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Some reactions of 2,4-diphosphaplatinocycles and the crystal structures of $[\text{Pt}(\text{CH}_2\text{PPh}_2\text{CH}_2\text{PPh}_2)(\text{PPh}_3)(\text{CH}_2\text{Cl})]\text{PF}_6$, $[\text{Pt}(\text{CH}_2\text{PPh}_2\text{CH}_2\text{PPh}_2)_2](\text{PF}_6)_2$, and $[\text{Pt}(\text{CH}_2\text{PPh}_2\text{CH}_2\text{PPh}_2)(\text{PPh}_3)(\text{OCMe}_2)](\text{PF}_6)_2$

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Abstract

The structure of the ring insertion product **1b** obtained from the reaction of $[\text{Pt}(\text{dppm})(\text{CH}_2\text{Cl})_2]$ ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) with triphenylphosphine has been confirmed by X-ray crystallography of the hexafluorophosphate salt. The bis-chelate complex $[\text{Pt}(\text{CH}_2\text{PPh}_2\text{CH}_2\text{PPh}_2)_2]\text{Cl}_2$ (**IIIa**) has been isolated from the reaction of $[\text{Pt}(\text{dppm})(\text{CH}_2\text{Cl})_2]$ (**II**) with diphenylphosphine in dichloromethane. Iodination of **1b** leads to selective cleavage of the chloromethyl group, and subsequent iodide abstraction with silver ion gives a solvated cation (**V**). The structures of the hexafluorophosphate salts of the bis-chelate **IIIb** and of the solvated cation **V** have been determined by X-ray diffraction.

Keywords: Platinum; Metallocycle; Phosphine; X-ray diffraction; Crystal structure

1. Introduction

Diphosphaplatinocycles (**I**) were recently reported as the products of the reaction between $[\text{Pt}(\text{dppm})(\text{CH}_2\text{Cl})_2]$ (**II**) and various Lewis bases [1]. It appeared likely that the product from diphenylphosphine (**Ia**) would offer the possibility of studying the reactivity of a secondary phosphine co-ordinated to platinum without complications arising from the formation of phosphido bridges.

Little experimental detail is given in the original report of the reaction of $[\text{Pt}(\text{dppm})(\text{CH}_2\text{Cl})_2]$ (**II**) with diphenylphosphine, although the product of the reaction after 2 h in dichloromethane is reported to be **Ia**. However, with longer reaction times we obtained a cation which we isolated as its hexafluorophosphate salt (**IIIb**). The earlier workers had obtained **IIIa** from **II** and dppm . The $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra of **IIIb** agreed closely with those reported for **IIIa**, and the structure of **IIIb** with the two carbon atoms remaining *cis* has been confirmed by X-ray crystallography.

The yield in the formation of **IIIa** from **II** and diphenylphosphine is 51% after recrystallisation, which suggests that the methylene group has been derived, at least partially, from the dichloromethane solvent. The alternative route involving redistribution of a dppm molecule from a second platinum ion seems rather unlikely in view of the strong complexing of phosphines to platinum. The detailed mechanism is unclear. The initial step may be the reaction of Ph_2PH with the co-ordinated chloromethyl group. Similar alkylation by a chloromethyl group attached to platinum has been observed by Lappert and coworkers [2], Scherer and Jungman [3], Engelter et al. [4] and Hoover and Stryker [5]. The formation of **III** could involve $\text{Ph}_2\text{PCH}_2\text{Cl}$ as an intermediate, although this compound is reported to be unstable [6]. A general review of the chemistry of halogenoalkyl complexes of the transition metals has appeared recently [7].

The reaction of **II** with triphenylphosphine seems to give mainly the ring insertion product **1b**, and we have confirmed by X-ray crystallography the structure suggested [1] on the basis of the NMR spectrum. The stereochemistry of the co-ordination sphere with the

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monodentate ligand **L** *trans* to the Pt–C bond in the platinumocycle ring is confirmed.

II has been reported to react with one equivalent of HCl with cleavage of a Pt–C bond [1]. We decided to try the iodination of **IIb** in which there are two types of Pt–C bond, and found that the chloromethyl group was cleaved off preferentially to give **IV**. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **IV** shows four phosphorus resonances, one is the hexafluorophosphate anion and two show large coupling constants to platinum, indicating that they are bonded directly to platinum.

There have been considerable refinements in our understanding of the metal–carbon bond energies in recent years [8,9], but it is not clear why the chloromethyl group is cleaved off preferentially. Possibly, the formal positive charge on P2 deters electrophilic attack on the Pt–C2 bond (see numbering scheme for **IIb** in Fig. 1). Reaction of **IV** with silver hexafluorophosphate gives the solvated cation **V**, which was characterised by analysis, NMR and X-ray crystallography. The $^{31}\text{P}\{^1\text{H}\}$ NMR data for **IV** and **V** are given in Table 1.

2. Description of the structures

Figs. 1–3 show the structures and atomic numbering schemes of **IIb**, **IIIb** and **V** respectively, Table 2 summarises the crystal data and Tables 3–5 give the positional and equivalent thermal parameters. The interatomic distances and bond angles are given in Table 6. All three structures contain a puckered five-membered ring with one platinum, two phosphorus and two carbon atoms. The bond distances and angles within the rings are as expected.

In **IIb** the bond Pt–C3 connecting the platinum to the chloromethyl group has length 2.185(21) Å, and the Pt–CH₂–Cl angle is 113.7(11)°. This Pt–C bond is slightly longer than other chloromethyl groups bonded to platinum [7]. This could be due to the *trans* influence [10] of the phosphorus P1, although in **II** the Pt–C bonds have an average length of 2.076(9) Å [1].

The structure of **IIIb** shows that the C1–Pt–C4 angle, which is only 84.2(4)° in **II** [1], is further reduced to 78.6(12)°. C2 is 0.44(4) Å below the best plane through the platinum atom and its four bonded atoms, and C3 is 0.29(4) Å above this plane. The structure of a nickel compound with the same ligands as **IIIb** but with a *trans*-configuration for the two phosphorus atoms has been reported [11].

In **V** the co-ordinated acetone is bonded through a lone pair on the oxygen. The Pt–O and O=C distances of 2.133(16) and 1.25(4) Å and the angle at oxygen of 126.3(18)° in **V** are similar to those found in [*trans*-(PhMe₂P)₂PtMe(acetone)]⁺PF₆[−], where the lengths and angle are 2.168(5), 1.226(9) Å and 129.3(5)° [12].

3. Experimental

3.1. Preparations

Reactions were generally carried out under a nitrogen atmosphere. NMR measurements were made on Bruker WM250 or AM360 instruments for which the ^{31}P frequencies are 101.25 and 145.78 MHz respectively. Chemical shifts are relative to external 85% phosphoric acid. [Pt(dppm)(CH₂Cl)₂] was prepared by the literature method [1], and we give a more detailed procedure for **IIb**, which we used as the hexafluorophosphate rather than the chloride.

3.1.1. [Pt(CH₂Cl)(CH₂PPh₂CH₂PPh₂)(PPh₃)]PF₆ (**IIb**)

A solution of [Pt(dppm)(CH₂Cl)₂] (0.3 g, 0.44 mmol) in dry dichloromethane (25 cm³) was treated with triphenylphosphine (1.0 g, 3.8 mmol) and stirred for 4 h at room temperature. The reaction mixture was concentrated under reduced pressure to ca. 10 cm³, addition of diethyl ether (20 cm³) precipitated the chloride as a cream powder which was filtered off and washed with diethyl ether. The chloride was then dissolved in acetone and treated with ammonium hexafluorophosphate to give the product. Recrystallisation from acetone/dichloromethane/methanol gave colourless crystals (0.27 g, 56%). M.p. 216°C. Anal. Found: C, 51.35; H, 4.14. C₄₅H₄₁ClF₆P₄Pt · 0.25CH₂Cl₂ Calc.: C, 50.74; H, 3.91%.

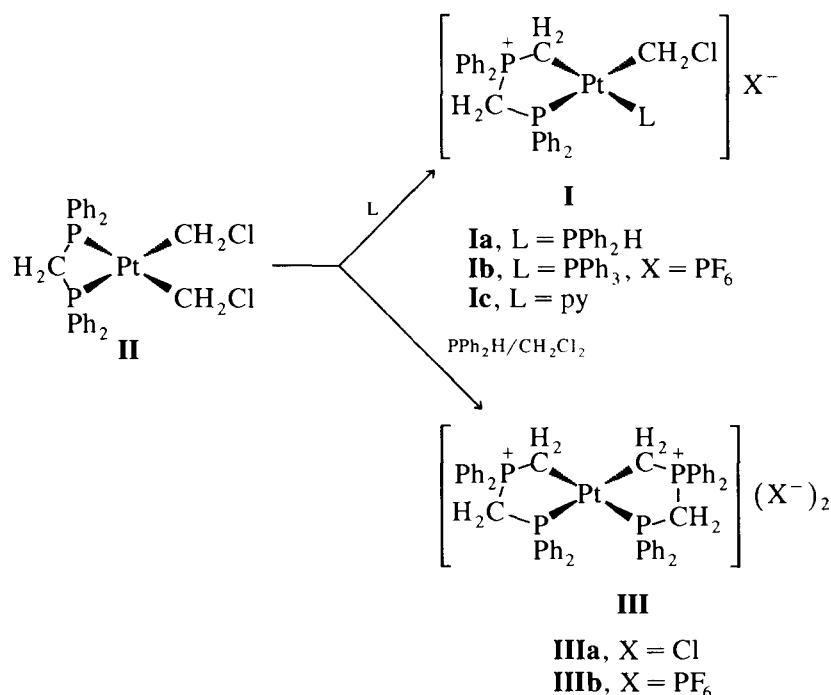
3.1.2. [Pt(CH₂PPh₂CH₂PPh₂)₂]Cl₂ (**IIIa**)

A solution of [Pt(dppm)(CH₂Cl)₂] (0.2 g, 0.295 mmol) in dry dichloromethane (15 cm³) was treated with diphenylphosphine (0.5 ml, 2.875 mmol) and stirred at room temperature in the dark for 5 days. The reaction mixture was concentrated under reduced pressure to ca. 5 cm³, when addition of diethyl ether and petroleum ether (60/80) precipitated the product as a cream powder, which was recrystallised from methanol/diethyl ether to give colourless crystals of the product (0.16 g, 51% yield). M.p. 218–220°C. The analysis we obtained corresponded to a hemi rather than a sesqui solvate as previously reported [1]. Anal. Found: C, 56.04; H 4.79. C₅₂H₄₈Cl₂P₄Pt · 0.5CH₂Cl₂ Calc.: C, 56.50; H, 4.52%.

The chloride was converted to the hexafluorophosphate (**IIIb**) by reaction with ammonium hexafluorophosphate in methanol. Anal. Found: C, 48.64; H, 3.93. C₅₂H₄₈F₁₂P₆Pt Calc.: C, 48.72; H, 3.77%.

3.1.3. [Pt(CH₂PPh₂CH₂PPh₂)(PPh₃)(I)]PF₆ (**IV**)

A solution of [Pt(CH₂Cl)(CH₂PPh₂CH₂PPh₂)(PPh₃)]PF₆ (**IIb**) (0.28 g, 0.27 mmol) in dichloromethane (25 cm³) was treated with iodine (0.20 g, 0.79 mmol) and stirred at room temperature overnight in air. The deep purple reaction mixture was partitioned with dilute



sodium thiosulphate solution to give a yellow organic layer, which was dried over anhydrous magnesium sulphate. The solvent was removed under reduced pressure to give a yellow residue which was recrystallised from dichloromethane/methanol to give yellow/orange crystals of the product (0.24 g, 79% yield). M.p. 187–189°C (dec.). Anal. Found: C, 43.91; H, 3.44. C₄₄H₃₉F₆IP₄Pt · 1.5CH₂Cl₂ Calc.: C, 43.54; H, 3.37%.

3.1.4. [Pt(CH₂PPh₂CH₂PPh₂)(PPh₃)(OCMe₂)](PF₆)₂ (V)

A warm solution of [Pt(CH₂PPh₂CH₂PPh₂)(PPh₃)(I)]PF₆ (IV) (0.17 g, 0.15 mmol) in methanol (25 cm³) was treated with silver hexafluorophosphate (0.08 g, 0.32 mmol) and refluxed for 2 h in air. The dark brown precipitate was filtered off and the colourless filtrate

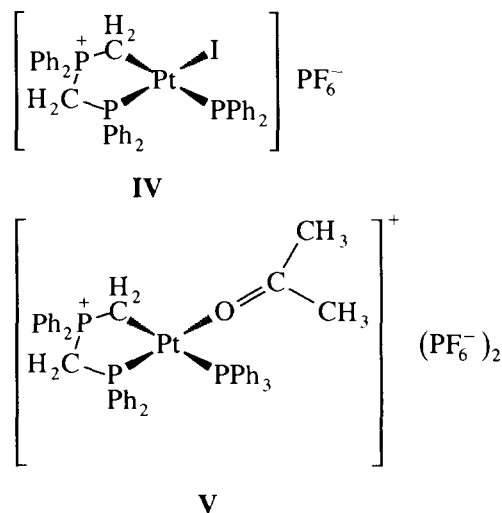


Table 1
³¹P{¹H} NMR data

Compound	Solvent	Chemical shift (ppm)			Coupling constants (Hz)
		P _A	P _B	P _C	
IV	(CD ₃) ₂ CO/CDCl ₃	15.9	48.8	12.9	¹ J _{P_A-Pt} = 3600
IV					¹ J _{P_C-Pt} = 2290
V	(CD ₃) ₂ CO/CDCl ₃	9.6	41.6	15.2	¹ J _{P_A-Pt} = 3340
V					¹ J _{P_C-Pt} = 2260

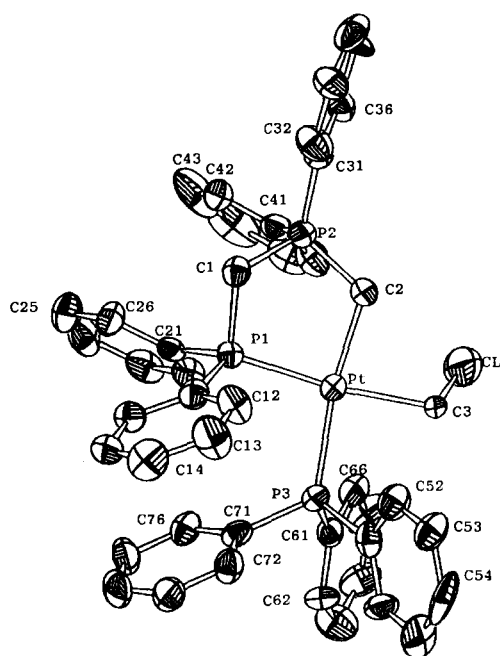


Fig. 1. ORTEP drawing of the unipositive ion of **Ib** showing the numbering scheme. The numbering within the phenyl rings is always sequential but labels are not shown for all atoms.

evaporated to dryness under reduced pressure to give a white residue, which was recrystallised from acetone/methanol containing ammonium hexafluorophosphate to give colourless crystals of the product (0.12 g, 66% yield). M.p. 269–271°C (dec.). Anal. Found: C, 46.56; H, 4.15; N, 0.98. $C_{47}H_{45}F_{12}OP_5Pt$

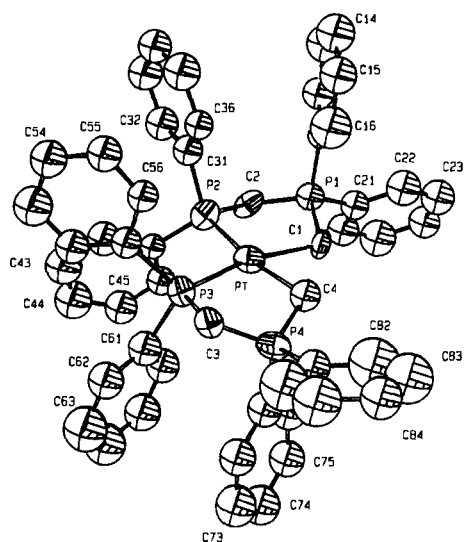


Fig. 2. ORTEP drawing of the dipositive ion of **IIIb** showing the numbering scheme. The numbering within the phenyl rings is always sequential but labels are not shown for all atoms.

Calc.: C, 46.88; H, 3.77%. We were only able to obtain a crystalline sample of **V** when we recrystallised in the presence of ammonium hexafluorophosphate, which accounts for the presence of a very small percentage of nitrogen.

3.2. Crystallography

The crystal data for **Ib**, **IIIb** and **V** are given in Table 6. Reflection data were collected on a Picker four-circle

Table 2
Crystal data for **Ib**, **IIIb** and **V**

Compound	Ib	IIIb	V
Formula	$C_{45}H_{41}ClF_6P_4Pt \cdot 0.25CH_2Cl_2$	$C_{52}H_{48}F_{12}P_6Pt$	$C_{47}H_{45}F_{12}OP_5Pt$
RMM	1135.181	1281.866	1203.811
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Space group	$Pcab$	$P2_12_12_1$	$P\bar{1}$
a (Å)	17.93(1)	20.05(1)	10.731(9)
b (Å)	28.05(1)	20.33(1)	12.928(10)
c (Å)	18.80(3)	13.34(1)	20.230(18)
α (deg)	90	90	96.31(7)
β (deg)	90	90	92.31(7)
γ (deg)	90	90	102.72(8)
Z	8	4	2
D_{calc} (g cm ⁻³)	1.50	1.57	1.47
D_{obs} (g cm ⁻³)	1.49	1.54	1.54
$F(000)$	4244	2538	1192
Crystal dimensions (mm ³)	0.60 × 0.38 × 0.28	0.33 × 0.30 × 0.18	0.95 × 0.40 × 0.30
μ (mm ⁻¹)	3.27	7.25	2.83
Transmission coefficients	0.36–0.45	0.13–0.35	0.30–0.41
2θ range (deg)	3–45	4–90	3–45
Radiation, λ (Å)	Mo, 0.7107	Cu, 1.5418	Mo, 0.7107
Temperature (K)	298	298	298
No. of reflections measured	6181	2482	7094
No. of reflections with $I_{net} > 2.5\sigma(I_{net})$	3676	2125	6105
Residual R	0.073	0.072	0.064
R_w	0.089	0.079	0.090
Quality of fit	4.22	8.47	5.22

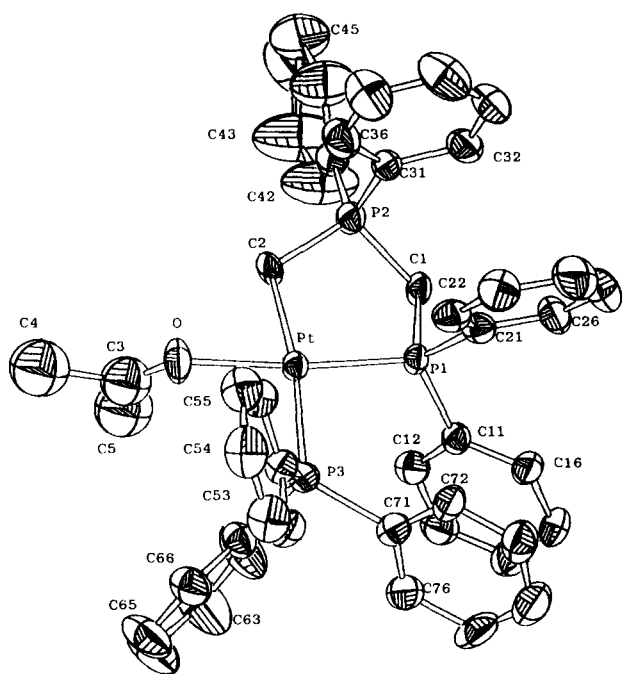


Fig. 3. ORTEP drawing of the dipositive ion of **V** showing the numbering scheme. The numbering within the phenyl rings is always sequential but labels are not shown for all atoms.

diffractometer interfaced to a 286 IBM-compatible microcomputer. **Ib** and **V** were examined using Zr-filtered Mo K α radiation. Very few crystals of **IIIb** were available and they diffracted Mo radiation very weakly. We therefore used Ni-filtered Cu K α radiation, and because of the large mosaic spread we used a 3° scan range for 2 θ . A standard reflection was measured every 25 reflections (every 50 reflections with Cu) and the reflections were scaled and corrected for Lorentz and polarisation effects. All three structures were solved by direct methods and Fourier difference synthesis. All computations were carried out using the NRCVAX program package [13]. Tables of H-atom co-ordinates and thermal parameters and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

3.2.1. Compound **Ib**

The crystal was obtained by crystallisation from dichloromethane–methanol. The intensity of the standard reflection fell by about 11% over the 14 days of the data collection. The difference map showed the presence of a solvent molecule, which was modelled as dichloromethane with geometry as found by Kawaguchi et al. [14] and one quarter occupancy. All non-hydrogen atoms except the dichloromethane solvate molecule were assigned anisotropic temperature factors. Idealised geometries were used for both the hexafluorophosphate and phenyl groups, and hydrogen atoms were placed in

Table 3
Positional and equivalent thermal parameters for **Ib**

Atom	x	y	z	B_{iso}
Pt	0.14662(5)	0.66972(3)	0.20602(5)	4.40(4)
P1	0.0663(3)	0.6118(2)	0.1680(3)	4.1(3)
P2	0.0796(4)	0.5971(2)	0.3212(3)	4.6(3)
P3	0.1597(3)	0.7098(2)	0.1008(3)	4.5(3)
C1	0.1879(7)	0.7505(4)	0.3261(5)	12.(1)
C1	0.0670(12)	0.5663(7)	0.2369(12)	5.(1)
C2	0.1544(13)	0.6348(8)	0.3034(12)	6.(1)
C3	0.2245(11)	0.7201(8)	0.2545(11)	4.(1)
C11	0.0935(10)	0.5799(6)	0.0923(7)	5.(1)
C12	0.1687(9)	0.5673(7)	0.0902(9)	6.(1)
C13	0.1972(8)	0.5429(8)	0.0315(11)	9.(2)
C14	0.1503(12)	0.5310(7)	-0.0250(9)	8.(2)
C15	0.0751(11)	0.5436(6)	-0.0229(7)	6.(1)
C16	0.0467(7)	0.5680(6)	0.0357(9)	5.(1)
C21	-0.0308(7)	0.6266(6)	0.1591(8)	5.(1)
C22	-0.0522(9)	0.6741(5)	0.1666(9)	6.(1)
C23	-0.1275(11)	0.6864(6)	0.1637(9)	7.(1)
C24	-0.1814(7)	0.6513(8)	0.1533(10)	8.(2)
C25	-0.1600(9)	0.6037(7)	0.1457(10)	7.(2)
C26	-0.0847(10)	0.5914(5)	0.1486(10)	6.(1)
C31	0.0928(10)	0.5538(6)	0.3915(8)	6.(1)
C32	0.1332(11)	0.5124(7)	0.3777(9)	7.(2)
C33	0.1475(11)	0.4800(5)	0.4324(14)	9.(2)
C34	0.1214(13)	0.4892(8)	0.5009(11)	10.(3)
C35	0.0810(12)	0.5307(9)	0.5148(7)	10.(3)
C36	0.0667(10)	0.5630(7)	0.4601(10)	7.(2)
C41	-0.0016(9)	0.6313(6)	0.3382(9)	6.(1)
C42	-0.0716(12)	0.6095(6)	0.3382(10)	6.(1)
C43	-0.1358(8)	0.6370(10)	0.3472(10)	12.(3)
C44	-0.1301(12)	0.6862(10)	0.3563(10)	11.(2)
C45	-0.0601(16)	0.7080(6)	0.3563(10)	9.(2)
C46	0.0041(11)	0.6805(6)	0.3473(10)	6.(1)
C51	0.2595(6)	0.7101(6)	0.0759(9)	5.1(1)
C52	0.3048(10)	0.6760(6)	0.1083(9)	6.(2)
C53	0.3797(9)	0.6721(6)	0.0890(11)	7.(2)
C54	0.4092(7)	0.7024(8)	0.0372(11)	9.(2)
C55	0.3639(10)	0.7365(7)	0.0048(9)	10.(2)
C56	0.2890(10)	0.7403(6)	0.0242(10)	7.(2)
C61	0.1237(9)	0.7733(5)	0.1045(9)	5.(1)
C62	0.1264(10)	0.8035(7)	0.0456(7)	6.(1)
C63	0.1032(12)	0.8508(7)	0.0519(11)	8.(2)
C64	0.0773(11)	0.8679(5)	0.1171(14)	8.(2)
C65	0.0745(11)	0.8376(7)	0.1759(10)	9.(2)
C66	0.0978(10)	0.7904(7)	0.1697(7)	7.(2)
C71	0.1176(8)	0.6885(6)	0.0181(7)	5.(1)
C72	0.1612(7)	0.6665(6)	-0.0338(9)	6.(1)
C73	0.1286(11)	0.6508(6)	-0.0970(8)	7.(1)
C74	0.0523(12)	0.6571(6)	-0.1081(8)	8.(2)
C75	0.0087(7)	0.6790(7)	-0.0562(10)	7.(2)
C76	0.0413(8)	0.6948(6)	0.0070(9)	6.(1)
SC1	0.6830(9)	0.5790(25)	0.3514(16)	3.(0)
SC11	0.6764(9)	0.6008(7)	0.4395(8)	3.(0)
SC12	0.5949(10)	0.5623(6)	0.3170(8)	3.(0)
P4	0.3672(6)	0.5400(3)	0.2318(4)	10.9(7)
F1	0.4018(14)	0.5244(10)	0.3056(6)	26.(4)
F2	0.3348(16)	0.4882(5)	0.2212(16)	26.(4)
F3	0.4415(9)	0.5247(11)	0.1929(9)	23.(3)
F4	0.3997(17)	0.5919(5)	0.2425(16)	29.(4)
F5	0.2930(11)	0.5554(11)	0.2708(10)	30.(4)
F6	0.3327(11)	0.5557(9)	0.1581(6)	19.(2)

Table 4
Positional and equivalent thermal parameters for **IIIb**

Atom	x	y	z	B_{iso}
Pt	0.28721(8)	0.74153(6)	0.02096(11)	6.50(7)
P1	0.3294(5)	0.8815(4)	0.1209(8)	6.0(5)
P2	0.2067(5)	0.8190(4)	0.0488(8)	6.6(5)
P3	0.2241(5)	0.6581(4)	-0.0390(8)	6.0(5)
P4	0.3565(6)	0.6092(5)	-0.0615(8)	7.0(6)
C1	0.365(1)	0.811(2)	0.062(3)	6(2)
C2	0.250(2)	0.897(1)	0.065(3)	7(2)
C3	0.277(2)	0.585(1)	-0.045(3)	6(2)
C4	0.372(2)	0.683(2)	0.011(3)	8(1)
C11	0.322(1)	0.865(1)	0.246(2)	6(1)
C12	0.300(2)	0.915(1)	0.311(2)	9(1)
C13	0.293(2)	0.902(2)	0.413(2)	13(2)
C14	0.309(2)	0.840(2)	0.451(2)	13(2)
C15	0.331(2)	0.791(1)	0.386(3)	11(1)
C16	0.338(2)	0.803(1)	0.284(3)	15(2)
C21	0.385(1)	0.947(1)	0.108(2)	8(1)
C22	0.442(2)	0.948(1)	0.168(2)	11(1)
C23	0.489(1)	0.998(2)	0.155(2)	12(1)
C24	0.479(1)	1.046(1)	0.082(3)	10(1)
C25	0.422(2)	1.044(1)	0.022(2)	14(2)
C26	0.375(1)	0.994(2)	0.035(2)	10(1)
C31	0.165(1)	0.810(1)	0.163(2)	8(1)
C32	0.115(2)	0.855(1)	0.183(2)	10(1)
C33	0.078(1)	0.851(1)	0.272(3)	11(1)
C34	0.092(1)	0.801(2)	0.341(2)	10(1)
C35	0.142(1)	0.756(1)	0.321(2)	12(1)
C36	0.179(1)	0.760(1)	0.232(2)	7(1)
C41	0.147(1)	0.834(1)	-0.049(2)	6(1)
C42	0.087(1)	0.799(1)	-0.047(2)	10(1)
C43	0.042(1)	0.804(2)	-0.126(3)	12(2)
C44	0.056(2)	0.845(2)	-0.207(2)	13(2)
C45	0.116(2)	0.881(1)	-0.209(2)	11(1)
C46	0.161(1)	0.875(1)	-0.130(2)	8(1)
C51	0.148(1)	0.634(1)	0.030(2)	7(1)
C52	0.083(2)	0.637(1)	-0.009(2)	9(1)
C53	0.029(1)	0.619(1)	0.051(3)	12(1)
C54	0.040(1)	0.597(1)	0.149(2)	10(1)
C55	0.104(2)	0.594(1)	0.187(2)	9(1)
C56	0.158(1)	0.612(1)	0.128(2)	7(1)
C61	0.196(2)	0.668(2)	-0.168(2)	9(1)
C62	0.167(1)	0.616(1)	-0.220(3)	10(1)
C63	0.156(2)	0.621(2)	-0.323(3)	16(2)
C64	0.174(2)	0.678(2)	-0.374(2)	15(2)
C65	0.203(2)	0.730(1)	-0.322(3)	11(1)
C66	0.214(1)	0.725(1)	-0.219(3)	10(1)
C71	0.364(2)	0.634(2)	-0.191(2)	9(1)
C72	0.351(2)	0.589(1)	-0.268(3)	10(1)
C73	0.363(2)	0.607(2)	-0.367(3)	14(2)
C74	0.388(2)	0.669(2)	-0.390(2)	13(2)
C75	0.401(1)	0.714(1)	-0.313(3)	11(1)
C76	0.389(2)	0.696(2)	-0.213(3)	11(1)
C81	0.414(2)	0.540(2)	-0.044(2)	8(1)
C82	0.479(2)	0.552(1)	-0.012(3)	19(2)
C83	0.522(1)	0.499(2)	0.006(3)	16(2)
C84	0.500(2)	0.435(2)	-0.008(3)	11(1)
C85	0.434(2)	0.423(1)	-0.039(3)	16(2)
C86	0.391(1)	0.476(2)	-0.057(3)	17(2)
PF1	0.6801(5)	0.0881(4)	0.1839(8)	8.5(7)
F1	0.6577(10)	0.0352(7)	0.1039(13)	13(2)
F2	0.6372(12)	0.0519(10)	0.2666(14)	19(3)
F3	0.7026(10)	0.1410(7)	0.2639(13)	15(2)
F4	0.7231(11)	0.1242(9)	0.1013(14)	21(3)

Table 4 (continued)

Atom	x	y	z	B_{iso}
F5	0.6179(8)	0.1321(8)	0.1557(19)	17(3)
F6	0.7423(9)	0.0441(8)	0.2122(19)	15(2)
PF2	0.3376(6)	0.9235(4)	0.7408(8)	8.3(8)
F7	0.3877(10)	0.8848(10)	0.6709(15)	17(3)
F8	0.2789(9)	0.8770(10)	0.7057(18)	16(2)
F9	0.2876(10)	0.9622(10)	0.8107(16)	18(3)
F10	0.3963(9)	0.9700(9)	0.7759(18)	17(3)
F11	0.3214(13)	0.9723(9)	0.6519(13)	17(3)
F12	0.3538(13)	0.8747(9)	0.8297(13)	20(4)

calculated positions. The final stages of refinement were carried out by full-matrix least-squares, and R converged to 0.073.

3.2.2. Compound **IIIb**

The crystal was obtained by recrystallisation from methanol/diethyl ether. Although we initially had problems with the data for this compound (see above), the solution of the structure was very straightforward once good data were obtained. The absorption correction was applied towards the end of the refinement and produced an improvement in the residual of ca. 0.015 when R was below 0.10. In the final stages of refinement all non-hydrogen atoms other than the phenyl rings were refined with anisotropic temperature factors. The phenyl and hexafluorophosphate groups were refined as idealised groups. The hydrogen atoms were placed in calculated positions and assigned isotropic temperature factors. The final value of R after full-matrix least-squares refinement was 0.072.

3.2.3. Compound **V**

The crystal was obtained by recrystallisation from acetone/methanol containing ammonium hexafluorophosphate. The refinement was originally carried out in $P1$, with two independent molecules per cell. As refinement proceeded it became clear that the structure was centrosymmetric, $P\bar{1}$, with two symmetry related molecules per cell. The non-hydrogen atoms of the five-membered ring, the phenyl carbon atoms and the oxygen atom were refined with anisotropic temperature factors, but the carbon atoms of the co-ordinated acetone molecule had rather large temperature factors and were refined isotropically. Both hexafluorophosphate anions and the phenyl groups attached to atom P1 were refined as idealised groups, but software limitations did not allow the remaining phenyl groups to be refined in this manner. Hydrogen atoms were placed in fixed positions, on the phenyl and methylene groups, but no hydrogen atoms were included in the refinement of the co-ordinated acetone molecule, where the rather large temperature factors suggest disorder. The last stages of refinement were carried out by full-matrix least-squares, giving a final R of 0.064

Table 5
Positional and equivalent thermal parameters for V

Atom	x	y	z	B_{iso}
Pt	0.35054(5)	0.25359(5)	0.22456(3)	3.73(3)
P1	0.1657(3)	0.2992(3)	0.2467(2)	3.8(2)
P2	0.1926(4)	0.1538(3)	0.3455(2)	4.5(2)
P3	0.4105(4)	0.3668(3)	0.1446(2)	4.3(2)
C1	0.0743(13)	0.1933(12)	0.2921(8)	4.1(1)
C2	0.3141(16)	0.1390(13)	0.2917(8)	5.1(1)
C3	0.5340(30)	0.1221(26)	0.1772(16)	11.1(1)
C4	0.6757(36)	0.0936(29)	0.1791(18)	15.1(1)
C5	0.4307(35)	0.0307(30)	0.1360(19)	14.1(1)
O	0.5227(13)	0.1989(12)	0.2126(8)	7.8(8)
C11	0.0505(9)	0.2934(8)	0.1767(4)	4.1(1)
C12	0.0272(10)	0.2013(7)	0.1308(5)	5.1(1)
C13	-0.0623(11)	0.1890(8)	0.0765(5)	6.1(1)
C14	-0.1286(10)	0.2687(11)	0.0681(5)	7.1(1)
C15	-0.1053(11)	0.3608(9)	0.1140(6)	7.1(1)
C16	-0.0158(10)	0.3732(7)	0.1683(5)	5.1(1)
C21	0.1845(10)	0.4221(7)	0.3012(5)	5.1(1)
C22	0.3074(8)	0.4830(10)	0.3214(6)	6.1(1)
C23	0.3235(11)	0.5780(9)	0.3643(7)	8.1(1)
C24	0.2167(15)	0.6121(9)	0.3869(7)	9.1(1)
C25	0.0938(12)	0.5512(11)	0.3666(7)	8.1(1)
C26	0.0777(8)	0.4562(10)	0.3238(6)	6.1(1)
C31	0.2467(14)	0.2531(13)	0.4129(8)	5.1(1)
C32	0.1615(17)	0.3099(16)	0.4459(9)	6.1(1)
C33	0.2056(21)	0.3855(18)	0.4986(10)	7.1(1)
C34	0.3308(26)	0.4076(21)	0.5233(12)	9.1(1)
C35	0.4163(22)	0.3551(22)	0.4925(13)	9.1(1)
C36	0.3729(18)	0.2794(18)	0.4388(10)	7.1(1)
C41	0.1211(18)	0.0320(16)	0.3764(10)	6.1(1)
C42	0.0498(36)	-0.0495(22)	0.3394(15)	14.2(1)
C43	0.0072(44)	-0.1465(26)	0.3617(20)	18.3(1)
C44	0.0253(43)	-0.1640(23)	0.4208(21)	13.2(1)
C45	0.1049(45)	-0.0851(35)	0.4614(21)	15.3(1)
C46	0.1536(32)	0.0186(23)	0.4401(16)	12.2(1)
C51	0.5610(15)	0.4642(12)	0.1696(8)	5.1(1)
C52	0.6095(17)	0.5407(15)	0.1274(10)	6.1(1)
C53	0.7243(20)	0.6141(16)	0.1480(13)	8.1(1)
C54	0.7916(20)	0.6119(18)	0.2068(15)	8.1(1)
C55	0.7437(19)	0.5357(18)	0.2495(11)	7.1(1)
C56	0.6276(16)	0.4619(14)	0.2296(9)	6.1(1)
C61	0.4271(16)	0.2864(14)	0.0689(8)	5.1(1)
C62	0.3279(21)	0.2045(20)	0.0447(13)	10.1(1)
C63	0.3261(26)	0.1464(26)	-0.0146(17)	13.2(1)
C64	0.4295(30)	0.1678(28)	-0.0541(14)	12.2(1)
C65	0.5329(24)	0.2516(25)	-0.0299(12)	10.2(1)
C66	0.5289(17)	0.3101(18)	0.0291(10)	7.1(1)
C71	0.3072(14)	0.4541(14)	0.1179(9)	5.1(1)
C72	0.3048(16)	0.5446(14)	0.1615(10)	6.1(1)
C73	0.2228(21)	0.6113(17)	0.1427(12)	7.1(1)
C74	0.1544(23)	0.5903(22)	0.0836(16)	9.2(1)
C75	0.1581(19)	0.5013(23)	0.0407(12)	8.1(1)
C76	0.2377(17)	0.4308(17)	0.0576(10)	7.1(1)
P4	0.0427(5)	-0.1172(4)	0.1302(3)	7.9(3)
F1	0.1220(9)	-0.0154(5)	0.1767(4)	11.1(1)
F2	-0.0366(8)	-0.2190(5)	0.0838(4)	11.1(1)
F3	0.0598(11)	-0.1893(7)	0.1867(4)	13.1(1)
F4	-0.0851(7)	-0.0977(8)	0.1596(5)	16.1(1)
F5	0.0256(11)	-0.0451(6)	0.0738(4)	13.1(1)
F6	0.1705(6)	-0.1368(8)	0.1009(5)	14.1(1)
F5	0.7374(4)	0.2695(4)	0.3855(2)	7.0(3)
F7	0.7863(8)	0.2798(8)	0.3136(3)	10.1(1)
F8	0.6885(8)	0.2592(8)	0.4574(3)	12.1(1)

Table 5 (continued)

Atom	x	y	z	B_{iso}
F9	0.6311(7)	0.1672(6)	0.3563(5)	11.1(1)
F10	0.6414(8)	0.3428(7)	0.3718(5)	13.1(1)
F11	0.8437(7)	0.3718(7)	0.4146(5)	15.1(1)
F12	0.8334(8)	0.1962(8)	0.3992(5)	14.1(1)

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Table 6
Selected geometric parameters (Å and deg)

Compound Ib			
Pt–P1	2.287(6)	P1–C1	1.817(23)
Pt–P3	2.287(7)	P2–C1	1.819(23)
Pt–C2	2.082(22)	P2–C2	1.740(24)
Pt–C3	2.185(20)	C1–C3	1.72(3)
Compound IIIb			
Pt–P2	2.285(9)	P1–C2	1.79(4)
Pt–P3	2.261(9)	P2–C2	1.82(3)
Pt–C1	2.16(3)	P3–C3	1.82(3)
Pt–C4	2.08(3)	P4–C3	1.68(3)
P1–C1	1.79(3)	P4–C4	1.80(4)
Compound V			
Pt–P1	2.242(4)	P2–C1	1.820(15)
Pt–P3	2.320(4)	P2–C2	1.768(14)
Pt–O	2.134(11)	O–C3	1.19(4)
Pt–C2	2.106(14)	C3–C4	1.64(5)
P1–C1	1.859(15)	C3–C5	1.56(5)
Compound Ib			
P1–Pt–P3	98.26(22)	Pt–P1–C1	105.7(7)
P1–Pt–C2	89.0(6)	C1–P2–C2	102.5(11)
P1–Pt–C3	173.0(5)	P1–C1–P2	106.9(11)
P3–Pt–C2	170.2(7)	Pt–C2–P2	113.8(12)
P3–Pt–C3	88.7(5)	Pt–C3–C1	113.7(11)
C2–Pt–C3	83.9(8)		
Compound IIIb			
P2–Pt–P3	100.3(4)	P3–Pt–C4	90.1(10)
P2–Pt–C1	91.1(8)	C1–Pt–C4	78.6(12)
Compound V			
P1–Pt–P3	97.95(15)	Pt–O–C3	126.3(18)
P1–Pt–C2	89.5(4)	P1–C1–P2	105.9(7)
P3–Pt–O	88.7(4)	Pt–C2–P2	114.7(7)
P3–Pt–C2	172.1(4)	O–C3–C4	117(3)
O–Pt–C2	83.9(5)	O–C3–C5	130(3)
Pt–P1–C1	106.7(4)	C4–C3–C5	111(3)

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