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

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The reactions of $[Pt_2(\mu-OH)_2(POPh_2)_2(PR_3)_2]$ with (i) HBF₄ or HPF₆ to give the triplatinum complexes $[Pt_3(\mu_3-OH)_{(\mu-OPPh_2)_3}(PR_3)_3]^{2+}$ (2) and (ii) alcohols to give the diplatinum complexes $[Pt_2(\mu-OPPh_2)_2(PR_3)_2]$ (4) are described; the X-ray crystal structures of (2a) and (4a) show the OPPh₂ ligand is capable of spanning Pt \cdots 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 (R₂PO) 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_sS -bridging in OSR₂ chemistry.⁵ In this paper we report the ready synthesis of a triplatinum(II) complex featuring the first example of a Pt₃(µ₃-OH) unit and a diplatinum complex which is the first reported O-donor complex of platinum(I); both of these complexes are stabilised by µ-OPPh₂ ligands.

We⁶ and others⁷ have previously shown that the diplatinum(1) complexes (**1a,b**) are readily made by base-promoted cleavage of the chelate [PtCl₂(dppm-PP')] (dppm = bisdiphenylphosphinomethane). When (1a,b) is treated with HPF₆ or HBF₄ a remarkably specific transformation takes place rapidly (upon mixing) to give the triplatinum(II) dication (2a) quantitatively (by ${}^{31}P{}^{1}H{}$ NMR). For (2a) elemental analysis, and IR, ${}^{31}P{}^{1}H{}$, and ${}^{1}H$ NMR spectroscopy† were consistent with the structure shown in Scheme 1 but its identity

[†] Spectroscopic data: ³¹P{¹H} NMR (**2a**) (isolated sample in dry CD₂Cl₂; ref. 85% H₃PO₄): δ 79.8 (OPPh₂, J_{PtP} 3760, J_{PP} 19 Hz), -8.1 (*P*MePh₂, J_{PtP} 4464, J_{PP} 19 Hz); (**2a**) (with water added to above solution): δ 85.5 (OPPh₂, J_{PtP} 4103, br), -9.2 (*P*MePh₂, J_{PtP} 3784 Hz); (**2b**) (CDCl₃) δ 79.3 (OPPh₂, J_{PtP} 3742, J_{PP} 22 Hz), 4.7 (*P*Ph₃, J_{PtP} 4464, J_{PP} 19 Hz); (**4a**) (CDCl₃): δ 49.8 (OPPh₂, J_{PtP} 4618, $3J_{PtP}$ 97, J_{PP} 9 Hz), -11.3 (*P*MePh₂, J_{PtP} 2882, $3J_{PtP}$ 361, $J_{PP'}$ 174 Hz); (**4b**) (CDCl₃): δ 49.4 (OPPh₂, J_{PtP} 4612, $3J_{PtP}$ 80, J_{PP} 9 Hz), 24.6 (*P*Ph₃, I_{PtP} , $3J_{PtP}$ not resolved).



Scheme 1. Reagents and conditions: (i) NaOH in water or dimethyl sulphoxide (dmso); (ii) concentrated aqueous HCl; (iii) HBF₄ in Et₂O or HPF₆ in water; (iv) EtOH at 70 °C.

could only be determined unambiguously by X-ray structure analysis of $(2a)(BF_4)_2 \cdot H_2O \cdot CH_2Cl_2$.‡ Figure 1 shows the molecular structure of the dication together with the water molecule that is hydrogen bonded to the μ_3 -OH group [O · · · 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 μ_3 -OH, and a PPh₂Me ligand. The Pt₃(μ_3 -OH) unit forms a shallow pyramid [Σ Pt-O-Pt angles 348.8(8)°], with non-bonding Pt · · · Pt edges (lengths 3.52— 3.71 Å). The ³¹P{¹H} 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

^{= 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, $\overline{\lambda}$ (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): C₅₀H₄₆O₂P₄Pt₂, 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, $D_x =$ $1.73 \text{ g cm}^{-3}, \overline{\lambda} (\text{Mo-}K_{\alpha}) = 0.71069 \text{ Å}, \mu = 32.7 \text{ cm}^{-1}, F(000) = 1156, T$ = 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 1. Molecular geometry of the dication (2a); important molecular geometry parameters include: interatomic distances (Å), Pt(1) \cdots Pt(2) 3.710(1), Pt(1) \cdots Pt(3) 3.700(1), Pt(2) \cdots Pt(3) 3.518(1), Pt(1)-P(2) 2.224(4), Pt(2)-P(3) 2.211(5), Pt(3)-P(1) 2.234(6), Pt(1)-O(1) 2.096(11), Pt(2)-O(2) 2.091(13), Pt(3)-O(3) 2.058(13), Pt(1)-P(5) 2.232(5), Pt(2)-P(6) 2.225(4), Pt(3)-P(4) 2.228(5), Pt(1)-O 2.157(12), Pt(2)-O 2.134(10), Pt(3)-O 2.153(11), P(1)-O(1) 1.554(12), P(2)-O(2) 1.548(12), P(3)-O(3) 1.565(12), O \cdots O(4a) 2.627(35); Bond angles (°) Pt(1)-O-Pt(2) 119.7(6), Pt(1)-O-Pt(3) 118.3(5), Pt(2)-O-Pt(3) 110.3(5).

general route to triplatinum complexes with μ -Ph₂PO ligands and indeed we have shown that such a route is viable for the synthesis of the Ph₃P complex (**2b**)[†] from (**1c**,d).

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



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(1) complex (4a) is deposited in *ca*. 50% yield. The ${}^{31}P{}^{1}H$ 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 BuⁱOH in reactions which may involve (as yet undetected) μ -OR intermediates. The Ph₃P analogue (4b) (characterised by its ³¹P{¹H} 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 Ph_2PO ligands can stabilise Pt–Pt bonds in low oxidation states and Pt_3 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).

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