

Opening of the P–N Bond of Bicyclic Phosphoranes. Synthesis and X-Ray Crystal and Molecular Structure of Rhodium Complexes of Perhydro-1,3,6,2-dioxazaphosphocine

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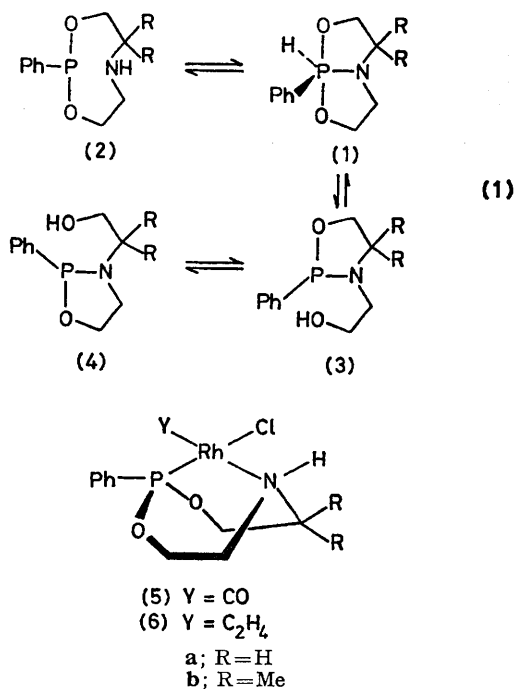
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Summary μ -Chloro binuclear rhodium(I) complexes trap the bidentate P^{III} – N^{III} tautomers of bicyclic phosphoranes containing a P–H bond to give monomeric rhodium(I) complexes, two of which [(5a) and (5b)] have been characterised by X-ray crystallography.

THE bicyclic phosphoranes (1)¹ formally arise from oxidative addition of the N–H or O–H groups of the intermediates (2), (3), or (4) to the P^{III} atom [reaction (1)]. However, neither (2) nor the equilibrium between (1) and (2), (3), or (4) have been observed spectroscopically. The presence of two donor atoms in the potentially bidentate ligand (2) prompted us to study the co-ordination chemistry of this class of compounds.

A solution of bis(dicarbonylchlororhodium) in toluene reacts at room temperature with the phosphoranes (1a) and (1b) with evolution of carbon monoxide, to form the yellow crystalline complexes (5a) [95% yield; m.p. 220 °C (decomp.); ν_{X-H} 3195, ν_{CO} 1991, and ν_{Rh-Cl} 285 cm^{-1} (Nujol); ^{31}P n.m.r.† δ + 162 p.p.m., $J(P-Rh)$ 190.5 Hz] and (5b) [98% yield; m.p. 220 °C (decomp.); ν_{X-H} 3178, ν_{CO} 1985, and ν_{Rh-Cl} 290 cm^{-1} ; ^{31}P n.m.r.: δ + 160.8 p.p.m., $J(P-Rh)$ 196.7 Hz], respectively.

Elemental analysis and mass spectrometry confirm the formation of phosphorane–Rh(CO)Cl adducts. There is no ν_{P-H} band. The position of ν_{X-H} suggests a co-ordinated



† All ^{31}P n.m.r. spectra were recorded for solutions in Me₂SO with H₃PO₄ as external reference.

N-H unit rather than co-ordination of an O-H unit.² There is no ν_{CO} splitting and only one $\nu_{\text{Rh-Cl}}$ absorption in (5a) and (5b). The relatively high value of ν_{CO} is in agreement with the expected *cis*-co-ordination of the CO and Cl ligands. Furthermore, the positions of ν_{CO} and $\nu_{\text{Rh-Cl}}$ in these complexes are similar to those observed for *cis*-[RhCl(CO)L(2,6-lutidine)] (L = PMe_3 , ν_{CO} 1979, $\nu_{\text{Rh-Cl}}$ 300; L = PMe_2Ph , ν_{CO} 1962, $\nu_{\text{Rh-Cl}}$ 295 cm^{-1}).³ These results suggest structure (5), in accordance with the anti-symbiotic rule.⁴ However, *o*-(diphenylphosphino)-*NN*-dimethylaniline was reported to lead to the other isomeric possibility.⁵ We have carried out single-crystal X-ray diffraction studies on (5a) and (5b).

Crystal data: (5a), $\text{C}_{11}\text{H}_{14}\text{ClNO}_3\text{PRh}$, $M = 377.57$, orthorhombic, $a = 7.031(1)$, $b = 11.509(2)$, $c = 33.400(9)$ Å, $Z = 8$, space group $Pbca$; $D_c = 1.855$, $D_m = 1.87$ g cm^{-3} ; $R = 0.0298$, $R_w = 0.0308$; 1860 unique data [$I > 2\sigma(I)$; $2\theta < 60^\circ$]; $\mu = 15.58$ cm^{-1} , $\mu R = 0.23$ (absorption corrections neglected); (5b), $\text{C}_{13}\text{H}_{18}\text{ClNO}_3\text{PRh}$, $M = 405.63$, monoclinic, $a = 11.692(2)$, $b = 15.447(4)$, $c = 9.202(2)$ Å, $\beta = 110.68(2)^\circ$, $Z = 4$, space group $P2_1/c$; $D_c = 1.727$, $D_m = 1.766$ g cm^{-3} ; $R = 0.0263$, $R_w = 0.0223$; 2340 unique data [$I > 2\sigma(I)$; $2\theta < 60^\circ$]; $\mu = 13.58$ cm^{-1} , $\mu R = 0.23$ (absorption corrections neglected). The data were collected on a NONIUS CAD-4 four-circle diffractometer, using Zr-filtered Mo- K_α radiation with a graphite monochromator and the ω - 2θ scan mode.†

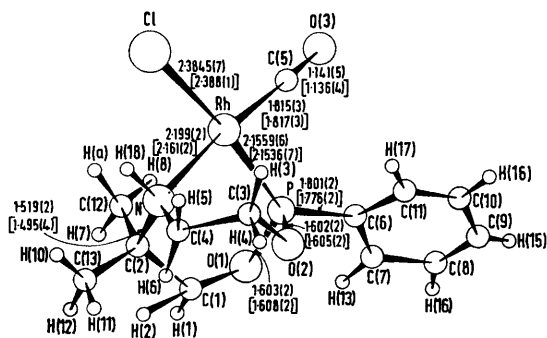


FIGURE. Molecular structure of complex (5b), with selected bond lengths in Å. The structure of (5a) is similar, with the omission of atoms C(12), C(13), and H(7)–H(12) of the two methyl groups; bond lengths in brackets are for (5a). $\text{P} \cdots \text{N} = 2.793(2)$ Å for (5a) and $2.788(2)$ Å for (5b); $\angle \text{P-Rh-N} = 80.68(6)^\circ$ for (5a) and $79.59(4)^\circ$ for (5b).

The molecular structures of (5a) and (5b) (Figure) show that the rhodium atom has a distorted square-planar co-ordination and the Cl and P atoms are in *trans* positions. The Cl–Rh–P angles are not strictly linear (respectively 170.0 and 168.5°), mainly owing to the geometrical constraints of the bidentate ligand. The distances of the Rh, Cl, P, N, C(5), and O(13) atoms from the least-mean squares

planes in (5a) and (5b), respectively, are 0.054 , 0.062 , 0.083 , -0.088 , 0.013 , and -0.088 ; 0.028 , -0.012 , -0.013 , -0.005 , 0.016 , and -0.015 Å; accordingly, (5b) is more distorted from planarity than (5a). The bond lengths in both structures are comparable to those in related compounds, e.g. [RhCl(CO)(C_2H_4)(HNEt₂)]⁶ and [RhCl(CO)-(PMe₂Ph)₂].³ The H–Cl distances in (5a) and (5b), 3.206 and 3.217 Å, respectively, indicate the presence of normal $\text{Cl} \cdots \text{H-N}$ hydrogen bonds in the crystals (normally accepted values in the range 3.16 – 3.26 Å⁷).

The only marked difference between the two structures is in the dihedral angles between the least-mean squares Rh, Cl, P, N, C(5), O(3), and phenyl planes, 122.4 and 64.2° , respectively. Both eight-membered ligand rings have a distorted crown conformation; the *gem*-dimethyl group does not lead to drastic modifications.

It is noteworthy that the $\text{P} \cdots \text{N}$ distances (respectively 2.793 and 2.788 Å) are significantly shorter than the sum of the van der Waals radii (3.4 Å) and are even smaller than the values (*ca.* 3.1 Å) reported by Verkade *et al.* for $\text{H}_3\text{B-P}(\text{OCH}_2\text{CH}_2)_3\text{N}$ ⁸ and $\text{S-P}(\text{OCH}_2\text{CH}_2)_3\text{N}$.⁹ This must be related to the relatively small N–Rh–P angles rather than to a $\text{P} \cdots \text{N}$ interaction as in [HP(OCH₂CH₂)₃N][BF₄]¹⁰ where a dative P→N bond (1.986 Å) is observed.

The $\text{P}^{\text{III}}\text{-N}^{\text{III}}$ tautomer (2) was also trapped using Cramer's complex [Rh(C_2H_4)₂Cl]₂, which leads to the formation of the yellow crystalline complexes (6a) [91% yield; m.p. 230°C (decomp.); $\nu_{\text{N-H}}$ 3185 , $\nu_{\text{C-C}}$ 1440 , and $\nu_{\text{Rh-Cl}}$ 290 cm^{-1} ; ³¹P n.m.r.:† $\delta + 165.3$ p.p.m., $J(\text{P-Rh})$ 232 Hz§] and (6b) [95% yield; m.p. 237°C (decomp.); $\nu_{\text{N-H}}$ 3180 , $\nu_{\text{C-C}}$ 1435 , and $\nu_{\text{Rh-Cl}}$ 293 cm^{-1} ; ³¹P n.m.r.: $\delta + 164.8$, $J(\text{P-Rh})$ 229.5 Hz], respectively. These compounds were further characterised by their reaction with carbon monoxide which leads to the complexes (5a) and (5b).

Reactions of an excess of the phosphoranes (1) with [Rh(CO)₂Cl]₂ or [Rh(C_2H_4)₂Cl]₂ proceed differently. 2:1 complexes are not observed in the reaction with [Rh(CO)₂Cl]₂, even in solution (i.r.); conversely, [Rh(C_2H_4)₂Cl]₂ reacts with 2 equiv. of (1a) and (1b) to give the yellow cationic complexes with two bidentate $\text{P}^{\text{III}}\text{-N}^{\text{III}}$ ligands (7a) [95% yield; m.p. 210°C (decomp.); $\nu_{\text{N-H}}$ 3050 cm^{-1} ; ³¹P n.m.r.:† $\delta + 172.7$ p.p.m., $J(\text{P-Rh})$ 218.6 Hz§] and (7b) [98% yield; m.p. 234°C (decomp.); $\nu_{\text{N-H}}$ 3060 cm^{-1} ; ³¹P n.m.r.: $\delta + 173.9$ p.p.m., $J(\text{P-Rh})$ 217.4 Hz§], respectively.

Compounds (5b) and (6b) react with an excess of triphenylphosphine to give respectively *trans*-[RhCl(CO)-(PPh₃)₂] (8) and (1b), and [RhCl(PPh₃)₃] (9) and (1b). Thus the sequence (1) → (5), (6) → (8), (9) + (1) demonstrates the reversibility of the oxidative addition in reaction (1).

The rhodium(I) complexes (5) and (6), which potentially contain up to three vacant co-ordination sites, and complexes (7) are being examined as homogeneous catalysts. Preliminary results indicate that (6a) and (6b) are hydro-

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ The Me₂SO solution decomposes slowly (even under argon) during the n.m.r. measurement and a new phosphorus species appears with a signal at $\delta + 15.6$ p.p.m. Me₂SO was the only solvent that was satisfactory for these measurements.

generation and hydroformylation catalysts. However, isomerisation is extensive and high ratios of linear to branched aldehydes in the hydroformylation of hex-1-ene are not observed.

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