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Preliminary communication

Preparation and crystal structure of $[\overline{\mathrm{Rh(COD)}(p\text{-}\mathrm{tolyl\text{-}N{=}PPh_2C}}\mathrm{HPPh_2NH}\text{-}p\text{-}\mathrm{tolyl})]$-$[\mathrm{Rh(COD)Cl_2}]$. A rhodium(I) complex containing a new σ-*N*,σ-*C*-chelating iminophosphoranylmethanide ligand

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Abstract

Reaction of the bis(iminophosphoranyl)methane $[(p\text{-tolyl-N{=}PPh}_2)_2\mathrm{CH_2}]$ with $[\mathrm{RhL_2Cl}]_2$ ($\mathrm{L} = \mathrm{CO}$ or $\mathrm{L_2} = \mathrm{COD}$) yields two different types of compounds. In one of these the bis(iminophosphoranyl)methane ligand is coordinated in a σ-*N*,σ-*N′*-chelating mode to form a six-membered metallaheterocycle, whereas in the other the ligand is coordinated in a σ-*N*,σ-*C*-chelating mode to form a novel four-membered ring. The solid state structure of $[\overline{\mathrm{Rh(COD)}(p\text{-}\mathrm{tolyl\text{-}N{=}PPh_2C}}\mathrm{HPPh_2NH}\text{-}p\text{-}\mathrm{tolyl})]$-$[\mathrm{Rh(COD)Cl_2}]$ has been determined by an X-ray diffraction study. The lithiated derivative $[(p\text{-tolyl-NPPh}_2)_2\mathrm{CHLi}]$ yields an organorhodium compound in which the bis(iminophosphoranyl)methanide ligand coordinates in a σ-*N*,σ-*C*-coordination mode towards rhodium(I).

Since the first synthesis of phosphinimides by Staudinger et al. [1] the chemistry of these iminophosphoranyl compounds has been thoroughly investigated [2]. Although bis(iminophosphoranyl)methane (= bipm) compounds containing two P=N groups can easily be synthesized [3], only little is known about their chemical behaviour, especially with respect to their organometallic and coordination chemistry.

Recently, new coordination compounds of bipm with early transition metals have been obtained by Katti et al. [4]. Our interest has been directed towards the activation of bipm using electron-rich transition metal complexes. Here we wish to report on the organometallic chemistry of bipm with rhodium(I) complexes.

Bipm may, in analogy to 1,3-diketones or bis(methylenephosphoranyl)methane, exist in two tautomeric forms [5]: groundstate I and tautomer II in which a

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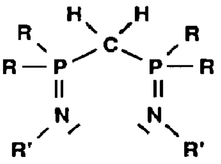
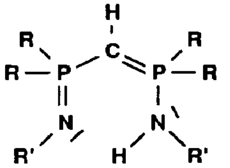
H-migration has occurred from the central C atom to one of the N atoms. We could not establish such a tautomeric behaviour for the free bipm, neither in solution nor in the solid state.



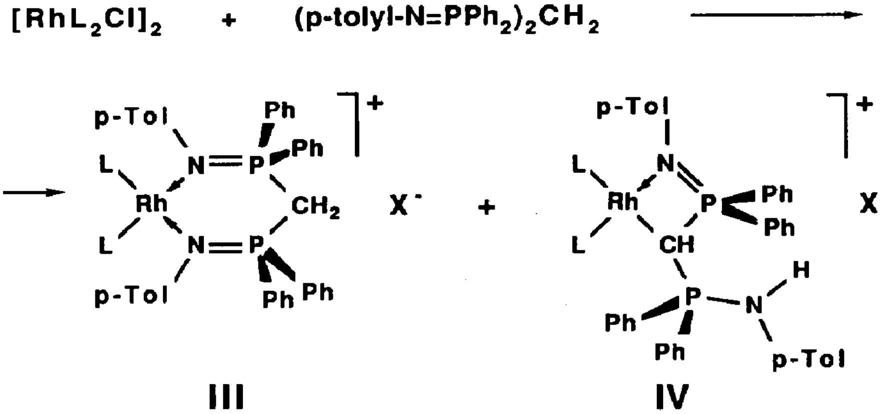
I



II

We have succeeded in the stabilisation of these tautomeric forms by coordination of the bipm ligand to rhodium(I), giving rise to σ-*N*,σ-*N*′ and σ-*N*,σ-*C*-chelate type coordination (complex III and IV respectively) *. When $[RhL_2Cl]_2$ ($L = CO$ or $L_2 = COD$) is treated with bis(*p*-tolyliminodiphenylphosphoranyl)methane (I; $R = Ph$, $R' = p$-tolyl) in C_6H_6 or CH_2Cl_2 a mixture of the complexes III and IV is formed (eq. 1). The products ratio IV/III is strongly influenced by variation of L: for $L = CO$ a higher ratio is obtained than for $L_2 = COD$ (ca. 4/1 and 1/1, respectively, at room temperature in C_6H_6).

The proposed structure for IV (based upon ^1H and ^{31}P NMR data) was confirmed by an X-ray structure determination. Single crystals of IV ($X = Rh(COD)Cl_2$, $L_2 = COD$) could be obtained by slow evaporation of a hexane/CH_2Cl_2 solution of a mixture of III and IV at room temperature. Crystallographic data: $[C_{47}H_{48}N_2P_2Rh][C_8H_{12}Cl_2Rh] \cdot 0.5CH_2Cl_2$, $M = 1112.5$, monoclinic, space group $P2_1/c$, a 22.395(5), b 12.704(3), c 20.019(3) Å, β 108.59(2)°, V 5398.11 Å^3, $Z = 4$, D_c 1.38 g cm^{-3}. A total of 7563 intensities ($2.5 < 2\theta < 60°$; h −21 to 20, k 0 to 12, l 0 to 19) were measured on a NONIUS CAD4 diffractometer employing graphite monochromated Mo-K_α radiation. Of these, 4313 intensities were below the $2.5\sigma(I)$ level and were treated as unobserved. The structure was solved using the



III IV (1)

$X = Cl, Rh(COD)Cl_2$; $L = CO$, $L_2 = COD$.

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* Complexes III and IV have been fully characterized by ^1H, ^{31}P NMR and IR spectroscopy, FDMS, and elemental analysis.

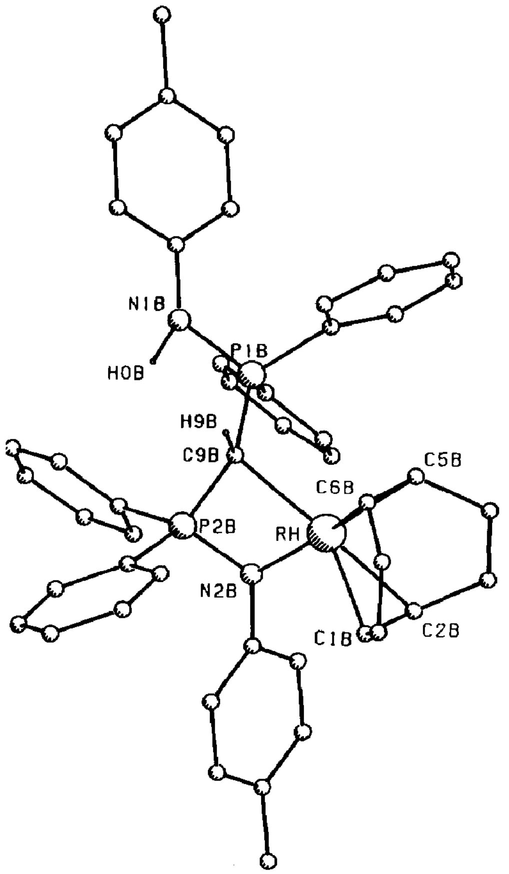
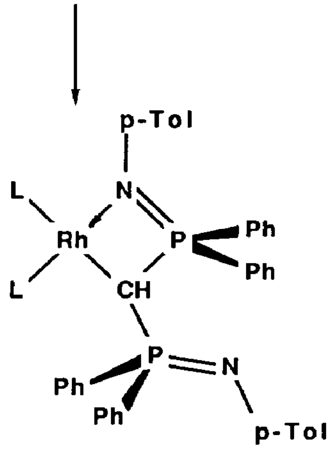


Fig. 1. Molecular structure of the $[\overline{\mathrm{Rh(COD)(}p\mathrm{\text{-}tolyl\text{-}N{=}PPh_2C}}\mathrm{HPPh_2NH\text{-}}p\mathrm{\text{-}tolyl)}]^+$ cation. The $[\mathrm{Rh(COD)Cl_2}]^-$ anion exhibits the normally observed features and has not been depicted in the figure. The hydrogen atoms have been omitted for clarity. Selected bond lengths and angles are: Rh–M(1) 1.999(1), Rh–M(2) 2.026(1), Rh–N(2b) 2.081(8), Rh–C(9b) 2.22(1), N(1b)–P(1b) 1.658(10), N(2b)–P(2b) 1.613(8), P(1b)–C(9b) 1.77(1), P(2b)–C9b) 1.771(10) Å, N(1b)–H(b) 1.30, C(9b)–H(9b) 1.05, N(2b)–Rh–C(9b) 73.1(1), M(1)–Rh–M(2) 86.45(5), N(1b)–P(1b)–C(9b) 108.6(7), N(2b)–P(2b)–C(9b) 98.3(7), P(1b)–C(9b)–P(2b) 120.4(6), Rh–C(9b)–P(1b) 117.2(6), Rh–C(9b)–P(2b) 85.9(6)°.

heavy atom method for Rh, P and Cl atoms and part of the remaining atoms in the structure. Analysis of the data was completed by means of subsequent difference Fourier syntheses. The H atoms were calculated, except for the H atoms on C(9b) and N(1b), which have been located from the ΔF synthesis. After anisotropic block diagonal least-squares refinement, convergence to a final R value of 0.060 was obtained. Tables of atomic coordinates, bond lengths and angles will be deposited with the Cambridge Crystallographic Data Centre.

An important feature of the structure of the cationic part of IV (Fig. 1) is the presence of the newly formed Rh–C(9b) (2.22(1) Å) and N(1b)–H(b) (1.30 Å) bonds, which indicates that upon coordination of the bipm ligand to rhodium there must have been a H migration from the central C atom to a terminal N atom. In this way a $\mathrm{Rh^I}$–C(sp^3) bond is formed, which is stabilized by internal coordination of the N atom of an iminophosphoranyl group, giving rise to a four-membered metallacycle. The N(1b) atom is protonated and the aminophosphonium moiety

$$[RhL_2Cl]_2 + 2/n \ \{(p\text{-tolylNPPh}_2)_2CHLi\}_n \qquad (2)$$



V

$L=CO$, $L_2=COD$

remains uncoordinated. The coordination geometry around Rh is almost square planar, the Rh atom is situated only 0.11(1) Å above the plane defined by M(1), M(2) *, C(9b) and N(2b).

The P(2b)–N(2b) distance of 1.613(8) Å, which is a normal value for a coordinated iminophosphoranyl group, is 0.045 Å longer than in the free ligand [6]. The bond distance in the uncoordinated P(1b)–N(1b) group (1.658(10) Å) is elongated by 0.090 Å as a result of protonation of the N atom. The P(1b)–C(9b) and P(2b)–C(9b) bond distances (1.77(1) and 1.771(10) Å) are significantly shorter than in a platinum system containing the comparable $[(Ph_2P(S))_2CH]^-$ ligand (1.838(11) and 1.821(12) Å, respectively) [7], suggesting that in complex IV there may be some ylide character.

From the reaction of $[RhL_2Cl]_2$ with $[(p\text{-tolyl-NPPh}_2)_2CHLi]$ (eq. 2) we were able to isolate a complex V, which has essentially the same structure as the cationic part of IV, except, of course, that both the charge and the hydrogen atom on one of the N atoms are now absent **. The coordination mode of the bis(iminophosphoranyl)methanide anion is reminiscent of that encountered in the previously mentioned $[\{(Ph_2P(S))_2CH\}Pt]$ system. It appears that in both IV and V the Rh^I to sp^3 carbon bond is effectively stabilized by internal coordination of an iminophosphoranyl group.

Further investigations into the organometallic and coordination chemistry of the bipm ligand, particularly with d^8 metal complex, is in progress.

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* M(1) and M(2) are the midpoints of C(5b)–C(6b) and C(1b)–C(2b) respectively.

** ^{31}P NMR (C_6D_6): L = CO, δ 24.0 ppm, ^2J(Rh–P) 7.3 Hz; L_2 = COD, δ 11.9 ppm, ^2J(Rh–P) 9.8 Hz.

helpful discussions, and Johnson–Matthey Technology Centre (Reading, UK) for a loan of $RhCl_3$.

References

1 H. Staudinger and J. Meyer, Helv. Chim. Acta, 2 (1919) 635.
2 See for instance: E.W. Abel, S.A. Mucklejohn, Phosphorus Sulfur, 9 (1981) 235.
3 A.M. Aguiar, H.J. Aguiar and T.G. Archibald, Tetrahedron Lett., (1966) 3187; V.A. Gilyarov, V.Yu. Kovtun and M.I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., 5 (1967) 1159; R. Appel and I. Ruppert, Z. Anorg. Allg. Chem., 406 (1974) 131.
4 K.V. Katti, H.W. Roesky and M. Rietzel, Z. Anorg. Allg. Chem., 553 (1987) 123; K.V. Katti, U. Seseke and H.W. Roesky, Inorg. Chem., 26 (1987) 814.
5 R. Appel, G. Haubrich and F. Knoch, Chem. Ber., 117 (1984) 2063.
6 P. Imhoff and C.J. Elsevier, unpublished results.
7 J. Browning, G.W. Bushnell, K.R. Dixon and A. Pidcock, Inorg. Chem., 22 (1983) 2226.