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Contribution from the Departments of Chemistry, The University of Western Ontario, London, Ontario, Canada N6A 5B7, and The University of Guelph, Guelph, Ontario, Canada N1G 2W1

Relative Stabilities of Monomeric and Dimeric Forms of Complexes $[PtCl_2(RR'PCH_2PRR')]$: Structure of *cis*-Tetrachlorobis[μ-bis(*tert*-butylphosphino)methane]diplatinum(II)

KAZI A. AZAM,† GEORGE FERGUSON,*‡ SAMSON S. M. LING,† MASOOD PARVEZ,‡
RICHARD J. PUDDEPHATT,*† and DEREK SROKOWSKI†

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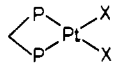
Reaction of $[PtCl_2(SMe_2)_2]$ with $Et_2PCH_2PEt_2$ (depm) or i-Pr_2PCH_2P-i-Pr_2 (dippm) gave mononuclear [PtCl$_2$(depm)] or [PtCl$_2$(dippm)]. In contrast, t-BuHPCH$_2$PH-t-Bu (dtbpm) gave the binuclear *cis*-[Pt$_2$Cl$_4$(μ-dtbpm)$_2$] and $Me_2PCH_2PMe_2$ (dmpm) gave insoluble [(PtCl$_2$(dmpm))$_n$], which, on the basis of IR and MS data, is thought to be *cis*-[Pt$_2$Cl$_4$(μ-dmpm)$_2$]. The structure of [Pt$_2$Cl$_4$(μ-dtbpm)$_2$] was established by an X-ray analysis of crystals of its methanol solvate. The crystals are monoclinic, space group $P2_1/c$, with two centrosymmetric molecules of the binuclear complex and four molecules of methanol of solvation in a unit cell of dimensions $a = 8.841$ (1) Å, $b = 9.708$ (1) Å, $c = 19.841$ (3) Å, and $\beta = 98.23$ (2)°. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations to $R = 0.059$ for 3525 observed reflections. The Pt atom has distorted square-planar geometry with cis Pt–P distances of 2.228 (2) and 2.229 (2) Å and cis Pt–Cl distances of 2.344 (2) and 2.360 (3) Å. The eight-membered ring (PtP$_2$C)$_2$ has a slightly deformed chair conformation.

Introduction

The ligand bis(diphenylphosphino)methane (dppm) is commonly used as a bridge between two metal atoms in forming stable binuclear or polynuclear complexes.[1,2] The factors that influence whether the chelated (**1**), the cis,cis-bridged (**2**), trans,trans-bridged (**3**), or other forms, will be most stable in complexes are only partially understood. For example, **1** is preferred when X = Cl, Br, or I, but **3** is preferred when X = alkynyl.[3,4] For X = Me, both **1** and **2** have been isolated but **1** is more stable.[5,6]



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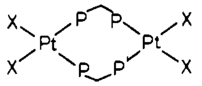

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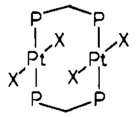

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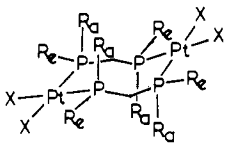

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In previous publications, the relative stabilities of mononuclear complexes [PtMe$_2$(R$_2$PCH$_2$PR$_2$)], and dinuclear complexes, *cis,cis*-[Pt$_2$Me$_4$(μ-R$_2$PCH$_2$PR$_2$)$_2$], of structures **1** and **2**, respectively, were examined as a function of the bulk of the substituents R.[7,8] It was concluded that angle strain was less in **2** than in **1**, since **1** contains a four-membered chelate ring, and therefore structure **2** was preferred when the R groups were small. However, steric effects were greater in the dinuclear form **2** than in **1**, and hence for large R groups the mononuclear form **1** was more stable. In this case, when R = Me or Et, the thermodynamically stable form was **2** whereas when R = Ph or i-Pr, the stable form was **1**. The greatest steric interactions in the twist-chair conformation of *cis,cis*-[PtMe$_4$(μ-Me$_2$PCH$_2$PMe$_2$)$_2$] were between the axial substituents on the phosphine ligands (shown as R$_a$ in structure **4**).

We have now studied the complexes [(PtCl$_2$(R$_2$PCH$_2$PR$_2$))$_n$] where R = Me, Et, and i-Pr in order to investigate the nuclearity, n, as a function of R. In addition, the related complex, with n = 2, of the ligand t-BuHPCH$_2$PH-t-Bu (dtbpm) has been characterized by a single-crystal X-ray structure determination and illustrates in a particularly clear fashion the role of steric effects in determining whether the monomer or dimer form will be the more stable.

Results and Discussion

Reaction of [PtCl$_2$(SMe$_2$)$_2$] with depm or dippm gave monomeric [PtCl$_2$(depm)] or [PtCl$_2$(dippm)] of structure **1**. These complexes were readily characterized by the $^{31}P\{^1H\}$ NMR spectra, which contained only a singlet with one-fourth intensity satellites due to coupling to ^{195}Pt as expected for a monomeric, but not for a dimeric, complex.[8] In addition, there was a high-field shift compared to that of the free phosphine ligands, as expected for a four-membered chelate complex.[9] Thus for [PtCl$_2$(R$_2$PCH$_2$PR$_2$)], the magnitudes of the coordination shift, defined as δ(coordinated phosphine) − δ(free phosphine), were −23.5, −29.8, and −41.1 for R = Et, i-Pr, and Ph, respectively.

Reaction of *trans*-[PtI$_2$(SMe$_2$)$_2$] with dmpm gave a mixture of monomeric [PtI$_2$(dmpm)] and *trans*-[Pt$_2$I$_4$(μ-dmpm)$_2$], with structure **3**. These were easily separated since the monomer was sparingly soluble in dichloromethane, whereas the dimer was more soluble. The $^{31}P\{^1H\}$ NMR spectrum of the monomer gave the expected high-field singlet with a coordination shift of −28.1 ppm. In contrast, the dimer gave a coordination shift of +21.7 ppm in the $^{31}P\{^1H\}$ NMR spectrum and the trans stereochemistry was indicated by the "triplet" appearance of the ^{195}Pt satellites[2] and by the magnitude of ^1J(PtP) of 2284 Hz. For comparison, ^1J(PtP) is 2200 Hz in *trans*-[PtI$_2$(PBu$_3$)$_2$] but 3372 Hz in *cis*-[PtI$_2$(PBu$_3$)$_2$].[10]

Greater difficulty was found in the characterization of the dmpm complex of PtCl$_2$. Three samples, each analyzing as [(PtCl$_2$(dmpm))$_x$] were prepared, and all were insoluble or very sparingly soluble in all common organic solvents and in water, so that NMR spectra could not be obtained. The first sample was prepared by reaction of [PtCl$_2$(SMe$_2$)$_2$] with dmpm. The second was prepared by heating the above sample in hydrochloric acid suspension (a procedure commonly used to isomerize complexes [PtCl$_2$L$_2$]), and the third was prepared by reaction of

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† University of Western Ontario.
‡ University of Guelph.

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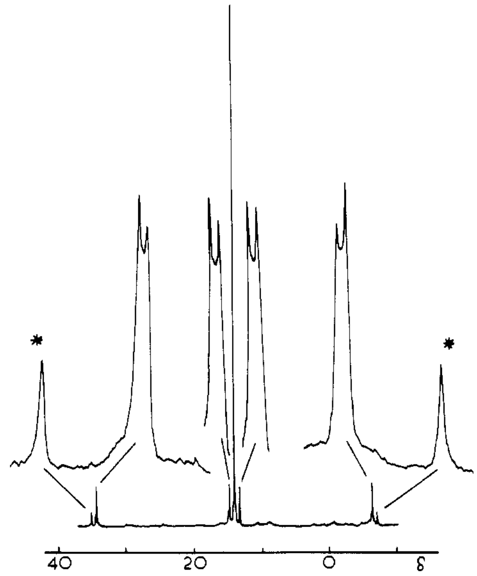

Figure 1. ^{31}P NMR spectrum (81 MHz) of $[Pt_2Cl_4(\mu\text{-}t\text{-}BuHPCH_2PH\text{-}t\text{-}Bu)_2]$, with expansions of the satellite peaks above. The peaks marked with an asterisk are due to the $^{195}Pt_2$ isotopomer and are separated by $^1J(PtP) + {}^3J(PtP)$.

cis-$[Pt_2Me_4(\mu\text{-dmpm})_2]$ with a large excess of HCl. The far-infrared spectra of all samples contained bands at 310 ± 5 and 292 ± 1 cm^{-1} due to $\nu(PtCl)$, suggesting the presence of *cis*-$[PtCl_2P_2]$ units,[10] and the mass spectra indicated that all complexes were dimers. We suggest therefore that they all have structure **2**, though the mass spectrometric determination of nuclearity is by no means definitive.[10] Chemical reactions that support the proposed structure **2** are the reaction with methyllithium to give *cis*-$[Pt_2Me_4(\mu\text{-dmpm})_2]$ and the reaction with $CH_3C{\equiv}CH$ and base to give *cis*-$[Pt_2(CCMe)_4(\mu\text{-dmpm})_2]$, both of which were soluble and were ppositively characterized as having structure **2**. It is unlikely that a major structural change accompanies these substitution reactions.[7,8] Extraction of the second sample above of $[PtCl_2(dmpm)]_n$ with dichloromethane, gave a very low yield of a complex that is characterized as the trans isomer, ***trans***-$[Pt_2Cl_4(\mu\text{-dmpm})_2]$ (**3**), by the $^{31}P\{^1H\}$ NMR spectrum. This spectrum (Experimental Section) was of low quality due to the tiny yield of complex, but it is very similar to that for *trans*-$[Pt_2I_4(\mu\text{-dmpm})_2]$. We initially suggested that this product was monomeric $[PtCl_2(dmpm)]$,[7] but it is now clear, by comparison with spectral parameters for $[PtCl_2(depm)]$ and $[PtCl_2(dippm)]$, that this was an error. This complex of structure **3** was apparently formed by partial isomerization of **2** on heating in hydrochloric acid.

In one attempt to prepare the ligand $t\text{-}Bu_2PCH_2P\text{-}t\text{-}Bu_2$ from $Cl_2PCH_2PCl_2$ and *t*-BuMgCl, the secondary phosphine *t*-$BuHPCH_2PH\text{-}t\text{-}Bu$ was isolated in almost pure form. Reaction of this ligand with $[PtCl_2(SMe_2)_2]$ gave the dimer *cis,cis*-$[Pt_2Cl_4(\mu\text{-}t\text{-}BuHPCH_2PH\text{-}t\text{-}Bu)_2]$. The cis,cis binuclear structure was established by an X-ray structure determination and was also consistent with the IR spectrum [$\nu(PtCl)$ at 318 and 295 cm^{-1}] and the $^{31}P\{^1H\}$ NMR spectrum (Figure 1). The ^{195}Pt satellites with doublet appearance are characteristic of this structure,[8] and the magnitude of $^1J(PtP)$ also suggests phosphine trans to Cl.[10] We were unable to identify a resonance due to the PH groups in the ^1H NMR spectrum, but this functional group was confirmed by recording the ^{31}P NMR spectrum without ^1H decoupling, when the central peak (Figure 1) appeared as a doublet with $^1J(PH) = 415$ Hz.

Table I. Molecular Dimensions for $[Pt_2Cl_4(\mu\text{-}t\text{-}BuHPCH_2PH\text{-}t\text{-}Bu)_2]\cdot 2CH_3OH$[a]

	a. Bond Distances (Å)		
Pt–Cl(1)	2.344 (2)	C(11)–C(12)	1.503 (15)
Pt–Cl(2)	2.360 (3)	C(11)–C(13)	1.540 (14)
Pt–P(1)	2.228 (2)	C(11)–C(14)	1.513 (14)
Pt–P(2)	2.229 (2)	C(21)–C(22)	1.544 (14)
P(1)–C(1)	1.837 (9)	C(21)–C(23)	1.526 (13)
P(1)–C(11)	1.868 (9)	C(21)–C(24)	1.490 (13)
P(2)–C(1)′	1.853 (9)	O(S)–C(S)	1.326 (21)
P(2)–C(21)	1.870 (8)		
	b. Bond Angles (deg)		
Cl(1)–Pt–Cl(2)	89.3 (1)	P(1)–C(11)–C(12)	110.9 (7)
Cl(1)–Pt–P(1)	88.5 (1)	P(1)–C(11)–C(13)	107.1 (7)
Cl(1)–Pt–P(2)	176.0 (1)	P(1)–C(11)–C(14)	106.7 (7)
Cl(2)–Pt–P(1)	174.0 (1)	C(12)–C(11)–C(13)	110.3 (9)
Cl(2)–Pt–P(2)	88.9 (1)	C(12)–C(11)–C(14)	110.3 (10)
P(1)–Pt–P(2)	92.9 (1)	C(13)–C(11)–C(14)	111.3 (10)
Pt–P(1)–C(1)	111.9 (3)	P(2)–C(21)–C(22)	105.0 (7)
Pt–P(1)–C(11)	121.9 (3)	P(2)–C(21)–C(23)	108.3 (7)
C(1)–P(1)–C(11)	105.9 (4)	P(2)–C(21)–C(24)	111.3 (7)
Pt–P(2)–C(1)′	111.6 (3)	C(22)–C(21)–C(23)	110.4 (9)
Pt–P(2)–C(21)	120.3 (3)	C(22)–C(21)–C(24)	110.8 (11)
C(1)′–P(2)–C(21)	106.4 (4)	C(23)–C(21)–C(24)	111.8 (10)
P(1)–C(1)–P(2)′	108.5 (5)		
	c. Torsion Angles (deg)		
P(2)Pt–P(1)C(1)	118.1 (5)	PtP(1)–C(1)P(2)′	−45.7 (7)
P(1)Pt–P(2)C(1)′	−120.9 (5)	PtP(2)–C(1)′P(1)′	52.2 (7)

[a] Primed atoms are related to unprimed atoms by the transformation −*x*, −*y*, −*z*. In this and succeeding tables estimated standard deviations are in parentheses.

Description of the Structure of $[Pt_2Cl_4(\mu\text{-}t\text{-}BuHPCH_2PH\text{-}t\text{-}Bu)_2]\cdot 2CH_3OH$

The crystals of **4** contain centrosymmetric molecules of the binuclear complex $[PtCl_2(\mu\text{-}t\text{-}BuHPCH_2PH\text{-}t\text{-}Bu)]_2$ (Figure 2), lying on an inversion center, and methanol of solvation; the shortest intermolecular contacts are between the loosely held methanol molecule and chlorine atoms of adjacent complex molecules. The molecular dimensions in **4** are given in Table I and are in accord with accepted values. In Table II the bond lengths of **4** are compared with those of related molecules. The cis Pt–P distances 2.228 (2) and 2.229 (2) Å lie within the range of values given in Table II. The cis Pt–Cl distances 2.344 (2) and 2.360 (3) Å

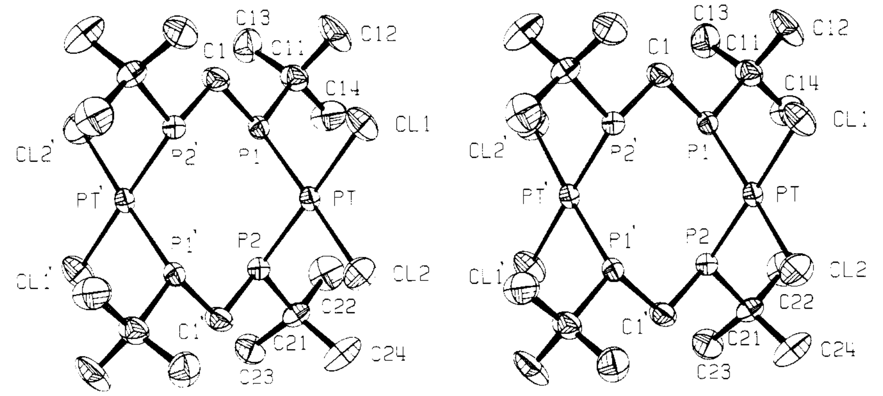

Figure 2. Stereoview of the $[Pt_2Cl_4(\mu\text{-}t\text{-}BuHPCH_2PH\text{-}t\text{-}Bu)_2]$ complex with the crystallographic numbering scheme.

Table II. Bond Lengths (Å) and Angles (deg) Involving Pt, Cl, and P in *cis*-Dichlorobis(phosphine)platinum Complexes

L in *cis*-$PtCl_2L$	Pt–P	P–Pt–P	Pt–Cl	Cl–Pt–Cl	ref
t-$BuHPCH_2PH$-*t*-Bu	2.228 (2) 2.229 (2)	92.9 (1)	2.344 (2) 2.360 (3)	89.3 (1)	this work
t-$Bu_2P(CH_2)_2P$-*t*-Bu_2	2.262 (3) 2.265 (3)	89.4 (1)	2.365 (4) 2.374 (3)	86.3 (1)	15
t-$Bu_2P(CH_2)_3P$-*t*-Bu_2	2.281 (3) 2.282 (3)	99.1 (1)	2.359 (3) 2.362 (3)	83.2 (1)	16
$Ph_2P(CH_2)_2PPh_2$	2.208 (6) 2.208 (6)	86.3 (2)	2.355 (6) 2.341 (6)	90.2 (2)	17
$(PMe_3)_2$	2.233 (3) 2.243 (3)	96.2 (1)	2.368 (3) 2.377 (3)	87.9 (1)	18
$(PPh_3)_2$	2.251 (2) 2.265 (2)	97.8 (1)	2.333 (2) 2.356 (2)	87.1 (1)	19

are comparable with those reported by others (Table II). The angles P–Pt–P (92.9 (1)°) and Cl–Pt–Cl (89.3 (1)°) are close to 90°. The coordination around the Pt atom is slightly distorted from square planar with Pt 0.075 Å below the $PtCl_2P_2$ plane, P(1) and Cl(2) being above (0.039 and 0.037 Å, respectively) and P(2) and Cl(1) in the plane. The atoms P(1), P(2), C(1), P(1)′, P(2)′, and C(1)′ are essentially coplanar with the plane necessarily passing through the origin; the plane of six atoms (P(1)–C(1)′) is inclined at an angle of 81.2° with the $PtCl_2P_2$ plane. The eight-membered ring $(PtP_2C)_2$ has a slightly twisted chair conformation. If the P–H distance has a normal value of 1.37 Å, the distance between the axial substituents R_a = H of structure **4** is calculated to be approximately 2.0 Å. This is unexceptional but does illustrate that steric hindrance would be severe with bulkier R_a groups.

The P–C and C–C distances in the phosphine ligand are normal (1.837–1.870 (8) Å, mean 1.857 (9) Å, and 1.490–1.544 (14) Å, mean 1.519 (14) Å, respectively). The Pt–P(1)–C(11) (121.9 (3)°) and Pt–P(2)–C(21) (120.3 (3)°) angles are larger than the Pt–P(1)–C(1) (111.9 (3)°) and Pt–P(2)–C(1)′ (111.6 (3)°) angles, reflecting the steric effect of Cl ligands and thus narrowing the C–P–C angles (C(1)–P (1)–C(11) = 105.9 (4)°, C(1)–P(2)–C(21) = 106.4 (4)°) from the normal tetrahedral value of 109.5°. There is also an effect on the angles at the *tert*-butyl carbon atoms C(11) and C(21); thus the methyl carbons closest to a chlorine atom (C(12)···Cl(1) = 3.471 Å, C(24)···Cl(2) = 3.496 Å) subtend the largest angles at C(11) and C(12) (P(1)–C(11)–C(12) = 110.9 (7)°, P(2)–C(21)–C(24) = 111.3 (7)°) compared with the other P–C–C angles, which are in the range 105.0 (7)–108.3 (7)°.

Conclusions

The chief difference between the dichloroplatinum complexes and the corresponding dimethylplatinum complexes, studied earlier,[5,7,8] is seen for the ligand $Et_2PCH_2PEt_2$, where chelate **1** is observed when X = Cl but the bridged **2** is more stable when X = Me. The chief steric hindrance in **2** occurs between axial substituents on the phosphorus ligands, labeled R_a in structure **4**. We suggest that, when X = Cl, the PtP bonds are shorter, due to the lower trans influence of chloride,[10] than when X = Me and hence that steric effects between the axial substituents, R_a, are of greater importance for the dichloroplatinum derivatives. The differences which result when X = Cl, rather than Me, are great enough to make **1** more stable than **2** in the depm complex. Presumably any slight lessening in ring strain for **1** when X = Me rather than Cl is not sufficient to counterbalance this effect.[11]

The crystal structure shows that [$Pt_2Cl_4(\mu$-*t*-$BuHPCH_2PH$-*t*-$Bu)_2$] has structure **4**, with all *t*-Bu groups in equatorial positions. Hence, steric effects between axial substituents R_a = H are very small. Under these circumstances the dimeric form is more stable than the chelate form **1**. Thus the unexpected result that this complex, having bulky substituents, is more stable in the binuclear form **2** is rationalized, and the result strongly supports the hypothesis that steric effects are of primary importance in determining the nuclearity of these complexes.

Experimental Section

NMR spectra were recorded on a Varian XL100 or XL200 spectrometer. Chemical shifts are quoted in ppm with respect to Me_4Si (^1H) or external H_3PO_4 (^{31}P). Mass spectra were obtained on a Varian MAT 311A spectrometer. Elemental analyses were carried out by Guelph Microanalytical Service.

[$PtCl_2(SMe_2)_2$] was prepared by the literature method.[12] The ligands $Cl_2PCH_2PCl_2$, dmpm, depm, and dippm were prepared by known methods.[13,14] All syntheses and reactions involving phosphine ligands were carried out under N_2 or vacuum. ^{31}P chemical shifts are as follows: dmpm, –56.5; depm, –28.6; dippm, –6.2; dppm, –28.6.

***t*-BuHPCH₂PH-*t*-Bu.** A solution of *t*-BuMgCl in ether (60 mL, 1.8 M) was added dropwise with stirring to a solution of $Cl_2PCH_2PCl_2$ (4 g) in ether (20 mL) cooled in an ice–salt bath. After addition was complete, the mixture was heated under reflux for 2 h and then hydrolyzed with cold concentrated NH_4Cl solution. The ether layer was separated and dried with $MgSO_4$ and the ether removed under vacuum. The residue was distilled under vacuum to give the product as a very air-sensitive liquid (1.5 g), bp 95–100 °C (0.5 mm). ^1H NMR (C_6D_6): 1.05 [m, *J*(PH) = 7.5 Hz, *t*-Bu], 1.60 [*J*(PH) = 3 Hz, CH_2P_2]. ^{31}P NMR: 64.7 (s). MS: *m/e* 192.

[$Pt_2Cl_4(\mu$-*t*-$BuHPCH_2PH$-*t*-$Bu)_2$]·2CH₃OH. To a solution of [$PtCl_2(SMe_2)_2$] (0.35 g) in CH_2Cl_2 (10 mL) was added *t*-$BuHPCH_2PH$-*t*-Bu (0.30 g), and the mixture was stirred for 1 h under N_2. The solution was evaporated to ~3-mL volume, and pentane was added to complete precipitation of a white solid, which was recrystallized from CH_2Cl_2/MeOH as colorless crystals that were subsequently shown to be the bis(methanol) solvate: yield 0.27 g; mp >300 °C. ^1H NMR (CD_2Cl_2): 1.38 [d, *J*(PH) = 18 Hz, *t*-Bu], 1.61 [CH_2P_2]. $^{31}P\{^1H\}$ NMR: 14.5 [s, $^1J(PtP)$ = 3328 Hz, $^3J(PtP)$ = 118 Hz, $^2J(P_AP^{B'})$ = 5 Hz]. ^{31}P NMR: 14.5 [d, $^1J(PH)$ = 415 Hz]. Anal. Calcd for $C_{20}H_{52}Cl_4O_2P_4Pt_2$: C, 24.5; H, 5.3. Found: C, 24.0; H, 5.1.

Crystal Data for [$Pt_2Cl_4(\mu$-*t*-$BuHPCH_2PH$-*t*-$Bu)_2$]·2CH₃OH: $C_{20}H_{52}Cl_4O_2P_4Pt_2$, M_r = 980.5, monoclinic, *a* = 8.841 Å, (1) *b* = 9.708 (1) Å, *c* = 19.841 (3) Å, β = 98.23 (2)°, *V* = 1686.0 Å^3, *Z* = 2, D_c = 1.93 g cm^{-3}, *F*(000) = 944, Mo Kα radiation, λ = 0.709 26 Å, μ(Mo Kα) = 89.0 cm^{-1}. Space group $P2_1/c$ from systematic absences *h0l*, *l* = 2*n* + 1, and 0*k*0, *k* = 2*n* + 1.

Structure Determination. Accurate unit cell constants and a crystal orientation matrix were determined on an Enraf-Nonius CAD4 diffractometer by a least-squares refinement of the setting angles of 25 reflections with θ in the range 10–20°. A small piece of crystal of dimensions 0.18 × 0.18 × 0.20 mm (with faces 100, $\bar{1}00$, 010, $0\bar{1}0$, 001, and $00\bar{1}$) was cut from a larger piece and used for data collection. Intensity data were collected by the $\omega/2\theta$ scan method using monochromatized Mo Kα radiation in the range $2 < \theta$ 30°. The intensities of three reflections, chosen as standards, were monitored at regular intervals and showed no reduction in intensity. Intensities of 4911 unique reflections were measured, of which 3525 had $I > 3\sigma(I)$, and were used in the structure solution and refinement. Data were corrected for Lorentz and polarization factors and for absorption.[20] Maximum and minimum values of

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Table III. Final Fractional Coordinates ($\times 10^5$ for Pt; $\times 10^4$ for the Remainder)

atom	x	y	z
Pt	2724 (3)	11141 (3)	8819 (1)
P(1)	−156 (3)	−1138 (2)	959 (1)
P(2)	−1831 (3)	1439 (2)	134 (1)
Cl(1)	2584 (3)	802 (3)	1606 (1)
Cl(2)	935 (3)	3439 (3)	736 (2)
C(1)	1378 (10)	−2170 (10)	676 (5)
C(11)	−562 (11)	−1950 (10)	1767 (4)
C(12)	846 (16)	−1968 (14)	2291 (5)
C(13)	−1111 (16)	−3430 (11)	1594 (6)
C(14)	−1802 (17)	−1096 (12)	2017 (7)
C(21)	−3455 (10)	2477 (9)	373 (5)
C(22)	−3821 (15)	1823 (14)	1041 (7)
C(23)	−4813 (12)	2325 (13)	−190 (6)
C(24)	−3020 (17)	3952 (10)	480 (10)
C(S)	3582 (20)	9545 (18)	6456 (9)
O(S)	4668 (19)	9598 (26)	6990 (9)

the transmission coefficients are 0.2976 and 0.1876, respectively.

The structure was solved by the heavy-atom method. With two molecules of the complex in the unit cell, space group $P2_1/c$ requires the molecules to lie on inversion centers; one pair of additional peaks was also found in the electron density maps, consistent with there being a methanol molecule of solvation. Refinement of the structure was by full-matrix least-squares calculations,[21] initially with isotopic and finally with anisotropic thermal parameters for the non-hydrogen atoms. At an intermediate stage in the refinement a difference map revealed all hydrogen atoms of the dimer in positions close to those expected. The H atoms were positioned geometrically (C–H = 0.95, P–H = 1.37 Å), and in subsequent cycles, although they were included, only an overall isotropic thermal parameter was refined for them; methanol hydrogen atoms could not be located from the differences map and were not included in the refinement. Refinement converged with $R = 0.059$ and $R_w = (\sum w\Delta^2/\sum F_o^2)^{1/2} = 0.057$. In the refinement cycles, weights were derived from the counting statistics, $w = 1/(\sigma^2(F) + 0.0126F^2)$. Scattering factors were those of Cromer and Mann[22] and Stewart, Davidson, and Simpson,[23] and allowance was made for anomalous dispersion.[24] 154 parameters were refined in the final cycles. The maximum shift/error was 0.064 for z/c of Pt and 0.085 for U_{33} of C(21). A difference map calculated at the conclusion of the refinement had no chemically significant features.

The final fractional coordinates with estimated standard deviations are given in Table III. Tables of hydrogen coordinates, anisotropic temperature factors, and structure factor listings have been deposited as supplementary material.

[PtCl$_2$(depm)]. This was prepared by reaction of $Et_2PCH_2PEt_2$ (0.40 g) with a solution of [PtCl$_2$(SMe$_2$)$_2$] (0.65 g) in CH_2Cl_2 (20 mL). After 1 h at room temperature, *n*-pentane (10 mL) was added and the solution was cooled to 0 °C. The white precipitate was recovered by filtration and dried under vacuum: yield 0.42 g; mp 300–305 °C dec. ^{1}H NMR (CDCl$_3$): 1.38 [m, ^3J(HH) = 7.5 Hz, ^3J(PH) = 8.5 Hz, CH$_3$C], 2.14 [m, CH$_2$C], 3.22 [t, ^2J(PH) = 10 Hz, ^3J(PtH) = 70.5 Hz, CH$_2$P$_2$]. ^{31}P NMR (CDCl$_3$): −52.1 [s, ^1J(PtP) = 3015 Hz]. Anal. Calcd for $C_9H_{22}Cl_2P_2Pt$: C, 23.6; H, 4.8. Found: C, 23.6; H, 4.9.

[PtCl$_2$(dippm)]. This was prepared similarly from [PtCl$_2$(SMe$_2$)$_2$] (0.63 g) and *i*-Pr$_2$PCH$_2$P-*i*-Pr$_2$ (0.45 g) in CH_2Cl_2 (20 mL); yield 0.35 g, mp >320 °C. ^{1}H NMR (CDCl$_3$): 1.39 and 1.43 [m, ^3J(HH) = 7 Hz, ^3J(PH) = 17 Hz, ^4J(PtH) = 19 Hz, (CH$_3$)$_2$C], 2.52 [m, ^3J(HH) = 7 Hz, J(PH) not resolved, CH], 3.10 [t, ^2J(PH) = 10 Hz, ^3J(PtH) = 68 Hz, CH$_2$P$_2$]. ^{31}P{^{1}H} NMR: −36.0 [s, ^1J(PtP) = 3043 Hz]. Anal. Calcd for $C_{13}H_{30}Cl_2P_2Pt$: C, 30.3; H, 5.8. Found: C, 30.3; H, 5.8.

[(PtCl$_2$(dmpm))$_x$]. This was prepared similarly from [PtCl$_2$(SMe$_2$)$_2$] (2.75 g) and $Me_2PCH_2PMe_2$ (0.96 g) in CH_2Cl_2 (50 mL). The product precipitated as a white solid: yield 1.72 g; mp 260–265 °C dec. Anal. Calcd for $C_5H_{14}Cl_2P_2Pt$: C, 14.9; H, 3.5. Found: C, 15.0; H, 3.5. MS: *m/e* 767 (Pt$_2$(dmpm)$_2$Cl$_3$), 732 (Pt$_2$(dmpm)$_2$Cl$_2$).

***cis*-[Pt$_2$Cl$_4$(μ-dmpm)$_2$].** (a) The above complex (1.0 g) was suspended in aqueous HCl solution (100 mL, 15%), and the mixture was heated under reflux for 1 h. The solution was cooled to room temperature, and the white solid was recovered by filtration: yield 0.65 g; mp 345 °C dec. MS: *m/e* 802 (P), 767 (P − Cl). Anal. Calcd for $(C_5H_{14}Cl_2P_2Pt)_2$: C, 14.9; H, 3.5. Found: C, 15.0; H, 3.5.

(b) A solution of [Pt$_2$Me$_4$(μ-dmpm)$_2$] (0.047 g) in CH_2Cl_2 (8 mL) was added dropwise, with stirring, to excess HCl in CH_2Cl_2 (15 mL, 0.17 M) at 0 °C. A white precipitate formed. The mixture was warmed to room temperature and then heated under reflux for 45 min. The white solid was washed with CH_2Cl_2 (5 mL) and dried under vacuum: yield 0.038 g; mp 324 °C dec. Anal. Calcd for $C_5H_{14}Cl_2P_2Pt$: C, 14.9; H, 3.5. Found: C, 15.8; H, 4.1.

***trans*-[Pt$_2$Cl$_4$(μ-dmpm)$_2$].** In the preparation of the cis isomer by method a, a trace amount of the trans isomer was detected by NMR. *trans*-[Pt$_2$Cl$_4$(μ-dmpm)$_2$] was separated from the bulk of the cis isomer by washing with CH_2Cl_2. ^{1}H NMR (CDCl$_3$): 1.77 [t, ^2J(PH) + ^4J(PH) = 7.0 Hz, ^3J(PtH) = 22.4 Hz, MeP], 3.84 [t, ^2J(PH) = 4.8 Hz, 3J(PtH) = 26 Hz, CH$_2$P$_2$]. ^{31}P{^{1}H} NMR: −17.1 [s, ^1J(PtP) = 2500 Hz].

[PtI$_2$(dmpm)]. To a solution of *trans*-[PtI$_2$(SMe$_2$)$_2$] (0.065 g) in CH_2Cl_2 (20 mL) was added $Me_2PCH_2PMe_2$ (0.019 mL). The mixture was allowed to stir for 4.5 h; then the volume was reduced under vacuum, and pentane was added to precipitate a brown solid, which was washed with CH_2Cl_2 (40 mL). The insoluble white solid was identified as [PtI$_2$(dmpm)]. Anal. Calcd for $C_5H_{14}I_2P_2Pt$: C, 10.3; H, 2.4. Found: C, 10.3; H, 2.4. ^{1}H NMR [(CD$_3$)$_2$CO]: 1.90 [m, ^2J + ^4J(PH) = 13 Hz, 3J(PtH) = 47 Hz, MeP], 4.02 [t, 2J(PH) = 12 Hz, ^3J(PtH) = 71 Hz, CH$_2$P$_2$]. ^{31}P{^{1}H} NMR: −84.6 [s, ^1J(PtP) = 2776 Hz, PtP].

The CH_2Cl_2 extract above was evaporated to give *trans*-[Pt$_2$I$_4$(μ-dmpm)$_2$] as a brown solid. Anal. Calcd for $C_{10}H_{28}I_4P_4Pt_2$: C, 10.3; H, 2.4. Found: C, 10.6; H, 2.4. ^{1}H NMR [CDCl$_3$]: 2.24 [t, ^2J(PH) + ^4J(PH) = 7 Hz, ^3J(PtH) = 22 Hz, MeP], 3.27 [t, ^2J(PH) = 4.5 Hz, ^3J(PtH) = 7 Hz, CH$_2$P$_2$]. ^{31}P{^{1}H} NMR: −35.8 (s, ^1J(PtP) = 2284 Hz, ^3J(PtP) = 6 Hz, ^2J(P^{A}P^B) = 33.4 Hz, ^3J(P^{A}P^{H}z, ^3J(P^{A}P$^{B'}$) = 12.4 Hz].

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Registry No. [Pt$_2$Cl$_4$(μ-*t*-BuHPCH$_2$PH-*t*-Bu)$_2$]·2CH$_3$OH, 97336-90-8; [PtCl$_2$(SMe$_2$)$_2$], 55449-91-7; [PtCl$_2$(depm)], 91491-50-8; [PtCl$_2$(dippm)], 94278-50-9; [PtCl$_2$(dmpm)], 88228-37-9; *cis*-[Pt$_2$Cl$_4$(μ-dmpm)$_2$], 94249-29-3; *trans*-[Pt$_2$Cl$_4$(μ-dmpm)$_2$], 97372-90-2; [PtI$_2$(dmpm)], 97336-91-9; *trans*-[PtI$_2$(SMe$_2$)$_2$], 18534-69-5; *trans*-[Pt$_2$I$_4$(μ-dmpm)$_2$], 97336-92-0; [Pt$_2$Me$_4$(μ-dmpm)$_2$], 88228-39-1; *t*-BuHPCH$_2$PH-*t*-Bu, 94478-02-1; Cl$_2$PCH$_2$PCl$_2$, 28240-68-8.

Supplementary Material Available: Tables of hydrogen atom coordinates, anisotropic temperature factors, and structure factors (17 pages). Ordering information is given on any current masthead page.

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