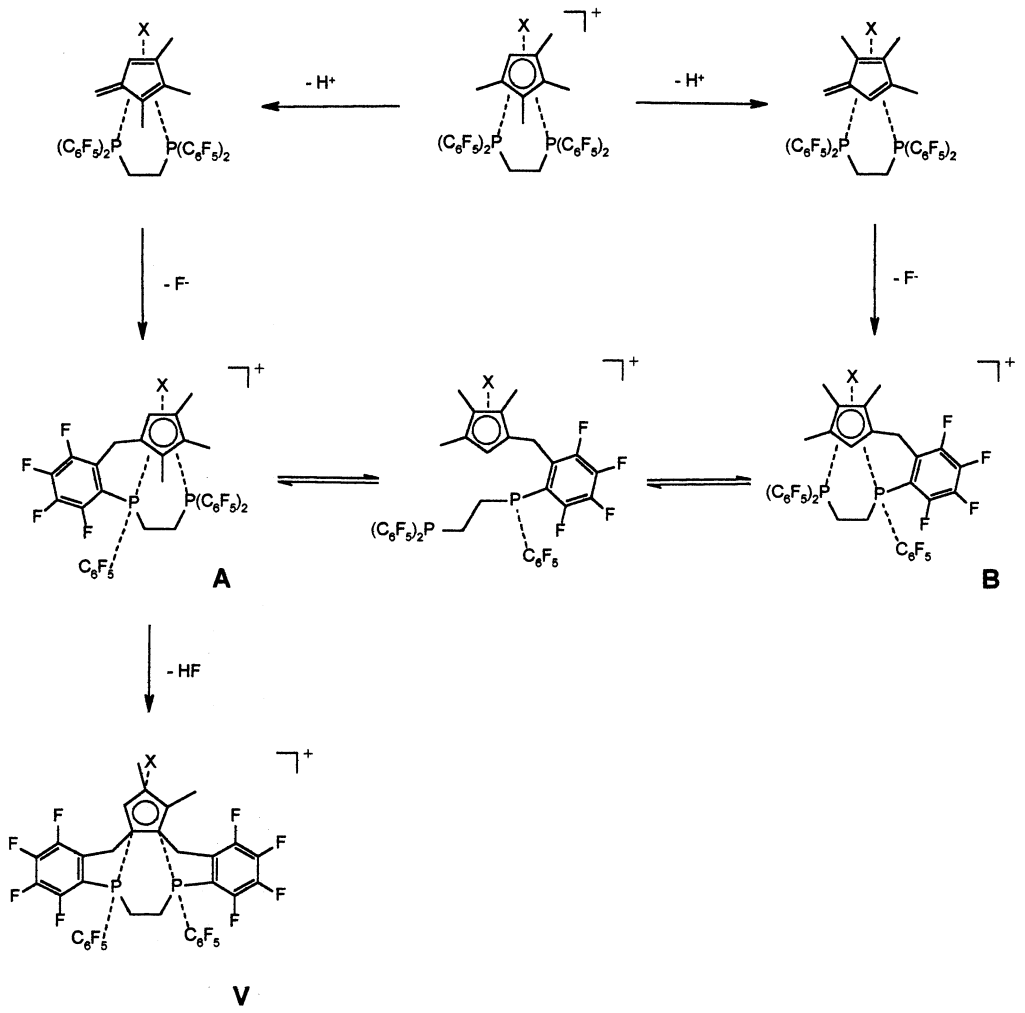


Fig. 4. Molecular structure of [{(η^5-C_5Me_4H)$RhCl_2$}$_2$]. Thermal ellipsoids are shown at the 30% probability level. The hydrogen atoms are omitted for clarity.



Scheme 2. Proposed mechanism. All cations are shown as viewed along the C_5 (centroid)–Rh axes. Only one enantiomer of each pair is shown.

4)PPhCH$_2$CH$_2$PPh$_2$}RhCl]$^+$ after isomerization involving cleavage of one Rh–P bond, which is the rate determining step [27]. However, at room temperature this reaction takes weeks to reach completion. Inversion at the phosphorus atom of phosphines is also known, although the activation energy for this process is usually high, typically 120–150 kJ mol^{-1} for PhPMeR [28,29], but is reduced by the presence of electron-withdrawing on the phosphorus substituents and also by π interactions between the phosphorus atom and the substituents. For example, the activation energy for inversion at the phosphorus atom of Me$_3$SiP(Pr^i)(C$_6$H$_4$-Me-4), which contains the electron-withdrawing silyl group is significantly lower than that of comparable non-silicon containing phosphines [28,29], and that of *cyclo*-{CH=C(Me)}$_2$PCHMe$_2$, in which there is significant delocalization, is only 65 kJ mol^{-1} [30]. Polyfluorinated aryl rings are electron-withdrawing and can provide π interactions with substituents and thus the barrier to inversion at the chiral phosphorus atom of the proposed intermediate might be expected to be relatively low. However, since this mechanism also involves the cleavage of two Rh–P bonds, the rate of the conversion of the two isomers is expected to be slow. Thus, although interconversion of **A** and **B** is possible, it is likely to be very slow at room temperature. The rapid reaction of **5** with proton sponge at room temperature militates against a mechanism involving conversion of **B** to **A**. Although the preferential formation of **A** seems unlikely in view of the unhindered rotation of the Cp* ligand about the Rh–C$_5$ (centroid) axis in **5**, there may be electronic or steric reasons for a preferential orientation of the η^4-fulvene ligand with respect to dfppe affording **A** preferentially or a large enhancement of the rate of reaction forming **A** over that forming **B** by, for example, the release of steric pressure. The observation that the reaction carried out at room temperature is almost quantitative, whereas that carried out in refluxing benzene or ethanol is less clean is consistent with this hypothesis, since other reactions and thus lower selectivity are expected at a higher temperature.

In an attempt to identify any singly coupled intermediates the reaction between $[\{(\eta^5\text{-}C_5Me_4H)RhCl_2\}_2]$ and dfppe in ethanol at approximately 60 °C was followed by multinuclear NMR spectroscopy. Although this might be expected to show side reactions, the rapid nature of the reaction of **5** with proton sponge precluded a study of this reaction. The ^1H and ^{19}F NMR spectra of the reaction mixture displayed several resonances, many coincident, which were difficult to assign. However, the $^{31}P\{^1H\}$ NMR spectra were much simpler and were easier to interpret. By comparison with the spectrum of **5**, a doublet of multiplets at δ 32.5 with a coupling $|^1J(P\text{–}H)|$ of 150 Hz is assigned to the cation $[(\eta^5\text{-}C_5Me_4H)RhCl(dfppe)]^+$, which will be present as the chloride salt. This resonance dominated the spectrum after 2 h, but had diminished at 4 h and had disappeared after 7 h. Resonances assigned to the product **2a** were observed at 2 h, and increased in intensity as the reaction proceeded. Two doublet of multiplet resonances at δ 74.4 and 33.8 with couplings $|^1J(P\text{–}H)|$ of 144 and 151 Hz, respectively, were present after 2 h, increased in intensity as those of $[(\eta^5\text{-}C_5Me_4H)RhCl(dfppe)]^+$ decreased and then decreased as **2a** was formed. The ratio of the integrals of these resonances was always 1:1. These resonances are assigned to one isomer of $[\{\eta^5,\eta^1,\eta^1\text{-}C_5HMe_3CH_2\text{-}2\text{-}C_6F_4P(C_6F_5)CH_2CH_2P(C_6F_5)_2\}RhCl]^+$ by comparison with those of the Cp* analogue [10]. At least seven other resonances showing Rh–P coupling, but all with small integrals, were present in the $^{31}P\{^1H\}$ NMR spectrum during the reaction. A doublet of multiplets at δ 7.7 with a coupling of 148 Hz was a major component of the reaction mixture after 2 h, but had diminished after 4 h and was absent after 7 h. On the basis that δ_P for the dinuclear complex $[(Cp^*IrCl_2)_2(\mu_2\text{-dfppe})]$ [12] is approximately 24 ppm to lower frequency of δ_P for $[Cp^*IrCl(dfppe)]BF_4$ [10], this resonance may be assigned to $[\{(\eta^5C_5Me_4H)RhCl_2\}_2(\mu_2\text{-dfppe})]$ or a complex containing monodentate dfppe. In support, $[Cp^*RhCl_2L]$ compounds containing monodentate diphosphine ligands (L), although not dfppe, have been reported [26]. Other, unidentified Rh–P complexes were observed. A doublet of multiplets at δ 50.4 with a coupling of approximately 125 Hz was present at 2 and 4 h, but absent after 7 h. A doublet of multiplets at δ 40.7 with a coupling of 149 Hz was present in all the spectra. There were also two doublet of multiplet resonances with couplings of approximately 150 Hz in the region 70–80 ppm which were present in the spectra recorded up to 7 h. As the reaction proceeded a doublet of multiplets at δ 20.1 with a coupling of only 59 Hz and a multiplet showing no coupling to rhodium at δ 19.4 arose. The former diminished after 7 h. The latter increased in intensity during the reaction and may be tentatively assigned to a product of oxidation of dfppe.

The phosphorus chemical shift in cationic complexes of the form $[Cp^*RhCl(P_2)]^+$, where P_2 is a chelating diphosphine, is very sensitive to the phosphorus environment. For example, the chemical shift difference between the two phosphorus atoms of both the chloride salts **2a** and **4a** is approximately 5 ppm, and of the tetrafluoroborate salts **2b** and **4b** is approximately 7 ppm, and [Cp*RhCl(prophos)]Cl (prophos=*R*-$Ph_2PCH_2CHMePPh_2$) exhibits chemical shifts for the two phosphorus atoms at δ 75.4 and 46.1 for the S_{Rh},R_C diastereoisomer and δ 63.9 and 57.0 for the R_{Rh},R_C diastereoisomer [26]. Therefore, the ^{31}P NMR spectra of **A** and **B** are expected to be different and the data for the reaction between $[\{(\eta^5\text{-}C_5Me_4H)RhCl_2\}_2]$ and dfppe strongly suggest the presence of only one isomer of $[\{\eta^5,\eta^1,\eta^1\text{-}C_5HMe_3CH_2\text{-}2\text{-}C_6F_4P(C_6F_5)CH_2\text{-}CH_2P(C_6F_5)_2\}RhCl]^+$ as an intermediate, but cannot confirm that the intermediate is **A**. The evidence supports the suggested mechanism in which one of the possible isomeric intermediates is formed with a high selectivity. The data also confirm that, as expected, the reaction carried out in hot ethanol is not clean.

4. Conclusion

The reaction between $[\{(\eta^5\text{-}C_5Me_4H)RhX_2\}_2]$ and dfppe proceeds thermally in benzene or ethanol to give the asymmetric cation $[\{\eta^5,\eta^1,\eta^1\text{-}C_5HMe_2\text{-}3,4\text{-}[CH_2\text{-}2\text{-}C_6F_4P(C_6F_5)CH_2]_2\text{-}1,2\}RhX]^+$ in high yield with high regioselectivity. The same product is obtained by treating $[(\eta^5\text{-}C_5Me_4H)RhCl(dfppe)]BF_4$ with proton sponge. The regioselectivity displayed by these reactions is in stark contrast to that displayed by the reaction between $[(Cp^*RhX_2)_2]$ and dfppe, which yields a product with a *cyclo*-pentadieneide ligand functionalized in the 1 and 3 positions. The reason for the difference in regioselectivity is not known, but presumably arises from geometric differences between the tetra- and penta-methyl-*cyclo*-poentadienyl intermediates $[(\eta^5\text{-}C_5Me_4R)RhX(dfppe)]^+$ and $[\{\eta^5,\eta^1,\eta^1\text{-}C_5Me_3RCH_2\text{-}2\text{-}C_6F_4P(C_6F_5)CH_2CH_2P\text{-}(C_6F_5)_2\}RhX]^+$. In support of this conclusion, distortions from local C_5 symmetry of the Rh–C_5 moiety is noted for $[(\eta^5\text{-}C_5Me_4H)RhCl_2P]$ but not $[Cp^*RhCl_2P]$ (P = phosphine). However, a similar difference between the structures of $[(\eta^5\text{-}C_5Me_4H)RhCl_2\}_2]$ and $[(Cp^*RhCl_2)_2]$ is not observed. A possible mechanism for the reaction has been proposed which requires the final dehydrofluorinative C–C coupling to occur for predominantly one isomer of $[\{\eta^5,\eta^1,\eta^1\text{-}C_5Me_3HCH_2\text{-}2\text{-}C_6F_4P(C_6F_5)CH_2CH_2P(C_6F_5)_2\text{-}1\}RhX]^+$ (**A**) in order to account for the high regioselectivity. The data suggest that this isomer is formed preferentially.

The reaction between $[\{(\eta^5\text{-}C_5Me_4H)RhX_2\}_2]$ and dfppe further demonstrates the synthetic potential of intramolecular dehydrofluorinative C–C coupling can

provide by facilitating the highly selective, high yield synthesis of complexes containing an asymmetric 1,2-substituted *cyclo*-pentadienyl-bis(phosphine) ligand. The reaction complements reaction 1, which yields the 1,3-substituted analogue exclusively. These reactions may be compared to the intramolecular hydroalkylation in $[Cp^*RhCl\{PPh_2(CH{=}CH_2)\}]^+$, which shows little regioselectivity and yields a mixture of the 1,2- and 1,3-isomers of $[(\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2CH_2CH_2PPh_2)_2\}\text{-}RhCl]^+$ [31,32].

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