

Synthesis and ^{31}P N.M.R. Spectroscopy of Platinum and Palladium Complexes containing Side-bonded Diphenyldiphosphene. The X-Ray Crystal and Molecular Structure of $[\text{Pd}(\text{PhP}=\text{PPh})\{\text{bis}(\text{diphenylphosphino})\text{ethane}\}]$

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The structure of $[\text{Pd}(\text{PhP}=\text{PPh})(\text{dppe})]$, dppe = bis(diphenylphosphino)ethane, obtained by a new and potentially general synthesis, is essentially planar with only a 3° twist between the two PdP_2 planes and a P–P bond distance of 2.121(4) Å; ^{31}P n.m.r. data on the analogous platinum complexes show very small s-character in the Pt–P(diphosphene) bonds, suggesting that the structure is essentially a diphosphene bound to Pt^0 rather than that of a diphosphido(2–) ligand bound to Pt^{II} .

Although preparation of $\text{PhP}=\text{PPh}$ was first claimed in 1877,¹ the product was actually $(\text{PhP})_2$,² and the first genuine diphosphene, bis(2,4,6-tri-*t*-butylphenyl)diphosphene, was reported only last year.³ Here the phosphorus–phosphorus double bond is apparently stabilised by the very bulky substituents. Stabilisation by η^2 co-ordination to a metal is also possible, but the three known examples^{4–6} all contain relatively unusual substituents on phosphorus and result from reactions unlikely to be of general application.† Moreover it is not clear with only P–P bond distance evidence available whether they should be regarded as diphosphene or diphosphido(2–) derivatives.

We have found that $\text{Li}_2(\text{PhPPP})$,⁷ reacts smoothly at 25 °C in tetrahydrofuran solution with *cis*- $[\text{MCl}_2\text{L}_2]$, to give good yields of air-stable orange or yellow crystals, $[\text{M}(\text{PhP}=\text{PPh})\text{L}_2]$, $\{\text{M} = \text{Pt}, \text{L}_2 = (\text{PPh}_3)_2 \text{ or } \text{Ph}_2\text{P}[\text{CH}_2]_2\text{PPh}_2 (\text{dppe}); \text{M} = \text{Pd}, \text{L}_2 = \text{dppe}\}$. The presence of side-bonded (η^2) diphenyldiphosphene in these complexes was confirmed by a single-crystal X-ray structure determination of $[\text{Pd}(\text{PhP}=\text{PPh})(\text{dppe})]$ (Figure 1).

Crystal data: $\text{C}_{38}\text{H}_{34}\text{P}_4\text{Pd}$, $M = 721.0$, monoclinic, $C2/c$, $a = 11.112(3)$, $b = 18.826(7)$, $c = 16.356(3)$ Å, $\beta = 99.59^\circ$, $Z = 4$. The structure was solved by heavy atom methods and refined by full-matrix least-squares to $R = 0.050$ for 1351 reflections with $I > \sigma(I)$ measured on an Enraf-Nonius CAD 4 diffractometer using Mo- K_α radiation.‡ The molecule lies on a crystallographic two-fold axis. The co-ordination about Pd is closely planar with only a 3° twist between the planes Pd–P(1)–P(1') and Pd–P(2)–P(2'). The diphosphene ligand is nearly planar with *trans*-phenyl substituents and the dihedral angle of 163° for C(1)–P(1)–P(1')–C(1') indicates a bending of the P(1)–C(1) bonds by 8.5° away from the metal. The P(1)–P(1') distance is 2.121(4) Å, similar to the *ca.* 2.15 Å in previous examples^{4–6} and significantly longer than in non-co-ordinated bis(2,4,6-tri-*t*-butylphenyl)diphosphene, 2.034(2) Å.³ The P–P single bond length in $(\text{PhP})_2$ is 2.217(6) Å.² Similar lengthening of multiple bonds on co-ordination is well known in alkene complexes⁸ and has also been reported very recently for the phospho-alkyne, $\text{Bu}^t\text{C}\equiv\text{P}$ (1.544 Å) in the complex, $[\text{Pt}(\eta^2\text{-P}\equiv\text{CBu}^t)(\text{PPh}_3)_2]$ (1.672 Å).⁹

$^{31}\text{P}\{^1\text{H}\}$ N.m.r. spectra of the complexes, $[\text{M}(\text{Ph}_2\text{P}_2)\text{L}_2]$, all consist basically of two triplets due to diphosphene and L_2 , respectively, with additional satellites arising from coupling to ^{195}Pt when $\text{M} = \text{Pt}$. The triplets may be interpreted as 'deceptively simple' examples of AA'XX' spectra§ and two highly unusual features are evident: (i) the apparent triplet couplings, $\frac{1}{2}[^2J(\text{PP } \textit{trans}) + ^2J(\text{PP } \textit{cis})]$, are only *ca.* 30 Hz indicating that $^2J(\text{PP } \textit{trans})$ must be much smaller than the 400–600 Hz normally observed in phosphine complexes¹⁰ and (ii) the coupling of diphosphene to ^{195}Pt is only *ca.* 280 Hz compared to values of 3000–4000 Hz in $\text{P}(\text{aryl})_3$ complexes.¹⁰ These effects are unprecedented except for the very recent data on $[\text{Pt}(\eta^2\text{-P}\equiv\text{CBu}^t)(\text{PPh}_3)_2]$; $^1J(\text{Pt}-\text{P})$ 62, $^2J(\text{PP } \textit{trans})$ 15, and $^2J(\text{PP } \textit{cis})$ 24 Hz.⁹ Based on the usual Fermi contact interpretation of $^1J(\text{Pt}-\text{P})$ values,¹¹ these data suggest a very small phosphorus 3s character for the Pt–P bonds in η^2 complexes. Precise comparisons with ^{13}C data for alkene and alkyne complexes are complicated by the variety of co-ligands (especially *trans*) and oxidation states in the literature exam-

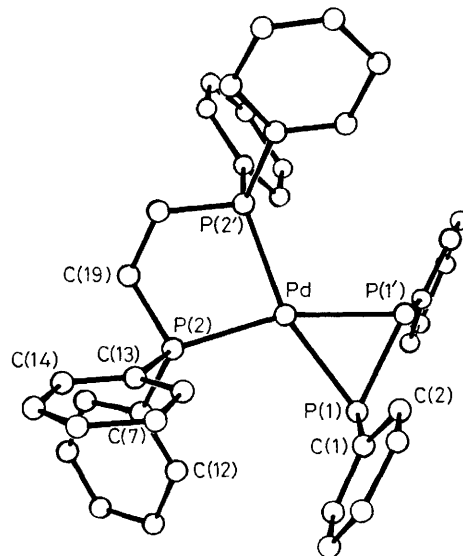


Figure 1. Molecular structure of $[\text{Pd}(\text{PhP}=\text{PPh})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]$. Some important dimensions are: Pd–P(1) 2.366(2), Pd–P(2) 2.304(2), P(1)–P(1') 2.121(4), and P(1)–C(1) 1.854(9) Å; C(1)–P(1)–P(1') $101.9(3)^\circ$.

† $[\text{MoH}_2(\eta^5\text{-C}_5\text{H}_5)_2] + \frac{1}{2}\text{P}_4 \rightarrow [\text{Mo}(\text{P}_2\text{H}_2)(\eta^5\text{-C}_5\text{H}_5)_2]$ (ref. 4); $[\text{Pt}(\text{PPh}_3)_2] + \frac{1}{2}[\text{P}_4(\text{C}_6\text{F}_5)_4] \rightarrow [\text{Pt}\{\text{P}_2(\text{C}_6\text{F}_5)_2\}(\text{PPh}_3)_2]$ (ref. 5); $[\text{NiCl}_2(\text{PEt}_3)_2] + \text{Li}[\text{P}(\text{SiMe}_3)_2] \rightarrow [\text{Ni}\{\text{P}_2(\text{SiMe}_3)_2\}(\text{PEt}_3)_2]$ (ref. 6).

‡ The atomic co-ordinates for this structure 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.

§ Additional fine structure of the triplets is observed in some spectra.

Table 1. Representative coupling constant data.

Complex	$^1J(\text{Pt-C})/\text{Hz}$	Complex	$^1J(\text{Pt-P})/\text{Hz}$
$[\text{PtCl}(\text{Me})(\text{AsMe}_2)_2]^{\text{a}}$	643 (Me <i>trans</i> to Cl)	$[\text{PtMe}(\text{PPh}_3)(\text{dppe})]^+{}^{\text{c}}$	2777 (PPh ₃)
$[\text{PtCl}(\text{Me})(\text{cod})]^{\text{a},\text{e}}$	214 (C=C <i>trans</i> to Cl)	$[\text{Pt}(\text{Ph}_2\text{P}[\text{CH}_2]_2\text{PPh}_2)_2]^{\text{d}}$	3644
$[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]^{\text{b}}$	194 (C=C)	$[\text{Pt}(\text{PhP}=\text{PPh})(\text{dppe})]^{\text{e}}$	288 (P=P)
$[\text{Pt}(\text{C}_2\text{Me}_2)(\text{PPh}_3)_2]^{\text{b}}$	52 (C=C)	$[\text{Pt}(\text{P}=\text{CBu}^t)(\text{PPh}_3)_2]^{\text{f}}$	62 (P=C)

^a M. H. Chisholm, H. C. Clark, L. E. Manzer, J. B. Stothers, and J. E. H. Ward, *J. Am. Chem. Soc.*, 1973, **95**, 8574; *ibid.*, 1975, **97**, 721. ^b B. E. Mann, *Adv. Organomet. Chem.*, 1974, **12**, 135, and references therein. ^c T. G. Appleton and M. A. Bennett, *Inorg. Chem.*, 1978, **17**, 738. ^d Ref. 10. ^e Present work. ^f Ref. 9. ^g cod = cyclo-octa-1,5-diene.

ples. However, the $^1J(\text{Pt-}^{13}\text{C})$ data in Table 1 do show a similar decrease in s-character on changing from a Pt-C(sp³) bond to an η^2 complex. The decrease is larger in the phosphorus case, presumably because the lone pairs have very high s-character. Table 1 also shows a close relationship between $^1J(\text{Pt-C})$ values in alkene and alkyne complexes and $^1J(\text{Pt-P})$ in diphosphene and phospho-alkyne complexes.

Overall, both the structural and n.m.r. evidence indicate that $\eta^2\text{-P}_2\text{R}_2$ complexes are best regarded as alkene analogues, face-bound to the metal with lone pairs occupying the *trans* 'trigonal' positions in the diphosphene.

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