^{31}P N.M.R. Evidence for a Di-*hapto*-bonded *Tetrahedro*-tetraphosphorus Ligand in [Rh(P_4)(PPh_3)$_2$Cl]

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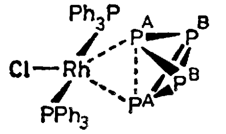
^{31}P{^{1}H} N.m.r. spectroscopic investigations of [Rh(P_4)(PPh_3)$_2$Cl] establish the presence of an η^2-P_4 ligand.

The complexes [M(P_4)(EAr_3)$_2$X] (**1**) (M = Rh, E = P, Ar = Ph, *m*- or *p*-tolyl, X = Cl, Br, I; M = Rh, E = As, Ar = Ph, X = Cl; M = Ir, E = P, Ar = Ph, X = Cl) prepared from white phosphorus have been described[1] and were the



(1a)

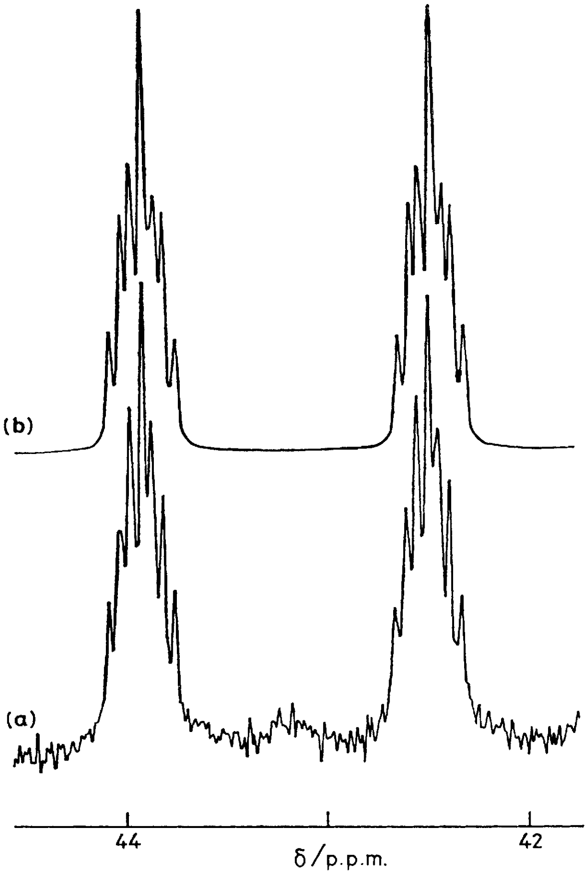


Figure 1. 81.02 MHz $^{31}P\{^1H\}$ resonance of the PPh$_3$ groups of (**1a**) in CD_2Cl_2 −22 °C: (a), experimental spectrum (line narrowed), (b), simulated spectrum (PANIC); δ 43.2 p.p.m.; ^1J (Rh–P) 115.3; ^2J (P–P^A) 4.7; ^3J (P–P^B) 8.6 Hz; linewidth = 2 Hz.

first examples of species containing the tetraphosphorus ligand. More recently, insoluble P$_4$ complexes [M{N(CH$_2$CH$_2$PPh$_2$)$_3$}(P$_4$)] (M = Ni, Pd),[2,3] with a tripod-phosphine ligand, have been reported and *X*-ray analysis has shown the presence of a simple mono-*hapto* η^1-P$_4$ ligand. The only other known complex in which a P$_4$ unit may be present is [Fe$_3$(CO)$_{12}$(P$_4$)],[4] but the mode of iron–phosphorus bonding has not been definitively established.

$$[M(P_4)(EAr_3)_2X] \qquad [Rh\{(Ph_2PCH_2)_3CMe\}(\eta^3\text{-}P_3)]$$
$$\textbf{(1)} \qquad\qquad\qquad \textbf{(2)}$$

a; M = Rh, E = P,
Ar = Ph, X = Cl

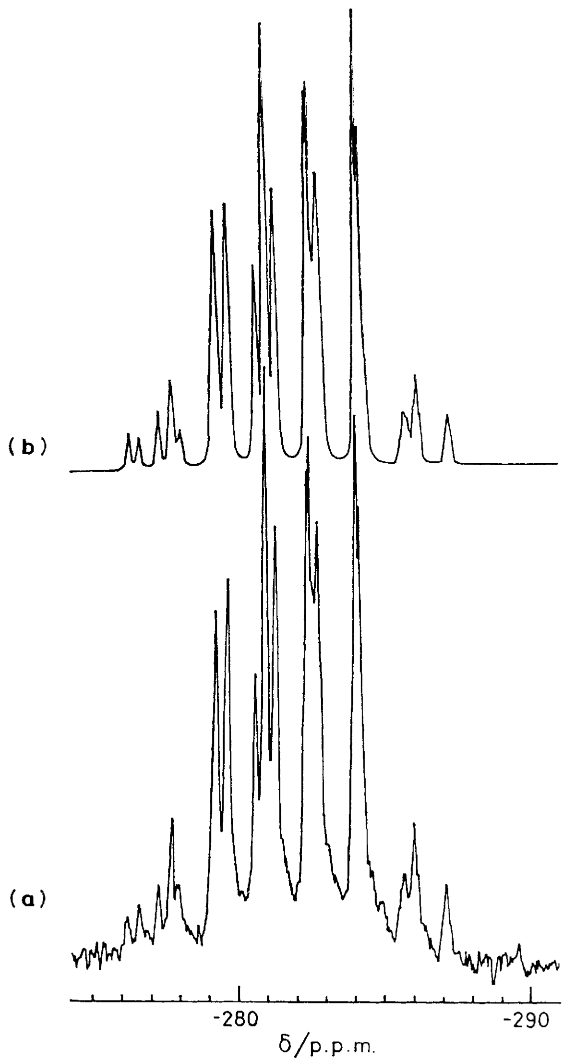


Figure 2. 81.02 MHz $^{31}P\{^1H\}$ resonance of the P$_4$ ligand of (**1a**) in CD_2Cl_2, −22 °C: (a), experimental spectrum, (b), simulated spectrum, A$_2$B$_2$ system (PANIC); δ(P^A) −279.4; δ(P^B) −284.0 p.p.m.; ^1J(P^A–P^B) 175; ^1J (Ph–P^A) 33.9; ^2J (Rh–P^B) 0; *J* (P^A–*P*Ph$_3$) 4.7; *J* (P^B–*P*Ph$_3$) 8.6 Hz; linewidth = 7 Hz.

The nature of the M–P$_4$ bond in the monomeric complexes (**1**) has not been determined though various possibilities of η^1-, η^2-, or η^3-interactions have been considered.[1] As yet, stable crystals of these complexes, suitable for *X*-ray analysis, have not been obtained but now low temperature $^{31}P\{^1H\}$ n.m.r. studies of [Rh(P$_4$)(PPh$_3$)$_2$Cl] (**1a**) have provided structural information.

The $^{31}P\{^1H\}$ n.m.r. spectrum of (**1a**) in CD_2Cl_2 solution (under N$_2$ or *in vacuo*) comprises two sets of resonances: one (δ + 43.2 p.p.m., −22 °C)† attributable to two equivalent PPh$_3$ groups (Figure 1) and the other, a second order multiplet at high field assigned to the P$_4$ group (Figure 2). The basic patterns of these resonances at 81.02 MHz are unchanged in the temperature range −70 to +40 °C (although minor changes in chemical shifts do occur). There is no evidence for fluxionality in this temperature range but at higher temperatures (> −10 °C), decomposition occurs, slowly on the n.m.r. time scale, and the intensity of the signals decreases.

Analysis shows that the high field multiplet arises from the P$_4$ unit acting as an A$_2$B$_2$ spin system with additional coupling to ^{103}Rh and the ^{31}P atoms of equivalent PPh$_3$ ligands (see

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† Positive chemical shifts are to low field of external 85% H$_3$PO$_4$.

Figure 2 for parameters). Similar reciprocal analysis may be made for the $^{31}P\{^1H\}$ resonance of the PPh_3 groups (Figure 1). This interpretation of the spectrum has been confirmed using both 81.02 and 145.8 MHz spectrometers.

The evidence supports the structure shown for (**1a**). The chemical shifts for atoms P^A and P^B are comparable to that of the η^3-P_3 ligand in the previously described $[Rh\{(Ph_2PCH_2)_3CMe\}(\eta^3\text{-}P_3)]$[5] (**2**) which has $^{31}P\{^1H\}$ parameters for η^3-P_3 [δ -270.8 p.p.m., dq, ^1J (Rh–P) 28.2; ^2J (P–P) 12.2 Hz in $CDCl_3$–CH_2Cl_2 (1 : 1)]. Also the ^1J (Rh–P^A) value for η^2-P_4 (**1a**) is small in comparison with normal Rh–P coupling constants in phosphine complexes[6] but comparable to the value in (**2**). The fact that ^2J (Rh–P^B) $= 0$ ($\pm$ $<$ *ca.* 1 Hz) supports no direct bonding between Rh and the two atoms P^B of the P_4 unit. The ^1J (Rh–P) coupling for PPh_3 ligands is slightly smaller than in some related rhodium(I)[6] complexes {*e.g.*, $[RhL(PPh_3)_2Cl]$, L = CO, C_2H_4, PPh_3}[7] but greater than values for rhodium(III)[6] species {*e.g.*, $[RhH(CO)(PPh_3)_2Cl_2]$ and *trans*-$[Rh(COR)(PPh_3)_2X_2]$}.[8] This raises the question of the oxidation state of Rh in (**1a**) and the oxidative–addition nature of the bonding of η^2-P_4. The order of coupling constants J (P^A–PPh$_3$) $<$ J (P^B–PPh$_3$) may reflect some 'through-space' interaction between P^B and the PPh_3 ligands.

At temperatures > -10 °C, the yellow solution in CD_2Cl_2 of (**1a**) turns dark brown; initially a singlet $^{31}P\{^1H\}$ n.m.r. resonance appears at +26.0 p.p.m. but this is followed by a resonance assignable to free PPh_3, increasing in intensity, plus a broad resonance (*ca.* +30 p.p.m.). There is a decomposition product (a brown solid) of unknown nature.

I thank the S.E.R.C. for support of this work, Dr. A. P. Ginsberg for helpful correspondence, Dr. I. H. Sadler for running the 145.8 MHz spectra, and Mr. W. P. Nethercote for some experimental assistance.

Received, 28th September 1982; Com. 1146

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