The Di-μ-bis(diphenylphosphino)methane-μ-hydrido-bis[methylplatinum(II)] Cation: Synthesis, Molecular Structure, and Chemical Properties

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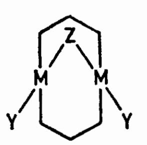
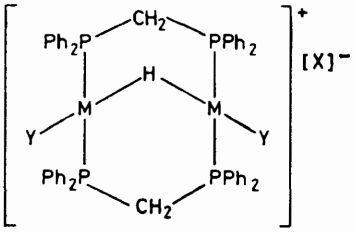
The binuclear title complex $[Pt_2Me_2(\mu\text{-}H)(\mu\text{-}dppm)_2][PF_6]$, dppm = $Ph_2PCH_2PPh_2$, has been prepared and characterized by ^1H and ^{31}P n.m.r. spectroscopy and by an *X*-ray structure determination. Crystals are monoclinic, with space group $P2_1/c$, a = 10.640(3), b = 20.341(3), c = 23.201(3) Å, β = 91.88(2)°, and Z = 4. The structure has been solved by the heavy-atom method and refined to R = 0.053 for 5 374 reflections with $I \geqslant 3\sigma(I)$. The cation has the ' A-frame ' structure with a Pt–Pt separation of 2.932(1) Å; a closed three-centre two-electron $Pt_2(\mu\text{-}H)$ bonding system is proposed. The complex undergoes slow reductive elimination of methane induced by added PMe_2Ph and is photochemically decomposed, but it has high thermal stability.

MANY complexes are now known to have the ' A-frame ' structure, (A),[1] and these include several in which the bridging group Z is a hydride ligand. The cations $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$ (1) [dppm = bis(diphenylphosphino)methane], $[Pt_2Cl_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$ (2),[2] and $[Rh_2(\mu\text{-}H)(CO)_2(\mu\text{-}dppm)_2]^+$ (3) [3] have this structure and $[Rh_2(\mu\text{-}H)(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]^+$ is similar but with an additional bridging carbonyl ligand in the ' pocket ' of the A-frame.[3] The methylplatinum analogue of complex (1), namely $[Pt_2Me_3(\mu\text{-}dppm)_2][PF_6]$, (5), is also known but does not have an ' A-frame ' structure probably due to the inability of the methyl group to form a three-centre two-electron $Pt_2(\mu\text{-}Me)$ grouping.[4,5] We now report the synthesis of the complex $[Pt_2Me_2(\mu\text{-}H)(\mu\text{-}dppm)_2][PF_6]$, (4), which like complexes (1)—(3) has the ' A-frame ' structure with an electron-deficient $Pt_2(\mu\text{-}H)$ bridge.

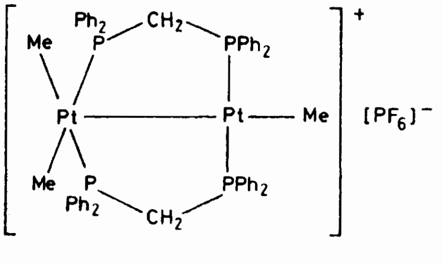


(A)

Alkyl(hydrido)metal complexes are important intermediates in several transition-metal-catalysed reactions but their chemistry has not been studied in depth.[6] This is due to the instability of many such complexes, *e.g.* *cis*-$[PtMe(H)(PPh_3)_2]$, which undergo very rapid reductive elimination of alkane.[7] The complex *cis*-$[OsMe(H)(CO)_4]$ readily decomposes by an intermolecular mechanism [8] whilst *cis*-$[OsMe(H)(CO)_2(PPh_3)_2]$ is more stable.[9] Several complexes of formula *trans*-$[PtR(H)L_2]$ (*e.g.* R = Me or Ph, L = PPh_3) have been isolated and have much better thermal stability than *cis* isomers.[10] Binuclear methyl(hydrido) transition-metal complexes are rare [8] and hence our interest in the new complex (4). A preliminary report has been published.[11]



	M	Y	X
(1)	Pt	H	Cl^- or PF_6^-
(2)	Pt	Cl	Cl^- or PF_6^-
(3)	Rh	CO	PF_6^-
(4)	Pt	Me	PF_6^-



(5)

RESULTS AND DISCUSSION

Synthesis and Properties.—The new complex $[Pt_2Me_2(\mu\text{-}H)(\mu\text{-}dppm)_2][PF_6]$, (4), was prepared in good yield by reaction of either $[Pt_2Me_3(\mu\text{-}dppm)_2][PF_6]$, (5),[4,5] or $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2][PF_6]$ [12] with sodium tetrahydroborate. The product decomposes slowly in the reaction mixture and it was necessary to follow the detailed experimental method closely in order to obtain good yields. Once isolated, the pure crystalline complex (4) was found to have good thermal stability and did not decompose upon heating to 70 °C in solution in dichloromethane or to 170 °C for one hour in the solid state. The complex failed to react with carbon monoxide, methanethiol, or ammonia at room temperature.

It has been shown that the trihydrido-complex (1) reacts rapidly with tertiary phosphine ligands, L, undergoing binuclear reductive elimination of H_2 and generating $[Pt_2H(L)(\mu\text{-dppm})_2][PF_6]$, (6), a diplatinum(I) complex containing a Pt–Pt σ bond.[13] By analogy, it was expected that (4) might react with these ligands to give $[Pt_2Me(L)(\mu\text{-dppm})_2][PF_6]$, (7), by binuclear reductive elimination of methane. Addition of PMe_2Ph to a dichloromethane solution of (4) gave an immediate yellow colouration. However, examination by ^1H n.m.r. spectroscopy showed that negligible reaction had occurred and by gas–liquid chromatography (g.l.c.) that almost no methane was evolved. With excess of PMe_2Ph, however, methane was evolved slowly and the solutions became orange. Details of methane evolution are given in Table 1. It was shown that PPh_3 or dppm were less effective than PMe_2Ph in inducing reductive elimination, and that photolysis of (4) caused elimination of methane in the absence of tertiary phosphines. Photolysis of (1) also causes reductive elimination of H_2. Examination of platinum-containing products after extended reaction of (4) with excess of PMe_2Ph, when almost quantitative formation of methane had occurred, showed that the expected cation (7) was not formed. This cation would be expected to exhibit a characteristic ^{31}P n.m.r. spectrum, similar to that of the analogous hydride (6), (6; L = PMe_2Ph). The products were not identified, but evidence for platinum(0) species was obtained and it appears that if (7) was formed, it must have undergone a disproportionation reaction. The ^{31}P n.m.r. spectra at room temperature of an unstable lemon-yellow solid isolated from one reaction contained only broad resonances with no coupling to ^{195}Pt, indicating an exchange process. At −10 °C, one sample gave a singlet [δ −48.0 p.p.m., $^1J(PtP)$ 2 185 Hz] and a multiplet [δ −44.2 p.p.m., $^1J(PtP)$ 1 907 Hz], but speculation about the precise structures is not justified.

TABLE 1

Elimination of methane from the reaction of $[Pt_2Me_2(\mu\text{-H})(\mu\text{-dppm})_2][PF_6]$ and PMe_2Ph [a]

Solvent	Mole ratio phosphine : complex	θ_c/°C	Duration of experiment /h	Yield of methane [b]
1,2-Dichloroethane	1.4	70	6	40
	2.4		3	95
	3.0	20	1	33
	3.0		24	65
	3.0		48	90
Acetone	1.4	50	3	50
	1.2		24	79
	10.0	20	48	80

[a] Control experiments at 20 and 70 °C showed the formation of only insignificant amounts of CH_4 (<1%) in the absence of PMe_2Ph. [b] Percentage of one molar proportion, estimated error within ±3%.

The Structure.—To establish the structure of (4) unambiguously we have carried out an *X*-ray diffraction study.

In the crystal structure the cations and anions are separated by van der Waals contacts. The geometry of the PF_6^- ions is as expected: P–F 1.49(2)—1.58(2) Å; F–P–F 85(1)—98(2) and 172(1)—177(1)°. The fluorine atoms undergo extremely high thermal vibrations [$U_{iso.}$ = 0.14(2)—0.24(3) Å²], suggesting that they may be involved in some kind of disorder.

In the cation (Figures 1 and 2) the metal centres are linked by two bridging dppm ligands to form a planar Pt_2P_4 unit which is roughly perpendicular to the C(3)-Pt(1)Pt(2)C(4) plane (dihedral angle 82.4°). The two PtP_2C(methyl) fragments are also planar and inclined to each other at a dihedral angle of 31.9°. The T-shaped geometries of the PtP_2C(methyl) fragments, evident from the P–Pt–C and P–Pt–P angles (Table 2), indicate that the platinum atoms are in square-planar environments sharing a ' vacant ' co-ordination site.[14] This site is available to the hydrido-ligand whose position was not established directly by the *X*-ray analysis. The presence of the bridging hydrido-ligand has, however, been revealed by the n.m.r. spectra of the compound (see later). Thus, the overall geometry of the cation is essentially that of the ' A-frame ' type structure.[1]

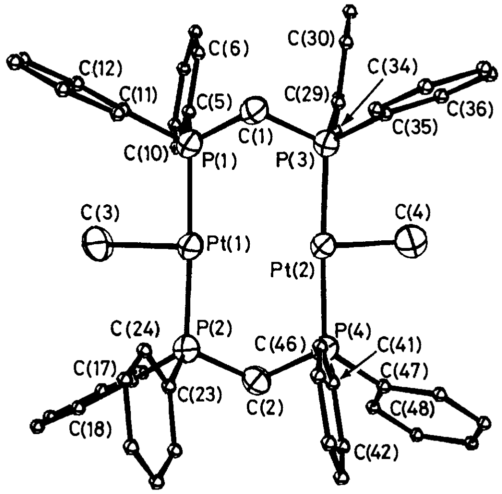


FIGURE 1 Structure of the $[Pt_2Me_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ cation. The vibrational ellipsoids of Pt, P, and C(sp^3) atoms display 50% probability. For clarity, C(sp^2) atoms are represented by spheres of arbitrary size; in each phenyl group the labelled C atoms indicate the direction of the progressive sequence C(n), C(n + 1) . . . C(n + 5)

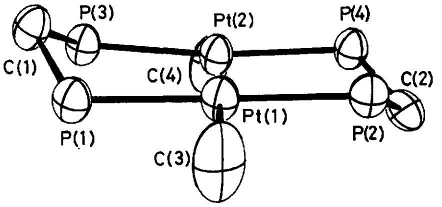


FIGURE 2 A view of the $Pt_2P_4C_4$ core, showing the co-ordination geometries of the Pt atoms and the conformation of the $Pt_2P_4C_2$ metallocycle

The dppm ligands adopt nearly staggered conformations about the P–C(sp^3) bonds, as is evident from the torsion angles listed in Table 2. Their orientation around the Pt–Pt vector is such as to afford a ***trans*** arrangement of the methylene groups with respect to the Pt_2P_4 plane, from which the C(1) and C(2) atoms are displaced by 0.76 and −0.64 Å, respectively (Figure 2). Thus, the $Pt_2P_4C_2$ metallocycle has an elongated chair conformation and the $Pt_2(\mu\text{-dppm})_2$ nucleus shows an approximate C_2 symmetry, the rotation axis coinciding with the direction of the Pt–Pt vector. Such a configuration of the $Pt_2(\mu\text{-dppm})_2$ nucleus distinguishes (4) from $[Pt_2(\mu\text{-}CH_2)Cl_2(\mu\text{-dppm})_2]$ [15] and from the other A-frame complexes (M = Pd or Pt),[16] where *cis* arrangement of the methylene groups and boat conformations of the $M_2P_4C_2$ rings have been observed. This feature is likely to reflect steric, and perhaps even electronic, properties of ligands in the V-shaped Me–Pt–H–Pt–Me fragment.

TABLE 2

Interatomic distances (Å) and angles (°) in $[Pt_2Me_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$

Pt(1)–Pt(2)	2.932(1)	P(2)–Pt(4)	2.295(3)
Pt(1)–C(3)	2.13(2)	P(1)–C(1)	1.83(1)
Pt(2)–C(4)	2.07(2)	P(3)–C(1)	1.83(1)
Pt(1)–P(2)	2.283(3)	P(4)–C(2)	1.84(1)
Pt(2)–P(3)	2.274(3)	P–C(sp^2)	1.801(10)— 1.845(9)
P(1) · · · P(3)	3.025(5)	C(4) · · · P(4)	3.15(2)
P(2) · · · P(4)	3.056(5)	C(4) · · · C(35)	3.47(2)
C(3) · · · P(1)	3.07(2)	C(4) · · · C(47)	3.36(2)
Pt(1)–P(1)	2.275(3)	P(2)–C(2)	1.83(1)
C(3) · · · P(2)	3.11(2)	Pt(1) · · · H(10) *	2.9
C(3) · · · C(11)	3.30(2)	Pt(1) · · · H(24)	2.9
C(3) · · · C(17)	3.25(2)	Pt(2) · · · H(34)	3.1
C(4) · · · P(3)	3.00(2)	Pt(2) · · · H(46)	2.9
P(1)–Pt(1)–C(3)	88.3(5)	C–P–C	102.1(6)— 106.8(5)
P(2)–Pt(1)–C(3)	89.4(5)		
P(1)–Pt(1)–P(2)	177.0(1)	Pt(1)–P(1)–C(1)	112.7(4)
P(3)–Pt(2)–C(4)	87.1(4)	Pt(2)–P(3)–C(1)	113.0(4)
P(4)–Pt(2)–C(4)	92.3(4)	Pt(1)–P(2)–C(2)	112.2(4)
P(3)–Pt(2)–P(4)	173.0(1)	Pt(2)–P(4)–C(2)	112.8(4)
Pt–P–C(sp^2)	112.4(3)— 119.5(3)	P(1)–C(1)–P(3)	111.4(6)
		P(2)–C(2)–P(4)	112.8(7)

Torsion angles (°)

Pt(1)–P(1)–C(1)–P(3)	51.2(7)
Pt(2)–P(3)–C(1)–P(1)	−46.2(7)
Pt(1)–P(2)–C(2)–P(4)	47.0(7)
Pt(2)–P(4)–C(2)–P(2)	−48.0(8)

* The Pt–H distances are derived from calculated positions of the hydrogen atoms; each hydrogen atom is labelled according to the carbon atom to which it is bonded.

The short non-bonding C · · · P and C · · · C distances (Table 2), illustrating contacts of each methyl ligand with two *cis* PPh groups, reveal the presence of some steric strain, which is also apparent from distortions of the co-ordination geometries of the metal atoms. These distortions are evident from the P–Pt–C and P–Pt–P bond angles and from displacements of atoms from the PtP_2C(methyl) planes of up to ±0.09 Å. The co-ordinatively unsaturated platinum atoms are each in contact with two phenyl hydrogens, at the Pt · · · H distances of 2.9—3.1 Å (Table 2).

In the dppm ligands the bond lengths and angles are as expected (Table 2). The Pt–P distances [2.274(3)—2.295(3) Å] are in the range of those observed in the other $Pt_2(\mu\text{-dppm})_2$ complexes with dppm ligands ***trans*** to one another [2.248(4)—2.308(5) Å].[13,17] The Pt–C bond lengths [2.07(2) and 2.13(2) Å] are in agreement with the corresponding ones [2.06(4)—2.10(3) Å] in $[Pt_2Me_3(\mu\text{-dppm})_2]^+$,[4,5] where the methyl groups are also expected to experience relatively high ***trans*** influence.

The Pt(1)–Pt(2) separation is not indicative of a normal single bond; it is *ca.* 0.16 Å longer than the upper limit of the range of Pt–Pt distances [2.620(1)—2.769(1) Å] in the binuclear $Pt_2(\mu\text{-dppm})_2$ complexes in which all structural features are compatible with the presence of covalent or donor–acceptor metal–metal bonding.[4,5,13,17] It is, however, *ca.* 0.23 Å shorter than the Pt · · · Pt distances [3.160(3) and 3.162(4) Å] in $[Pt_2(\mu\text{-}CH_2)Cl_2(\mu\text{-dppm})_2]$ [15] and $[Pt_2Cl_2(\mu\text{-CO})(\mu\text{-}Ph_2AsCH_2AsPh_2)_2]$,[18] where metal–metal bonding is neither suggested by structural evidence nor required for 16-electron configuration of the metal atoms, normally obtained in platinum chemistry. It has been commonly observed that in the A-frame $[M_2(\mu\text{-dppm})_2]$ complexes (M = Pt, Pd, or Rh) the non-bonding M · · · M distances are longer than the intraligand P · · · P distances.[15,16,19] In (4) the opposite is true; the Pt(1)–Pt(2) distance [2.932(1) Å] is significantly shorter than the P · · · P distances [3.025(5) and 3.056(5) Å], suggesting a weak metal–metal interaction. It is thus possible that this electron-deficient complex contains a closed, rather than open,[14] PtHPt system in which the metal-atom orbitals involved in bonding with the hydrido-ligand overlap significantly with one another.

N.M.R. Studies.—As discussed earlier,[20] the ^1H and ^{31}P n.m.r. spectra of binuclear platinum complexes consist of superimposed spectra due to isotopomers containing no ^{195}Pt atoms (43.8%), one ^{195}Pt atom (44.8%), and two ^{195}Pt atoms (11.4%) based on the natural abundance of ^{195}Pt ($I = \frac{1}{2}$) of 33.8%. The spectra are therefore rich in detail and very useful for studies of structure and bonding.[21]

The ^{31}P-{^1H} n.m.r. spectrum of (4) in CH_2Cl_2 solution was very similar to spectra of analogous complexes such as (1), (2),[2] and $[Pt_2Me_2(\mu\text{-Cl})(\mu\text{-dppm})_2][PF_6]$.[12] The peaks due to isotopomers containing two ^{195}Pt atoms were very clearly resolved (Figure 3) and this allowed the coupling ^1J(PtPt) to be determined accurately.[22] The full analysis gave δ(^{31}P) 13.5 p.p.m., ^1J(PtP) 2 884, ^2J(PtP) +24, ^2J(PP) 51, ^3J(PP) 15, and ^1J(PtPt) 464 ± 5 Hz and, as expected, the couplings are similar to those in (1).[2]

The presence of a symmetrically bridging hydride in (4) is shown by the ^1H n.m.r. spectrum at high field. A resonance at δ −7.26 p.p.m., with the appearance of a 1 : 8 : 18 : 8 : 1 quintet due to coupling with ^{195}Pt and with each peak further split into a 1 : 4 : 6 : 4 : 1 quintet due to coupling with ^{31}P, was observed [^1J(PtH) 512 and ^2J(PH) 9 Hz] as expected.[2]

In the ^1H n.m.r. spectrum, the methylplatinum resonance appeared as an apparent triplet, due to coup-

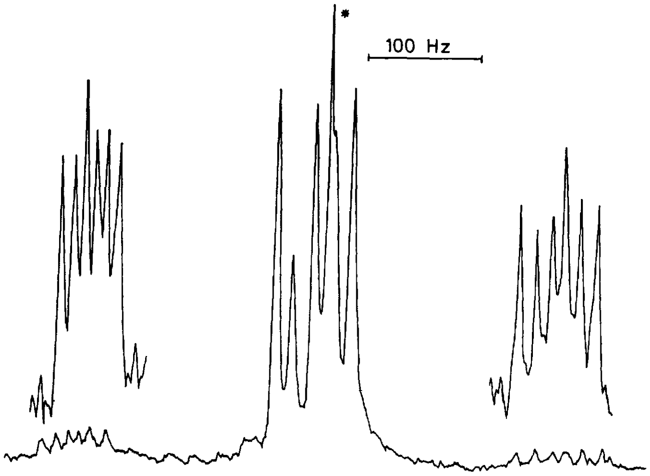


FIGURE 3 High-field ^{195}Pt satellites in the ^{31}P-{^{1}H} n.m.r. spectrum (40.5 MHz) of [Pt_2Me_2(μ-H)(μ-dppm)$_2$][PF_6], (4). The peak marked * and the two groups of very weak outer peaks, also shown inset at higher amplitude and slightly different sweep width (from a spectrum at 36.2 MHz), are due to the $^{195}Pt_2$ isotopomer

ling with ^{31}P at $\delta = 0.19$ p.p.m. The methyl protons and phosphorus atoms give an [$A_3X_2X'_2A'_3$] spin system and the apparent triplet splitting of 6.5 Hz is not necessarily given by ^3J(PH).[23] Two sets of satellites due to coupling with ^{195}Pt were observed with ^2J(PtMe) = 67 and ^3J(PtMe) = 7 Hz. The outer set of satellites also gave a triplet splitting but the relative intensities of the satellites were not the same as for the central triplet, no doubt due to the changed spin system on introduction of the ^{195}Pt. In addition, decoupling of either the Pt_2(μ-H) or CH_2P_2 protons in the 400-MHz ^{1}H n.m.r. spectra led to narrowing of the peaks, indicating unresolved couplings between these protons and methyl protons. In the 100-MHz n.m.r. spectra the doublet splitting due to coupling to the Pt_2(μ-H) proton with ^3J(HH) 0.75 Hz was resolved.

The methylene protons of the dppm ligands together with ^{31}P atoms give an [$A_2X_2X'_2A'_2$] spin system (assuming equivalence of the CH_2 protons, see later) and the central resonance ($\delta = 4.63$ p.p.m.) appeared as an apparent quintet due to coupling with ^{31}P, with individual lines separated by 4.5 Hz [Figure 4(*a*)]. Coupling to ^{195}Pt gave the usual two sets of satellites and an overall 1 : 8 : 18 : 8 : 1 pattern. Decoupling at the central methylplatinum resonance frequency caused a narrowing of the central CH_2P_2 resonance and a doublet splitting due to coupling with the μ-H proton [^4J(HH) = 2 Hz] was then clearly resolved [Figure 4(*b*)]. The splitting disappeared with resulting line narrowing on decoupling the central part of the Pt_2(μ-H) resonance [Figure 4(*c*)]. This coupling to the Pt_2(μ-H) proton was clearly resolved in the 100-MHz spectrum without decoupling.

The apparent equivalence of the PCH_2P protons is worthy of brief comment. The *X*-ray structural determination clearly shows that this complex cation has the A-frame structure (A) although the μ-H atom has not been directly located. It might therefore have been expected that the PCH_2P resonance would resemble those of the A-frame complexes [Pt_2Cl_2(μ-Z)(μ-dppm)$_2$] (Z = S, SO_2, or CH_2) [24,25] and show inequivalence of these protons. However, instead the resemblance is with the cations of complexes (1), (2), and [Pt_2(μ-Cl)H_2(μ-dppm)$_2$]-[PF_6]^2 which at ambient temperatures appear to undergo a rapid fluxional process which makes the PCH_2P

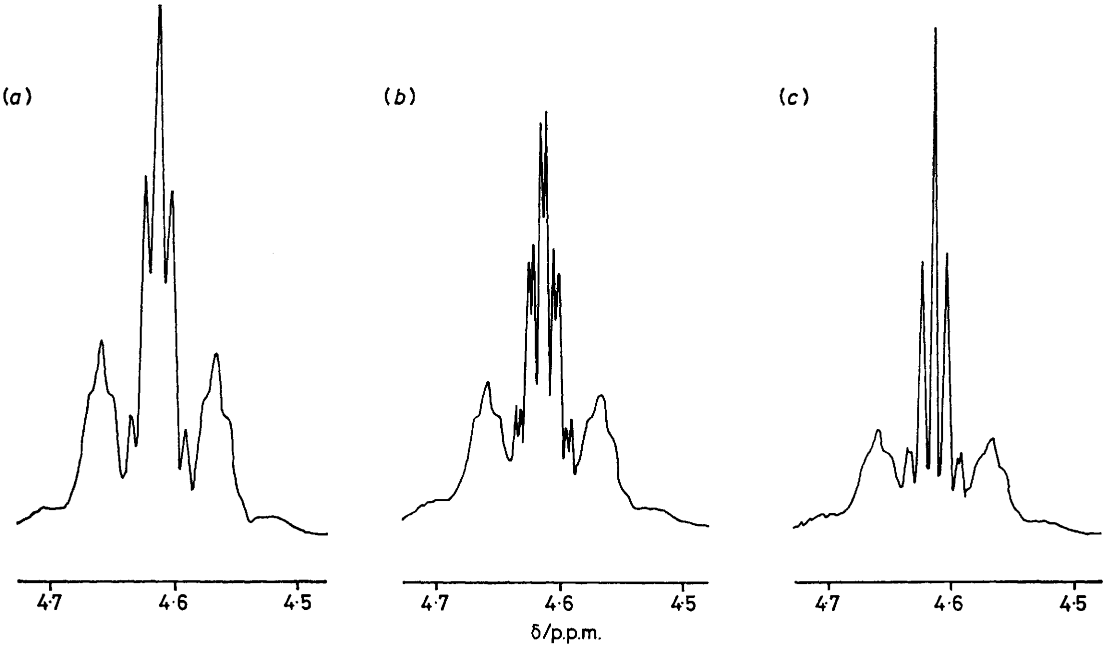


FIGURE 4 The ^{1}H n.m.r. spectrum (400.1 MHz) of [Pt_2Me_2(μ-H)(μ-dppm)$_2$][PF_6], (4), in the region of the PCH_2P resonances; (*a*) the fully coupled spectrum, (*b*) decoupling at the central part of the MePt resonance, and (*c*) decoupling at the centre of the Pt_2(μ-H) resonance

protons equivalent on the n.m.r. time scale. The fluxionality of these and other related A-frame complexes is currently being investigated.

EXPERIMENTAL

The n.m.r. spectra were recorded on Varian XL-100, JEOL FX90Q, and Bruker WH-400 spectrometers. The reference for ^{31}P chemical shifts was trimethyl phosphate and the convention of negative upfield shifts and positive downfield shifts was adopted. The complexes $[Pt_2Me_3(\mu\text{-dppm})_2][PF_6]$ [4] and $[Pt_2Me_2(\mu\text{-Cl})(\mu\text{-dppm})_2][PF_6]$ [12] were prepared as described elsewhere.

Preparation of $[Pt_2Me_2(\mu\text{-H})(\mu\text{-dppm})_2][PF_6]$.—(*a*) *From* $[Pt_2Me_3(\mu\text{-dppm})_2][PF_6]$. In a typical experiment, $[Pt_2Me_3(\mu\text{-dppm})_2][PF_6]$ (1.32 g, 0.98 mmol) was dissolved in methanol (110 cm^3). Potassium hexafluorophosphate (0.60 g, 3.25 mmol) was added to provide an excess of PF_6^- ions and facilitate crystallization of the product. The solution was cooled to 0 °C and sodium tetrahydroborate in methanol (0.4% w/v) at 0 °C was added slowly with stirring until the yellow colour of the starting material had completely disappeared. This required a total of 27 cm^3 of solution (2.9 mmol of $Na[BH_4]$). At the end of the reaction, a creamy coloured precipitate of the product had formed and the solution was pale brown. The precipitate was recovered by filtration and recrystallized from dichloromethane–n-hexane to afford pure $[Pt_2Me_2(\mu\text{-H})(\mu\text{-dppm})_2][PF_6]$ (0.85 g, 65%) as a white solid (Found: C, 46.7; H, 3.8; F, 8.4; P, 11.8. $C_{52}H_{51}F_6P_5Pt_2$ requires C, 46.8; H, 3.9; F, 8.5; P, 11.6%). A second crop of slightly less pure material (0.25 g, 19%) was obtained by further crystallization of the mother-liquor.

Consistently high yields were obtained from similar experiments provided the addition of tetrahydroborate solution was carefully controlled. It was found particularly necessary to add this reagent slowly towards the end of the reaction otherwise a darker brown solution was formed and a poor yield of product was obtained.

(*b*) *From* $[Pt_2Me_2(\mu\text{-Cl})(\mu\text{-dppm})_2][PF_6]$. A suspension of $[Pt_2Me_2(\mu\text{-Cl})(\mu\text{-dppm})_2][PF_6]$ (0.200 g, 0.146 mmol) in methanol (75 cm^3) was rapidly heated to the boiling point when most of the solid dissolved. The solution was then rapidly cooled. Sodium tetrahydroborate (0.08 g, 2.1 mmol) in ethanol (4 cm^3) was then fairly rapidly added to the supersaturated solution. The solution was stirred during the addition and then for another 15 min. The pale brown solution was decanted from a small amount of white residue, presumably unreacted starting material, and treated with aqueous $K[PF_6]$ (0.2 g, 1.09 mmol in *ca.* 50 cm^3) to produce a pale brown precipitate which was allowed to form completely over 1 h. The product, slightly impure (i.r.) $[Pt_2Me_2(\mu\text{-H})(\mu\text{-dppm})_2][PF_6]$ (0.149 g, 77%), was then recovered by filtration, washed with water, and dried *in vacuo*. On recrystallization from dichloromethane–n-hexane, pure material (0.093 g, 48%) was obtained.

This was found to be a less satisfactory preparation than (*a*). The μ-chloro-complex has only a low solubility in methanol and its reaction with $Na[BH_4]$ is slow, presumably as a consequence of this. The desired μ-hydrido complex also reacts slowly with $Na[BH_4]$ and much of it was therefore consumed when the reaction time was much longer. The above procedure was found largely to overcome this problem by utilizing a supersaturated solution of the μ-chloro-complex.

Reaction of $[Pt_2Me_2(\mu\text{-H})(\mu\text{-dppm})_2][PF_6]$ *with Organophosphines*.—In a typical experiment, the complex (0.050 g, 0.037 mmol) and 1,2-dichloroethane (1.2 cm^3) were placed in a reaction tube (40 cm^3) fitted with a Teflon stopcock and cooled to nearly −196 °C. Dimethylphenylphosphine (0.012 g, 0.087 mmol) in 1,2-dichloroethane (0.8 cm^3) was then added under a blanket of nitrogen and the vessel evacuated. The reaction mixture was allowed to warm to room temperature, when a yellow colour rapidly developed, and was then heated at 70 °C for 3 h by which time it was deep orange.

After cooling to room temperature, nitrogen was admitted (1 atm).* Analysis of the gases by g.l.c. showed the presence of methane (0.035 mmol, 95%). Equilibrated standards of methane in nitrogen were prepared in an identical vessel containing the same volume of solvent, thus compensating for the small amount of methane in solution.

The results of a series of experiments with PMe_2Ph are summarized in Table 1. Other experiments, with triphenylphosphine and dppm, showed that these phosphines react even more slowly. To avoid photodecomposition of the starting complex it was necessary to exclude light from the reaction vessels.

Attempts to isolate pure platinum complexes from reactions with PMe_2Ph at elevated temperatures, either in dichloromethane or acetone, were unsuccessful. However, from reactions in acetone at room temperature, which proceeded essentially to completion after 2—3 days provided a large excess of the phosphine (10—11 molar proportions) was used, an unidentified, nicely crystalline, lemon-yellow solid (Found: C, 63.1; H, 4.3; P, 13.1%) was obtained.

Determination of the Crystal Structure.—*Crystal data*. $[C_{52}H_{51}P_4Pt_2][PF_6]$, $M = 1\,335.0$, Monoclinic, space group $P2_1/c$ (C_{2h}^5), with $a = 10.640(3)$, $b = 20.341(3)$, $c = 23.201(3)$ Å, $\beta = 91.88(2)°$, $U = 5\,019$ Å^3, $Z = 4$, $D_c = 1.77$ g cm^{-3}, $F(000) = 2\,592$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, and μ(Mo-K_α) = 55.4 cm^{-1}.

Measurements. After optical goniometry measurements, a highly transparent, plate-like crystal of approximate dimensions 0.6 × 0.5 × 0.02 mm was centred on an Enraf-Nonius CAD-4F diffractometer equipped with a graphite monochromator. Further photodecomposition of the crystal was prevented by maintaining darkness in the laboratory.

The unit-cell dimensions were determined from the setting angles of 25 reflections with $12 \leqslant \theta(\text{Mo-}K_\alpha) \leqslant 14°$. The space group was derived from systematically absent reflections. The intensities of 9 518 hkl and $hk\bar{l}$ reflections with $2 \leqslant \theta(\text{Mo-}K_\alpha) \leqslant 25°$ were measured using continuous θ—2θ scans of 0.75° in θ, increased by 25% at each end to allow for background effects. A reflection was scanned either until $\sigma(I)/I < 0.02$ or for 100 s, whichever required less time. The intensities of two reflections remeasured every 2 h displayed random fluctuations of up to 6% of their mean values.

The integrated intensities and their standard deviations, derived as described earlier ($q = 0.04$),[26] were corrected for Lorentz, polarization, and absorption effects, but not for extinction. Only 5 374 reflections met the condition $I \geqslant 3\sigma(I)$ and were used in further analysis.

Structure determination and refinement. The structure was solved by the heavy atom method and refined by full-matrix least-squares minimization of the function $\Sigma w\Delta^2$, where $w = 1/\sigma^2(|F_o|)$ and $\Delta = |F_o| - |F_c|$. The eight phenyl groups of the cation were constrained to D_{6h} sym-

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* Throughout this paper: 1 atm = 101 325 Pa.

metry and the C–C bond length to **1.395** Å, but their carbon atoms were assigned individual isotropic thermal parameters. The remaining non-hydrogen atoms were allowed anisotropic thermal vibrations. Electron-density difference syntheses revealed the positions of all hydrogen atoms, except for those of the CH_3 groups and the hydrido-ligand. Hence, only the C_6H_5 and CH_2 hydrogens were included in the structural model, but with fixed positions assuming idealized geometry around the C atoms in the C–H bonds of 1.08 Å. The refinement converged at $R = 0.053$ ($R' = 0.070$), with no parameter changing by $>0.05\sigma$. The final difference synthesis displayed peaks of up to 2.6 e Å^{-3} in the immediate vicinity of the Pt atoms, but none elsewhere that is >1.0 e Å^{-3}. An analysis of $\langle w\Delta^2\rangle$ as a function of $\sin\theta$, $|F_o|$, and Miller indices showed no unexpected trends. The atomic scattering factors, and the anomalous-dispersion corrections for Pt and P atoms, were taken from ref. 27.

TABLE 3

Fractional atomic co-ordinates ($\times 10^n$; $n = 5$ for Pt and $n = 4$ for other atoms)

Atom	*x*	*y*	*z*
Pt(1)	1 925(5)	25 242(3)	−1 040(2)
Pt(2)	25 173(5)	18 070(3)	−3 272(2)
P(1)	−672(3)	2 159(2)	−955(1)
P(2)	996(3)	2 939(2)	745(1)
P(3)	1 786(3)	1 492(2)	−1 217(1)
P(4)	3 431(3)	2 202(2)	513(1)
P(5)	2 489(5)	724(3)	3 196(2)
F(1)	2 699(15)	205(8)	2 729(6)
F(2)	1 202(16)	426(11)	3 287(8)
F(3)	3 655(15)	1 091(12)	3 053(11)
F(4)	3 036(29)	308(12)	3 671(8)
F(5)	2 252(20)	1 286(9)	3 648(7)
F(6)	1 803(22)	1 152(9)	2 734(7)
C(1)	503(12)	2 012(7)	−1 499(5)
C(2)	2 269(13)	2 431(6)	1 050(5)
C(3)	−1 618(14)	2 874(12)	111(7)
C(4)	3 827(16)	1 060(9)	−380(6)
C(5)	−1 600(9)	1 411(4)	−914(4)
C(6)	−2 004(9)	1 076(4)	−1 411(4)
C(7)	−2 757(9)	518(4)	−1 367(4)
C(8)	−3 105(9)	295(4)	−827(4)
C(9)	−2 701(9)	630(4)	−330(4)
C(10)	−1 948(9)	1 188(4)	−373(4)
C(11)	−1 714(8)	2 757(4)	−1 309(4)
C(12)	−3 014(8)	2 668(4)	−1 332(4)
C(13)	−3 793(8)	3 149(4)	−1 581(4)
C(14)	−3 272(8)	3 719(4)	−1 806(4)
C(15)	−1 971(8)	3 808(4)	−1 784(4)
C(16)	−1 192(8)	3 327(4)	−1 535(4)
C(17)	−99(8)	2 975(5)	1 345(3)
C(18)	−604(8)	3 566(5)	1 536(3)
C(19)	−1 505(8)	3 563(5)	1 959(3)
C(20)	−1 902(8)	2 969(5)	2 192(3)
C(21)	−1 397(8)	2 378(5)	2 001(3)
C(22)	−496(8)	2 381(5)	1 578(3)
C(23)	1 592(10)	3 765(4)	707(4)
C(24)	1 268(10)	4 143(4)	222(4)
C(25)	1 652(10)	4 797(4)	192(4)
C(26)	2 360(10)	5 075(4)	647(4)
C(27)	2 683(10)	4 697(4)	1 132(4)
C(28)	2 300(10)	4 043(4)	1 162(4)
C(29)	1 133(10)	678(4)	−1 306(4)
C(30)	797(10)	460(4)	−1 859(4)
C(31)	190(10)	−143(4)	−1 936(4)
C(32)	−80(10)	−529(4)	−1 458(4)
C(33)	257(10)	−311(4)	−904(4)
C(34)	863(10)	292(4)	−828(4)
C(35)	2 956(8)	1 541(5)	−1 771(4)
C(36)	3 609(8)	972(5)	−1 915(4)
C(37)	4 532(8)	998(5)	−2 327(4)
C(38)	4 803(8)	1 592(5)	−2 596(4)
C(39)	4 150(8)	2 161(5)	−2 453(4)
C(40)	3 227(8)	2 135(5)	−2 041(4)
C(41)	4 361(9)	2 930(4)	398(4)
C(42)	5 114(9)	3 177(4)	852(4)
C(43)	5 715(9)	3 782(4)	796(4)
C(44)	5 564(9)	4 140(4)	285(4)
C(45)	4 811(9)	3 893(4)	−168(4)
C(46)	4 210(9)	3 289(4)	−112(4)
C(47)	4 515(8)	1 677(4)	937(3)
C(48)	4 141(8)	1 326(4)	1 418(3)
C(49)	5 013(8)	943(4)	1 730(3)
C(50)	6 257(8)	911(4)	1 561(3)
C(51)	6 630(8)	1 262(4)	1 079(3)
C(52)	5 759(8)	1 645(4)	767(3)

The positional parameters of non-hydrogen atoms are listed in Table 3. The structure factors and the thermal atomic parameters are given in Supplementary Publication No. SUP 23197 (35 pp.).*

The calculations were carried out using programs listed elsewhere [13] and the ICL 2976 computer at the University of Glasgow.

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