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Note

Regioselective C–F and C–H bond activation: synthesis and structure of an asymmetric rhodium complex comprising a η^5:η^1:η^1-cyclopentadienyl-bis(phosphine) ligand

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Abstract

The reaction between $[(\eta^5\text{-}C_5Me_4H)RhBr(\mu\text{-}Br)]_2$ and $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ proceeds in refluxing benzene via the cleavage of two C–F and C–H bonds and the formation of two C–C bonds to give the unexpected asymmetric compound $[\{\eta^5\text{-}C_5HMe_2\text{-}3,4\text{-}[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,2\}RhBr]Br$ with high selectivity. The formulation has been confirmed by single-crystal X-ray diffraction. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Rhodium; Carbon–fluorine bond activation; Carbon–hydrogen bond activation

Recently we reported the reaction between $[(\eta^5\text{-}C_5Me_4H)RhCl(\mu\text{-}Cl)]_2$ and the fluorinated diphosphine $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ (dfppe), which proceeded via C–F and C–H bond activation to give an asymmetric rhodium complex cation **1** with high selectivity [1]. The formulation $[\{\eta^5\text{-}C_5HMe_2\text{-}2,4\text{-}[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}RhCl]^+$ was proposed on the basis of the spectroscopic data and the completely regiospecific synthesis of $[\{\eta^5\text{-}C_5Me_3[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}MX]^+$ (**2** M = Rh, X = Cl; **3** M = Rh, X = Br; **4** M = Ir, X = Cl) from $[(\eta^5\text{-}C_5Me_5)MX(\mu\text{-}X)]_2$ (Scheme 1) [2–4]. The identities of cations **2** [2] and **3** [4] were confirmed by single-crystal X-ray diffraction. Unfortunately, although crystals of the tetrafluoroborate salt of **1** were obtained, these were found to be unsuitable for X-ray diffraction and the proposed formulation could not be confirmed by a structural study. Here we report the unexpected product of the reaction between $[(\eta^5\text{-}C_5Me_4H)RhBr(\mu\text{-}Br)]_2$ and dfppe, and its structural characterisation by single-crystal X-ray diffraction, which indicates that the structure originally proposed for cation **1** is wrong.

Treatment of $[(\eta^5\text{-}C_5Me_4H)RhBr_2]_2$ with dfppe in refluxing benzene proceeded via C–F and C–H bond activation and C–C bond formation to afford a salt of formula $[\{\eta^5\text{-}C_5HMe_2[CH_2C_6F_4P(C_6F_5)CH_2]_2\}RhBr]Br$ (**5**), as a yellow precipitate in 53% yield (Scheme 1).[1] Spectroscopic studies indicated that **5** was also the major component of the mother liquor. Salt **5** was fully characterised by analytical and spectroscopic tech-

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[1] Spectroscopic and analytical data for **5**: ^{1}H-NMR [$(CD_3)_2CO$, 300.01 MHz]: δ 5.48 (1H, d, $^3J_{P-H}$ 6.6, C_5H), 4.75 (1H, d, $^2J_{H-H}$ 18.3, $CHH'C_6F_4$), 4.59 (1H, d, $^2J_{H-H}$ 17.5, CH'' $H'''C_6F_4$), 4.24 (1H, m, PCH_2), 4.13 (1H, dd, $^2J_{H-H}$ 18.3, $^4J_{P-H}$ 9.6, CHH' C_6F_4), 4.06 (1H, dd, $^2J_{H-H}$ 17.5, $^4J_{P-H}$ 8.4, $CH''H'''C_6F_4$), 3.68 (3H, m, PCH_2), 2.13 (3H, dd, $^4J_{P-H}$ 3.3, $^4J_{P-H}$ 1.5, Me), 1.94 (3H, dd, $^4J_{P-H}$ 9.1, $^4J_{P-H}$ 1.3, Me); ^{19}F-NMR [$(CD_3)_2CO$, 282.29 MHz]: δ −120.26 (1F, d, $^3J_{F-F}$ 11.4, C_6F_4), −120.53 (1F, dd, $^3J_{F-F}$ 20.9, $^4J_{F-F}$ 9.8, C_6F_4), −129.25 (2F, s, F_{ortho} of C_6F_5), −131.53 (2F, br s, F_{ortho} of C_6F_5), −134.34 (1F, m, C_6F_4), −135.17 (1F, m, C_6F_4), −143.19 (1F, m, C_6F_4), −143.48 (1F, m, C_6F_4), −144.76 (1F, t, $^3J_{F-F}$ 20.4, F_{para} of C_6F_5), −145.05 (1F, t, $^3J_{F-F}$ 20.4, F_{para} of C_6F_5), −152.63 (1F, dd, $^3J_{F-F} \approx 22.0$, $^3J_{F-F} \approx 22.0$, C_6F_4), −153.11 (1F, dd, $^3J_{F-F} \approx 22.0$, $^3J_{F-F} \approx 22.0$, C_6F_4), −158.20 (4F, m, F_{meta} of C_6F_5); ^{31}P-NMR [$(CD_3)_2CO$, 121.45 MHz]: δ 73.8 (dm, $^1J_{Rh-P}$ 144), 68.3 (dm, $^1J_{Rh-P}$ 138). FAB MS (m/z): 1023, 1021 ($[M-Br]^+$), 941 ($[M-2Br]^+$). Anal. Found C, 38.25; H, 1.45. $C_{35}H_{15}Br_2F_{18}P_2Rh$ Calc.: C, 38.1; H, 1.4%.

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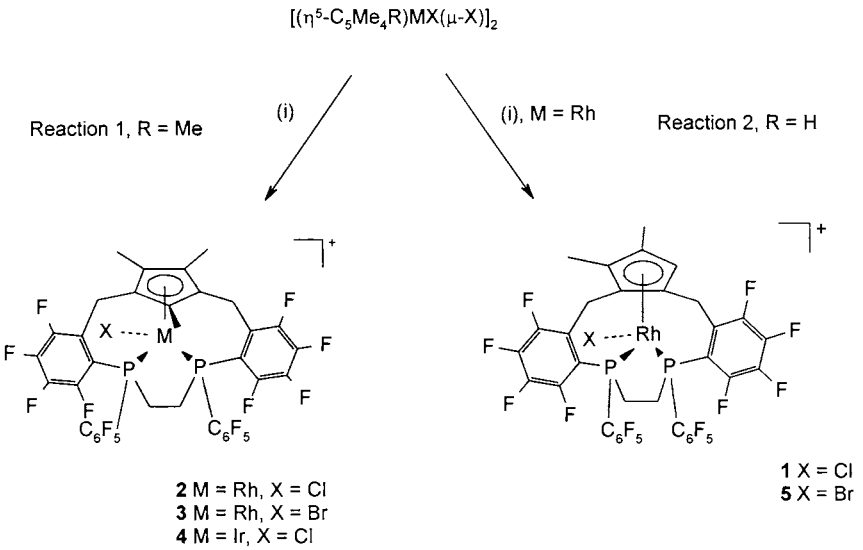

Scheme 1. (i) dfppe, C_6H_6, reflux.

niques, and also by single-crystal X-ray diffraction[2]. The structure clearly establishes that **5** is [{η5-C_5HMe_2-3,4-[$CH_2C_6F_4P(C_6F_5)CH_2$]2-1,2}RhBr]Br, formed by activation of C–H bonds of methyl groups in a 1,2-disposition (Fig. 1). The two phosphorus atoms of **5** are chiral and the complex also exhibits planar chirality, but due to geometric constraints only one pair of enantiomers is formed as a racemic mixture. Compound **5** crystallised in the chiral space group $Pna2_1$ with two independent ion pairs in the unit cell. The two independent cations are of similar structure and have the same configuration. The absolute configuration was determined by refinement of the Flack parameter [5] to a value of 0.49(6), indicating that the crystal was racemically twinned.

The mass and NMR spectra are entirely consistent with the formulation. Further, the NMR spectra of the crystals, from which one was taken for structure determination, were identical to those of the bulk material, confirming that **5** is a homogeneous solid, and not a mixture of isomers. The positive-ion FAB mass spectrum shows the parent cation (M^+) at 1023 and 1021 (Br^{81}, Br^{79}). The $^{31}P\{^1H\}$-NMR spectrum shows two doublets of multiplet resonances at δ 73.8 and 68.3 with

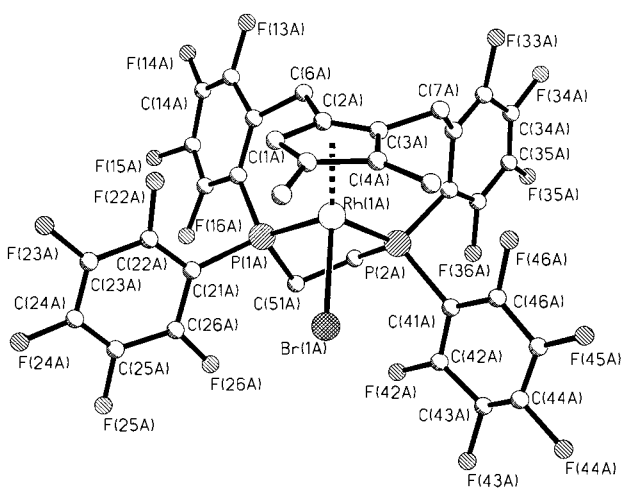

Fig. 1. Molecular structure of the cation of one of the independent ion pairs of [{η5-C_5HMe_2-3,4-[$CH_2C_6F_4P(C_6F_5)CH_2$]2-1,2}RhBr]Br (**5**). Selected bond distances (Å): $Cp^\dagger$–Rh(1A) 1.830, $Cp^\dagger$–Rh(1B) 1.832, Rh(1A)–Br(1A) 2.514(4), Rh(1B)–Br(1B) 2.506(4), Rh(1A)–P(1A) 2.260(10), Rh(1A)–P(2A) 2.246(10), Rh(1B)–P(1B) 2.261(9), Rh(1B)–P(2B) 2.264(10). Selected angles (°): $Cp^\dagger$–Rh(1A)–Br(1A) 128.1, $Cp^\dagger$–Rh(1B)–Br(1B) 128.2, $Cp^\dagger$–Rh(1A)–P(1A) 122.3, $Cp^\dagger$–Rh(1A)–P(2A) 126.6, $Cp^\dagger$–Rh(1B)–P(1B) 126.9, $Cp^\dagger$–Rh(1B)–P(2B) 122.4, P(1A)–Rh(1A)–P(2A) 86.0(3), P(1B)–Rh(1B)–P(2B) 86.7(3), P(1A)–Rh(1A)–Br(1A) 90.5(3), P(2A)–Rh(1A)–Br(1A) 91.1(3), P(1B)–Rh(1B)–Br(1B) 87.7(3), P(2B)–Rh(1B)–Br(1B) 92.9(3).

[2] Crystallographic data for **5**·H_2O: $C_{35}H_{15}Br_2F_{18}P_2Rh.H_2O$, M = 1120.16, orthorhombic, space group $Pna2_1$; a = 17.805(2), b = 18.172(2), c = 22.729(4) Å, V = 7354.0(20) Å^3, Z = 8; $D_{calc.}$ = 2.023 Mg m^{-3}, Mo–K_α radiation, λ = 0.71073 Å, μ = 2.848 mm^{-1}; T = 153 K, $F(000)$ = 4336. Crystal dimensions 0.36 × 0.32 × 0.14 mm. Diffractometer: Siemens P4; 2θ range 4.5–45.0°, index ranges $-19 \le h \le 1$, $-19 \le k \le 1$, $-1 \le l \le 24$, measured reflections 5952, independent reflections 5169 (R_{int} = 0.0865), observed reflections 2911 ($I > 2\sigma(I)$), number of parameters 528, number of restraints 1, Goodness-of-fit on F^2 = 1.029, R ($I > 2\sigma(I)$) = 0.0836, wR_2 = 0.1554, R (all data) = 0.1691, wR_2 = 0.1961, maximum/minimum residual electron density 1.017/ − 0.751 e Å^{-3}. An empirical absorption correction was applied using psi scans, maximum/minimum transmission 0.921/0.664. The rhodium, bromine and phosphorus atoms were refined with anisotropic thermal parameters. All other non-hydrogen atoms were refined with isotropic thermal parameters. The hydrogen atoms were added at idealised positions and a riding model with fixed thermal parameters was used in the subsequent refinement. Structure determination in the higher symmetry space group *Pnma* was attempted, and whilst it was possible to discern the cations, they were substantially disordered. Consequently, the lower symmetry system was chosen.

couplings to rhodium, $|^1J_{Rh-P}|$, of 144 and 138 Hz, respectively, confirming the non-equivalence of the phosphorus atoms. This is corroborated by the ^{19}F-NMR spectrum, which shows eight signals assigned to the two non-equivalent $PC_6F_4CH_2$ groups, and two signals assigned to the *para* fluorine atoms of the two C_6F_5 rings. The *ortho* fluorine resonances are broad, indicative of hindered rotation about the P–C_6F_5 bonds. Variable-temperature ^{19}F-NMR studies gave values of $\Delta G^{\ddagger}$, the activation energies for these processes, of 45 ± 2 and 47 ± 2 kJ mol^{-1}. These values are significantly lower than the value of 52.5 kJ mol^{-1} for rotation about the P–C_6F_5 bonds of **1** [2], indicating lower steric pressure in the cation of **5**. The ^{1}H-NMR spectrum shows a resonance at δ 5.48 with coupling to only one phosphorus assigned to the cyclopentadienyl hydrogen atom. Each pair of $C_5CH_2C_6F_4$ hydrogen atoms occurs in the region δ 4–5 as mutually coupled resonances. One resonance of each pair is further coupled to one phosphorus to give a doublet of doublets. The PCH_2 hydrogen atom resonances are multiplets at δ 4.24 and 3.68 and the methyl resonances occur as doublets of doublets, due to coupling to both phosphorus atoms, at δ 2.13 and 1.94. The NMR spectroscopic data for **5** are similar to those of the chloride salt of **1** [1] and strongly suggest that the latter is the chloride analogue of the former. Thus, the formulation originally proposed for **1** is incorrect.

The regioselectivity displayed in the activation of the C–H bonds of methyl groups in a 1,2 disposition in the synthesis of **5** is surprising in view of the complete regiospecificity in the activation of C–H bonds of methyl groups in a 1,3 disposition in reactions involving the pentamethylcyclopentadienyl complexes $[(\eta^5\text{-}C_5Me_5)MX(\mu\text{-}X)]_2$ [2–4,6]. Unfortunately the large estimated standard deviations in the structural data of **5** prevent a meaningful comparison between the bond distances and angles of **1** and **5** being made. Recent structure determinations of the tetramethylcyclopentadienyl rhodium phosphine complexes $(\eta^5\text{-}C_5Me_4H)RhCl(PPh_2R)$ (R = Ph or C_6F_5) have revealed that the Rh–CH distance and Rh–CMe distances for the 1 and 4 positions are significantly shorter than the Rh–CMe distances for the 2 and 3 positions [7], whereas for similar pentamethylcyclopentadienyl complexes the Rh–CMe distances are identical [8]. This geometric difference between tetramethyl- and pentamethyl-cyclopentadienyl complexes may account, at least in part, for the difference between reactions 1 and 2. The Rh–C distances of **5** are identical within experimental error (2.09–2.26 Å), but the e.s.d. values are large (0.03–0.05 Å). We are currently investigating these reactions further to gain a better understanding of the regioselectivity.

Reactions 1 and 2 provide convenient high-yield routes to complexes comprising η^5:η^1:η^1 hybrid cyclopentadienyl-bis(phosphine) ligands. There is considerable current interest in organometallic complexes of this type, since greater control of reactivity and regio- and stereoselectivity can be exerted than in complexes comprising separate cyclopentadienyl and phosphine ligands [9–11]. However, to date complexes of cyclopentadienyl-bis(phosphine) ligands are restricted to those reported by ourselves [2–4,6], $\{\eta^5\text{-}C_5Me_3(SiMe_2CH_2PPr^i_2)_2\}ZrCl_3$ and derivatives [10] and the 1,2 and 1,3 isomers of $[\{\eta^5\text{-}C_5Me_3[CH_2CH_2CH_2PPh_2]_2\}RhCl]^+$, which are formed by the reaction between $[(\eta^5\text{-}C_5Me_4H)RhCl(\mu\text{-}Cl)]_2$ and $Ph_2PCH{=}CH_2$ [11]. In contrast to the last reaction, which shows little regioselectivity and gives roughly equal amounts of the 1,2 and 1,3 isomers, reactions 1 and 2 allow the selective syntheses of complexes formed by activation of C–H bonds of methyl groups in a 1,2 or 1,3 disposition.

In conclusion, the reaction between $[(\eta^5\text{-}C_5Me_4H)RhBr_2]_2$ and dfppe yielded, selectively, salt **5**, which contains the asymmetric cation $[\{\eta^5\text{-}C_5HMe_2\text{-}3,4\text{-}[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,2\}RhBr]^+$, comprising a cyclopentadienyl-bis(phosphine) ligand. The structure of **5** was determined by single-crystal X-ray diffraction, confirming its identity. The regioselectivity displayed in the syntheses of **1** and **5** (reaction 2) complements that of reactions between the pentamethylcyclopentadienyl complexes $[(\eta^5\text{-}C_5Me_5)MX(\mu\text{-}X)]_2$ (M = Rh, X = Cl or Br; M = Ir, X = Cl) and dfppe, which yield exclusively $[\{\eta^5\text{-}C_5Me_3[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}MX]^+$ (**2**–**4**) (reaction 1).

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 127551 (compound **5**). Copies of the information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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