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Polyphosphinoylmethanide complexes of tin(II). Crystal and molecular structure of $\{[(C_6H_5)_2PO]_3C\}_2Sn$

Daniel L. Reger*, Steven J. Knox and **Lukasz Lebioda**
Department of Chemistry, University of South Carolina, Columbia, SC 29208 (U.S.A.)

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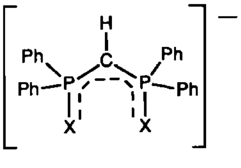
Abstract

The reaction of $SnCl_2$ and two equiv. of $Na\{[(C_6H_5)_2PO]_3C\}$ yields $\{[(C_6H_5)_2PO]_3C\}_2Sn$ (**1**). The solid state structure of **1** has been determined by X-ray crystallography: trigonal, space group $R\bar{3}c$, with $a=29.216(3)$, $c=42.120(5)$ Å, $V=31.136$ Å^3 and $Z=18$. Both potentially tridentate $[(C_6H_5)_2PO]_3C$–ligands are coordinated to the tin atom in a bidentate manner. The coordination geometry about tin is a pseudo trigonal bipyramid. Each phosphinoylmethanide ligand occupies an axial and equatorial site with the remaining equatorial site filled by the lone pair on tin. The reaction of $Na\{[(C_6H_5)_2PO]_2CH\}$ and $SnCl_2$ yields the analogous complex $\{[(C_6H_5)_2PO]_2CH\}_2Sn$ (**2**).

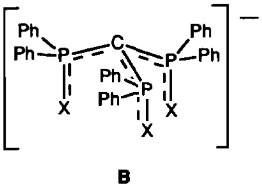
Introduction

We have recently been exploring the chemistry of the metals in groups 13 and 14 using anionic, chelating ligands. Our initial interest has been with the poly(pyrazolyl)borate family of ligands [1]. An interesting feature of this ligand family is the potential to prepare similar complexes from both the bidentate bis(pyrazolyl)borate ligands and tridentate tris(pyrazolyl)borate ligands. Thus, for example, we have prepared and are exploring the chemistry of $[H_2B(pz)_2]_mMCl_n(CH_3)_p$ [2] and $[HB(pz)_3]_mMCl_n(CH_3)_p$ [3] ($M=Ga$, In; $m+n+p=3$) complexes. Similar tin(II) complexes are also under investigation [3].

Another class of anionic ligands for which both the bidentate and umbrella type tridentate forms are known are the polyphosphinoylmethanides, **A** and **B**.



A



B

The coordination chemistry of the bidentate ligands ($X=S$, Se) has been explored previously by one of us [4] and has also been used by others [5]. Recently, Grim *et al.* have published the synthesis of most members of the potentially tridentate ligands **B**, including unsymmetrical cases with both mixed donor atoms and mixed R groups [6].

Reported here is the synthesis and characterization of the tin(II) complexes $\{[(C_6H_5)_2PO]_3C\}_2Sn$ (**1**) and $\{[(C_6H_5)_2PO]_2CH\}_2Sn$ (**2**). Of interest to us was the structural impact of the lone pair on tin(II). In particular, tridentate coordination of these sterically bulky ligands could force a geometry in which the planes of the O_3 donor atoms of each ligand were parallel. This unusual geometry is forced by the bulky pentaphenylcyclopentadienyl ligands in $[C_5(C_6H_5)_5]_2Sn$, the structure of which has been determined crystallographically [7]. We report here that in the solid state, as determined by X-ray crystallography, the ligands in **1** are coordinated in only a bidentate fashion.

Experimental

General procedure

All operations were carried out under a nitrogen atmosphere either by standard Schlenk techniques or in a Vacuum Atmospheres HE-493 drybox. All solvents were dried, degassed, and distilled before use. Infrared spectra were recorded on a Nicolet DX V4.56 spectrometer. The ^1H solution NMR spectra were recorded on a Bruker AM300 spectrometer using a 5 mm broad band probe. Proton chemical shifts are reported in ppm versus Me_4Si. Mass spectra were run on a Finnigan 4521 GC-mass

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*Author to whom correspondence should be addressed.

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spectrometer or a VG 70SQ spectrometer. Clusters assigned to specific ions show appropriate isotopic patterns as calculated for the atoms present Elemental analyses were performed by Robertson Laboratory, Inc Anhydrous $SnCl_2$ was purchased from Aldrich Chemical Company $Li\{[(C_6H_5)_2PO]_2CH\}$ [8] and $Na\{[(C_6H_5)_2PO]_3C\}$ [6] were prepared as in the literature $[(C_6H_5)_2PO]_2CH_2$ [8] and $[(C_6H_5)_2PO]_3CH$ [6] were prepared as outlined by Grim *et al* [6], however, we found an excess of H_2O_2 (Fisher Brand 30–35%) was necessary to ensure complete oxidation of the tripodal ligand

Bis[tris(diphenyloxophosphinoyl)methanido]tin(II) $\{[(C_6H_5)_2PO]_3C\}_2Sn$ (1)

$SnCl_2$ (0 15 g, 0 79 mmol) and $Na\{[(C_6H_5)_2PO]_3C\}$ (1 0 g, 1 6 mmol) were placed in a round bottomed flask THF (40 ml) was added via syringe The suspension was stirred overnight at room temperature, and the solvent evaporated under vacuum The residue was extracted with benzene (20 ml), centrifuged and filtered The benzene was removed under vacuum to yield a white solid (0 94 g, 0 70 mmol, 88%), m p 239–241 °C ^1H NMR (C_6D_6) δ 8 04, 6 80 (2, 3, m, m, (C_6H_5)) ^{31}P NMR (C_6D_6) δ 36 4 (s) The mass spectrum shows a cluster for $M^+ - C_{37}H_{30}P_3O_3$ at *m/e* 735 *Anal* Calc for $C_{74}H_{60}P_6O_6Sn$ C, 65 84, H, 4 49 Found C, 66 04, H, 5 00%

TABLE 1 Crystallographic data for the structural analysis of $\{[(C_6H_5)_2PO]_3C\}_2Sn$

Formula	$C_{74}H_{60}O_6P_6Sn$
Molecular weight	1352
Crystal system	trigonal
Space group	*R*3*c*
a (Å)	29 216(3)
b (Å)	29 216(3)
c (Å)	42 120(5)
α (°)	90
β (°)	90
γ (°)	120
V (Å^3)	31 136
Z	18
Crystal size (mm)	0 5 × 0 4 × 0 4
Monochromator	graphite
Radiation	Mo Kα (0 71073 Å)
D_{calc} (g cm^{-3})	1 298
Temperature (K)	298
2θ range (°)	4–46 ($-h$, $+k$, $+l$)
No reflections measured	9277
No reflections	
symmetry independent	4731
observed	1709
Linear absorption coefficient (cm^{-1})	5 54
Transmission factors	
max	1 432
min	0 571
average	0 859
Crystal decay (%)	31% over 175 h of exposure
Corrections	
max	1 21
average	1 09
R_F	0 078
R_{WF}	0 103

TABLE 2 Positional parameters for $\{[(C_6H_5)_2PO]_3C\}_2Sn$ with e s d.s in parentheses

Atom	*x*	*y*	*z*	*B* (Å^2)
Sn	0 36259(5)	0 000	0 250	5 00(5)
C1	0 3965(5)	−0 0968(5)	0 2980(3)	4 6(4)
P1	0 4091(1)	−0 0358(1)	0 3118(1)	5 0(1)
P2	0 4679(1)	0 1283(1)	0 2247(1)	5 4(1)
P3	0 4258(1)	−0 1352(2)	0 3091(1)	5 7(1)
O1	0 4154(3)	0 0033(3)	0 2845(2)	6 0(3)
O2	0 4173(3)	0 0882(3)	0 2405(2)	4 8(3)
O3	0 3862(3)	−0 1919(3)	0 3101(3)	7 6(3)
C11	0 4666(5)	−0 0022(5)	0 3362(4)	5 5(4)
C12	0 5142(6)	0 0296(5)	0 3201(4)	8 2(5)
C13	0 5617(6)	0 0613(6)	0 3387(4)	7 7(5)
C14	0 5612(6)	0 0638(7)	0 3679(4)	9 2(6)
C15	0 5126(9)	0 0316(7)	0 3849(4)	10 8(6)
C16	0 4652(6)	−0 0002(6)	0 3674(3)	6 9(5)
C21	0 3570(4)	−0 0435(4)	0 3388(4)	4 5(4)
C22	0 3280(5)	−0 0861(5)	0 3576(4)	5 7(4)
C23	0 2909(6)	−0 0906(7)	0 3794(5)	8 5(6)
C24	0 2824(6)	−0 0498(6)	0 3832(5)	9 0(6)
C25	0 3078(5)	−0 0059(5)	0 3641(5)	7 5(5)
C26	0 3464(6)	−0 0034(6)	0 3414(4)	6 6(5)
C31	0 4642(5)	−0 1115(6)	0 3466(4)	7 4(5)
C32	0 4339(6)	−0 1311(6)	0 3740(5)	9 6(6)
C33	0 4575(7)	−0 1200(8)	0 4049(4)	11 1(7)
C34	0 5121(8)	−0 0864(9)	0 4059(6)	14 8(8)
C35	0 5421(7)	−0 0693(7)	0 3761(5)	11 9(7)
C36	0 5152(6)	−0 0836(7)	0 3482(4)	8 9(6)
C41	0 4740(4)	−0 1270(5)	0 2798(4)	4 9(4)
C42	0 5029(5)	−0 0818(5)	0 2641(4)	6 3(5)
C43	0 5390(6)	−0 0761(6)	0 2398(5)	8 3(6)
C44	0 5465(6)	−0 1181(6)	0 2331(5)	8 9(6)
C45	0 5169(6)	−0 1634(6)	0 2489(5)	8 8(6)
C46	0 4804(5)	−0 1688(5)	0 2720(5)	7 4(5)
C51	0 4498(5)	0 1699(5)	0 2034(3)	5 4(4)
C52	0 3993(5)	0 1623(6)	0 2077(4)	8 3(5)
C53	0 3878(6)	0 2003(6)	0 1895(4)	11 9(5)
C54	0 4191(9)	0 2351(7)	0 1712(4)	12 6(7)
C55	0 4716(7)	0 2443(7)	0 1680(5)	9 9(6)
C56	0 4868(6)	0 2121(5)	0 1827(4)	7 2(5)
C61	0 5143(5)	0 1691(5)	0 2551(4)	5 8(4)
C62	0 5465(6)	0 2223(6)	0 2544(4)	8 1(6)
C63	0 5786(7)	0 2516(7)	0 2767(4)	10 8(6)
C64	0 5799(7)	0 2284(7)	0 3046(5)	11 7(6)
C65	0 5453(7)	0 1720(7)	0 3083(5)	11 8(7)
C66	0 5131(7)	0 1415(6)	0 2818(4)	8 2(6)

Bis[bis(diphenyloxophosphinoyl)methanido]tin(II) $\{[(C_6H_5)_2PO]_2CH\}_2Sn$ (2)

$SnCl_2$ (0 11 g, 0 58 mmol) and $Li\{[(C_6H_5)_2PO]_2CH\}$ (0 52 g, 1 2 mmol) were placed in a round bottomed flask THF (30 ml) was added via syringe The suspension was stirred at room temperature for 5 h, and the solvent evaporated under vacuum. The residue was extracted with benzene (30 ml), centrifuged and filtered. The benzene was removed under vacuum to yield a white solid (0.29 g, 0.31 mmol, 53%); m.p. 174–177 °C. ^{1}H NMR ($CDCl_3$): δ 7.94, 7.33, 7.21 (2, 1, 2; m, m, m; (C_6H_5)); 4.24 (1; t; $J=10$ Hz; (CH)). ^{31}P NMR ($CDCl_3$): δ 29.8 (s). The mass spectrum shows a cluster for $M^+ - C_{25}H_{21}P_2O_2$ at *m/e* 536.

Crystallographic analysis of $\{[(C_6H_5)_2PO]_3C\}_2Sn$ *(1)*

A transparent crystal of **1** was mounted in a thin-walled capillary tube on a CAD-4 diffractometer. The unit cell was determined and refined from 25 general reflections. Crystal data, data collection parameters, and results of the analysis are listed in Table 1. The structure was solved by the heavy atom method and refined with anisotropic temperature factors for the non-hydrogen atoms by using SDP (Enraf-Nonius Structure Determination Package: Frenz, B.A. (1983)). Hydrogen atoms were placed in calculated positions and not refined. Full-matrix least-squares refinements were carried out with weights $w=(\sigma^2(F)+0.0004F^2)^{-1}$ for reflections with $I>3\sigma(I)$. Absorption corrections were by the method of Walker and Stuart [9]. Table 2 shows the atomic parameters for **1**. Bond distances and angles are given in Table 3.

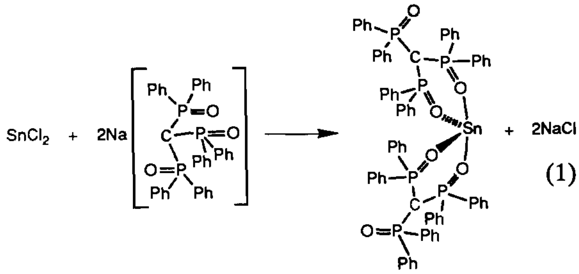
TABLE 3. Selected bond distances (Å) and bond angles (°) for $\{[(C_6H_5)_2PO]_3C\}_2Sn$ with e.s.d.s in parentheses

Bond distances					
Sn	O1	2.089(6)	P1	C21	1.82(2)
Sn	O2	2.289(6)	P2	O2	1.506(6)
C1	P1	1.730(9)	P2	C51	1.79(1)
C1	P2	1.731(9)	P2	C61	1.81(1)
C1	P3	1.782(9)	P3	O3	1.472(7)
P1	O1	1.562(7)	P3	C31	1.86(1)
P1	C11	1.79(1)	P3	C41	1.79(1)

Bond angles							
O1	Sn	O1′	88.5(3)	O3	P3	C41	107.0(7)
O1	Sn	O2	89.3(2)	C31	P3	C41	104.3(6)
O1	Sn	O2′	79.6(2)	P1	C11	C12	116(2)
O2	Sn	O2′	164.5(3)	P1	C11	C16	124(1)
P1	C1	P2	112.7(5)	P1	C21	C22	125(1)
P1	C1	P3	129.8(5)	P1	C21	C26	119(2)
P2	C1	P3	116.5(5)	P3	C31	C32	114(1)
O1	P1	C11	106.6(5)	P3	C31	C36	125(1)
O1	P1	C21	109.7(5)	P3	C41	C42	123(1)
C11	P1	C21	101.9(5)	P3	C41	C46	120(1)
O2	P2	C51	103.8(6)	P2	C51	C52	119(1)
O2	P2	C61	108.8(5)	P2	C51	C56	121.9(9)
C51	P2	C61	106.5(6)	P2	C61	C62	127(1)
O3	P3	C31	112.7(6)	P2	C61	C66	114(2)

Results and discussion

The complex $\{[(C_6H_5)_2PO]_3C\}_2Sn$ (**1**) was prepared from tin(II) chloride as shown in eqn. (1).



1

(1)

It is soluble in aromatic solvents and in halocarbon solvents, but is not soluble in saturated hydrocarbon solvents. Complex **1** is a high melting air stable solid and only slowly decomposes in air in solution.

The solid state structure of **1** has been determined by X-ray crystallography. An ORTEP drawing of the molecule, with the phenyl groups omitted for clarity, is shown in Fig. 1. The molecule crystallizes in the space group $R\bar{3}c$ with a crystallographically imposed two-fold rotational axis.

Both potentially tridentate $[(C_6H_5)_2PO]_3C$–ligands are coordinated to the tin atom in a bidentate fashion. The third P–O group on each ligand is flipped back and away from the tin atom leading to trigonal planar geometry about the methine carbon atoms, C(1). The sum of the three P–C(1)–P bond angles is 359° with the lowest angle of 112.7(5)° formed by the atoms in the chelate rings. The C–P bond distances within the chelate rings are short (1.730(9) and 1.731(9) Å) when compared to the distance for the uncoordinated phosphoryl group (1.782(9) Å) and the average of the P–C(phenyl) distances (1.81(1)

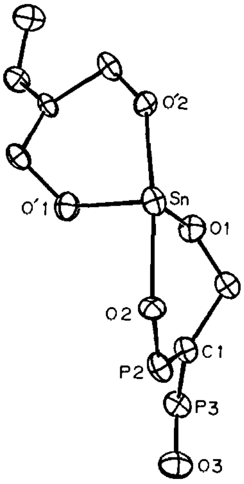


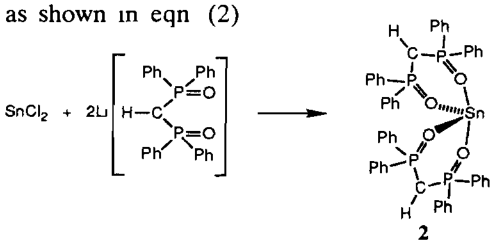
Fig. 1. ORTEP drawing of $\{[(C_6H_5)_2PO]_3C\}_2Sn$. The phenyl groups have been omitted for clarity.

Å) The P–C bond lengths in simple ylides are 1 71 Å [10] Thus, the lone pair on the sp^2 hybridized C(1) carbon atoms is delocalized over the chelate portion of the ligand

The coordination geometry about tin is a pseudo trigonal bipyramid with one equatorial site filled by the lone pair The two-fold rotational axis is coincident with this empty equatorial site Each phosphinoylmethanide ligand occupies an axial and equatorial site The bite angle of the ligands coordinated to the tin(II) atom is 89 3(2)°, as expected for a trigonal bipyramid The equatorial O(1)–Sn–O(1′) bond angle is considerably compressed from the 120° angle of a trigonal bipyramid to 88 5(3)° The axial O(2)–Sn–O(2′) bond angle (164 5(3)°) is also compressed, but to a lesser extent The axial Sn–O(2) bond lengths are considerably longer (2 289(6) Å) than the equatorial Sn–O(1) bond lengths (2 089(6) Å) Compression of the equatorial bond angle and shorter equatorial bond distances are a general feature of four-coordinate, pseudo trigonal bipyramidal tin(II) structures [11]

Bidentate coordination of the potentially tridentate $[(C_6H_5)_2PO]_3C$–ligand appears to be general [12] Presumably, steric crowding caused by the six phenyl rings prevents tridentate coordination Also, the planarity at the methine carbon atom would introduce considerable strain if the ligand were tridentate The sulfur analog, $\{[(C_6H_5)_2PS]_3C\}^-$, does act as either a tridentate [13] or bidentate [14] ligand depending on the metal system, but the longer metal–S bonds help alleviate the steric problems Bidentate coordination in **1** might also have been anticipated due to the fact that tin(II) has been found to generally form three- and four-coordinate complexes [15]

The complex $\{[(C_6H_5)_2PO]_2CH\}_2Sn$ (**2**) is prepared as shown in eqn (2)



(2)

2

This complex has similar chemical and physical properties to **1** and presumably has a similar structure

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