Novel Intramolecular Michael-type Reactions between Vinyldiphenylphosphine and Pentamethylcyclopentadienyl Coordinated to Rhodium(III): Formation and X-Ray Structures of Heptadentate 10-Electron Donor Ligands

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The reaction between vinyldiphenylphosphine and $[\{(\eta^5\text{-}C_5Me_5)RhCl_2\}_2]$ proceeds *via* an intramolecular hydroalkyl addition to yield the two isomeric products **1a** and **2a**.

While investigating the substitution chemistry of $[\{(\eta^5\text{-}C_5Me_5)RhCl_2\}_2]$ with vinyldiphenylphosphine, we observed a novel intramolecular Michael-type reaction to give the unexpected formation of two heptadentate bis(diphenylphosphinopropyl)trimethylcyclopentadienide ligands. To the best of our knowledge, this is the first example of such a reaction and only the second example[1] of a reaction of a phosphine ligand with a coordinated pentamethylcyclopentadienyl ligand. A species with a structure analogous to one of the products {*viz.* $[\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2CH_2PPr^i_2)_2]ZrCl_3$} has been reported,[2] but the phosphinomethylsilyl groups were attached to the cyclopentadienyl ligand prior to its coordination to the metal centre. Activation of the C–H bonds of the methyl groups of a coordinated $\eta^5\text{-}C_5Me_5$ ligand is not uncommon.[3–5] However, the formation of new C–C bonds to provide chelating phosphino(alkyl or aryl)cyclopentadienides is rare.

Treatment of $[\{(\eta^5\text{-}C_5Me_5)RhCl_2\}_2]$ with vinyldiphenylphosphine and AIBN in refluxing benzene for 48 h gave the two complexes $[\{\eta^5\text{-}C_5Me_3\text{-}1,3\text{-}[CH_2CH_2CH_2P(C_6H_6)_2]_2\}RhCl]Cl$ **1a** and $[\{\eta^5\text{-}C_5Me_3\text{-}1,2\text{-}[CH_2CH_2CH_2P(C_6H_6)_2]_2\}RhCl]Cl$ **2a** in a 1 : 2 ratio. The compounds were separated by fractional crystallization as their hexafluorophosphate salts **1b** and **2b** in 29 and 59% yields, respectively. A single-crystal X-ray diffraction study of **1b** shows that each terminal vinylic carbon atom formed a C–C bond with one of the methyl groups of the $\eta^5\text{-}C_5Me_5$ ring with concomitant C–H bond cleavage and hydrogen migration to the vinylic carbon atom that is alpha to the phosphorus atom. Two of the methyl groups of the $\eta^5\text{-}C_5Me_5$ ligand have formally undergone a hydroalkyl addition[6] to the vinylphosphine (Fig. 1).† In the solid state, **1b** is chiral with no symmetry operation relating the two phosphine ligands. In solution the phosphine ligands are equivalent due to rapid ring inversions and only one doublet is observed in its $^{31}P\{^1H\}$ NMR spectrum. Complex **1b** is similar to the recently reported[1] $[\{\eta^5\text{-}C_5Me_3\text{-}1,3\text{-}[CH_2C_6F_4P(C_6F_5)CH_2]_2\}RhCl]BF_4$ only in that the methyl groups in the 1,3-positions of the C_5Me_5 ligand were activated in both cases. In addition to the formation of complex **1a**, the methyl groups in the 1,2 positions also undergo the hydroalkyl addition to form complex **2a**. A single-crystal X-ray diffraction study of the tetraphenylborate salt **2c**, formed by anion metathesis, established the structure of this product (Fig. 2).‡

The ^1H§ and $^{31}P\{^1H\}$ NMR spectroscopic data are in agreement with the structures. The $^{31}P\{^1H\}$ NMR spectrum of **1b** exhibits a doublet (δ 21, $^1J(RhP)$ 134 Hz) while that of **2c** is a doublet (δ 17, $^1J(RhP)$ 133 Hz). The progress of the reaction can be monitored by $^{31}P\{^1H\}$ NMR spectroscopy which shows the initial formation of an unidentified intermediate observed as a doublet (δ 25, $^1J(RhP)$ 140 Hz), followed by the formation of **1a** and then **2a**. Presumably, this intermediate is the bis(phosphine)rhodium $\eta^5\text{-}C_5Me_5$ complex cation which forms before the intramolecular hydroalkyl additions occur.

The ratio of **1a** to **2a** varies depending on the solvent and other conditions. Mixing the same reagents in refluxing acetonitrile for one week gives a ratio of 2 : 1 for **1a** and **2a**. The variable product ratio suggests that the reaction mechanism may involve a radical pathway. Attempts to probe the generality of this reaction with other ligands are in progress.

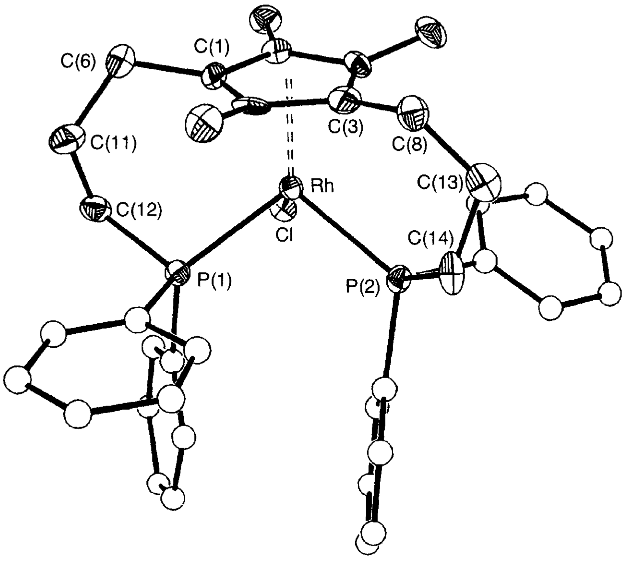

Fig. 1 Structure of the cation of **1b**. Selected interatomic distances (Å) and angles (°): Rh–P(1) 2.324(3), Rh–P(2) 2.309(3), Rh–Cl 2.393(3), Rh–cp′ 1.875, P(1)–C(12) 1.819(12), C(11)–C(12) 1.520(18), C(6)–C(11) 1.498(20), C(1)–C(6) 1.546(19), P(2)–C(14) 1.836(12), C(13)–C(14) 1.501(20), C(8)–C(13) 1.540(19), C(3)–C(8) 1.444(18); P(1)–Rh–P(2) 102.4(1), Cl–Rh–P(1) 84.3(1), Cl–Rh–P(2) 94.0(1), Rh–P(1)–C(12) 104.6(4), P(1)–C(12)–C(11) 113.8(9), C(6)–C(11)–C(12) 116.7(12), Rh–P(2)–C(14) 110.6(4), P(2)–C(14)–C(13) 112.9(8), C(8)–C(13)–C(14) 116.8(11). cp′ denotes the centroid of the cyclopentadienyl ring.

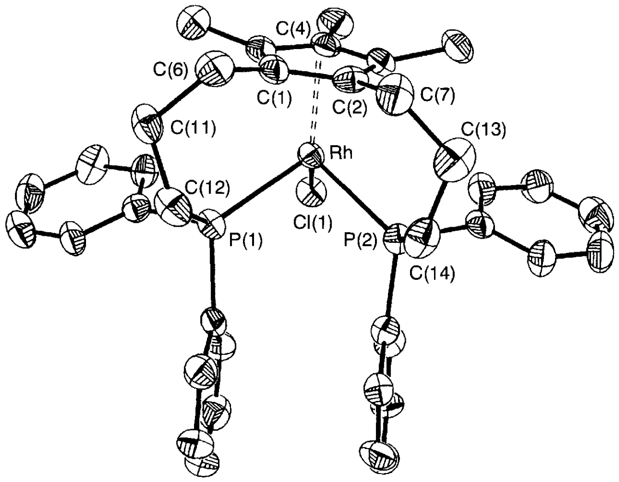

Fig. 2 Structure of the cation of **2c**. Selected interatomic distances (Å) and angles (°): Rh–P(1) 2.332(3), Rh–P(2) 2.316(3), Rh–Cl(1) 2.387(3), Rh–cp′ 1.856, P(1)–C(12) 1.828(12), C(11)–C(12) 1.532(20), C(6)–C(11) 1.536(16), C(1)–C(6) 1.514(15), P(2)–C(14) 1.823(11), C(13)–C(14) 1.533(19), C(7)–C(13) 1.544(18), C(2)–C(7) 1.521(13); P(1)–Rh–P(2) 98.1(1), P(1)–Rh–Cl(1) 92.7(1), P(2)–Rh–Cl(1) 90.1(1), Rh–P(1)–C(12) 110.3(4), P(1)–C(12)–C(11) 112.8(7), C(6)–C(11)–C(12) 112.8(9), Rh–P(2)–C(14) 108.0(4), P(2)–C(14)–C(13) 113.0(8), C(7)–C(13)–C(14) 115.6(9). cp′ denotes the centroid of the cylcopentadienyl ring.

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Footnotes

† *Crystal data* for **1b**: $C_{38}H_{41}ClF_6P_3Rh·0.5\ CH_2Cl_2$, $M = 885.5$, orthorhombic, space group $Pna2_1$, $a = 17.426(7)$, $b = 14.815(3)$, $c = 14.976(3)$ Å, $V = 3866(2)$ Å^3, $Z = 4$, $D_c = 1.519$ Mg m^{-3}, μ(Mo-Kα) = 0.761 mm^{-1}, crystal dimensions 1.0 × 0.8 × 0.8 mm. A suitable crystal of **1b** was coated with a hydrocarbon oil and placed in the −100 °C nitrogen stream on a Siemens P4 diffractometer, Mo-Kα radiation. 3626 Reflections with $2\theta < 45°$ were measured (ω-scans) and corrected for Lorentz and polarization effects to yield 2634 independent reflections with $R_{int} = 0.032$, with 2601 having $F > 5\sigma(F)$ regarded as observed. An absorption correction was applied.[7] The structure was solved by direct methods using the Siemens SHELXTL PLUS version 4.0 software package. All non-hydrogen atoms except the phenyl ring carbons and the solvate carbon were refined with anisotropic thermal parameters. Final cycle of refinement gave $R = 0.055$, $R_w = 0.087$ $[w^{-1} = \sigma^2F + 0.004F^2]$, $\Delta\rho_{max} = 1.32$ e Å^{-3} and is 0.66 Å from C(30).

‡ *Crystal data* for **2c**: $C_{62}H_{61}BClP_2Rh·0.5\ CH_2Cl_2$, $M = 1059.7$, monoclinic, space group $P2_1/c$, $a = 13.356(1)$, $b = 26.801(2)$, $c = 15.907(1)$ Å, $\beta = 110.38(1)°$, $V = 5338.3(1)$ Å^3, $Z = 4$, $D_c = 1.320$ Mg m^{-3}, μ(Mo-Kα) = 0.519 mm^{-1}, crystal dimensions 0.35 × 0.35 × 0.4 mm. A suitable crystal of **2c** was coated with epoxy resin, mounted on a glass fibre and placed on a Siemens P4 diffractometer, Mo-Kα radiation. 8534 Reflections with $2\theta < 45°$ were measured (ω-scans). The data were corrected for Lorentz and polarization effects and merged to give 6964 independent reflections with $R_{int} = 0.044$, with 4675 having $F > 4\sigma(F)$ regarded as observed. The data were corrected for absorption using a semi-empirical model (max and min transmission factors, 0.58 and 0.52) derived from an azimuthal data collection. Scattering factors and corrections for anomalous dispersion were taken from a standard source.[8] The structure was solved by Patterson methods. Anisotropic thermal parameters were assigned to all non-hydrogen atoms except the solvent carbon. The dichloromethane solvent refined well at one-half occupancy. Final cycles of refinement gave $R = 0.067$, $R_w = 0.088$ $[w^{-1} = \sigma^2F + 0.001F^2]$, $\Delta\rho_{max} = 1.56$ e Å^{-3} and is 0.914 Å from Cl(2).

Atomic coordinates, bond lengths and angles, and thermal parameters for both structures have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ *Spectroscopic data* for **1b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–6.97 (m, 20 H, Ph), 5.30 (s, 1 H, 0.5 CH_2Cl_2), 2.46 (m, 8 H, CH_2), 2.20 (m, 2 H, CH_2), 1.86 [t, $|^4J(PH) + {}^4J(P'H)|$ 6.50 Hz, 6 H, CH_3], 1.80 (m, 2 H, CH_2), 1.07 (s, 3 H, CH_3); for **2c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84–6.68 (m, 40 H, Ph), 5.30 (s, 1 H, 0.5 CH_2Cl_2), 2.43 (m, 2 H, CH_2), 2.16 (m, 2 H, CH_2), 1.94 (m, 6 H, CH_2), 1.82 (s, 3 H, CH_3), 1.46 (m, 2 H, CH_2), 1.34 [t, $|^4J(PH) + {}^4J(P'H)|$ 10.50 Hz, 6 H, CH_3].

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