

The Flexibility of Bridging Phosphinoyl Ligands: New Classes of Triplatinum(II) and Diplatinum(I) Complexes

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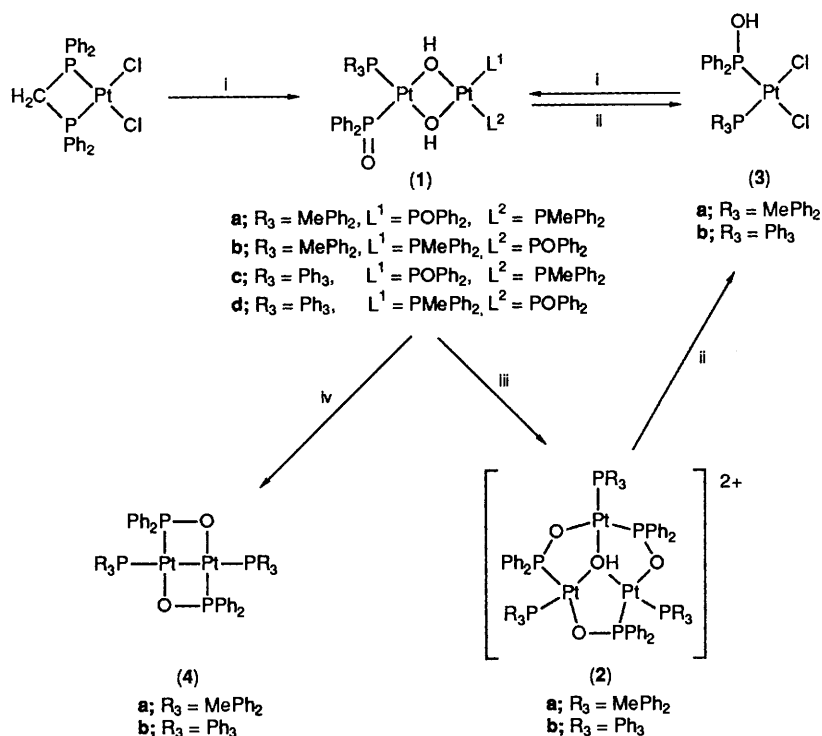
The reactions of $[\text{Pt}_2(\mu\text{-OH})_2(\text{POPh}_2)_2(\text{PR}_3)_2]$ with (i) HBF_4 or HPF_6 to give the triplatinum complexes $[\text{Pt}_3(\mu_3\text{-OH})(\mu\text{-OPPh}_2)_3(\text{PR}_3)_3]^{2+}$ (**2**) and (ii) alcohols to give the diplatinum complexes $[\text{Pt}_2(\mu\text{-OPPh}_2)_2(\text{PR}_3)_2]$ (**4**) are described; the X-ray crystal structures of (**2a**) and (**4a**) show the OPPh_2 ligand is capable of spanning Pt...Pt distances of 2.55 to 3.71 Å.

The study of diorganophosphido-bridged polynuclear complexes has been, and continues to be, a vigorously researched area of inorganic chemistry.¹ In contrast, the chemistry of diorganophosphinoyl (R_2PO) complexes remains almost unexplored²⁻⁴ despite the intriguing combination of soft (P) and hard (O) donors in this ligand and the well established co-ordination chemistry of the isoelectronic diorganosulphoxide ligand. We note that there is apparently no evidence for *O,S*-bridging in OSR_2 chemistry.⁵ In this paper we report the ready synthesis of a triplatinum(II) complex featuring the first example of a $\text{Pt}_3(\mu_3\text{-OH})$ unit and a diplatinum complex which is the first reported *O*-donor complex of platinum(I); both of these complexes are stabilised by $\mu\text{-OPPh}_2$ ligands.

We⁶ and others⁷ have previously shown that the diplatinum(II) complexes (**1a,b**) are readily made by base-promoted cleavage of the chelate $[\text{PtCl}_2(\text{dppm-PP}')]$ (dppm = bisdi-

phenylphosphinomethane). When (**1a,b**) is treated with HPF_6 or HBF_4 a remarkably specific transformation takes place rapidly (upon mixing) to give the triplatinum(II) dication (**2a**) quantitatively (by $^{31}\text{P}\{^1\text{H}\}$ NMR). For (**2a**) elemental analysis, and IR, $^{31}\text{P}\{^1\text{H}\}$, and ^1H NMR spectroscopy† were consistent with the structure shown in Scheme 1 but its identity

† Spectroscopic data: $^{31}\text{P}\{^1\text{H}\}$ NMR (**2a**) (isolated sample in dry CD_2Cl_2 ; ref. 85% H_3PO_4): δ 79.8 (OPPh_2 , J_{PtP} 3760, J_{PP} 19 Hz), -8.1 (PMePh_2 , J_{PtP} 4464, J_{PP} 19 Hz); (**2a**) (with water added to above solution): δ 85.5 (OPPh_2 , J_{PtP} 4103, br), -9.2 (PMePh_2 , J_{PtP} 3784 Hz); (**2b**) (CDCl_3) δ 79.3 (OPPh_2 , J_{PtP} 3742, J_{PP} 22 Hz), 4.7 (PPh_3 , J_{PtP} 4464, J_{PP} 19 Hz); (**4a**) (CDCl_3): δ 49.8 (OPPh_2 , $^1J_{\text{PtP}}$ 4618, $^3J_{\text{PtP}}$ 97, J_{PP} 9 Hz), -11.3 (PMePh_2 , $^1J_{\text{PtP}}$ 2882, $^3J_{\text{PtP}}$ 361, J_{PP} 174 Hz); (**4b**) (CDCl_3): δ 49.4 (OPPh_2 , $^1J_{\text{PtP}}$ 4612, $^3J_{\text{PtP}}$ 80, J_{PP} 9 Hz), 24.6 (PPh_3 , $^1J_{\text{PtP}}$, $^3J_{\text{PtP}}$ not resolved).



Scheme 1. Reagents and conditions: (i) NaOH in water or dimethyl sulphoxide (dmsO); (ii) concentrated aqueous HCl; (iii) HBF_4 in Et_2O or HPF_6 in water; (iv) EtOH at 70°C .

could only be determined unambiguously by X-ray structure analysis of $(2a)(\text{BF}_4)_2 \cdot \text{H}_2\text{O} \cdot \text{CH}_2\text{Cl}_2$.[‡] Figure 1 shows the molecular structure of the dication together with the water molecule that is hydrogen bonded to the $\mu_3\text{-OH}$ group [$\text{O} \cdots \text{O}(4a)$ 2.627(35) Å]. Each platinum(II) is approximately square-planar co-ordinated by O and P atoms of μ -phosphinoyl ligands, the $\mu_3\text{-OH}$, and a PPh_2Me ligand. The $\text{Pt}_3(\mu_3\text{-OH})$ unit forms a shallow pyramid [$\Sigma\text{Pt-O-Pt}$ angles $348.8(8)^\circ$], with non-bonding $\text{Pt} \cdots \text{Pt}$ edges (lengths 3.52–3.71 Å). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum[†] of $(2a)$ is sensitive to the presence of water indicating that the hydrogen bonding detected in the crystal structure prevails in solution.

It was observed that addition of aqueous HCl to $(2a)$ gave the hydroxyphosphine complex $(3a)$ quantitatively and that $(3a)$ can be reconverted to $(2a)$ via $(1a,b)$ (see Scheme 1). This suggested that complexes analogous to $(3a)$ would provide a

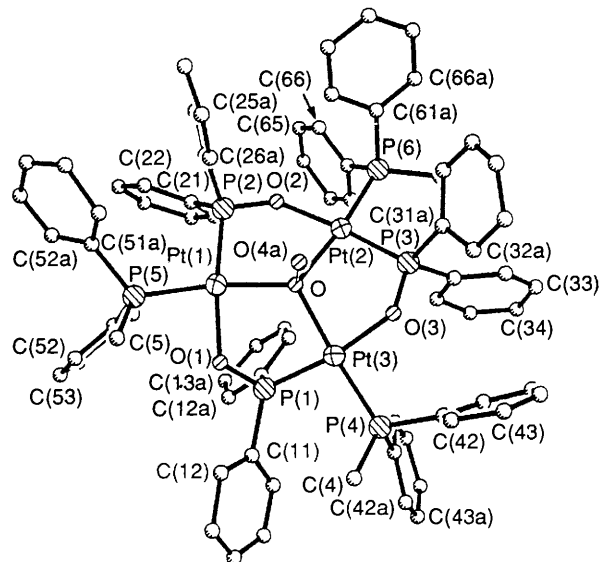


Figure 1. Molecular geometry of the dication $(2a)$; important molecular geometry parameters include: interatomic distances (Å), $\text{Pt}(1) \cdots \text{Pt}(2)$ 3.710(1), $\text{Pt}(1) \cdots \text{Pt}(3)$ 3.700(1), $\text{Pt}(2) \cdots \text{Pt}(3)$ 3.518(1), $\text{Pt}(1)\text{-P}(2)$ 2.224(4), $\text{Pt}(2)\text{-P}(3)$ 2.211(5), $\text{Pt}(3)\text{-P}(1)$ 2.234(6), $\text{Pt}(1)\text{-O}(1)$ 2.096(11), $\text{Pt}(2)\text{-O}(2)$ 2.091(13), $\text{Pt}(3)\text{-O}(3)$ 2.058(13), $\text{Pt}(1)\text{-P}(5)$ 2.232(5), $\text{Pt}(2)\text{-P}(6)$ 2.225(4), $\text{Pt}(3)\text{-P}(4)$ 2.228(5), $\text{Pt}(1)\text{-O}$ 2.157(12), $\text{Pt}(2)\text{-O}$ 2.134(10), $\text{Pt}(3)\text{-O}$ 2.153(11), $\text{P}(1)\text{-O}(1)$ 1.554(12), $\text{P}(2)\text{-O}(2)$ 1.548(12), $\text{P}(3)\text{-O}(3)$ 1.565(12), $\text{O} \cdots \text{O}(4a)$ 2.627(35); Bond angles ($^\circ$) $\text{Pt}(1)\text{-O-Pt}(2)$ 119.7(6), $\text{Pt}(1)\text{-O-Pt}(3)$ 118.3(5), $\text{Pt}(2)\text{-O-Pt}(3)$ 110.3(5).

general route to triplatinum complexes with $\mu\text{-Ph}_2\text{PO}$ ligands and indeed we have shown that such a route is viable for the synthesis of the Ph_3P complex $(2b)$ [†] from $(1c,d)$.

When $(1a,b)$ is refluxed in ethanol for 5 min the bright

[‡] *Crystal data:* $(2a)(\text{BF}_4)_2 \cdot \text{H}_2\text{O} \cdot \text{CH}_2\text{Cl}_2$: $\text{C}_{76}\text{H}_{68}\text{B}_2\text{Cl}_2\text{F}_8\text{O}_5\text{P}_6\text{Pt}_3$, $M = 2077.0$, monoclinic, space group Cc (No. 9), $a = 13.559(2)$, $b = 24.493(8)$, $c = 25.048(5)$ Å, $\beta = 105.16(2)^\circ$, $V = 8029(4)$ Å³, $Z = 4$, $D_x = 1.72$ g cm⁻³, λ (Mo- K_α) = 0.71069 Å, $\mu = 55.2$ cm⁻¹, $F(000) = 4016$, $T = 295$ K. Data were collected on a Nicolet P3m diffractometer for $4 < 2\theta < 50^\circ$. The structure was solved by heavy-atom methods and refined by least-squares to R 0.046 for 6428 unique, observed [$I > 1.5\sigma(I)$], absorption-corrected intensity data. The chirality was confirmed by an η refinement [$\eta = 0.84(5)$]. $(4a)$: $\text{C}_{50}\text{H}_{46}\text{O}_2\text{P}_4\text{Pt}_2$, $M = 1193.0$, monoclinic, space group $P2_1/n$ (No. 14), $a = 18.349(5)$, $b = 9.095(3)$, $c = 13.647(3)$ Å, $\beta = 90.38(2)^\circ$, $V = 2289(1)$ Å³, $Z = 2$, $D_x = 1.73$ g cm⁻³, λ (Mo- K_α) = 0.71069 Å, $\mu = 32.7$ cm⁻¹, $F(000) = 1156$, $T = 295$ K. Data were collected on a Nicolet P3m diffractometer for $4 < 2\theta < 50^\circ$. The structure was solved by heavy-atom methods and refined by least-squares to R 0.028 for 3710 unique, observed [$I > 2\sigma(I)$], absorption-corrected intensity data. Molecules of $(4a)$ have crystallographically imposed 1 symmetry. For both structures, atomic co-ordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

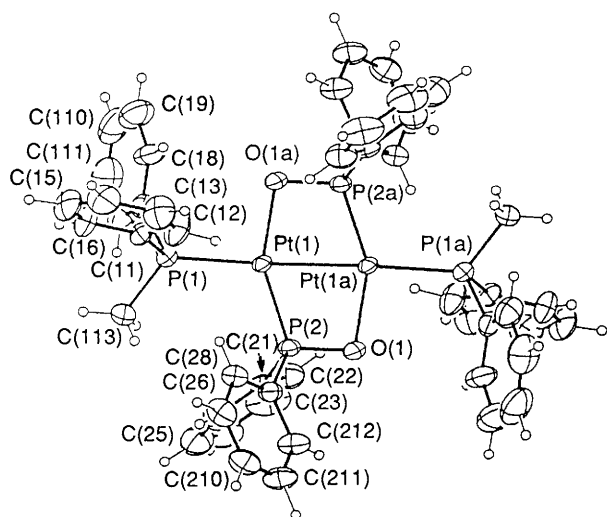


Figure 2. Molecular geometry of (**4a**); important bond lengths (Å) include: Pt(1)–Pt(1a) 2.554(1), Pt(1)–P(1) 2.301(1), Pt(1)–P(2) 2.203(1), Pt(1)–O(1a) 2.167(3), P(2)–O(1) 1.565(3); bond angles (°): P(1)–Pt(1)–P(2) 111.1(1), P(1)–Pt(1)–Pt(1a) 176.8(1), P(2)–Pt(1)–Pt(1a) 71.9(1), P(1)–Pt(1)–O(1a) 95.2(1), P(2)–Pt(1)–O(1a) 153.7(1).

yellow, crystalline, air-stable diplatinum(I) complex (**4a**) is deposited in *ca.* 50% yield. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum[†] of (**4a**) is characteristic of a diplatinum complex and its structure has been confirmed by X-ray crystallography.[‡] The molecular structure of (**4a**) is illustrated in Figure 2. The two platinum atoms are linked by a single bond [Pt(1)–Pt(1a) 2.554(1) Å] and bridged by μ -PPh₂O ligands, with their square-planar co-ordination completed by a PPh₂Me ligand *trans* to the Pt–Pt bond. One remarkable feature of the structure is the planarity of the entire Pt₂P₂O₂ unit. A comparison of the metrical parameters for (**4a**) and (**2a**) reveals that the

Pt–OPPh₂ distance [2.167(3) Å] in the platinum(I) complex (**4a**) is significantly longer than in the platinum(II) complex (**2a**) [2.058(13) to 2.096(11) Å].

The reduction of (**1a,b**) to (**4a**) can also be achieved using MeOH, PrⁱOH, or Bu^tOH in reactions which may involve (as yet undetected) μ -OR intermediates. The Ph₃P analogue (**4b**) (characterised by its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum[†]) can be made similarly from the corresponding precursors (**1c,d**). Complex (**4a**) has several potentially reactive sites and preliminary experiments show that it reacts with RC≡CR, HCl, Ph₂PCl, CO, and PR₃ to give products which we are presently characterising.

The above chemistry shows that Ph₂PO ligands can stabilise Pt–Pt bonds in low oxidation states and Pt₃ triangles containing μ_3 -OH bridges. The flexibility of the μ -PPh₂O ligands is further shown by the range of Pt...Pt distances bridged in (**4a**) and (**2a**) (2.55–3.71 Å).

We thank NATO and SERC for support and Johnson Matthey for the loan of platinum salts.

Received, 6th March 1990; Com. 0/00994F

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