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Article

Biphenolate Phosphine Complexes of Tin(IV)

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The preparation and structural characterization of tin(IV) complexes supported by (2,2′-phenylphosphino)bis(4,6-di-*tert*-butylphenolate) ($[OPO]^{2-}$) are described. The reaction of in-situ prepared $Li_2[OPO]$ with $SnCl_4$ in THF at –35 °C produced $[OPO]SnCl_2(THF)$ as a THF adduct. Addition of $SnCl_4$ to a THF solution of $H_2[OPO]$ in the presence of 2 equiv of NEt_3 at room temperature led to the formation of the "ate" complex $\{[OPO]SnCl_3\}(HNEt_3)$. The metathetical reactions of $Li_2[OPO]$ with R_2SnCl_2 (R = Me, *n*-Bu) in THF at –35 °C generated the corresponding five-coordinate dialkyl complexes $[OPO]SnR_2$. In addition to the multinuclear NMR spectroscopic data for all new compounds, X-ray structures of $[OPO]SnCl_2(THF)$, $[OPO]SnMe_2$, and $[OPO]Sn(n\text{-}Bu)_2$ are presented.

Introduction

We are currently exploring the coordination chemistry of main-group and transition metals involving *o*-phenylene-derived hybrid chelating ligands that contain both soft and hard donors.[1−14] For instance, the structural characterization of a series of group 4 complexes supported by the tridentate biphenolate phosphine ligand (2,2′-phenylphosphino)bis(4,6-di-*tert*-butylphenolate) ($[OPO]^{2-}$) has recently been described.[14] The chelating (poly)phenolate ligands such as $[OPO]^{2-}$ are currently receiving considerable attention, particularly for group 4 chemistry, due, at least in part, to their potential use as homogeneous catalyst precursors for polymerization of terminal olefins and ring-opening polymerization of heterocyclic molecules.[15−24] Interestingly, it has been demonstrated that the bond distances of Ti−P in titanium(IV) complexes of $[OPO]^{2-}$[14] are shorter than those of Ti−S in the corresponding complexes of the sulfide-bridged 2,2′-thiobis(6-*tert*-butyl-4-methylphenolate) ligand[21,25,26] as evidenced by single-crystal X-ray diffraction analysis. This phenomenon is notably unusual in consideration of the relative atomic size and hardness of these donor atoms but

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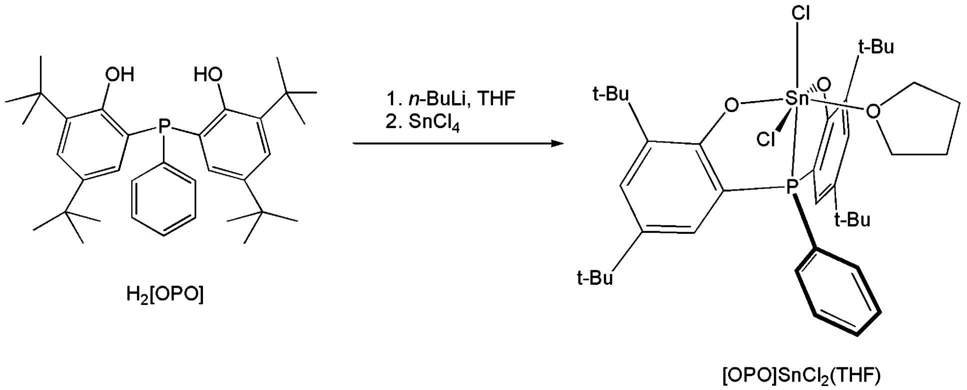
Scheme 1



likely suggestive of a stronger chemical bond for the former than the latter. In view of the close resemblances of Ti(IV) to Sn(IV)[27] and the potential transmetalation characteristic of tin complexes with other metal halides,[28,29] we have set out to explore the coordination chemistry of $[OPO]^{2-}$ involving Sn(IV). In this contribution, we describe the preparation and structural characterization of a series of tin(IV) complexes containing $[OPO]^{2-}$, including X-ray structures of $[OPO]SnCl_2(THF)$, $[OPO]SnMe_2$, and $[OPO]Sn(n\text{-}Bu)_2$. Interestingly, both facial and meridional coordination modes are observed for $[OPO]^{2-}$ in this study, in spite of the intrinsic pyramidal nature of the phosphorus donor. It is worth noting that compounds described herein represent rare examples of structurally characterized biphenolate phosphine complexes of main-group metals,[13] although ligands of this type have been known since 1980.[30]

Results and Discussion

It has been shown that attempts to prepare $[OPO]TiCl_2(THF)$ from the reactions of $Li_2[OPO]$ with 1 equiv of $TiCl_4(THF)_2$ in a variety of solvents led to a complicated mixture from which the bis-ligand complex $Ti[OPO]_2$ may be selectively isolated.[14] Subsequent comproportionation of $Ti[OPO]_2$ with $TiCl_4(THF)_2$ produced effectively the desired $[OPO]TiCl_2(THF)$. In contrast, the analogous metathetical reaction of $Li_2[OPO]$ with $SnCl_4$ in THF at −35 °C generated $[OPO]SnCl_2(THF)$ (Scheme 1) as a pale yellow solid as judged by the ^1H and $^{31}P\{^1H\}$ NMR spectra. The phosphorus donor of $[OPO]SnCl_2(THF)$ in C_6D_6 appears as a singlet resonance at −61.7 ppm in the $^{31}P\{^1H\}$ NMR spectrum, a value that is significantly shifted upfield as compared to those of $Li_2[OPO]$ (−32 ppm)[13] and $[OPO]TiCl_2(THF)$ (18 ppm).[14] The *tert*-butyl groups in $[OPO]SnCl_2(THF)$ are observed as two sharp singlet resonances in the ^1H NMR spectrum at room temperature, consistent with a C_s-symmetric geometry for this complex. Reminiscent of what has been reported for $[OPO]TiCl_2(THF)$,[14] the coordinated THF molecule is presumably labile and tends to dissociate from the Sn(IV) center as only one set of THF resonances is observed in the ^1H NMR spectrum of a C_6D_6 solution containing $[OPO]SnCl_2(THF)$ and an excess amount of THF (e.g., 10 equiv). The solubility of $[OPO]SnCl_2(THF)$, however, is too low in all commonly used solvents to acquire interpretable low-temperature ^1H NMR spectra. The determination of the static structure of this molecule in solution is thus hampered and inconclusive. The tin atom may be observed in a saturated THF solution as a doublet resonance centered at −55.1 ppm with $^1J_{PSn}$ of 1886 Hz (Table 1) in the $^{119}Sn\{^1H\}$ NMR spectrum, indicating the coordination of the phosphorus donor to the tetravalent tin center. Attempts to obtain satisfactory analysis data for $[OPO]SnCl_2(THF)$ were unsuccessful, due presumably to the facile dissociation of the coordinated THF molecule and/or the incorporation of cocrystallized toluene molecule upon recrystallization (vide infra).

Table 1. Selected NMR Data[a]

compd	$\delta_{^{31}P}$	$\delta_{^{119}Sn}$	$^1J_{^{119}SnP}$	$^1J_{^{117}SnP}$
$[OPO]SnCl_2(THF)$[b]	−58.9	−55.1	1886	1802
$\{[OPO]SnCl_3\}(HNEt_3)$	−56.5	−37.6	2009	1920
$[OPO]SnMe_2$	−76.5	342.1	1094	1047
$[OPO]Sn(n\text{-}Bu)_2$	−76.5	309.4	881	842

[a] All spectra were recorded in C_6D_6 at room temperature unless otherwise noted; chemical shifts in ppm, and coupling constants in Hz. [b] Data obtained in THF due to low solubility in C_6D_6.

Though indeterminate in solution, the solid-state structure of $[OPO]SnCl_2(THF)$ was established by an X-ray diffraction study. Colorless crystals of $[OPO]SnCl_2(THF)$ suitable for X-ray diffraction analysis were grown from a concentrated toluene solution at −35 °C. Crystallographic details are summarized in Table 2. As depicted in Figure 1, $[OPO]SnCl_2(THF)$ is a six-coordinate species with the coordinated THF molecule trans to one of the phenolate oxygen atoms of the *fac*-$[OPO]^{2-}$ ligand. As a result, this compound is C_1-symmetric in the solid state. The C_s symmetry found for $[OPO]SnCl_2(THF)$ in solution thus presumably arises from the facile dissociation and recoordination of the THF molecule as illustrated in Scheme 2. The Sn−O(phenolate), Sn−O(THF), and Sn−Cl distances are all within the expected values for a six-coordinate tin(IV) complex.[31−34] The Sn−P

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Table 2. Crystallographic Data for [OPO]$SnCl_2$(THF), [OPO]$SnMe_2$, and [OPO]Sn(*n*-Bu)$_2$

Compound	{[OPO]$SnCl_2$(THF)}(toluene)	{[OPO]$SnMe_2$}(pentane)
Formula	$C_{45}H_{61}Cl_2O_3PSn$	$C_{41}H_{63}O_2PSn$
Fw	870.50	737.57
crystal size (mm^3)	0.32 × 0.28 × 0.15	0.27 × 0.23 × 0.17
D_{calc} (Mg/m^3)	1.267	1.208
crystal syst	Triclinic	Monoclinic
space group	$P\bar{1}$	$P2_1/n$
a (Å)	11.2833(2)	13.2078(5)
b (Å)	13.1780(3)	20.1362(8)
c (Å)	16.6922(5)	15.8305(7)
α (deg)	77.8660(10)	90
β (deg)	75.9260(10)	105.598(2)
γ (deg)	73.4790(10)	90
V (Å^3)	2281.39(9)	4055.1(3)
Z	2	4
T (K)	200(2)	150(2)
diffractometer	Kappa CCD	SMART APEX II
radiation, (Å)	Mo K_α, 0.71073	Mo K_α, 0.71073
2 range (deg)	4.18 < 2 < 50.72	3.20 < 2 < 57.64
index ranges (h;k;l)	−13, 13; −15, 15; −20, 20	−12, 13; −23, 17; −24, 24
total no. of reflns	29396	33224
no. of indep reflns	8327	10512
R_{int}	0.0725	0.0275
Absorp coeff (mm^{-1})	0.748	0.700
no. of data/restraints/parameters	8327/0/453	10512/97/452
goodness of fit	1.090	1.050
final *R* indices [*I* > 2(*I*)]	R1 = 0.0504	R1 = 0.0413
	wR2 = 0.1249	wR2 = 0.1139
R indices (all data)	R1 = 0.0744	R1 = 0.0634
	wR2 = 0.1454	wR2 = 0.1240
residual density (e/Å^3)	−0.703 to 0.839	−0.872 to 0.942

Compound	[OPO]Sn(*n*-Bu)$_2$
Formula	$C_{42}H_{63}O_2PSn$
Fw	749.58
Crystal size (mm^3)	0.25 × 0.14 × 0.11
D_{calc} (Mg/m^3)	1.227
Crystal syst	Monoclinic
space group	$P2_1/n$
a (Å)	10.9360(7)
b (Å)	19.4210(13)
c (Å)	19.1740(14)
α (deg)	90
β (deg)	94.957(4)
γ (deg)	90
V (Å^3)	4057.1(5)
Z	4
T (K)	200(2)
diffractometer	Kappa CCD
radiation, *λ* (Å)	Mo K_α, 0.71073
2*θ* range (deg)	4.20 < 2 < 50.02
index ranges (h;k;l)	−13, 12; −22, 23; −22, 18
total no. of reflns	28062
no. of indep reflns	7124
R_{int}	0.1217
Absorp coeff (mm^{-1})	0.701
no. of data/restraints/parameters	7124/96/471
goodness of fit	1.033
final *R* indices [*I* > 2*σ*(*I*)]	R1 = 0.0765
	wR2 = 0.1725
R indices (all data)	R1 = 0.1321
	wR2 = 0.2007
residual density (e/Å^3)	−0.618 to 1.145

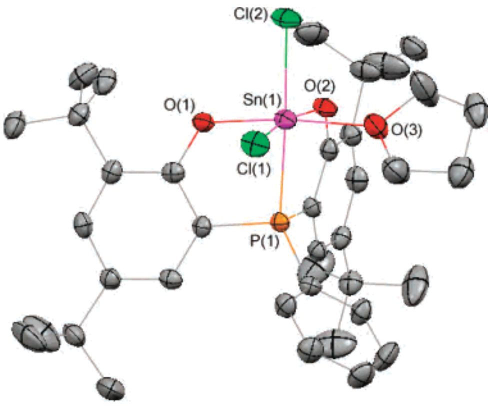

Figure 1. Molecular structure of [OPO]$SnCl_2$(THF) with thermal ellipsoids drawn at the 35% probability level. The asymmetric unit cell contains one disordered toluene molecule, which is omitted for clarity. Selected bond distances (Å) and angles (deg): Sn(1)−O(2) 2.049(3), Sn(1)−O(1) 2.053(3), Sn(1)−O(3) 2.221(3), Sn(1)−Cl(2) 2.3401(12), Sn(1)−Cl(1) 2.4049(12), Sn(1)−P(1) 2.5311(11), O(2)−Sn(1)−O(1) 93.89(12), O(2)−Sn(1)−O(3) 83.79(13), O(1)−Sn(1)−O(3) 173.10(12), O(2)−Sn(1)−Cl(2) 88.24(8), O(1)−Sn(1)−Cl(2) 95.25(9), O(3)−Sn(1)−Cl(2) 91.18(10), O(2)−Sn(1)−Cl(1) 169.01(9), O(1)−Sn(1)−Cl(1) 95.13(9), O(3)−Sn(1)−Cl(1) 86.52(10), Cl(2)−Sn(1)−Cl(1) 97.15(5), O(2)−Sn(1)−P(1) 80.50(8), O(1)−Sn(1)−P(1) 77.55(8), O(3)−Sn(1)−P(1) 95.63(10), Cl(2)−Sn(1)−P(1) 166.10(4), Cl(1)−Sn(1)−P(1) 95.35(4).

distance of 2.531(1) Å, however, is notably shorter than those found in six-coordinate tin(IV) complexes of alkylphosphines such as $SnF_4(Et_2PCH_2CH_2PEt_2)$ (2.6058(9) Å),[35] $SnCl_4(Et_2PCH_2CH_2PEt_2)$ (2.6481(17) Å),[35] and *trans*-$SnF_4(PCy_3)_2$ (2.6538(11) Å)[35] but comparable to those of five-coordinate derivatives of aryl phosphines such as $SnPh[P(C_6H_4\text{-}2\text{-}S)_3]$ (2.5161(11) Å),[29] $SnPh[P(C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3]$ (2.5132(14) Å),[29] and $SnPh[P(C_6H_3\text{-}5\text{-}Me\text{-}2\text{-}S)_3]$ (2.5124(9) Å).[28,29] The molecular structure of [OPO]$SnCl_2$(THF) resembles closely that of [OPO]$TiCl_2$(THF).[14] The [OPO]$^{2-}$ ligand in both [OPO]$SnCl_2$(THF) and [OPO]$TiCl_2$(THF) adopts a *facial* coordination mode with the dihedral angle of the two O−M−P planes being 96.2° for Sn and 100.9° for Ti. The somewhat smaller dihedral angle found for [OPO]$SnCl_2$(THF) than [OPO]$TiCl_2$(THF) is consistent with the longer Sn−O(phenolate) bond distances (2.049(3) and 2.053(3) Å) than Ti−O(phenolate) (1.848(8) and 1.858(7) Å). Interestingly, the Sn−P distance is in the former complex is slightly shorter than Ti−P (2.596(3) Å) in the latter, despite the smaller octahedral covalent radius of Ti(IV) (1.36 Å) than Sn(IV) (1.45 Å).[27] The Sn(1)−Cl(1) distance of 2.405(1) Å is slightly longer than the Sn(1)−Cl(2) distance of 2.340(1) Å, consistent with the relatively higher trans influence of the phenolate oxygen atom than the phosphorus donor in [OPO]$^{2-}$. As anticipated, the Sn−O(THF) distance of 2.221(3) Å is longer than the Sn−O(phenolate) lengths.

Addition of $SnCl_4$ to a THF solution of H_2[OPO] in the presence of 2 equiv of NEt_3 at room temperature produced the "ate" complex {[OPO]$SnCl_3$}($HNEt_3$) (Scheme 3). This result is notably different from what has been observed for the titanium(IV) chemistry, which led instead to the formation of the bis-ligand complex Ti[OPO]$_2$ under similar conditions.[14] The propensity to form a six-coordinate

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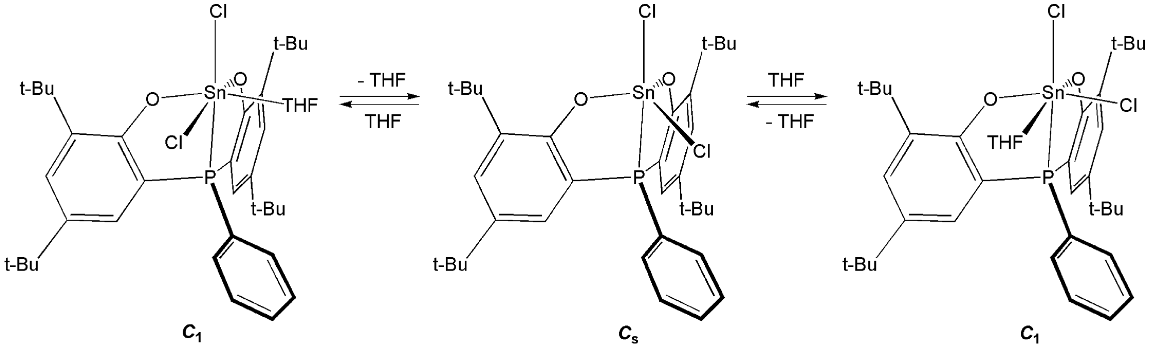
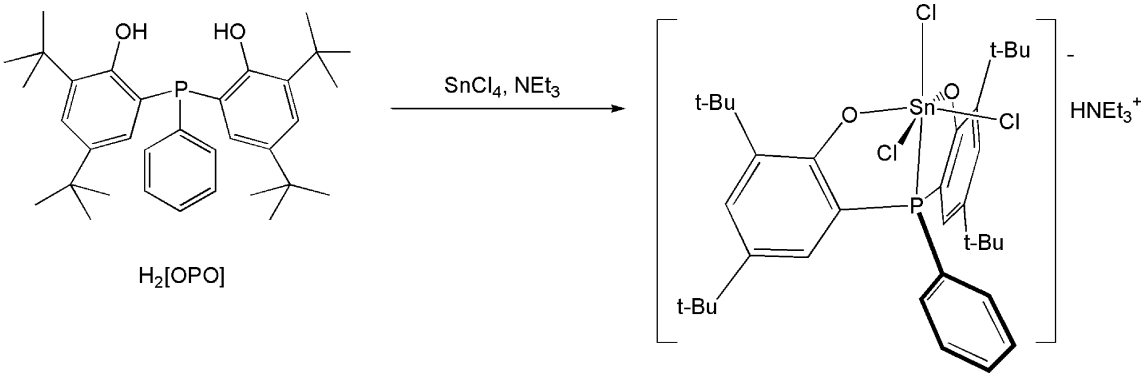
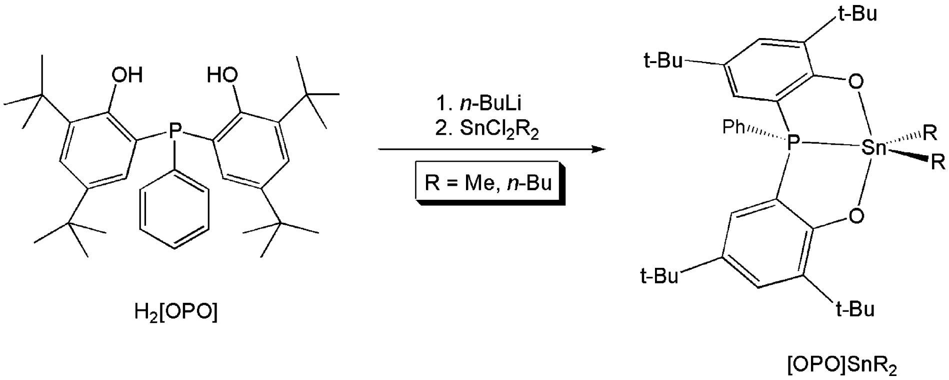
Scheme 2



Scheme 3



Scheme 4



$\{[OPO]SnCl_3\}^-$ and $[OPO]SnCl_2(THF)$ rather than a five-coordinate $[OPO]SnCl_2$ is likely reflective of the highly electrophilic nature of the putative $[OPO]SnCl_2$. Surprisingly, $\{[OPO]SnCl_3\}(HNEt_3)$ is much more soluble than $[OPO]SnCl_2(THF)$ even in nonpolar solvents, although the former complex is characteristic of an ion pair. The ^1H NMR spectrum of $\{[OPO]SnCl_3\}(HNEt_3)$ in C_6D_6 exhibits two sharp singlet resonances for the *tert*-butyl groups, indicating the presence of a symmetry plane in this molecule. The phosphorus donor appears as a singlet resonance at −56.5 ppm flanked by ^{117}Sn and ^{119}Sn satellite signals with $^1J_{SnP}$ of 1920 and 2009 Hz, respectively Consistently, the $^{119}Sn\{^1H\}$ NMR spectrum reveals a doublet resonance centered at −37.6 ppm due to the coupling between ^{119}Sn and ^{31}P nuclei.

The metathetical reactions of $Li_2[OPO]$ with R_2SnCl_2 (R = Me, *n*-Bu) in THF at −35 °C generated the corresponding five-coordinate dialkyl complexes $[OPO]SnR_2$ (Scheme 4). Interestingly, these dialkyl species are not associated with coordinating solvents (e.g., THF or diethyl ether) or the eliminated LiCl salt, a phenomenon that is in sharp contrast to that of the dichloride derivative (vide supra). This result is reflective of a less electrophilic tin(IV) center of the dialkyl complexes than that of the putative five-coordinate dichloride species due to the difference in electronegativity of these donor atoms (C, 2.55; Cl, 3.16).[36] The ^1H NMR spectrum of $[OPO]SnMe_2$ in C_6D_6 at room temperature reveals two sharp singlet resonances at 1.70 and 1.33 ppm for the *tert*-butyl groups of $[OPO]^{2-}$ and two doublet resonances at 0.53 ($^3J_{HP} = 3$ Hz) and 0.44 ppm ($^3J_{HP} = 2$ Hz) with tin satellites for the tin-bound methyl groups, consistent with C_s symmetry for this molecule. The C_s symmetry is anticipated in view of the inherent pyramidal geometry of the phosphorus donor. The phenolate oxygen atoms are likely positioned axially in a trigonal bipyramial structure on the basis of their relatively high electronegativity as compared to those of the other donor

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[36] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 93.

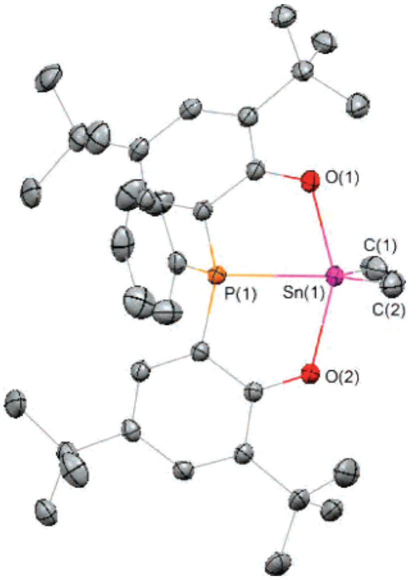

Figure 2. Molecular structure of [OPO]SnMe$_2$ with thermal ellipsoids drawn at the 35% probability level. The asymmetric unit cell contains one disordered pentane molecule, which is omitted for clarity. Selected bond distances (Å) and angles (deg): C(1)−Sn(1) 2.119(3), C(2)−Sn(1) 2.129(4), O(1)−Sn(1) 2.154(2), O(2)−Sn(1) 2.150(2), P(1)−Sn(1) 2.5118(7), C(1)−Sn(1)−C(2) 121.53(16), C(1)−Sn(1)−O(2) 103.99(12), C(2)−Sn(1)−O(2) 89.89(13), C(1)−Sn(1)−O(1) 103.31(12), C(2)−Sn(1)−O(1) 91.80(12), O(2)−Sn(1)−O(1) 146.73(9), C(1)−Sn(1)−P(1) 109.96(12), C(2)−Sn(1)−P(1) 128.51(11), O(2)−Sn(1)−P(1) 76.77(6), O(1)−Sn(1)−P(1) 76.29(6).

atoms present in this molecule (Bent's rule).[37,38] The symmetry plane of this compound thus coincides with the equatorial plane that contains the tin center and the two α-carbon atoms. As a result, the two tin-bound methyl groups are chemically inequivalent. The phosphorus donor in [OPO]SnMe$_2$ appears as a singlet resonance at −76.5 ppm flanked by ^{117}Sn and ^{119}Sn satellite signals with $^1J_{\mathrm{SnP}}$ of 1047 and 1094 Hz, respectively. The tin atom is observed as a doublet resonance at 342.1 ppm in the ^{119}Sn{^{1}H} NMR spectrum, a value that is shifted significantly downfield as compared to those of [OPO]SnCl$_2$(THF) and {[OPO]SnCl$_3$}(HNEt$_3$). The discrepancy in ^{119}Sn chemical shifts observed for five-coordinate [OPO]SnMe$_2$ and six-coordinate [OPO]SnCl$_2$X (X = THF, Cl$^-$) is consistent with the lower coordination number[39] for the former than the latter. Similar phenomena were also found for [OPO]Sn(*n*-Bu)$_2$.

Colorless crystals of [OPO]SnMe$_2$ and [OPO]Sn(*n*-Bu)$_2$ suitable for X-ray diffraction analysis were grown from a concentrated pentane solution at −35 °C. Figures 2and 3 illustrate the molecular structures of [OPO]SnMe$_2$ and [OPO]Sn(*n*-Bu)$_2$, respectively. Consistent with the solution NMR spectroscopic data, these compounds are C_s-symmetric, five-coordinate species. The coordination geometry of these complexes is best described as distorted trigonal bipyramidal with the two phenolate oxygen atoms occupying the axial positions. The tin center lies perfectly on the equatorial plane as indicated by the sum of the three equatorial bond angles of 359.99° for [OPO]SnMe$_2$ and 360° for [OPO]Sn(*n*-Bu)$_2$. The dihedral angle between the two O−Sn−P planes in [OPO]SnMe$_2$ (160.3°) and [OPO]Sn(*n*-Bu)$_2$ (173.0°) is notably wider than those of the *fac*-[OPO]$^{2-}$-derived [OPO]SnCl$_2$(THF) and [OPO]TiCl$_2$(THF) (vide supra) but smaller than the ideal value of 180° due likely to the constraint imposed by the two fused five-membered chelate rings and the distortion arisen from the pyramidal phosphorus donor. The O−Sn−O bond angle ([OPO]SnMe$_2$, 146.73(9)°; [OPO]Sn(*n*-Bu)$_2$, 150.5(2)°) is thus relatively small, and the two *o*-phenylene rings are tilted away from the phosphorus-bound phenyl group with respect to the [OPO]$^{2-}$ coordination plane. The preference for [OPO]$^{2-}$ to adopt the meridional instead of facial geometry in a trigonal bipyramid is reminiscent of what has been reported for 5-coordinate tin(IV) complexes of [ONO]$^{2-}$ such as Sn[(OCH$_2$CH$_2$)$_2$NMe](*t*-Bu)$_2$[40] and Sn[(O$_2$CCH$_2$)$_2$NCH$_2$-*m*-tolyl](*n*-Bu)$_2$.[41] Though anticipated in view of the Bent's rule, the meridional geometry of [OPO]$^{2-}$ found in [OPO]SnMe$_2$ and [OPO]Sn(*n*-Bu)$_2$ is virtually unprecedented for [XPX]$^{2-}$- or [LPL]-derived (X = anionic donor, L = neutral donor) five-coordinate complexes as indicated by the Cambridge Structural Database to date. With the incorporation of a phosphorus donor at the central position, the tridentate di(donor)/phosphine ligands are usually forced to adopt a facial coordination mode in five-coordinate species due to its intrinsic pyramid geometry.[42−48] The Sn−P distance of 2.5118(7) Å in [OPO]SnMe$_2$ and

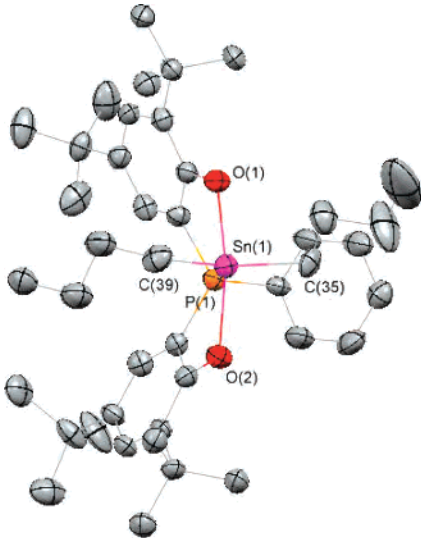

Figure 3. Molecular structure of [OPO]Sn(*n*-Bu)$_2$ with thermal ellipsoids drawn at the 35% probability level. Selected bond distances (Å) and angles (deg): Sn(1)−C(35) 2.128(7), Sn(1)−C(39) 2.146(8), Sn(1)−O(1) 2.178(5), Sn(1)−O(2) 2.183(6), Sn(1)−P(1) 2.480(2), C(35)−Sn(1)−C(39) 119.7(3), C(35)−Sn(1)−O(1) 100.3(3), C(39)−Sn(1)−O(1) 94.5(3), C(35)−Sn(1)−O(2) 98.5(3), C(39)−Sn(1)−O(2) 95.6(3), O(1)−Sn(1)−O(2) 150.5(2), C(35)−Sn(1)−P(1) 116.7(2), C(39)−Sn(1)−P(1) 123.6(3), O(1)−Sn(1)−P(1) 76.0(1), O(2)−Sn(1)−P(1) 75.4(1).

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2.480(2) Å in [OPO]Sn(n-Bu)$_2$ is slightly shorter than that of 2.531(1) Å in [OPO]SnCl$_2$(THF), a result that is ascribed to the higher percentage of s character that the Sn−P bond possesses in the hybrid orbitals for the former (sp^2) than the latter (d^2sp^3).[37,38] Consistently, the Sn−O distances in [OPO]SnR$_2$ (R = Me, 2.152 Å average; R = n-Bu, 2.181 Å average) are longer than those of [OPO]SnCl$_2$(THF) (2.052 Å average). The Sn−C bond lengths of [OPO]SnR$_2$ are comparable to those reported for five-coordinate organotin(IV) complexes such as Sn[(OCH$_2$CH$_2$)$_2$NMe](t-Bu)$_2$[40] and Sn[(O$_2$CCH$_2$)$_2$NCH$_2$-m-tolyl](n-Bu)$_2$.[41]

Conclusions

In summary, we have prepared a series of five- and six-coordinate tin(IV) complexes of the tridentate biphenolate phosphine ligand [OPO]$^{2-}$ and established the solution and solid-state structures of these molecules by multinuclear NMR spectroscopy and X-ray crystallography, respectively. Of particular interest are the divergent coordination modes of [OPO]$^{2-}$, which may bind to tin(IV) either facially or meridionally depending on the overall geometry of the derived complexes. The meridional geometry of [OPO]$^{2-}$ verified in this study is particularly remarkable in view of the involvement of a pyramidal phosphorus donor at the central position in the chelating ligand employed. Studies directed to delineate the reactivity of these compounds are currently under way.

Experimental Section

General Procedures. Unless otherwise specified, all experiments were performed under nitrogen using standard Schlenk or glovebox techniques. All solvents were reagent grade or better and purified by standard methods. The NMR spectra were recorded on Varian Unity or Bruker AV instruments. Chemical shifts (δ) are listed as parts per million downfield from tetramethylsilane, and coupling constants (J), in hertz. ^{1}H NMR spectra are referenced using the residual solvent peak at δ 7.16 for C$_6$D$_6$ and δ 7.27 for CDCl$_3$. ^{13}C NMR spectra are referenced using the residual solvent peak at δ 128.39 for C$_6$D$_6$. The assignment of the carbon atoms is based on the DEPT ^{13}C NMR spectroscopy. ^{31}P NMR spectra are referenced externally using 85% H$_3$PO$_4$ at δ 0. ^{119}Sn NMR spectra are referenced externally using SnMe$_4$ (at δ 0)[39] or a saturated SnCl$_2$ (anhydrous) solution in THF (at δ 236).[49] Routine coupling constants are not listed. All NMR spectra were recorded at room temperature in specified solvents unless otherwise noted. Elemental analysis was performed on a Heraeus CHN-O Rapid analyzer.

Materials. Compounds H$_2$[OPO][50] and Li$_2$[OPO][13] were prepared according to the literature procedures. All other chemicals were obtained from commercial vendors and used as received.

X-ray Crystallography. Table 2 summarizes the crystallographic data for [OPO]SnCl$_2$(THF), [OPO]SnMe$_2$, and [OPO]Sn(n-Bu)$_2$. Data were collected on a Bruker-Nonius Kappa CCD diffractometer or a SMART APEX II diffractometer with graphite monochromated Mo Kα radiation (λ = 0.7107 Å). Structures were solved by direct methods and refined by full matrix least-squares procedures against F^2 using WinGX crystallographic software package or SHELXL-97. All full-weight non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. In [OPO]SnMe$_2$, one of the *tert*-butyl groups is disordered with the methyl substituents being in the ratio of ca. 74:26 over two conformations. In [OPO]Sn(n-Bu)$_2$, one *tert*-butyl and one n-butyl groups are disordered with the methyl or n-butyl (excluding C$_\alpha$) moieties being in the ratio of ca. 55:45 and ca. 37:63, respectively, over two conformations. A semiempirical absorption correction was applied using the SADABS program.[51]

Synthesis of [OPO]SnCl$_2$(THF). Solid H$_2$[OPO] (200 mg, 0.39 mmol) was dissolved in THF (4 mL), and the solution was cooled to −35 °C. To this was added n-BuLi (0.48 mL, 1.6 M in hexane, Aldrich, 0.77 mmol, 2 equiv) dropwise. The reaction mixture was stirred at room temperature for 1 h. The resultant solution was cooled to −35 °C again, and a prechilled solution of SnCl$_4$ (101 mg, 0.39 mmol) in THF (10 mL) at −35 °C was added dropwise. The reaction mixture was stirred at room temperature for 16 h and evaporated to dryness under reduced pressure. The solid thus obtained was extracted with diethyl ether (20 mL × 2) and filtered through a pad of Celite. The combined filtrate was evaporated to dryness under reduced pressure to afford a pale yellow solid, which was washed with pentane (1 mL × 3) and dried in vacuo; yield 251 mg (84%). Colorless crystals suitable for X-ray diffraction analysis were grown from a concentrated toluene solution at −35 °C. ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ 7.88 (m, 2, Ar), 7.66 (d, 2, Ar), 7.50 (dd, 2, Ar), 7.03 (m, 3, Ar), 3.63 (t, 4, OCH_2CH$_2$), 1.69 (s, 18, CMe_3), 1.18 (s, 22, CMe_3 + OCH$_2$CH_2). ^{1}H NMR (CDCl$_3$, 200 MHz): δ 7.68 (m, 2, Ar), 7.50 (m, 2, Ar), 7.45 (m, 3, Ar), 7.22 (d, 2, Ar), 3.64 (t, 4, OCH_2CH$_2$), 1.71 (t, 4, OCH$_2$CH_2), 1.42 (s, 18, CMe_3), 1.21 (s, 18, CMe_3). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 80.95 MHz): δ −61.70. ^{31}P{^{1}H} NMR (CDCl$_3$, 80.95 MHz): δ −62.40. ^{31}P{^{1}H} NMR (THF, 202.31 MHz): δ −58.85 ($^1J_{\mathrm{PSn}^{119}}$ = 1886, $^1J_{\mathrm{PSn}^{117}}$ = 1802). ^{119}Sn{^{1}H} NMR (THF, 186.38 MHz): δ −55.11 (d, $^1J_{\mathrm{PSn}^{119}}$ = 1886).

Synthesis of {[OPO]SnCl$_3$}(HNEt$_3$). Neat SnCl$_4$ (0.02 mL, 0.17 mmol) was added to a mixture of H$_2$[OPO] (88.3 mg, 0.17 mmol) and NEt$_3$ (37.8 mg, 0.37 mmol, 2.2 equiv) in THF (6 mL) at room temperature. The reaction solution was stirred at room temperature for 17 h and evaporated to dryness under reduced pressure. The solid residue was triturated with pentane (2 mL × 2) and dissolved in toluene (6 mL). The toluene solution was filtered through a pad of Celite and evaporated to dryness under reduced pressure to afford the product as a pale yellow solid; yield 92 mg (65%). ^{1}H NMR (C$_6$D$_6$, 500 MHz): δ 8.47 (br s, 1, NH), 7.97 (dd, 2, Ar), 7.67 (d, 2, Ar), 7.59 (dd, 2, Ar), 7.04 (m, 3, Ar), 2.40 (dq, 6, NCH_2Me), 1.82 (s, 18, CMe_3), 1.23 (s, 18, CMe_3), 0.71 (t, 9, NCH$_2$$Me$). ^{31}P{^{1}H} NMR (C$_6D_6$, 202.31 MHz): δ −56.52 ($^1J_{\mathrm{PSn}^{119}}$ = 2009, $^1J_{\mathrm{PSn}^{117}}$ = 1920). ^{31}P{^{1}H} NMR (THF, 80.95 MHz): δ −58.61. ^{119}Sn{^{1}H} NMR (C$_6$D$_6$, 186.38 MHz): δ −37.61 (d, $^1J_{\mathrm{PSn}^{119}}$ = 2009). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.70 MHz): δ 164.88 (d, J_{CP} = 13.32, C), 139.71 (d, J_{CP} = 4.15, C), 138.98 (d, J_{CP} = 7.79, C), 134.88 (d, J_{CP} = 10.43, CH), 131.20 (d, J_{CP} = 3.27, CH), 129.23 (d, J_{CP} = 11.94, CH), 128.87 (s, CH), 126.16 (s, CH), 124.06 (d, J_{CP} = 61.84, C), 110.35 (d, J_{CP} = 68.26, C), 46.87 (s, NCH$_2$Me), 36.47 (d, J_{CP}

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= 2.26, $C\mathrm{Me}_3$), 34.77 (s, $C\mathrm{Me}_3$), 32.09 (s, $\mathrm{C}Me_3$), 30.49 (s, $\mathrm{C}Me_3$), 8.84 (s, NCH_2Me). Anal. Calcd for $\mathrm{C_{40}H_{61}Cl_3NO_2PSn}$: C, 56.93; H, 7.29; N, 1.66. Found: C, 56.59; H, 7.29; N, 1.73.

Synthesis of [OPO]SnMe$_2$. Solid $\mathrm{H_2}$[OPO] (200 mg, 0.39 mmol) was dissolved in THF (4 mL), and the solution was cooled to −35 °C. To this was added *n*-BuLi (0.48 mL, 1.6 M in hexane, Aldrich, 0.77 mmol, 2 equiv) dropwise. The reaction mixture was stirred at room temperature for 1 h. The resultant solution was cooled to −35 °C again, and a prechilled solution of $\mathrm{Me_2SnCl_2}$ (85 mg, 0.39 mmol) in THF (10 mL) at −35 °C was added dropwise. The reaction mixture was stirred at room temperature for 16 h and evaporated to dryness under reduced pressure. The pale yellow solid thus obtained was dissolved in pentane (6 mL). The pentane solution was filtered through a pad of Celite and evaporated to dryness to afford the product as a pale yellow solid; yield 248 mg (96%). Colorless crystals suitable for X-ray diffraction analysis were grown from a concentrated pentane solution at −35 °C. ^{1}H NMR ($\mathrm{C_6D_6}$, 500 MHz): δ 7.92 (dd, 2, Ar), 7.79 (d, 2, Ar), 7.37 (dd, 2, Ar), 6.83 (m, 1, Ar), 6.78 (m, 2, Ar), 1.70 (s, 18, $\mathrm{C}Me_3$), 1.33 (s, 18, $\mathrm{C}Me_3$), 0.53 (d, 3, $^3J_{\mathrm{HP}} = 3$, $^2J_{\mathrm{HSn}} = 67$, $\mathrm{SnC}H_3$), 0.44 (d, 3, $^3J_{\mathrm{HP}} = 2$, $^2J_{\mathrm{HSn}} = 77$, $\mathrm{SnC}H_3$). ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$, 202.31 MHz): δ −76.479 ($^1J_{\mathrm{PSn}^{119}} = 1094$, $^1J_{\mathrm{PSn}^{117}} = 1047$). ^{31}P{^{1}H} NMR (THF, 80.95 MHz): δ −77.733. ^{119}Sn{^{1}H} NMR ($\mathrm{C_6D_6}$, 186.38 MHz): δ 342.127 ($^1J_{\mathrm{PSn}^{119}} = 1094$). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 125.70 MHz): δ 168.00 (d, $J_{\mathrm{CP}} = 14.71$, C), 140.42 (d, $J_{\mathrm{CP}} = 2.263$, C), 138.93 (d, $J_{\mathrm{CP}} = 4.59$, C), 132.47 (d, $J_{\mathrm{CP}} = 6.41$, CH), 130.99 (d, $J_{\mathrm{CP}} = 1.82$, CH), 130.23 (s, CH), 129.85 (d, $J_{\mathrm{CP}} = 5.97$, CH), 126.50 (d, $J_{\mathrm{CP}} = 1.76$, CH), 108.78 (s, C), 108.15 (s, C), 36.50 (s, $C\mathrm{Me}_3$), 34.77 (s, $C\mathrm{Me}_3$), 32.03 (s, $\mathrm{C}Me_3$), 30.23 (s, $\mathrm{C}Me_3$), 1.66 (s, $\mathrm{Sn}Me$), −5.06 (d, $^2J_{\mathrm{CP}} = 12.82$, $\mathrm{Sn}Me$). Anal. Calcd for $\mathrm{C_{36}H_{51}O_2PSn}$: C, 64.98; H, 7.72. Found: C, 65.07; H, 8.05.

Synthesis of [OPO]Sn(*n*-Bu)$_2$. Solid $\mathrm{H_2}$[OPO] (100 mg, 0.19 mmol) was dissolved in THF (4 mL), and the solution was cooled to −35 °C. To this was added *n*-BuLi (0.24 mL, 1.6 M in hexane, Aldrich, 0.38 mmol, 2 equiv) dropwise. The reaction mixture was stirred at room temperature for 1 h. The resultant solution was cooled to −35 °C again, and a prechilled solution of (*n*-Bu)$_2$SnCl$_2$ (58.7 mg, 0.19 mmol) in THF (4 mL) at −35 °C was added dropwise. The reaction mixture was stirred at room temperature for 16 h and evaporated to dryness under reduced pressure. The pale yellow solid thus obtained was dissolved in pentane (6 mL). The pentane solution was filtered through a pad of Celite and evaporated to dryness to afford the product as a pale yellow solid; yield 133 mg (92%). Crystals suitable for X-ray diffraction analysis were grown from a concentrated pentane solution at −35 °C; yield 61 mg (43%). ^{1}H NMR ($\mathrm{C_6D_6}$, 500 MHz): δ 7.888 (dd, 2, Ar), 7.779 (d, 2, Ar), 7.345 (ddd, 2, Ar), 6.816 (m, 3, Ar), 1.729 (s, 18, $\mathrm{C}Me_3$), 1.582 (m, 4, $\mathrm{Sn(C}H_2\mathrm{)_3CH_3}$), 1.480 (m, 2, $\mathrm{Sn(C}H_2\mathrm{)_3CH_3}$), 1.331 (s, 18, $\mathrm{C}Me_3$), 1.283 (m, 2, $\mathrm{Sn(C}H_2\mathrm{)_3CH_3}$), 1.236 (q, 2, $\mathrm{Sn(C}H_2\mathrm{)_3CH_3}$), 1.162 (q, 2, $\mathrm{Sn(C}H_2\mathrm{)_3CH_3}$), 0.730 (t, 3, $\mathrm{Sn(CH_2)_3C}H_3$), 0.695 (t, 3, $\mathrm{Sn(CH_2)_3C}H_3$). ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$, 202.31 MHz): δ −76.520 ($^1J_{\mathrm{PSn}^{119}} = 881$, $^1J_{\mathrm{PSn}^{117}} = 842$). ^{31}P{^{1}H} NMR (THF, 80.95 MHz): δ −76.922. ^{119}Sn{^{1}H} NMR ($\mathrm{C_6D_6}$, 186.38 MHz): δ 309.444 (d, $^1J_{\mathrm{PSn}^{119}} = 881$). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 125.70 MHz): δ 168.39 (d, $J_{\mathrm{CP}} = 15.59$, C), 140.07 (d, $J_{\mathrm{CP}} = 4.53$, C), 138.75 (d, $J_{\mathrm{CP}} = 8.17$, C), 132.56 (d, $J_{\mathrm{CP}} = 12.82$, CH), 130.81 (d, $J_{\mathrm{CP}} = 2.65$, CH), 130.13 (s, CH), 129.71 (d, $J_{\mathrm{CP}} = 11.94$, CH), 129.38 (d, $J_{\mathrm{CP}} = 60.46$, C), 126.54 (d, $J_{\mathrm{CP}} = 1.89$, CH), 108.43 (d, $J_{\mathrm{CP}} = 77.81$, C), 36.50 (d, $J_{\mathrm{CP}} = 2.77$, $C\mathrm{Me}_3$), 34.74 (s, $C\mathrm{Me}_3$), 32.03 (s, $\mathrm{C}Me_3$), 30.27 (s, $\mathrm{C}Me_3$), 28.55 (s, $\mathrm{Sn(}C\mathrm{H_2)_3Me}$), 28.36 (s, $\mathrm{Sn(}C\mathrm{H_2)_3Me}$), 27.49 (s, $\mathrm{Sn(}C\mathrm{H_2)_3Me}$), 26.97 (s, $\mathrm{Sn(}C\mathrm{H_2)_3Me}$), 23.72 (s, $\mathrm{Sn(}C\mathrm{H_2)_3Me}$), 16.56 (d, $J_{\mathrm{CP}} = 11.94$, $\mathrm{Sn(}C\mathrm{H_2)_3Me}$), 14.07 (s, $\mathrm{Sn(CH_2)_3}Me$), 13.91 (s, $\mathrm{Sn(CH_2)_3}Me$). Anal. Calcd for $\mathrm{C_{42}H_{63}O_2PSn}$: C, 67.30; H, 8.47. Found: C, 67.38; H, 8.49.

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Supporting Information Available: X-ray crystallographic data in CIF format for [OPO]SnCl$_2$(THF), [OPO]SnMe$_2$, and [OPO]Sn(*n*-Bu)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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