Organometallic Chemistry of Diphosphazanes. Part 7.[1] Platinum(II), Palladium-(0), -(I) and -(II) Complexes of RN[P(OPh)$_2$]$_2$ (R = Me or Ph)†

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The reactions of [MCl$_2$(cod)] (M = Pd or Pt, cod = cycloocta-1,5-diene) with RN[P(OPh)$_2$]$_2$ [R = Me (L^1) or Ph (L^2)] afford the chelate complexes [MCl$_2$L^1] and [MCl$_2$L^2]. The dinuclear palladium(0) complex, [Pd$_2$L$^1_3$] has been synthesized by starting from [Pd$_2$(dba)$_3$] (dba = dibenzylideneacetone). Redox condensation of [Pd$_2$(dba)$_3$] and [PdCl$_2$(PhCN)$_2$] in the presence of the diphosphazane ligands gives the dinuclear palladium(I) complexes [Pd$_2$Cl$_2$L$^1_2$] and [Pd$_2$Cl$_2$L$^2_2$]. The structures of the complexes have been deduced from ^{1}H and ^{31}P NMR spectroscopic data. Single-crystal X-ray diffraction studies confirm the structures of [Pd$_2$L$^1_3$] and [Pd$_2$Cl$_2$L$^2_2$].

Continuing our interest in the organometallic chemistry of diphosphazanes,[2–5] we report in this paper the synthesis and structural characterization of palladium-(0), -(I), -(II) and platinum(II) complexes of RN[P(OPh)$_2$]$_2$ [R = Me (L^1) or Ph (L^2)] ligands. Diphosphazane complexes of Group 6, 7, 8 and 9 elements have been investigated extensively. Among the Group 10 elements, only the nickel chemistry has received some attention; studies of platinum and palladium complexes of diphosphazanes surprisingly have been sparse[6] although the first palladium complex of a diphosphazane *viz.* [PdCl$_2${EtN(PPh$_2$)$_2$}] was reported by Ewart *et al.*[7] in 1964. Subsequently, Du Preez *et al.*[8] have reported the synthesis of [MCl$_2${EtN[P(OR)$_2$]$_2$}] (M = Pd or Pt, R = Pr^i or Ph). Recently Uson *et al.*[9] have reported the synthesis and the crystal structure of the dipalladium(I) complex, [Pd$_2$Cl$_2$(dppa)$_2$].‡ A preliminary account of the work described in this paper has appeared in the proceedings of two conferences.[4,5]

Experimental

All manipulations were carried out under a nitrogen atmosphere by using standard Schlenk-line techniques.[10] Solvents were distilled under nitrogen and degassed prior to use. The ligands L^1 and L^2 were prepared as described previously.[11] Palladium and platinum complexes such as [MCl$_2$(cod)] (M = Pd or Pt), [PdCl$_2$(PhCN)$_2$] and [Pd$_2$(dba)$_3$]·CHCl$_3$ used as precursors were prepared according to standard literature methods.[12,13]

The NMR spectra were recorded on Varian T-60 (^{1}H NMR, standard SiMe$_4$) and Varian FT-80A spectrometers (^{31}P NMR, 85% H$_3$PO$_4$ external reference). All NMR chemical shifts are expressed on the δ scale with upfield shifts negative. Elemental analyses were obtained from City University London.

Syntheses.—*cis*-[MCl$_2$L] (M = Pd, L = L^1 **1** *or* L^2 **2**; M = Pt, L = L^1 **3** *or* L^2 **4**). A mixture of [MCl$_2$(cod)] (1.0 mmol) and L (1.0 mmol) in CH$_2$Cl$_2$ (30 cm^3) was stirred at 30 °C for 30 min. The solution was filtered, the filtrate concentrated to 10 cm^3 and light petroleum (b.p. 60–80 °C) (50 cm^3) was added to obtain a precipitate of *cis*-[MCl$_2$L] **1**–**4**. Analytically pure samples were obtained by recrystallization from a 1:3 mixture of CH$_2$Cl$_2$ and light petroleum. The IR spectra of complexes **1**–**4** show ν(M–Cl) in the range 285–300 cm^{-1}.

[Pd$_2$Cl$_2$L$_2$] (L = L^1 **5** *or* L^2 **6**). Under a nitrogen atmosphere, a 100 cm^3 Schlenk flask containing a magnetic stirrer bar was charged with oxygen-free CH$_2$Cl$_2$ (30 cm^3), [PdCl$_2$(PhCN)$_2$] (2.0 mmol), [Pd$_2$(dba)$_3$]·CHCl$_3$ (1.0 mmol) and L (4.0 mmol). The mixture was heated under reflux for 50 min. The orange-red solution was cooled and filtered. The filtrate was concentrated to 10 cm^3 and methanol (25 cm^3) was added. The solution was cooled to 0 °C to obtain [Pd$_2$Cl$_2$L$_2$] **5** or **6**. IR (Nujol): ν(Pd–Cl) 270 (**5**), 275 cm^{-1} (**6**).

[Pd$_2$L$^1_3$] **7**. The complex [Pd$_2$(dba)$_3$]·CHCl$_3$ (0.30 g, 0.29 mmol) was dissolved in benzene (25 cm^3) and L^1 (0.53 g, 1.15 mmol) also in benzene (15 cm^3) was added dropwise with stirring. Stirring was continued for 2 h and the solvent was evaporated under reduced pressure. The oily residue was dissolved in a 1:3 mixture of CH$_2$Cl$_2$ and light petroleum and the solution was cooled to 0 °C to give an orange-red precipitate of **7** along with dba. The precipitate was washed three or four times with hot light petroleum to remove the latter. An analytically pure sample was obtained by recrystallization from a 1:3 mixture of CH$_2$Cl$_2$ and light petroleum.

X-Ray Crystal Structure Analyses of [Pd$_2$Cl$_2$L$^2_2$] **6** *and* [Pd$_2$L$^1_3$] **7**.—Single crystals of the compounds **6** and **7** for X-ray diffraction study were grown from CH$_2$Cl$_2$–light petroleum (1:2). A suitable crystal of each compound was glued to a glass fibre and coated with paraffin oil to protect it from air and moisture. Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα radiation. The unit-cell parameters of **6** were obtained and refined by using 25 randomly selected well-centred reflections in the range 20 < 2θ < 40°; the cell parameters of **7** were similarly determined by using 25 reflections in the range 18 < 2θ < 38°. Three reflections, monitored throughout the data collection, showed no significant change in intensities for either structure. The details pertaining to data collection and refinement are listed in Table 1. The structures were solved by conventional Patterson and Fourier techniques and refined by full-matrix

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

‡ Abbreviations used: cod = cycloocta-1,5-diene; dba = dibenzylideneacetone; dppm = bis(diphenylphosphino)methane; dppe = 1,2-bis(diphenylphosphino)ethane; dppp = 1,3-bis(diphenylphosphino)propane; dppa = bis(diphenylphosphino)amine; dmpm = bis(dimethylphosphino)methane.

Table 1 Crystal data for complexes **6** and **7**

	6	**7**
Formula	$C_{60}H_{50}Cl_2N_2O_8P_4Pd_2$	$C_{75}H_{69}N_3O_{12}P_6Pd_2$
M	1334.7	1603.0
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbcn*	*C*2/*c*
a/Å	12.942(1)	22.228(6)
b/Å	20.043(2)	15.989(5)
c/Å	22.246(2)	44.279(8)
β/°	—	94.07(1)
U/Å^3	5771(1)	15 697(7)
Z	4	8
D_c/g cm^{-3}	1.536	1.357
Crystal size/mm	0.3 × 0.3 × 0.2	0.25 × 0.25 × 0.15
F(000)	2696	6544
μ(Mo-Kα)/cm^{-1}	8.71	6.28
T/°*C*	19	19
Scan method	ω–2θ	ω–2θ
Octants (collected)	$+h, +k, +l$	$+h, +k, \pm l$
2θ Range/°	50	46
Decay (%)	< 1	< 2
Total reflections	5220	11 838
Unique reflections	4657	10 874
Observed reflections (N_o)	2396 [$I \geqslant 2.5\sigma(I)$]	4426 [$I \geqslant 3\sigma(I)$]
No. of parameters refined (N_p)	354	883
R^a	0.040	0.079
R'^b	0.045	0.085
g	0	0.0097
S^c	1.63	1.02
Maximum shift/e.s.d.	0.017	0.028

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$ $w = [(\sigma^2|F_o|) + g(|F_o|)^2]^{-1}$ [c] $S = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{\frac{1}{2}}$

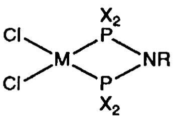
least-squares treatment.[14a] The scattering factors of the various atoms were taken from refs. 14(*a*) and 14(*b*). For compound **7**, in the final difference map, a few peaks with electron density in the range 1.00–1.33 e Å^{-3} were observed near one of the phenyl rings. The ^{1}H NMR spectrum of the compound showed a peak at δ 5.29 due to the presence of CH_2Cl_2 while the C, H, N analytical data were in accord with the incorporation of half a molecule of CH_2Cl_2 per molecule of **7**. Attempts to refine the structure by assigning the residual peaks to solvent molecules were not successful presumably because of disorder in their positions in the lattice. Recollection of the data using a different crystal with a slower scan rate did not improve the data quality; the residual peaks also remained. The final positional parameters are listed in Tables 2 and 3 for compounds **6** and **7** respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

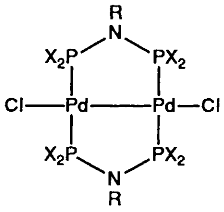
Results and Discussion

Synthesis.—Treatment of [MCl_2(cod)] (M = Pt or Pd) with 1 : 1 molar proportion of diphosphazane ligands L in dichloromethane yields the chelate complexes [MCl_2L] **1**–**4**. The palladium chloride complexes **1** and **2** can also be prepared by the reaction of *trans*-[$PdCl_2(PhCN)_2$] with L in CH_2Cl_2 or by refluxing a solution of $PdCl_2$ and L in acetonitrile. These complexes are soluble in CH_2Cl_2 and $CHCl_3$ and are stable in air both as solids and in solution.

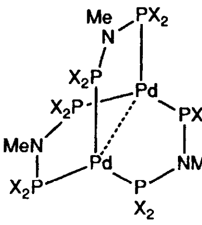
Redox condensation of the palladium-(II) and -(0) derivatives, [$PdCl_2(PhCN)_2$] and [$Pd_2(dba)_3$]·$CHCl_3$ in the presence of ligands L^1 or L^2 in CH_2Cl_2 yields the palladium(I) complexes [$Pd_2Cl_2L_2$] **5** or **6**. These complexes are soluble in benzene, tetrahydrofuran (thf), CH_2Cl_2 or $CHCl_3$. They are air-stable both in the solid state and in solution. Unlike the analogous dppm complex [$Pd_2Cl_2(dppm)_2$],[15] the diphosphazane complexes **5** or **6** do not react with CO or CS_2 to form A-frame type complexes and the starting complexes are recovered unchanged. Treatment of [$Pd_2(dba)_3$]·$CHCl_3$ with L^1 yields the dinuclear palladium(0) complex, [$Pd_2(\mu\text{-}L^1)_3$] **7** in 55% yield. This complex is a red crystalline solid soluble in benzene, thf, CH_2Cl_2 or $CHCl_3$. The solid is moderately air-stable but the orange-red solution of the complex decomposes when exposed to air. An analogous reaction of [$Pd_2(dba)_3$]·$CHCl_3$ with the *N*-phenyldiphosphazane L^2 did not afford a readily identifiable dinuclear complex. The ^{31}P NMR spectrum of the product shows a resonance at δ 87.3 suggesting that presumably a bis-chelated complex of the type [$PdL_2{}^2$] is formed in the reaction. Attempts to prepare the palladium(0) complex, [$Pd_2L^1{}_3$] **7** by reduction of [$PdCl_2L^1$] **1** with $NaBH_4$ were unsuccessful. When CO is bubbled through a solution of [$Pd_2L^1{}_3$] in CH_2Cl_2, decomposition occurs to give an insoluble black residue of metallic palladium. This is in contrast to the behaviour of [$Pd(PMe_3)_4$] which yields a cluster complex under similar reaction conditions.[16]



	M	R
1	Pd	Me
2	Pd	Ph
3	Pt	Me
4	Pt	Ph



	R
5	Me
6	Ph



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X = OPh

The physical properties of the complexes, analytical and spectroscopic data are summarised in Table 4.

Spectroscopic Features.—The structures of the platinum- and palladium-diphosphazane complexes **1**–**7** have been deduced from ^{1}H and ^{31}P NMR spectroscopic data (Table 4). The structures of the dinuclear palladium-(0) and -(I) complexes (**6** and **7**) have been confirmed by single crystal X-ray diffraction (see below).

Table 2 Fractional atomic coordinates for complex **6**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pd(1)	0.0	0.360 89(3)	0.25
Pd(2)	0.0	0.230 19(3)	0.25
Cl(1)	0.0	0.480 0(1)	0.25
Cl(2)	0.0	0.112 4(1)	0.25
P(1)	−0.056 5(1)	0.356 4(1)	0.153 4(1)
P(2)	0.054 2(1)	0.236 0(1)	0.154 2(1)
N(1)	−0.006 0(5)	0.293 9(3)	0.112 5(2)
O(1)	−0.175 9(4)	0.344 7(3)	0.138 5(2)
O(2)	−0.037 3(4)	0.420 3(3)	0.111 8(2)
O(3)	0.174 8(4)	0.252 8(3)	0.145 5(2)
O(4)	0.050 5(4)	0.172 2(2)	0.111 1(2)
C(1)	−0.013 9(6)	0.289 8(4)	0.047 3(3)
C(2)	−0.109 8(6)	0.271 5(4)	0.022 1(3)
C(3)	−0.118 5(7)	0.265 4(4)	−0.040 6(3)
C(4)	−0.030 5(8)	0.276 6(5)	−0.076 2(4)
C(5)	0.064 2(7)	0.295 7(5)	−0.050 5(4)
C(6)	0.074 5(6)	0.302 2(4)	0.012 5(3)
C(11)	−0.259 9(5)	0.387 4(4)	0.149 9(3)
C(12)	−0.347 8(6)	0.371 6(5)	0.117 9(4)
C(13)	−0.436 7(7)	0.410 6(5)	0.128 7(5)
C(14)	−0.435 6(7)	0.461 3(5)	0.171 0(4)
C(15)	−0.348 8(7)	0.476 1(4)	0.200 7(4)
C(16)	−0.255 7(6)	0.438 5(4)	0.191 8(4)
C(21)	0.056 3(8)	0.454 7(4)	0.105 0(3)
C(22)	0.148 2(7)	0.429 1(5)	0.126 7(4)
C(23)	0.239 4(10)	0.466 3(7)	0.118 6(6)
C(24)	0.231 0(15)	0.526 7(9)	0.086 4(9)
C(25)	0.138 4(18)	0.550 6(7)	0.065 8(9)
C(26)	0.047 8(11)	0.514 5(5)	0.074 5(5)
C(31)	0.243 3(6)	0.226 1(4)	0.189 3(3)
C(32)	0.260 6(7)	0.158 9(5)	0.190 5(5)
C(33)	0.330 5(9)	0.132 6(7)	0.234 1(7)
C(34)	0.380 4(10)	0.177 2(10)	0.272 4(6)
C(35)	0.361 0(11)	0.240 8(10)	0.269 7(6)
C(36)	0.294 0(9)	0.272 8(7)	0.224 5(6)
C(41)	−0.039 8(6)	0.137 4(4)	0.091 8(3)
C(42)	−0.022 4(7)	0.100 2(4)	0.041 0(4)
C(43)	−0.107 3(8)	0.062 9(5)	0.018 5(4)
C(44)	−0.201 9(8)	0.064 1(5)	0.049 2(5)
C(45)	−0.213 9(7)	0.101 9(5)	0.099 7(4)
C(46)	−0.131 9(6)	0.139 9(4)	0.122 1(4)

The ^{31}P NMR spectra of the mononuclear chelate complexes **1**–**4** show single resonances which are upfield of the signals of the respective free ligands. The shielding is less pronounced for the *N*-phenyl ligand L^2 compared to that for the *N*-methyl ligand L^1. Another noticeable feature is that the replacement of methyl by phenyl on the nitrogen of the diphosphazane ligand reduces the ^1J(PtP) value very markedly, from 5040 Hz for **3** to 3630 Hz for **4**. For both **1** and **3**, the *N*-methyl resonance appears as a triplet (coupling to phosphorus) at δ 3.05 and 3.00 respectively. The chemical shifts of the *N*-methyl protons of L^1 appear to be structure-sensitive. For the palladium-(0) and -(I) complexes, $[Pd_2L^1_3]$ **7** and $[Pd_2Cl_2L^1_2]$ **6**, these resonances appear at δ 2.85 and 2.80 compared to δ 3.05 for the palladium(II) complex **1**. More interestingly, the ^3J(PH) value for the dinuclear complexes is appreciably reduced (4–5 Hz) relative to the value of 11 Hz observed for the palladium(II) complex **1**. A similar trend is noted for the analogous palladium complexes of dppm.[17]

The ^{31}P chemical shifts for the dipalladium(I) complexes **5** and **6** are shifted upfield compared to the free ligands but much less so than for the corresponding palladium(II) complexes **1** and **2**. The upfield shift is even less for the dipalladium(0) complex **7**. The ^{31}P chemical shifts for the palladium- and platinum-(II) complexes **1**–**4** are unusual because they occur at very much lower frequencies than for the free ligands; generally co-ordination of diphosphines results in a shift of the ^{31}P resonances to higher frequencies. The same unusual trend is however observed for complexes of dppm such as $[MCl_2(dppm)]$ (M = Pt or Pd)[17,18] and $[PdMe_2(dppm)]$.[19] The ^{31}P resonances for five- and six-membered chelate complexes such as $[PdCl_2(dppe)]$ and $[PdCl_2(dppp)]$ show the normal high frequency shifts compared to the free ligands.[20] The anomalous ^{31}P chemical shifts for palladium- and platinum-(II) complexes of dppm and diphosphazanes (L^1 or L^2) cannot be simply related to the presence of a four-membered chelate ring[20] since the tetracarbonyl chelates of these ligands *viz.* $[M(CO)_4L]$ (M = Cr or Mo) show high-frequency shifts of their ^{31}P resonances compared to the free ligands.[11]

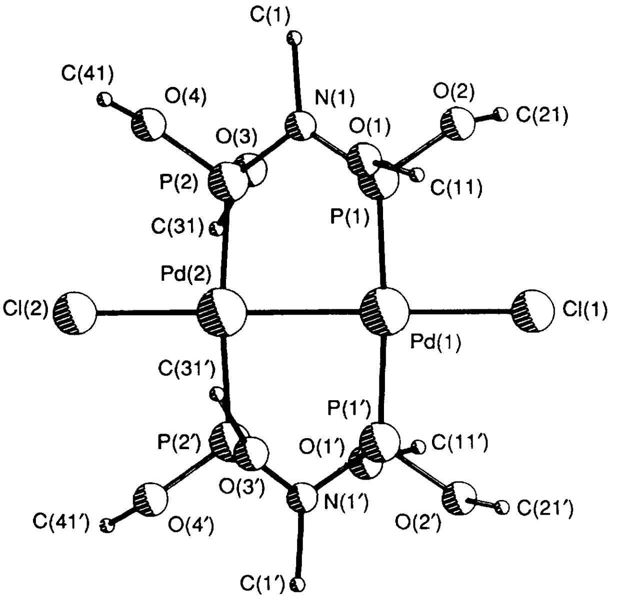

Fig. 1 Molecular structure of $[Pd_2Cl_2L^2_2]$ **6**. For clarity only the *ipso* carbons of the phenyl rings are shown

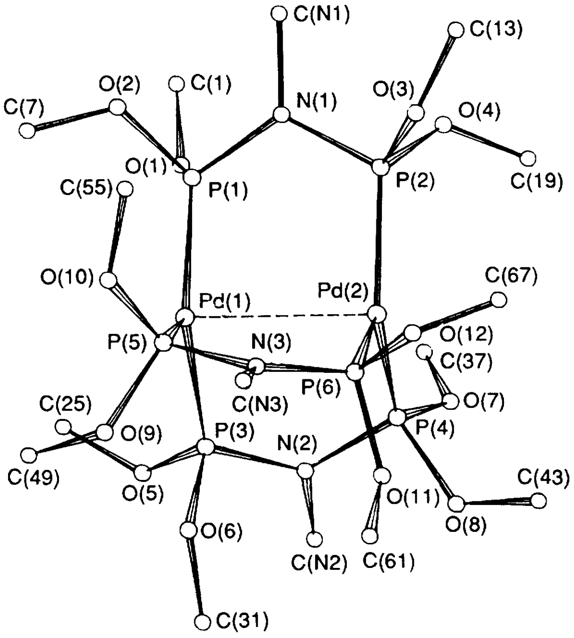

Fig. 2 Molecular structure of $[Pd_2L^1_3]$ **7**. For clarity only the *ipso* carbons of the phenyl rings are shown

Crystal Structures of $[Pd_2Cl_2L^2_2]$ **6** *and* $[Pd_2L^1_3]$ **7**.—The molecular structures of the dinuclear palladium-(I) and -(0) complexes **6** and **7** have been confirmed by single-crystal X-ray diffraction. Perspective views of the structures along with the numbering scheme are shown in Figs. 1 and 2 respectively. Selected structural parameters are listed in Tables 5 and 6 respectively.

Table 3 Fractional atomic coordinates for complex **7**

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Pd(1)	0.168 1(1)	−0.170 7(1)	0.368 46(3)	C(24)	0.144 2(11)	0.197 8(16)	0.414 7(5)
Pd(2)	0.180 4(1)	0.006 9(1)	0.371 45(3)	C(25)	0.043 6(11)	−0.282 3(17)	0.326 0(5)
P(1)	0.132 5(2)	−0.165 9(4)	0.415 2(1)	C(26)	0.062 2(12)	−0.356 7(13)	0.316 4(5)
P(2)	0.167 3(2)	0.008 7(3)	0.421 4(1)	C(27)	0.038 4(18)	−0.423 9(20)	0.330 8(9)
P(3)	0.117 2(2)	−0.149 7(3)	0.322 8(1)	C(28)	−0.006 6(28)	−0.419 1(42)	0.352 6(2)
P(4)	0.107 1(2)	0.027 3(3)	0.333 9(1)	C(29)	−0.012 8(21)	−0.348 5(44)	0.362 2(9)
P(5)	0.267 8(2)	−0.190 2(3)	0.363 2(1)	C(30)	0.004 5(13)	−0.270 4(25)	0.349 1(6)
P(6)	0.274 2(2)	−0.012 3(3)	0.354 8(1)	C(31)	0.147 0(8)	−0.150 1(15)	0.263 8(4)
O(1)	0.058 4(6)	−0.176 1(9)	0.416 8(3)	C(32)	0.163 4(10)	−0.071 8(18)	0.252 3(6)
O(2)	0.156 6(6)	−0.236 4(8)	0.440 0(3)	C(33)	0.150 2(11)	−0.061 6(16)	0.221 8(6)
O(3)	0.224 1(5)	0.039 9(9)	0.442 4(3)	C(34)	0.120 6(11)	−0.117 0(21)	0.203 0(5)
O(4)	0.112 5(6)	0.065 6(8)	0.434 5(3)	C(35)	0.108 4(14)	−0.194 4(16)	0.215 4(6)
O(5)	0.062 5(7)	−0.208 0(9)	0.311 2(4)	C(36)	0.119 0(9)	−0.212 0(16)	0.246 3(5)
O(6)	0.161 4(6)	−0.164 4(9)	0.295 4(3)	C(37)	−0.003 9(9)	0.051 7(14)	0.352 3(5)
O(7)	0.044 4(6)	0.076 4(9)	0.337 4(3)	C(38)	−0.005 0(9)	−0.027 1(14)	0.367 7(5)
O(8)	0.124 2(6)	0.083 5(8)	0.305 1(3)	C(39)	−0.056 8(12)	−0.050 2(17)	0.381 0(4)
O(9)	0.286 7(6)	−0.243 7(8)	0.333 0(3)	C(40)	−0.107 8(11)	−0.004 5(21)	0.379 0(6)
O(10)	0.314 3(6)	−0.242 6(8)	0.386 0(3)	C(41)	−0.105 9(12)	0.071 8(22)	0.364 8(6)
O(11)	0.274 7(6)	0.014 0(8)	0.319 7(3)	C(42)	−0.055 4(11)	0.097 9(16)	0.350 1(6)
O(12)	0.330 2(6)	0.040 6(10)	0.370 6(4)	C(43)	0.152 2(9)	0.159 7(13)	0.307 6(5)
N(1)	0.150 0(7)	−0.084 4(11)	0.438 3(3)	C(44)	0.136 5(10)	0.226 0(13)	0.325 3(6)
N(2)	0.084 8(7)	−0.057 3(9)	0.314 0(3)	C(45)	0.163 7(16)	0.300 5(20)	0.325 7(6)
N(3)	0.307 7(6)	−0.103 9(9)	0.357 4(4)	C(46)	0.211 5(15)	0.313 7(19)	0.309 5(6)
C(N1)	0.152 5(10)	−0.088 1(16)	0.472 3(4)	C(47)	0.231 0(12)	0.254 9(18)	0.288 7(6)
C(N2)	0.035 1(9)	−0.047 6(12)	0.288 7(4)	C(48)	0.199 6(10)	0.175 5(17)	0.288 3(5)
C(N3)	0.376 6(9)	−0.115 8(16)	0.354 9(5)	C(49)	0.256 9(8)	−0.313 6(13)	0.323 5(4)
C(1)	0.027 9(8)	−0.182 0(20)	0.443 6(5)	C(50)	0.238 4(10)	−0.372 1(15)	0.343 7(5)
C(2)	0.018 6(12)	−0.256 7(18)	0.457 3(7)	C(51)	0.211 7(12)	−0.447 9(19)	0.332 7(6)
C(3)	−0.015 5(15)	−0.249 6(26)	0.483 0(7)	C(52)	0.203 2(13)	−0.459 8(17)	0.302 0(7)
C(4)	−0.035 8(16)	−0.176 3(40)	0.493 1(8)	C(53)	0.221 9(13)	−0.398 7(19)	0.282 6(6)
C(5)	−0.028 0(18)	−0.101 5(26)	0.478 3(10)	C(54)	0.248 4(10)	−0.326 5(13)	0.293 1(5)
C(6)	0.007 6(12)	−0.102 3(20)	0.453 0(6)	C(55)	0.326 5(9)	−0.227 6(15)	0.417 8(4)
C(7)	0.166 4(9)	−0.319 4(13)	0.431 7(4)	C(56)	0.360 8(10)	−0.289 6(17)	0.431 2(5)
C(8)	0.215 8(11)	−0.355 9(15)	0.450 8(5)	C(57)	0.376 5(12)	−0.283 1(19)	0.462 5(7)
C(9)	0.227 3(12)	−0.441 7(16)	0.443 1(7)	C(58)	0.354 8(10)	−0.210 8(17)	0.478 5(5)
C(10)	0.192 4(17)	−0.481 1(16)	0.422 4(8)	C(59)	0.318 2(10)	−0.149 0(15)	0.462 6(4)
C(11)	0.146 7(13)	−0.445 7(19)	0.405 6(6)	C(60)	0.303 5(9)	−0.157 3(11)	0.430 8(5)
C(12)	0.130 3(12)	−0.361 2(18)	0.409 3(7)	C(61)	0.321 0(9)	0.003 6(17)	0.300 4(5)
C(13)	0.237 4(11)	0.075 7(14)	0.470 9(4)	C(62)	0.322 4(13)	−0.068 7(19)	0.283 7(5)
C(14)	0.294 5(11)	0.084 0(19)	0.482 1(7)	C(63)	0.371 0(15)	−0.077 6(31)	0.263 3(5)
C(15)	0.308 8(16)	0.132 0(21)	0.508 1(7)	C(64)	0.412 5(14)	−0.009 5(29)	0.261 1(8)
C(16)	0.268 5(17)	0.158 2(17)	0.525 0(5)	C(65)	0.412 3(15)	0.059 0(23)	0.279 7(8)
C(17)	0.208 7(14)	0.151 5(16)	0.515 0(6)	C(66)	0.365 7(10)	0.066 4(15)	0.300 5(5)
C(18)	0.190 4(10)	0.110 4(15)	0.487 2(4)	C(67)	0.328 4(9)	0.119 4(15)	0.382 3(5)
C(19)	0.099 2(12)	0.145 1(12)	0.422 8(4)	C(68)	0.357 5(13)	0.133 1(20)	0.410 8(5)
C(20)	0.039 0(10)	0.167 7(15)	0.419 9(5)	C(69)	0.360 6(14)	0.216 9(23)	0.422 0(6)
C(21)	0.026 9(16)	0.251 9(19)	0.408 5(6)	C(70)	0.327 5(13)	0.281 9(17)	0.405 5(6)
C(22)	0.074 4(26)	0.304 6(16)	0.403 1(9)	C(71)	0.298 3(12)	0.263 5(18)	0.376 3(6)
C(23)	0.131 4(14)	0.274 9(21)	0.405 2(6)	C(72)	0.297 6(14)	0.183 5(18)	0.366 8(6)

Table 4 Physical properties, analytical and NMR data for complexes **1**–**7**

				Analyses (%)[a]			NMR data		
Compound	Colour	M.p./°C	Yield (%)	C	H	N	δ_H	δ_P	$\Delta\delta$[b]
1 $[PdCl_2L^1]$	Yellow	130 (decomp.)	85	50.3 (51.2)	3.7 (3.5)	1.8 (2.0)	3.05 (t, NMe)	65.5	69.6
2 $[PdCl_2L^2]$	Colourless	120 (decomp.)	89	54.0 (54.0)	3.7 (3.8)	2.0 (2.1)	—	82.2	45.5
3 $[PtCl_2L^1]$	Colourless	95–97	61	41.4 (41.1)	3.0 (3.1)	1.8 (1.9)	3.00 (t, NMe)	46.5	88.6
4 $[PtCl_2L^2]$	Colourless	148 (decomp.)	80	45.3 (45.5)	3.1 (3.2)	1.6 (1.8)	—	78.3	49.4
5 $[Pd_2Cl_2L^1{}_2]$	Orange-yellow	165 (decomp.)	50	51.9 (52.4)	4.0 (4.0)	2.4 (2.3)	2.85 (t, NMe)	112.1	23.0
6 $[Pd_2Cl_2L^2{}_2]$	Orange-yellow	170 (decomp.)	52	54.0 (54.0)	3.7 (3.8)	2.0 (2.1)	—	111.5	16.2
7 $[Pd_2L^1{}_3]$	Orange-red	135–137	55	55.2 (55.1)[c]	4.6 (4.3)	2.7 (2.6)	2.80 (t, NMe)	124.5	10.6

[a] Required values given in parentheses. [b] $\Delta\delta = \delta_P(\text{ligand}) - \delta_P(\text{complex})$; δ_P values for L^1 and L^2 are 135.1 and 127.7 respectively.[11] [c] The values in parentheses are those calculated for the solvate **7**·$0.5CH_2Cl_2$ (see text).

Table 5 Selected structural parameters for complex **6**

Pd(1)–Pd(2)	2.6196(9)	Pd(1)–Cl(1)	2.387(2)
Pd(2)–Cl(2)	2.361(2)	Pd(1)–P(1)	2.272(2)
Pd(2)–P(2)	2.247(2)	P(1)–N(1)	1.681(6)
P(2)–N(1)	1.678(6)	P(1)–O(1)	1.598(5)
P(1)–O(2)	1.599(6)	P(2)–O(3)	1.608(5)
P(2)–O(4)	1.599(5)	N(1)–C(1)	1.456(8)
O(1)–C(11)	1.407(9)	O(2)–C(21)	1.402(11)
O(3)–C(31)	1.422(9)	O(4)–C(41)	1.427(9)
Pd(2)–Pd(1)–Cl(1)	180.0	Pd(1)–Pd(2)–Cl(2)	180.0
Cl(1)–Pd(1)–P(1)	92.3(1)	Pd(2)–Pd(1)–P(1)	87.7(1)
Pd(1)–Pd(2)–P(2)	87.0(1)	Cl(2)–Pd(2)–P(2)	93.0(1)
Pd(1)–P(1)–O(2)	117.8(2)	Pd(1)–P(1)–O(1)	120.9(2)
Pd(1)–P(1)–N(1)	114.6(2)	O(1)–P(1)–O(2)	98.5(3)
N(1)–P(1)–O(2)	102.9(3)	N(1)–P(1)–O(1)	98.9(3)
Pd(2)–P(2)–O(4)	121.2(2)	Pd(2)–P(2)–O(3)	115.3(2)
Pd(2)–P(2)–N(1)	114.5(2)	O(3)–P(2)–O(4)	97.1(3)
N(1)–P(2)–O(4)	102.0(3)	N(1)–P(2)–O(3)	103.9(3)
P(1)–N(1)–P(2)	113.4(3)	P(2)–N(1)–C(1)	123.0(5)
P(1)–N(1)–C(1)	123.6(5)	P(1)–O(1)–C(11)	128.4(5)
P(1)–O(2)–C(21)	126.2(5)	P(2)–O(3)–C(31)	116.4(4)
P(2)–O(4)–C(41)	126.6(4)		

Table 6 Selected structural parameters for complex **7**

Pd(1) • • • Pd(2)	2.855(2)	Pd(1)–P(1)	2.269(5)
Pd(1)–P(3)	2.271(5)	Pd(1)–P(5)	2.266(5)
Pd(2)–P(2)	2.251(5)	Pd(2)–P(4)	2.267(5)
Pd(2)–P(6)	2.281(5)	P(1)–N(1)	1.69(2)
P(2)–N(1)	1.72(2)	P(3)–N(2)	1.68(2)
P(4)–N(2)	1.67(1)	P(5)–N(3)	1.67(2)
P(6)–N(3)	1.64(1)	P(1)–O(1)	1.66(1)
P(1)–O(2)	1.64(1)	P(2)–O(3)	1.59(1)
P(2)–O(4)	1.66(1)	P(3)–O(5)	1.59(2)
P(3)–O(6)	1.63(1)	P(4)–O(7)	1.62(1)
P(4)–O(8)	1.63(1)	P(5)–O(9)	1.67(1)
P(5)–O(10)	1.63(1)	P(6)–O(11)	1.61(1)
P(6)–O(12)	1.62(2)	N(1)–C(N1)	1.50(2)
N(2)–C(N2)	1.52(2)	N(3)–C(N3)	1.56(2)
P(3)–Pd(1)–P(5)	111.0(2)	P(1)–Pd(1)–P(5)	120.4(2)
P(1)–Pd(1)–P(3)	128.6(2)	P(4)–Pd(2)–P(6)	114.1(2)
P(2)–Pd(2)–P(6)	120.3(2)	P(2)–Pd(2)–P(4)	125.6(2)
Pd(1)–P(1)–N(1)	112.0(6)	Pd(1)–P(1)–O(2)	118.0(5)
Pd(1)–P(1)–O(1)	116.5(5)	O(2)–P(1)–N(1)	94.3(7)
O(1)–P(1)–N(1)	103.7(8)	O(1)–P(1)–O(2)	100.5(7)
Pd(2)–P(2)–N(1)	117.7(6)	Pd(2)–P(2)–O(4)	120.0(5)
Pd(2)–P(2)–O(3)	115.1(5)	O(4)–P(2)–N(1)	97.5(7)
O(3)–P(2)–N(1)	102.1(7)	O(3)–P(2)–O(4)	101.3(7)
Pd(1)–P(3)–N(2)	121.0(5)	Pd(1)–P(3)–O(6)	110.6(5)
Pd(1)–P(3)–O(5)	121.5(6)	O(6)–P(3)–N(2)	103.0(7)
O(5)–P(3)–N(2)	97.8(8)	O(5)–P(3)–O(6)	99.4(8)
Pd(2)–P(4)–N(2)	116.2(6)	Pd(2)–P(4)–O(8)	117.3(5)
Pd(2)–P(4)–O(7)	125.4(5)	O(8)–P(4)–N(2)	96.4(7)
O(7)–P(4)–N(2)	102.6(8)	O(7)–P(4)–O(8)	93.3(7)
Pd(1)–P(5)–N(3)	115.9(5)	Pd(1)–P(5)–O(10)	126.2(5)
Pd(1)–P(5)–O(9)	117.2(5)	O(10)–P(5)–N(3)	101.6(7)
O(9)–P(5)–N(3)	97.7(7)	O(9)–P(5)–O(10)	92.8(7)
Pd(2)–P(6)–N(3)	121.2(6)	Pd(2)–P(6)–O(12)	118.8(6)
Pd(2)–P(6)–O(11)	110.2(5)	O(12)–P(6)–N(3)	96.0(8)
O(11)–P(6)–N(3)	105.4(8)	O(11)–P(6)–O(12)	102.9(8)
P(1)–N(1)–P(2)	117.0(8)	P(2)–N(1)–C(N1)	118.4(14)
P(1)–N(1)–C(N1)	124.6(14)	P(3)–N(2)–P(4)	119.0(9)
P(4)–N(2)–C(N2)	118.5(12)	P(3)–N(2)–C(N2)	122.5(12)
P(5)–N(3)–P(6)	120.3(9)	P(6)–N(3)–C(N3)	123.2(13)
P(5)–N(3)–C(N3)	116.5(13)		

Compound **7** is the first example of a palladium(0) complex of an acyclic diphosphazane ligand. The structure is very similar to that of $[Pd_2(dppm)_3]$[21] and $[Pt_2(dppm)_3]$.[22] The co-ordination geometry around each palladium centre is approximately trigonal planar, the displacement of the Pd atoms from their local P_3 planes being <0.05 Å. The two P_3 planes are nearly parallel to one another (dihedral angle 2.0°) and the two PdP_3 moieties adopt an eclipsed configuration. In the dinuclear palladium(I) complex **6**, the Cl–Pd–Pd–Cl axis coincides with the crystallographic two-fold axis. The geometry around each palladium atom is square planar; the two PdP_2Cl planes are inclined at an angle of 37°.

Table 7 Comparison of M–M and M–P distances in selected dinuclear palladium and platinum compounds

Compound	M–M/Å	Mean M–P/Å	Ref.
$[Pd_2L^1{}_3]$	2.855	2.269	This work
$[Pd_2Cl_2L^2{}_2]$	2.620	2.259	This work
$[Pd_2Cl_2(dppa)]$	2.638	2.272	9
$[Pd_2Br_2(dppm)_2]$	2.699	2.288	23
$[Pt_2Cl_2(dppm)_2]$	2.652	2.278	18
$[Pt_2I_2Me_2(dmpm)_2]$	3.353	2.276	24
$[Pd_2(dba)_3]$	3.245	—	13
$[Pd_2(dppm)_3]$	2.959	2.310	21
$[Pt_2(dppm)_3]$	3.023	2.266	22
$[Pd_8(CO)_8(PMe_3)_7]$	2.703–3.138	—	16

The geometry around the nitrogen atoms in both **6** and **7** is strictly planar. The P–N–P angles in **7** range between 117.0 and 120.3° whereas for **6** the P–N–P angle is 113.4°. The mean P–N distance in both compounds [1.68(1)] is shorter than the accepted value for a P–N single bond (1.77–1.80 Å) implying partial double bond character.

The most interesting aspect of the two structures is the short Pd–Pd separation [2.855(2) Å for the palladium(0) complex **7**, 2.620(1) Å for the palladium(I) complex **6**]. These values are significantly shorter than those observed for analogous complexes with the metal in the same oxidation state (zero or +1 respectively). There is also a corresponding decrease in the Pd–P distances in **6** and **7** (Table 7).

The Pd • • • Pd separation for the dipalladium(0) complex **7** lies only slightly outside the range of bonding distances found in dinuclear palladium(I) complexes (Table 7) and is comparable to the values (2.70–3.14 Å) found for $Pd^0 \cdots Pd^0$ distances in $[Pd_8(\mu_3\text{-}CO)_2(\mu\text{-}CO)_6(PMe_3)_7]$.[16] Consistent with the strong metal–metal interaction, the electronic spectrum of complex **7** in CH_2Cl_2 shows an intense characteristic visible absorption band at 446 nm (ε = 21 700 dm^3 mol^{-1} cm^{-1}). Gray and co-workers[25] have investigated the electronic and spectroscopic properties of d^{10}–d^{10} dinuclear complexes $[M_2L_3]$ (M = Pd or Pt, L = dppm or dba) and from absorption and emission spectral studies concluded that the absorption bands in the region 400–500 nm arise as a result of metal–metal interaction and can be assigned to $p \longleftarrow d_\sigma$ transitions. They also point out that the blue shift of the singlet $p \longleftarrow d_{\sigma^*}$ band for $[Pd_2(dppm)_3]$ (440 nm) compared to the diplatinum analogue (487 nm) suggests that the M–M interaction is weaker in $[Pd_2(dppm)_3]$. They calculated a value of 3.043 Å for the Pd • • • Pd distance in $[Pd_2(dppm)_3]$ from resonance-Raman spectroscopic data using an empirical relationship. Subsequently the structure of $[Pd_2(dppm)_3]$ has been determined by single-crystal X-ray diffraction[21] and the Pd • • • Pd distance (2.959 Å) is shorter than that for $[Pt_2(dppm)_3]$ (3.025 Å) contrary to the prediction of Gray and co-workers.[25] Even though the Pd • • • Pd distance in $[Pd_2L^1{}_3]$ **7** [2.855(2) Å] is shorter than that in $[Pd_2(dppm)_3]$, there is a slight red shift of the $p \longleftarrow d_{\sigma^*}$ transition of 6 nm. These data indicate that there is no direct correlation between metal–metal distance and the position of the $p \longleftarrow d_{\sigma^*}$ transition for d^{10}–d^{10} dipalladium(0) or diplatinum(0) complexes.

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