

A DINUCLEAR HYDRIDE COMPLEX OF PLATINUM(I) CONTAINING BOTH BIDENTATE AND MONODENTATE BIS(DIPHENYLPHOSPHINO)METHANE LIGANDS: THE CRYSTAL STRUCTURE OF $[\text{Pt}_2\text{H}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2][\text{PF}_6]$

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Summary

The crystal structure of the title compound has been determined from 6049 X-ray diffractometric intensities with $I > 3\sigma(I)$, and refined by a least-squares procedure to $R = 0.050$. The crystals are monoclinic, space group $P2_1/n$, $a = 13.702(2)$, $b = 14.255(2)$, $c = 39.556(6)$ Å, $\beta = 94.75(1)^\circ$, $Z = 4$. The structure of the cation displays two different coordination modes of the $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ligands. Two of these are bidentate, bridging the Pt–Pt bond [$2.769(1)$ Å] to form a $\text{Pt}_2(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2$ nucleus, while the third acts as a monodentate two-electron donor. The hydrido ligand was not located, but its position is inferred from the coordination geometry of the platinum atom to which it is bonded. The metal–ligand distances are: Pt–P(*trans* to P) $2.248(3)$ – $2.289(4)$ and Pt–P(*trans* to Pt) $2.347(4)$ Å.

Introduction

The chemistry of the transition metal hydrides is rich in platinum(II) species: numerous mononuclear, and more recently novel dinuclear, mono- and poly-hydrides have been reported and their involvement in homogeneous catalysis has been recognised [1]. In contrast, platinum(I) hydrides, first discovered in 1979, are still rare [2,3]. The compounds $[\text{Pt}_2\text{H}(\text{L})(\text{dppe})_2][\text{X}]$ (L = CO, CNR; R = *p*-tolyl, methyl, *t*-butyl; dppe = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$; X = BF_4 , I), containing bridging or terminal hydrido ligands, have been characterised spectroscopically and by a preliminary X-ray structure analysis of $[\text{Pt}_2(\mu\text{-H})(\mu\text{-CO})(\text{dppe})_2][\text{BF}_4]$ [2].

The title compound was first obtained by a dppm-induced reductive elimination of dihydrogen from $[\text{Pt}_2\text{H}_3(\mu\text{-dppm})_2][\text{PF}_6]$ (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$). On the basis of the observed stoichiometry of the reaction it was formulated as $[\text{Pt}_2\text{H}(\text{dppm})_3][\text{PF}_6]$ [3]. The IR spectrum indicated the presence of a terminal

hydrido ligand, but the ^1H and ^{31}P NMR spectra were not sufficiently resolved to allow structural assignments. To establish the solid state structure of this novel hydride, which can be considered as a protonated form of the catalytically active platinum(0) complex $[\text{Pt}_2(\mu\text{-dppm})_3]$ [4], we subjected it to an X-ray diffraction study, the account of which is presented herein. Preliminary results of this work have been published elsewhere [3].

Experimental

Crystals of $[\text{Pt}_2\text{H}(\text{dppm})_3][\text{PF}_6]$, obtained from a 1 : 1 mixture of 1,2-dichloroethane and propan-1-ol, were pale yellow pseudohexagonal prisms highly sensitive to loss of solvent.

Crystal data

$[\text{C}_{75}\text{H}_{67}\text{P}_6\text{Pt}_2][\text{PF}_6] \cdot \text{C}_2\text{H}_4\text{Cl}_2$, $M = 1788.3$. Monoclinic, $a = 13.702(2)$, $b = 14.255(2)$, $c = 39.556(6)$ Å, $\beta = 94.75(1)^\circ$, $U = 7700$ Å³, $Z = 4$, $D_c = 1.54$ g cm⁻³, $F(000) = 3528$, space group $P2_1/n$ (C_{2h}^5 , No. 14). Mo- K_α radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 39$ cm⁻¹.

Measurements

A crystal of approximate dimensions $0.025 \times 0.025 \times 0.025$ cm was sealed in a Lindemann glass capillary, together with some mother liquor, and used in all measurements. The orientation of the crystal, on an Enraf-Nonius CAD4F diffractometer equipped with a graphite monochromator, and the unit-cell dimensions were determined from the setting angles of 24 reflections with $15 \leq \theta(\text{Mo-}K_\alpha) \leq 18^\circ$. The space group was derived from systematically absent reflections. The intensities of 10 364 reflections with $3 \leq \theta(\text{Mo-}K_\alpha) \leq 22^\circ$ were measured using continuous $\theta/2\theta$ scans of 0.70° in θ , increased by 25% at each end of the scan range to allow for background effects. A reflection was scanned either until $\sigma(I)/I < 0.03$ or for 70 s, whichever required less time. For each reflection the intensity measurement was repeated until consistent results were obtained. The crystal orientation and the intensities of two strong reflections were measured periodically throughout the experiment. The random fluctuations of the monitored intensities did not exceed 4% of their mean values.

The integrated intensities, I , and their standard deviations, $\sigma(I)$, were derived as described elsewhere [5], using a q value of 0.05. They were corrected for Lorentz-polarisation effects, but not for absorption nor extinction. Only 6049 independent reflections met the condition $I > 3\sigma(I)$, and they were used in the subsequent structure analysis.

Structure determination and refinement

The positions of the platinum atoms were determined from a Patterson function and those of the phosphorus, carbon and fluorine atoms from the subsequent electron density syntheses. At a later stage of the analysis a difference Fourier synthesis revealed three regions of significant electron density, which were separated from one another and also from the cation and anion. One of these regions displayed discrete peaks upon which a molecule of 1,2-di-

TABLE 1

FRACTIONAL ATOMIC COORDINATES ($\times 10^5$ for Pt and $\times 10^4$ for other atoms)

Atom	x	y	z
Pt(1)	37192(4)	25916(5)	15050(2)
Pt(2)	18238(4)	21359(4)	12635(1)
P(1)	3302(3)	3324(3)	1975(1)
P(2)	1749(3)	1939(3)	1829(1)
P(3)	4462(3)	1807(3)	1105(1)
P(4)	2510(3)	2114(3)	755(1)
P(5)	161(3)	2054(3)	1068(1)
P(6)	-366(3)	3812(3)	1509(1)
P(7)	2434(5)	3086(4)	4110(2)
F(1)	3423(8)	3347(9)	4318(3)
F(2)	1877(12)	3594(15)	4361(5)
F(3)	1475(11)	2849(11)	3893(4)
F(4)	2433(20)	2153(12)	4246(7)
F(5)	2494(11)	4079(11)	3941(4)
F(6)	3009(14)	2759(15)	3816(4)
C(1)	2046(11)	2991(10)	2083(4)
C(2)	3601(11)	1307(10)	775(4)
C(3)	-737(10)	2670(9)	1315(3)
C(4)	4029(8)	3086(8)	2365(2)
C(5)	4836(8)	2490(8)	2363(2)
C(6)	5345(8)	2225(8)	2668(2)
C(7)	5046(8)	2556(8)	2975(2)
C(8)	4239(8)	3152(8)	2977(2)
C(9)	3731(8)	3418(8)	2672(2)
C(10)	3274(8)	4605(6)	1939(3)
C(11)	4000(8)	5169(6)	2102(3)
C(12)	3996(8)	6134(6)	2045(3)
C(13)	3267(8)	6536(6)	1824(3)
C(14)	2541(8)	5973(6)	1661(3)
C(15)	2544(8)	5007(6)	1718(3)
C(16)	2560(7)	993(6)	200(2)
C(17)	2862(7)	317(6)	1778(2)
C(18)	3483(7)	-406(6)	1898(2)
C(19)	3802(7)	-454(6)	2242(2)
C(20)	3500(7)	223(6)	2466(2)
C(21)	2879(7)	946(6)	2346(2)
C(22)	591(6)	1594(7)	1996(2)
C(23)	36(6)	2225(7)	2170(2)
C(24)	-846(6)	1938(7)	2290(2)
C(25)	-1172(6)	1019(7)	2236(2)
C(26)	-618(6)	388(7)	2062(2)
C(27)	264(6)	676(7)	1942(2)
C(28)	1840(7)	1576(6)	383(2)
C(29)	1718(7)	606(6)	393(2)
C(30)	1274(7)	134(6)	112(2)
C(31)	953(7)	634(6)	-179(2)
C(32)	1075(7)	1605(6)	-189(2)
C(33)	1519(7)	2076(6)	92(2)
C(34)	2945(8)	3227(6)	611(3)
C(35)	3388(8)	3298(6)	307(3)
C(36)	3693(8)	4171(6)	196(3)
C(37)	3555(8)	4972(6)	389(3)
C(38)	3112(8)	4901(6)	693(3)
C(39)	2807(8)	4028(6)	804(3)
C(40)	5298(9)	2397(9)	854(3)
C(41)	5831(9)	1871(9)	635(3)
C(42)	6475(9)	2318(9)	432(3)
C(43)	6587(9)	3290(9)	448(3)

TABLE 1 (continued)

Atom	x	y	z
C(44)	6054(9)	3815(9)	666(3)
C(45)	5410(9)	3369(9)	869(3)
C(46)	5182(9)	840(8)	1290(3)
C(47)	4921(9)	-98(8)	1240(3)
C(48)	5473(9)	-802(8)	1410(3)
C(49)	6285(9)	-567(8)	1630(3)
C(50)	6546(9)	372(8)	1679(3)
C(51)	5994(9)	1076(8)	1509(3)
C(52)	-390(7)	893(5)	1047(3)
C(53)	-1403(7)	766(5)	1028(3)
C(54)	-1792(7)	-135(5)	1047(3)
C(55)	-1169(7)	-909(5)	1085(3)
C(56)	-156(7)	-781(6)	1104(3)
C(57)	233(7)	120(5)	1085(3)
C(58)	-144(7)	2554(7)	651(2)
C(59)	256(7)	3432(7)	591(2)
C(60)	-10(7)	3905(7)	289(2)
C(61)	-676(7)	3498(7)	46(2)
C(62)	-1076(7)	2619(7)	105(2)
C(63)	-810(7)	2147(7)	408(2)
C(64)	-1351(8)	3959(8)	1792(3)
C(65)	-2274(8)	3551(8)	1729(3)
C(66)	-2965(8)	3632(8)	1967(3)
C(67)	-2732(8)	4121(8)	2269(3)
C(68)	-1809(8)	4528(8)	2332(3)
C(69)	-1119(8)	4448(8)	2093(3)
C(70)	-670(9)	4677(7)	1176(3)
C(71)	-1529(9)	4646(7)	961(3)
C(72)	-1726(9)	5348(7)	719(3)
C(73)	-1064(9)	6082(7)	693(3)
C(74)	-205(9)	6114(7)	908(3)
C(75)	-8(9)	5411(7)	1149(3)
C(76)	9807(40)	4062(38)	4584(12)
C(77)	9863(39)	2944(36)	4537(12)
C(78)	7778(14)	2005(13)	3124(5)
C(79)	9671(18)	799(16)	3735(6)
Cl(1)	8830(10)	4338(9)	4820(3)
Cl(2)	8536(13)	2436(11)	4378(4)

chloroethane could be superimposed; each of the other two regions showed a peak of height comparable with that of the other carbon atoms in this structure, and also a broad plateau of significant, but unresolved electron density. Hence, the non-hydrogen atoms of a $C_2H_4Cl_2$ molecule [designated as C(76), C(77), Cl(1) and Cl(2) in Table 1] and, in addition, two carbon atoms thought to be associated with two unidentified and probably disordered solvent molecules [C(78) and C(79)] were included in all further calculations.

The positional and thermal atomic parameters were refined by full-matrix least-squares minimisation of the function $\sum \omega \Delta^2$ ($\omega = 1/\sigma^2(|F_0|)$, $\Delta = |F_0| - |F_c|$). An allowance was made for anisotropy of the thermal vibrations of the platinum, phosphorus and fluorine atoms. The twelve phenyl rings of the cation were constrained to $6/mmm$ symmetry and a C—C bond length of 1.395 Å, but their carbon atoms were assigned individual isotropic thermal parameters. The neutral-atom scattering factors for the non-hydrogen atoms and the anomalous

dispersion corrections for platinum, phosphorus and chlorine were taken from the literature [6]. Scattering of the hydrogen atoms was not accounted for. The refinement converged at $R = 0.050$ and $R' = 0.074$ [$R' = (\sum \omega \Delta^2 / \sum \omega F_0^2)^{1/2}$], with no parameter changing by more than 0.1σ . An analysis of $\langle \omega \Delta^2 \rangle$ as a function of $|F_0|$, $\sin \theta$ and Miller indices revealed no unexpected trends. The highest electron density peaks in the final difference synthesis ($0.8\text{--}1.3 \text{ e}\text{\AA}^{-3}$) are associated with solvent molecules or lie close to the platinum and phosphorus atoms.

The final positional atomic parameters are listed in Table 1. The vibrational atomic parameters and the observed and calculated structure factors are available from the authors.

The calculations were carried out using CAD4 data processing program (M.B. Hursthouse), a local version of SHELX system (G.M. Sheldrick), GEOM molecular functions program (P.R. Mallinson) and ORTEP (C.K. Johnson), adapted for the ICL 2976 computer by P.R. Mallinson and K.W. Muir.

Results and discussion

The crystal structure is built of the cations, anions and solvent molecules, separated by Van der Waals distances. The asymmetric unit contains three solvent molecules per ion pair, but only one of these has been identified as 1,2-dichloroethane.

Geometries of the $[\text{PF}_6]^-$ anion and $\text{C}_2\text{H}_4\text{Cl}_2$ molecule have been determined rather poorly [P—F 1.44(2)—1.57(2) Å, F—P—F 84(1)—101(1)° and 168(1)—178(1)°; C—C 1.61(8), C—Cl 1.74(6), 2.01(6) Å and C—C—Cl 110(4), 110(3)°]. This however is not surprising, considering that the two entities display large thermal vibrations. Indeed, it is likely that not only two, but all three solvent molecules are involved in disorder. In the cation the atomic vibrations are much smaller and its geometry has been determined with correspondingly higher accuracy (Table 2). Similar features have emerged from the crystal structure analysis of $[\text{Pt}_2\text{Me}_3(\mu\text{-dppm})_2][\text{PF}_6] \cdot 3 \text{ CH}_2\text{Cl}_2$ [7], where the solvent molecules and the anion are also much smaller than the cation.

The structure of the cation (Fig. 1) contains a $\text{Pt}_2(\text{dppm})_2$ nucleus in which the metal atoms are held in close proximity by the two bridging dppm ligands and linked directly by a covalent Pt—Pt bond. The square planar environment of the Pt(2) centre is completed by the third dppm ligand acting as a monodentate two-electron donor. The T-shaped arrangement of the Pt(1), Pt(2), P(1) and P(3) atoms suggests a square planar geometry around the Pt(1) centre, in which the fourth coordination site is available to the hydrido ligand, whose position has not been directly revealed by this analysis. However, the length of the Pt—Pt bond is compatible with the presence of a linear H—Pt—Pt system (see later) and, as is evident from the Pt(2)—Pt(1)—P angles (Table 2), the Pt(1)—P bonds are bent towards the site of the hydrido ligand - a feature commonly observed in transition metal hydrides containing bulky tertiary phosphines [8]. Further support for this interpretation comes from the IR spectrum of the compound [3] which shows an absorption at ca. 2010 cm^{-1} characteristic of a terminal Pt—H bond.

The cation is subject to considerable steric strain which is evident from

TABLE 2

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN $[\text{Pt}_2\text{H}(\text{dppm})(\mu\text{-dppm})_2]^+$

<i>(a) Bond lengths</i>		<i>(b) Non-bonding distances</i>	
Pt(1)—Pt(2)	2.769(1)	P(1)⋯P(2)	2.925(5)
Pt(1)—P(1)	2.248(4)	P(3)⋯P(4)	2.940(5)
Pt(1)—P(3)	2.249(4)	P(5)⋯P(6)	3.169(5)
Pt(2)—P(2)	2.264(4)	P(2)⋯P(5)	3.568(5)
Pt(2)—P(4)	2.289(4)	P(4)⋯P(5)	3.544(5)
Pt(2)—P(5)	2.347(4)	C(23)⋯C(64)	3.39(2)
		C(28)⋯C(58)	3.31(2)
<i>(c) Bond angles</i>			
Pt(2)—Pt(1)—P(1)	95.7(1)	P(2)—Pt(2)—P(4)	157.1(1)
Pt(2)—Pt(1)—P(3)	96.1(1)	P(2)—Pt(2)—P(5)	101.3(1)
P(1)—Pt(1)—P(3)	167.0(1)	P(4)—Pt(2)—P(5)	99.7(1)
Pt(1)—Pt(2)—P(2)	78.8(1)	P(1)—C(1)—P(2)	104.5(7)
Pt(1)—Pt(2)—P(4)	82.2(1)	P(3)—C(2)—P(4)	104.8(7)
Pt(1)—Pt(2)—P(5)	169.2(1)	P(5)—C(3)—P(6)	117.6(8)
<i>(d) Torsion angles</i>			
P(6)—C(3)—P(5)—C(58)	-89.0(8)	Pt(1)—Pt(2)—P(2)—C(1)	59.0(5)
P(5)—C(3)—P(6)—C(70)	86.2(8)	Pt(1)—Pt(2)—P(4)—C(2)	54.2(5)
Pt(2)—P(2)—C(1)—P(1)	-57.2(7)	C(1)—P(1)—Pt(1)—Pt(2)	19.0(5)
Pt(2)—P(4)—C(2)—P(3)	-61.3(7)	C(2)—P(3)—Pt(1)—Pt(2)	5.3(5)
P(2)—C(1)—P(1)—Pt(1)	15.2(8)	P(1)—Pt(1)—Pt(2)—P(2)	-37.4(1)
P(4)—C(2)—P(3)—Pt(1)	29.0(8)	P(3)—Pt(1)—Pt(2)—P(4)	-30.0(1)
		P(2)—Pt(2)—P(5)—C(3)	42.2(5)

several short non-bonding interatomic distances (Table 2) and also from the large distortions of the coordination geometries of the metal atom. Around the Pt(1) centre, the Pt_2P_2 fragment is planar to within ± 0.07 Å, and the Pt—Pt(1)—P and P—Pt(1)—P angles are ca. $6^\circ > 90^\circ$ and $13^\circ < 180^\circ$ (Table 2). The tetrahedral distortion around the Pt(2) centre is much larger and unusually severe: the Pt(2), Pt(1), P(2), P(4) and P(5) atoms are displaced from their mean plane by 0.01, -0.25, 0.23, 0.22 and -0.21 Å, respectively, and the Pt—Pt(2)—P and P—Pt(2)—P angles deviate from 90° by ca. -9.5 and 10.50° and from 180° by -11 and -23° . Thus, to lower steric strain, all four Pt—P(*trans* to P) bonds are bent away from the axial dppm ligand (Fig. 1).

The three dppm ligands display different conformations, which are defined by the torsion angles listed in Table 2. In the axial ligand conformations about both P—C(sp^3) bonds are practically half way between eclipsed and staggered; in the bridging ligands conformations about the P(2)—C(1) and P(4)—C(2) bonds are staggered, but that about the P(1)—C(1) bond is closer to eclipsed while that about the P(3)—C(2) bond is half way between staggered and eclipsed. Such conformations of the bridging ligands enable the $\text{Pt}_2(\mu\text{-dppm})_2$ nucleus to adopt a twisted configuration in which the coordination planes of the two metal atoms are rotated about the Pt—Pt bond to give a dihedral angle of 33.5° , and thus lower considerably any antibonding interactions between filled d_π metal orbitals. They are also reflected in the conformations of the five-membered $\text{Pt}_2\text{P}_2\text{C}$ metallocycles. The ring containing methylenic carbon C(2) is nearly an envelope, with the atoms C(2) and P(4) lying 0.16 and 1.13 Å above the $\text{Pt}_2\text{P}(3)$ plane. The conformation of the other ring is intermediate

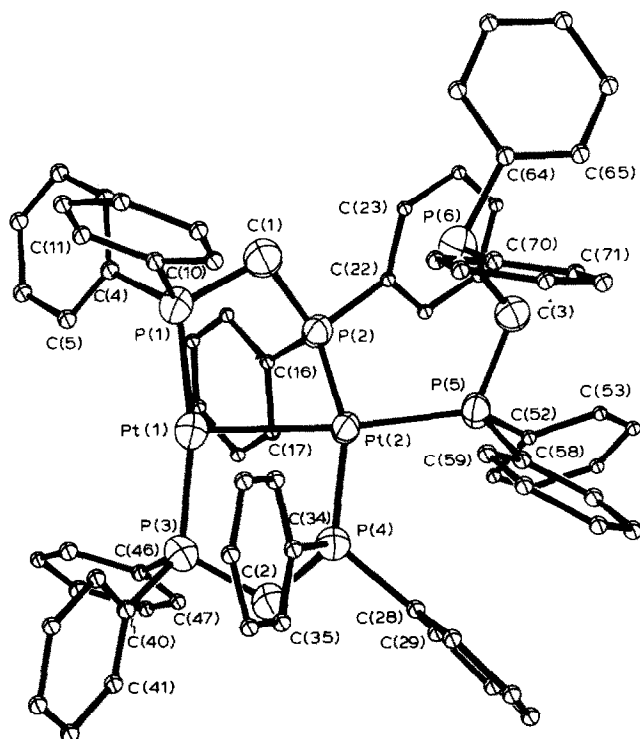


Fig. 1. The structure of the $[\text{Pt}_2\text{H}(\text{dppm})(\mu\text{-dppm})_2]^+$ cation. The vibrational ellipsoids of Pt, P and C(sp^3) atoms display 50% probability. For clarity, C(sp^2) atoms are represented by spheres of arbitrary size; in each phenyl group only two C atoms are labelled and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

between an envelope and a half-chair, with the C(1) and P(2) atoms displaced by 0.56 and 1.35 Å from the $\text{Pt}_2\text{P}(1)$ plane. The bond lengths and angles in the dppm ligands are unexceptional: P—C(sp^3) 1.829(14)—1.883(15), P—C(sp^2) 1.788(13)—1.842(10) Å, C—P—C 97.0(5)—107.2(6), P—C—P 104.5(7)—117.6(8) and Pt—P—C 110.7(5)—120.4(5)°.

The Pt—P(*trans* to P) bonds involving the Pt(1) atom [2.248(4), 2.249(4) Å] are shorter than those involving the Pt(2) atom [2.264(4), 2.289(4) Å], and this is compatible with different steric and electronic properties of the *cis* hydrido and phosphine ligands. The axial Pt(2)—P(5) bond [2.347(4) Å] is ca. 0.07 Å longer than the average Pt(2)—P(*trans* to P) distance, and this lengthening is likely to reflect the *trans*-influence of the Pt—Pt bond, and perhaps also the steric requirements of this bulky ligand. The NMR spectra of the platinum(I) complexes $[\text{Pt}_2(\text{CNMe})_{6-n}(\text{PMe}_2\text{Et})_n][\text{PF}_6]_2$ ($n = 1, 2$ or 3) also suggest that the Pt—Pt bond exerts a large *trans* influence on the Pt—P bond [9].

The Pt(1)—Pt(2) separation [2.769(1) Å] is indicative of a σ -bonding interaction and lies within the range of Pt—Pt single bond distances usually found in dinuclear complexes [2.531(1)—2.890(2) Å] [1,10–12]. It is however, much longer than the Pt—Pt bonds of 2.620(1) and 2.651(1) Å in the related complex $[\text{Pt}_2\text{Cl}(\text{CO})(\mu\text{-dppm})_2][\text{PF}_6]$ [11] and $[\text{Pt}_2\text{Cl}_2(\mu\text{-dppm})_2]$ [13], and this lengthen-

ing may be ascribed to high *trans*-influencing abilities of the axial hydrido and phosphine ligands.

The results of the work described here therefore show that this dinuclear hydride should be formulated as $[\text{Pt}_2\text{H}(\text{dppm})(\mu\text{-dppm})_2]^+$ (I). It has since been suggested that its low temperature ^1H and ^{31}P solution NMR spectra are compatible with the solid state structure, and that its fluxionality at higher temperatures arises from a dynamic behaviour of the monodentate dppm ligand, in which an exchange of the two phosphorus atoms appears more likely than a rotation about the $\text{Pt}-\text{P}(\eta^1\text{-dppm})$ bond [14]. The $^3J(\text{HP})$ value of 45 Hz at -30°C has been assigned to an effective transmission of coupling through the $\text{Pt}-\text{Pt}$ bond in the linear $\text{H}-\text{Pt}-\text{Pt}-\text{P}$ system.

A novel feature of I is that it displays two different modes of coordination of the dppm ligands. The ability of dppm to act as a bidentate four-electron donor, either by ligating one metal atom to form chelate complexes or by spanning two metal centres ca. 2.5–3.4 Å apart to form bridged dinuclear or polynuclear species, is now well established [15]. Complexes in which it acts as a monodentate two-electron donor are less common and some have been characterised spectroscopically [16]. As far as we are aware, the structure of I provides the first example of a monodentate dppm ligand characterised crystallographically. The three coordination modes of dppm reflect its ability to adopt different conformations by rotating internally around the $\text{P}-\text{C}(sp^3)$ bonds, and to distort considerably the bond angle subtended at the methylenic carbon. Thus, for example, the $\text{P}-\text{C}-\text{P}$ angle is only 95° in the platinum(II) chelate $[\text{Pt}_2\text{Ph}_2(\text{dppm})]$ [17], but it is ca. 105° in the bridging, and 118° in the monodentate, dppm ligands in I (Table 2).

Another noteworthy structural feature of I is that it contains two coordinatively unsaturated metal centres in sterically different environments (Fig. 1). The platinum atom attached to the hydrido ligand is effectively shielded by six phenyl groups, while that bonded to the $\eta^1\text{-dppm}$ is in a more open environment, and thus potentially more easily accessible in the attack by small molecules. It has been shown that I undergoes readily a reversible reaction with MeSH , to eliminate one dppm ligand and produce the 'A-frame' complex $[\text{Pt}_2\text{H}_2(\mu_2\text{-SMe})(\mu\text{-dppm})_2]^+$ [3,18]. Although this reaction is a binuclear oxidative addition, it is possible that the attack by MeSH occurs initially at a single platinum centre, namely that bonded to the $\eta^1\text{-dppm}$.

Realisation that one dppm ligand in the structure of I is monodentate has indicated that the reductive elimination of dihydrogen from the $[\text{Pt}_2\text{H}_2(\mu_2\text{-H})(\mu\text{-dppm})_2]^+$ could be induced not only by dppm but also by other two-electron donors, such as monotertiary phosphines and carbon monoxide. Since the preliminary results of this work have been published [3], a series of novel dinuclear platinum(I) hydrides of the formula $[\text{Pt}_2\text{H}(\text{L})(\mu\text{-dppm})_2]^+$, where $\text{L} = \text{PMe}_2\text{Ph}$, PMePh_2 , PPh_3 or CO , has been obtained [14,19]. By analogy with I, and in accordance with their IR and NMR spectra, the new complexes have been assigned the same structural type as that displayed by I.

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