

## 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  $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2]_2$  proceeds *via* an intramolecular hydroalkyl addition to yield the two isomeric products **1a** and **2a**.

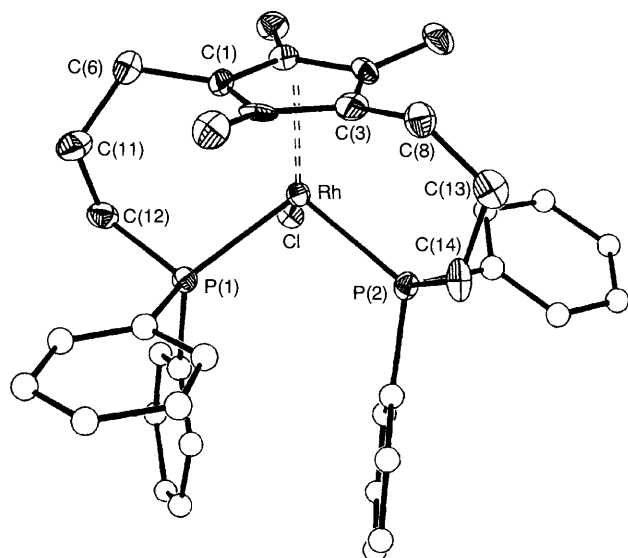
While investigating the substitution chemistry of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2]_2$  with vinyldiphenylphosphine, we observed a novel intramolecular Michael-type reaction to give the unexpected formation of two heptadentate bis(diphenylphosphino)propyl)trimethylcyclopentadienyl ligands. To the best of our knowledge, this is the first example of such a reaction and only the second example<sup>1</sup> of a reaction of a phosphine ligand with a coordinated pentamethylcyclopentadienyl ligand. A species with a structure analogous to one of the products [*viz.*  $[\eta^5\text{-C}_5\text{H}_3\text{-1,3-(SiMe}_2\text{CH}_2\text{PPr}_2)_2]\text{ZrCl}_3$ ] has been reported,<sup>2</sup> 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  $\eta^5\text{-C}_5\text{Me}_5$  ligand is not uncommon.<sup>3–5</sup> However, the formation of new C–C bonds to provide chelating phosphino(alkyl or aryl)cyclopentadienyls is rare.

Treatment of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2]_2$  with vinyldiphenylphosphine and AIBN in refluxing benzene for 48 h gave the two complexes  $[(\eta^5\text{-C}_5\text{Me}_3\text{-1,3-}[\text{CH}_2\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2)\text{RhCl}]\text{Cl}$  **1a** and  $[(\eta^5\text{-C}_5\text{Me}_3\text{-1,2-}[\text{CH}_2\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2)\text{RhCl}]\text{Cl}$  **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  $\eta^5\text{-C}_5\text{Me}_5$  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  $\eta^5\text{-C}_5\text{Me}_5$  ligand have formally undergone a hydroalkyl addition<sup>6</sup> to the vinylphosphine (Fig. 1).<sup>†</sup> 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  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum. Complex **1b** is similar to the recently reported<sup>1</sup>  $[(\eta^5\text{-C}_5\text{Me}_3\text{-1,3-}[\text{CH}_2\text{C}_6\text{F}_4\text{P}(\text{C}_6\text{F}_5)\text{CH}_2]_2)\text{RhCl}]\text{BF}_4$  only in that the methyl groups in the 1,3-positions of the  $\text{C}_5\text{Me}_5$  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).<sup>‡</sup>

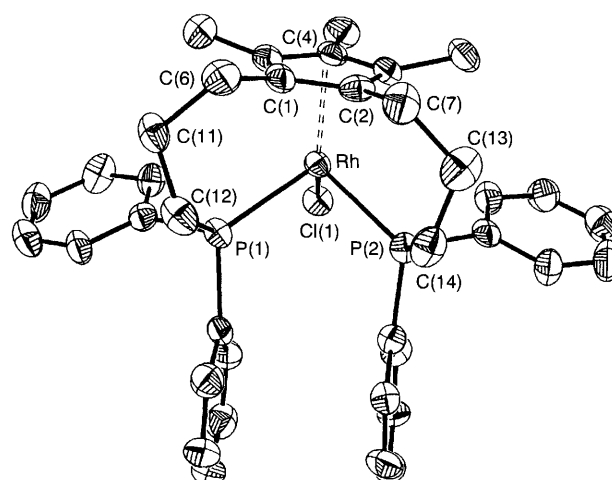
The  $^1\text{H}\{\}^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopic data are in agreement with the structures. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **1b** exhibits a doublet ( $\delta$  21,  $^1J(\text{RhP})$  134 Hz) while that of **2c** is a doublet ( $\delta$  17,  $^1J(\text{RhP})$  133 Hz). The progress of the reaction can be monitored by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy which shows the initial formation of an unidentified intermediate observed as a doublet ( $\delta$  25,  $^1J(\text{RhP})$  140 Hz), followed by the formation of **1a** and then **2a**. Presumably, this intermediate is the bis-(phosphine)rhodium  $\eta^5\text{-C}_5\text{Me}_5$  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.

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**Fig. 1** Structure of the cation of **1b**. Selected interatomic distances (Å) and angles ( $^\circ$ ): 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 ( $^\circ$ ): 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 cyclopentadienyl ring.

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### Footnotes

† *Crystal data* for **1b**:  $\text{C}_{38}\text{H}_{41}\text{ClF}_6\text{P}_3\text{Rh} \cdot 0.5 \text{CH}_2\text{Cl}_2$ ,  $M = 885.5$ , orthorhombic, space group  $Pna2_1$ ,  $a = 17.426(7)$ ,  $b = 14.815(3)$ ,  $c = 14.976(3)$  Å,  $V = 3866(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.519$  Mg m<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 0.761$  mm<sup>-1</sup>, crystal dimensions  $1.0 \times 0.8 \times 0.8$  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-K $\alpha$  radiation. 3626 Reflections with  $2\theta < 45^\circ$  were measured ( $\omega$ -scans) and corrected for Lorentz and polarization effects to yield 2634 independent reflections with  $R_{\text{int}} = 0.032$ , with 2601 having  $F > 5\sigma(F)$  regarded as observed. An absorption correction was applied.<sup>7</sup> 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  $R = 0.055$ ,  $R_w = 0.087$  [ $w^{-1} = \sigma^2F + 0.004F^2$ ],  $\Delta\rho_{\text{max}} = 1.32$  e Å<sup>-3</sup> and is 0.66 Å from C(30).

‡ *Crystal data* for **2c**:  $\text{C}_{62}\text{H}_{61}\text{BClP}_2\text{Rh} \cdot 0.5 \text{CH}_2\text{Cl}_2$ ,  $M = 1059.7$ , monoclinic, space group  $P2_1/c$ ,  $a = 13.356(1)$ ,  $b = 26.801(2)$ ,  $c = 15.907(1)$  Å,  $\beta = 110.38(1)^\circ$ ,  $V = 5338.3(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.320$  Mg m<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 0.519$  mm<sup>-1</sup>, crystal dimensions  $0.35 \times 0.35 \times 0.4$  mm. A suitable crystal of **2c** was coated with epoxy resin, mounted on a glass fibre and placed on a Siemens P4 diffractometer, Mo-K $\alpha$  radiation. 8534 Reflections with  $2\theta < 45^\circ$  were measured ( $\omega$ -scans). The data were corrected for Lorentz and polarization effects and merged to give 6964 independent reflections with  $R_{\text{int}} = 0.044$ , 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.<sup>8</sup> 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  $R = 0.067$ ,  $R_w = 0.088$  [ $w^{-1} = \sigma^2F + 0.001F^2$ ],  $\Delta\rho_{\text{max}} = 1.56$  e Å<sup>-3</sup> 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**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.36–6.97 (m, 20 H, Ph), 5.30 (s, 1 H, 0.5 CH<sub>2</sub>Cl<sub>2</sub>), 2.46 (m, 8 H, CH<sub>2</sub>), 2.20 (m, 2 H, CH<sub>2</sub>), 1.86 [t,  $|^4J(\text{PH}) + ^4J(\text{P}^*\text{H})|$  6.50 Hz, 6 H, CH<sub>3</sub>], 1.80 (m, 2 H, CH<sub>2</sub>), 1.07 (s, 3 H, CH<sub>3</sub>); for **2c**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.84–6.68 (m, 40 H, Ph), 5.30 (s, 1 H, 0.5 CH<sub>2</sub>Cl<sub>2</sub>), 2.43 (m, 2 H, CH<sub>2</sub>), 2.16 (m, 2 H, CH<sub>2</sub>), 1.94 (m, 6 H, CH<sub>2</sub>), 1.82 (s, 3 H, CH<sub>3</sub>), 1.46 (m, 2 H, CH<sub>2</sub>), 1.34 [t,  $|^4J(\text{PH}) + ^4J(\text{P}^*\text{H})|$  10.50 Hz, 6 H, CH<sub>3</sub>].

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