

## X-Ray Crystal Structure of a Binuclear Platinum Complex, $[\text{Pt}(\text{Cl})\{\text{P}(\text{:O})\text{F}_2\}(\text{Et}_3\text{P})]_2$ , involving a Bridging Difluorophosphonate Ligand

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**Summary** A single crystal X-ray structure determination of the binuclear complex,  $[\text{Pt}(\text{Cl})\{\text{P}(\text{:O})\text{F}_2\}(\text{Et}_3\text{P})]_2$  has revealed the presence of the group  $[\text{P}(\text{:O})\text{F}_2]^-$  as both a terminal and a bridging ligand.

WE have recently reported the synthesis of a series of complexes of the platinum metals, especially Pt and Pd in which the anionic group,  $[\text{POF}_2]^-$ , functions as a terminal monodentate ligand, attached to the metal atom

via phosphorus, rather than oxygen;<sup>1,2</sup> structural characterization was by i.r. and n.m.r. spectroscopy,<sup>2,3</sup> and by X-ray crystallography.<sup>4,5</sup> We have now determined the structure of a binuclear complex of the composition  $[\text{Pt}(\text{Cl})\{\text{P}(\text{:O})\text{F}_2\}(\text{Et}_3\text{P})]_2$  (**1**) (Figure) by single crystal X-ray crystallography. A structure with two bridging chlorine atoms and two terminal difluorophosphonate ligands was originally suggested, although not unambiguously established, for this compound.<sup>2†</sup>

† *Crystal data*: (**1**), monoclinic  $P2_1/n$ ,  $a = 14.992(9)$ ,  $b = 13.496(6)$ ,  $c = 13.137(5)$  Å;  $\beta = 112.29(4)^\circ$ ;  $Z = 4$ ;  $D_c$  2.34 g cm<sup>-3</sup>.

The intensity data were collected on a Stoe diffractometer using Mo- $K_\alpha$  radiation by the  $\theta$ - $2\theta$  scan technique at a scan rate of 3° min<sup>-1</sup>. 4552 unique reflections were measured in the range of  $2\theta \leq 50^\circ$ . Data reduction included an absorption correction by a Gauss-numerical method (DRABSO, D. Schomburg) because of the very high absorption coefficient of 114.03 cm<sup>-1</sup>. Transmission factors varied between 3.06 and 15.06%. The structure was determined by Patterson and Fourier techniques (SHELX-76, G. M. Sheldrick). Least-square refinement using 3447 reflections with  $I \geq 2\sigma(I)$  led to reliability factors of  $R = 0.058$  and  $R_G = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{0.5} = 0.072$ .

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Compound (1), m.p. 192 °C, forms a dimer, involving bridging chlorine and a bridging  $[\text{POF}_2]^-$  group, with phosphorus and oxygen atoms being bonded to the two platinum atoms. The resulting five-membered ring is planar within experimental error. As a further consequence of this all the heavier atoms of the molecule are situated in one plane. In order to achieve planarity the angle at the bridging chlorine had to be widened to 111.9°, compared to angles of <100° which are found in four-membered  $\text{PtCl}_2\text{Pt}$  rings.<sup>6</sup>

The bond lengths for the Pt-Cl-Pt bridge of 2.382(4) and 2.408(5) Å are significantly greater than the terminal

Pt-Cl bond [2.325(4) Å] which is comparable to that in *trans*- $[\text{Pt}(\text{POF}_2)(\text{PEt}_3)_2\text{Cl}]$ .<sup>5</sup> The fact that the oxygen atom of the bridging  $[\text{POF}_2]^-$  group forms a dative bond to platinum causes a slight increase in the P-O bond length [1.498(16) Å], compared to 1.465(14) Å for the terminal P-O group. Bond angles at platinum are close to 90°; deviations are <7.5°, and are apparently dictated by the steric requirements of the ligands.

It has been observed that the group  $[\text{P}(\text{:O})(\text{OR})_2]^-$  can function as a bridging ligand between transition metal atoms<sup>7</sup> (*cf.* also ref. 8). We have observed for the first time that the difluorophosphonate group can form a bridge between metal atoms in a binuclear complex, and that it can be present both as a mono- and a bi-dentate ligand in the same complex. A system bearing some resemblance to ours has recently been discovered by Maitlis and his co-workers<sup>9</sup> who have observed the difluorophosphate ion  $\text{P}(\text{:O})\text{F}_2\text{O}^-$  to function as a bridging ligand between rhodium and iridium atoms.

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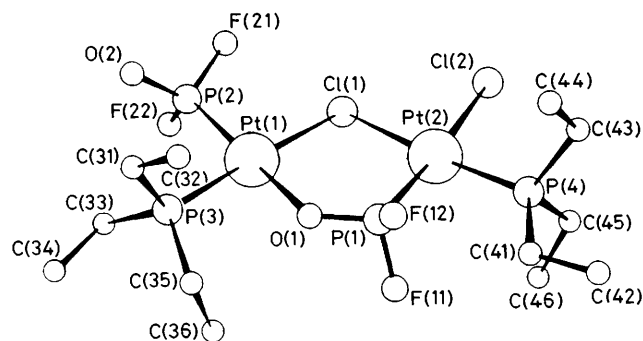


FIGURE. The structure of  $[\text{Pt}(\text{Cl})\{\text{P}(\text{:O})\text{F}_2\}(\text{Et}_3\text{P})]_2$  (1).

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<sup>1</sup> J. Grosse and R. Schmutzler, *Z. Naturforsch.*, 1973, **28b**, 515.

<sup>2</sup> J. Grosse and R. Schmutzler, *J.C.S. Dalton*, 1976, 405.

<sup>3</sup> J. Grosse and R. Schmutzler, *J.C.S. Dalton*, 1976, 412.

<sup>4</sup> J. Grosse, R. Schmutzler, and W. S. Sheldrick, *Acta Cryst.*, 1974, **B30**, 1623.

<sup>5</sup> D. Schomburg, unpublished results.

<sup>6</sup> M. Black, R. H. Mais, and P. G. Owston, *Acta Cryst.*, 1969, **B25**, 1760.

<sup>7</sup> For a recent review on complexes of substituted phosphinites and secondary phosphites, see: D. M. Roundhill, R. P. Sperline, and W. B. Beaulieu, *Coord. Chem. Rev.*, 1978, **26**, 263.

<sup>8</sup> W. Kläni and K. Dehnicke, *Chem. Ber.*, 1978, **111**, 451; H. Werner and T. N. Khac, *Inorg. Chim. Acta*, 1978, **30**, L347, and references quoted therein.

<sup>9</sup> S. J. Thompson, P. M. Bailey, C. White, and P. M. Maitlis, *Angew. Chem.*, 1976, **88**, 506; C. White, S. J. Thompson, and P. M. Maitlis, *J. Organometallic Chem.*, 1977, **134**, 319; P. M. Maitlis, personal communication.