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The Preparation and X-ray Characterisation of $[(PPh_2Me)_2Pt(\mu\text{-}PPhH)_2Pt(PPh_2Me)_2][Cl]_4\cdot\frac{3}{2}CH_2Cl_2$ and $[(PPh_2Me)_2Pt(\mu\text{-}PPhH)Pt(PPh_2Me)_2][Cl]_2[PhPO_2OH]_2[PhPO(OH)_2]_2$

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Abstract

Reaction of $(PPh)_5$ with $PtCl_2(PR_3)_2$ in CH_2Cl_2 gives $[(PPh_2Me)_2Pt(\mu\text{-}PPhH)_2Pt(PPh_2Me)_2][Cl]_4\cdot\frac{3}{2}CH_2Cl_2$ (**1**) or $[(PPh_2Me)_2Pt(\mu\text{-}PPhH)Pt(PPh_2Me)_2][Cl]_2[PhPO_2OH]_2[PhPO(OH)_2]_2$ (**2**) as shown by microanalyses and X-ray crystallography. The reaction appears (on the basis of ^{31}P NMR) to proceed via *trans*-$Pt(PR_3)_2(PPhH)Cl$. The X-ray structures of **1** and **2** reveal, in both cases, planar coordination of the platinum atoms with a planar Pt_2P_2 central ring. The P–Pt–P and Pt–P–Pt angles are 105 and 75°, respectively. All Pt–P bond lengths are equivalent.

Introduction

Although bimetallic platinum compounds are quite common when bridged by halides, chelating phosphorus–oxygen and phosphite ligands [1], binuclear platinum compounds with pnictide group bridging atoms are rare. Examples are $[Rh(\mu\text{-t-Bu(H)P})(PMe_3)_2]_2$ and $[Ni(\mu\text{-t-Bu(H)P})(PMe_3)_2]_2$ [2] formed from the reaction of the appropriate dichlorobis(trimethylphosphine)metal complex and (H)(t-Bu)PLi. We have synthesised $[(R_3P)_2Pt(\mu\text{-}NH_2)_2Pt(PR_3)_2][BF_4]_2$ from the reaction of $PtCl_2(PR_3)_2$ with sodium metal and HBF_4 in liquid ammonia [3]. We are involved in the study of $(PPh)_5$ with a variety of reagents [4, 5]. Here we report the reaction of $PtCl_2(PR_3)_2$ with $(PPh)_5$ which yields compounds with the central $Pt(\mu\text{-}PPhH)_2Pt$ dimer core. The compounds have been characterised by microanalyses, X-ray crystallography and infrared spectroscopy.

Experimental

General

All reactions were carried out under an inert atmosphere using standard Schlenk line techniques unless stated otherwise. Solvents were distilled prior to use; CH_2Cl_2 from CaH_2 and n-hexane from Na/benzophenone. C_6D_6 was dried over 3A molecular sieves. $^{31}P\{^1H\}$ NMR spectra were obtained on a Jeol FX90Q spectrometer operating at 36.21 MHz and referenced to external H_3PO_4. Infrared spectra were obtained on a Perkin-Elmer 1720X instrument using KBr discs. Microanalyses was provided by the Imperial College Microanalytical Service and Pascher Microanalytical laboratory, F.R.G., $PtCl_2(PR_3)_2$ were prepared from $Pt(COD)Cl_2$ and the stoichiometric quantity of free phosphine [6]. $(PPh)_5$ was made by reaction of $PPhCl_2$ and magnesium in toluene by the standard procedure [7].

Preparation of the Complexes

Cyclopentaphosphine $(PPh)_5$ (0.0243 g, 0.045 mmol) was dissolved in degassed CH_2Cl_2 (20 ml) at room temperature. $PtCl_2(PMePh_2)_2$ (0.060 g, 0.090 mmol) was added and the mixture stirred at room temperature for five days. The solvent was reduced to *c.* 2 ml *in vacuo*. Degassed C_6D_6 (0.5 ml) was added and the $^{31}P\{^1H\}$ spectra recorded. Addition of n-hexane (15 ml) gave colourless crystals of $(Pt(\mu\text{-}PPhH)(PMePh_2)_2Cl_2)_2$ (**1**) (0.038 g, 0.0245 mmol, 54%). *Anal.* Calc. for $[Pt(\mu\text{-}PPhH)(PMePh_2)_2]_2Cl_4\cdot 1.5CH_2Cl_2$: C, 48.6; H, 4.1; Cl, 9.5. Found: C, 48.7; H, 4.1; Cl, 7.9.

When the reaction was carried out in non-degassed solvents in air, the product was (in the case of $PtCl_2(PMePh_2)$) $[(PPh_2Me)_2Pt(\mu\text{-}PPhH)_2Pt(PPh_2Me)_2]Cl_2[PhPO_2OH]_2[PhPO(OH)_2]_2$ (**2**) in 42% yield. *Anal.* Calc. for CH_2Cl_2 solvate: C, 48.2; H, 4.2; Cl, 6.4; P, 14.1; O, 8.7. Found: C, 48.5; H, 4.3; Cl, 5.8; P, 13.1; O, 8.5.

X-ray Studies

Crystal data: $C_{64}H_{64}P_6Pt_2\cdot 4Cl\cdot 1.5(CH_2Cl_2)$ (**1**), $M = 1674.0$, monoclinic, $a = 13.812(8)$, $b = 12.481(6)$, $c = 20.339(10)$ Å, $\beta = 91.90(5)°$, $V = 3504$ Å^3, space group $P2_1/n$, $Z = 2$ (the molecule is disposed about a centre of symmetry), $D_c = 1.59$ g cm^{-3}, Cu radiation, $\lambda = 1.54178$ Å, $\mu(\text{Cu K}\alpha) = 116$ cm^{-1}, $F(000) = 1642$.

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Data were measured on a Nicolet R3m diffractometer with Cu Kα radiation (graphite monochromator) using ω-scans. A crystal of dimensions 0.17 X 0.17 X 0.23 mm was used. A total of 3840 independent reflections ($2\theta < 116°$) were measured, of which 3458 had $|F_o| > 3\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarisation factors. Due to a *c.* 50% decomposition of the sample during the data collection and also its encapsulation in epoxy resin no absorption correction was applied. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. A ΔF map revealed the presence of a 75% dichloromethane molecule. The positions of the hydrogen atoms were idealised, C–H = 0.96 Å, P–H = 1.33 Å, assigned isotropic thermal parameters, $U(\mathrm{H}) = 1.2\ U_{eq}(\mathrm{C})$ and allowed to ride on their parent carbon atoms. The methyl groups were refined as idealised rigid bodies. Refinement was by block-cascade full-matrix least-squares to $R = 0.063$, $R_w = 0.060$ [$w^{-1} = \sigma^2(F) + 0.00050F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 4.18 and -1.59 e A^{-3}, respectively. The mean and maximum shift/error in the final refinement were 0.015 and 0.094, respectively.

Crystal data: [$C_{64}H_{64}P_6Pt_2$]·2[Cl]·2[$C_6H_6O_3P$]·2[$C_6H_7O_3P$] (2), $M = 2111$, triclinic, $a = 13.375(2)$, $b = 13.520(2)$, $c = 15.052(2)$ Å, $\alpha = 92.55(1)$, $\beta = 107.02(1)$, $\gamma = 118.86(1)°$, $V = 2223$ Å^3, space group $P\bar{1}$, $Z = 1$ (the molecule is disposed about a centre of symmetry), $D_c = 1.58$ g cm^{-3}, Cu radiation, $\lambda = 1.54178$ Å, μ(Cu Kα) = 86 cm^{-1}, $F(000) = 1050$.

Data were measured on a Nicolet R3m diffractometer with Cu Kα radiation (graphite monochromator) using ω scans. A crystal of dimensions 0.07 X 0.07 X 0.33 mm was used. A total of 6001 independent reflections ($2\theta \leqslant 116°$) were measured, of which 5456 had $|F_o| > 3\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarisation factors; a numerical absorption correction (face-indexed crystal) was applied; maximum and minimum transmission factors 0.638 and 0.311. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The hydroxy protons on the alkylphosphates were located from a ΔF map and refined isotropically. The positions of the remaining hydrogen atoms were idealised, C–H = 0.96 Å, P–H = 1.33 Å, assigned isotropic thermal parameters, $U(\mathrm{H}) = 1.2\ U_{eq}(\mathrm{C})$ and allowed to ride on their parent carbon atoms. The methyl groups were refined as rigid bodies. Refinement was by block-cascade full-matrix least-squares to $R = 0.042$, $R_w = 0.043$ [$w^{-1} = \sigma^2(F) + 0.00094F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 1.37 and -1.79 e Å^{-3}, respectively. The mean and maximum shift/error in the final refinement were 0.010 and 0.147, respectively. Computations were carried out on an Eclipse S140 computer using the SHELXTL program system [8].

Results and Discussion

Treatment of $PtCl_2(PR_3)_2$ with $(PPh)_5$ in CH_2Cl_2 produces Pt(μ-PPhH)$_2$Pt dimers **1** and **2** in reasonable yield. We have performed the reaction under an inert atmosphere and in air. Monitoring of the anaerobic reaction by $^{31}P\{^1H\}$ NMR (Fig. 1) reveals an intermediate whose spectrum consists of a triplet and a doublet ($^2J(^{31}P-^{31}P)$ 20 Hz) with platinum satellites as well as minor impurities. The intermediate is postulated as *trans*-PtCl(PPhH)(PR$_3$)$_2$. It is observed in solution after *c.* 1 day and is the main species in the solution after five days. The intermediate has $^1J\{^{195}Pt-^{31}P\}$ couplings of *c.* 2400 Hz (2P, doublet) and *c.* 3500 Hz (1P, triplet) (Table 1). This is consistent with the structure proposed in Fig. 1. The *trans* PR$_3$ groups would account for the low value of ^1J coupling (*trans*-$PtCl_2(PR_3)_2$ has a

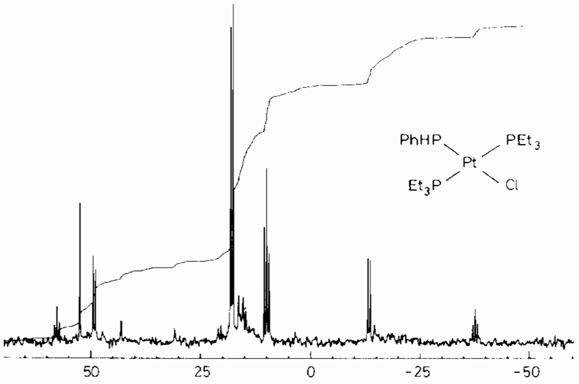

Fig. 1. $^{31}P\{^1H\}$ NMR ($CDCl_3$ solution) of the crude reaction between $PtCl_2(PEt_3)_2$ and $(PPh)_5$.

TABLE 1. ^{31}P NMR data for the intermediates observed during the formation of 1 and 2[a]

Compound	δ_A	δ_X		^1J_A	^1J_X	$^2J_{AX}$
1a	17.9	10.0		2270	3460	21
1c	10.4	−4.3		2428	3620	20
	δ_A	δ_X	δ_M	^1J_A	^1J_X	$^2J_{AX}$
2a	16.5	49.6	21.4	2240	3883	22
2b	−4.8	47.9	22.3	2250	3882	22
2c	10.4	48.5	21.9	2272	3804	22

[a] a = PEt$_3$, b = PMe$_2$Ph, c = PMePh$_2$; $^1J = {}^{31}P-{}^{195}Pt$; $^2J = {}^{31}P-{}^{31}P$; resonance A is a doublet of intensity 2, resonance X is a triplet intensity 1, resonance M is a singlet.

^1J coupling of *c.* 2400 Hz [9]. The $PPhH^-$ anion *trans* to chloride would be expected to have a large value of ^1J ($^1J\{^{195}Pt-^{31}P\}$ in *cis*-$PtCl_2(PR_3)_2$ is *c.* 3500 Hz). The two equivalent PR_3 groups are split by the *cis* PPhH phosphorus into a doublet (*cis* ^2J $\{^{31}P-^{31}P\}$ = 19 Hz) and the PPhH phosphorus consequently appears as a triplet. Without proton decoupling the triplet is split into two sets of multiplets with ^1J $\{^1H-^{31}P\}$ of 460 Hz, confirming the presence of a P–H bond.

In the case of the reaction carried out in air the ^{31}P NMR of the intermediate has a similar pattern although the triplet is shifted to higher field by *c.* 50 ppm adn the magnitude of the ^1J $\{^{195}Pt-^{31}P\}$ coupling constant has increased by *c.* 200 Hz. The resonance due to the *trans*-PR_3 ligands is unaltered from the anaerobic case. The large change in δ ^{31}P for the triplet implies that the group *trans* to $PPhH^-$ is different, possibly of the type OPO since we observe additional ^{31}P resonances around *c.* 25 ppm in this case; we propose that the intermediate includes coordinated $PhPO_3{}^{2-}$.

The study of the reactivity of $(PPh)_5$ with $PtCl_2(PR_3)_2$ where PR_3 is PEt_3 or PMe_2Ph, failed to produce crystals of the expected dimeric compound yielding instead yellow oils. No reaction occurred in the case of PR_3 = dppe, probably as the required *trans* geometry of the intermediate could not be obtained for this chelating ligand.

The product in both the aerobic and anaerobic reactions where PR_3 = $PMePh_2$ crystallised out of the reaction mixture on the addition of n-hexane. Once formed both $[(PPh_2Me)_2Pt(\mu\text{-}PPhH)_2Pt(PPh_2Me)_2][Cl]_4\cdot 3/2CH_2Cl_2$ (**1**) and $[(PPh_2Me)_2Pt(\mu\text{-}PPhH)Pt(PPh_2Me)_2][Cl]_2[PhPO_2OH]_2[PhPO(OH)_2]_2$ (**2**) are insoluble in all common organic solvents, thus no ^{31}P NMR studies on these species were possible. Furthermore the mass spectra of these species (in the FAB mode) were unsatisfactory due to the solubility problems. In the EI mode no M^+ was observable although fragmentation ions due to $[PtCl_2(PR_3)_2]^+$ and $PPhH^+$ were seen.

The infrared spectrum of **1** shows the expected vibrations due to the PPh_2Me ligand in addition to a ν(P–H) vibration at 2580 cm^{-1}. **2** has the ν(O–H) vibration at 3440 cm^{-1} and δ(O–H) at 1630m cm^{-1}. The ν(P–H) vibration occurs at 2680s cm^{-1} and P=O vibrations occur at 1130vs, 998vs and 921vs cm^{-1}. The other observed ligand vibrations are identical to those in **1**.

Fractional atomic coordinates for the non-hydrogen atoms in **1** and **2** are given in Tables 2 and 3, respectively with selected comparative bond lengths and angles listed in Table 4. Figure 2 shows a perspective view of **2** with phenyl rings omitted for clarity. The geometries of the central cores of **1** and **2** are identical. Both platinum atoms have essentially planar coordination geometries with a maximum deviation of 0.1 Å (for P(3)). Both **1** and **2** possess a crystallographic centre of symmetry at the centre of the Pt_2P_2 ring resulting in the ring being planar. All of the Pt–P bond lengths are identical and the bridging is symmetric. The phosphorus bridges produce a contraction of the P(3)–Pt–P(3′) angle (75°) form normal square planar geometry. This is undoubtedly due to the desire of the bridging phosphorus atoms to retain normal tetrahedral geometry. The Pt–P(3)–Ph and Pt′–P(3)–Ph angles are 110.1(4) and 113.7(4)° in **1** and 109.4(3) and 111.6(3)° in **2**. The Pt–P(3)–Pt′ angles are 104.9(1)

TABLE 2. Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for **1** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	U_{eq}[a]
Pt	3921(1)	4231(1)	225(1)	26(1)*
P(1)	2257(2)	4583(2)	124(1)	31(1)*
C(1)	1905(10)	5648(9)	−445(5)	39(3)*
C(2)	2192(11)	5535(11)	−1089(7)	62(3)*
C(3)	1925(12)	6337(13)	−1566(7)	77(3)*
C(4)	1371(13)	7211(13)	−1372(9)	96(3)*
C(5)	1115(11)	7285(11)	−740(11)	91(3)*
C(6)	1359(10)	6537(10)	−267(7)	52(3)*
C(7)	1741(10)	4978(8)	894(5)	37(3)*
C(8)	792(10)	4794(12)	1042(7)	58(3)*
C(9)	430(11)	5124(12)	1632(7)	69(3)*
C(10)	1000(13)	5601(12)	2066(8)	78(3)*
C(11)	1944(15)	5827(12)	1946(7)	85(3)*
C(12)	2354(11)	5492(10)	1364(6)	56(3)*
C(13)	1498(10)	3509(9)	−207(6)	48(3)*
P(2)	3760(2)	2485(2)	623(1)	31(1)*
C(14)	2749(9)	2238(9)	1144(5)	38(3)*
C(15)	2645(10)	2893(11)	1679(5)	50(3)*
C(16)	1844(12)	2801(12)	2073(6)	68(3)*
C(17)	1182(12)	2060(12)	1958(7)	74(3)*
C(18)	1238(11)	1379(12)	1429(8)	74(3)*
C(19)	2036(11)	1467(10)	1009(7)	59(3)*
C(20)	4773(9)	1975(8)	1123(4)	34(2)*
C(21)	5194(10)	2613(9)	1604(5)	41(3)*
C(22)	5930(11)	2248(11)	1998(5)	55(3)*
C(23)	6282(11)	1193(12)	1917(6)	59(3)*
C(24)	5860(11)	563(10)	1448(7)	60(3)*
C(25)	5135(10)	952(9)	1049(6)	43(3)*
C(26)	3625(10)	1572(9)	−72(5)	40(3)*
P(3)	5595(2)	4123(2)	195(1)	29(1)*
C(31)	5940(9)	2999(9)	−293(5)	38(3)*
C(32)	6633(10)	2235(9)	−50(7)	46(3)*
C(33)	6899(12)	1394(10)	−423(8)	70(3)*
C(34)	6521(12)	1248(10)	−1043(9)	76(3)*
C(35)	5844(12)	1945(11)	−1289(6)	63(3)*
C(36)	5538(10)	2845(9)	−927(5)	45(3)*
Cl(1)	3004(4)	2596(4)	−1712(2)	87(1)*
Cl(2)	4193(4)	4549(3)	−2172(2)	99(2)*
C(40)	651(6)	1170(6)	−1354(3)	104(3)*
Cl(3)	999(6)	435(6)	−684(3)	191(3)*
Cl(4)	−479(6)	1702(6)	−1310(3)	198(3)*

[a] Starred items: equivalent isotropic *U* defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE 3. Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for 2 with e.s.d.s in parentheses

Atom	x	y	z	U_{eq}[a]
Pt	4476(1)	3693(1)	507(1)	33(1)*
P(1)	2553(2)	2057(1)	209(1)	37(1)*
C(1)	1294(5)	2272(5)	−381(5)	41(2)*
C(2)	1274(6)	3204(6)	58(5)	50(2)*
C(3)	341(7)	3379(7)	−351(6)	60(2)*
C(4)	−613(7)	2639(8)	−1193(7)	74(2)*
C(5)	−599(7)	1722(8)	−1616(6)	68(2)*
C(6)	348(6)	1537(6)	−1220(5)	50(2)*
C(7)	2273(6)	795(5)	−539(5)	41(2)*
C(8)	2906(7)	970(6)	−1156(5)	50(2)*
C(9)	2766(8)	22(7)	−1700(6)	65(2)*
C(10)	1995(8)	−1089(7)	−1629(6)	68(2)*
C(11)	1364(8)	−1253(7)	−1029(7)	69(2)*
C(12)	1505(7)	−322(6)	−474(6)	55(2)*
C(13)	2226(7)	1632(6)	1268(5)	50(2)*
P(2)	5561(2)	3207(2)	1748(1)	39(1)*
C(14)	4955(6)	1691(6)	1783(5)	45(2)*
C(15)	4697(7)	929(6)	990(6)	55(2)*
C(16)	4230(7)	−245(7)	980(7)	65(2)*
C(17)	4033(8)	−661(7)	1770(7)	76(2)*
C(18)	4268(9)	94(7)	2542(7)	83(2)*
C(19)	4734(7)	1272(7)	2572(6)	63(2)*
C(20)	7074(6)	3638(6)	1718(5)	45(2)*
C(21)	7200(7)	3534(6)	845(5)	51(2)*
C(22)	8312(7)	3800(7)	785(6)	62(2)*
C(23)	9302(8)	4201(8)	1595(7)	79(2)*
C(24)	9193(8)	4306(9)	2462(8)	92(2)*
C(25)	8074(8)	4020(8)	2528(6)	74(2)*
C(26)	5810(8)	3933(7)	2901(5)	58(2)*
P(3)	6179(2)	5509(2)	704(1)	41(1)*
C(31)	6675(8)	6376(7)	1869(5)	69(2)*
C(32)	5838(11)	6517(7)	2150(6)	90(2)*
C(33)	6215(15)	7174(10)	3036(9)	174(3)*
C(34)	7392(16)	7681(11)	3639(9)	238(3)*
C(35)	8217(14)	7560(12)	3376(8)	205(3)*
C(36)	7880(10)	6917(10)	2485(7)	128(3)*
Cl	2733(3)	6105(2)	1819(2)	96(1)*
P(4)	3115(2)	4225(2)	3665(2)	66(1)*
O(1)	2795(8)	4199(6)	2586(5)	106(2)*
O(2)	4478(5)	4813(5)	4137(5)	84(2)*
O(3)	2543(6)	4757(5)	4102(5)	90(2)*
C(41)	2416(7)	2731(7)	3696(5)	59(2)*
C(42)	3112(8)	2247(8)	4059(6)	73(2)*
C(43)	2559(10)	1099(9)	4056(7)	89(2)*
C(44)	1308(10)	391(9)	3694(7)	93(2)*
C(45)	631(9)	854(8)	3339(8)	100(2)*
C(46)	1165(8)	2008(8)	3314(7)	83(2)*
P(5)	3602(3)	7821(2)	4542(2)	77(1)*
O(4)	3842(7)	6889(5)	4819(5)	91(2)*
O(5)	3095(11)	7692(9)	3449(6)	151(2)*
O(6)	4759(7)	8976(6)	5000(6)	104(2)*
C(51)	2385(10)	7709(9)	4891(7)	92(2)*
C(52)	1294(15)	6816(18)	4522(17)	440(3)*
C(53)	393(17)	6699(19)	4841(18)	362(3)*
C(54)	514(16)	7375(18)	5435(11)	241(3)*
C(55)	1557(14)	8539(15)	5685(9)	185(3)*
C(56)	2456(13)	8608(13)	5426(9)	135(3)*

[a] Starred items; equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE 4. Selected bond lengths (Å) and angles (°) in 1 and 2[a]

	1	2
Pt–P(1)	2.341(3)	2.336(1)
Pt–P(2)	2.338(3)	2.339(2)
Pt–P(3)	2.319(3)	2.334(1)
Pt–P(3′)	2.330(3)	2.326(2)
P(3)–C(31)	1.792(11)	1.809(8)
Pt–P(3)–Pt′	104.9(1)	105.4(1)
P(3)–Pt–P(3′)	75.1(1)	74.6(1)
P(1)–Pt–P(2)	93.5(1)	96.5(1)
P(1)–Pt–P(3′)	95.5(1)	95.9(1)
P(2)–Pt–P(3)	93.5(1)	93.3(1)
Pt–P(3)–C(31)	110.1(4)	109.4(3)
Pt′–P(3)–C(31)	113.7(4)	111.6(3)

[a] P–C bond lengths in the $PMePh_2$ ligands are normal, in the range 1.81–1.83 Å.

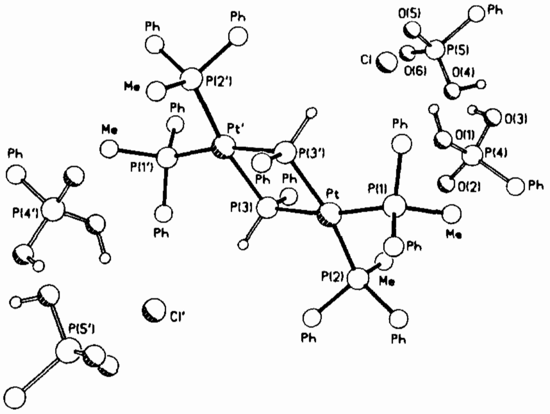

Fig. 2. The X-ray crystal structure of $[(PPh_2Me)_2Pt(\mu\text{-}PPhH)Pt(PPh_2Me)_2][Cl]_2[PhPO_2(OH)]_2[PhPO(OH)_2]_2$ (2), phenyl rings omitted for clarity. The central, metal containing core in 1 has an identical structure.

and 105.4(1)° in 1 and 2, respectively. The *trans*-annular P(3)...P(3′) distance is 2.82 Å and the Pt...Pt′ separation is 3.7 Å in both structures. In 1 there are no anion–cation interactions although, interestingly, there is a short Cl(1)...Cl(2) contact of 3.10 Å. In 2 the alkylphosphate groups hydrogen bond to the chloride ion (H(10)...Cl 2.0 Å, O(1)...Cl 2.90 Å, O(1)–H(10)...Cl 152°) and there is a strong O–H...O bond between adjacent alkylphosphates (H(30)...O(4) 1.56 Å, O(3)...O(4) 2.51 Å, O(3)–H(30)...O(4) 163°).

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References

1 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, London, 5th edn., 1988.
2 R. A. Jones and M. H. Seeberger, *Inorg. Synth., 25* (1989) 173.
3 I. P. Parkin, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *Polyhedron, 8* (1989) 1979.
4 P. T. Wood and J. D. Woollins, *J. Chem. Soc., Chem. Commun.*, (1988) 1190.
5 J. C. Fitzmaurice, D. J. Williams, P. T. Wood and J. D. Woollins, *J. Chem. Soc., Chem. Commun.*, (1988) 741.
6 J. C. Bailar and H. Itatani, *Inorg. Chem., 4* (1965) 1618.
7 W. M. A. Henderson, M. Epstein and F. S. Seichter, *J. Am. Chem. Soc., 85* (1963) 2462.
8 G. M. Sheldrick, *SHELXTL*, an integrated system for solving, refining and displaying crystal structures from diffraction data, University of Gottingen, 1978; Revision 4.1, 1983.
9 P. S. Pregosin and R. W. Kunz, *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*, Springer, Berlin, 1979.