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1 : 1 Complexes of dimethyltin dihalides with tris(2,6-dimethoxyphenyl)-phosphine oxide, its sulphide, and related compounds

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Abstract

Dimethyltin dihalides Me_2SnX_2 (X = Cl, Br) only form 1:1 complexes with 2,6-dimethoxyphenylphosphine oxides $\Phi_3P{=}O$, $Ph\Phi_2P{=}O$ and $Ph_2\Phi P{=}O$ ($\Phi = 2,6\text{-}(MeO)_2C_6H_3$) even though the ligands are used in excess. 2,6-Dimethoxyphenylphosphine sulphides $\Phi_3P{=}S$ and $Ph\Phi_2P{=}S$ also form analogous 1:1 complexes, while $Ph_2\Phi P{=}S$ and $Ph_3P{=}S$ do not react. X-Ray crystal structural analysis of $Me_2SnCl_2 \cdot O{=}P\Phi_3$ reveals that the tin atom is penta-coordinated in a distorted trigonal bipyramidal arrangement, with a chlorine and two methyl carbon atoms in the equatorial positions and the other chlorine and the $\Phi_3P{=}O$ oxygen atom in the axial positions.

1. Introduction

Organotin halides comprise one of the most convenient systems for the investigation of Lewis acid–base interactions, and it has long been known that dialkyltin dihalides form complexes with a variety of Lewis bases [1,2]. Triphenylphosphine oxide is one of the strongest bases towards dialkyltin dihalides, and both 1:2 and 1:1 complexes $Me_2SnX_2 \cdot n(O{=}PPh_3)$ (X = Cl, Br; n = 1, 2) are known [3–8]. Extending our own study of the chemistry of tris(2,6-dimethoxyphenyl)phosphine oxide $\Phi_3P{=}O$ and the sulphide $\Phi_3P{=}S$ ($\Phi = 2,6\text{-}(MeO)_2C_6H_3$, see Scheme 1) [9–12], we report here the preparation and properties of their dimethyltin dihalide complexes together with those of the related complexes.

2. Experimental details

2.1. *Physical measurements*

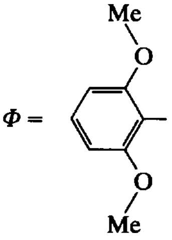
^1H and ^{13}C NMR spectra were recorded for solutions in $CDCl_3$ using a JEOL model JNM-GX-270 spectrometer, and the spectral data are summarized in Tables 1 and 2, respectively. IR spectra (Nujol mulls) were recorded using a Shimadzu FTIR-4200 spectrophotometer.

2.2. *Preparation of 2,6-dimethoxyphenylphosphine derivatives*

Φ_3P was kindly provided by K.I. Kasei Co., Ltd. $Ph\Phi_2P$ and $Ph_2\Phi P$ were prepared as previously reported [9].

2.2.1. $\Phi_3P{=}O$

To a suspension of Φ_3P (5 mmol) in methanol (25 ml) was added 30% aqueous hydrogen peroxide (1 ml, excess). The mixture was stirred at room temperature



Scheme 1.

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TABLE 1. ^{1}H NMR spectral data [a] for $Me_2SnX_2 \cdot L$

L [b]	Me_2SnX_2 [c]	δ (ppm) [d]
Φ_3P=O	F	7.23, 6.47, 3.50, -
	C	7.35, 6.51, 3.51, 0.98 (92)
	B	7.36, 6.52, 3.51, 1.21 (91)
PhΦ_2P=O	F	- [e], 6.50, 3.46, -
	C	- [e], 6.52, 3.46, 1.04 (89)
	B	- [e], 6.52, 3.47, 1.27 (84)
Ph$_2\Phi$P=O	F	- [e], 6.51, 3.34, -
	C	- [e], 6.56, 3.38, 1.12 (84)
	B	- [e], 6.55, 3.38, 1.33 (82)
Φ_3P=S [f]	C	7.26, 6.51, 3.54, 1.20 (75)
	B	7.25, 6.50, 3.54, 1.37 (70)
PhΦ_2P=S [f]	C	- [e], 6.49, 3.46, 1.19 (69)
	B	- [e], 6.49, 3.47, 1.37 (66)
Nil	C	1.21 (67)
	B	1.37 (66)

[a] In $CDCl_3$. [b] Φ = 2,6-$(MeO)_2C_6H_3$. [c] F = free ligand; C = Me_2SnCl_2; B = Me_2SnBr_2. [d] In the order of 4-H (triplet with J(H) 8–9 Hz), 3,5-H (double doublets with J(H) 8–9 Hz and J(P) 4–6 Hz), 2,6-MeO (singlet), and Me–Sn, of which the coupling constant $J(^{119}Sn)$ (in Hz) is given in brackets. [e] Obscured by phenyl proton resonances. [f] The spectral data for the free ligand have been reported in ref. 12.

for 1 h to give a clear solution. The solvent was removed under reduced pressure, and the residual solid was recrystallized from toluene. The crystals thus obtained were contaminated with water and were dried at 120°C for 16 h to give pure Φ_3P=O in 88% yield. M.p. 212–214°C. Anal. Found C 62.7, H 6.0%. Calc. for $C_{24}H_{27}O_7P_1$: C, 62.9; H, 5.9%. This compound is highly soluble in water (1 g/8 ml).

The other new triarylphosphine oxides were prepared by analogous procedures.

2.2.2. PhΦ_2P=O

Yield: 50–70%. M.p. 124°C. This compound is also hygroscopic with a lower melting point if wet, and no satisfactory elemental analysis was obtained. In the following experiments, normality was estimated from the ^{1}H NMR spectrum (MeO proton resonance) for each sample.

2.2.3. Ph$_2\Phi$P=O

Yield: 51%. M.p. 164–165°C. Anal. Found C, 70.5; H, 5.8%. Calc. for $C_{20}H_{19}O_3P_1$: C, 71.0; H 5.7%.

The sulphides *Φ_3P=S*, *PhΦ_2P=S*, and *Ph$_2\Phi$P=S* were prepared as reported [12].

2.3. Preparation of complexes

$Me_2SnCl_2 \cdot O{=}P\Phi_3$. A solution of dimethyltin dichloride (0.110 g, 0.5 mmol) in 2 propanol (5 ml) was added to a solution of Φ_3P=O (0.229 mg, 0.5 mmol) in 2-propanol (10 ml). The resulting suspension was filtered to give the 1 : 1 complex in 77% yield. The analytical sample was obtained by recrystallization from 2-propanol. M.p. 204–205°C. Anal. Found: C, 45.7; H, 4.9%. Calc. for $C_{26}H_{33}Cl_2O_7P_1Sn_1$: C, 46.0; H, 4.9%.

In an analogous manner to the above, the following complexes were obtained. In some cases, the mixture in 2-propanol was cooled to −30°C to give the crystals. These were characterized by the relative peak intensities of the Me–O protons and the Me–Sn protons in ^{1}H NMR spectra and by elemental analysis for some representative complexes. *$Me_2SnBr_2 \cdot O{=}P\Phi_3$*: 76% yield; m.p. 185–186°C. *$Me_2SnCl_2 \cdot O{=}PPh\Phi_2$*: 67% yield; m.p. 197–198°C. *$Me_2SnBr_2 \cdot O{=}PPh\Phi_2$*: 63% yield; m.p. 193–195°C. *$Me_2SnCl_2 \cdot O{=}PPh_2\Phi$*: 70% yield; m.p. 133–134°C. *$Me_2SnBr_2 \cdot O{=}PPh_2\Phi$*: 70% yield; m.p. 111–113°C. *$Me_2SnCl_2 \cdot O{=}PPh_2(C_6H_4\text{-}OMe\text{-}2)$*: 62% yield; m.p. 144–145°C. Anal. Found: C, 47.7; H, 4.4%. Calc. for $C_{21}H_{23}Cl_2O_2P_1Sn_1$: C, 47.8; H, 4.4%. *$Me_2SnBr_2 \cdot O{=}PPh_2(C_6H_4OMe\text{-}2)$*: 65% yield; m.p. 134–135°C. *$Me_2SnCl_2 \cdot S{=}P\Phi_3$*: 65% yield; m.p.

TABLE 2. ^{13}C NMR spectral data [a] for $Me_2SnX_2 \cdot L$

L [b]	Me_2SnX_2 [c]	δ/ppm [d]
Φ_3P=O	F	116.9 (115), 162.6, 105.1 (8), 131.4, 56.2
	C	111.9 (121), 162.2, 104.4 (8), 133.1, 55.8, 14.1
	B	111.6 (121), 162.2, 104.4 (6), 133.2, 55.9, 17.1
PhΦ_2P=O	F	112.9 (110), 162.4, 104.9 (6), 130.0, 55.8; 138.0 (113), 130.9 (10), 127.3 (12), 133.0
	C	109.6 (113), 162.1, 104.4 (6), 130.8, 55.6, 13.4; 135.6 (120), 130.6 (12), 127.6 (14), 134.3
	B	109.8 (114), 162.2, 104.4 (8), 130.7, 55.6, 15.2; 135.7 (119), 130.6 (12), 127.5 (14), 134.2
Ph$_2\Phi$P=O	F	108.8 (110), 163.3, 104.8 (6), 130.5, 55.5; 136.6 (110), 130.9 (10), 127.9 (14), 134.9
	C	- [e], 163.2, 104.8 (6), 131.4, 55.5, 11.9; 133.9 (114), 130.6 (10), 128.2 (14), 136.1
	B	- [e], 163.2, 104.8 (8), 131.3, 55.5, 14.1; 134.2 (113), 130.6 (12), 128.2 (14), 136.0
Φ_3P=S	C [f]	- [e], 161.6, 105.1 (8), 131.3, 55.9, 9.4
	B	- [e], 161.6, 105.7 (6), 131.2, 55.9, 9.4
PhΦ_2P=S	C [f]	114.4 (90), 161.0, 105.0 (8), 129.6, 55.7, 7.4; 137.3 (90), 131.2 (12), 127.2 (14), 132.0
	B	114.5 (92), 161.0, 105.0 (8), 129.6 (4), 55.7, 7.8; 137.4 (92), 131.2 (12), 127.1 (14), 131.9
Nil	C	6.3
	B	7.3

[a] In $CDCl_3$. [b] Φ = 2,6-$(MeO)_2C_6H_3$. [c] F = free ligand; C = Me_2SnCl_2; B = Me_2SnBr_2. [d] In the order of 1–C, 2,6–C, 3,5–C, 4–C, 2,6–MeO, (Sn–)C, and Ph carbons; the coupling constant value J(P) is shown in brackets. [e] These resonances were not well observed. [f] The spectral data for the free ligand have been reported in ref. 12.

135–136°C. Anal. Found: C, 45.4; H, 4.9%. Calc. for $C_{26}H_{33}Cl_2O_6P_1S_1Sn_1$: C, 45.0; H 4.8%. *$Me_2SnBr_2$, $S{=}P\Phi_3$*: 62% yield; m.p. 137–138°C. Anal. Found C 39.9, H, 4.3%. Calc. for $C_{26}H_{33}Br_2O_6P_1S_1Sn_1$: C, 39.9; H, 4.25%. *$Me_2SnCl_2$,$S{=}PPh\Phi_2$*: 57% yield; m.p. 167–168°C. *Me_2SnBr_2,$S{=}PPh\Phi_2$*: 68% yield; m.p. 169–171°C.

2.4. Structure of Me_2SnCl_2,$O{=}P\Phi_3$.

Single crystals were grown from toluene. Accurate unit-cell parameters were determined from 25 reflections with 2θ values from 53 to 56°, measured with a Rigaku four-circle diffractometer at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University.

2.5. Crystal data

$C_{26}H_{33}Cl_2O_7PSn$, $M = 678.24$, triclinic, space group $P\bar{1}$, $a = 14.774(2)$, $b = 10.3822(9)$, $c = 10.307(3)$ Å, $\alpha = 82.22(2)$, $\beta = 109.42(2)$, $\gamma = 83.84(1)°$, $U = 1457.6(6)$ Å^3, $Z = 2$, $D_c = 1.545(1)$ g cm^{-3}, D_m(flotation) = 1.54 g cm^{-3}, $F(000) = 688.0$, μ(Cu-Kα) = 97.8 cm^{-1}.

Intensities were collected in the range of $6 < 2\theta < 120°$ for a crystal with approximate dimensions 0.2 × 0.3 × 0.35 mm, using monochromatized Cu Kα (λ = 1.5415 Å) radiation at the ω-2θ scan rate of 8° min^{-1}. No significant variation of intensity was observed throughout the data collection. Lorentz and polarization effects were applied and an absorption correction was made [13]. A total of 4617 unique reflections was measured, of which 4223 ($|F_o| > 3\sigma(F)$) were used for the structure determination.

The final refinement with anisotropic thermal parameters for the non-hydrogen atoms converged at $R = 0.059$ and $R' = 0.086$, using the weighting scheme $w^{-1} = \sigma^2(F_o) + 0.0005F_o^{\,2}$. Atomic scattering factors were taken from ref. 14. Fractional atomic coordinates with estimated standard deviations are listed in Table 3.

Crystallographic calculations were performed, using the programs of Professor K. Nakatsu, Kwansei Gakuin University, on an ACOS 930S computer at the Research Center of Protein Engineering, Institute for Protein Research, Osaka University. Figure 1 was drawn with a local version of ORTEP-II [15].

Additional material available from the Cambridge Crystallographic Data Center comprises thermal parameters and remaining bond distances and angles.

TABLE 3. Fractional atomic coordinates for $Me_2SnCl_2 \cdot O{=}P\Phi_3$

Atom	x	y	z
Sn	0.28079(2)	0.39295(3)	0.22708(4)
Cl(1)	0.2823(2)	0.5965(2)	0.0575(2)
Cl(2)	0.1542(1)	0.5085(2)	0.2762(2)
P	0.24555(9)	0.1537(1)	0.4795(1)
O(1)	0.2722(3)	0.2106(3)	0.3566(4)
O(2)	0.4496(3)	0.1131(5)	0.6084(5)
O(3)	0.1704(4)	0.3546(4)	0.6303(6)
O(4)	0.1951(3)	−0.0155(4)	0.2843(4)
O(5)	0.3573(3)	−0.0365(4)	0.7639(4)
O(6)	0.0728(3)	0.2460(4)	0.1965(4)
O(7)	0.1578(3)	0.0854(4)	0.6735(4)
C(1)	0.2500(6)	0.2807(7)	0.0636(7)
C(2)	0.4179(4)	0.4069(7)	0.3755(7)
C(3)	0.3099(4)	0.2306(5)	0.6226(6)
C(4)	0.4130(4)	0.2039(6)	0.6672(6)
C(5)	0.4710(5)	0.2702(7)	0.7635(7)
C(6)	0.4291(6)	0.3650(7)	0.8144(7)
C(7)	0.3283(6)	0.3960(6)	0.7730(7)
C(8)	0.2679(5)	0.3292(6)	0.6756(7)
C(9)	0.5482(5)	0.0516(10)	0.6718(9)
C(10)	0.1243(8)	0.4704(9)	0.6579(10)
C(11)	0.2811(4)	−0.0247(5)	0.5226(6)
C(12)	0.2489(4)	−0.0932(5)	0.4108(6)
C(13)	0.2714(5)	−0.2313(6)	0.4259(8)
C(14)	0.3234(5)	−0.2994(6)	0.5590(9)
C(15)	0.3534(5)	−0.2397(6)	0.6733(8)
C(16)	0.3310(4)	−0.1022(5)	0.6564(6)
C(17)	0.1541(7)	−0.0759(8)	0.1681(8)
C(18)	0.4023(7)	−0.1125(9)	0.9035(8)
C(19)	0.1151(4)	0.1738(5)	0.4411(6)
C(20)	0.0437(4)	0.2177(5)	0.3075(7)
C(21)	−0.0551(4)	0.2325(6)	0.2902(8)
C(22)	−0.0822(5)	0.1952(7)	0.4058(9)
C(23)	−0.0130(5)	0.1498(6)	0.5372(8)
C(24)	0.0847(4)	0.1357(5)	0.5528(7)
C(25)	−0.0001(6)	0.3064(9)	0.0652(8)
C(26)	0.1394(7)	0.0767(9)	0.8037(8)

3. Results and discussion

3.1. Preparation of complexes

While treatments of triphenylphosphine oxide with dimethyltin dihalides have been known to afford 2 : 1 complexes [3], analogous treatments of tris(2,6-dimethoxyphenyl)phosphine oxide $\Phi_3P{=}O$ afforded crystals of 1 : 1 complexes, even though the ligand was used in excess. Bis(2,6-dimethoxyphenyl)phenylphosphine oxide $Ph\Phi_2P{=}O$, (2,6-dimethoxyphenyl)diphenylphosphine oxide $Ph_2\Phi P{=}O$, and even (2-methoxyphenyl)diphenylphosphine oxide $Ph_2(2\text{-}MeOC_6H_4)P{=}O$ afforded only the 1 : 1 complexes. Both tris(2,6-dimethoxyphenyl)phosphine sulphide $\Phi_3P{=}S$ and bis(2,6-dimethoxyphenyl)phenylphosphine sulphide $Ph\Phi_2P{=}S$ also afforded analogous 1 : 1 complexes, while (2,6-dimethoxyphenyl)diphenylphosphine sulphide $Ph_2\Phi P{=}S$ and triphenylphosphine sulphide $Ph_3P{=}S$ were recovered unreacted. Few such S-donor complexes of dimethyltin dihalide are known, except for the trimethylstibine sulphide complex $Me_2SnX_2 \cdot 2S{=}SbMe_3$ [16].

It is worth noting that the tertiary phosphine Φ_3P itself reacts with dimethyltin dihalide in toluene or in

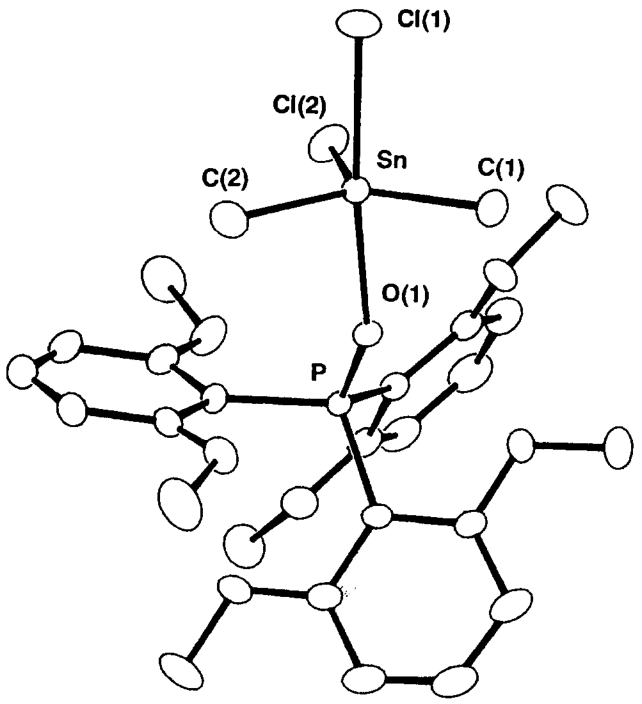

Fig. 1. Molecular geometry of Me_2SnCl_2,$O{=}P\Phi_3$, with the atom-labelling scheme.

2-propanol to form precipitates. Unfortunately, they are very sensitive towards both oxygen and moisture to give complex mixtures including tetramethyl-1,3-dichlorodistannoxane $ClMe_2SnOSnMe_2Cl$, tris(2,6-dimethoxyphenyl)phosphonium tetrachlorodimethylstannate $[\Phi_3P\text{-}H]_2[Me_2SnCl_4]$, and $Me_2SnCl_2 \cdot O{=}P\Phi_3$ during the manipulation.

The tin-methyl proton chemical shift δ_H(Me-Sn) of $Me_2SnX_2 \cdot L$ was observed at magnetic fields decreasing in the order $L = \Phi_3P{=}O > Ph\Phi_2P{=}O > Ph_2\Phi P{=}O > \Phi_3P{=}S \approx Ph\Phi_2P{=}S$ (Table 1), while the ^{13}C chemical shift δ_C(Me-Sn) was observed in the reverse order (Table 2). It is well-known for the ^1H NMR spectroscopy of methyltin derivatives that the magnitude of the magnetic coupling constant of the methyl protons with ^{119}Sn is a useful guide to the conformation around the tin atom, since it is intimately connected with the relative degree of s character in the tin-methyl bond [17-19]. The value $J(^{119}Sn)$ for dimethyltin derivatives has been known to vary between 66 Hz (sp^3) and 117 Hz (sp) depending on the configuration. The $J(^{119}Sn)$ value of the complexes prepared here increased in the order of $L = \text{nil} < Ph\Phi_2P{=}S < \Phi_3P{=}S < Ph_2\Phi P{=}O < Ph\Phi_2P{=}O < \Phi_3P{=}O$. These values, as well as δ_H(Me-Sn), did not vary even in the presence of three-fold excesses of the ligands. When an equimolar amount of dimethyltin dichloride was added, both $J(^{119}Sn)$ and δ_H(Me-Sn) decreased towards those of free dimethyltin dichloride. These observations may suggest the existence of fast ligand exchange in solution.

IR spectroscopy in the region 600-500 cm^{-1} is another useful tool for estimating the conformation around the tin atom [1]. Unfortunately, our complexes showed a very strong band in this region, due to the 2,6-dimethoxyphenyl group, obscuring the symmetric SnC_2 stretching band.

3.2. *Crystal structure of* $Me_2SnCl_2 \cdot O{=}P\Phi_3$.

Figure 1 shows the molecular structure of the complex, together with the atom-labelling scheme. Selected bond distances and angles are listed in Table 4. The 1:1 complex molecules are isolated in the unit cell having no intermolecular tin-chlorine and tin-oxygen contacts within 4 Å. The tin atom is penta-coordinated in a distorted trigonal bipyramidal arrangement. A chlorine and two methyl carbon atoms are located in the equatorial positions of the tin atom forming what is almost a plane with the bond angles totalling 359.8°, where the tin atom deviates only slightly (0.057 Å) from the Cl(2)-C(1)-C(2) equatorial plane. The axial Sn-Cl(1) bond (2.561(2) Å) is longer than the equatorial Sn-Cl(2) bond (2.347(2) Å). This is consistent with the prediction from Gillespie's VSEPR theory [1,20] and analogous results have been reported for a variety of dimethyltin dichloride complexes (Table 5) [21-30]. It is noteworthy that in the present complex the difference (0.214 Å) between these bonds is appreciably larger than those of the other complexes (0.056-0.140 Å), which comes from the strong coordination of the oxygen atom *trans* to Cl(1), as described below. The two Sn-C bonds (2.130(8) and 2.128(6) Å) retain the C(1)-Sn-C(2) bite angle of 128.7(3)°, which is much closer to the regular sp^2 angle than those reported for the other complexes (Table 5). The large deviations from the regular sp^2 angle have been attributed for some complexes to the presence of intermolecular interaction between Sn and Cl (or O) atoms to produce a weak sixth coordination of the tin atom [21-30]. The present complex has the shortest Sn-O bond observed

TABLE 4. Selected bond lengths (Å) and angles (°) for $Me_2SnCl_2 \cdot O{=}P\Phi_3$

Sn-Cl(1)	2.561(2)	Sn-Cl(2)	2.347(2)
Sn-C(1)	2.130(8)	Sn-C(2)	2.128(6)
Sn-O(1)	2.205(4)	P-O(1)	1.513(4)
Cl(1)-Sn-Cl(2)	90.4(1)	Cl(1)-Sn-C(1)	91.0(2)
Cl(1)-Sn-C(2)	93.1(2)	Cl(1)-Sn-O(1)	174.9(1)
Cl(2)-Sn-C(1)	120.7(2)	Cl(2)-Sn-C(2)	110.4(2)
C(1)-Sn-C(2)	128.7(3)	Cl(2)-Sn-O(1)	90.6(1)
Sn-O(1)-P	145.3(2)	O(1)-Sn-C(1)	84.2(2)
O(1)-Sn-C(2)	91.3(2)		

TABLE 5. Structural data for $Me_2SnCl_2 \cdot$ donor 1:1 adducts

Donor	Sn–C (Å)	Sn–Cl (Å)	Sn–O (Å)	Sn--Cl (Å)	C–Sn–C (°)	Ref.
$(O{=}CH)(OH)C_6H_4$ [a]	2.098 2.107	2.347 2.403	2.680		131	21
$O{=}C(NMe_2)_2$	2.110(7) 2.107(7)	2.372(2) 2.497(2)	2.357(4)	3.66	146.6(3)	22
$ONC_5H_3Me_2$	2.110(4) 2.112(4)	2.400(1) 2.528(1)	2.289(3)	3.399(1)	145.3(2)	23
$O{=}CC_2Ph_2$	2.111(3) 2.116(3)	2.3713(6) 2.4745(7)	2.380(2)	3.5607(7)	142.2(1)	24
$O{=}S{=}C(Ph)(NMePh)$	2.109(4) 2.109(4)	2.4043(9) 2.544(1)	2.268(3)	3.307(1)	153.4(2)	26
$HOCH_2C_3N_2H_3$	2.085(7) 2.108(8)	2.363(2) 2.448(3)	2.502(6)	3.916	138.7(4)	30
$O{=}S(CH_2Ph)_2$	2.109(16) 2.128(15)	2.392(6) 2.464(6)	2.319(10)		136.4(9)	29
$O{=}P[C_6H_3(OMe)_2]_3$	2.128(6) 2.130(8)	2.347(2) 2.561(2)	2.205(4)		128.7(3)	This work
$1/2NC_4H_4N$ [b]	2.095(8) 2.102(8)	2.366(2) 2.424(2)		3.48	136.5(4)	27, 28

[a] Sn--O Bridging [3.366(11) Å]. [b] Sn–N, 2.746(6) Å.

in the analogous 1:1 complexes (Table 5) and 1:2 complexes such as $Me_2SnCl_2,2O{=}SMe_2$ (2.27 and 2.31 Å) [31], $Me_2SnCl_2 \cdot (salen)H_2$ (2.22(2) and 2.23(2) Å) [32], and $Me_2SnCl_2 \cdot Ni(salen)$ (2.403 and 2.558 Å) [33], where salen is *N,N'*-ethylenebis(salicylideneiminate). The shortest distance between the tin atom and the methoxyl oxygen atom is 3.516(4) Å. Recently, Dunbar *et al.* also reported for the 1:1 complex $\Phi_3P{=}O \cdot FeCl_3$ that the O–Fe coordination bond distance was much shorter than the metal–oxygen distances found in similar tetrahedral phosphine oxide complexes and that the P=O distance (1.550(7) Å) is much longer than the average corresponding distance in $CoCl_2 \cdot 2O{=}PPh_3$ [34]. The P=O distance observed for our complex was 1.513(4) Å. We are interested in the interatomic distances between the phosphorus atom and the six methoxyl oxygen atoms (2.778(5), 2.817(5), 2.818(4), 3.086(6), 3.116(4), and 3.120(4) Å). Three of them were much shorter than the sum of van der Waals' radii (3.3 Å). The overall intramolecular electron donating interaction from six methoxyl oxygens must increase the basicity on the P=O oxygen atom, which best explains the unique effects observed for tris(2,6-dimethoxyphenyl)phosphine derivatives, as discussed elsewhere [12,35]. An analogous result has been reported by Wood *et al.* for benzyl(2-methoxyphenyl)diphenylphosphonium bromide [36]. The true reason why all the present triarylphosphine oxides formed the 1:1 complexes exclusively is unknown, although both steric and electronic effects of these ligands may be necessary to explain it.

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