The Nature of the Co-ordinate Link. Part 11.[1] Synthesis and Phosphorus-31 Nuclear Magnetic Resonance Spectroscopy of Platinum and Palladium Complexes containing Side-bonded (*E*)-Diphenyldiphosphene. *X*-Ray Crystal and Molecular Structures of $[Pd\{(E)\text{-}PhP{=}PPh\}(Ph_2PCH_2CH_2PPh_2)]$ and $[Pd\{[(E)\text{-}PhP{=}PPh][W(CO)_5]_2\}(Ph_2PCH_2CH_2PPh_2)]$ †

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The complexes *cis*-$[MCl_2L_2]$ react with $Li_2(PhPPPh)$ to give $[M(PhP{=}PPh)L_2]$ [M = Pd, L_2 = 1,2-bis(diphenylphosphanyl)ethane (dppe), (1); M = Pt, L_2 = dppe or $(PPh_3)_2$]. Complex (1) reacts with $[W(CO)_5(thf)]$ (thf = tetrahydrofuran) to give $[Pd\{(PhP{=}PPh)[W(CO)_5]_2\}(dppe)]$ (2). Complexes were characterized by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy. *X*-Ray crystal-structure determinations of complexes (1) and (2) reveal nearly identical and planar PdP_4 moieties comprising the donor atoms of L_2 and η^2-[(*E*)-diphenyldiphosphene] ligands. In (2) the two diphosphene lone pairs co-ordinate to $W(CO)_5$ groups and the W–P bonds are bent 32° away from the Pd atom. The diphosphene P–P bond in (2) [2.186(6) Å] is 0.06 Å longer than that in (1) [2.121(4) Å], which is similar to that in other diphosphene complexes and is approximately mid-way between the P–P single and double bond lengths. Small values of the coupling constants $^1J(PtP)$ and $^2J(PP)$ involving the diphosphene ligand indicate that the diphosphene uses electrons of low *s* character in η^2-co-ordination.

Diorganodiphosphenes RP=PR tend to polymerize to cyclopolyphosphanes such as $\overline{\mathrm{PhP(PPh)}}_4$, because the bond energy per phosphorus atom is smaller in the diphosphene (*i.e.* half the P=P bond energy) than in the polyphosphane (*i.e.* the P–P bond energy). Although $p_\pi\text{-}p_\pi$ bonding between elements X from the second and later rows of the Periodic Table leads to the expected maximum in the X_2 bond dissociation energies at Group 5, the ratio of the bond energies per atom in X_2 to that in the polymers containing single bond X–X is too small for the diatomic molecules X_2 to be thermodynamically stable at 25 °C.[2] At high temperatures entropy favours the smaller molecules X_2, and the π-bonded molecules X_2 for most of the Main Group elements have been known for a long time. Recent success in the stabilization at room temperature of molecules RP=PR has been achieved by the use of bulky substituents R. In the (*E*)-configuration of the diphosphene the interaction between the two R groups is minimized, whereas the number and intensity of the steric interactions tend to be greater in the polymeric forms. With sufficiently bulky substituents R, the doubly-bonded molecules become thermodynamically stable at room temperature, and even when full thermodynamic stabilization is not achieved, the bulky R groups reduce the rate of polymerization or attack by other reagents. The molecules RP=PR have been prepared and studied for R = $C_6H_2Bu^t_3$-2,4,6 and other bulky aryl groups,[3-10] $C(SiMe_3)_3$,[5,9,11,12] $N(SiMe_3)_2$,[13] and $N(SiMe_2Bu^t)_2$.[13]

The early report [14] of the detection of monomeric and dimeric forms of PPh by ^{31}P n.m.r. in melts of $\overline{\mathrm{PhP(PPh)}}_4$ now appears to be unreliable in view of the wide disparity between the shifts found and the very high frequency shifts established for the diphosphenes with bulky groups R.[4-7,11,13,15]

Stabilization of molecules RP=PR with less-bulky substituents R, such as C_6F_5,[16] Ph,[17] $SiMe_3$,[18,19] and even H,[20,21] has been achieved by η^2-co-ordination to transition metals. Co-ordination obviously leads to kinetic stabilization through the interaction of the $p_\pi\text{-}p_\pi$ electrons of RP=PR with the metal acceptor orbitals; whether or not co-ordination also affords thermodynamic stabilization against polymerization is unclear.

Our interest in this area derived from the expectation that the lithium compound $Li_2(PhPPPh)$ [22] would provide a rational and possibly more general route to transition-metal complexes of diphosphenes than found hitherto, and from the prospects for detailed ^{31}P n.m.r. studies. Although alkali-metal compounds such as $K_2(Bu^tPPBu^t)$ react with a wide range of Main Group element dichloro-compounds to form three-membered rings containing two P atoms and an atom of B, C, Si, Ge, Sn, As, or Sb,[23] so far as we are aware, attempts to apply this method to transition-metal dichloro-complexes have not been reported. A preliminary account of part of our work has been published.[17]

Experimental

Complexes were prepared and handled under an atmosphere of dry oxygen-free nitrogen. Solvents were dried and distilled before use. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra were recorded at 32.44 MHz on a Bruker WP80SY spectrometer and are referred to external 85% H_3PO_4. The ^{19}F n.m.r. spectra of $CDCl_3$ solutions were also recorded on this instrument and are referred to external CCl_3F. Positive shifts are to high frequency of the reference. Elemental analyses were by the Microanalytical Laboratory of this School.

Preparations.—*Pentaphenylcyclopentaphosphane.* This compound was obtained from dichlorophenylphosphane and

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† 1,2-Bis(diphenylphosphanyl)ethane[(*E*)-η^2-diphenyldiphosphene]-palladium(0) and 1-[1′,2′-bis(diphenylphosphanyl)ethane]-2,2,2,2,2,3,3,3,3,3-decacarbonyl-[(*E*)-μ_3-η-diphenyldiphosphene-*P*(Pd^1W^2)*P*′(Pd^1W^3)]-palladium(0)ditungsten(0) respectively.

Supplementary data available (No. SUP 23947, 30 pp.): thermal parameters, H-atom co-ordinates, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

magnesium turnings [24] [δ_P −3.8 p.p.m. for a tetrahydrofuran (thf) solution] (Found: C, 66.0; H, 4.7. Calc. for $C_{30}H_{25}P_5$: C, 66.7; H, 4.7%).

1,2-*Dilithio*-1,2-*diphenyldiphosphane*. This compound was obtained as the thf solvate after stirring pentaphenylcyclopentaphosphane with lithium in thf under argon for 2 d.[22]

Tetra(*pentafluorophenyl*)*cyclotetraphosphane*. Prepared from dibromo(pentafluorophenyl)phosphane and mercury. N.m.r. spectra of a solution in diethyl ether: δ_P −63.7 p.p.m.; δ_F 127, 151, and 162 p.p.m. (lit.,[25] 126.4, 149.5, and 160 p.p.m.).

1,2-*Bis*(*diphenylphosphanyl*)*ethane*[(E)-η^2-*diphenyldiphosphene*]*palladium*(0), (1). Equimolar proportions of [$PdCl_2$(dppe)] [dppe = 1,2-bis(diphenylphosphanyl)ethane] (0.39 g) and Li_2(PhPPPh)·thf in thf (5 cm^3) were heated under reflux for 5 min. The resulting red-brown solution was evaporated to dryness and extracted with benzene (5 cm^3). The mixture was filtered through Celite to remove LiCl, and the solvent removed under reduced pressure. The orange residue was recrystallized from hot toluene to give the complex as orange crystals, m.p. 200—204 °C (Found: C, 61.9; H, 4.7. $C_{38}H_{34}P_4Pd$ requires C, 63.3; H, 4.7%).

Similarly prepared and characterized by $^{31}P-\{^1H\}$ n.m.r. spectroscopy (Table 1) were 1,2-bis(diphenylphosphanyl)ethane[(*E*)-η^2-diphenyldiphosphene]platinum(0), as orange crystals from toluene–light petroleum, and [(*E*)-η^2-diphenylphosphene]bis(triphenylphosphane)platinum(0) from *cis*- or *trans*-[$PtCl_2(PPh_3)_2$]. Application of a similar method using [$PdCl_2(PPh_3)_2$] or [$PtCl_2(PMe_2Ph)_2$] as starting complex gave products for which the $^{31}P-\{^1H\}$ n.m.r. spectra showed the presence of the free phosphane; however, clear evidence of formation of a diphenyldiphosphene complex was obtained by $^{31}P-\{^1H\}$ n.m.r. for [Pt(PhP=PPh)$(PMe_2Ph)_2$] (see Results and Discussion section).

1-[1′,2′-*Bis*(*diphenylphosphanyl*)*ethane*]-2,2,2,2,2,3,3,3,3,3-*decacarbonyl*-[(E)-μ_3-η-*diphenyldiphosphene*-P(*Pd*^{1}*W*^{2})P′(*Pd*^{1}-*W*^{3})]-*palladium*(0)*ditungsten*(0), (2). A solution of [Pd(PhP=PPh)(dppe)] (0.04 g) in thf (5 cm^3) was treated with two molar equivalents of [$W(CO)_5$(thf)] in thf (20 cm^3). The resulting orange-yellow solution was evaporated to dryness. The residue was dissolved in diethyl ether and chromatographed using a GF 254 silica-gel column and diethyl ether. A fast-moving yellow band was collected, and the residue after evaporation of the solvent was recrystallised from [$^2H_6$]benzene–n-pentane to give the complex as yellow crystals, containing 1 mol of C_6D_6 of crystallization, m.p. 120 °C (decomp.) [ν(CO) 2 062w, 1 985vw, 1 945s, 1 933m (sh), 1 922w (sh) cm^{-1}] (Found: C, 44.5; H, 3.0. $C_{48}H_{34}O_{10}P_4PdW_2$ requires C, 44.8; H, 2.8%).

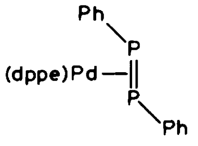
1-[1′,2′-*Bis*(*diphenylphosphanyl*)*ethane*]-2,2,2,2,2-*pentacarbonyl*[(E)-μ-η-*diphenyldiphosphene*-P(*Pd*^{1}*W*^{2})P′(*Pd*^{1})]*palladium*(0)*tungsten*(0). A solution of [$W(CO)_5$(thf)] (0.08 g) in thf (20 cm^3) was added dropwise to a solution of [Pd(PhP=PPh)(dppe)] (0.07 g) in thf (10 cm^3). Chromatography and recrystallisation as described above gave the product as yellow crystals, m.p. 156—158 °C [ν(CO) 2 058w, 1 977w, 1 943s, 1 909m (sh) cm^{-1}] (Found: C, 48.1; H, 3.6. $C_{43}H_{34}O_5P_4PdW$ requires C, 49.4; H, 3.3%).

η^2-1-[1′,2′-*Bis*(*diphenylphosphanyl*)*ethane*]-2,3-*dichloro*-[(E)-μ_3-η-*diphenyldiphosphene*-P(*Pd*^{1}*Pd*^{2})P′(*Pd*^{1}*Pd*^{3})]-2,2,3,3-*tetrakis*(*triphenylphosphane*)*tripalladium*(0)(II)(II) *bis*(*tetrafluoroborate*). An equimolar mixture of [Pd(PhP=PPh)(dppe)] (0.057 g) and [$Pd_2(\mu\text{-}Cl)_2(PPh_3)_4$][$BF_4$]$_2$ (0.095 g) in dichloromethane (7 cm^3) was stirred at room temperature for a few minutes. The orange solution which formed was filtered, and the filtrate was treated with n-pentane to give the product as yellow crystals, m.p. 197—200 °C (decomp.) [ν(PdCl) 350, ν(BF) 1 050br cm^{-1}] (Found: C, 57.2; H, 4.1. $C_{110}H_{94}B_2Cl_2F_8P_8Pd_3$ requires C, 57.0; H, 4.1%).

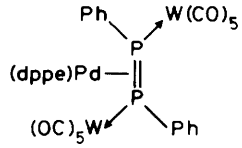
{(E)-η^2-[*Bis*(*pentafluorophenyl*)*diphosphene*]}*bis*(*triphenylphosphane*)*palladium*(0). This complex (m.p. 153—155 °C), and the analogous platinum complex [m.p. 180 °C (decomp.)], were obtained as described previously.[16] Satisfactory analytical results were obtained, and the ^{19}F n.m.r. spectra for both complexes were similar to that reported for the platinum complex.

1,2-*Bis*(*diphenylphosphanyl*)*ethane*{(E)-η^2-[*bis*(*pentafluorophenyl*)*diphosphene*]}*palladium*(0). An equimolar mixture of [Pd{$(C_6F_5)P{=}P(C_6F_5)$}$(PPh_3)_2$] (0.087 g) and dppe (0.034 g) in benzene were heated under reflux for 1 h. Removal of solvent under vacuum gave a pale yellow oil, which on washing with light petroleum (b.p. 60—80 °C) gave the product as a yellow solid, m.p. 126—128 °C (Found: C, 50.3; H, 2.8. $C_{38}H_{24}F_{10}P_4Pd$ requires C, 50.7; H, 2.7%).

X-*Ray Crystal-structure Determinations*.—The structure determination for [Pd(PhP=PPh)(dppe)] (1) has previously been described briefly.[17] Details for this complex and for [Pd{(PhP=PPh)[$W(CO)_5$]$_2$}(dppe)] (2) [line drawings of (1) and (2) are shown below] are as follows.



(1)



(2)

Crystal data. (1) $C_{38}H_{34}P_4Pd$, M = 721.0, monoclinic, a = 11.112(3), b = 18.826(7), c = 16.356(3) Å, β = 99.59(2)°, U = 3 373.8 Å^3, Z = 4, D_c = 1.42 g cm^{-3}, F(000) = 1 472. Monochromated Mo-K_α radiation, λ = 0.710 69 Å, μ = 7.6 cm^{-1}. Space group $C2/c$ from systematic absences of hkl for $h + k$ odd and $h0l$ for l odd, and successful refinement.

Crystal data. (2) $C_{48}H_{34}O_{10}P_4PdW_2 \cdot C_6D_6$, M = 1 452.9, monoclinic, a = 16.718(3), b = 18.805(6), c = 34.576(10) Å, β = 95.76(2)°, U = 10 815.2 Å^3, Z = 8, D_c = 1.78 g cm^{-3}, F(000) = 5 584. Monochromated Mo-K_α radiation, λ = 0.710 69 Å, μ = 49.8 cm^{-1}. Space group $C2/c$ from systematic absences of hkl for $h + k$ odd, and successful structure refinement. The sample from which the data crystal was chosen had crystallised from a deuteriated benzene solution used for n.m.r. measurements.

Data were measured on an Enraf-Nonius CAD4 diffractometer using crystals of approximate sizes 0.2 × 0.2 × 0.2 mm (1) and 0.4 × 0.3 × 0.3 mm (2). Preliminary cell dimensions were found using the SEARCH and INDEX routines of the CAD4 and final values were calculated from the setting angles for 25 reflections with θ = 15°. Intensities for $hk + l$ reflections with $2 < \theta < 20°$ (1) or $2 < \theta < 22°$ (2) were measured by a $\theta/2\theta$ scan with a scan width of $\Delta\theta = (1.0 + 0.35\tan\theta)°$ (1) or $\Delta\theta = (0.8 + 0.35\tan\theta)°$ (2). The scan rate for each reflection was determined by a rapid pre-scan at 10° min^{-1} in θ at which point any reflection with $I < \sigma(I)$ was coded as unobserved. The remaining reflections were rescanned at such a speed as to give a minimum value of $\sigma(I)/I$ of 0.1 [for (1)] or 0.05 [for (2)] subject to a maximum scan time of 60 s. Two standard reflections monitored every hour showed no significant variation. Data were corrected for Lorentz polarization (Lp) effects and for absorption, and after averaging any equivalent reflections 1 351 (1) and 4 404 (2) reflections with $|F|^2 > \sigma(F)^2$ were used in the structure refinements. The values of $\sigma(F)^2$ were taken as $[\sigma^2(I) + (0.02I)^2]^{\frac{1}{2}}/\text{Lp}$.

The structures were solved by routine heavy-atom methods and (2) proved to contain a molecule of C_6D_6 in the lattice. For (1) refinement of non-hydrogen atoms with anisotropic temperature factors was by full-matrix least squares. Hydrogen atoms were placed at calculated positions (C–H 1.08 Å) and held fixed with a common isotropic temperature factor of $B = 6.0$ Å^2. Refinement converged at $R = 0.050$, $R' = 0.055$, when the maximum shift/error was 0.01 and the weighting scheme was $w = 1/\sigma^2(F)$. A final difference map was everywhere featureless. For (2) refinement was by full-matrix least squares with the W, Pd, and P atoms anisotropic. Refinement converged at $R = 0.099$, $R' = 0.118$, when the maximum shift/error was 0.09 and the weighting scheme was $w = 1/\sigma^2(F)$. A final difference map had peaks up to 2.6 e Å^{-3} near the W atoms, but was elsewhere featureless.

Table 1. Fractional atomic co-ordinates (× 10^4) for [Pd(PhP=PPh)(dppe)] (1) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Pd	5 000	1 845.4(5)	2 500
P(1)	4 226(3)	2 969(1)	2 802(2)
P(2)	3 801(2)	956(1)	2 903(1)
C(1)	2 964(9)	3 111(5)	1 922(6)
C(2)	3 083(11)	3 236(7)	1 140(7)
C(3)	2 034(13)	3 315(9)	525(8)
C(4)	915(11)	3 291(7)	743(8)
C(5)	786(11)	3 204(8)	1 518(9)
C(6)	1 834(11)	3 124(7)	2 127(7)
C(7)	3 298(8)	939(4)	3 896(5)
C(8)	3 382(9)	358(6)	4 413(6)
C(9)	2 970(9)	374(6)	5 154(6)
C(10)	2 453(10)	983(7)	5 404(6)
C(11)	2 372(12)	1 558(6)	4 908(7)
C(12)	2 784(10)	1 540(5)	4 158(6)
C(13)	2 409(7)	759(5)	2 186(5)
C(14)	1 763(8)	139(5)	2 221(6)
C(15)	710(9)	17(5)	1 665(7)
C(16)	273(9)	504(6)	1 080(6)
C(17)	908(11)	1 110(7)	1 034(7)
C(18)	1 997(10)	1 247(6)	1 587(7)
C(19)	4 691(7)	138(5)	2 881(5)

The structure solutions and refinements were carried out on a PDP 11/34 computer using the Enraf-Nonius Structure Determination Package. Scattering factors for neutral atoms were taken from ref. 26. Final atom co-ordinates are listed in Tables 1 and 2.

Simulation of ^{31}P *N.M.R. Spectra.*—The ^{31}P n.m.r. spectra of four complexes were simulated by use of the PANIC 80 program of the Bruker spectrometer; initial choices of shifts and coupling constants were refined by iteration. The final parameters were in accord with the symmetry of the complexes and gave a fit to the observed line positions to within 2.5 Hz. To determine the reliability of the coupling constants thus obtained, spectra were simulated with $|^1J(\mathrm{PP})| = 350$, 400, 640, 669, 690, 900, and 1 300 Hz and other parameters as given in Table 6 for [Pt(PhP=PPh)(PPh$_3$)$_2$] (see Results and Discussion section).

Results and Discussion

The lithium compound Li$_2$(PhPPPh) reacts smoothly at 25 °C in tetrahydrofuran (thf) solution with the complexes *cis*-

Table 2. Fractional atomic co-ordinates (× 10^4) for [Pd{(PhP=PPh)[W(CO)$_5$]$_2$}(dppe)] (2) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1)	1 549.5(8)	1 052.7(6)	−343.8(4)	C(20)	3 007(26)	−1 190(21)	−2 782(13)
W(2)	3 354.2(8)	1 599.0(7)	−1 823.9(4)	C(21)	3 395(31)	−1 750(25)	−2 611(15)
Pd	2 505.1(14)	−330.3(11)	−1 228.4(8)	C(22)	3 593(28)	−1 796(23)	−2 146(14)
P(1)	1 900(5)	721(4)	−1 013(3)	C(23)	2 994(20)	−2 048(16)	−1 290(10)
P(2)	3 053(5)	820(4)	−1 255(3)	C(24)	2 037(20)	−2 052(16)	−1 354(10)
P(3)	1 650(5)	−1 265(4)	−1 139(3)	C(25)	1 182(17)	1 028(14)	−1 398(9)
P(4)	3 331(6)	−1 194(4)	−1 447(3)	C(26)	769(20)	544(16)	−1 664(10)
O(1)	1 106(20)	1 563(16)	455(10)	C(27)	138(23)	822(18)	−1 951(11)
O(2)	673(18)	−391(15)	−152(9)	C(28)	−28(25)	1 552(20)	−1 959(12)
O(3)	−186(19)	1 608(15)	−694(9)	C(29)	422(19)	2 015(15)	−1 725(9)
O(4)	3 184(16)	452(13)	94(8)	C(30)	1 009(20)	1 776(15)	−1 418(10)
O(5)	2 206(15)	2 606(12)	−467(7)	C(31)	1 744(19)	−1 528(15)	−638(10)
O(6)	1 743(19)	1 161(15)	−2 361(9)	C(32)	2 350(21)	−1 155(17)	−398(10)
O(7)	5 040(17)	2 060(14)	−1 363(8)	C(33)	2 393(21)	−1 365(17)	32(10)
O(8)	4 330(19)	412(16)	−2 206(10)	C(34)	1 820(24)	−1 851(20)	184(12)
O(9)	3 699(17)	2 585(14)	−2 511(9)	C(35)	1 257(24)	−2 148(20)	−81(12)
O(10)	2 589(15)	2 848(12)	−1 414(7)	C(36)	1 183(21)	−2 000(17)	−464(10)
C(1)	1 310(21)	1 367(17)	140(10)	C(37)	581(20)	−1 190(16)	−1 320(10)
C(2)	1 030(19)	153(16)	−212(10)	C(38)	43(28)	−1 025(23)	−1 104(14)
C(3)	468(20)	1 390(17)	−572(10)	C(39)	−831(35)	−870(29)	−1 282(17)
C(4)	2 645(20)	687(16)	−83(10)	C(40)	−836(28)	−1 016(23)	−1 694(13)
C(5)	2 020(17)	2 018(14)	−437(9)	C(41)	341(32)	−1 248(26)	−1 898(16)
C(6)	2 322(27)	1 291(22)	−2 181(13)	C(42)	445(28)	−1 369(23)	−1 744(14)
C(7)	4 461(28)	1 879(23)	−1 541(14)	C(43)	4 414(22)	−1 248(18)	−1 299(11)
C(8)	3 966(21)	879(17)	−2 036(11)	C(44)	4 675(24)	−1 534(20)	−937(12)
C(9)	3 523(23)	2 176(18)	−2 236(12)	C(45)	5 536(27)	−1 492(22)	−810(13)
C(10)	2 815(18)	2 353(15)	−1 577(9)	C(46)	6 010(27)	−1 177(23)	−1 052(13)
C(11)	3 816(17)	902(14)	−834(9)	C(47)	5 804(26)	−881(21)	−1 418(13)
C(12)	3 860(20)	1 558(16)	−645(10)	C(48)	4 910(23)	−950(19)	−1 542(11)
C(13)	4 481(21)	1 720(17)	−324(10)	C(49)	3 228(34)	766(28)	−3 869(17)
C(14)	5 035(24)	1 116(19)	−240(12)	C(50)	3 464(32)	928(26)	−3 464(16)
C(15)	4 993(21)	460(17)	−452(11)	C(51)	2 920(36)	1 060(28)	−3 222(17)
C(16)	4 341(20)	316(16)	−733(10)	C(52)	2 131(32)	1 014(26)	−3 351(15)
C(17)	3 202(21)	−1 205(17)	−1 973(10)	C(53)	1 920(35)	814(29)	−3 716(18)
C(18)	2 753(21)	−699(17)	−2 190(10)	C(54)	2 498(37)	644(31)	−3 994(19)
C(19)	2 663(30)	−719(23)	−2 583(15)				

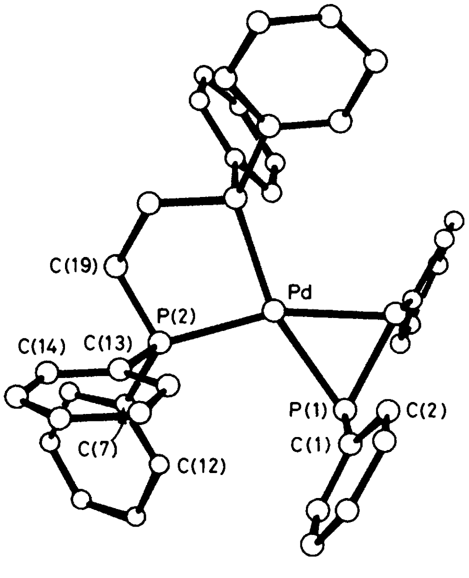


Figure 1. Molecular structure of [Pd(PhP=PPh)(dppe)] (1)

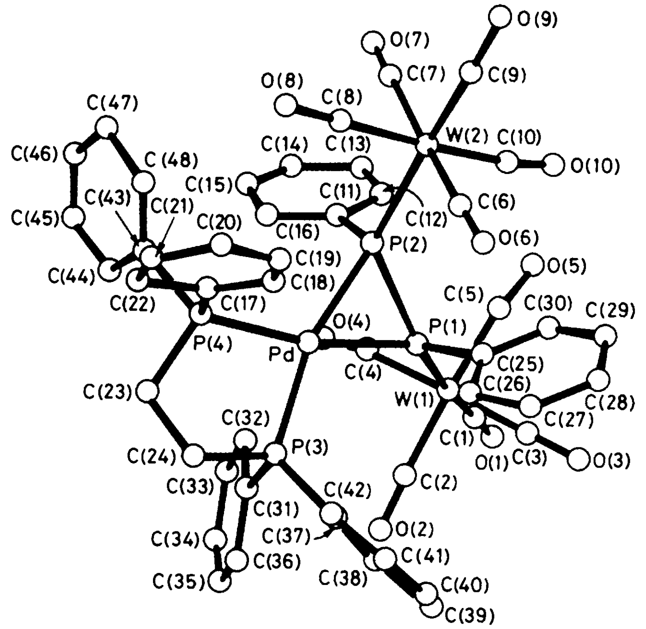


Figure 2. Molecular structure of [Pd{(PhP=PPh)[W(CO)$_5$]$_2$}(dppe)] (2)

[MCl$_2$L$_2$] to give good yields of air-stable orange or yellow crystals, [M(PhP=PPh)L$_2$] [M = Pd, L$_2$ = 1,2-bis(diphenylphosphanyl)ethane (dppe) (1); M = Pt, L$_2$ = dppe or (PPh$_3$)$_2$]. An *X*-ray crystal-structure determination of [Pd(PhP=PPh)(dppe)] (1) and the exceptionally small values of the n.m.r. coupling constants ^1J(PtP) and ^2J(PP$_{trans.}$) led us to suggest that these complexes are best regarded as containing a η^2-(*E*)-diphenyldiphosphene ligand side bonded to palladium(0) or platinum(0).[17]

The η^2-diphosphene has a lone pair of electrons on each of the phosphorus atoms, and the preparation of complexes in which these electrons were also used in co-ordination proved to be straightforward. The reaction between [Pd(PhP=PPh)(dppe)] (1) and two molar proportions of [W(CO)$_5$(thf)] in thf solution at 25 °C gave [Pd{(PhP=PPh)[W(CO)$_5$]$_2$}(dppe)] (2), which was characterized by an *X*-ray crystal-structure determination and by ^{31}P-{^{1}H} n.m.r. spectroscopy. With one molar proportion of [W(CO)$_5$(thf)] complex (1) appeared to give [Pd{(PhP=PPh)[W(CO)$_5$]}(dppe)], a complex in which only one of the diphosphene lone pairs was co-ordinated to tungsten. This product gave satisfactory microanalytical results and a ^{31}P-{^{1}H} n.m.r. spectrum that differed from that of [Pd(PhP=PPh)(dppe)] (1) or its bis(pentacarbonyltungsten) derivative. However, we were not able to simulate the n.m.r. spectrum, so we cannot exclude the possibility that the complex was not pure or undergoes some disproportionation in solution. Treatment of [Pd(PhP=PPh)(dppe)] with an equimolar proportion of [Pd$_2$(μ-Cl)$_2$(PPh$_3$)$_4$][BF$_4$]$_2$ gave a product with microanalysis results in accord with those of the expected product, [Pd{(PhP=PPh)[PdCl(PPh$_3$)$_2$]$_2$}(dppe)][BF$_4$]$_2$, but the complex was not further characterized. Preparations starting from Li$_2$(PhPPPh) are thus capable of leading to heteronuclear complexes with a significant degree of synthetic control, and it is clear that the ligand diphosphenes are suitable for grouping different metal centres in close proximity. The related trinuclear complexes [{M(CO)$_5$}$_3$(PhX=XPh)] (M = Cr, X = As; M = W, X = Sb) have been reported by Huttner *et al.*[27] One of their synthetic methods, the reaction between XPhCl$_2$ and Na$_2$[M$_2$(CO)$_{10}$], appears to be best suited to the formation of homonuclear complexes, but their alternative method (used for the Cr compound) of treating [M(CO)$_5$(AsPhLi$_2$)] with [M(CO)$_5$(AsPhCl$_2$)] may have some potential for the preparation of heterometallic complexes, if, for example, the lithium compound reacts cleanly with AsPhCl$_2$ complexes of other metals.

Crystal-structure Determinations.—The results of the *X*-ray crystal-structure determinations for complexes (1) and (2) are given in Figures 1 and 2 and in Tables 1—5. The crystal of (2) contained a molecule of C$_6$D$_6$ of crystallisation [atoms C(49)—C(54)]. The P–P bond length in (1) [2.121(4) Å] is similar to those in other η^2-diphosphene complexes ([Pt{(C$_6$F$_5$)P=P(C$_6$F$_5$)}(PPh$_3$)$_2$], 2.156(7);[16] [Mo(HP=PH)(η-C$_5$H$_5$)$_2$], 2.146(3);[21] and [Ni(Me$_3$SiP=PSiMe$_3$)(PEt$_3$)$_2$], 2.148(2) Å[19]) and it is about half-way between the lengths (*l*) of the double bonds in the free diphosphenes RP=PR [R, *l*/Å: C$_6$H$_2$Bu$^t_3$-2,4,6, 2.034(2);[3] N(SiMe$_3$)$_2$, 2.034;[13] and C(SiMe$_3$)$_3$, 2.002-(3)[12]] and the single bonds in $\overline{PhP(PPh)_4}$ [2.217(6) Å],[24] and a variety of three-membered rings comprised of two P atoms and one Main Group atom, M (M = B, Si, Ge, P, or S) (2.185—2.246 Å).[23] It is evident that a substantial π-component is retained in the P–P bonds of the η^2 complexes, and the torsion angle C–P–P–C in (1) (163°) shows that the diphosphene is nearly planar and that the C–P bonds are bent away from the Pd atom by only 8.5°.

In the closely related complex [Pt{(C$_6$F$_5$)P=P(C$_6$F$_5$)}(PPh$_3$)$_2$], the angle between the PtP$_2$ planes associated with each ligand is relatively large (20.4°), and there are significant differences between the Pt–P bond lengths for each ligand.[16] These distortions were ascribed to steric effects, and they are not present in (1) where the ligands are less bulky. In particular, pairs of Pd–P bonds in (1) are related by a C_2 axis through the Pd atom and the centre of the P–P bond, and the co-ordination about the Pd atom is nearly planar, with only a 3° twist between the PdP(1)P(1′) and PdP(2)P(2′) planes.

The Pd–P(2) bond length [2.034(2) Å] in (1) is similar to that *trans* to S in [Pd(η^2-S=CS)(PPh$_3$)$_2$] [2.136(8) Å],[28] and it is shorter by 0.062(2) Å than the Pd–P(1) bond. A similar difference (0.07 Å) was found for [Ni(Me$_3$SiP=PSiMe$_3$)(PEt$_3$)$_2$],[19] but the corresponding bonds in [Pt{(C$_6$F$_5$)P=P(C$_6$F$_5$)}(PPh$_3$)$_2$], which are probably perturbed by steric effects,[16] are not significantly different in length.

Table 3. Intramolecular distances (Å) and angles (°) for [Pd(PhP=PPh)(dppe)] (1) with estimated standard deviations in parentheses

Pd–P(1)	2.366(2)	Pd–P(2)	2.304(2)
P(1)–P(1$^{\mathrm{I}}$)	2.121(4)	P(1)–C(1)	1.854(9)
P(2)–C(7)	1.804(7)	P(2)–C(13)	1.816(7)
P(2)–C(19)	1.834(7)	C(1)–C(2)	1.329(12)
C(1)–C(6)	1.353(12)	C(2)–C(3)	1.414(14)
C(3)–C(4)	1.350(15)	C(4)–C(5)	1.310(15)
C(5)–C(6)	1.408(15)	C(7)–C(8)	1.376(11)
C(7)–C(12)	1.368(11)	C(8)–C(9)	1.366(11)
C(9)–C(10)	1.374(14)	C(10)–C(11)	1.345(14)
C(11)–C(12)	1.380(12)	C(13)–C(14)	1.376(10)
C(13)–C(18)	1.365(10)	C(14)–C(15)	1.377(11)
C(15)–C(16)	1.355(12)	C(16)–C(17)	1.350(13)
C(17)–C(18)	1.408(12)	C(19–C(19$^{\mathrm{I}}$)	1.520(13)
Pd–P(1)–P(1$^{\mathrm{I}}$)	63.4(1)	Pd–P(1)–C(1)	102.8(3)
P(1$^{\mathrm{I}}$)–P(1)–C(1)	101.9(3)	Pd–P(2)–C(7)	123.4(2)
Pd–P(2)–C(13)	115.8(3)	Pd–P(2)–C(19)	105.4(2)
C(7)–P(2)–C(13)	102.7(3)	C(7)–P(2)–C(19)	104.6(3)
C(13)–P(2)–C(19)	102.7(3)	P(1)–C(1)–C(2)	126.1(8)
P(1)–C(1)–C(6)	115.1(8)	C(2)–C(1)–C(6)	119(1)
C(1)–C(2)–C(3)	120(1)	C(2)–C(3)–C(4)	120(1)
C(3)–C(4)–C(5)	121(1)	C(4)–C(5)–C(6)	119(1)
C(1)–C(6)–C(5)	121(1)	P(2)–C(7)–C(8)	124.6(7)
P(2)–C(7)–C(12)	118.4(6)	C(8)–C(7)–C(12)	117.0(7)
C(7)–C(8)–C(9)	122.0(9)	C(8)–C(9)–C(10)	120.0(9)
C(9)–C(10)–C(11)	118.8(9)	C(10)–C(11)–C(12)	121(1)
C(7)–C(12)–C(11)	121.1(9)	P(2)–C(13)–C(14)	122.7(7)
P(2)–C(13)–C(18)	118.3(6)	C(14)–C(13)–C(18)	119.1(7)
C(13)–C(14)–C(15)	120.3(8)	C(14)–C(15)–C(16)	121.3(8)
C(15)–C(16)–C(17)	118.8(8)	C(16)–C(17)–C(18)	121.3(9)
C(13)–C(18)–C(17)	119.2(8)	P(2)–C(19)–C(19$^{\mathrm{I}}$)	109.6(4)
P(1)–Pd–P(1$^{\mathrm{I}}$)	53.3(1)	P(2)–Pd–P(2$^{\mathrm{I}}$)	86.7(1)
P(1)–Pd–P(2)	110.0(1)		

Symmetry element: I 1 − *x*, *y*, 0.5 − *z*.

Table 4. Deviations (Å) (shown in square brackets) of atoms from various mean planes for [Pd(PhP=PPh)(dppe)] (1)

Plane 1: Pd, P(1), P(1$^{\mathrm{I}}$)
Plane 2: Pd, P(2), P(2$^{\mathrm{I}}$)
Plane 3: C(1), P(1), P(1$^{\mathrm{I}}$)
Plane 4: P(1), P(1$^{\mathrm{I}}$), C(1$^{\mathrm{I}}$)
Plane 5: C(1) [0.03], C(2) [−0.02], C(3) [0.00], C(4) [0.01], C(5) [0.00], C(6) [−0.02]
Plane 6: C(7) [0.00], C(8) [0.00], C(9) [0.00], C(10) [0.00], C(11) [0.00], C(12) [0.00]
Plane 7: C(13) [0.01], C(14) [0.00], C(15) [0.01], C(16) [−0.01], C(17) [0.00], C(18) [0.01]

Angles (°) between planes: 1—2, 3; 3—4, 17; 3—5, 3; and 6—7, 97.

The results for complexes (1) and (2) permit for the first time a comparison to be made between structures containing a single diphosphene (PhP=PPh) in different states of co-ordination. The crystallographic C_2 axis in (1) is replaced by a similar approximate axis in (2), and for the purpose of discussion we use the average of values of parameters related by this axis. Apart from the changes imposed by the difference in the lengths of the P–P bonds, the immediate co-ordination spheres of the Pd atoms are remarkably similar in the two complexes. Comparison between (1) and (2) of the corresponding bond angles at Pd reveals no difference greater than 2°, the corresponding Pd–P bond lengths are identical, and in both complexes the angle between the PdP$_2$(dppe) and the PdP$_2$(diphosphene) planes is 3°. This suggests that any electronic effects induced by the W(CO)$_5$ groups may be confined mainly to the diphosphene moiety.

In (2) the tungsten atoms and the carbon atoms C(11) and C(25) occupy quite different positions in relation to the P–P bond. The C–P–P angles (104.7°) are slightly wider than in (1) (101.9°), and the P–C bonds are bent away from the Pd atom by 12° compared with 8.5° in (1). The W–P–P angles (127.7°) and the bending back of the P–W bonds (32°) are much greater, and although these angles could indicate the directions of the diphosphene lone pairs, there are indications that the bulk of the W(CO)$_5$ groups has some effect on the structure. Comparison of Figures 1 and 2 shows that the phenyl groups change position to accommodate the W(CO)$_5$ groups, and the steric pressure on the W(CO)$_5$ groups is evident from the nonlinearity of several of the W–CO groups and in some anomalous bond angles subtended by the tungsten atoms (Table 5).

Steric pressures involving the W(CO)$_5$ groups may also contribute to the lengthening of the P–P bond from 2.121(4) Å in (1) to 2.186(6) Å in (2). In the complex $[\{\mathrm{Fe(CO)_4}\}_2\{(\mathrm{Me_3Si})_2\mathrm{CHP{=}PCH(SiMe_3)_2}\}]$,[29] in which the diphosphene is planar and co-ordinates to Fe through the lone pairs, the P–P bond [2.039(1) Å] is only slightly longer than in the free diphosphene $(\mathrm{Me_3Si})_3\mathrm{CP{=}PC(SiMe_3)_3}$ (2.002 Å).[12] Steric or electronic effects on the length of the P–P bond in (2) are, however, expected to be larger, because the potential energy curve for the longer P–P bond in (2) will be less steep than that for the free diphosphene.

The W–P bonds in (2) [2.521(5) Å] are shorter than in $[\mathrm{W(CO)_5(PBu^t{}_3)}]$ [2.686(4) Å],[30] which contains a very hindered phosphane, and they are slightly longer than those in $[\mathrm{W(CO)_4}\{\overline{\mathrm{MeP}}(\mathrm{PMe})_5\}]$ [2.502(7) Å],[31] but the assessment of the significance of the W–P bond length is inhibited by the paucity of results for W^0 complexes with P *trans* to CO.

^{31}P-{^{1}H} *N.M.R. Spectra.*—The ^{31}P-{^{1}H} n.m.r. spectra of the complexes [M(PhP=PPh)L$_2$] comprise two groups of lines each of which is roughly triplet in character (with additional coupling to ^{195}Pt for M = Pt), but which shows the fine structure expected from an [AX]$_2$ system. This establishes that any rotation of the diphosphene about the C_2 axis must be slow on the n.m.r. time-scale. Similar spectra have been reported for the nickel complexes $[\mathrm{Ni(Me_3SiP{=}PSiMe_3)(PR_3)_2}]$ (R = Me, Et, or Bu^n), for which the triplet character was attributed to the near equality of the indirect couplings ^2J(PP)(*trans*) and ^2J(PP)(*cis*) between the non-equivalent ^{31}P nuclei.[18] However, such triplet character may also arise from strong coupling between one of the pairs of chemically equivalent nuclei. Thus the ^{1}H n.m.r. spectrum of the HP=PH moiety in the complex $[\mathrm{Mo(HP{=}PH)(\eta\text{-}C_5H_5)_2}]$, which is also triplet in character,[20] suggests strongly that ^1J(PP) is relatively large for the diphosphene ligands. This was confirmed by the simulation of the spectra of the complexes [M(PhP=PPh)L$_2$], which showed that $|^1J(\mathrm{PP})|$ is greater than *ca.* 350 Hz (Figure 3, Table 6). The form of the spectra was shown to be rather insensitive to the value of $|^1J(\mathrm{PP})|$ for $|^1J(\mathrm{PP})| > 340$ Hz, so the values given are best regarded as giving an approximate lower limit to the magnitude of $|^1J(\mathrm{PP})|$.

The results of the simulation were in accord with our earlier conclusion that the magnitudes of the couplings between the *trans* disposed ^{31}P nuclei, ^2J(PP)(*trans*), are unusually small (*ca.* 60 Hz).[17] The couplings between the ^{31}P nuclei in *cis* disposition are expectedly close to zero. The small magnitudes of the *trans* couplings and of the couplings to platinum, ^1J(PtP) (*ca.* 260 Hz), appear to provide a striking illustration of the dependence of such couplings on the *s* character of the phosphorus donor orbital. For square-planar triorganophosphane complexes of Pd or Pt, *trans* couplings ^2J(PP) are

Table 5. Intramolecular distances (Å) and angles (°) for $[\mathrm{Pd}\{(\mathrm{PhP{=}PPh})[\mathrm{W(CO)_5}]_2\}(\mathrm{dppe})]$ (2) with estimated standard deviations in parentheses

W(1)–P(1)	2.521(5)	W(1)–C(1)	1.86(2)
W(1)–C(2)	1.98(2)	W(1)–C(3)	2.00(2)
W(1)–C(4)	2.08(2)	W(1)–C(5)	2.02(2)
W(2)–P(2)	2.542(5)	W(2)–C(6)	2.10(3)
W(2)–C(7)	2.07(3)	W(2)–C(8)	1.89(2)
W(2)–C(9)	1.83(2)	W(2)–C(10)	1.92(2)
Pd–P(1)	2.375(4)	Pd–P(2)	2.355(4)
Pd–P(3)	2.305(4)	Pd–P(4)	2.307(5)
P(1)–P(2)	2.186(6)	P(1)–C(25)	1.80(2)
P(2)–C(11)	1.84(2)	P(3)–C(24)	1.81(2)
P(3)–C(31)	1.79(2)	P(3)–C(37)	1.84(2)
P(4)–C(17)	1.81(2)	P(4)–C(23)	1.80(2)
P(4)–C(43)	1.84(2)	O(1)–C(1)	1.23(2)
O(2)–C(2)	1.21(2)	O(3)–C(3)	1.20(2)
O(4)–C(4)	1.13(2)	O(5)–C(5)	1.16(2)
O(6)–C(6)	1.12(2)	O(7)–C(7)	1.15(2)
O(8)–C(8)	1.25(2)	O(9)–C(9)	1.28(2)
O(10)–C(10)	1.17(2)	C(11)–C(12)	1.39(2)
C(11)–C(16)	1.43(2)	C(12)–C(13)	1.47(2)
C(13)–C(14)	1.48(2)	C(14)–C(15)	1.43(2)
C(15)–C(16)	1.41(2)	C(17)–C(18)	1.38(2)
C(17)–C(22)	1.45(3)	C(18)–C(19)	1.35(3)
C(19)–C(20)	1.29(3)	C(20)–C(21)	1.34(3)
C(21)–C(22)	1.61(4)	C(23)–C(24)	1.59(2)
C(25)–C(26)	1.42(2)	C(25)–C(30)	1.44(2)
C(26)–C(27)	1.47(2)	C(27)–C(28)	1.40(2)
C(28)–C(29)	1.36(2)	C(29)–C(30)	1.44(2)
C(31)–C(32)	1.43(2)	C(31)–C(36)	1.47(2)
C(32)–C(33)	1.53(3)	C(33)–C(34)	1.46(3)
C(34)–C(35)	1.37(3)	C(35)–C(36)	1.35(3)
C(37)–C(38)	1.26(3)	C(37)–C(42)	1.50(3)
C(38)–C(39)	1.55(4)	C(39)–C(40)	1.45(4)
C(40)–C(41)	1.22(3)	C(41)–C(42)	1.39(3)
C(43)–C(44)	1.39(3)	C(43)–C(48)	1.36(3)
C(44)–C(45)	1.46(3)	C(45)–C(46)	1.35(3)
C(46)–C(47)	1.39(3)	C(47)–C(48)	1.52(3)
C(49)–C(50)	1.45(4)	C(49)–C(54)	1.27(4)
C(50)–C(51)	1.32(4)	C(51)–C(52)	1.35(4)
C(52)–C(53)	1.33(4)	C(53)–C(54)	1.47(4)

P(1)–W(1)–C(1)	175.7(6)	P(1)–W(1)–C(2)	98.5(5)
P(1)–W(1)–C(3)	90.0(6)	P(1)–W(1)–C(4)	92.3(5)
P(1)–W(1)–C(5)	86.9(5)	C(1)–W(1)–C(2)	85.7(8)
C(1)–W(1)–C(3)	89.3(8)	C(1)–W(1)–C(4)	88.5(8)
C(1)–W(1)–C(5)	88.8(7)	C(2)–W(1)–C(3)	87.8(7)
C(2)–W(1)–C(4)	90.3(7)	C(2)–W(1)–C(5)	174.2(7)
C(3)–W(1)–C(4)	177.2(8)	C(3)–W(1)–C(5)	90.2(6)
C(4)–W(1)–C(5)	91.5(6)	P(2)–W(2)–C(6)	94.7(7)
P(2)–W(2)–C(7)	91.0(7)	P(2)–W(2)–C(8)	92.5(6)
P(2)–W(2)–C(9)	177.4(7)	P(2)–W(2)–C(10)	86.8(5)
C(6)–W(2)–C(7)	172(1)	C(6)–W(2)–C(8)	91.1(9)
C(6)–W(2)–C(9)	83.6(9)	C(6)–W(2)–C(10)	94.1(8)
C(7)–W(2)–C(8)	82.7(9)	C(7)–W(2)–C(9)	90.9(9)
C(7)–W(2)–C(10)	92.3(8)	C(8)–W(2)–C(9)	89.5(8)
C(8)–W(2)–C(10)	174.9(8)	C(9)–W(2)–C(10)	91.4(8)
P(1)–Pd–P(2)	55.1(2)	P(1)–Pd–P(3)	107.6(2)
P(1)–Pd–P(4)	167.6(2)	P(2)–Pd–P(3)	162.6(2)
P(2)–Pd–P(4)	112.7(2)	P(3)–Pd–P(4)	84.7(2)
W(1)–P(1)–Pd	129.8(2)	W(1)–P(1)–P(2)	128.8(2)
W(1)–P(1)–C(25)	113.6(5)	Pd–P(1)–P(2)	62.0(2)
Pd–P(1)–C(25)	108.0(5)	P(2)–P(1)–C(25)	103.8(6)
W(2)–P(2)–Pd	131.9(2)	W(2)–P(2)–P(1)	126.6(2)
W(2)–P(2)–C(11)	112.9(5)	Pd–P(2)–P(1)	62.9(1)
Pd–P(2)–C(11)	106.6(5)	P(1)–P(2)–C(11)	105.7(6)
Pd–P(3)–C(24)	108.5(6)	Pd–P(3)–C(31)	110.2(6)
Pd–P(3)–C(37)	119.4(6)	C(24)–P(3)–C(31)	99.9(8)
C(24)–P(3)–C(37)	107.3(8)	C(31)–P(3)–C(37)	109.8(8)
Pd–P(4)–C(17)	108.8(6)	Pd–P(4)–C(23)	108.3(6)
Pd–P(4)–C(43)	123.7(6)	C(17)–P(4)–C(23)	106.5(8)
C(17)–P(4)–C(43)	107.1(9)	C(23)–P(4)–C(43)	101.3(8)

Table 5 *(continued)*

W(1)–C(1)–O(1)	176(2)	W(1)–C(2)–O(2)	176(2)
W(1)–C(3)–O(3)	177(2)	W(1)–C(4)–O(4)	171(2)
W(1)–C(5)–O(5)	171(1)	W(2)–C(6)–O(6)	175(2)
W(2)–C(7)–O(7)	175(2)	W(2)–C(8)–O(8)	175(2)
W(2)–C(9)–O(9)	175(2)	W(2)–C(10)–O(10)	171(1)
P(2)–C(11)–C(12)	116(1)	P(2)–C(11)–C(16)	119(1)
C(12)–C(11)–C(16)	124(1)	C(11)–C(12)–C(13)	122(2)
C(12)–C(13)–C(14)	112(2)	C(13)–C(14)–C(15)	124(2)
C(14)–C(15)–C(16)	121(2)	C(11)–C(16)–C(15)	116(1)
P(4)–C(17)–C(18)	123(2)	P(4)–C(17)–C(22)	114(2)
C(18)–C(17)–C(22)	123(2)	C(17)–C(18)–C(19)	122(2)
C(18)–C(19)–C(20)	123(2)	C(19)–C(20)–C(21)	122(3)
C(20)–C(21)–C(22)	122(2)	C(17)–C(22)–C(21)	108(2)
P(4)–C(23)–C(24)	107(1)	P(3)–C(24)–C(23)	110(1)
P(1)–C(25)–C(26)	121(1)	P(1)–C(25)–C(30)	118(1)
C(26)–C(25)–C(30)	121(1)	C(25)–C(26)–C(27)	119(1)
C(26)–C(27)–C(28)	119(2)	C(27)–C(28)–C(29)	121(2)
C(28)–C(29)–C(30)	122(2)	C(25)–C(30)–C(29)	117(1)
P(3)–C(31)–C(32)	115(1)	P(3)–C(31)–C(36)	125(1)
C(32)–C(31)–C(36)	120(2)	C(31)–C(32)–C(33)	114(2)
C(32)–C(33)–C(34)	123(2)	C(33)–C(34)–C(35)	117(2)
C(34)–C(35)–C(36)	124(2)	C(31)–C(36)–C(35)	122(2)
P(3)–C(37)–C(38)	123(2)	P(3)–C(37)–C(42)	111(2)
C(38)–C(37)–C(42)	126(2)	C(37)–C(38)–C(39)	121(3)
C(38)–C(39)–C(40)	105(3)	C(39)–C(40)–C(41)	134(3)
C(40)–C(41)–C(42)	120(3)	C(37)–C(42)–C(41)	113(2)
P(4)–C(43)–C(44)	119(2)	P(4)–C(43)–C(48)	117(2)
C(44)–C(43)–C(48)	124(2)	C(43)–C(44)–C(45)	117(2)
C(44)–C(45)–C(46)	117(2)	C(45)–C(46)–C(47)	129(2)
C(46)–C(47)–C(48)	112(2)	C(43)–C(48)–C(47)	120(2)
C(50)–C(49)–C(54)	122(4)	C(49)–C(50)–C(51)	121(3)
C(50)–C(51)–C(52)	119(3)	C(51)–C(52)–C(53)	119(3)
C(52)–C(53)–C(54)	124(3)	C(49)–C(54)–C(53)	114(4)

typically *ca.* 500 Hz, and values of ^1J(PtP) are usually greater than 2 000 Hz.[32] The structure of (1) shows that the diphosphene in the η^2 configuration remains nearly planar (C–P–P–C torsion angle 163°), which implies a hybridization scheme in which the diphosphene uses orbitals of high *p*- and low *s*-character to bind to the metal. The coupling ^2J(PP)(*trans*) is of larger magnitude in the bis(pentacarbonyltungsten) derivative (2) (Table 1) and in (2) the torsion angles W–P–P–W (−116°) and C–P–P–C (156°) indicate that the *s* character of the electrons in the η^2 linkage may be increased by the co-ordination to tungsten.

The close parallel between the coupling constants ^1J(PtC) in organoplatinum compounds and ^1J(PtP) in their phospha-analogues has been described in our earlier report.[17] However, it is known, for example from studies of ^1J(PtSe) in $\mathrm{SeMe_2}$ complexes,[33] that the presence of a lone pair on the donor atom can give a negative contribution to the coupling constants. The direct dependence of the Fermi-contact contribution to the couplings on the *s* character of the phosphorus bonding orbital ensures that the couplings are small when the *s* character is low, and, as indicated above, a simple hybridization model based on the structures of the η^2 complexes implies that the phosphorus donor orbital has a low *s* character. Nevertheless, the coupling constants in the phosphorus-containing η^2 complexes in comparison with the coupling constants ^1J(PtC) in the η^2-alkene and -alkyne complexes are smaller than expected from hybridization effects alone, so it is probable that excitations involving the phosphorus lone pair lead to a further reduction in the magnitudes of the coupling constants in the η^2 complexes.

We also prepared the known complexes $[\mathrm{M}\{(\mathrm{C_6F_5})\mathrm{P{=}P}(\mathrm{C_6F_5})\}(\mathrm{PPh_3})_2]$ (M = Pd or Pt)[16] in order to record their ^{31}P-{^{1}H} n.m.r. spectra. The chemical shifts, ^1J(PtP) for the $\mathrm{PPh_3}$ ligand, and $|^2J(\mathrm{PP})(trans) + {}^2J(\mathrm{PP})(cis)|$ are all similar to the values in our complexes. Unfortunately, the spectra of

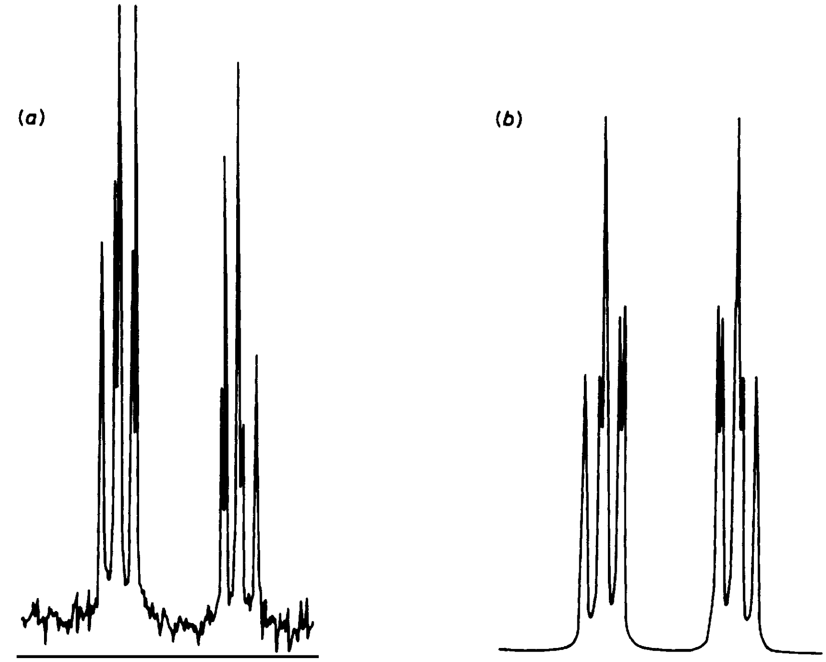


Figure 3. (*a*) ^{31}P-{^{1}H} N.m.r. spectrum of [Pd(PhP=PPh)(dppe)] (1); (*b*) spectrum simulated with parameters as given in Table 6

Table 6. ^{31}P-{^{1}H} N.m.r. parameters of complexes [M(diphosphene)L$_2$] in benzene

	Diphosphene					L_2	
Complex	δ/p.p.m.	^{1}J(PtP)/Hz	^{1}J(PP)/Hz [a]	^{2}J(PP)(*trans*)/Hz [a]	^{2}J(PP)(*cis*)/Hz [a]	δ/p.p.m.	^{1}J(PtP)/Hz
[Pd(PhP=PPh)(dppe)] (1)	34.3	—	348 [b]	+60	+1	41.0	—
[Pd{(PhP=PPh)[W(CO)$_5$]$_2$}(dppe)] (2)	17.0	—	344 [c]	+155	14	39.0	—
[Pd{(C$_6$F$_5$)P=P(C$_6$F$_5$)}(PPh$_3$)$_2$]	32.0	—	*d*	← *ca.* 50 [e] →		24.8	—
[Pd{(C$_6$F$_5$)P=P(C$_6$F$_5$)}(dppe)]	1.7	—	*d*	← *ca.* 62 [e] →		52.1	—
[Pt(PhP=PPh)(dppe)]	−23.5	264	350 [b]	+64	0	55.6	3 071
[Pt(PhP=PPh)(PPh$_3$)$_2$]	18.1	288	669 [b]	+60	+4	28.3	3 353
[Pt(PhP=PPh)(PMe$_2$Ph)$_2$]	4.5	239	*f*	*f*		−9	*f*
[Pt{(C$_6$F$_5$)P=P(C$_6$F$_5$)}(PPh$_3$)$_2$]	−22	—	*c*	← *ca.* 65 [e] →		27.8	3 405

[a] Coupling constants and their relative signs were determined by iteration. The signs given are based on ^{1}J(PP) < 0 (E. G. Finer and R. K. Harris, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1971, **6**, 61). [b] Simulated spectrum is insensitive to larger values of $|^{1}J(\mathrm{PP})|$; see text. [c] Simulated spectrum significantly dependent on ^{1}J(PP). [d] Spectrum complicated by coupling to ^{19}F. [e] $|^{2}J(\mathrm{PP})(trans) + {}^{2}J(\mathrm{PP})(cis)|$ estimated from separation of outer lines of 'virtual triplet'. [f] Resonance of PMe$_2$Ph broadened by exchange.

the diphosphene ligand were greatly complicated by coupling to ^{19}F, and even when the palladium complex was converted to its dppe analogue to increase the shift difference between the non-equivalent ^{31}P nuclei and thus reduce the second-order character of the spectrum, the complexity of the spectrum still precluded the determination of the coupling constants involving the diphosphene ligand. Since, however, the overall width of the diphosphene spectrum in the platinum complex is *ca.* 375 Hz, it is clear that the magnitude of ^{1}J(PtP) cannot differ substantially from those in the PhP=PPh complex.

When the complex [PtCl$_2$(PMe$_2$Ph)$_2$] was treated with Li$_2$(PhPPPh), an orange product was obtained, but the microanalytical results were unsatisfactory, and the product had a strong odour of the phosphane. The ^{31}P-{^{1}H} n.m.r. spectrum of a solution in thf comprised a resonance at $\delta_P = -4.5$ p.p.m. with ^{1}J(PtP) = 239 Hz, and a second broad resonance at −9 p.p.m. which did not become sharp when the solution was cooled to −60 °C. The magnitude of the coupling constant ^{1}J(PtP) is sufficiently distinctive to be certain that a diphosphene complex is formed; evidently the PMe$_2$Ph ligands undergo rapid and reversible dissociation, thus averaging to zero all the couplings to them.

The chemical shifts of the diphosphenes in all the complexes we examined lie within 35 p.p.m. of the reference (85% H$_3$PO$_4$) and the coupling constants ^{1}J(PP) derived from the simulated spectra are greater than 340 Hz in the η^2-PhP=PPh complexes and *ca.* 350 Hz in [Pd{(PhP=PPh)[W(CO)$_5$]$_2$}(dppe)] (2). These values differ substantially from those for free diphosphenes, for which the shifts lie between 450 and 600 p.p.m. and the couplings ^{1}J(PP) between 540 and 590 Hz.[3–7,11,13,15] This comparison could be affected by differences in the organic substituents in the free and co-ordinated diphosphenes, but the shifts for the free diphosphenes do not depend greatly on the bulk or composition of the organic groups. The closest comparison that can be made with the PhP=PPh complexes is with an unstable compound with an unsubstituted phenyl substituent, PhP=PC$_6$H$_2$Bu$^t_3$-2,4,6, for which ^{1}J(PP) = 549 Hz and the shift of the PPh moiety is 525.5 p.p.m.[7]

The very high frequency shifts of the free diphosphenes appear to derive from the electrons in the unperturbed P–P double bond. The small shift difference (17 p.p.m.) between (1) and its bis(pentacarbonyltungsten) derivative (2) indicates that the high-frequency shifts do not derive from the lone pairs on phosphorus, which would be perturbed by donation to tungsten. The shift for $[\{Fe(CO)_4\}_2(Me_3SiP{=}PSiMe_3)]$,[29] in which only the phosphorus lone pairs are used in co-ordination, is 384.5 p.p.m., and this differs by *ca.* 130 p.p.m. from the shift reported for the $(Me_3Si)_2CH$-substituted P in $(Me_3Si)_2CHP{=}PC_6H_2Bu^t_3$-2,4,6 (513 p.p.m.).[15] However, the P–P double bond may be slightly perturbed in the Fe compound, since, as noted above, the P–P bond is likely to be slightly longer than in the free diphosphene. In the RP=PR (R = Ph or C_6F_5) complexes of Table 6, and in the complexes $[Ni(Me_3SiP{=}PSiMe_3)(PR_3)_2]$ (R = Me, Et, or Bu^n), where the shifts are at much lower frequencies ($\delta_P = -61.5$ to -71.5 p.p.m. for the Ni complexes),[18] the P–P bonds are at least 0.08 Å longer than in the free diphosphenes,[16,18] indicating extensive perturbation of the P–P π electrons.

In $[Pd\{(PhP{=}PPh)[W(CO)_5]_2\}(dppe)]$ (2), the only diphosphene complex for which a reliable result appears to be available, the coupling constant $^1J(PP)$ (344 Hz) is smaller by more than 200 Hz than in the free diphosphenes. This is probably a consequence of the lengthening of the bond on co-ordination, since in the three-membered ring compounds, $Bu^tP{-}P(Bu^t){-}XR_n$ (X = Si, Ge, P, or another Main Group element), where the P–P bonds are even longer (*e.g.* 2.226 Å for X = Si), the coupling constants $^1J(PP)$ are relatively small (75—250 Hz).[23]

Comparison with Organometallic Compounds.—There are close analogies between the diphosphene complexes studied here and the alkene and alkyne complexes extensively studied at the ICI laboratories at 'The Frythe' (ref. 34 and earlier papers in the same series). The idea that π electrons of alkenes could function in the same way as a lone pair on simple Lewis bases came from F. G. Mann in his undergraduate lectures (Cambridge, 1936); the concept of dative π-bonding or back-donation was added in 1949.[35] The acceptor orbitals on the alkene were identified by Dewar,[36] and the resulting bonding model as developed for platinum complexes accommodated the i.r. and other physical measurements and provided the prototype for the bonding between unsaturated molecules and transition metals.[37] In the η^2-diphosphene complexes the donation from the p_π–p_π orbital is accompanied by back-donation into the corresponding π^* orbital, and their structures and n.m.r. coupling constants confirm that little *s* character is present in the η^2 linkage.

The possibilities for attaching other acceptors to the lone pairs of the diphosphenes is an additional feature not possessed by the alkenes, and in the tetrahedral cluster $[Fe_2(CO)_6(Bu^tPPBu^t)]$ the analogy (or more explicitly, the isolobal relationship[38]) between $(RP{=}PR)^{2+}$ and alkynes is exemplified.[39]

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