Platinum(II) Complexes with Ligands $(RO)_2PCH_2P(OR)_2$ (R = Me, Et, Ph, or C_6H_4Me-4); Crystal Structure of *cis,cis*-$[Pt_2Me_4\{\mu\text{-}(EtO)_2PCH_2P(OEt)_2\}_2]$†

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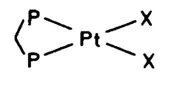
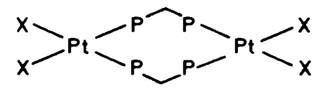
Reaction of the ligands $(RO)_2PCH_2P(OR)_2$ (R = Me, Et, Ph, or C_6H_4Me-4) with the compounds $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ or $[PtX_2(SMe_2)_2]$ (X = Cl, Br, or I) gives the corresponding complexes *cis,cis*-$[Pt_2Me_4\{\mu\text{-}(RO)_2PCH_2P(OR)_2\}_2]$ (**1**) and *cis,cis*-$[Pt_2X_4\{\mu\text{-}(RO)_2PCH_2P(OR)_2\}_2]$ (**2**). Complexes (**2**) with R = Me or Et were also prepared by treating $[PtX_2(SMe_2)_2]$ with $Cl_2PCH_2PCl_2$ followed by reaction with methanol or ethanol respectively. The crystal structure of the complex *cis,cis*-$[Pt_2Me_4\{\mu\text{-}(EtO)_2PCH_2P(OEt)_2\}_2]$ has been determined by *X*-ray diffraction methods [space group $P2_1/a$, a = 28.792(8), b = 10.560(2), c = 11.660(5) Å, β = 99.63(3)°, and Z = 4; R = 0.051 for 3 525 independent reflections with $I \geqslant 2.5\sigma(I)$]. In the molecular structure, two *cis*-$PtMe_2$ fragments are bridged by two $(EtO)_2PCH_2P(OEt)_2$ ligands to form an eight-membered $Pt_2P_4C_2$ ring with C_s boat–chair conformation and a Pt ··· Pt separation of 3.459(1) Å. Studies by ^1H and ^{31}P n.m.r. spectroscopy indicate that all complexes (**1**) have this conformation but that complexes (**2**) adopt a chair conformation. The factors affecting both the formation of mononuclear or binuclear complexes with diphosphinomethane ligands and the conformations adopted by binuclear complexes are interpreted in terms of steric effects of the ligands.

The rapid development of the chemistry of binuclear and cluster complexes in recent years has been aided by the use of bridging ligands of general formula X_2PYPX_2, of which the most common is $Ph_2PCH_2PPh_2$ (dppm).[1,2] However the ligands $Me_2PCH_2PMe_2$ (dmpm), $Et_2PCH_2PEt_2$, and $(EtO)_2POP(OEt)_2$ and many other related ligands have also been used and may give different chemistry as a result of changes in electronic or steric effects compared to dppm.[3–11]

In order further to develop the chemistry of binuclear and cluster complexes of platinum with bridging diphosphine ligands, a comparative study of the chemistry of the ligands $R_2PCH_2PR_2$ (R = Ph, Me, Et, or Pr^i) and $RHPCH_2PHR$ (R = Pr^i or Bu^t) has been made.[3,12–19] Both mononuclear derivatives, (I), and binuclear derivatives, (II), have been identified (X = anionic ligand, $\widehat{\mathrm{P\,P}}$ = $R_2PCH_2PR_2$ or $RHPCH_2PHR$), as well as isomers of (II) with *trans* stereochemistry about platinum.


(I)


(II)

It has been argued that the relative stability of (I) *versus* (II) depends primarily on the bulk of the substituents R in $R_2PCH_2PR_2$, with bulky substituents favouring (I) and small substituents favouring (II).[3] There is also some dependence on the nature of X; for example, when $\widehat{\mathrm{P\,P}}$ = $Et_2PCH_2PEt_2$ the mononuclear form (I) is more stable when X = Cl but the binuclear form (II) is more stable when X = Me.[3,14] There are also dramatic differences in the conformations of the eight-membered ring in (II) and in the reactivity of (II), which have also been attributed to steric effects.[3]

This paper describes a study of related platinum(II) complexes with the ligands $(RO)_2PCH_2P(OR)_2$, where R = Me (dmopm), Et (deopm), Ph (dpopm), or C_6H_4Me-4 (dtopm). These ligands should give small cone angles. For example, the related monophosphines have the cone angles: PPh_3, 145; PEt_3, 132; $P(OPh)_3$, 128; PMe_3, 118; $P(OEt)_3$, 109; and $P(OMe)_3$, 107°, and the diphosphines will follow the same trend. Thus, the series studied spans a range of cone angles from considerably less to considerably higher than dmpm, which has been studied previously. The ligands will all be much weaker donors than dmpm, and so any major differences in the chemistry due to possible electronic effects should be obvious.

Results and Discussion

Ligand Synthesis.—The ligands were prepared by reacting the required alcohol or phenol with $Cl_2PCH_2PCl_2$ in the presence of base [equation (1), Z = base], according to modified literature methods.[20–23]

$$Cl_2PCH_2PCl_2 + 4ROH + 4Z \longrightarrow (RO)_2PCH_2P(OR)_2 + 4ZH^+Cl^- \quad (1)$$

The ligands were stable liquids at reduced temperatures when R = Et, Ph, or C_6H_4Me-4 but, when R = Me, the ligand was thermally unstable and it was prepared and stored at −40 °C at which temperature decomposition occurred within 2—3 months.

Synthesis of Complexes.—Binuclear methylplatinum complexes were synthesized following equation (2).

No mononuclear complexes were detected and the same binuclear complexes were formed using the mononuclear precursor *cis*-$[PtMe_2(SMe_2)_2]$. Thus, the binuclear form (II) is

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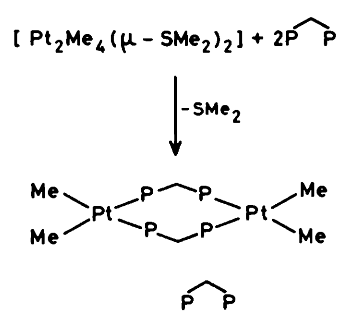
† *cis,cis*-Bis-μ-[bis(diethoxyphosphino)methane-*PP′*]-bis[dimethylplatinum(II)].

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: mmHg ≈ 133 Pa.

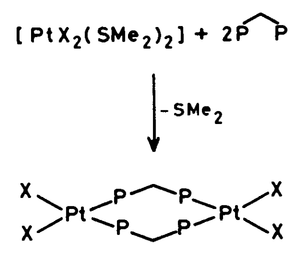


(2)

(1a)	dmopm
(1b)	deopm
(1c)	dpopm
(1d)	dtopm

more stable than the mononuclear form (**I**) with these ligands. Complexes (**1**) were stable colourless solids.

In a similar way, treating the ligands with $[PtX_2(SMe_2)_2]$, as either the *cis* or *trans* isomer, gave the binuclear complexes (**2**) [equation (3)].



(3)

	X	P P
(2a)	Cl	dmopm
(2b)	Cl	deopm
(2c)	Br	deopm
(2d)	I	deopm
(2e)	Cl	dpopm
(2f)	Cl	dtopm

In most cases, the products (**2**) were formed in high yield and purity. However, the reaction with dmopm was not selective and, even when the reaction was carried out at low temperature, several other complexes as well as (**2a**) were formed. The reaction of dmopm with $[PtX_2(SMe_2)_2]$ (X = Br or I) was also not selective. The reaction of *trans*-$[PtI_2(SMe_2)_2]$ with deopm gave some of the monomeric $[PtI_2(deopm)]$ as well as (**2d**). However, pure (**2d**) was easily prepared by treating (**2b**) with sodium iodide.

The ligands in (**2**) are not sufficiently inert to allow the synthesis of organometallic complexes from these precursors. Thus, treating (**2b**) with methyl-lithium or sodium tetrahydroborate failed to give the methylplatinum complex (**1b**) or a hydride derivative respectively.

Another route to (**2**) was developed based on reaction of $[PtCl_2(SMe_2)_2]$ with $Cl_2PCH_2PCl_2$ to give an uncharacterized product $[\{PtCl_2(Cl_2PCH_2PCl_2)\}_n]$ (**3**), followed by solvolysis with alcohol. Thus, treatment of (**3**) with ethanol gave (**2b**) and treatment with methanol gave (**2a**). This is a useful synthetic method for (**2a**) since the unstable ligand dmopm need not be isolated.

Treatment of $[PdCl_2(PhCN)_2]$ with deopm gave the dimer *cis,cis*-$[Pd_2Cl_4(\mu\text{-deopm})_2]$ but no attempt was made to synthesize further palladium derivatives with the other diphosphine ligands.

Table 1. Selected bond lengths (Å) and angles (°) for *cis,cis*-$[Pt_2Me_4\{\mu\text{-}(EtO)_2PCH_2P(OEt)_2\}_2]$ (**1b**)

Pt(1)–C(1)	2.15(3)	P(3)–C(6)	1.81(2)
Pt(1)–C(2)	2.10(3)	P(4)–C(6)	1.80(3)
Pt(2)–C(3)	2.17(3)	P(1)–O(1)	1.61(1)
Pt(2)–C(4)	2.07(3)	P(1)–O(2)	1.59(1)
Pt(1)–P(1)	2.233(6)	P(2)–O(3)	1.58(2)
Pt(1)–P(4)	2.242(6)	P(2)–O(4)	1.57(1)
Pt(2)–P(2)	2.230(5)	P(3)–O(5)	1.60(2)
Pt(2)–P(3)	2.243(6)	P(3)–O(6)	1.57(2)
P(1)–C(5)	1.84(2)	P(4)–O(7)	1.59(2)
P(2)–C(5)	1.83(2)	P(4)–O(8)	1.59(3)
C(1)–Pt(1)–C(2)	83.5(10)	Pt(2)–P(2)–C(5)	117.3(7)
C(1)–Pt(1)–P(1)	87.4(7)	Pt(2)–P(3)–C(6)	115.6(7)
C(2)–Pt(1)–P(4)	91.7(8)	Pt(1)–P(4)–C(6)	113.6(7)
P(1)–Pt(1)–P(4)	97.4(2)	Pt(1)–P(1)–O(1)	116.6(6)
C(1)–Pt(1)–P(4)	174.8(7)	Pt(1)–P(1)–O(2)	117.1(6)
C(2)–Pt(1)–P(1)	170.8(8)	Pt(2)–P(2)–O(3)	116.5(6)
C(3)–Pt(2)–C(4)	84.2(9)	Pt(2)–P(2)–O(4)	114.8(6)
C(3)–Pt(2)–P(2)	87.8(6)	Pt(2)–P(3)–O(5)	118.0(7)
C(4)–Pt(2)–P(3)	91.6(7)	Pt(2)–P(3)–O(6)	113.1(7)
P(2)–Pt(2)–P(3)	96.4(2)	Pt(1)–P(4)–O(7)	119.0(6)
C(3)–Pt(2)–P(3)	175.8(6)	Pt(1)–P(4)–O(8)	117.8(10)
C(4)–Pt(2)–P(2)	171.9(7)	P(1)–C(5)–P(2)	112.4(10)
Pt(1)–P(1)–C(5)	114.7(6)	P(3)–C(6)–P(4)	116.1(11)

Torsion angles (°)

Pt(2)–P(2)–C(5)–P(1)	58.4(8)	P(2)–Pt(2)–P(3)–C(6)	55.9(8)
Pt(1)–P(1)–C(5)–P(2)	–55.9(8)	P(1)–Pt(1)–P(4)–C(6)	–59.4(8)
Pt(2)–P(3)–C(6)–P(4)	57.2(10)	P(3)–Pt(2)–P(2)–C(5)	–112.1(7)
Pt(1)–P(4)–C(6)–P(3)	–55.9(10)	P(4)–Pt(1)–P(1)–C(5)	112.4(7)

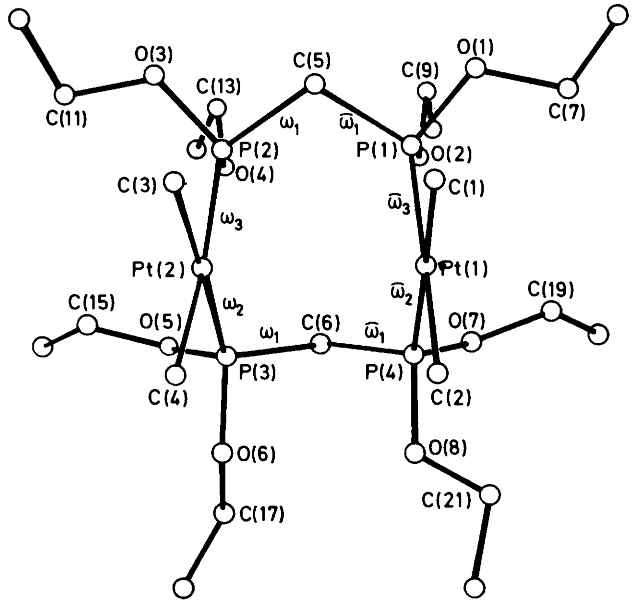


Figure 1. A view of the molecular structure of *cis,cis*-$[Pt_2Me_4\{\mu\text{-}(EtO)_2PCH_2P(OEt)_2\}_2]$ (**1b**), with atoms represented by spheres of arbitrary radius. In each ethyl group the carbon atoms are numbered by C(n) and C(n + 1). Hydrogen atoms are omitted. The sequence of internal ring torsion angles, ω, assumes exact C_s point-group symmetry

Characterization of the Complexes.—Complexes (**1**) and (**2**) were characterized by elemental analysis and by ^1H and ^{31}P n.m.r. spectroscopy. In addition a typical example was fully characterized by an *X*-ray structure determination.

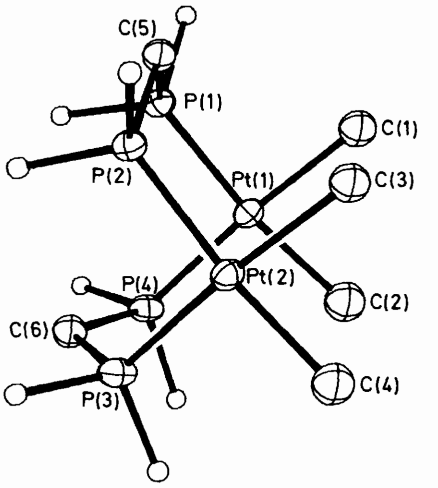
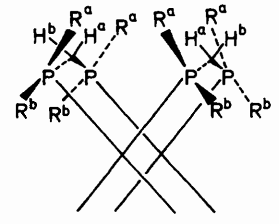


Figure 2. Conformation of the $Pt_2P_4C_2$ heterocycle in *cis*, *cis*-$[Pt_2Me_4\{\mu\text{-}(EtO)_2PCH_2P(OEt)_2\}_2]$ (**1b**). Thermal ellipsoids of the ring atoms are shown with 20% probability. Oxygen atoms are represented by spheres of arbitrary size and the ethyl groups are omitted for clarity

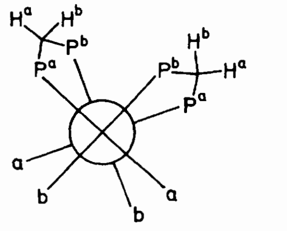
A single-crystal *X*-ray diffraction study of complex (**1b**) established the structural parameters shown in Table 1 and revealed no intramolecular approaches shorther than the appropriate van der Waals distances. The molecular structure is similar to those of the derivatives *cis,cis*-$[Pt_2Me_4(\mu\text{-}R_2PCH_2PR_2)_2]$ [R = Me (**4**) or Ph (**5**)].[3] It comprises two *cis*-$PtMe_2$ fragments locked together by two mutually *cis* deopm ligands to form an eight-membered diplatinaheterocycle, in which both metal centres display square-planar co-ordination geometry (Figure 1). Individual displacements of the ligand donor atoms from their *cis*-PtC_2P_2 planes do not exceed 0.028(1) Å.

In the local environment of each metal centre, the methyl ligands are in close contact with ethoxy oxygens [C(1) ··· O(1) 3.25(3), C(2) ··· O(8) 3.12(4), C(3) ··· O(3) 3.24(3), and C(4) ··· O(6) 2.99(3) Å], despite substantial opening of the Pt–P–O angles relative to the tetrahedral value of 109.5° (Table 1). The C(2) ··· C(21) and C(3) ··· C(11) distances [3.48(5) and 3.49(3) Å] are also short. Steric repulsions among mutually *cis* ligands [which are also evident from short intramolecular non-bonding distances P ··· P 3.334(7), 3.361(7); P ··· C(Me) 3.02(2)—3.12(3); C(Me) ··· C(Me) 2.83(4), 2.84(3) Å] are further balanced by considerable opening of P–Pt–P and closing of C–Pt–C [mean values 96.9(5) and 83.9(7)°]. Similar distortions have been observed in the *cis*-$PtMe_2P_2$ fragments of (**4**) and (**5**), where the C–Pt–C angles average 82.9(6) and 77(3)°.[3] Such acute L–M–L angles subtended by *cis* monodentate ligands are unusual in square-planar d^8 platinum complexes.

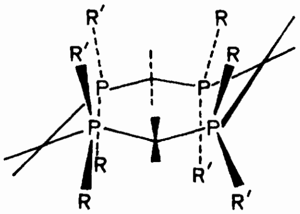
The mean Pt–C bond length in (**1b**) [2.12(2) Å] is practically the same as those in (**4**) and (**5**) [2.16(2) and 2.09(2) Å respectively]. However, the Pt–P bond lengths are sensitive to the phosphine substituents, increasing along the series OEt < Me < Ph [mean values 2.237(3), 2.275(4), and 2.299(2) Å]. This series is the reverse of that expected on the basis of electronic effects, but can be readily rationalized in terms of the steric requirements of R.[24,25] The P ··· P distances and P–C–P angles in the $R_2PCH_2PR_2$ ligands of (**1b**), (**4**), or (**5**) display similar trends [3.055(10), 3.115(7), and 3.193(10) Å; 114(2), 115.1(7), and 118.5(14)°]. In $[Me_2Pt(\mu\text{-dppm})_2Pt(C_6H_4Me\text{-}2)_2]$ (**6**) the P–C–P angles are 119.2(9) and 124.6(9)° and the P ··· P distances are 3.22 and 3.33 Å in this very congested molecule.[19]



(III)



(IV)



(V)

In (**1b**) each deopm ligand shows two Pt–P–C–P torsion angles of opposite sign and nearly equal size, and the absolute values of four such angles (Table 1) average at $|\omega_1| = 56.9(6)°$. Thus the deopm ligands adopt staggered conformations about P–CH_2 bonds and display approximate C_s symmetry. Orientation of the two ligands about the Pt $\longrightarrow$ Pt vector is such as to yield a C_s boat–chair, eight-membered $Pt_2P_4C_2$ ring, in which the distribution and sign sequence of the torsion angles are shown in Figure 1, and the mean torsion angles about the mutually *cis*-Pt–P bonds are $|\omega_2| = 57.7(18)$ and $|\omega_3| = 112.3(5)°$. In cyclo-octane, whose conformations have been studied in detail,[26,27] the C_s boat–chair, which represents the most stable conformer, is characterized by torsion angles $|\omega_1| = 65.0$, $|\omega_2| = 44.7$, and $|\omega_3| = 102.2°$. Such a conformation of the heterocycle in (**1b**) affords an eclipsed configuration of the two *cis*-$PtMe_2P_2$ fragments (Figure 2) and, as found by inspection of a space-filling model of the molecular structure, it leaves the *exo* sides of the metal centres exposed to the environment and hence to attack by reagents. It permits an intramolecular Pt ··· Pt separation of 3.459(1) Å, which is too long to be considered indicative of a bonding interaction. In (**4**) and (**5**), where the dmpm and dppm ligands show C_2 and C_1 symmetry and the $Pt_2P_4C_2$ rings adopt C_{2h} twist–chair and S_4 twist–boat conformations, respectively, the metal centres are much further apart [Pt ··· Pt 4.198(1) and 4.276(1) in (**4**)* and 4.361(2) Å in (**5**)]. In the even more hindered complex (**6**), the Pt ··· Pt distance is 4.91 Å.[19]

In summary, complexes (**1b**), (**4**), and (**5**) respond to different steric requirements of the phosphine substituents, R, by altering the conformation of the $R_2PCH_2PR_2$ ligands and the eight-membered $Pt_2P_4C_2$ dimetallacycle, while retaining the *cis* geometry of the $Pt_2(\mu\text{-}R_2PCH_2PR_2)_2$ nucleus and changing the mutual approach of the metal centres by *ca.* 0.90 Å.

The n.m.r. spectra of the complexes give interesting additional information about the conformations in solution. The three conformations found by *X*-ray methods are shown in simplified form as (**III**) [for (**1b**)], (**IV**) [for (**5**) and (**6**)], and (**V**) [for (**4**)].[3,19] Each gives different n.m.r. properties. For (**III**), assuming rapid twisting of the PCH_2 units (as appears to occur in all molecules of this type) to make the two PCH_2P groups equivalent (*cf.* Figure 2), there is non-equivalence within the $P_2CH^aH^b$ and PR^aR^b groups but all the methylplatinum and

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* There are two molecules in the asymmetric unit of (**4**).

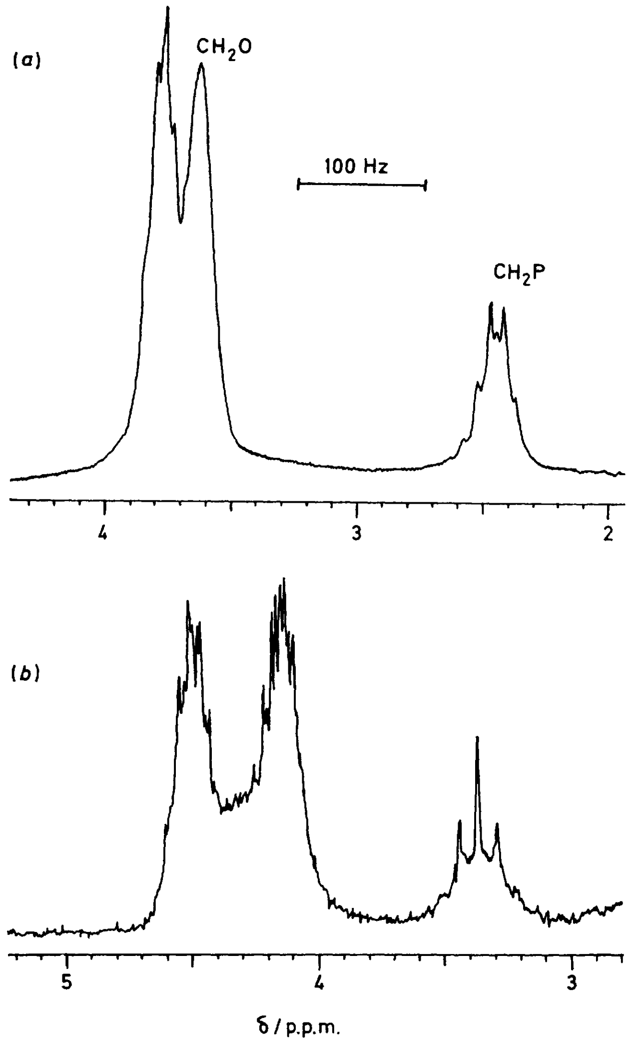


Figure 3. Typical ^1H n.m.r. spectra (200 MHz): (*a*) *cis,cis*-$[Pt_2Me_4(\mu\text{-deopm})_2]$ (**1b**), showing the '$(ABX_2)_2$' resonances for the CH_2P_2 protons as expected for the boat–chair configuration (**III**); (*b*) *cis,cis*-$[Pt_2Cl_4(\mu\text{-deopm})_2]$ (**2b**), showing a single resonance for the CH_2P_2 protons and thus suggesting the chair configuration (**V**). In both spectra only two of the expected four resonances for the $CH_3C\mathit{H}_2OP$ protons are resolved

platinum–phosphorus groups are equivalent. The expected patterns, except for apparent accidental degeneracy of chemical shift for the PR^aR^b groups in some cases (see below), are observed for all the complexes (**1**) and strongly suggest that all have the conformation (**III**) proved crystallographically for (**1b**). Figures 3 and 4 show typical spectra for (**1b**) and (**1d**) showing the '$(ABX_2)_2$' resonances for the $CH^aH^bP_2$ protons as expected for (**III**). Inversion of the boat would lead to coalescence of these signals to an '$(A_2X_2)_2$' spectrum and is obviously slow at room temperature. No splitting of the ^{31}P or MePt resonances occurred at low temperature, as would be expected for an equilibrating twist–boat structure (**IV**) and observed experimentally for complex (**5**).[3] The resonances due to the PR_2 groups were less useful. For complex (**1d**) two MeC_6H_4 resonances were observed as expected for conformation (**III**) (Figure 4), but for (**1a**) only one broad *Me*O signal was observed. When R = EtO, four CH_2O resonances are expected because the CH^aH^bO protons of each ethyl group are diastereotopic, but only two broad resonances were resolved in the spectrum of (**1b**) (Figure 3).

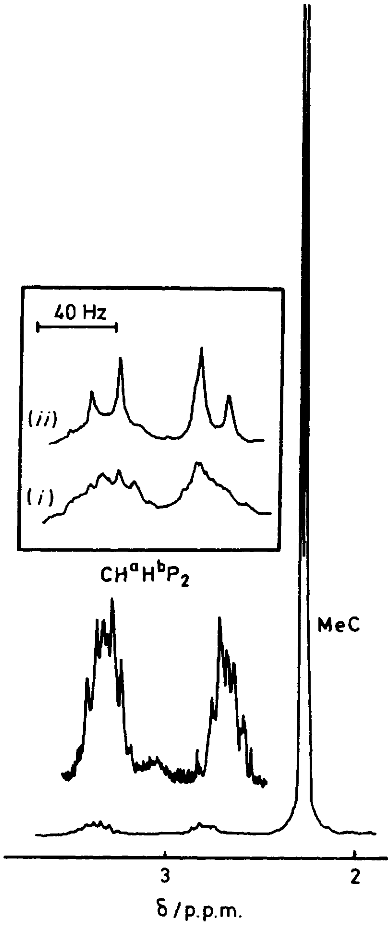


Figure 4. ^1H N.m.r. spectra (200 MHz) of *cis,cis*-$[Pt_2Me_4(\mu\text{-dtopm})_2]$ (**1d**) in the $CH^aH^bP_2$ and MeC regions. The inset shows the $CH^aH^bP_2$ signal at 100 MHz: (*i*) ^{31}P coupled and (*ii*) ^{31}P decoupled, to emphasize the 'AB' quartet due to $^2J(H^aH^b)$ coupling

In conformation (**V**), the CH_2P_2 protons, MePt groups, and phosphorus atoms are all equivalent. This type of spectrum has been observed previously for complex (**4**) and was observed for all of the complexes (**2**). A typical spectrum for (**2b**) showing a single resonance for the CH_2P_2 protons [complex since the hydrogen and phosphorus atoms make up an $(A_2X_2)_2$ spin system] is shown in Figure 3. Again accidental degeneracy of the chemical shifts due to PR^aR^b groups appeared to occur in some cases, and the assignment of conformation is less certain in these instances. Complex (**2f**) gave two resonances for the $\mathit{Me}C_6H_4$ groups as expected for conformation (**V**), but only one *Me*O resonance was observed for (**2a**). Only two resonances for the $CH_3C\mathit{H}_2O$ protons of (**2b**) were resolved (Figure 3) whereas four resonances are expected. We suggest therefore that complexes (**2**) have conformation (**V**), which is also the conformation determined crystallographically for *cis,cis*-$[Pt_2Cl_4\{\mu\text{-}(EtO)_2POP(OEt)_2\}]$[9] and *cis,cis*-$[Pt_2Cl_4\{\mu\text{-}Bu^tHPCH_2PHBu^t\}_2]$.[4] The n.m.r. criterion to distinguish between conformations (**III**) and (**V**) relies on the appearance of the $C\mathit{H}_2P_2$ resonance in the ^1H n.m.r. and may be expected to fail if there is accidental degeneracy of chemical shifts of the CH^aH^b protons for conformation (**III**). In general, therefore it will be a more positive test for conformation (**III**) than for (**V**).

The ^{31}P n.m.r. spectra of complexes (**1**) and (**2**) were characteristic of the *cis,cis* stereochemistry, and the couplings $^1J(PtP)$ were strongly dependent on the *trans* influence of the ligand *trans* to phosphorus. The spectra were analysed as described elsewhere.[9]

Discussion

All of the ligands studied here have low steric effects and all give binuclear rather than mononuclear complexes. Complexes (**2**), with halide substituents, are the first such complexes with $R_2PCH_2PR_2$ ligands to be characterized. When R = Et or Ph, the monomeric form (**I**) is formed and, when R = Me, the complex probably has structure (**II**) but is too insoluble to characterize fully.[13,14]

The conformations adopted by the eight-membered rings in (**1**) and (**2**) are of interest. The results described above for the methyl derivatives (**1**), (**4**), (**5**), and (**6**) suggest that two factors are important in determining the most stable conformation. It seems that the natural stability sequence is the same as for cyclooctane, *i.e.* (**III**) > (**V**) > (**IV**), but that steric effects involving substituents on phosphorus also follow this sequence. Hence for the smallest substituents on phosphorus (**III**) is most stable, for intermediate sized substituents (**V**) is preferred, and for large substituents (**IV**) is preferred. However, we note that the ligands dpopm and dtopm are larger than dmpm, yet both complexes (**1c**) and (**1d**) appear to adopt conformation (**III**), whereas (**4**) adopts conformation (**V**).

Why do the halide derivatives (**2**) adopt a different conformation from the methyl derivatives (**1**)? First, the Pt–P bonds will be shorter for the halide derivatives, due to the lower *trans* influence of the halide, and this will lead to slightly greater steric hindrance between substituents on phosphorus and hence favour conformation (**V**) over (**III**). Also, the halide ligands on different platinum atoms are close together in conformation (**III**) and unfavourable electrostatic repulsions are expected. This would not be present for the methyl derivatives (**1**) which are much less polar.

This work, in conjunction with earlier papers,[1–12] shows clearly how steric effects of ligands $R_2PCH_2PR_2$ can determine the nuclearity of complexes and also the conformations adopted by binuclear complexes.

Experimental

Proton and ^{31}P n.m.r. spectra were recorded using Varian T60, EM360L, XL100 (^1H), XL200 (^1H and ^{31}P), or XL300 (^{31}P) spectrometers. Chemical shifts are quoted with respect to $SiMe_4$ (^1H n.m.r.) or external $PO(OMe)_3$ (^{31}P n.m.r.). Carbon and H analyses were performed by Guelph Chemical Laboratories Ltd.

Complexes *cis*- and *trans*-$[PtCl_2(SMe_2)_2]$, *trans*-$[PtI_2(SMe_2)_2]$, and *cis,cis*-$[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ were prepared with modifications of known procedures.[28,29] Solvents were dried and distilled immediately before use, and all syntheses involving phosphine ligands were carried out under dry N_2 using standard Schlenk techniques.

Preparations.—*trans*-$[PtBr_2(SMe_2)_2]$. To a stirred solution of LiBr (1.53 g) in acetone (20 cm^3) was added a solution of $[PtCl_2(SMe_2)_2]$ (2.00 g as a mixture of *cis* and *trans* isomers) in CH_2Cl_2 (10 cm^3). The solution was stirred at room temperature for 0.5 h and then filtered to remove lithium chloride. The resulting orange solution was washed with water (2 × 20 cm^3). Additional dimethyl sulphide (0.25—0.50 cm^3) was added to ensure complete substitution of the halides. The methylene chloride solution was dried with anhydrous $MgSO_4$, then the filtrate was added to pentane (*ca.* 30 cm^3) and evaporated to dryness under vacuum to give the product as an orange crystalline solid. Yield: 1.11 g, 79%; m.p. 165—167 °C. N.m.r. in $CDCl_3$: ^1H, δ 2.52 [$^2J(PtH)$ 21 Hz, MeS].

$Cl_2PCH_2PCl_2$. A suspension of Al (granulated form, 32 g) in dry CH_2Cl_2 (300 cm^3) and $BrCH_2CH_2Br$ (10 cm^3) under dry N_2 was heated under reflux until no metallic Al remained (*ca.* 48 h). A black suspension in a yellow solution had formed and the mixture was allowed to cool and settle. The resulting solution of $Cl_2AlCH_2AlCl_2$ was decanted off into a dropping funnel, and added dropwise to a rapidly stirred solution of PCl_3 (107 cm^3) in CH_2Cl_2 (100 cm^3) at a rate sufficient to maintain a gentle reflux. The mixture was then heated under reflux for 3 h and allowed to cool to room temperature. Next, $POCl_3$ (108 cm^3) was added dropwise to the stirred solution followed by addition of dry, powdered KCl (94.5 g). The solution was heated under reflux for a further 3 h and then allowed to cool. The solution was decanted off from precipitated salts and the solids were washed with CH_2Cl_2 (2 × 50 cm^3). The solvent was removed under vacuum from the combined CH_2Cl_2 solutions. The residue was then extracted with dry diethyl ether (300 cm^3), the diethyl ether layer decanted off, and the diethyl ether removed under vacuum to yield the product which was purified by vacuum distillation. Yield: 30%; b.p. 40 °C/0.5 mmHg. N.m.r. in $CDCl_3$: ^1H, δ 3.58 [t, $^2J(PH)$ 17 Hz, CH_2P_2]; ^{31}P, δ 172.4 (s).

$(RO)_2PCH_2P(OR)_2$ (R = Me *or* Et). A solution of $Cl_2PCH_2PCl_2$ (6.2 cm^3, 0.046 mol) in dry diethyl ether (25 cm^3) was added dropwise with stirring to a solution of the appropriate dry alcohol (0.184 mol) and NEt_3 (51.1 cm^3, 0.367 mol) in dry diethyl ether (100 cm^3) cooled to −78 °C. After mixing, hexane (50 cm^3) was added. The mixture was stirred at −78 °C for 2 h and then at −7 °C for 1 h, and then filtered to remove $[NHEt_3]Cl$. The solvent was removed from the filtrate at reduced temperature under high vacuum to yield the product (yield *ca.* 45%) which was purified by vacuum distillation. B.p.: dmopm, 45 °C/0.5 mmHg; deopm, 50 °C/0.5 mmHg. N.m.r. in $CDCl_3$: dmopm, ^1H, δ 3.43 [m, $^2J + {}^4J(PH)$ 12, CH_3O], 1.90 [t, $^2J(PH)$ 7, CH_2P_2]; ^{31}P, δ 178.7 (s); deopm, ^1H, δ 3.89 [m, $^2J(HH)$ 7, CH_3CH_2O], 2.12 [t, $^2J(PH)$ 7, CH_2P_2], 1.27 [t, $^2J(HH)$ 7 Hz, CH_3CH_2]; ^{31}P, δ 173.3 (s).

$(RO)_2PCH_2P(OR)_2$ (R = Ph *or* C_6H_4Me-4). A solution of *p*-cresol or phenol respectively (0.029 mol) in dry diethyl ether (25 cm^3) was added dropwise with stirring to a solution of $Cl_2PCH_2PCl_2$ (1.0 cm^3, 0.007 mol) and pyridine (py) (2.35 cm^3, 0.029 mol) in dry diethyl ether (100 cm^3) cooled to −7 °C. The mixture was allowed to stir for 1 h at −7 °C and then warmed to room temperature over a period of 1 h. After filtering off the [Hpy]Cl the solvent was removed from the filtrate under high vacuum to yield the product (yield 70%). N.m.r. in $CDCl_3$: dtopm, ^1H, δ 2.28 and 2.24 (s, $CH_3C_6H_4$), 2.64 [t, $^2J(PH)$ 9, CH_2P_2], 7.02 and 6.93 (s, $CH_3C_6H_4$); ^{31}P, δ 174.1 (s); dpopm, ^1H, δ 2.92 [t, $^2J(PH)$ 9 Hz, CH_2P_2], 7.45 (t, C_6H_5O), 7.28 (d, C_6H_5O); ^{31}P, δ 174.3 (s).

cis,cis-$[Pt_2Cl_4(\mu\text{-deopm})_2]$ (**2b**). *Method* 1. To a stirred solution of $[PtCl_2(SMe_2)_2]$ (0.5 g, 1.28 mmol) in dry CH_2Cl_2 (10 cm^3) was added a solution of deopm (0.33 g, 1.28 mmol) in CH_2Cl_2 (2 cm^3) under an atmosphere of N_2. The solution was allowed to stir for 1.5 h. The product was precipitated by addition of hexane (20 cm^3), and dried under vacuum to give a light yellow powder. Yield: 0.74 g, 42%; m.p. 175—185 °C (Found: C, 20.70; H, 4.25. Calc. for $C_{18}H_{14}Cl_4O_8P_4Pt_2$: C, 20.7; H, 4.2%).

Method 2. To a stirred solution of $[PtCl_2(SMe_2)_2]$ (0.38 g, 1.00 mmol) in dry CH_2Cl_2 (10 cm^3) was added a solution of $Cl_2PCH_2PCl_2$ (0.22 g, 1.01 mmol) in dry CH_2Cl_2 (2 cm^3) under an atmosphere of N_2. The pale yellow mixture was stirred overnight. The reaction mixture was added to pentane (20 cm^3), and then evaporated to dryness under vacuum to yield an air-sensitive light yellow powder. This solid was immediately dissolved in dry ethanol (5 cm^3) under N_2 and stirred for 1 h. CH_2Cl_2 (5 cm^3) and pentane (20 cm^3) were added and the product was isolated by evaporation under vacuum as a light yellow powder. Yield: 0.50 g, 49%; m.p. 175—185 °C (Found:

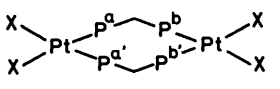
Table 2. Crystal data for *cis,cis*-$[Pt_2Me_4\{\mu\text{-}(EtO)_2PCH_2P(OEt)_2\}_2]$ (**1b**)

Empirical formula	$C_{22}H_{56}O_8P_4Pt_2$
M	962.76
Crystal system	Monoclinic
Space group	$P2_1/a$
a/Å	28.792(8)
b/Å	10.560(2)
c/Å	11.660(5)
β/°	99.63(3)
U/Å^3	3 495
Z	4
F(000)	1 872
D_c/g cm^{-3}	1.830
μ(Mo-K_α)/cm^{-1}	83.0
T/°C	22.5

Table 3. Fractional atomic co-ordinates for *cis,cis*-$[Pt_2Me_4\{\mu\text{-}(EtO)_2PCH_2P(OEt)_2\}_2]$ (**1b**)

Atom	X/a	Y/b	Z/c
Pt(1)	0.116 84(3)	−0.118 87(7)	−0.071 11(6)
Pt(2)	0.152 96(3)	−0.185 92(7)	−0.332 95(6)
P(1)	0.165 8(2)	−0.273 3(5)	0.003 3(4)
P(2)	0.196 6(2)	−0.332 9(5)	−0.228 1(4)
P(3)	0.086 3(2)	−0.299 8(6)	−0.367 1(4)
P(4)	0.054 2(2)	−0.241 3(6)	−0.135 1(4)
O(1)	0.196 9(5)	−0.247 1(14)	0.129 0(10)
O(2)	0.143 3(5)	−0.408 8(11)	0.017 3(11)
O(3)	0.247 4(5)	−0.356 4(14)	−0.258 1(11)
O(4)	0.173 9(5)	−0.468 7(11)	−0.233 6(12)
O(5)	0.087 3(5)	−0.431 9(15)	−0.434 6(12)
O(6)	0.043 7(5)	−0.224 5(17)	−0.437 2(13)
O(7)	0.035 0(5)	−0.333 8(17)	−0.046 1(11)
O(8)	0.008 4(8)	−0.174 6(23)	−0.204 3(15)
C(1)	0.174 4(8)	0.011 0(22)	−0.021 5(19)
C(2)	0.080 5(10)	0.044 8(27)	−0.136 8(23)
C(3)	0.214 8(7)	−0.065 2(20)	−0.308 1(17)
C(4)	0.121 3(8)	−0.035 5(23)	−0.429 4(20)
C(5)	0.215 7(6)	−0.300 5(17)	−0.073 6(15)
C(6)	0.065 2(7)	−0.358 7(19)	−0.239 1(16)
C(7)	0.171 8(10)	−0.199 7(27)	0.220 6(24)
C(8)	0.197 8(11)	−0.231 7(30)	0.336 5(26)
C(9)	0.169 2(9)	−0.508 9(25)	0.085 5(21)
C(10)	0.134 5(11)	−0.620 7(31)	0.078 6(27)
C(11)	0.254 4(9)	−0.363 1(24)	−0.379 1(21)
C(12)	0.306 0(11)	−0.315 6(30)	−0.380 3(26)
C(13)	0.198 0(10)	−0.583 7(28)	−0.196 6(24)
C(14)	0.168 7(13)	−0.693 3(35)	−0.252 7(30)
C(15)	0.116 2(11)	−0.445 4(30)	−0.520 0(27)
C(16)	0.102 8(14)	−0.541 5(42)	−0.601 0(36)
C(17)	−0.000 2(16)	−0.281 3(41)	−0.482 2(38)
C(18)	−0.023 4(14)	−0.214 8(40)	−0.581 8(36)
C(19)	0.039 7(10)	−0.297 0(26)	0.073 9(24)
C(20)	0.005 0(12)	−0.361 2(33)	0.128 0(29)
C(21)	−0.023 9(15)	−0.123 6(39)	−0.142 4(36)
C(22)	−0.065 2(12)	−0.075 6(34)	−0.226 6(30)

C, 20.85; H, 4.40. Calc. for $C_{18}H_{44}Cl_4O_8P_4Pt_2$: C, 20.7; H, 4.2%). N.m.r. in $CDCl_3$: ^1H, δ 1.40 [t, $^2J(HH)$ 7, $C\mathit{H}_3CH_2O$], 3.38 [m, ^2J + $^4J(PH)$ 30, $^3J(PtH)$ 28, CH_2P_2], 4.50 and 4.16 (m, $CH_3C\mathit{H}_2O$); ^{31}P, δ 88.8 [s, $^1J(PtP)$ 4 846, $^3J(PtP)$ 67, $^2J(P^aP^b)$ 79, $^2J(P^aP^{a'})$ −16 Hz, PPt].



(**II**)

cis,cis-$[Pt_2Br_4(\mu\text{-}deopm)_2]$ (**2c**). To a stirred solution of *trans*-$[PtBr_2(SMe_2)_2]$ (0.35 g, 0.73 mmol) in dry CH_2Cl_2 (25 cm^3) was added a solution of deopm (0.182 cm^3, 0.73 mmol) in dry CH_2Cl_2 (10 cm^3) under N_2. An immediate colour change to yellow was observed and the solution was stirred for 1 h. The product was isolated by the introduction of hexane (20 cm^3) and evaporated to dryness. After washing with diethyl ether (10 cm^3) and pentane (10 cm^3) and drying under vacuum, a light yellow powder remained. Yield: 0.38 g, 85%; m.p. 310 °C (decomp.) (Found: C, 18.35; H, 3.90. Calc. for $C_{18}H_{44}Br_4O_8P_4Pt_2$: C, 17.7; H, 3.6%). N.m.r. in $CDCl_3$: ^1H, δ 1.36 [t, $^3J(HH)$ 7, $C\mathit{H}_3CH_2O$], 1.22 (t, $C\mathit{H}_3CH_2O$), 3.44 [m, ^2J + $^4J(OH)$ 30, CH_2P_2], 4.48 and 4.04 (m, $CH_3C\mathit{H}_2O$); ^{31}P, δ 89.6 [s, $^1J(PtP)$ 4 797, $^3J(PtP)$ 19, $^2J(P^aP^b)$ 80, $^2J(P^aP^{a'})$ −57 Hz, PPt].

cis,cis-$[Pt_2I_4(\mu\text{-}deopm)_2]$ (**2d**). *Method* 1. To a stirred solution of *trans*-$[PtI_2(SMe_2)_2]$ (0.06 g, 0.11 mmol) in dry CH_2Cl_2 (10 cm^3) was added an equimolar amount of deopm in dry diethyl ether (1 cm^3) and the mixture stirred for *ca.* 1 h. A yellow solid was isolated after adding pentane (20 cm^3) and evaporation under vacuum. Yield: 0.04 g, 56%.

Method 2. To a stirred solution of *cis,cis*-$[Pt_2Cl_4(\mu\text{-}deopm)_2]$ (0.05 g, 0.05 mmol) in CH_2Cl_2 was added a solution of sodium iodide (0.08 g, 0.5 mmol) in acetone (3 cm^3). The cloudy lime-green solution was stirred for 0.5 h. Now a yellow mixture, the organic phase was washed with water (5 cm^3) and then dried to yield a clear yellow solution. The filtrate was added to hexane (5 cm^3) and the product precipitated by evaporation under vacuum as a bright yellow powder. Yield: 0.05 g, 66%; m.p. 325 °C (decomp.) (Found: C, 15.55; H, 3.25. Calc. for $C_{18}H_{44}I_4O_8P_4Pt_2$: C, 15.3; H, 3.1%). N.m.r. in $CDCl_3$: ^1H, δ 1.36 [t, $^3J(HH)$ 7, $C\mathit{H}_3CH_2O$], 3.67 [m, ^2J + $^4J(PH)$ 29, CH_2P_2], 4.44 and 4.04 (m, $CH_3C\mathit{H}_2O$); ^{31}P, δ 91.1 [s, $^1J(PtP)$ 4 609, $^3J(PtP)$ −4, $^2J(P^aP^b)$ 71, $^2J(P^aP^{a'})$ −24 Hz, PPt].

cis,cis-$[Pt_2Me_4(\mu\text{-}deopm)_2]$ (**1b**). To a stirred solution of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (0.34 g, 0.59 mmol) in dry CH_2Cl_2 (10 cm^3) was added a solution of deopm (0.31 g, 1.2 mmol) in dry CH_2Cl_2 (2 cm^3). The solution was stirred for 0.5 h and then added to hexane (5 cm^3) to give a light yellow solid. Yield: 0.25 g, 44%; m.p. 135—185 °C (decomp.) (Found: C, 27.45; H, 5.75. Calc. for $C_{22}H_{56}O_8P_4Pt_2$: C, 27.4; H, 5.9%). N.m.r. in $CDCl_3$: ^1H, δ 1.00 [t, $^3J(HH)$ 7, $C\mathit{H}_3CH_2O$], 2.49, 2.40 [q, $^2J(HH)$ 10, CH_2P_2], 3.77 and 3.62 (m, $CH_3C\mathit{H}_2O$), 0.23 [s, $^2J(PtH)$ 67, $^3J(PH)$ 8, MePt]; ^{31}P, δ 147.5 [s, $^1J(PtP)$ 2 705, $^3J(PtP)$ 7, $^2J(P^aP^b)$ 96, $^2J(P^aP^{a'})$ −16 Hz, PPt].

cis,cis-$[Pt_2Me_4(\mu\text{-}dmopm)_2]$ (**1a**). To a stirred solution of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (85.7 mg, 0.149 mmol) in dry CH_2Cl_2 (10 cm^3) was added a solution of dmopm (53.6 µl, 0.298 mmol) in dry CH_2Cl_2 (5 cm^3). The solution was stirred for 30 min. White crystals were isolated by addition of hexane (15 cm^3) followed by evaporation under vacuum. The product was washed with diethyl ether and pentane and dried under vacuum. Yield: 91.7 mg, 72%; m.p. 220—230 °C (decomp.) (Found: C, 19.80; H, 4.55. Calc. for $C_{14}H_{40}O_8P_4Pt_2$: C, 19.75; H, 4.75%). N.m.r. in $CDCl_3$: ^1H, δ 2.75 and 2.64 [q, $^3J(PtH)$ 21, CH_2P_2], 3.58 (br, CH_3O), 0.49 [s, $^2J(PtH)$ 67, $^3J(PH)$ 8, MePt]; ^{31}P, δ 153.6 [s, $^1J(PtP)$ 2 680, $^3J(PtP)$ 7, $^2J(P^aP^b)$ 98, $^2J(P^aP^{a'})$ −17 Hz, PPt].

cis,cis-$[Pt_2Cl_4(\mu\text{-}dtopm)_2]$ (**2f**). To a stirred solution of $[PtCl_2(SMe_2)_2]$ (0.20 g, 0.51 mmol) in dry CH_2Cl_2 (10 cm^3) cooled to 0 °C was added a solution of dtopm [0.26 g (0.26 cm^3 assuming $\rho \cong 1$ g cm^{-3}), 0.51 mmol] in dry CH_2Cl_2 (10 cm^3). The resulting light yellow solid was crystallized from acetone and n-pentane. Yield: 0.24 g, 59%; m.p. 117—160 °C (Found: C, 42.50; H, 3.95. Calc. for $C_{58}H_{60}Cl_4O_8P_4Pt_2$: C, 45.20; H, 3.9%).

N.m.r. in $CDCl_3$: ^1H, δ 2.33 and 2.31 (s, $CH_3C_6H_4$), 7.07 [m, $^3J(HH)$ 7, $CH_3C_6H_4$], 3.52 [m, $^2J + ^4J(PH)$ 32, CH_2P_2]; ^{31}P, δ 82.2 [s, $^1J(PtP)$ 5 162, $^3J(PtP)$ 30, $^2J(P^aP^b)$ 96, $^2J(P^aP^{a'})$ −36 Hz, PPt].

cis,cis-[$Pt_2Me_4(\mu\text{-dtopm})_2$] (**1d**). To a stirred solution of [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] (0.199 g, 0.346 mmol) in dry CH_2Cl_2 (10 cm^3) cooled to −7 °C was added a solution of dtopm [0.349 g (*ca.* 350 μl assuming $\rho \cong 1$ g cm^{-3}), 0.69 mmol] in dry CH_2Cl_2 (5 cm^3). The solution was stirred for 1 h and then allowed to cool slowly to room temperature. The light yellow solid was precipitated from solution with diethyl ether and dried under vacuum. Yield: 81 mg, 16%; m.p. 210—225 °C (Found: C, 49.40; H, 4.75. Calc. for $C_{62}H_{72}O_8P_4Pt_2$: C, 51.05; H, 4.95%). N.m.r. in $CDCl_3$: ^1H, δ 2.25, 2.28 (s, $CH_3C_6H_4$), 6.87, 6.92 (s, $CH_3C_6H_4$), 2.82 and 3.36 [q, $^2J(HH)$ 14, CH_2P_2], 0.68 [s, $^2J(PtH)$ 72, $^3J(PH)$ 9, MePt]; ^{31}P, δ 138.4 [s, $^1J(PtP)$ 2 625, $^3J(PtP)$ 15, $^2J(P^aP^b)$ 150, $^2J(P^aP^{a'})$ −105 Hz, PPt].

cis,cis-[$Pt_2Cl_4(\mu\text{-dmopm})_2$] (**2a**). To a stirred solution of [$PtCl_2(SMe_2)_2$] (0.400 g, 1.03 mmol) in dry CH_2Cl_2 (15 cm^3) was added a solution of $Cl_2PCH_2PCl_2$ (0.137 cm^3, 1.03 mmol) in dry CH_2Cl_2 (5 cm^3). The mixture was stirred for 3 h. Pentane (20 cm^3) was introduced and the solvent was taken off under vacuum and immediately dry methanol (5 cm^3) added to dissolve the light yellow solid. The mixture was stirred for 2 h after which CH_2Cl_2 (*ca.* 5 cm^3) was added to give a yellow solution. Pentane (20 cm^3) was introduced and the solvent removed; the yellow powder was washed with diethyl ether (10 cm^3) and pentane (10 cm^3) and dried under vacuum. Yield: 0.400 g, 84%; ^{31}P n.m.r. indicates two distinct products, (**A**) and (**B**), that are very difficult to isolate. In a mixture of (**A**):(**B**) = 5:1, m.p. 290—320 °C (decomp.) (Found: C, 12.95; H, 3.05. Calc. for $C_{10}H_{28}Cl_4O_8P_4Pt_2$: C, 12.90; H, 3.05%). N.m.r. in $CDCl_3$: (**A**), ^1H, δ 3.75 (m, CH_3O), 3.37 [m, $^2J + ^4J(PH)$ 32, CH_2P_2]; ^{31}P, δ 89.3 [s, $^1J(PtP)$ 4 925, $^3J(PtP)$ 8, $^2J(P^aP^b)$ 67, $^2J(P^aP^{a'})$ −12, PPt]; (**B**) ^1H, same as (**A**); ^{31}P, δ 94.9 [s, $^1J(PtP)$ 4 886, $^3J(PtP)$ 10, $^2J(P^aP^b)$ 87 Hz, PPt].

X-*Ray Structure Analysis of cis,cis*-[$Pt_2Me_4\{\mu\text{-}(EtO)_2PCH_2P(OEt)_2\}_2$] (**1b**).—Straw-coloured, prismatic crystals of (**1b**) were grown from a mixture of $ClCH_2CH_2Cl$ and hexane (1:5).

Measurements. A crystal of approximate dimensions 0.85 × 0.55 × 0.20 mm was sealed in a Lindemann glass capillary, mounted on an Enraf–Nonius CAD4 diffractometer, and exposed to graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å).

The unit-cell dimensions (Table 2) were determined by a least-squares treatment of 25 high-angle reflections. The observed systematic absences established the space group as $P2_1/a$.

Intensities of 9 229 reflections with $2 \leqslant \theta \leqslant 27°$ were measured by continuous θ–2θ scans of 0.86 + 0.35 tanθ in θ. Scan speeds were adjusted to give $\sigma(I)/I < 0.02$, subject to a time limit of 90 s. Two strong reflections, remeasured every 2 h, showed no systematic variation of intensity during the experiment. Intensities of all reflections were corrected for background, Lorentz, polarization and absorption effects. The absorption factors (0.64—1.44 on *F*) were calculated by an empirical method.[30] 2 658 Reflections related by symmetry were averaged to yield 1 286 independent structure amplitudes which gave *R*(internal) of 0.101 before, and 0.045 after, absorption correction. Only 3 525 reflections were considered observed [$I \geqslant 2.5\sigma(I)$] and used in the structure analysis.

Structure solution and refinement. The positions of the platinum atoms were obtained from a Patterson function and those of the phosphorus, oxygen, and carbon atoms from difference Fourier syntheses. Hydrogen atoms were neither located in electron-density maps nor included in the structural model. The structure was refined by full-matrix least squares, minimizing the function $\Sigma w\Delta^2$, where $w = 1/\sigma^2(F_o)$ and $\Delta = (|F_o| - |F_c|)$. The platinum, phosphorus, and oxygen atoms were allowed anisotropic thermal vibrations. The refinement of 215 parameters converged at R = 0.051 and R' = 0.071, with the largest parameter shift/error ratio of 0.20. The weighting scheme $w = \{1 + [(|F_o| - 55)/165]^2\}^{-2}$ was used and an analysis of $w\Delta^2$ values revealed no unexpected trends. In the final difference electron-density map the function values ranged from −1.47 to +0.97 e Å^{-3}.

All calculations were performed on a GOULD SEL 32/27 super minicomputer, using the locally developed 'GX' program package.[31] Neutral-atom scattering factors and anomalous dispersion corrections were taken from ref. 32.

The final atomic co-ordinates are given in Table 3.

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