# $\eta^2$-Co-ordination in a 1,3-Diphospha-allene complex of Platinum(0). Synthesis and Solution $^{31}$P N.M.R. Spectrum of $[Pt(PPh_3)_2(RP{=}C{=}PR)]$ (R = 2,4,6-$Bu^t_3C_6H_2$)

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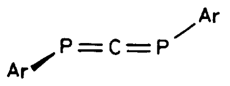
The first example of a co-ordination complex containing the novel diphospha-allene ligand RP=C=PR (R = 2,4,6-$Bu^t_3C_6H_2$) is reported and solution $^{31}$P n.m.r. studies indicate that in solution the ligand is bonded in an $\eta^2$-fashion to the metal as in the isoelectronic allene and $CS_2$ (or $CO_2$) complexes.

The co-ordination chemistry of phospha-alkenes, $R_2C{=}PR'$, and phospha-alkynes, $RC{\equiv}P$, is developing rapidly[1—4] and both $\eta^1$- and $\eta^2$-bonding of phospha-alkenes has been observed in transition metal complexes. Furthermore in the case of the complex $[Pt(PPh_3)_2\{P(mesityl){=}CPh_2\}]$ the phospha-alkene is bonded in an $\eta^2$-fashion in solution but is $\eta^1$-bonded in the solid state as demonstrated by solution and solid-state $^{31}$P n.m.r. spectroscopy[3,4] and a single-crystal *X*-ray crystallographic study.[3]

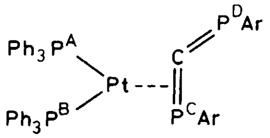
Members of the interesting heterocumulene family RP=C=X (X = NR,[5] O,S,[6] and $CR_2$[6,7]) have only been described very recently using a variety of synthetic methods and we now report the first example of a co-ordination complex of the novel, stable, diphospha-allene ArP=C=PAr (**1**) (Ar = 2,4,6-$Bu^t_3C_6H_2$).[8]

Treatment of $[Pt(PPh_3)_2(C_2H_4)]$ with (**1**) in dry toluene at room temperature rapidly gave an orange solution from which the orange solid diphospha-allene complex $[Pt(PPh_3)_2(ArP{=}C{=}PAr)]$ (**2**) can be isolated. Although the $^{31}P\{^1H\}$ n.m.r. spectrum of (**2**) in toluene shows rather broad resonances at room temperature the spectrum sharpens at −40 °C (see Figure 1a) and shows all the expected features of an $\eta^2$-bonded complex.

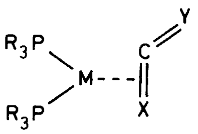
Evidence for the proposed $\eta^2$-structure is based on the observation of separate resonances for $P^A$, $P^B$, $P^C$, and $P^D$,† and the very low value of $^1J(PtP^C)$ (318 Hz) compared with the typically large values of $^1J(PtP^A)$ and $^1J(PtP^B)$ for the $\eta^1$-co-ordinated $PPh_3$ ligands. Interestingly the magnitude of $^1J(PtP^C)$ in (**2**) lies between the corresponding values found for the related phospha-alkene $[Ph_2C{=}P(mesityl)$, 498 Hz$]$[3,4] and phospha-alkyne ($Bu^tCP$, 62 Hz)[2] complexes. The $^{31}P\{^1H\}$ n.m.r. spectrum of (**2**) (neglecting $^{195}$Pt satellites) has been simulated using the coupling constant data and is shown in Figure 1(b).



(**1**)



(**2**) Ar = 2,4,6-$Bu^t_3C_6H_2$



(**3**)

The non-magnetic equivalence of the two $PPh_3$ ligands is consistent with either the diphospha-allene lying in the plane containing platinum and the two $PPh_3$ ligands, similar to the mode of bonding found for related allene complexes $[M(PPh_3)_2(allene)]$ (M = Pt, allene = $CH_2{=}C{=}CH_2$, $CH_2{=}C{=}CHMe$, or $CH_2{=}C{=}CMe_2$; M = Pd, allene = $CH_2{=}C{=}CH_2$],[9] or the perpendicular mode established for certain $Rh^I$ allene complexes.[10] The former structure seems to be most likely.

Thus (**2**) represents a new member of the well known class of metal systems (**3**) (M = Ni, Pd, or Pt; CXY = $CS_2$, COS, $CO_2$, $C_2R_4$, or $CR_2PR$).[3,4,11]

No evidence for fluxional behaviour was found for (**2**) in which the metal moves between the two P=C bonds of the diphospha-allene and the four distinct phosphorus resonances were still observed in the $^{31}P\{^1H\}$ n.m.r. spectrum recorded above room temperature. The broader spectrum might arise

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† For (**2**) $\delta(P^A)$ −119.0, $\delta(P^B)$ −114.5, $\delta(P^C)$ 97.2 $\delta(P^D)$ −187.2 p.p.m. (rel. trimethyl phosphite); $^1J(PtP^A)$ 3457, $^1J(PtP^B)$ 3127, $^1J(PtP^C)$ 318, $^1J(PtP^D)$ 239, $^2J(P^AP^B)$ 26.3, $^2J(P^AP^C)$ 72.5, $^2J(P^BP^C)$ 75.6, $^3J(P^BP^D)$ 52.8, $^3J(P^CP^D)$ 10.9, $^3J(P^AP^D)$ = 0 Hz.

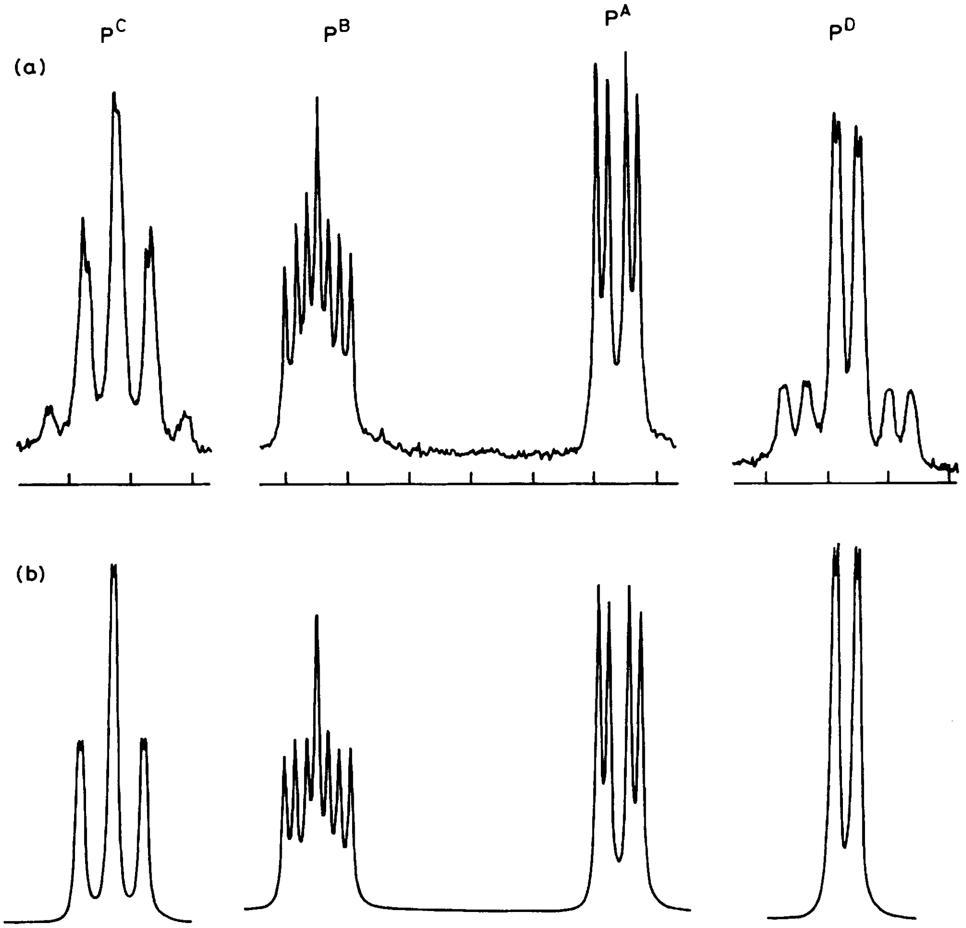

**Figure 1.** $^{31}P$ N.m.r. spectra of complex (**2**); (a) in toluene at −40 °C; (b) simulation from coupling constant data.

from phosphine ligand exchange with trace amounts of $Pt(PPh_3)_3$ present in solution. A study of the solid-state $^{31}P$ n.m.r. spectrum of (**2**) is planned.

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