Binuclear Methylplatinum(II) Complexes. The Molecular Structure and Fluxional Behaviour of the Face-to-face Dimer $[Pt_2I_2Me_2(\mu\text{-}Me_2PCH_2PMe_2)_2]$†

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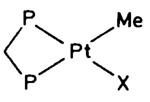
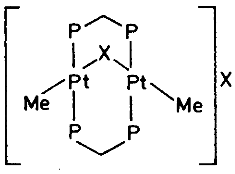
The complexes *cis,cis*-$[Pt_2Cl_2Me_2(\mu\text{-dmpm})_2]$ (**6**), *trans,trans*-$[Pt_2I_2Me_2(\mu\text{-dmpm})_2]$ (**8**), and $[Pt_2(\mu\text{-I})Me_2(\mu\text{-dmpm})_2][PF_6]$ (**11**) (dmpm = $Me_2PCH_2PMe_2$) have been prepared and characterized spectroscopically. The crystal structure of (**8**) was determined by *X*-ray diffraction techniques and refined to $R = 0.036$ for 2 598 unique reflections with $I \geqslant 3\sigma(I)$. The crystals are monoclinic, space group $P2_1/n$, $a = 8.611(2)$, $b = 16.971(3)$, $c = 8.405(1)$ Å, $\beta = 102.83(2)°$, $Z = 2$. The molecular structure shows a face-to-face geometry with crystallographically imposed C_i symmetry. It contains two square-planar metal centres [Pt · · · Pt 3.353 5(4) Å] bridged by mutually *trans* dmpm ligands to afford an eight-membered $Pt_2P_4C_2$ dimetallacycle with an *anti* configuration of the *trans*-PtIMe groups. Complex (**8**) has been shown to undergo a novel fluxional process involving overall inversion of the face-to-face structure. Differences in properties between the dmpm complexes (**6**), (**8**), and (**11**) and related known $Ph_2PCH_2PPh_2$ complexes are rationalized in terms of steric effects.

Following an interest in the effects of steric properties of the substituents, R, on the co-ordination chemistry of the ligands $R_2PCH_2PR_2$,[1-4] we report a study of the derivatives $[Pt_2X_2Me_2(Me_2PCH_2PMe_2)_2]$ (X = Cl or I). The analogous complexes with the ligand $Ph_2PCH_2PPh_2$ (dppm) have been reported earlier, and could exist either as the mononuclear form (**1**), with chelating diphosphine, or as the ionic binuclear A-frames (**2**).[5,6] In this paper we show that the new complexes of the $Me_2PCH_2PMe_2$ (dmpm) ligand adopt the *cis,cis* and *trans,trans* binuclear structures (**3**) and (**4**), respectively. A new ionic dmpm A-frame is also described.



(**1**)



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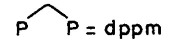

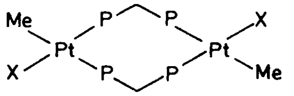

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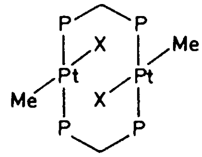

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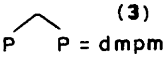
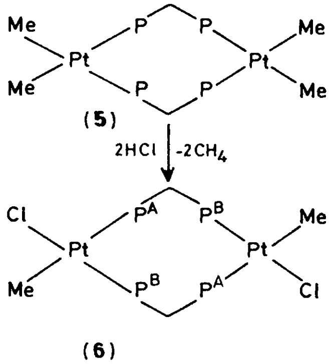
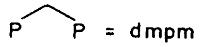




(**6**)



Results and Discussion

The compound *cis,cis*-$[Pt_2Cl_2Me_2(\mu\text{-dmpm})_2]$ (**6**) was obtained by reaction of two equivalents of HCl with *cis,cis*-$[Pt_2Me_4(\mu\text{-dmpm})_2]$ (**5**), according to the equation shown. Addition of one equivalent of HCl to (**5**) gave a mixture of (**5**) and (**6**) and none of the expected $[Pt_2ClMe_3(\mu\text{-dmpm})_2]$.

Complex (**6**) was characterized by its ^1H and ^{31}P n.m.r. spectra. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum gave an [AA′BB′] pattern, with satellites due to coupling to ^{195}Pt. The coupling constants $^1J(PtP^A)$ and $^1J(PtP^B)$ were 1 758 and 4 148 Hz respectively, thus proving the *cis* stereochemistry at each platinum centre with P^A *trans* to methyl and P^B *trans* to chloride.[7,8] In confirmation, the MePt signal in the ^1H n.m.r. spectrum appeared as a doublet of doublets, due to coupling to two non-equivalent ^{31}P atoms attached to the same platinum centre, as expected for structure (**6**). Only one ^1H n.m.r. resonance was observed for the PCH_2P protons, thus vindicating the more symmetrical structure (**6**), rather than (**7**) which would give two such resonances due to non-equivalent dmpm ligands.

Complex (**6**) was stable both in the solid state and in solution in CD_2Cl_2 or $CDCl_3$. No isomerisation to the A-frame structure (**2**) or to (**4**) was observed, as monitored by recording the ^1H and ^{31}P n.m.r. spectra of the solutions several days after preparation.

The complex *trans,trans*-$[Pt_2I_2Me_2(\mu\text{-dmpm})_2]$ (**8**) was prepared by reaction of *trans*-$[PtIMe(SMe_2)_2]$ with dmpm and shown, by spectroscopic and *X*-ray diffraction techniques, to

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† Bis[μ-bis(dimethylphosphino)methane]-bis[iodo(methyl)-platinum(II)].

Supplementary data available (No. SUP 56347, 4 pp.): fractional co-ordinates and thermal parameters of all atoms (including H). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

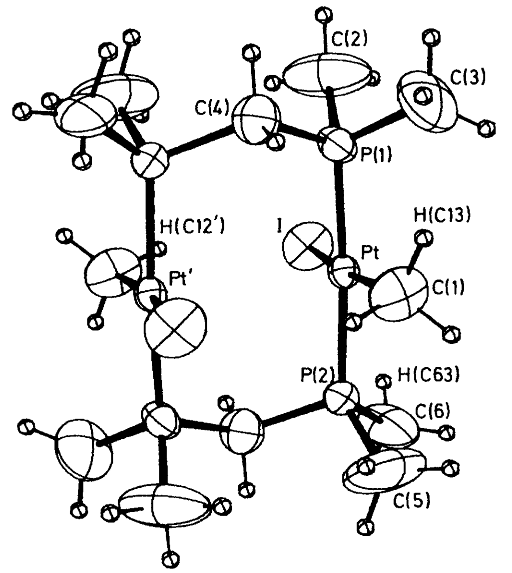


Figure 1. The molecular structure of *trans,trans*-$[Pt_2I_2Me_2(\mu\text{-}Me_2PCH_2PMe_2)_2]$ (**8**), with vibrational ellipsoids of non-hydrogen atoms displaying 50% probability. The mid-point of the Pt ⟶ Pt' vector coincides with a crystallographically imposed centre of symmetry which relates primed with the corresponding unprimed atoms

Table 1. Selected parameters of the molecular geometry of *trans,trans*-$[Pt_2I_2Me_2(\mu\text{-}Me_2PCH_2PMe_2)_2]$ (**8**)*

Bond lengths (Å)

Pt–I	2.696(1)	P(1)–C(3)	1.84(2)
Pt–P(1)	2.274(3)	P(1)–C(4)	1.83(1)
Pt–P(2)	2.278(3)	P(2)–C(4')	1.86(1)
Pt–C(1)	2.10(1)	P(2)–C(5)	1.75(2)
P(1)–C(2)	1.76(2)	P(2)–C(6)	1.78(1)

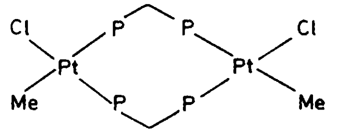
Bond angles (°)

I–Pt–P(1)	93.6(1)	Pt–P(2)–C(4')	112.6(4)
I–Pt–P(2)	90.2(1)	Pt–P(2)–C(5)	122.1(7)
C(1)–Pt–P(1)	87.2(3)	Pt–P(2)–C(6)	118.8(6)
C(1)–Pt–P(2)	89.8(3)	C(2)–P(1)–C(3)	99.8(8)
C(1)–Pt–I	170.0(4)	C(2)–P(1)–C(4)	105.4(7)
P(1)–Pt–P(2)	173.7(1)	C(3)–P(1)–C(4)	96.4(6)
Pt–P(1)–C(2)	123.5(5)	C(5)–P(2)–C(4')	105.3(9)
Pt–P(1)–C(3)	115.1(5)	C(6)–P(2)–C(4')	99.5(6)
Pt–P(1)–C(4)	112.6(4)	C(5)–P(2)–C(6)	94.9(9)
P(1)–C(4)–P(2')	116.8(6)		

Torsion angles (°)

Pt–P(1)–C(4)–P(2')	−52.3(5)
C(2)–P(1)–C(4)–P(2')	85.0(8)
C(3)–P(1)–C(4)–P(2')	−172.9(8)
Pt'–P(2')–C(4)–P(1)	56.4(5)
C(5')–P(2')–C(4)–P(1)	−79.0(9)
C(6')–P(2')–C(4)–P(1)	−176.8(8)

* Primed atoms are related to the unprimed ones by the symmetry operation −*x*, −*y*, −*z*.



(**7**)

adopt a face-to-face structure (**4**). In platinum chemistry such a structural type is unusual and has been previously observed only in complexes where the bridging diphosphine ligand is dppm.[9–11] Examples of crystallographically characterised transition-metal binuclear complexes of the sterically less demanding dmpm ligand are still rare and each has been found to display a different type of molecular structure: $[Ag_2(\mu\text{-}dmpm)_2]^{2+}$,[12] *cis,cis*-$[Pt_2Me_4(\mu\text{-}dmpm)_2]$ (**5**),[1,3] $[LPt(\mu\text{-}I)(\mu\text{-}dmpm)_2PtMe_3]^+$ (1:1 mixture of complexes with L = I or Me),[2,4] $[Pt_2(\mu\text{-}I)Me_6(\mu\text{-}dmpm)_2]^+$,[13] and $[Pd_2Cl_2(\mu\text{-}CO)(\mu\text{-}dmpm)_2]$.[14]

In the solid state the molecular dimer of (**8**) has an exact C_i symmetry, the mid-point of the Pt ⟶ Pt' vector coinciding with a crystallographic centre of inversion. The molecular structure is shown in Figure 1 and characterised by bond lengths and angles listed in Table 1. It comprises two *trans*-PtIMe fragments bridged by two mutually *trans* dmpm ligands to form an eight-membered dimetallacycle with an *anti* arrangement of iodide as well as methyl ligands. The $Pt_2P_4C_2$ ring shows a chair conformation and the $Pt_2(\mu\text{-}dmpm)_2$ nucleus approximate $C_2{}^h$ symmetry, with the non-crystallographic two-fold axis passing through the platinum atoms. The square-planar co-ordination environments of the metal centres practically eclipse one another and both are normal to the Pt_2P_4 plane (dihedral angle 88.5°). Tetrahedral distortions of the co-ordination geometries of the metal centres are large and characterised by displacements of the Pt, P(1), P(2), I, and C(1) atoms from their best plane by −0.0389(3), −0.143(2), −0.144(2), 0.138(1), and 0.19(1) Å respectively.

Steric crowding in (**8**) is balanced by large angular distortions. In the local environment of each metal centre, the iodide and methyl ligands are separated from the substituents at phosphorus by short intramolecular distances: I···C(2) 3.64(1), I···C(6) 3.72(2), I···H(C63) 2.9, C(1)···C(3) 3.23(2), C(1)···C(5) 3.27(2), and H(C13)···C(3) 2.4 Å. These distances would have been even shorter if it were not for opening of the Pt–P–C(methyl) angles to 115.1(5)—123.5(5)°. Within the $Pt_2P_4C_2$ ring the bond angles at the phosphorus and carbon atoms are much larger than the tetrahedral value of 109.5°, and at platinum smaller than 180° (Table 1). Despite this, and the closure of the C(1)–Pt–I angle to 170.0(4)°, the methyl and iodide ligands attached to adjacent platinum atoms are in close transannular contact: C(1')···I 3.83(1), H(C12')···I 2.9 Å. Thus the steric congestion leaves only the *exo* sides of the metal centres open to external environment and to attack by small molecules. The observed details of the molecular geometry and a comparison of the Pt···Pt separation [3.353 5(4) Å] with the van der Waals radius of iodine (2.15 Å)[15] suggest that the steric requirements of the ligands could play an important role in precluding formation of the *syn* isomer of (**8**).

Conformation of the dmpm ligands is practically staggered about both $P\text{–}CH_2$ bonds and characterised by torsion angles shown in Table 1. Distortions from the conformation of exact C_s symmetry reflect steric interactions discussed above. The dmpm $P\text{–}CH_2\text{–}P$ angle [116.8(6)°] and the P···P bite [3.140(3) Å] are similar to those previously observed in (**5**) [114.4(7), 115.7(5)° and 3.108(4), 3.122(4) Å].[3]

The metal–ligand bond lengths (Table 1) are as expected in square-planar d^8 platinum complexes.[16] The Pt–P(*trans* to P) bonds are 0.1 Å shorter than those of 2.374(3) and 2.378(3) Å in the d^6,d^6 complex $[Pt_2(\mu\text{-}I)Me_6(\mu\text{-}dmpm)_2]^+$,[13] and this difference can be readily rationalised in terms of the change in oxidation state of the metal centres.[17] The intramolecular

Pt $\cdots$ Pt separation [3.353 5(4) Å] is too large to be considered indicative of a significant bonding interaction.

The ^{1}H and ^{31}P n.m.r spectra of (**8**) (see Experimental section) were as expected for a face-to-face dimer,[9–11] except that only one *Me*P resonance was observed in the ambient-temperature ^{1}H n.m.r. spectrum. However, at lower temperatures this signal broadened and then split into two separate signals (Figure 2). There is thus a fluxional process which leads to an effective molecular plane of symmetry containing the Pt_2P_4 unit at higher temperatures (Scheme).

There are two likely mechanisms for this process. The first involves a concerted exchange of iodide ligands, through an intermediate with two five-co-ordinate platinum centres, (**9**), while the second involves displacement of one iodide with reversible formation of an A-frame intermediate, (**10**) (Scheme). The former mechanism is favoured, on the basis of the following observations. First, the coalescence temperature was the same in the solvents $CDCl_3$ and $(CD_3)_2CO$, which have different solvating abilities for ionic complexes and, secondly, the coalescence temperature was not changed on addition of sodium iodide to a solution in $(CD_3)_2CO$. This would be expected to inhibit formation of an A-frame intermediate like (**10**). A complex similar to (**9**) has been proposed previously as an intermediate in the interconversion of $[Pd_2Cl_4(\mu\text{-dppm})_2]$ to $[PdCl_2(dppm)]$.[18]

The A-frame derivative $[Pt_2(\mu\text{-I})Me_2(\mu\text{-dmpm})_2][PF_6]$ (**11**) was prepared by reaction of $[Pt_2I_2Me_2(\mu\text{-dmpm})_2]$ (**8**) with silver nitrate, followed by precipitation of the cation by addition of $K[PF_6]$. This complex is not fluxional and has n.m.r. properties very similar to those[6] of the $[Pt_2(\mu\text{-I})Me_2(\mu\text{-dppm})_2]^+$ analogue. For example, in the ^{1}H n.m.r. spectrum, one *Me*Pt resonance was observed, but the $CH^AH^BP_2$ protons gave an AB quartet in the ^{1}H-{^{31}P} n.m.r. spectrum, as expected for an A-frame structure, and two separate Me_2P resonances were also observed. Clearly, inversion of the A-frame is slow on the n.m.r. time-scale, in contrast to the behaviour of (**8**). The methyl resonances of the dmpm ligands are obviously very useful for studying these fluxional processes, and the absence of this probe in dppm complexes probably explains why the fluxionality of face-to-face complexes had not been established earlier.[18,19]

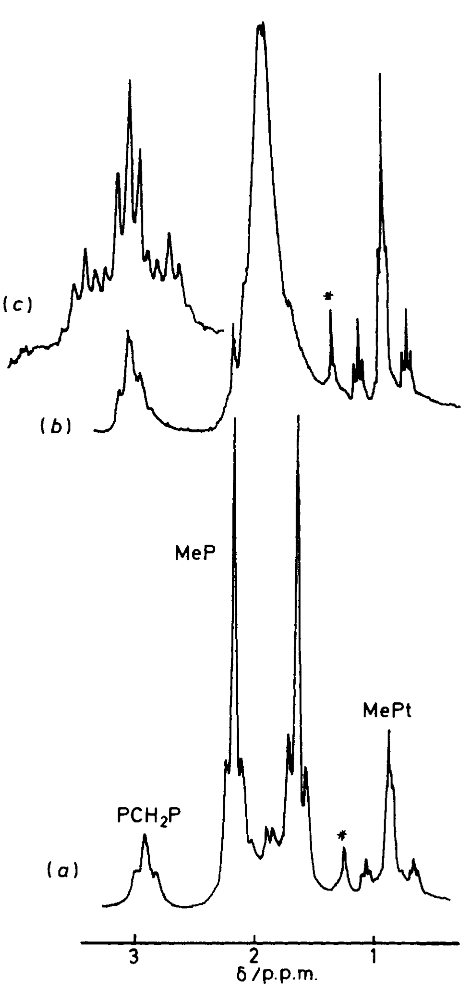
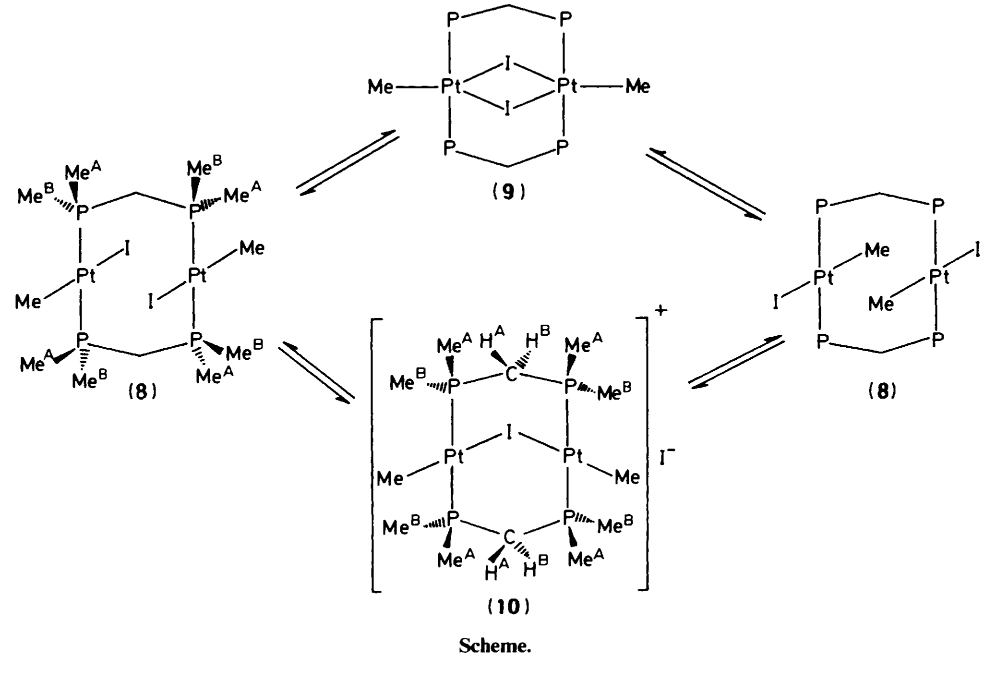


Figure 2. Hydrogen-1 n.m.r. spectra (200 MHz) of complex (**8**): (*a*) at −42 °C, (*b*) at 20 °C, (*c*) expansion of PCH_2P resonance showing the quintet structure with ^{195}Pt satellites (recorded at 100 MHz and 25 °C). The asterisk indicates an impurity



Scheme.

Isolation of the neutral derivatives $[Pt_2X_2Me_2(P\text{-}P)_2]$ when P–P = dmpm, but ionic complexes $[Pt_2(\mu\text{-}X)Me_2(P\text{-}P)_2]X$ when P–P = dppm (X = Cl or I) is considered to be due to lower steric requirements of dmpm compared with dppm. Ionisation of halide to give a cationic A-frame relieves steric congestion in the face-to-face structure, especially between terminal ligands and the substituents on phosphorus, and so becomes more favourable as these substituents increase in steric bulk.

Experimental

Hydrogen-1 and $^1H\text{-}\{^{31}P\}$ n.m.r. spectra were recorded using a Varian XL100 spectrometer, and $^{31}P\text{-}\{^1H\}$ n.m.r. spectra using a Varian XL200 spectrometer. Chemical shifts are quoted with respect to $SiMe_4$ or $(MeO)_3PO$ respectively, *J* values in Hz. $[Pt_2Me_4(\mu\text{-dmpm})_2]$ was prepared as described elsewhere.[1,3]

Preparations.—*cis,cis*-$[Pt_2Cl_2Me_2(\mu\text{-dmpm})_2]$ (**6**). A solution of HCl in dry diethyl ether (0.6 cm^3, 0.454 mol) was added dropwise to a solution of $[Pt_2Me_4(\mu\text{-dmpm})_2]$ (0.08 g) in CH_2Cl_2 (15 cm^3), cooled in an ice-bath. After 30 min the solvent volume was reduced under vacuum and n-pentane (20 cm^3) was added to precipitate the product as a pale yellow solid. Yield 0.074 g, m.p. 180 °C (Found: C, 17.7; H, 4.5; Cl, 9.5. Calc. for $C_{12}H_{34}Cl_2P_4Pt_2$: C, 18.9; H, 4.5; Cl, 9.3%). N.m.r. in CD_2Cl_2: ^1H, 0.54 [dd, $^3J(PH)$ 7.0, 4.0 $^2J(PtH)$ 52, MePt], 1.72 and 1.84 (m, MeP), 2.53 [m, $^3J(PtH)$ 34, PCH_2P]; ^{31}P, -8.1 [m, $^1J(PtP)$ 1 758, $^3J(PtP)$ 75, $^2J(P^AP^B)$ 12.5, $^2J(P^AP^{A'})$ 52.0, PtP^A *trans* to Me], -21.2 [m, $^1J(PtP)$ 4 148, $^3J(PtP)$ 110, $^2J(P^AP^B)$ 12.5, $^2J(P^BP^{B'})$ 20.5, PtP^B *trans* to Cl]. This complex was spectroscopically pure and we are unable to explain the poor carbon analysis.

trans,trans-$[Pt_2I_2Me_2(\mu\text{-dmpm})_2]$ (**8**). A solution of *trans*-$[PtIMe(SMe_2)_2]$ was prepared by reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (0.052 g), SMe_2 (0.0133 cm^3), and *trans*-$[PtI_2(SMe_2)_2]$ (0.104 g) in CH_2Cl_2 (9 cm^3) at room temperature for 24 h. To this solution, cooled to 0 °C, was added dmpm (0.060 cm^3) and, after 30 min, hexane (30 cm^3) was added to precipitate the product. Yield 0.145 g (Found: C, 15.3, H, 3.3. Calc. for $C_{12}H_{34}I_2P_4Pt_2$: C, 15.2; H, 3.6%). N.m.r. ($CDCl_3$ at 25 °C): ^1H, 0.81 [t, $^3J(PH)$ 7.5, $^2J(PtH)$ 81.5, $^4J(PtH)$ 7.5, MePt], 1.82 [s, $^3J(PtH)$ 29, MeP], 2.91 [quintet, $^2J(PH) + {}^4J(PH)$ 8.5, $^3J(PtH)$ 34.5, PCH_2P]; ^{31}P, -19.7 [s, $^1J(PtP)$ 2 859, $^3J(PtP)$ 33, $^2J(PP'') = {}^4J(PP''') = 28$, PtP]. N.m.r. in $CDCl_3$ at -50 °C was the same except that two MeP resonances were observed at δ 1.53 [s, $^3J(PtH)$ 30] and 2.05 [s, $^3J(PtH)$ 26]. The coalescence temperature was 11 °C.

$[Pt_2(\mu\text{-}I)Me_2(\mu\text{-dmpm})_2][PF_6]$ (**11**). A solution of $Ag[NO_3]$ (0.009 g) in MeOH (10 cm^3) was added to a solution of $[Pt_2I_2Me_2(\mu\text{-dmpm})_2]$ (0.05 g) in CH_2Cl_2 (30 cm^3). A trace of charcoal was added to aid coagulation of the AgI precipitate and the mixture was filtered. A solution of $K[PF_6]$ (0.097 g) in MeOH (10 cm^3) was added to the filtrate to precipitate the product as a pale yellow solid. Yield 0.02 g (Found: C, 15.2; H, 3.7. Calc. for $C_{12}H_{34}F_6IP_5Pt_2$: C, 15.0; H, 3.55%). N.m.r. ($CDCl_3$): ^1H, 0.77 [t, $^3J(PH)$ 7, $^2J(PtH)$ 88, MePt], 1.56 [m, $^2J(PH) + {}^4J(PH)$ 9, $^3J(PtH)$ 32, Me^AP], 1.75 [m, $^2J(PH) + {}^4J(PH)$ 6, $^3J(PtH)$ 30, Me^BP], 3.46 [m, $^2J(H^AH^B)$ 14, $^3J(PtH)$ ~0, PCH^AH^BP] 3.59 [m, $^2J(H^AH^B)$ 14, $^3J(PtH)$ 48, PCH^AH^BP]; ^{31}P, -18.0 [s, $^1J(PtP)$ 2 670, $^3J(PtP)$ 30, $^2J(PP'')$ 25, $^4J(PP''')$ 4, PtP].

X-*Ray Structure Analysis of trans,trans*-$[Pt_2I_2Me_2(\mu\text{-dmpm})_2]$ (**8**).—Transparent yellow crystals of prismatic habit were grown from a trichloromethane–cyclohexane mixture.

Crystal data. $C_{12}H_{34}I_2P_4Pt_2$, *M* = 946.3, monoclinic, space group $P2_1/n$ (an alternative setting of $P2_1/c$, no. 14), *a* = 8.611(2), *b* = 16.971(3), *c* = 8.405(1) Å, β = 102.83(2)°, *U* = 1 197.7 $Å^3$, *Z* = 2, D_c = 2.624 g cm^{-3}, *F*(000) = 856, μ(Mo-K_α) = 146.0 cm^{-1}, *T* = 22.5 °C.

Table 2. Fractional atomic co-ordinates for *trans,trans*-$[Pt_2I_2Me_2(\mu\text{-}Me_2PCH_2PMe_2)_2]$ (**8**), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Pt	−0.181 47(3)	0.030 15(2)	0.015 56(3)
I	−0.244 79(10)	0.117 78(4)	−0.258 76(8)
P(1)	−0.282 79(25)	−0.081 97(12)	−0.115 76(29)
P(2)	−0.055 15(26)	0.134 62(14)	0.158 57(28)
C(1)	−0.170 3(17)	−0.030 9(6)	0.235 3(12)
C(2)	−0.389 9(21)	−0.084 0(8)	−0.319 6(20)
C(3)	−0.421 2(19)	−0.136 8(8)	−0.018 8(21)
C(4)	−0.134 4(12)	−0.160 1(6)	−0.099 4(13)
C(5)	−0.011 2(28)	0.137 5(11)	0.372 0(17)
C(6)	−0.149 3(15)	0.228 2(7)	0.133 6(23)

Measurements. A crystal fragment of dimensions *ca.* 0.5 × 0.5 × 0.7 mm was mounted on an Enraf-Nonius CAD4F diffractometer and exposed to graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å). The unit-cell dimensions were determined by a least-squares treatment of 25 high-angle reflections. Intensities of 6 693 $h \pm k \pm l$ reflections ($2 \leqslant \theta \leqslant 30°$) were measured by θ/2θ scans, following a procedure described elsewhere.[20] Only 2 598 unique reflections were considered observed $[I \geqslant 3\sigma(I)]$ and used in the structure analysis. They were corrected empirically for absorption effects.[21]

Structure solution and refinement. The crystal structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares methods. In the final cycles of refinement the platinum, phosphorus, and carbon atoms were assigned anisotropic thermal parameters. The hydrogen atoms were located in difference electron-density maps and included in the structural model, but their co-ordinates were adjusted to comply with idealised tetrahedral geometry around the carbon atoms with C–H bonds of 1.07 Å. They were allowed to ride on the carbon atoms to which they are bonded, with individual isotropic thermal parameters constrained to $U_H = 1.2\ U_C$, where $U_C = \frac{1}{3}(U_{11} + U_{22} + U_{33})$. The refinement converged at $R(= \Sigma||F_o| - |F_c||/\Sigma|F_o|) = 0.036$ and $R'\{= [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\} = 0.045$, with the largest parameter-shift-error ratio of 0.11. The weighting scheme $w = [\sigma^2(F_o)]^{-1}$ was found adequate. In the final difference electron-density synthesis the function values ranged from −1.7 to +1.9 e $Å^{-3}$; the extreme values, associated with the positions of platinum and iodine atoms, are likely to reflect residual absorption effects.

All calculations were performed on a GOULD SEL 32/27 super minicomputer, using the locally developed 'GX Package' programs.[22] Neutral-atom scattering factors and anomalous dispersion corrections were taken from ref. 23. Final atomic co-ordinates of the non-hydrogen atoms are given in Table 2.

Acknowledgements

We thank the S.E.R.C. (U.K.) and the University of Glasgow for the diffractometer and computer purchasing grants and the N.S.E.R.C. (Canada) for financial support (to R. J. P.) and for the award of a scholarship (to S. S. M. L.).

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Received 4th March 1985; *Paper* 5/355