η^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$^t{}_3$C$_6$H$_2$)

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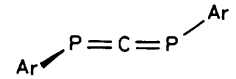
The first example of a co-ordination complex containing the novel diphospha-allene ligand RP=C=PR (R = 2,4,6-Bu$^t{}_3$C$_6$H$_2$) is reported and solution ^{31}P n.m.r. studies indicate that in solution the ligand is bonded in an η^2-fashion to the metal as in the isoelectronic allene and CS$_2$ (or CO$_2$) complexes.

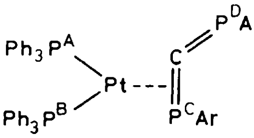
The co-ordination chemistry of phospha-alkenes, R$_2$C=PR′, and phospha-alkynes, RC≡P, is developing rapidly[1—4] and both η^1- and η^2-bonding of phospha-alkenes has been observed in transition metal complexes. Furthermore in the case of the complex [Pt(PPh$_3$)$_2${P(mesityl)=CPh$_2$}] the phospha-alkene is bonded in an η^2-fashion in solution but is η^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$^t{}_3$C$_6$H$_2$).[8]

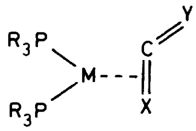
Treatment of [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] with (**1**) in dry toluene at room temperature rapidly gave an orange solution from which the orange solid diphospha-allene complex [Pt(PPh$_3$)$_2$(ArP=C=PAr)] (**2**) can be isolated. Although the ^{31}P{^{1}H} n.m.r. spectrum of (**2**) in toluene shows rather broad resonances at room temperature the spectrum sharpens at −40 °C (see Figure 1a) and shows all the expected features of an η^2-bonded complex.



(**1**)



(**2**) Ar = 2,4,6-Bu$^t{}_3$C$_6$H$_2$



(**3**)

Evidence for the proposed η^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 η^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$_2$C=P(mesityl), 498 Hz][3,4] and phospha-alkyne (Bu^{t}CP, 62 Hz)[2] complexes. The ^{31}P{^{1}H} 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).

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$^{\rm I}$ 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$_2$R$_4$, or CR$_2$PR).[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{^{1}H} n.m.r. spectrum recorded above room temperature. The broader spectrum might arise

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† For (**2**) δ(P^A) −119.0, δ(P^B) −114.5, δ(P^C) 97.2 δ(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^{A}P^B) 26.3, ^2J(P^{A}P^C) 72.5, ^2J(P^{B}P^C) 75.6, ^3J(P^{B}P^D) 52.8, ^3J(P^{C}P^D) 10.9, ^3J(P^{A}P^D) = 0 Hz.

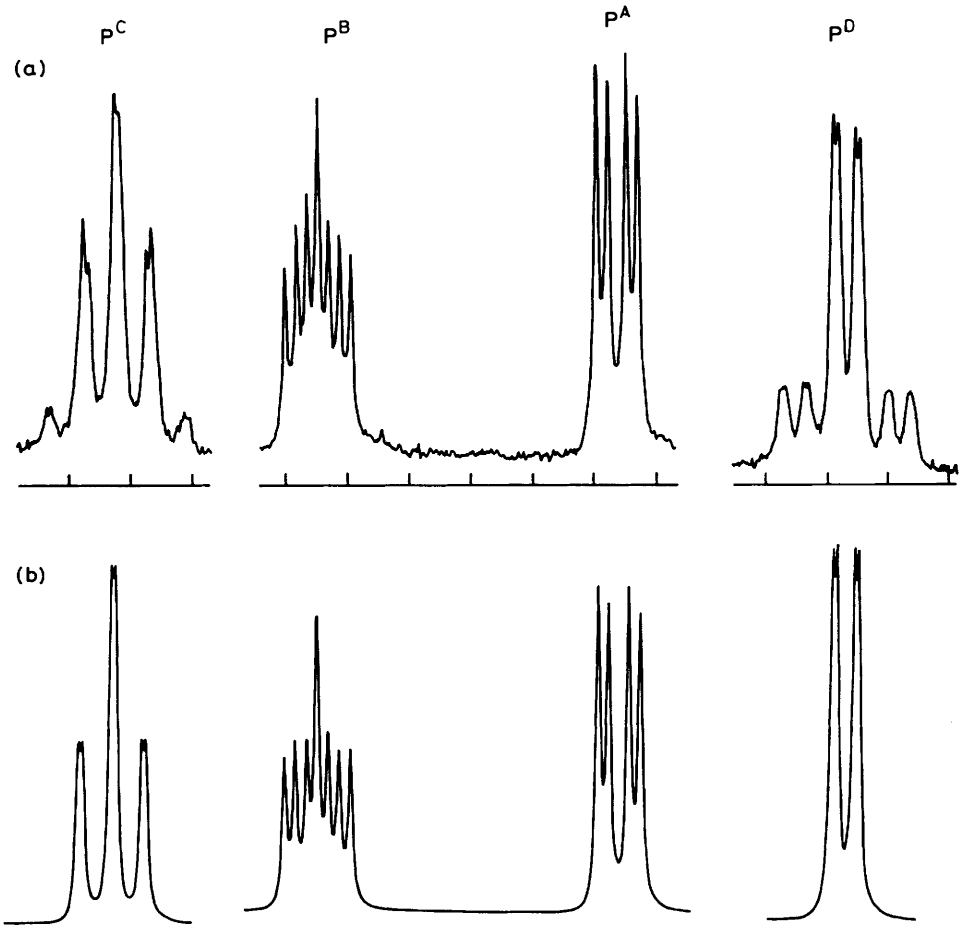

Figure 1. ^{31}P N.m.r. spectra of complex (2); (a) in toluene at −40 °C; (b) simulation from coupling constant data.

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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References

1 H. Eshtiagh-Hosseini, H. W. Kroto, J. F. Nixon, M. J. Maah, and M. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 1981, 199; Th. C. Klebach, R. Lourens, F. Bickelhaupt, C. H. Stam, and A. van Herk, *J. Organomet. Chem.*, 1981, **210**, 211; H. W. Kroto, J. F. Nixon, M. J. Taylor, A. A. Frew, and K. W. Muir, *Polyhedron*, 1982, **1**, 89; S. I. Al-Resayes, S. I. Klein, H. W. Kroto, M. F. Meidine, and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1983, 930; A. H. Cowley, R. A. Jones, C. A. Stewart, A. L. Stuart, J. L. Atwood, W. E. Hunter, and H. M. Zhang, *J. Am. Chem. Soc.*, 1983, **105**, 3737; T. A. van der Knapp, L. W. Jenneskens, H. W. Meeuwissen, F. Bickelhaupt, D. Walther, E. Dinjus, E. Uhlig, and A. L. Spek, *J. Organomet. Chem.*, 1983, **254**, C33; S. I. Al-Resayes, P. B. Hitchcock, M. F. Meidine, and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1984, 1080; S. I. Resayes, P. B. Hitchcock, J. F. Nixon, and D. M. P. Mingos, *J. Chem. Soc., Chem. Commun.*, 1985, 365; J. C. T. R. Burckett-St. Laurent, P. B. Hitchcock, H. W. Kroto, M. F. Meidine, and J. F. Nixon, *J. Organomet. Chem.*, 1982, **238**, C82; R. Bartsch, P. B. Hitchcock, M. F. Meidine, and J. F. Nixon, *ibid.*, 1984, **266**, C41.

2 J. C. T. R. Burckett-St. Laurent, P. B. Hitchcock, H. W. Kroto and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1981, 1141.

3 Th. C. van der Knapp, F. Bickelhaupt, H. van der Poel, G. van Koten, and C. H. Stam, *J. Am. Chem. Soc.*, 1982, **104**, 1756.

4 H. W. Kroto, S. I. Klein, M. F. Meidine, J. F. Nixon, R. K. Harris, K. J. Packer, and P. Reams, *J. Organomet. Chem.*, 1985, **280**, 281; Th. A. van der Knaap, F. Bickelhaupt, J. G. Kraaykamp, G. Van Koten, J. P. C. Bernards, H. T. Edzes, W. S. Veeman, E. de Boer, and E. J. Baerends, *Organometallics*, 1984, **3**, 1804.

5 O. I. Kolodiazhnyi, *Tetrahedron Lett.*, 1982, **23**, 4933; C. Wentrup, H. Briehl, G. Becker, G. Uhl, H. J. Wessely, A. Maquestiau, and R. Flammang, *J. Am. Chem. Soc.*, 1983, **105**, 7194; M. Yoshifuji, K. Toyota, K. Shibayomo, and N. Inamoto, *Tetrahedron Lett.*, 1984, **25**, 1809.

6 R. Appel and W. Paulen, *Tetrahedron Lett.*, 1983, **24**, 2639; *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 785; R. Appel, P. Fölling, L. Krieger, M. Siray, and F. Knoch, *ibid.*, 1984, **23**, 970.

7 R. Appel, P. Fölling, B. Josten, M. Siray, V. Winkaus, and F. Knoch, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 619.

8 M. Yoshifuji, K. Toyota, and N. Imamoto, *J. Chem. Soc., Chem. Commun.*, 1984, 689; H. H. Karsch, H-U Reisacher, and G. Muller, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 618; *Tetrahedron Lett.*, 1984, **25**, 3687.

9 M. Kadonaga, N. Yasuoka, and N. Kasai, *Chem. Commun.*, 1971, 1597; K. Okamoto, N. Yasuoka, and N. Kasai, unpublished results; N. Yasuoka, M. Morita, M. Kai, and N. Kasai, *J. Organomet. Chem.*, 1975, **90**, 111; K. Okamoto, Y. Kai, N. Yasuoka, and N. Kasai, *ibid.*, 1974, **65**, 427.

10 P. Racanelli, G. Pantini, A. Immirizi, G. Allegra, and L. Porri, *Chem. Commun.*, 1969, 361; T. G. Hewitt and J. J. De Boer, *J. Chem. Soc. (A)*, 1971, 817.

11 R. Mason and A. I. M. Rac, *J. Chem. Soc. (A)*, 1970, 1767; T. Kashiwagi, N. Yasuoka, T. Ueki, N. Kasai, M. Kakudo, S. Takahashi, and N. Hagihara, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 296; J. A. Ibers, *Chem. Soc. Rev.*, 1982, **11**, 57, and references therein.