oriented within the same plane containing the presumed planar $Co_2(CO)_2$ core as found[15] for each of the two centrosymmetrically related methylcyclopentadienyl rings in the $Ni_2(\eta^5\text{-}C_5H_4Me)_2(\mu\text{-}CO)_2$ dimer, which contains a planar $Ni_2(CO)_2$ core) and (2) the solid-state structure of the $[Co_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2]^-$ monoanion as the $[Na(2,2,2\text{-crypt})]^+$ salt exhibiting a large sterically induced distortion from planar C_{2v} symmetry in contrast to that found for its oxidized neutral parent. It is also evident that dilute single-crystal ESR studies of these monoanions doped in suitable diamagnetic hosts are highly desirable in order to reveal the full nature of the hyperfine interaction and thereby enable one to delineate more clearly a comparative bonding description of the unpaired electron in these dimeric radicals.

Acknowledgment. We are pleased to acknowledge support of this research by the National Science Foundation. We also wish to thank Mr. Mark A. Murphy and Mr. Don M. Washecheck for special experimental assistance.

Registry No. 1a, 80127-68-0; **1b**, 58636-28-5; **3a**, 72271-22-8; **4**, 69657-52-9; $[Na]^+[Co_2(\eta^5\text{-}C_5H_5)_2(CO)_2]^-$, 62602-00-0; $[Na]^+$-$[Co_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2]^-$, 71618-09-2; $Co(\eta^5\text{-}C_5H_5)(CO)_2$, 12078-25-0; $Co(\eta^5\text{-}C_5Me_5)(CO)_2$, 12129-77-0; $Co_2(CO)_8$, 10210-68-1.

Supplementary Material Available: Selected least-squares planes (Tables III, VI, and IX) together with a listing of the observed and calculated structure factor amplitudes for $[AsPh_4]^+[Co_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)_2]^-$ and $Co_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2$ (25 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of Victoria, Victoria, British Columbia, Canada, V8W 2Y2

Coordination Chemistry of Bridging PR_2-O Ligands. Crystal and Molecular Structure of Bis(bis(dimethyl phosphito)difluoroborato)platinum(II), $[Pt((P(OMe)_2O)_2BF_2)_2]$

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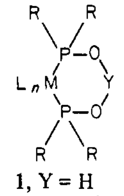
Crystals of $[Pt((P(OMe)_2O)_2BF_2)_2]$ are triclinic, space group $P\bar{1}$, with a = 8.331 (3) Å, b = 9.794 (4) Å, c = 7.840 (2) Å, α = 96.19 (5)°, β = 99.65 (3)°, and γ = 111.92 (4)° for Z = 1. The structure shows square-planar platinum coordination and a chair conformation for the six-membered rings, $\overline{\mathrm{PtP(OMe)_2OB(F_2)OP}}\mathrm{(OMe)_2}$, such that the platinum and boron atoms lie respectively +0.623 and −0.543 Å on opposite sides of the mean plane defined by the P_2O_2 ring section. A reinvestigation by ^{31}P NMR does not support a previous claim for formation of tetraphosphorus macrocyclic ligands by hydrolysis of $[Pt((P(OMe)_2O)_2BF_2)_2]$.

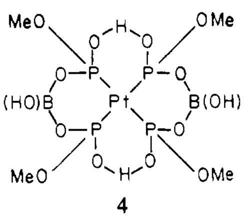
Introduction

Several recent studies have shown that whenever PR_2O^- and PR_2OH ligands occupy mutually cis positions in a coordination complex, a hydrogen-bonded system, **1**, is formed.[1,2] Removal of the hydrogen-bonded proton yields an anionic ligand, formally analogous to acetylacetonate, which can coordinate to a second metal[1,3,4] or be capped by groups such as BF_2.[1,3] Bimetallic complexes such as **2** are of considerable interest both as a means of holding two different metals in close proximity for catalysis studies and as a possible route to chain oligomers having different metal ions in specific ligand sites.[4]



1, Y = H
2, Y = M′
3, Y = BF_2

The range of potential geometries for the six-membered ring systems in complexes **1**–**3** may be illustrated by the related bis(pyrazolyl)-bridged complexes where conformations range from the chair structure of $[(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}C_3N_2H_3)]_2$[5] through planar for $[Ni(NO)(\mu\text{-}C_3N_2HMe_2)]_2$[6] to boat shaped in a cobalt(I) analogue.[7] For the present complexes the only available crystal structure determinations are for the hydrogen-bonded rings in $[Pd_2(\mu\text{-}NCS)_2((PPh_2O)_2H)_2]$[8] and $[Pd(S_2PMe_2)((PPh_2O)_2H)]$,[9] where it was not possible to locate the hydrogen atoms and hence establish the ring conformation. We have experienced difficulty in obtaining suitable crystals of several bimetallic systems of type **2** and hence decided to study initially the ring conformation in the known BF_2 capped complex $[Pt((P(OMe)_2O)_2BF_2)_2]$.[10] This system is also of interest because of earlier uncertainty as to whether $[Pt((P(OMe)_2O)_2BF_2)_2]$ or $[Pt((P(OMe)_2O)_2BF)_2]F_2$ is the correct formulation and because of the suggestion that hydrolysis leads to the macrocyclic complex, **4**, which may be converted to **5** by further reaction with BF_3·OEt_2.[10] Macrocyclic phosphorus ligands are very rare,[11] and we were therefore interested in obtaining definitive evidence for complexes **4** and **5**. We now



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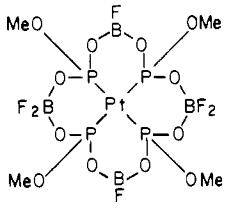

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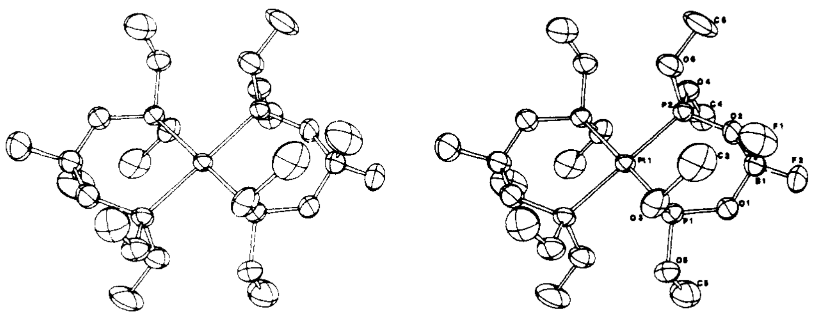

Figure 1. Stereoview of the molecular structure of $[Pt((P(OMe)_2O)_2BF_2)_2]$.

report (i) a crystal and molecular structure determination of $[Pt((P(OMe)_2O)_2BF_2)_2]$, which confirms the nonionic formulation and shows chair conformations for the six-membered rings and (ii) reactivity and NMR studies which indicate that formation of macrocyclic ligands probably does not occur in these systems.

During the preparation of this work for publication we became aware of a study by Roundhill and Roundhill on the related complex $[PtCl((P(OMe)_2O)_2BF_2)(PEt_3)]$.[12]

Results and Discussion

(A) Synthetic and ^{31}P NMR Studies. As reported previously, $[Pt((P(OMe)_2O)_2H)_2]$ is readily prepared from trimethyl phosphite and aqueous potassium tetrachloroplatinite(II).[10,13] Subsequent reaction with excess boron trifluoride etherate generates $[Pt((P(OMe)_2O)_2BF_2)_2]$,[10] which we have completely characterized by the X-ray diffraction study reported below. However, when the reaction with $BF_3 \cdot OEt_2$ is conducted by careful addition of successive aliquots of the etherate, with monitoring of the reaction by ^{31}P NMR spectroscopy at each stage, an intermediate product is observed. Thus, addition of 1 equiv of $BF_3 \cdot OEt_2$ to $[Pt((P(OMe)_2O)_2H)_2]$ results, over 20 h, in gradual replacement of ^{31}P NMR signals due to the starting material (−49.9 ppm, J(Pt–P) = 3473 Hz) by signals due to the intermediate (−52.6 ppm, J(Pt–P) = 3517 Hz). Addition of a second equivalent (or excess) of $BF_3 \cdot OEt_2$ then results in rapid formation of $[Pt((P(OMe)_2O)_2BF_2)_2]$ (−55.5 ppm, J(Pt–P) = 3580 Hz). All three ^{31}P NMR spectra consist of simple 1:4:1 triplets due to coupling of a single phosphorus environment with Pt ($I = ^1/_2$, 33.8% abundant).

The previous suggestion that hydrolysis of $[Pt((P(OMe)_2O)_2BF_2)_2]$ yields the macrocycle **4** which may be converted to **5** by subsequent reaction with $BF_3 \cdot OEt_2$[10] was based only on analytical and infrared evidence. In our hands the literature hydrolysis procedure gave a product mixture shown by ^{31}P NMR to contain only the unknown intermediate and unreacted $[Pt((P(OMe)_2O)_2BF_2)_2]$. Reaction of this mixture with $BF_3 \cdot OEt_2$ regenerated pure $[Pt((P(OMe)_2O)_2BF_2)_2]$. Unfortunately, although the reaction of $[Pt((P(OMe)_2O)_2H)_2]$ with 1 equiv of $BF_3 \cdot OEt_2$ generates the unknown intermediate ~90% pure by ^{31}P NMR spectroscopy, all attempts to obtain crystalline samples gave good crystals only of $[Pt((P(OMe)_2O)_2BF_2)_2]$. The most likely formulation of the unknown seems to be $[Pt((P(OMe)_2O)_2BF_2)((P(OMe)_2O)_2H)]$ with the AA′BB′ spin system so closely coupled that it appears as a singlet in the ^{31}P NMR spectrum even at 101.2 MHz. The unknown is formed by $[Pt((P(OMe)_2H)_2]$ with 1 equiv of $BF_3 \cdot OEt_2$ and is subsequently converted to $[Pt((P(OMe)_2O)_2BF_2)_2]$ by excess $BF_3 \cdot OEt_2$; hence, the unknown cannot be either of the macrocycles **4** or **5**, and there is no evidence for production of macrocycles from hydrolysis of $[Pt((P(OMe)_2O)_2BF_2)_2]$.

Table I. Fractional Atomic Coordinates (×10^4)[a]

atom	x	y	z
Pt	0	0	0
P(1)	1976 (2)	−377 (2)	2120 (2)
P(2)	1600 (2)	2547 (2)	825 (2)
F(1)	6231 (7)	3167 (6)	3282 (8)
F(2)	4023 (11)	2857 (8)	4737 (8)
O(1)	3870 (7)	873 (6)	2686 (7)
O(2)	3558 (8)	3069 (6)	1759 (8)
O(3)	2358 (8)	−1822 (6)	1706 (8)
O(4)	1710 (8)	3512 (6)	−668 (7)
O(5)	1113 (8)	−648 (7)	3748 (7)
O(6)	596 (8)	3153 (6)	2015 (8)
C(3)	3415 (17)	−1933 (13)	481 (20)
C(4)	2723 (15)	3432 (11)	−1964 (14)
C(5)	2029 (19)	−877 (16)	5374 (13)
C(6)	1240 (20)	4720 (10)	2835 (17)
B	4436 (11)	2519 (8)	3185 (11)

[a] Estimated standard deviations are given in parentheses.

Table II. Bond Lengths (Å)[a]

Pt–P(1)	2.297 (2)	Pt–P(2)	2.302 (2)
P(1)–O(1)	1.547 (5)	P(2)–O(2)	1.534 (6)
P(1)–O(3)	1.576 (6)	P(2)–O(4)	1.576 (5)
P(1)–O(5)	1.566 (6)	P(2)–O(6)	1.561 (6)
O(1)–B	1.486 (9)	O(2)–B	1.49 (1)
O(3)–C(3)	1.43 (1)	O(4)–C(4)	1.44 (1)
O(5)–C(5)	1.46 (1)	O(6)–C(6)	1.45 (1)
B–F(1)	1.37 (1)	B–F(2)	1.36 (1)

[a] Estimated standard deviations are given in parentheses.

Table III. Bond Angles (Deg)[a]

P(1)–Pt–P(2)	89.70 (6)		
Pt–P(1)–O(1)	116.5 (2)	Pt–P(2)–O(2)	116.5 (2)
Pt–P(1)–O(3)	117.3 (2)	Pt–P(2)–O(4)	117.4 (2)
Pt–P(1)–O(5)	106.9 (2)	Pt–P(2)–O(6)	106.9 (2)
O(1)–P(1)–O(3)	102.1 (3)	O(2)–P(2)–O(4)	102.4 (3)
O(3)–P(1)–O(5)	102.6 (3)	O(4)–P(2)–O(6)	102.5 (3)
O(5)–P(1)–O(1)	110.5 (3)	O(6)–P(2)–O(2)	110.3 (3)
P(1)–O(1)–B	129.4 (5)	P(2)–O(2)–B	131.3 (5)
P(1)–O(3)–C(3)	121.4 (6)	P(2)–O(4)–C(4)	121.1 (6)
P(1)–O(5)–C(5)	122.1 (7)	P(2)–O(6)–C(6)	122.9 (7)
O(1)–B–F(1)	107.2 (6)	O(2)–B–F(1)	107.1 (6)
O(1)–B–F(2)	110.2 (7)	O(2)–B–F(2)	110.7 (7)
O(1)–B–O(2)	109.5 (6)	F(1)–B–F(2)	112.1 (7)

[a] Estimated standard deviations are given in parentheses.

(B) Crystal and Molecular Structure of $[Pt((P(OMe)_2O)_2BF_2)_2]$. Stereoscopic views of the molecular structure and the crystal packing are shown in Figure 1 and 2. Figure 1 also shows the atom labeling scheme and the thermal vibration ellipsoids. Fractional atomic coordinates, bond lengths, and bond angles are collected in Tables I–III, respectively, and further tables of anisotropic temperature factors, atomic coordinates for the hydrogen atoms, intermolecular contacts, and structure factors have been deposited.

The platinum coordination is exactly planar by symmetry since the symmetric unit is half of the molecule which is

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(12) Roundhill, S. G. N.; Roundhill, D. M., private communication.
(13) Troitskaya, A. D.; Itskovich, T. B. *Tr. Kazan. Khim.-Teknol. Inst.*, **1954–55**, 79.

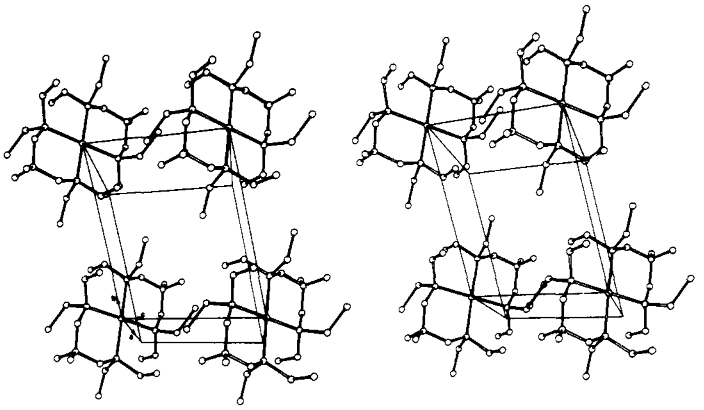

Figure 2. Stereoview of the crystal packing in $[Pt((P(OMe)_2O)_2BF_2)_2]$.

repeated by inversion through the origin at the platnium atom. The angles about platinum are close to 90°, and the bond lengths (mean 2.300 Å) are normal for Pt–P bonds trans to phosphorus.[14] The geometry about boron is closely tetrahedral. Within the six-membered rings, the 90° angle at platinum is accommodated by the larger (relative to tetrahedral) angles at phosphorus (Pt–P(1)–O(1) and Pt–P(2)–O(2) are 116.5 (2)°). However, angles of this magnitude at phosphorus are not specific to the ring systems as similar angles have been observed in platinum $P(OR)_3$ complexes,[17] and M–P–C angles in $M(PR_3)$ complexes are greater than the ideal tetrahedral value. The relative small size of the oxygen and boron atoms at the BF_2 end of the ring is accommodated by the large B–O(1)–P(1) and B–O(2)–P(2) angles (129.4 (5) and 131.3 (5)°, respectively).

The six-membered rings adopt a distorted chair conformation in which the platinum and boron atoms lie respectively at +0.623 and –0.543 Å on opposite sides of the mean plane defined by the two P–O bonds (i.e., P(1), P(2), O(1), and O(2)). In the previous X-ray study of $[Pd(S_2PMe_2)((PPh_2O)_2H)]$ the palladium was 0.661 Å from the corresponding plane.[9] The authors viewed this displacement as a rotation of each ligand about the Pd–P bond from the position in which the P_2O_2 plane would coincide with the Pd coordination plane. They considered the actual angle of rotation to be a compromise between the tendency for smaller rotations to decrease the O···O separation and of greater rotations to bring two phenyl rings into contact.[9] The conformation in our complex may be viewed in a similar way. The O(1)···O(2) distance is constrained by the bonding to boron, rather than the more flexible hydrogen bond found in the palladium complex, and the exact displacement of platinum from the P(1),P(2),O(1),O(2) plane is apparently controlled by steric interactions between the methoxy oxygens. Thus the degree of rotation about the Pt–P bond is such that the methoxy oxygens on one asymmetric unit interlock with those on the inverse unit, the important intramolecular contacts being O(3)′–O(4) = O(3)–O(4)′ = 3.080 Å and O(4)–O(5)′ = O(4)′–O(5) = 3.308 Å.[18]

A further interesting feature of these structures is the great geometrical similarity of the MP_2O_2 ring section in the present complex and in the previous examples where the ring was completed by a hydrogen bond instead of the BF_2 group.[19] Thus the Pt–P(1)–O(1) and Pt–P(2)–O(2) angles are 116.5 (2)° in our structure compared with 114.6 (4)° in $[Pd(S_2PMe_2)((PPh_2O)_2H)$;[9] the ring P–O bond lengths are 1.54 Å (av) compared with 1.545 Å in $[Pd(S_2PMe_2)((PPh_2O)_2H)]$[9] and 1.543 Å in $[Pd_2(\mu\text{-}NCS)_2((PPh_2O)_2H)_2]$, and the nonbonded distance between the ring oxygens is 2.43 Å compared with 2.414 Å in $[Pd(S_2PMe_2)((PPh_2O)_2H)]$.[9] The constancy of the ring P–O lengths is especially interesting in that a reduction in bond order might have been expected on replacing the hydrogen bond by BF_2.

The shortest of the intermolecular contacts are of the F–C(methyl) type. In the range 3.00–3.30 Å there are three such contacts which probably involve weak hydrogen bonding.

Experimental Section

(A) Synthetic and NMR Studies. Phosphorus-31 NMR spectra were recorded in dichloromethane solution at 24.29 MHz on a Nicolet TT14 Fourier transform spectrometer using a Varian HA60 magnet. Protons were decoupled by broad-band ("noise") irradiation at appropriate frequencies. $P(OCH_3)_3$ was used as external reference and C_6D_6 as external lock. Negative chemical shifts are upfield from the reference. A ^{31}P spectrum of the unknown intermediate was also recorded at 101.2 MHz on a Bruker WP250 spectrometer.

Microanalyses were by Canadian Microanalytical Service Ltd., Vancouver, B.C.

$[Pt((P(OMe)_2O)_2H)_2]$. This complex was prepared essentially as previously described.[10,13] $P(OMe)_3$ (0.60 mL, 5.1 mmol) was added to a solution of K_2PtCl_4 (0.50 g, 1.2 mmol) in water (35 mL) and the mixture stirred under a nitrogen atmosphere for 48 h. The product was obtained as a white precipitate (0.33 g, 0.52 mmol) and purified by crystallization from dichloromethane solution by addition of diethyl ether; mp 172–173 °C. Anal. Calcd for $C_8H_{26}O_{12}P_4Pt$: C, 15.2; H, 4.11. Found: C, 15.3; H, 4.14.

Reaction of $[Pt((P(OMe)_2O)_2H)_2]$ with $BF_3{\cdot}OEt_2$. Successive aliquots of a solution of $BF_3{\cdot}OEt_2$ in diethyl ether (0.50 mL diluted to 10 mL, i.e., 1 mL solution contains 1.19 mmol of BF_3) were added to an NMR tube containing $[Pt((P(OMe)_2O)_2H)_2]$ (0.215 g, 0.339 mmol) in dichloromethane. The reaction was monitored by ^{31}P NMR spectroscopy during gradual addition of 1.02 mmol of BF_3 over a total period of ~48 h. The final product, $[Pt((P(OMe)_2O)_2BF_2)_2]$ was isolated by evaporation of the solution under reduced pressure and recrystallization of the residues from dichloromethane solution by addition of diethyl ether; mp 223–225 °C. Samples were also prepared as previously described.[10] Anal. Calcd for $C_8H_{24}B_2F_4O_{12}P_4Pt$: C, 13.2; H, 3.3. Found: C, 13.5; H, 3.1.

Hydrolysis of $[Pt((P(OMe)_2O)_2BF_2)_2]$. This was carried out exactly as previously described.[10] $[Pt((P(OMe)_2O)_2BF_2)_2]$ (0.085 g, 0.12 mmol) was heated under reflux for 55 h in a mixture of chloroform (70 mL), tetrahydrofuran (12 mL), pinene (0.15 mL), and water (0.02 mL). The products and their subsequent reaction with $BF_3{\cdot}OEt_2$ were characterized by ^{31}P NMR spectroscopy as described in Results.

(B) Crystal Measurements. Crystals of $[Pt((P(OMe)_2O)_2BF_2)_2]$ were grown by vapor diffusion of diethyl ether into a solution in

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(14) See, for example, the Pt–P bonds in *trans*-$[PtCl_2(PEt_3)_2]$, 2.300 (19) Å,[15] and *trans*-$[Pt(SC_6F_5)_2(P\text{-}n\text{-}Bu_3)_2]$, 2.329 Å.[16]

(15) Messmer, G. G.; Amma, E. L. *Inorg. Chem.* **1966**, *5*, 1775.

(16) Fenn, R. H.; Segrott, G. R. *J. Chem. Soc. A* **1970**, 2781.

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(18) It is interesting that in the structure of $[PtCl((P(OMe)_2O)_2BF_2)(PEt_3)]$, determined by Roundhill and Roundhill,[12] there are no such steric constraints and the Pt atom lies only 0.122 Å from the P_2O_2 plane.

(19) Similar Pt–P–O angles and P–O and O···O lengths are also found in $[PtCl((P(OMe)_2O)_2BF_2)(PEt_3)]$.[12]

dichloromethane. X-ray photographs were taken with Cu Kα radiation. A Picker 4-circle diffractometer automated by a PDP-11 computer, with Zr-filtered Mo K$\bar{\alpha}$ X-rays ($\lambda = 0.71069$ Å) was then used. The unit cell was refined by least-squares methods employing 21 pairs of centering measurements (obtained at $\pm 2\theta$) in the range $|2\theta| = 21$–44°. The crystal was mounted along the *b* axis. The crystal data at 25 °C are as follows: space group $P\bar{1}$; $a = 8.331$ (3), $b = 9.794$ (4), $c = 7.840$ (2) Å; $\alpha = 96.19$ (5), $\beta = 99.65$ (3), $\gamma = 111.92$ (4)°; (Delaunay reduced cell) V(cell) = 574.8 (3) Å^3; $D_m = 2.113$ (5) g cm^{-3} (flotation in $CCl_4/CHBr_3$) $D_c = 2.105$ g cm^{-3}; $Z = 1$; formula $C_8H_{24}B_2F_4O_{12}P_4Pt$; $M_r = 728.75$. One reciprocal space hemisphere of intensity measurements ($h \geq 0$) were done up to $2\theta = 60°$. A $\theta/2\theta$ step scan was used with 50 steps of 0.04° in 2θ, counting for 1 s per step. Background measurements were for 25 s at each end of the scan. Three standards, −2,−2,0, 4,−1,−4, and 0,−4,0, preceded each batch of 50 intensity measurements and were used to correct the intensities for instrument instability and beam variations. The intensities were corrected with the Lorentz and polarization factors. Absorption corrections were applied with a numerical integration procedure utilizing a Gaussian grid (4 × 12 × 12). The crystal shape was defined by perpendicular distances to crystal faces from a central origin as follows: {100}, 0.0517 mm; {010}, 0.222 mm; {001}, 0.187 mm. The absorption coefficient was 68.1 cm^{-1}, and the range of correction factors was 0.12–0.52. The computer program has been tested.[20] The final file contained 3124 independent reflections.

(C) Crystal Structure Solution and Refinement. The structure was solved by standard heavy-atom methods. The refinement was by least squares, using a full matrix, and minimizing $\sum w(|F_o| - |F_c|)^2$. The atomic scattering factors were from ref 21 with Pt treated as an anomalous scatterer. A weighting scheme was used in the final stages of refinement: $w = (A + Bx + Cx^2 + Dx^3)^{-1}$, where $x = |F_o|$ and $A = 17.1221$, $B = -1.52881$, $C = 5.2126 \times 10^{-2}$, $D = -1.96 \times 10^{-4}$. The positions of the methyl hydrogen atoms were calculated with the assumption that the POCH torsion angles are consistent with staggered geometry as seen along the O–C bond directions and that the C–H bond lengths were 1.09 Å. The final two cycles of least squares gave convergence at $R = 0.050$ with a maximum change/error ratio of 0.47. The final difference map was satisfactory. The errors in bond lengths and angles were calculated from all components of the variance/covariance matrix. The main computer programs used for this work were supplied by Penfold[22] and are modified versions of ORFLS, FORDAP, ORFFE, and ORTEP. The diffractometer programs were written in this laboratory. The determined atomic coordinates are given in Table I. The hydrogen atom coordinates, the temperature factors, intermolecular contacts, and the structure factor tables have been deposited.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the University of Victoria for research grants, Bruker Canada Ltd. for recording a ^{31}P NMR spectrum at 101.2 MHz, Mrs. K. Beveridge for technical assistance in the crystal structure determination, and Dr. S. J. Cartwright for some preliminary synthetic work.

Registry No. $Pt((POMe)_2O)_2BF_2)_2$, 80041-62-9; $Pt((P(OMe)_2O)_2H)_2$, 30053-63-5; $BF_3 \cdot OEt_2$, 109-63-7.

Supplementary Material Available: Tables of calculated fractional atomic coordinates of the hydrogen atoms (Table S1), interatomic distances (Table S2), anisotropic temperature parameters (Table S3), and observed and calculated structure factor amplitudes (Table S4) (13 pages). Ordering information is given on any current masthead page.

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Oxy and Thio Phosphorus Acid Derivatives of Tin. 10. Crystal and Molecular Structure of Triphenyltin(IV) Diphenyl Phosphate, a Cyclic Hexamer[1]

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(Diphenyl phosphato)triphenyltin(IV), $C_{30}H_{25}O_4PSn$, forms colorless crystals, mp = 178–180 °C, in the triclinic space group $P\bar{1}$ with $a = 21.814$ (16) Å, $b = 20.724$ (9) Å, $c = 10.117$ (5) Å, $\alpha = 99.25$ (3)°, $\beta = 92.70$ (3)°, $\gamma = 114.52$ (4)°, $V = 4073.9$ Å^3, $Z = 6$, and $\rho_{calcd} = 1.465$ g cm^{-3}. The structure was solved by three-dimensional Patterson and difference Fourier techniques from 9953 reflections measured at 138 ± 2 K on an Enraf-Nonius CAD/4 automatic diffractometer using monochromated Mo Kα radiation to a final R value of 0.048 for the 8336 reflections included in the least-squares sums. The molecular units associate to form a centrosymmetric, cyclic hexamer in which planar triphenyltin(IV) groups are axially bridged by –O–P–O– linkages of the diphenyl phosphate ligand to form almost perfect trigonal bipyramids at tin. The structure of the ring is linear at tin but bent through an average O–P–O angle of 118.5°. The intrachain tin–oxygen and phosphorus–oxygen bonds are virtually symmetrical, indicating extensive delocalization of the P=O double bond. The ring is slightly puckered into a chair conformation with the phenoxy groups at each phosphorus pointing out from the center in an eclipsed array of phosphorus connections. However, one of the phenyl groups on each tin atom protrudes toward the center of the ring, with such phenyls lying alternately above and below the ring plane to produce a staggered array of triphenyltin groups. The adjacent hexameric unit along the *c* axis then nestles into the stack to fill space efficiently. A pentameric ring would be the smallest that could accommodate the axially bridged triphenyltin trigonal bipyramids, but expansion to the hexamer is necessary to accommodate the phenyl rings in the interior of the ring. No other examples of small oligomeric rings containing axially bridged trigonal-bipyramidal tin(IV) of any size are known.

We have been investigating the syntheses[1,3,4] and structures[5-8] of organotin(IV) derivatives of oxy and thio phosphorus acids in which biocidal activity is a property of both the tin and phosphorus portions of the molecule. As part of this

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(1) For the previous paper in this series see: Molloy, K. C.; Nasser, F. A. K.; Zuckerman, J. J. *Inorg. Chem.*, in press.

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