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Bis(diphenylphosphinomethyl)phenylphosphine as a Chelating and Bridging Ligand.

The Preparations and Molecular Structures of Palladium Complexes

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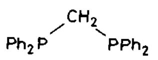
The following three complexes of bis(diphenylphosphinomethyl)phenylphosphine (dpmp) have been isolated from the reaction of the ligand with palladium chloride complexes: (dpmp)$PdCl_2$, (CH_3CN)$PdCl_2$(μ-dpmp)$PdCl_2$ and $(dpmp)_2Pd_3Cl_6$. The structures of the first two have been established by X-ray crystallography. (Dpmp)$PdCl_2 \cdot CH_2Cl_2$ crystallizes in the space group $P2_1/m$ (No. 11) with cell dimensions (determined at 140 K) of a = *9.864(10),* b = *17.513(8),* c = *10.706(10) Å, β = 112.85(6)°, Z = 2, V = 1704(3) Å^3. The structure was refined by blocked-cascade least-squares to a conventional* R *value of 0.073 using 2021 significant data. The structure consists of square planar palladium bound in a six-membered chelate ring. The central phosphorus atom is not coordinated. (CH_3CN)$PdCl_2$(μ-dpmp)$PdCl_2 \cdot CH_3CN$ crystallizes in the space group $P2_12_12_1$ (No. 19) with cell dimensions (at 140 °K) of* a = *12.302(4),* b = *12.483(3),* c = *24.316 Å, Z = 4, V = 3734 Å^3. It was refined as described above to an* R *value of 0.069 using 3193 significant reflections. The structure consists of two square planar palladium atoms. One is bound to two chlorine atoms and the chelating phosphine. The other palladium is bound to a linear acetonitrile molecule, two* trans *chlorine atoms, and to the central atom of the triphosphine ligand. The two palladium atoms are separated by 5.854 Å. The chelate ring conformations differ in the two structures ((dpmp)$PdCl_2$, boat; (CH_3CN)$PdCl_2$(μ-dpm)$PdCl_2$, symmetric skew boat). The flexibility of chelate ring conformation in chelated dpmp coupled with the ability of the central phosphorus to bind a second metal ion suggests that this ligand will be a versatile unit in the preparation of binuclear transition metal complexes.*

Introduction

The use of polydentate phosphine ligands for the control of coordination number, stereochemistry, and ligand lability of mononuclear transition metal complexes is wide spread [1–4]. The most striking example of the degree of reaction control that these phosphines give has been in the design of ligands which provide for catalytic asymmetric homogeneous hydrogenation [5–8].

Phosphine ligands have also been demonstrated to be useful in the construction of bi- and polynuclear metal complexes. The versatility of bis(diphenylphosphino)methane, *1* (dpm) in binding two metals while allowing considerable variation in coordination stereochemistry and metal–metal separation is well established [9–11].

Recently a number of ligands have been developed which have two distinct coordination sites available for binding two different metal ions. Such ligands can utilize differences such as hardness or softness in the two binding sites to discriminate between metal ions. Examples of such ligands include: 2-(diphenylphosphino)pyridine, *2*, [11–16]



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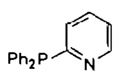

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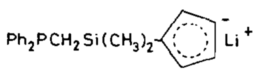

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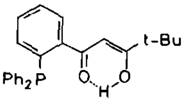

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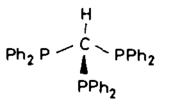

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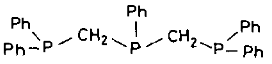

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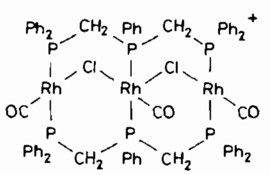
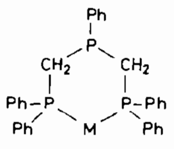
[dimethyl(diphenylphosphinomethyl)silyl] cyclopentadienyl lithium, *3* [17, 18] and [*o*-(diphenylphosphino)benzoyl] pinacolone, *4* [19].

Another development in the use of polydentate ligands as templates for the design of polynuclear complexes involves the use of the tripod ligand *5*. This presents a triangular array of lone pairs which are adept at binding to the triangular faces of metal clusters [20] and, more significantly, at inducing the formation of new triangular arrays of metal atoms [21].

Here we report on investigations of the tridentate ligand, bis(diphenylphosphinomethyl)phenylphosphine, *6*. This ligand represents an elaboration on the structural elements of bis(diphenylphosphino)methane. While unsuited for binding to triangular groups of metal atoms, it has the potential for binding three metal atoms in a nearly linear array as found for *7* [22]. However, by leaving the central phosphorus atom uncoordinated, it also has the potential of forming a strain-free, six-membered chelate rings as shown in *8*.



7 $Rh_3(\mu\text{-dpmp})_2(\mu\text{-Cl})Cl(CO)_3^+$



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Here we describe structural studies of two palladium(II) complexes, both of which incorporate the chelate structure *8*. In one the central phosphorus is free while in the other it binds to a second palladium(II) atom. The results reveal considerable flexibility in the chelate ring and suggest that the chelated structure *8* will represent a common, basic structural element in the coordination chemistry of this ligand. Preliminary reports of parts of this work have appeared [22, 23].

Experimental

Preparation of Compounds

Bis(diphenylphosphinomethyl)phenylphosphine [24] and bis(benzonitrile)palladium(II) chloride [25] were prepared by established routes.

$\{(C_6H_5)_2PCH_2\}_2P(C_6H_5)PdCl_2\cdot CH_2Cl_2$

A solution of 76.7 mg (0.200 mmol) of bis(benzonitrile) palladium(II)chloride in 5 ml of dichloromethane was added to a solution of 100.0 mg (0.198 mmol) of bis(diphenylphosphinomethyl)phenylphosphine in 7 ml of dichloromethane. The solution was stirred for 5 min after mixing. Its volume was reduced to about 5 ml with the use of a rotary evaporator. Ethyl ether was slowly added to the solution. The product precipitated as fine, cream colored crystals. These were collected by filtration, washed with ether and dried under vacuum; yield 76%. *Anal.* Calcd. for $C_{33}H_{31}Cl_4P_3Pd$: C, 51.70; H, 3.81. Found: C, 51.68; H, 4.11.

$(CH_3CN)PdCl_2[\mu\text{-}(C_6H_5)P\{CH_2P(C_6H_5)_2\}_2]PdCl_2\cdot CH_3CN$

A solution containing 56.1 mg (0.146 mmol) of bis(benzonitrile)palladium(II)chloride in 3 ml of dichloromethane was added to a solution of 100.0 mg (0.130 mmol) of $(C_6H_5)P\{CH_2P(C_6H_5)_2\}_2PdCl_2$ in 20 ml of dichloromethane. The solution was stirred for 5 min and then evaporated on a rotary evaporatory until its volume was *ca.* 3 ml. Dropwise addition of ethyl ether produced fine yellow crystals. These were collected by filtration and washed with ether. Recrystallization from hot acetonitrile gave a 48% yield of the yellow, crystalline product. *Anal.* Calcd. for $C_{36}H_{35}Cl_4N_2P_3Pd_2$: C, 45.84; H, 3.74, N, 2.97. Found: C, 45.50; H, 3.79; N, 3.03.

$\{(C_6H_5)_2PCH_2\}_2P(C_6H_5)\}_2Pd_3Cl_6$

A solution of 42.3 mg (0.148 mmol) of $(C_8H_{12})PdCl_2$ in 2 ml of dichloromethane was added to 50 mg (0.10 mmol) of bis(diphenylphosphinomethyl)phenylphosphine in 3 ml of dichloromethane. After 5 min of stirring, the volume was reduced under vacuum on a rotary evaporator to two thirds its original volume. Ether was added slowly to precipitate the yellow product which was collected by filtration, washed with the ether, and vacuum dried: yield 64%. *Anal.* Calcd. for $C_{64}H_{58}Cl_6P_6Pd_3$: C, 49.75; H, 3.76. Found: C, 49.32; H, 3.89.

X-ray Data Collection, Solution and Refinement

$(dpmp)PdCl_2\cdot CH_2Cl_2$

Small crystals were obtained from dichloromethane/ether. The largest that could be found was mounted with its needle axis parallel to ϕ on a Syntex P2$_1$ diffractometer equipped with a low-temperature apparatus. Reflections initially were located from a rotation photograph. A typical reflexion had a width at half-height of 0.32° on an ω scan. With the use of 10 centered reflections and the P2$_1$ automatic indexing program, the lattice was assigned as monoclinic P. This was confirmed by axial photographs. Quick scans of the reflections for space group determination yielded the condition 0k0, k = 2n, consistent with space groups P2$_1$ (No. 4) or P2$_1$/m (No. 11). The density was measured by flotation in sym-$C_2H_2Br_4/CCl_4$. Final cell dimensions were obtained from a least-squares fit of 20 reflections having a 21–29° range in 2θ. The results of these measurements as well as data collection parameters are summarized in Table I. No decay in the intensity

TABLE I. Summary of Crystal Parameters, Data Collection and Refinement.

	$(dmp)PdCl_2 \cdot CH_2Cl_2$	$(CH_3CN)PdCl_2(\mu\text{-dpmp})PdCl_2 \cdot CH_3CN$
Formula	$PdCl_4P_2C_{33}H_{31}$	$Pd_2Cl_4P_3N_2C_{36}H_{35}$
fw	768.75	943.23
a, Å	9.864(10)	12.302(4)
b, Å	17.513(8)	12.483(3)
c, Å	10.706(10)	24.316(5)
β, deg	112.85(6)	
V, Å^3	1704(3)	3734(2)
Z	2	4
density, g/cm^3	1.498(calcd) (140 K) 1.47(1) (exptl) (298 K)	1.678(calcd) (140 K) 1.61(1) (exptl) (289 K)
space group	$P2_1/m$ (No. 11)	$P2_12_12_1$ (No. 19)
cryst. dimens., mm	0.07 × 0.15 × 0.25	0.25 × 0.35 × 0.42
cryst color	pale yellow	orange
cryst shape	needle	irregular
radiatn	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
temp, K	140	140
μ, cm^{-1}	10.1	13.8
absorption correction factor	1.01–1.29	1.77–2.21
2θ max, deg	50	50
scan type	ω	ω
scan speed, deg/min	4–60	60
scan range, deg	1.2	1.2
bkgd offset, deg	1	1
bkgd time/peak scan time	1	1
refl between check refl	118	118
no. check refl	2	2
unique data measd	3291	3723
unique data used	2021	3193
final no. of variables	214	234
mean shift/esd max	0.001	0.006
G.O.F.	1.453	1.178
R	0.073	0.069
R_w	0.073	0.068

of the check reflections was observed. Reflections were scaled to the random 2% fluctuation in check reflections that took place. Net intensities were computed from the relationship I = (P–LB–RB)(SR) where P is the peak count, LB and RB are left and right background counts, and SR is the scan rate. The standard deviation σ(I) is given by (P + LB + RB)$^{1/2}$(SR). The usual Lorentz and polarization corrections were made to the data. No correction was made for absorption.

A statistical analysis of the E-values indicated the structure was likely to be centrosymmetric. Solution of the structure by direct methods under this assumption (space group $P2_1/m$) proceeded smoothly. One-half of the complex molecule is contained in the asymmetric unit; the other half is generated by the presence of a mirror plane. The palladium atom lies in the mirror plane. There is also a disordered dichloromethane of crystallization that has its carbon atom and one chlorine atom in the mirror plane. The other chlorine atom is disordered with respect to position and with respect to the mirror plane. The occupancies of the two positions for this chlorine atom Cl(3) and Cl(4) were allowed to vary during refinement and converged at 0.49 and 0.51 respectively. Thereafter they were fixed at 0.50 each. Another test was made to see if $P2_1$ might be the correct space group, in light of the dis-

TABLE II. Atom Coordinates ($\times 10^4$) and Temperature Factors (A × 10^3), for (dpm)$PdCl_2 \cdot CH_2Cl_2$.

Atom	x	y	z	U
Pd	8197(2)	2500	7071(1)	29(1)
Cl(1)	6828(3)	1560(1)	7639(3)	41(1)
Cl(2)	6951(5)	2500	11203(4)	54(2)
Cl(3)	4526(7)	3337(3)	9458(6)	47(2)
Cl(4)	4179(6)	3315(3)	9616(5)	39(2)
P(1)	9390(3)	1517(1)	6580(3)	32(1)
P(2)	10190(6)	2500	4565(4)	48(2)
C(1)	8070(12)	866(5)	5418(10)	33(4)
C(2)	7853(13)	132(5)	5840(11)	40(4)
C(3)	6771(13)	−342(5)	4939(12)	46(5)
C(4)	5941(14)	−79(7)	3658(12)	54(5)
C(5)	6114(13)	646(6)	3261(11)	52(5)
C(6)	7195(13)	1109(6)	4132(11)	47(5)
C(7)	10497(11)	974(5)	8078(10)	35(4)
C(8)	10527(13)	1182(6)	9327(10)	45(5)
C(9)	11400(14)	770(6)	10479(11)	55(5)
C(10)	12179(14)	167(6)	10364(11)	55(5)
C(11)	12183(14)	−44(6)	9128(12)	59(6)
C(12)	11346(13)	363(6)	7948(11)	43(5)
C(13)	10712(13)	1716(5)	5768(11)	43(5)
C(14)	11768(18)	2500	3940(17)	38(7)
C(15)	11438(22)	2500	2595(16)	58(8)
C(16)	12481(19)	2500	2106(16)	47(7)
C(17)	13884(18)	2500	2949(16)	41(7)
C(18)	14326(22)	2500	4338(16)	55(8)
C(19)	13209(24)	2500	4894(17)	56(8)
C(20)	5427(18)	2500	9646(15)	38(6)

ordered solvent molecule. With isotropic thermal parameters (168 total variables), refinement in $P2_1$ converged at R = 0.164. The comparable stage in $P2_1/m$ (95 variables) converged at R = 0.169. Since similar agreement was achieved using fewer parameters, the original choice of $P2_1/m$ was probably correct. In the last stage of refinement, non-hydrogen atoms were assigned anisotropic thermal parameters, and hydrogen atoms were assigned isotropic thermal parameters 1.2 times the equivalent isotropic value of the anisotropic thermal parameters for the bonded carbon atom. Hydrogen atoms were given computed positions riding on the bonded carbon atom. A blocked-cascade least-squares refinement procedure [26] was employed with the function minimized during refinement given by $\Sigma w(|F_o| - |F_c|)^2$; $w = 1/\sigma^2(F_o) + 0.001 F_o^2$. Neutral atom scattering factors and corrections for anomalous scattering were from vol. IV of the International Tables. Refinement of 214 least-squares variables using 2021 unique data ($I > 3\sigma(I)$) converged with R = 0.073. The final difference map was essentially featureless. An analysis of the reflections with the largest variance did not show any systematic trends among these reflections. Positional parameters and equivalent isotropic values of the anisotropic thermal parameters for non-hydrogen atoms are given in Table II. Selected interatomic distances and angles are given in Tables III and IV. Hydrogen atom positions, anisotropic thermal parameters, and structure factor tables are available as supplementary material.

TABLE III. Selected Interatomic Distances (Å) in (dpmp)-$PdCl_2 \cdot CH_2Cl_2$.

Pd–Cl(1)	2.354(3)	Pd–P(1)	2.259(3)
P(1)–C(1)	1.812(9)	P(1)–C(7)	1.818(9)
P(1)–C(13)	1.860(15)	P(2)–C(13)	1.815(10)
P(2)–C(14)	1.919(22)	P(1)–P(2)	3.043(7)
P(1)–P(1')	3.443(7)	Pd–P(2)	3.893(5)

(CH_3CN)Pd_2Cl_2(μ-dpmp)$PdCl_2 \cdot CH_3CN$

Irregular-shaped, orange crystals of this compound crystallized from acetonitrile solution. The procedure followed for X-ray data collection was similar to that used for the previous compound. Crystal data and data collection parameters are summarized in Table I. A 1.7° peak scan was used during data collection due to the fairly broad peak width at half height along the *b* axis (0.57° along *b*, 0.37° along *a* and *c*). This width was presumed due to fine cracks since the crystal appeared normal in other respects. The observation of conditions h00, h = 2n; 0k0, k = 2n; 00l, l = 2n; 0kl, h0l, hk0, no conditions indicated the space group to be $P2_12_12_1$ (No. 19).

TABLE IV. Selected Bond Angles in (dpmp)$PdCl_2 \cdot CH_2Cl_2$.

Cl(1)–Pd–P(1)	86.0(1)	Cl(1)–Pd–Cl(1A)	88.7(2)
P(1)–Pd–Cl(1A)	174.7(1)	Cl(1)–Pd–P(1A)	174.7(1)
Pd–P(1)–C(1)	109.8(4)	Pd–P(1)–C(7)	112.4(4)
C(1)–P(1)–C(7)	107.6(4)	Pd–P(1)–C(13)	119.2(3)
C(1)–P(1)–C(13)	104.1(5)	C(7)–P(1)–C(13)	102.7(5)
C(13)–P(2)–C(14)	101.7(6)	C(13)–P(2)–C(13A)	98.3(7)
C(14)–P(2)–C(13A)	101.7(6)		
Pd–P(1A)–C(13A)	119.2(3)	P(2)–C(13A)–P(1A)	114.6(7)

TABLE V. Atom Coordinates ($\times 10^4$) and Temperature Factors (Å $\times$ 10^3) for $(CH_3CN)PdCl_2(\mu\text{-dpmp})PdCl_2 \cdot CH_3CN$.

Atom	x	y	z	U
Pd(1)	2352(1)	1848(1)	7788(1)	13(1)*
Pd(2)	5355(1)	–447(1)	9194(1)	18(1)*
P(1)	2312(3)	2154(3)	8703(1)	15(1)*
Cl(2)	1138(3)	3393(3)	7722(2)	22(1)*
Cl(1)	2603(3)	1915(3)	6841(1)	26(1)*
P(3)	3300(3)	416(3)	7828(1)	14(1)*
Cl(3)	4632(3)	–2127(3)	9065(2)	29(1)*
P(2)	3658(3)	140(3)	9077(2)	16(1)*
Cl(4)	6014(3)	1233(3)	9371(2)	27(1)*
C(3)	1118(12)	1627(12)	9040(6)	18(3)
C(9)	2457(11)	3558(11)	8889(5)	13(3)
C(16)	5406(12)	–320(12)	7905(6)	21(3)
C(33)	7704(14)	–1522(13)	9340(6)	27(4)
N(1)	6875(11)	–1115(11)	9299(5)	31(3)
C(17)	6571(11)	–229(12)	7828(6)	17(3)
C(15)	4766(10)	553(11)	7779(5)	12(3)
C(6)	–721(15)	872(14)	9559(7)	32(4)
C(10)	3385(13)	4107(13)	8739(6)	24(4)
C(22)	1891(13)	–974(12)	7291(6)	24(4)
C(11)	3485(15)	5153(14)	8875(7)	30(4)
C(14)	1629(12)	4082(12)	9183(6)	22(3)
C(2)	3032(11)	–320(12)	8458(5)	16(3)
C(19)	6330(14)	1575(15)	7498(7)	31(4)
C(8)	297(14)	1166(13)	8738(6)	26(4)
C(20)	5178(14)	1465(14)	7569(7)	29(4)
C(12)	2746(13)	5710(13)	9149(6)	29(4)
C(5)	70(12)	1305(12)	9867(6)	21(3)
C(7)	–632(14)	799(14)	9000(7)	30(4)
C(34)	8751(14)	–2051(15)	9387(7)	35(4)
C(1)	3513(11)	1583(11)	9052(6)	15(3)
C(26)	3675(12)	–810(12)	6896(6)	19(3)
C(4)	1020(13)	1706(13)	9607(6)	25(4)
C(24)	2411(13)	–2006(13)	6481(6)	26(4)
C(18)	6992(14)	682(13)	7620(6)	28(4)
C(23)	1624(15)	–1719(14)	6890(7)	32(4)
C(36)	191(17)	6059(16)	8094(8)	49(5)
N(2)	1025(16)	7782(16)	8455(7)	64(5)
C(35)	669(16)	7007(18)	8298(8)	48(6)
C(13)	1779(16)	5170(15)	9301(8)	42(5)
C(29)	1411(15)	–1309(14)	10066(7)	33(4)
C(31)	2594(14)	–233(14)	10632(7)	33(4)
C(32)	3184(13)	69(13)	10177(6)	27(4)
C(21)	2937(11)	–517(12)	7291(5)	14(3)
C(25)	3409(13)	–1536(12)	6488(6)	23(4)
C(27)	2774(13)	–416(14)	9708(6)	25(4)
C(28)	2004(14)	–980(14)	9605(7)	31(4)
C(30)	1748(12)	–934(12)	10580(6)	21(3)

*Equivalent isotropic U defined as one third of the trace of the orthogonalised U tensor.

TABLE VI. Selected Interatomic Distances in $(CH_3CN)PdCl_2(\mu\text{-dpmp})PdCl_2 \cdot CH_3CN$.

Pd(1)–P(1)	2.239(4)	Pd(1)–Cl(2)	2.348(4)
Pd(1)–Cl(1)	2.324(3)	Pd(1)–P(3)	2.241(4)
Pd(2)–Cl(3)	2.300(4)	Pd(2)–P(2)	2.230(4)
Pd(2)–Cl(4)	2.288(4)	Pd(2)–N(1)	2.065(14)
P(1)–C(3)	1.806(15)	P(1)–C(9)	1.819(14)
P(1)–C(1)	1.847(15)	P(3)–C(15)	1.816(13)
P(3)–C(2)	1.818(14)	P(3)–C(21)	1.806(14)
P(2)–C(27)	2.006(14)	P(3)–P(1)	3.270(8)
P(2)–P(3)	3.088(8)	P(2)–P(1)	3.146(8)
N(1)–C(33)	1.14(2)	C(33)–C(34)	1.45(2)
N(2)–C(35)	1.13(3)	C(35)–C(36)	1.41(3)

The structure was solved by Patterson and Fourier methods. The handedness was determined by the Rogers procedure in which a parameter times Δf″ is refined to ±1 [24]. This procedure indicated that the inverted enantiomer was correct, and the positions of all atoms were moved accordingly. Blocked-cascade least-squares refinement was carried out with anisotropic thermal parameters for Pd, Cl and P and a riding model for hydrogen atoms as for the previous structure. Convergence occurred at *R* = 0.069 for 234 variables and 3193 unique data. A difference map computed after the last cycle of refinement was featureless. Positional and thermal parameters for this structure are given in Table V. Selected interatomic distances and bond angles are presented in Tables VI and VII, respectively. Hydrogen atom positions, anisotropic thermal parameters and structure factor tables are available as supplementary material.

Results

Reactions of Bis(diphenylphosphinomethyl)phenylphosphine with Bis(benzonitrile)palladium(II) Chloride

The reaction of equimolar quantities of bis(diphenylphosphinomethyl)phenylphosphine with bis(benzonitrile)palladium(II) chloride in dichloromethane solution yields the cream colored complex *9* in 76% yield. The ^{31}P-NMR spectrum of the complex consists of a doublet at 18.3 ppm due to the two terminal phosphorus atoms of the chelate ring and a triplet at –40.7 due to the internal phosphorus. The phosphorus-phosphorus coupling constant is 62 Hz. For comparison ^{31}P-NMR spectrum of the free ligand is an A_2B pattern with δ_A, –33.0 ppm; δ_B, –22.8 ppm and J(AB) = 115 Hz. Thus chelation of the triphosphine ligand results in a shift of the resonance of the terminal, coordinated phosphorus atoms to high frequency as is usually observed upon coordi-

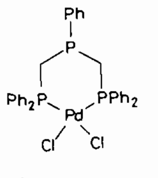

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TABLE VII. Selected Bond Angles for $(CH_3CN)PdCl_2(\mu\text{-dpmp})PdCl_2 \cdot CH_3CN$.

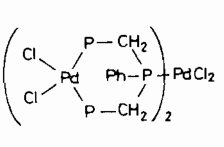
P(1)–Pd(1)–Cl(2)	88.0(1)	P(1)–Pd(1)–Cl(1)	171.5(1)
Cl(2)–Pd(1)–Cl(1)	91.8(1)	P(1)–Pd(1)–P(3)	93.8(1)
Cl(2)–Pd(1)–P(3)	171.7(1)	Cl(1)–Pd(1)–P(3)	87.6(1)
Cl(3)–Pd(2)–P(2)	85.4(1)	Cl(3)–Pd(2)–Cl(4)	176.5(2)
P(2)–Pd(2)–Cl(4)	93.2(1)	Cl(3)–Pd(2)–N(1)	89.9(4)
P(2)–Pd(2)–N(1)	175.3(4)	Cl(4)–Pd(2)–N(1)	91.5(4)
Pd(1)–P(1)–C(3)	115.2(5)	Pd(1)–P(1)–C(9)	110.8(4)
C(3)–P(1)–C(9)	108.5(7)	Pd(1)–P(1)–C(1)	113.2(5)
C(3)–P(1)–C(1)	107.6(7)	C(9)–P(1)–C(1)	100.3(6)
Pd(1)–P(3)–C(15)	115.7(5)	Pd(1)–P(3)–C(2)	111.9(5)
C(15)–P(3)–C(2)	106.4(6)	Pd(1)–P(3)–C(21)	113.0(5)
C(15)–P(3)–C(21)	105.0(6)	C(2)–P(3)–C(21)	103.8(7)
Pd(2)–P(2)–C(2)	114.0(5)	Pd(2)–P(2)–C(1)	115.0(5)
C(2)–P(2)–C(1)	104.4(7)	C(2)–P(2)–C(27)	107.5(7)
C(1)–P(2)–C(27)	108.4(7)	Pd(2)–P(2)–C(27)	107.2(5)
N(1)–C(33)–C(34)	179(1)	N(2)–C(35)–C(36)	178(2)

nation. The resonance of the free phosphorus atom is shifted to lower frequency in the chelated complexes.

The free phosphorus atom of *9* is capable of binding an additional metal atom. Titration of *9* with bis(benzonitrile)palladium(II) chloride in dichloromethane solution reveals that a reaction occurs with the stoichiometry shown in eqn. 1. The product may also be prepared directly from the reaction between dpmp and (1,5-cyclooctadiene)-palladium(II) chloride. It has been isolated as fine

$$2(\text{dpmp})PdCl_2 + (PhCN)_2PdCl_2 \longrightarrow (\text{dpmp})_2Pd_3Cl_6 + 2PhCN \qquad (1)$$

yellow crystals. The formation of $(\text{dpmp})_2Pd_3Cl_6$ is readily followed by ^{31}P NMR spectroscopy, which shows the direct transformation of the spectrum of $(\text{dpmp})PdCl_2$ into the spectrum of $(\text{dpmp})_2Pd_3Cl_6$ without the appearance of any intermediates. The ^{31}P-NMR spectrum of $(\text{dpmp})_2Pd_3Cl_6$ consists of two narrow singlets at 23.0 and –5.3 ppm with an intensity ratio of 2:1. The chemical shifts of both types of phosphorus atoms are at higher frequency of those of the free phosphine and consequently suggest that all of the phosphorus atoms of the ligand are coordinated. Because of the narrow lines J(P,P) must be less than 10 Hz. These data are consistent with either structure *10* or *11* for the product. Because of the structural results on a related derivative (*vide infra*), we feel that *10* is the more likely structure.



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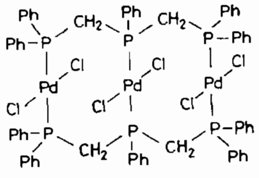

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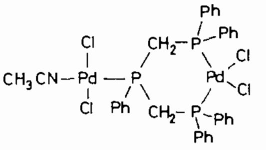
Although ^{31}P-NMR spectra of mixtures of $(\text{dpmp})PdCl_2$ and $(PhCN)_2PdCl_2$ indicate that, in dichloromethane solution the reaction terminates with the formation of $(\text{dpmp})_2Pd_3Cl_6$ as the sole product, mixing equimolar quantities of the mononuclear palladium complexes followed by precipitation with ethyl ether yields another palladium complex. This species, unlike $(\text{dpmp})_2Pd_3Cl_6$ does not redissolve in dichloromethane. However it may be recrystallized from acetonitrile to yield yellow crystals with the composition $(\text{dpmp})Pd_2Cl_4(CH_3CN)_2$. In acetonitrile, this complex has a ^{31}P-NMR spectrum which consists of two singlets at 22.4 and 5.6 ppm with a 2:1 intensity ratio. No P–P coupling is apparent in the spectrum. The chemical shifts of both phosphorus atoms are indicative of coordination. An X-ray crystal structure (*vide infra*) indicates that this material possesses the structure *12*.



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The Molecular Structure of $(\text{dpmp})PdCl_2$

Atomic coordinates are given in Table II. Tables III and IV give a selection of pertinent interatomic distances and angles. Figure 1 shows a perspective drawing of the molecule along with the numbering scheme. Figure 2 is a stereoscopic view of the molecule. The complex possesses crystallographically imposed mirror symmetry. In addition to one-

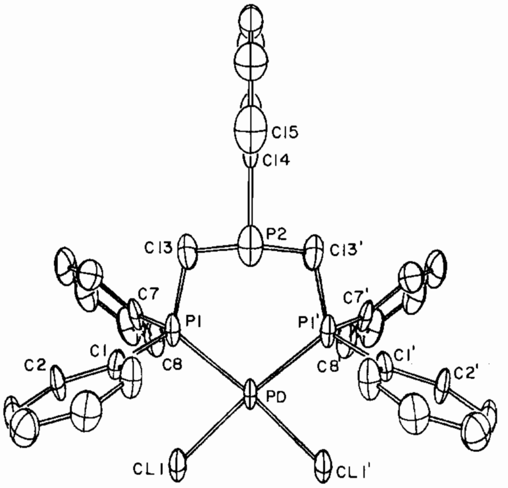


Fig. 1. A perspective view of (dpmp)$PdCl_2$.

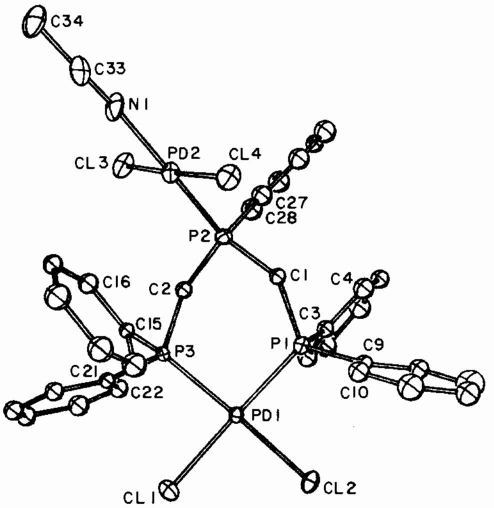


Fig. 3. A perspective view of $(CH_3CN)PdCl_2(\mu$-dpmp)$PdCl_2$.

half of a molecule of the complex, the asymmetric unit contains one-half a molecule of dichloromethane. There are no unusual contacts between these species.

The coordination about the palladium ion is strictly planar. The Pd–P and Pd–Cl bond lengths fall within normal limits. The largest deviation from normal bond angles about palladium involves the P–Pd–P angle which is 99.3° rather than the expected 90°. The structure is readily compared to those of $(Ph_2P(CH_2)_nPPh_2)PdCl_2$ (n = 1, 2, 3) [27] and of *cis*-$(PhMe_2P)_2PdCl_2$ [28]. In the chelate complexes, the P–Pd–P angles increase as the ring size expands (n = 1, 72.7°; n = 2, 85.8°; n = 3, 90.6°) while this angle is considerably larger in the nonchelate compound (97.8°).

The triphosphine ligand is coordinated through the terminal phosphorus atoms only. The central phosphorus atom is not bonded to palladium. Not only is the Pd···P(2) separation long (3.893 Å) but the phosphorus lone pair is not directed toward palladium at all. This is readily apparent in the stereoscopic drawing. The C–P–C bond angles about the central, uncoordinated phosphorus atom (98.3, 101.7°) are significantly smaller than the related angles at the terminal, palladium bond phosphorus atoms (107.6, 104.1 and 102.7). Similar differences in bond angles for free and coordinated tertiary phosphine have been noted before [28] and can be attributed in the increase in s orbital character in the bonds about a metal-bound phosphine.

The Molecular Structure of $(CH_3CN)PdCl_2(\mu$-dpmp)-$PdCl_2 \cdot CH_3CN$

The atomic coordinates for this binuclear complex are given in Table V. Selected interatomic distances and angles are presented in Tables VI and VII respectively. Figure 3 shows a perspective drawing of the molecule and our numbering scheme. A stereoscopic drawing of the molecule is presented

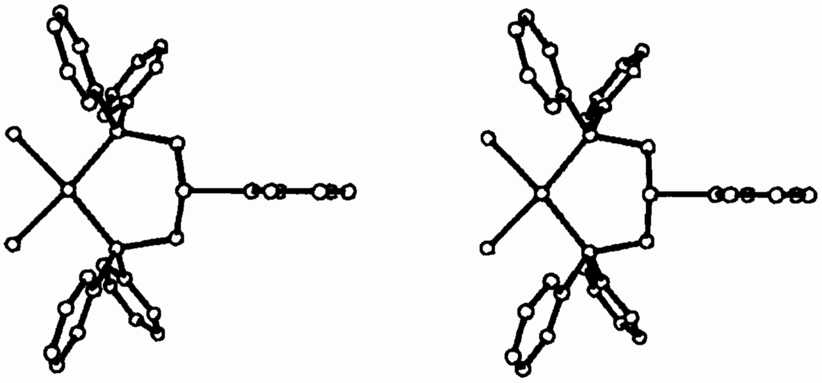


Fig. 2. A stereoscopic drawing of (dpmp)$PdCl_2$.

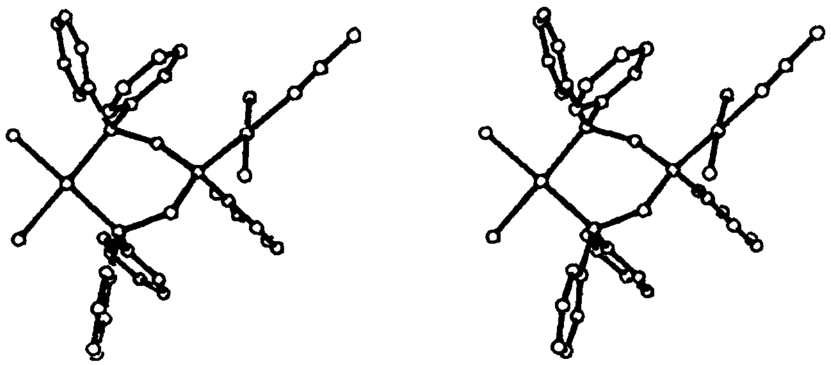


Fig. 4. A stereoscopic drawing of $(CH_3CN)PdCl_2(\mu\text{-dpmp})PdCl_2$.

in Fig. 4. There is no symmetry crystallographically imposed on the complex. The asymmetric unit contains the dinuclear complex along with a molecule of acetonitrile. These are well separated, and there are no unusual intermolecular contacts in the solid.

Both palladium atoms are four coordinate and planar. One, Pd(1), is bound to two phosphorus atoms from the chelating triphosphine and two *cis* chloride ligands. The other, Pd(2), is bound to two *trans* chloride ligands, an acetonitrile ligand and the internal phosphorus atom of the triphosphine ligand. The environment of Pd(1) is somewhat distorted from planarity. The dihedral angle between the planes defined by Pd(1)P(1)P(3) and Pd(1)Cl(1)-Cl(2) is 11.5°. The corresponding dihedral angles in related palladium complexes are less: $(dpmp)PdCl_2$, 0°; *cis*$(PhMe_2P)_2PdCl_2$, 8.7°; $(Ph_2P)(CH_2)_n PPh_2)PdCl_2$: n = 1, 8.4°; n = 2, 3.0°; n = 3, 8.1°. The P(1)–Pd(1)–P(3) angle, 93.8°, in $(CH_3CN)PdCl_2(dpmp)PdCl_2$ is reduced relative to the corresponding angle in $(dpmp)PdCl_2$. The bond distances about Pd(1) are all within their normal values.

The coordination geometry about Pd(2) is more nearly planar than it is about Pd(1). All of the bond angles between *cis* ligands are close to 90°. The presence of the *trans* Cl–Pd–Cl unit produces shorter Pd(2)–Cl bonds than the corresponding bond lengths at Pd(1) where *cis* phosphines are involved. The acetonitrile ligand is coordinated in the normal, linear fashion. There are no significant differences between the free and the coordinated acetonitrile molecules in the solid.

The triphosphine ligand uses its two terminal phosphorus atoms to bind Pd(1) while the internal phosphorus binds Pd(2). As a result of coordination at Pd(2), the C–P–C angles about P(2) (104.4, 107.5, 108.4) have opened up relative to the corresponding values in $(dpmp)PdCl_2$.

Chelate Ring Conformations

The chelate ring conformations in these two complexes are best described using the nomenclature developed for propylenediamine chelate rings [30].

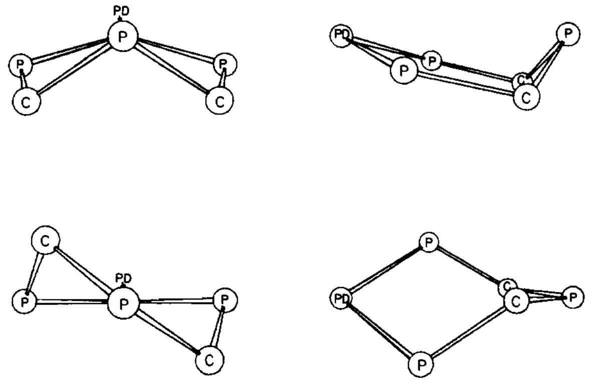


Fig. 5. A comparison of the chelate ring conformations in $(dpmp)PdCl_2$ at the top and $(CH_3CN)PdCl_2(\mu\text{-dpmp})PdCl_2$ at the bottom. The two views on the left side look down the phosphorus-palladium axis and the palladium atom is hidden from view.

The chelate ring in $(dpmp)PdCl_2$ has a boat conformation. In the solid the ring is bisected by a crystallographically imposed mirror plane which passes through the palladium and interior phosphorus atoms. The conformation is best appreciated by turning to Fig. 5 which presents, in its upper half, two views of the six atoms comprising the chelate ring. While the interior phosphorus atom is bent up toward the palladium, it is clearly not within bonding distance of that metal atom.

Upon binding a second palladium, the ring conformation, at least in the solid state, is altered. Views of the chelate ring in $(CH_3CN)PdCl_2(\mu\text{-dpmp})PdCl_2$ are shown in the lower half of Fig. 5. In this case the chelate ring possesses a symmetric skew-boat conformation. The chelate ring is dissymmetric. On crystallization the complex undergoes spontaneous resolution. In the particular crystal chosen for study, the absolute configuration of the chelate ring is λ.

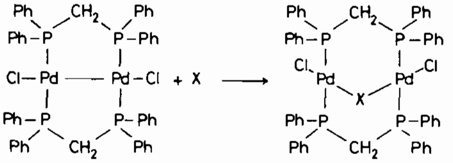
The change in ring conformation from boat to symmetric skew-boat allows for a large non-bonded Pd•••Pd separation in the binuclear complex. In crystalline $(CH_3CN)PdCl_2(\mu\text{-dpmp})PdCl_2$ this separation is 5.854 Å. If an imaginary palladium atom were added to the central phosphorus atom of (dpmp)PdCl$_2$ (at a Pd–P distance of 2.226 Å) while maintaining the boat conformation, the hypothetical Pd•••Pd separation would be 4.31 Å. Thus the change in ring conformation accomodates a greater separation between the metal ions and serves to minimized non-bonded interactions between their coordination environments. It is interesting to note, however, that the non-bonded Pd(1)–P(2) separations in the two structures (3.893 in (dpmp)PdCl$_2$ and 4.182 Å in (CH$_3$CN)PdCl$_2$(dpmp)PdCl$_2$ are not greatly different.

Discussion

In utilizing polydentate phosphine ligands to construct polynuclear complexes, it is necessary to understand how these ligands wrap themselves about metal centers. The present work establishes the ability of bis(diphenylphosphinomethyl)phenylphosphine to form six-membered chelate rings. Further investigation, on going in this laboratory, suggest that this is the most common mode of binding of this ligand to a single metal center. Additionally we have demonstrated that the chelated ligand is capable of binding a second metal through the internal phosphorus atom. Preliminary results using other metal ions suggest that this is also a common mode of reaction for this ligand [23].

It is instructive to compare the mode of chelating of bis(diphenylphosphinomethyl)phenylphosphine found here with comparable behavior of other tridentate phosphine ligands. Meek and coworkers [31] have examined the products of interaction of a dimethylplatinum(II) fragment with several polydentate phosphine ligands. The dimethylplatinum(II) fragment and a dichloropalladium(II) unit will have similar bonding requirements and the comparison seems reasonable. The linear triphosphine ligands $Ph_2P(CH_2)_2P(Ph)(CH_2)_2PPh_2$, $Ph_2P(CH_2)_2P(Ph)(CH_2)_3PPh_2$, and $Ph_2P(CH_2)_3P(Ph)(CH_2)_3PPh_2$ form complexes in which one terminal phosphorus atom is uncoordinated while the other two form a chelate ring. However, the ^{31}P-NMR spectra of all of these complexes are temperature dependent and show that the platinum atom can move between alternate chelate rings. With the tripod ligand, $CH_3C(CH_2PPh_2)_3$, a six-membered chelate ring, similar to that found in (dpmp)PdCl$_2$, is formed while the remaining phosphorus atom is uncoordinated [31]. All of these complexes have the potential for adding a second metal to the uncoordinated phosphorus atom but this area has not been explored. On the other hand the triphosphine, $PhP\{(CH_2)_3PPh_2\}_2$ reacts with tetrachloroplatinum(II) to yield the salt $[PhP\{(CH_2)_3PPh_2\}_2PtCl]Cl$ in which all three of the phosphorus atoms are coordinated to platinum [32].

The flexibility of the phosphine ligand in accomodating a variety of metal–metal separations as well as differing coordination geometries has been shown to be an important aspect of some of the novel chemical reactions of complexes containing bridging bis(diphenylphosphino)methane ligands. For example, the insertion of small molecules into the metal–metal bond of Pd$_2$(μ-dpm)$_2$X$_2$, which occurs *via* eqn. 2 (X = CO, SO$_2$, CNR, RC≡CR), results in an expansion of the Pd–Pd distance of about 0.5 Å [9, 10, 34, 35]. In comparison Pd$_2$(μ-Ph$_2$Ppy)$_2$Cl$_2$, *13*, which is isoelectronic with Pd$_2$(μ-dpm)$_2$Cl$_2$, does not undergo facile insertions of similar small molecules [14]. We have attributed this lack of reactivity to the more rigid nature of the phosphinopyridine ligand. The fixed bite of this ligand appears to restrict the metal–metal separation to less than 2.7 Å whenever two such *trans* bridging ligands are present.



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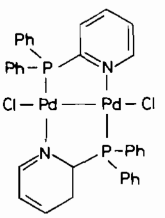

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We believe that bis(diphenylphosphinomethyl)phenylphosphine has the ability to act as an extremely flexible connection between metal atoms. Here chelate ring conformation can play a major role in accomodating a variety of bonding possibilities. The structural results concerning (CH$_3$CN)PdCl$_2$(μ-dpmp)PdCl$_2$ already demonstrate the ability of this ligand to bridge two metal atoms which are quite remote from one-another. The symmetric skew-boat ring conformation is certainly capable of insuring maximal separation of the two metals. However, in the boat conformation found in (dpmp)PdCl$_2$, the lone pair of the internal phosphorus atom is directed over and above the chelated palladium. Inspection of space filling models suggests that in this conformation it should be possible to bind a second metal atom to both the internal phosphorus atom and to the chelated metal atom.

Acknowledgements

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