

## Structure of $\{[\text{Bis}(\text{dimethyl phosphito})\text{difluoroborato}]-O,O'\}$ chloro-(triethylphosphine)platinum(II); $\text{PtCl}\{[\text{OP}(\text{OMe})_2]_2\text{BF}_2\}\text{PEt}_3$

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**Abstract.**  $\text{C}_{10}\text{H}_{27}\text{BClF}_2\text{O}_6\text{P}_3\text{Pt}$ ,  $M_r = 615.60$ , monoclinic,  $P2_1/c$ ,  $a = 7.980$  (3),  $b = 19.248$  (7),  $c = 14.240$  (5) Å,  $\beta = 93.72$  (2)°,  $Z = 4$ ,  $D_c = 1.873$  Mg m<sup>-3</sup>, Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å),  $\mu = 71.41$  mm<sup>-1</sup>.  $R = 0.090$  for 2032 reflections. The distances Pt–P(1), Pt–P(2) and Pt–P(3) are 2.263 (6), 2.194 (5) and 2.340 (6) Å and Pt–Cl is 2.338 (6) Å. The distances B–O(3), B–O(4), B–F(1) and B–F(2) are 1.46 (3), 1.46 (3), 1.31 (3), 1.40 (3) Å, and the Pt and  $\text{BF}_2$  groups have a chair conformation about the P–O plane.

**Introduction.** Dimethyl phosphite is a ligand of some potential advantage for use as a bridging ligand to link two dissimilar metal ions in regiospecific sites. The preferred synthetic approach to such compounds is to treat a complex of the first metal ion with dimethyl phosphite to yield a monomeric phosphorus-bonded complex. Commonly two or three dimethyl phosphite ligands coordinate, and the oxygen atoms are linked by a hydrogen bond (Roundhill, Sperline & Beaulieu, 1978). Removal of this proton yields a multidentate anionic ligand for coordination to a second metal ion (Sperline & Roundhill, 1977; Dixon & Rattray, 1977; Klaui, 1977, 1979, 1980; Dubler, Linowsky & Klaui, 1979; Harder, Dubler & Werner, 1974; Klaui & Werner, 1976; Werner & Khac, 1979; Robertson & Stephenson, 1980), or to capping by groups such as  $\text{BF}_2$  (Austin, 1966; Lovell, 1969; Klaui, Neukomm & Werner, 1977; Klaui & Dehnicke, 1978; Beaulieu, Rauchfuss & Roundhill, 1975). For complexes having a bis(dimethyl phosphite) ligand, either a chair or a boat form is possible. Previously it has been suggested that the hydrogen atoms in the compound  $\text{Pt}[(\text{OPPh}_2)_4\text{H}_2]$  are out of the P–O plane (Dixon & Rattray, 1971), but it is only when this proton has been replaced by a group such as  $\text{BF}_2$  that this premise can be verified.

The compound  $\text{PtCl}\{[\text{OP}(\text{OMe})_2]_2\text{BF}_2\}\text{PEt}_3$  has been prepared previously by treating the complex  $\text{PtCl}\{[\text{OP}(\text{OMe})_2]_2\text{H}\}\text{PEt}_3$  with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (Beaulieu, Rauchfuss & Roundhill, 1975). Since there has been no previous report of the crystal structure of a bidentate phosphinito mixed-metal complex we have solved the

structure of the title compound to find the platinum–boron separation and to deduce whether the six-membered ring adopts the chair or boat conformation. Since completion of this work we have learned of the structure determination of  $\text{Pt}\{[\text{OP}(\text{OMe})_2]_2\text{BF}_2\}_2$  (Berry, Bushnell & Dixon, 1982) which shows essentially the same structural features as  $\text{PtCl}\{[\text{OP}(\text{OMe})_2]_2\}\text{PEt}_3$ .

The compound  $\text{PtCl}\{[\text{OP}(\text{OMe})_2]_2\text{BF}_2\}\text{PEt}_3$  was prepared by published procedures. Slow evaporation of a dichloromethane solution left the compound as one crystal of approximate dimensions  $3 \times 3 \times 3$  mm.

A single piece of crystal was cut from the large crystal block. Lengths 0.091, 0.149, and 0.133 mm were measured along the faces of the crystal and the axes identified. The crystal was mounted on a glass fiber. From the observed extinctions  $h0l, l = 2n + 1, 0k0, k = 2n + 1$  the space group was identified as  $P2_1/a$ . The final lattice constants were determined from least-squares refinement of the reciprocal-lattice coordinates of 12 accurately centered reflections.

Intensity data were collected on an automated Picker full-circle diffractometer with Zr-filtered Mo  $K\alpha$  radiation. 2032 unique reflections were collected in the range  $4 \leq 2\theta \leq 40^\circ$  with a  $\theta$ – $2\theta$  scan with a scan width of  $1.8^\circ$  with 20 steps deg<sup>-1</sup> and 3.0 s step<sup>-1</sup>. The reflections  $4 \leq 2\theta \leq 20^\circ$  and  $20 \leq 2\theta \leq 40^\circ$  were collected with two separate filters of approximate transmission ratio 1:5. Of the 2032 reflections, 1565 were regarded as observed, *i.e.* with  $I \geq 3\sigma(I)$ . The standard deviation of each reflection was calculated by  $\sigma^2(I) = \text{TC} + \text{BG} + 0.03^2 I^2$ , where TC is total counts, BG is background counts, and  $I = \text{TC} - \text{BG}$ . The intensities of three reflections were monitored every 40 reflections to check for decomposition *etc.* These intensities decreased by approximately 15% during data collection, and a decay correction was applied to the data by using the *DIFFDAT* program before proceeding with further data treatment.

Data were corrected for absorption ( $\mu = 71.41$  mm<sup>-1</sup>, transmission factors ranged from 0.33 to 0.52) from optically measured crystal dimensions using *DIFFDAT*, and the position for the platinum atom was found from *MULTAN* (Main, Fiske, Hull, Les-

Table 1. Final fractional positional parameters and isotropic temperature factors with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> * (Å <sup>2</sup> )
Pt	0.1732 (1)	0.13506 (4)	0.25661 (6)	0.050
Cl	0.0450 (9)	0.1771 (4)	0.3883 (5)	0.089
P(1)	0.1173 (9)	0.0267 (3)	0.3078 (5)	0.078
P(2)	0.2874 (6)	0.0953 (3)	0.1313 (4)	0.048
P(3)	0.2305 (8)	0.2516 (3)	0.2244 (5)	0.065
O(1)	-0.066 (3)	0.011 (1)	0.329 (2)	0.122
O(2)	0.217 (3)	0.0186 (9)	0.411 (1)	0.111
O(3)	0.164 (3)	-0.0344 (7)	0.246 (1)	0.108
O(4)	0.272 (2)	0.0156 (7)	0.1117 (9)	0.059
O(5)	0.215 (2)	0.1276 (7)	0.0359 (9)	0.060
O(6)	0.479 (2)	0.1179 (7)	0.136 (1)	0.067
B	0.286 (4)	-0.044 (2)	0.176 (2)	0.073
F(1)	0.258 (2)	-0.1028 (6)	0.131 (1)	0.084
F(2)	0.446 (3)	-0.0416 (9)	0.221 (2)	0.146
C(1)	0.331 (3)	0.275 (1)	0.117 (2)	0.080
C(2)	0.366 (3)	0.286 (1)	0.321 (2)	0.078
C(3)	0.036 (3)	0.302 (1)	0.224 (2)	0.086
C(4)	0.358 (3)	0.353 (1)	0.101 (2)	0.095
C(5)	0.525 (4)	0.244 (2)	0.338 (2)	0.113
C(6)	-0.086 (4)	0.281 (2)	0.153 (2)	0.109
C(7)	-0.202 (5)	0.037 (2)	0.272 (3)	0.131
C(8)	0.226 (5)	-0.038 (2)	0.462 (3)	0.144
C(9)	0.056 (4)	0.111 (2)	-0.005 (2)	0.101
C(10)	0.579 (3)	0.100 (1)	0.055 (2)	0.089

\* Calculated for non-hydrogen atoms from anisotropic thermal parameters of the form  $\exp[-(\beta_{11}h^2 + \dots + 2\beta_{12}hk + \dots)]$  as  $U_{eq} = (a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33})/6\pi^2$ .

Table 2. Interatomic distances (Å) and angles (°)

Pt-P(1)	2.263 (6)	P(1)-Pt-P(2)	92.4 (2)
Pt-P(2)	2.194 (5)	P(1)-Pt-P(3)	172.5 (2)
Pt-P(3)	2.340 (6)	P(1)-Pt-Cl	87.4 (2)
Pt-Cl	2.338 (6)	P(2)-Pt-P(3)	94.4 (2)
Pt-B	3.76 (3)	P(2)-Pt-Cl	178.6 (2)
		P(3)-Pt-Cl	85.8 (2)
P(1)-O(1)	1.55 (2)	Pt-P(1)-O(1)	117.0 (9)
P(1)-O(2)	1.63 (2)	Pt-P(1)-O(2)	106.7 (7)
P(1)-O(3)	1.53 (2)	Pt-P(1)-O(3)	117.7 (7)
		O(1)-P(1)-O(2)	102.4 (14)
		O(1)-P(1)-O(3)	103.3 (12)
		O(2)-P(1)-O(3)	108.7 (11)
P(2)-O(4)	1.56 (1)	Pt-P(2)-O(4)	117.0 (5)
P(2)-O(5)	1.57 (1)	Pt-P(2)-O(5)	114.6 (5)
P(2)-O(6)	1.59 (1)	Pt-P(2)-O(6)	108.7 (5)
		O(4)-P(2)-O(5)	102.3 (7)
		O(4)-P(2)-O(6)	110.1 (7)
		O(5)-P(2)-O(6)	103.2 (8)
P(3)-C(1)	1.83 (3)	Pt-P(3)-C(1)	120.0 (8)
P(3)-C(2)	1.82 (3)	Pt-P(3)-C(2)	108.3 (8)
P(3)-C(3)	1.83 (3)	Pt-P(3)-C(3)	109.2 (9)
		C(1)-P(3)-C(2)	105.8 (11)
		C(1)-P(3)-C(3)	106.7 (12)
		C(2)-P(3)-C(3)	106.0 (12)
O(1)-C(7)	1.41 (4)	P(1)-O(1)-C(7)	121 (2)
O(2)-C(8)	1.31 (4)	P(1)-O(2)-C(8)	125 (2)
O(3)-B	1.46 (3)	P(1)-O(3)-B	134 (2)
O(4)-B	1.46 (3)	P(2)-O(4)-B	131 (2)
O(5)-C(9)	1.40 (3)	P(2)-O(5)-C(9)	123 (2)
O(6)-C(10)	1.49 (3)	P(2)-O(6)-C(10)	117.9 (13)
C(1)-C(4)	1.54 (3)	P(3)-C(1)-C(4)	116 (2)
C(2)-C(5)	1.51 (4)	P(3)-C(2)-C(5)	112 (2)
C(3)-C(6)	1.42 (4)	P(3)-C(3)-C(6)	113 (2)
B-F(1)	1.31 (3)	F(1)-B-F(2)	112 (3)
B-F(2)	1.40 (3)	F(1)-B-O(3)	110 (2)
B-O(3)	1.46 (3)	F(1)-B-O(4)	112 (2)
B-O(4)	1.46 (3)	F(2)-B-O(3)	108 (2)
		F(2)-B-O(4)	107 (2)
		O(3)-B-O(4)	107 (2)

singer, Germain, Declercq & Woolfson, 1980) and Patterson maps. The positions for other nonhydrogen atoms were found from Fourier mapping techniques. At the stage of refinement where all atoms other than C and H were anisotropic, and all C atoms were isotropic, all nonhydrogen parameters for 1565 reflections with  $I \geq 3\sigma(I)$  converged to an  $R = \sum |F_o| - |F_c| / \sum |F_o|$  of 0.063 and  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$  of 0.060. The hydrogen atoms in the molecule were identified using a combination of Fourier-difference mapping techniques and the *HYDRA* program. Final refinement using all 2032 reflections with the hydrogen atoms in fixed positions led to  $R = 0.090$  and  $R_w = 0.068$ . Refinement was not continued beyond this point because the somewhat high thermal parameters of C(7) and C(8) indicated possible disorder.

The parameter shifts on the last cycle were less than 5% of the value of their estimated error. The goodness of fit was 1.337 with  $w = 1/\sigma^2(F)$ . Scattering factors for Pt, Cl, P, C, O, B, and F were taken from *International Tables for X-ray Crystallography* (1968). Computer programs used are part of a local library. Final parameters are listed in Table 1 and bond distances and angles are given in Table 2.\*

**Discussion.** The crystal structure of PtCl{[OP(OMe)<sub>2</sub>]<sub>2</sub>BF<sub>2</sub>}PEt<sub>3</sub> shows a planar coordination about platinum and a tetrahedral geometry around boron. The bidentate phosphito ligand adopts a P(1)-Pt-P(2) bite angle of 92.4 (2)° which is close to the ideal value about platinum. The high *trans* influence (Roundhill, Sperline & Beaulieu, 1978; Bennett, Pidcock, Waterhouse, Coggon & McPhail, 1970; Chatt & Heaton, 1968) of the secondary phosphite ligand is shown by the long Pt-PEt<sub>3</sub> distance of 2.340 (6) Å as compared to the Pt-P distances 2.263 (6) and 2.194 (5) Å to the dimethyl phosphito ligand. The short Pt-P(2) distance is a consequence of the low *trans* influence of the Cl ligand. The angles about P(1) and P(2) show significant deviation from the tetrahedral values. The ring angles Pt-P(1)-O(3) and Pt-P(2)-O(4) have values of 117.7 (7) and 117.0 (5)°, indicating that the chelated BF<sub>2</sub> introduces some steric constraints into the ring. This, consequently, reflects in two of the other O-P-O angles about each phosphorus being 103.2 (8) and 102.3 (7) and 102.4 (14) and 103.3 (12)°. These small angles are the angles subtended by the methoxy groups at platinum, and the angles between the ring oxygen and an axial and an equatorial methoxy-group oxygen respectively. The angles about boron are the same, within experimental error, with the value of tetrahedral angles.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36885 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

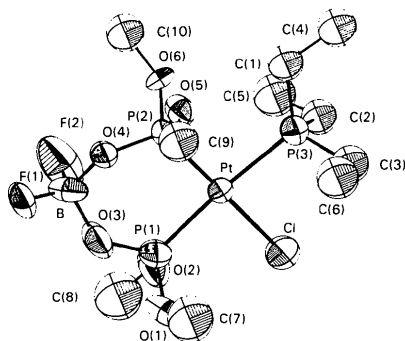


Fig. 1. ORTEP (Johnson, 1965) drawing of PtCl{[OP(OMe)<sub>2</sub>]<sub>2</sub>BF<sub>2</sub>}PEt<sub>3</sub> with 50% probability thermal ellipsoids showing stereochemistry and ring structure.

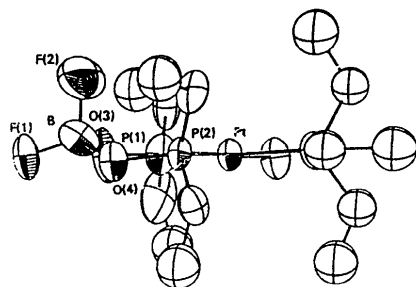


Fig. 2. ORTEP (Johnson, 1965) drawing of PtCl{[OP(OMe)<sub>2</sub>]<sub>2</sub>BF<sub>2</sub>}PEt<sub>3</sub> with 50% probability thermal ellipsoids showing chair conformation of the ring.

From Figs. 1 and 2 it is apparent that the ring has a chair conformation with the platinum and BF<sub>2</sub> substituents on opposite sides of the P–O plane. This conformation causes Pt and BF<sub>2</sub> to be widely separated at 3.76 (3) Å. We believe that this is the first determination of the conformation of a complexed phosphinito or secondary phosphito ring. This conformation is the anticipated one but there is no literature on the energetics of the boat–chair interconversion in such compounds. The smaller O(1)–P(1)–O(3) and O(4)–P(2)–O(5) angles of 103.3 (12) and 102.3 (7)° represent an axial and an equatorial angle to the respective ring oxygens O(3) and O(4).

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