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Cyclometalation of *o*-Arylphenoxide and Alkoxide Ligands at Tin(IV) Metal Centers: Reaction Scope and Product Characterization

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The reaction of $LiOC_6H_3Ph_2$-2,6 ($OC_6H_3Ph_2$-2,6 = 2,6-diphenylphenoxide) with $SnCl_4$ leads to the formation of the dimeric compound $[Sn(OC_6H_3Ph\text{-}C_6H_4)Cl_2]_2$ (1) containing cyclometalated 2,6-diphenylphenoxide ligands. Similarly, treatment of $Sn(NMe_2)_4$ with $HOC_6H_3Ph_2$-2,6 (2 equiv) in hydrocarbon solvents at 50 °C leads to the bis-cyclometalated compound $[Sn(OC_6H_3Ph\text{-}C_6H_4)_2(HNMe_2)_2]$ (2). Single-crystal X-ray diffraction analyses of 1 and 2 show the presence of six-membered metallacycle rings formed by metalation of a substituent aryl group of the aryloxide ligands. In compound 1 the dinuclear unit is held together by asymmetric oxygen bridges, while in 2 the dimethylamine ligands are mutually cis. Attempts to induce cyclometalation of 2,6-diphenylphenoxide ligands utilizing an alkyl leaving group at tin failed. Compounds $[Me_3Sn(OC_6H_3Ph_2\text{-}2,6)]$ (3) and $[Me_2Sn(OC_6H_3Ph_2\text{-}2,6)_2]$ (4) are stable at 150 °C for days. The treatment of $Sn(NMe_2)_4$ with the asymmetric phenol $HOC_6H_2Bu^t_2$-2,4-Ph-6 initially led to the bis-substituted compound $[Sn(OC_6H_2Bu^t_2\text{-}2,4\text{-}Ph\text{-}6)_2(NMe_2)_2]$ (5). Thermolysis of 5 leads to the five-coordinate, bis-cyclometalated compound $[Sn(OC_6H_2Bu^t_2\text{-}C_6H_4)_2(HNMe_2)]$ (6). No evidence for metalation of the *tert*-butyl substituent was observed. The solid-state structure of 6 shows the geometry about tin to be trigonal bipyramidal with trans, axial oxygen atoms. Treatment of $Sn(NMe_2)_4$ with various alcohols containing aryl substituents leads to the isolation of the alkoxide compounds $[Sn(OCH_2Ph)_4(HNMe_2)]_2$ (7), $[Sn(OCMe_2Ph)_4]$ (8), and $[Sn(OCPh_3)_2(NMe_2)_2]$ (9). A single-crystal X-ray diffraction analysis of 7 shows a dinuclear unit held together by two alkoxide bridges. The dimethylamine ligands occupy axial sites in the edge-shared bis-octahedral structure, which contains a crystallographic inversion center. Thermolysis at 110 °C of the 2-phenylpropoxide compound 8 results in elimination of $HOCMe_2Ph$ and formation of a bis-cyclometalated complex $[Sn(OCMe_2\text{-}C_6H_4)_2]_2$ (10). Crystallographic studies show the dinuclear unit in 10 is held together by two bridging oxygen atoms within two of the new five-membered metallacycle rings. The spectroscopic properties of 7 and 10 are consistent with the dinuclear units being maintained in solution. Thermolysis of the bis(amido) complex $[Sn(OCPh_3)_2(NMe_2)_2]$ (9) also leads to a bis-cyclometalated compound $[Sn(OCPh_2\text{-}C_6H_4)_2(HNMe_2)_2]$ (11). The solid-state structure of octahedral 11 shows the dimethylamine ligands to be mutually trans. In a related study, treatment of $Sn(NMe_2)_4$ with 2-*tert*-butyl-1-naphthol (HO-tbn) initially leads to the intermediate $[Sn(O\text{-}tbn)_2(NMe_2)_2]$, which converts slowly at room temperature to the bis-cyclometalated complex $[Sn(O\text{-}tbn\text{-}H)_2(NHMe_2)_2]$ (12). The cyclometalation of the O-tbn ligands at the 8-position of the naphthalene ring was confirmed by a single-crystal X-ray diffraction analysis of 12. Crystal data: for $Sn_2Cl_4O_2C_{42}H_{30}$ (1) at 20 °C, a = 11.680 (1) Å, b = 26.909 (3) Å, c = 12.884 (1) Å, β = 110.720 (8)°, Z = 4, d_{calc} = 1.659 g cm^{-3} in space group $P2_1/n$; for $SnO_2N_2C_{40}H_{38}$ (2) at 22 °C, a = 18.223 (1) Å, b = 7.644 (2) Å, c = 13.709 (1) Å, β = 121.440 (7)°, Z = 2, d_{calcd} = 1.422 g cm^{-3} in space group $C2$; for $SnO_2NC_{42}H_{55}$ (6) at 20 °C, a = 20.878 (3) Å, b = 7.024 (1) Å, c = 27.150 (3) Å, β = 95.37 (1)°, Z = 4, d_{calcd} = 1.214 g cm^{-3} in space group $P2_1/n$; for $Sn_2O_8N_2C_{60}H_{70}$ (7), a = 10.701 (2) Å, b = 11.208 (1) Å, c = 23.322 (2) Å, α = 91.386 (9)°, β = 98.05 (1)°, γ = 92.62 (1)°, Z = 2, d_{calcd} = 1.423 g cm^{-3} in space group $P\bar{1}$; for $Sn_2O_4C_{36}H_{40}$ (10) at 20 °C, a = 24.101 (2) Å, b = 9.972 (1) Å, c = 19.678 (1) Å, β = 135.489 (8)°, Z = 4, d_{calcd} = 1.551 g cm^{-3} in space group $C2/c$; for $SnO_2N_2C_{42}H_{42}$ (11) at 20 °C, a = 9.175 (1) Å, b = 9.3158 (9) Å, c = 12.033 (2) Å, α = 76.20 (1)°, β = 68.03 (1)°, γ = 67.65 (1)°, Z = 1, d_{calcd} = 1.374 g cm^{-3} in space group $P\bar{1}$; for $SnO_2N_2C_{32}H_{42}$ (12) at 20 °C, a = 10.3832 (9) Å, b = 9.075 (1) Å, c = 17.255 (2) Å, β = 112.600 (8)°, Z = 2, d_{calcd} = 1.339 g cm^{-3} in space group $P2_1/c$.

Introduction

The study of transition-metal alkoxide, aryloxide, and siloxide chemistry has increased dramatically over the last ten years.[1-5] More recently, interest has also focused on the structure, bonding, and reactivity of alkoxide and related derivatives of the s- and p-block elements.[5-10] During

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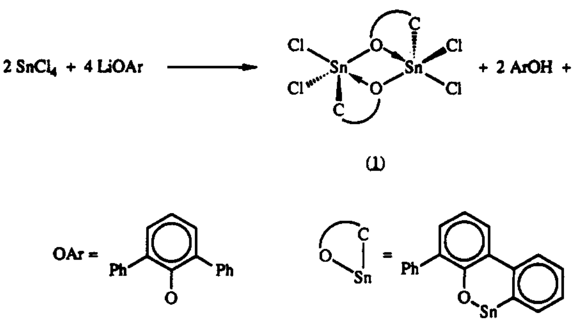
Scheme I



our studies of early d-block element chemistry that can be supported by aryloxide ligation,[11-14] we have demonstrated that cyclometalation of aryloxide ligands is sometimes a facile reaction.[15] While expanding our studies to include the aryloxide chemistry of the group 14 metals Ge and Sn, we discovered that the ligand 2,6-diphenylphenoxide will undergo rapid cyclometalation when coordinated to suitable tin(IV) metal centers.[16] Further work has now shown that tin(IV) metal centers have the ability to metalate a wide range of simple alkoxide ligands that contain suitable aryl substituents. The fact that alkoxide ligands may undergo sometimes facile cyclometalation by tin is of relevance to the developing field of metal oxide synthesis via MOCVD of metal–alkoxide precursors.[1] In this paper we report upon the scope of these cyclometalation reactions as well as upon the spectroscopic and structural characteristics of the products.

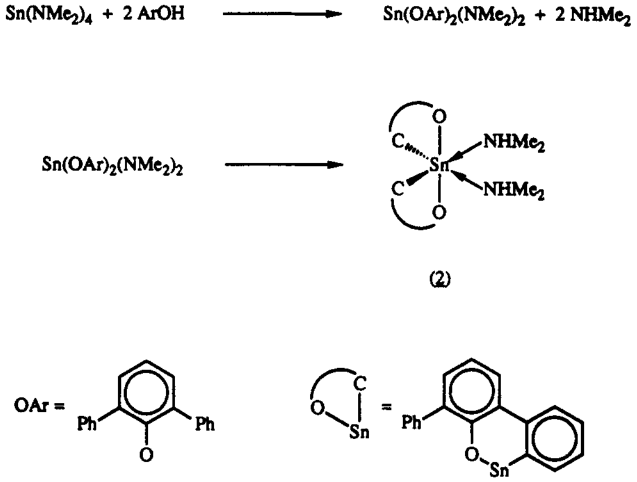
Table I. Selected Bond Distances (Å) and Angles (deg) for $[Sn(OC_6H_3Ph\text{-}C_6H_4)Cl_2]_2$ (1)

Sn(1)–Sn(2)	3.4192 (4)	Sn(2)–Cl(21)	2.363 (1)
Sn(1)–Cl(11)	2.354 (1)	Sn(2)–Cl(22)	2.29 (1)
Sn(1)–Cl(12)	2.290 (1)	Sn(2)–O(10)	2.035 (2)
Sn(1)–O(10)	2.326 (2)	Sn(2)–O(20)	2.259 (2)
Sn(1)–O(20)	2.045 (2)	Sn(2)–C(222)	2.103 (5)
Sn(1)–C(122)	2.133 (4)		
Cl(11)–Sn(1)–Cl(12)	102.91 (4)	Cl(21)–Sn(2)–C(222)	103.2 (1)
Cl(11)–Sn(1)–O(10)	160.74 (6)	Cl(22)–Sn(2)–O(10)	108.07 (8)
Cl(11)–Sn(1)–O(20)	93.86 (7)	Cl(22)–Sn(2)–O(20)	89.77 (7)
Cl(11)–Sn(1)–C(122)	104.6 (1)	Cl(22)–Sn(2)–C(222)	118.8 (1)
CL(12)–Sn(1)–O(10)	87.36 (7)	O(10)–Sn(2)–O(20)	68.42 (9)
Cl(12)–Sn(1)–O(20)	115.60 (8)	O(10)–Sn(2)–C(222)	124.2 (1)
Cl(12)–Sn(1)–C(122)	125.9 (1)	O(20)–Sn(2)–C(222)	82.7 (1)
O(10)–Sn(1)–O(20)	66.92 (9)	Sn(1)–O(10)–Sn(2)	103.1 (1)
O(10)–Sn(1)–C(122)	81.4 (1)	Sn(1)–O(10)–C(11)	113.0 (2)
O(20)–Sn(1)–C(122)	107.9 (1)	Sn(2)–O(10)–C(11)	128.3 (2)
Cl(21)–Sn(2)–Cl(22)	102.09 (5)	Sn(1)–O(20)–Sn(2)	105.1 (1)
Cl(21)–Sn(2)–O(10)	94.37 (7)	Sn(1)–O(20)–C(21)	132.1 (2)
Cl(21)–Sn(2)–O(20)	161.65 (7)	Sn(2)–O(20)–C(21)	116.7 (2)

Table II. Selected Bond Distances (Å) and Angles (deg) for $[Sn(OC_6H_3Ph\text{-}C_6H_4)_2(HNMe_2)_2]$ (2)

Sn–O(1)	2.091 (8)	Sn–C(162)	2.12 (1)
Sn–N(1)	2.32 (1)		
O(1)–Sn–O(1)	157.0 (4)	N(1)–Sn–C(162)	146.2 (4)
O(1)–Sn–N(1)	71.2 (3)	N(1)–Sn–C(162)	92.1 (4)
O(1)–Sn–N(1)	89.0 (3)	C(162)–Sn–C(162)	118.7 (5)
O(1)–Sn–C(162)	86.5 (3)	Sn–O(1)–C(11)	122.8 (7)
O(1)–Sn–C(162)	105.3 (4)	Sn–N(1)–C(1)	112.5 (9)
N(1)–Sn–N(1)	63.3 (5)	Sn–N(1)–C(2)	114 (2)

Scheme II



Results and Discussion

Cyclometalation of *o*-Arylphenoxide Ligands. Attempts to prepare simple 2,6-diphenylphenoxide ($OC_6H_3Ph_2$-2,6) derivatives of tin by reaction of $LiOC_6H_3Ph_2$-2,6 with $SnCl_4$ in benzene or toluene as solvent lead to a complex mixture of products. When 2 equiv of lithium salt is used, it is possible to isolate the cyclometalated dimer $[Sn(OC_6H_3Ph\text{-}C_6H_4)Cl_2]_2$ (1) as large colorless crystals of the hydrocarbon solvate (Scheme I). The yield of 1 can be increased to 75% by refluxing the reaction mixture. It seems reasonable to believe that the formation of 1 occurs via an intermediate aryloxide compound of the type $[Sn(OC_6H_3Ph_2\text{-}2,6)Cl_3]$, which undergoes elimination of HCl to form the new metallacycle ring. The eliminated HCl then reacts with the extra equivalent of lithium aryloxide to produce $HOC_6H_3Ph_2$-2,6. The facile cyclometalation observed for the tin(IV) chloride system contrasts with the high thermal stability of $M(OC_6H_3Ph_2\text{-}2,6)_2Cl_2$ and $M(OC_6H_3Ph_2\text{-}2,6)_3Cl$ (M = Ge,

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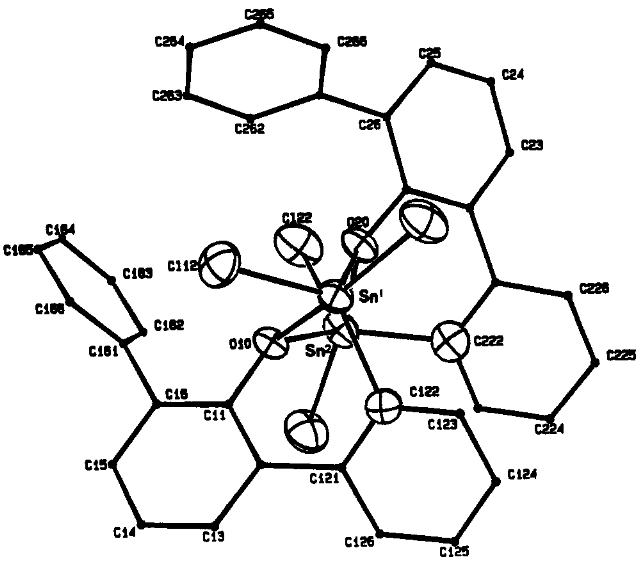

Figure 1. ORTEP view of $[Sn(OC_6H_3Ph\text{-}C_6H_4)Cl_2]_2$ (1).

Ti);[17,18] neither undergo cyclometalation after extended heating (days at 150 °C).

The ^1H NMR spectrum of 1 shows a total of 10 nonequivalent aromatic signals as anticipated for a cyclometalated 2,6-diphenylphenoxide ligand. A single-crystal X-ray diffraction analysis of $1\cdot C_6H_6$ was carried out (Figure 1). Selected bond distances and angles are collected in Table I. The molecular structure of 1 can be seen to consist of two five-coordinate tin metal centers held together by two oxygen atom bridges. These oxygen atoms are themselves part of the new metallacycle rings. The geometry about each tin metal center is best described as trigonal bipyramidal. The bridging oxygen and one terminal chlorine atom occupy the axial sites. An interesting feature of the structure of 1 involves the distinctly asymmetric oxygen bridges.[19] For example O(10) is strongly bound to Sn(2) with a distance of 2.035 (2) Å but O(10) is weakly bound to Sn(1) with a distance of 2.326 (2) Å. The shorter distances are consistent with normal, covalent tin–aryloxide bonds, while the longer distances correspond to dative interactions between oxygen lone pairs and tin(IV).[19] The alternating covalent/dative bonds shown for 1 in Scheme I are hence structurally vertical. A similar situation has been noticed in other tin compounds containing oxygen bridging ligands.[19,20] It is also of note that the long, dative bonds to the metal centers are from oxygen atoms chelated via the metallacycle ring (Scheme I).

Metal amido compounds have been shown to be valuable substrates for the synthesis of metal alkoxide and aryloxide compounds.[21,22] The reaction of $Sn(NMe_2)_4$ with $HOC_6H_3Ph_2$-2,6 (2 equiv) in hydrocarbon solvents at 50 °C generates the bis-cyclometalated compound $[Sn(OC_6H_3Ph\text{-}C_6H_4)_2(HNMe_2)_2]$ (2) (Scheme II). The intermediate bis(amido) compound $[Sn(OC_6H_3Ph_2\text{-}2,6)_2(NMe_2)_2]$ was detected spectroscopically but not isolated. The facile formation of 2 contrasts with the thermal stability of the bis(amido) structurally characterized[17] compounds $[Ge(OC_6H_3Ph_2\text{-}2,6)_2(NMe_2)_2]$ and $[Sn(OC_6H_3Bu^t{}_2\text{-}2,6)_2(NMe_2)_2]$. The molecular structure of monomeric 2 (Figure 2; Table II) consists of a pseudooctahedral environment about the tin metal center with the dimethylamine ligands being mutually cis. The two new metallacycle rings are oriented with their oxygen atoms trans to each other. A crystallographically imposed 2-fold axis is present.

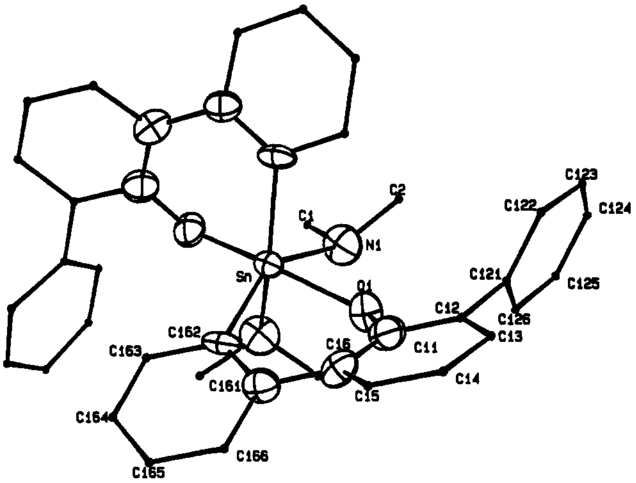

Figure 2. ORTEP view of $[Sn(OC_6H_3Ph\text{-}C_6H_4)_2(HNMe_2)_2)]$ (2).

The formation of 1 and 2 involve cyclometalation at tin with chloride and dimethylamido ligands acting as leaving groups. For high-valent, early d-block metals, halide and dialkylamido ligands rarely act as leaving groups in CH bond activation reactions.[23,24] Instead, the more common method of CH bond activation involves σ-bond metathesis with M–C or M–H bonds. In complete contrast, cyclometalation at tin does not occur with alkyl leaving groups. The methyl derivatives $[Me_3Sn(OC_6H_3Ph_2\text{-}2,6)]$ (3) and $[Me_2Sn(OC_6H_3Ph_2\text{-}2,6)_2]$ (4) can be readily obtained from the corresponding chloride compounds and $LiOC_6H_3Ph_2$-2,6. Both 3 and 4 are stable at 150 °C for 24 h. No evidence (^1H NMR) for elimination of either methane or 2,6-diphenylphenol was obtained for either compound. There are a number of possible explanations for the dramatic difference in the reactivity of tin versus early d-block metals such as titanium or zirconium. In the case of tin, the pathway for aromatic CH bond activation appears to proceed via electrophilic aromatic substitution.[25] The presence of alkyl groups will have the effect of reducing the electrophilic (Lewis acidic) nature of the metal center, and hence, attack on aromatic rings should be reduced. More electronegative, anionic ligands such as Cl^-, OR^-, or NR_2^- should increase the Lewis acidity of the tin metal center. In the case of the early d-block metals, CH bond activation occurs via 4-center, 4-electron transition

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Scheme III

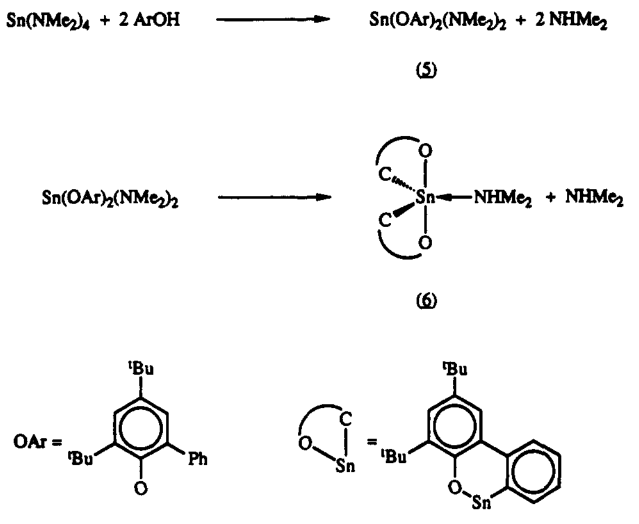

Table III. Selected Bond Distances (Å) and Angles (deg) for $[Sn(OC_6H_2Bu^t{}_2\text{-}C_6H_4)_2(HNMe_2)]$ (6)

Sn–O(10)	2.097 (4)	Sn–C(122)	2.111 (7)
Sn–O(20)	2.077 (4)	Sn–C(222)	2.105 (6)
Sn–N(30)	2.220 (6)		
O(10)–Sn–O(20)	165.8 (2)	N(30)–Sn–C(122)	108.7 (2)
O(10)–Sn–N(30)	83.6 (2)	N(30)–Sn–C(222)	112.1 (3)
O(10)–Sn–C(122)	87.7 (2)	C(122)–Sn–C(222)	139.1 (3)
O(10)–Sn–C(222)	93.4 (2)	Sn–O(10)–C(11)	119.0 (4)
O(20)–Sn–N(30)	82.5 (2)	Sn–O(20)–C(21)	120.6 (4)
O(20)–Sn–C(122)	99.7 (2)	Sn–N(30)–C(31)	113.2 (5)
O(20)–Sn–C(122)	88.9 (2)	Sn–N(30)–C(32)	112.3 (5)

states.[23,24] For these metals, metal–carbon bond dissociation energies are much lower than for metal–halide or metal–dialkylamido bonds.[26] Hence, from a kinetic viewpoint the transition-state energy is much lower for alkyl leaving groups.

Another consequence of the differing mechanisms evident for CH bond activation by tin and the d-block metals is that the latter have the ability to activate aliphatic CH bonds. In the case of tin, CH bond activation appears to be limited to aromatic substrates. This is highlighted by the fact that 2,6-di-*tert*-butylphenoxide derivatives of tin are stable,[17] while cyclometalation of this ligand occurs rapidly at d^0-metal centers.[15] The treatment of $Sn(NMe_2)_4$ with 2,4-di-*tert*-butyl-6-phenylphenol (2 equiv) initially generates the bis(aryloxide) $[Sn(OC_6H_2Bu^t{}_2\text{-}2,4\text{-}Ph\text{-}6)_2(NMe_2)_2]$ (5). Thermolysis of 5 leads to the five-coordinate, bis-cyclometalated compound $[Sn(OC_6H_2Bu^t{}_2\text{-}C_6H_4)_2(HNMe_2)]$ (6), in which metalation of the *o*-aryl rings has occurred (Scheme III). No evidence (^1H NMR) for metalation of the *tert*-butyl groups was obtained. The solid-state structure of 6 (Figure 3; Table III) is best described as a distorted trigonal bipyramid with trans, axial oxygen atoms. The fact that only one dimethylamine ligand remains bound in contrast to related bis-cyclometalated compound 2 is probably a consequence of the steric demands of the *tert*-butyl substituents in 6.

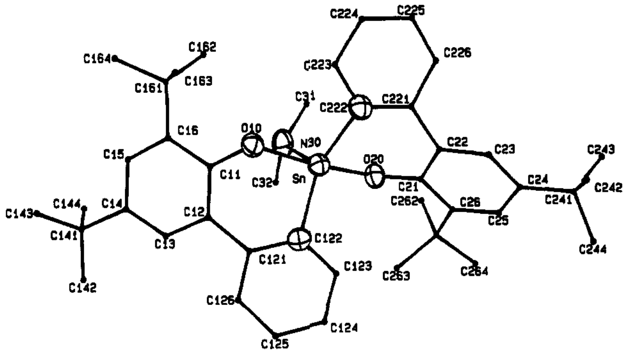

Figure 3. ORTEP view of $[Sn(OC_6H_2Bu^t{}_2\text{-}C_6H_4)_2(HNMe_2)]$ (6).

Scheme IV

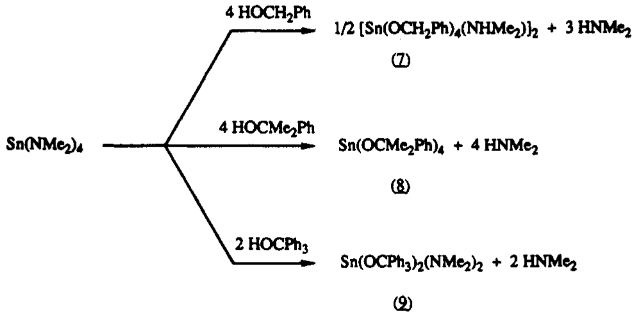

Table IV. Selected Bond Distances (Å) and Angles (deg) for $[Sn(OCH_2Ph)_4(HNMe_2)]_2$ (7)

Sn(1)–O(110)	2.126 (3)	Sn(2)–O(210)	2.113 (3)
Sn(1)–O(110)	2.117 (3)	Sn(2)–O(210)	2.133 (3)
Sn(1)–O(120)	1.978 (3)	Sn(2)–O(220)	1.984 (3)
Sn(1)–O(130)	1.979 (3)	Sn(2)–O(230)	1.984 (3)
Sn(1)–O(140)	1.994 (3)	Sn(2)–O(240)	2.010 (3)
Sn(1)–N(150)	2.259 (4)	Sn(2)–N(250)	2.243 (4)
O(110)–Sn(1)–O(110)	72.2 (1)	O(230)–Sn(2)–O(240)	96.6 (1)
O(110)–Sn(1)–O(120)	160.3 (1)	O(230)–Sn(2)–N(250)	88.5 (1)
O(110)–Sn(1)–O(130)	96.3 (1)	O(240)–Sn(2)–N(250)	165.9 (1)
O(110)–Sn(1)–O(140)	82.5 (1)	Sn(1)–O(110)–Sn(1)	107.8 (1)
O(110)–Sn(1)–N(150)	85.4 (1)	Sn(1)–O(110)–C(110)	126.5 (3)
O(120)–Sn(1)–O(130)	103.2 (1)	Sn(1)–O(120)–C(120)	125.5 (3)
O(120)–Sn(1)–O(140)	96.4 (1)	Sn(1)–O(130)–C(130)	124.7 (3)
O(120)–Sn(1)–N(150)	93.9 (1)	Sn(1)–O(140)–C(140)	124.1 (3)
O(130)–Sn(1)–O(140)	99.9 (1)	Sn(2)–O(210)–Sn(2)	105.8 (1)
O(130)–Sn(1)–N(150)	84.3 (1)	Sn(2)–O(210)–C(210)	122.3 (3)
O(140)–Sn(1)–N(150)	167.6 (1)	Sn(2)–O(220)–C(220)	121.8 (3)
O(210)–Sn(2)–O(210)	74.2 (1)	Sn(2)–O(230)–C(230)	122.2 (3)
O(210)–Sn(2)–O(220)	162.2 (1)	Sn(2)–O(240)–C(240)	121.9 (3)
O(210)–Sn(2)–O(230)	96.7 (1)	Sn(1)–N(150)–C(151)	115.7 (3)
O(210)–Sn(2)–O(240)	83.8 (1)	Sn(1)–N(150)–C(152)	114.0 (3)
O(210)–Sn(2)–N(250)	82.5 (1)	C(151)–N(150)–C(152)	108.7 (4)
O(220)–Sn(2)–O(230)	100.5 (1)	Sn(2)–N(250)–C(251)	116.5 (3)
O(220)–Sn(2)–O(240)	98.0 (1)	Sn(2)–N(250)–C(252)	114.8 (3)
O(220)–Sn(2)–N(250)	93.1 (1)		

Cyclometalation of Alkoxide Ligands. Following the observation of facile cyclometalation of *o*-arylphenoxides by tin, we have investigated the reaction of $Sn(NMe_2)_4$ with a number of alcohols that contain at least one phenyl ring in a position suitable for cyclometalation (Scheme IV). In the case of benzyl alcohol, complete substitution of all dimethylamido groups is observed leading to the alkoxide dimer $[Sn(OCH_2Ph)_4(HNMe_2)]_2$ (7) and 3 equiv of dimethylamine (Scheme IV). The solid-state structure of 7 confirms the dimeric nature of the compound deduced from spectroscopic evidence (vide infra). An ORTEP view of the molecule is given in Figure 4, while Table IV contains selected bond distances and angles. The molecule adopts an edge-shared bis-octahedral structure with a pair of bridging alkoxide oxygen atoms. There is a crystallographically imposed inversion center within the molecule. Unlike the cyclometalated compound 1, the bonding to the bridging alkoxide ligands in 7 are symmetric.

The spectroscopic properties of 7 are consistent with it rigidly maintaining the observed solid-state structure in solution. In the ^1H NMR spectrum in $CDCl_3$, the $Sn-NHMe_2$ group appears as a well-resolved doublet and septet, the doublet due to the methyl protons having satellites due to coupling to ^{117}Sn and ^{119}Sn nuclei. The

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[26] Simoes, J. A. M.; Beauchamp, J. L. *Chem. Rev.* 1990, *90*, 629 and references therein.

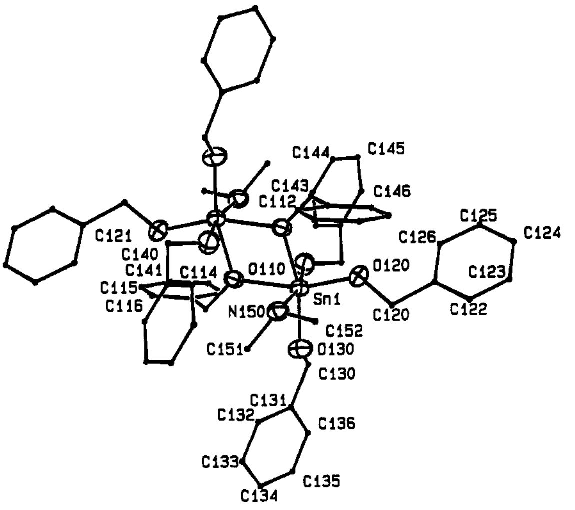


Figure 4. ORTEP view of $[Sn(OCH_2Ph)_4(HNMe_2)]_2$ (7), emphasizing the central coordination sphere.

Table V. Selected Bond Distances (Å) and Angles (deg) for $[Sn(OCMe_2\text{-}C_6H_4)_2]_2$ (10)

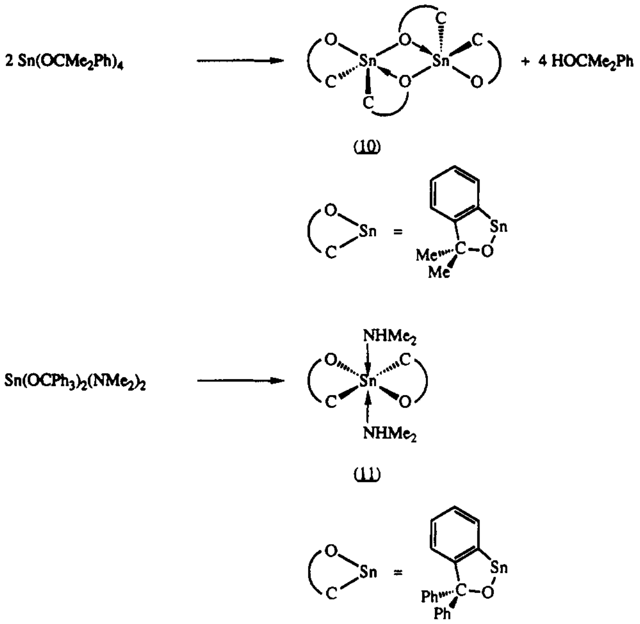
Sn–Sn	3.4296 (5)	Sn–O(2)	2.258 (2)
Sn–O(1)	2.007 (3)	Sn–C(12)	2.101 (4)
Sn–O(2)	2.056 (2)	Sn–C(22)	2.100 (4)
O(1)–Sn–O(2)	98.0 (1)	O(2)–Sn–C(22)	121.5 (1)
O(1)–Sn–O(2)′	168.8 (1)	C(12)–Sn–C(22)	128.6 (1)
O(1)–Sn–C(12)	84.6 (1)	Sn–O(2)–Sn	105.2 (1)
O(1)–Sn–C(22)	104.2 (1)	Sn–O(2)–C(20)	127.6 (2)
O(2)–Sn–O(2)	72.6 (1)	Sn–O(1)–C(10)	114.2 (2)
O(2)–Sn–C(12)	106.6 (1)		

SnOC*H*$_2$Ph methylene protons appear as two overlapping AB patterns and a singlet in the δ 4.8–5.5 ppm region. The singlet can be assigned to the nondiastereotopic methylene protons of the benzyl alkoxide group trans to the dimethylamine nitrogen atom. In the ^{13}C NMR spectrum, three nonequivalent $Sn\text{–}OCH_2Ph$ ligands are also indicated. Hence, in solution neither dissociation of the $HNMe_2$ ligands nor exchange of bridge and terminal alkoxide groups is rapid on the NMR time scale.

The reaction of $Sn(NMe_2)_4$ with the more bulky alcohols 2-phenylpropan-2-ol ($HOCMe_2Ph$) or triphenylmethanol ($HOCPh_3$) led to the mononuclear alkoxide compounds $[Sn(OCMe_2Ph)_4]$ (**8**) and $[Sn(OCPh_3)_2(NMe_2)_2]$ (**9**), respectively (Scheme IV). The homoleptic alkoxide **8** was obtained as a colorless liquid, while the mixed alkoxide–amido complex **9** is a white, powdery solid. In both the ^1H and ^{13}C NMR spectra of **8**, only one set of 2-phenylpropoxide resonances were observed. In the case of $[Sn(OCPh_3)_2(NMe_2)_2]$ (**9**) the Sn–N*Me*$_2$ protons appear as a very sharp resonance at δ 2.14 ppm with two sets of satellites due to coupling to ^{117}Sn (68 Hz) and ^{119}Sn (71 Hz).

Thermolysis of the 2-phenylpropoxide compound **8** at 110 °C in the absence of solvent leads to the formation of 2-phenylpropanol and the cyclometalated compound $[Sn(OCMe_2\text{-}C_6H_4)_2]_2$ (**10**) (Scheme V). Compound **10** is formed in the reaction mixture as large colorless blocks and can be purified by simply washing with hexane and drying. The solid-state structure of **10** is shown in Figure 5, while Table V contains selected bond distances and angles. The dinuclear molecule contains a crystallographically imposed 2-fold axis making the two tin metal centers equivalent. The cyclometalation of the 2-phenylpropoxide ligands results in the formation of two, nonequivalent five-membered metallacycle rings. One of these rings, bound to the metal through O(1) and C(12), forms an essentially planar chelate ring to the metal with a bite of 84.6 (1)°. The other metallacycle ring has its oxygen atom, O(2), bridging between the two metal centers. The overall geometry about each metal center is distorted trigonal bipyramidal, with the two new Sn–C(aryl) bonds occupying equatorial positions. The bridging oxygen atoms occupy an axial site at one metal and an equatorial site at the other. There is a definite asymmetry to the $Sn(\mu\text{-}O)_2Sn$ bridging unit. One of the Sn–O(2) distances is short, 2.056 (2) Å, comparable to the terminal Sn–O(1) distance of 2.007 (3) Å, while the other Sn–O(2) distance is long, 2.258 (2) Å. This latter distance is consistent with a simple dative bond between oxygen and tin(IV). The alternating covalent/dative bonding shown in Scheme V has excellent structural support. As in the case of compound **1** (Figure 1), the longer Sn–O dative bond occurs to the metal center to which the oxygen atom is chelated.

Scheme V



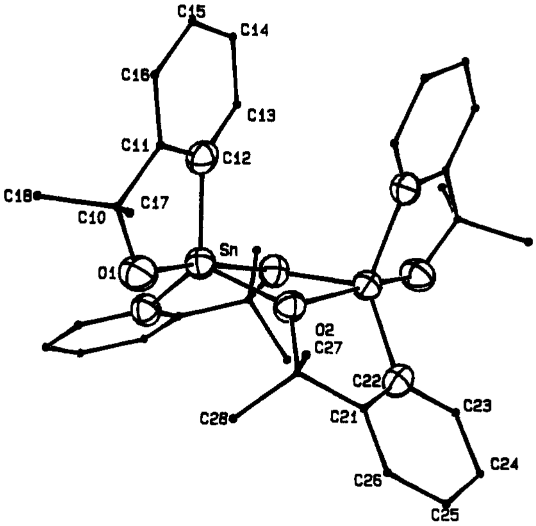


Figure 5. ORTEP view of $[Sn(OCMe_2\text{-}C_6H_4)_2]_2$ (10).

The NMR spectroscopic properties of $[Sn(OCMe_2\text{-}C_6H_4)_2]_2$ (**10**) indicate the solid-state structure is maintained in solution. The molecular structure of **10** (Figure 5) indicates that the OC*Me*$_2$ groups should be diastereotopic, and the resulting ^1H NMR spectrum (Figure 6) shows four nonequivalent methyl resonances of equal intensity. Furthermore, one of the protons ortho to the new

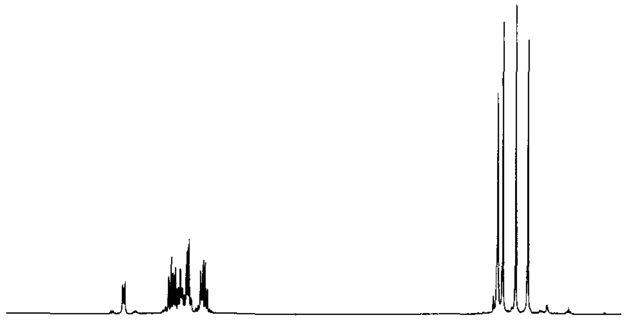


Figure 6. ^1H NMR (200 MHz) spectrum of $[Sn(OCMe_2\text{-}C_6H_4)_2]_2$ (**10**).

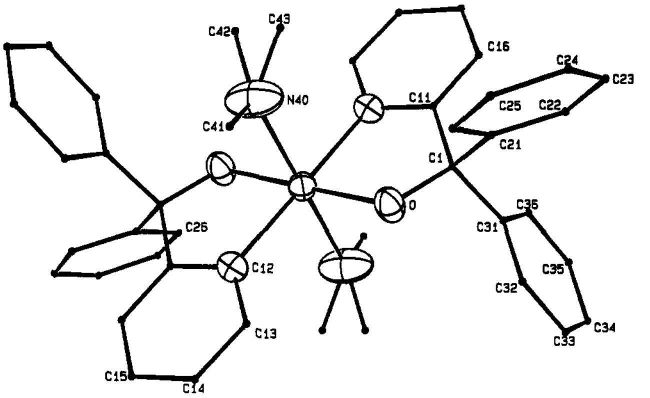


Figure 7. ORTEP view of $[Sn(OCPh_2\text{-}C_6H_4)_2(HNMe_2)_2]$ (**11**).

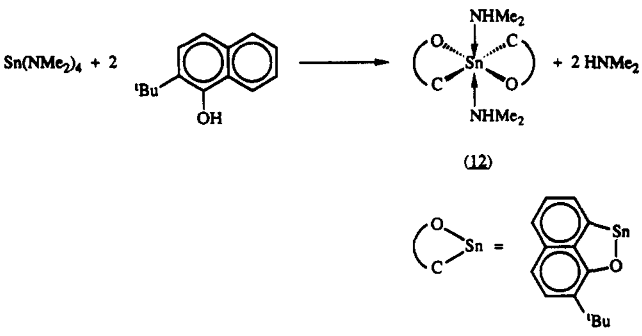
Table VI. Selected Bond Distances (Å) and Angles (deg) for $[Sn(OCPh_2\text{-}C_6H_4)_2(HNMe_2)_2]$ (11)

Sn–O	2.072 (3)	Sn–C(12)	2.119 (4)
Sn–N(4)	2.394 (4)		
O–Sn–O	180 (0)	O–Sn–C(12)	99.0 (1)
O–Sn–N(4)	90.0 (2)	N(40)–Sn–N(40)	180 (0)
O–Sn–N(40)	90.0 (2)	N(40)–Sn–C(12)	91.7 (2)
O–Sn–C(12)	99.0 (1)	N(40)–Sn–C(12)	88.3 (2)
O–Sn–C(12)	81.0 (1)	N(40)–Sn–C(12)	88.3 (2)
O–Sn–N(40)	90.0 (2)	N(40)–Sn–C(12)	91.7 (2)
O–Sn–N(40)	90.0 (2)	C(12)–Sn–C(12)	180 (0)
O–Sn–C(12)	81.0 (1)	Sn–O–C(1)	116.2 (2)

Sn–C(aryl) bonds resonates at low field, with $^{117}Sn/^{119}Sn$ satellites. In the ^{13}C NMR spectrum of **10** the two Sn-*C*-(aryl) carbon atoms of the two nonequivalent metallacycle rings resonate downfield at δ 155.6 and 160.0 ppm. A total of 12 (6 pairs) aromatic signals are resolved.

Thermolysis of the bis(amido) complex $[Sn(OCPh_3)_2(NMe_2)_2]$ (**9**) in hydrocarbon solvents leads to formation of the octahedral, bis-cyclometalated complex $[Sn(OCPh_2\text{-}C_6H_4)_2(HNMe_2)_2]$ (**11**) (Scheme V). The formation of **11** from **9** involves an intramolecular transfer of the hydrogen atom from the aromatic CH bond to the dimethylamido nitrogen atom. In the ^1H NMR spectrum of **11** the characteristic downfield multiplet with satellite peaks of the proton ortho to the new Sn–C(aryl) bond is present. In the solid state (Figure 7; Table VI), the two $HNMe_2$ ligands in **11** can be seen to occupy mutually trans sites about the crystallographically imposed inversion center. The two five-membered metallacycle rings in **11** are coplanar. This contrasts with the situation in the bis-cyclometalated compound $[Sn(OC_6H_3Ph\text{-}C_6H_4)_2(HNMe_2)_2]$ (**2**), where the two dimethylamine ligands are mutually cis (Figure 2). Molecular models show that a coplanar arrangement of the two metallacycles formed by cyclometalation of 2,6-diphenylphenoxide groups is sterically unfavored.

Scheme VI



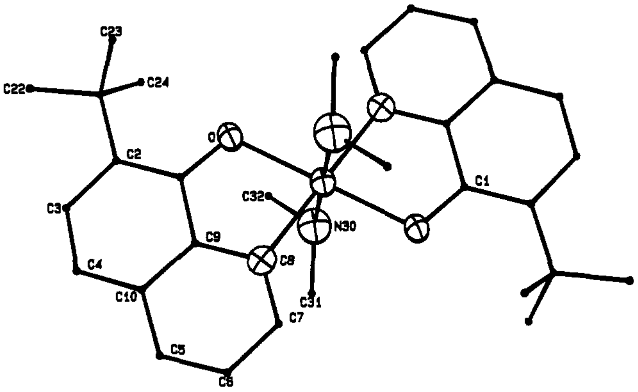


Figure 8. ORTEP view of $[Sn(O\text{-}tbn\text{-}H)_2(HNMe_2)_2]$ (**12**).

Table VII. Selected Bond Distances (Å) and Angles (deg) for $[Sn(O\text{-}tbn\text{-}H)_2(HNMe_2)_2]$ (12)

Sn–O	2.126 (3)	Sn–C(8)	2.131 (5)
Sn–N(30)	2.380 (4)		
O–Sn–O	180 (0)	N(30)–Sn–N(30)	180 (0)
O–Sn–N(30)	92.1 (1)	N(30)–Sn–C(8)	89.8 (2)
O–Sn–N(3)	87.9 (1)	N(30)–Sn–C(8)′	90.2 (2)
O–Sn–C(8)	80.7 (1)	C(8)–Sn–C(8)′	180 (0)
O–Sn–C(8)′	99.3 (1)	Sn–O–C(1)	112.3 (3)

In a related study, we have investigated the reaction of 2-*tert*-butyl-1-naphthol (HO-tbn) with $Sn(NMe_2)_4$. The geometry of the 2-*tert*-butyl-1-naphthoxide ligand offers the possibility for the formation of either five-membered (aromatic CH bond activation) or six-membered (less likely aliphatic CH bond activation) metallacyclic rings. The formation of a five-membered ring via attack at the 8-position of the naphthalene ring system may, however, be inhibited by the rigid nature of the ligand backbone. Initial coordination through the oxygen atom does not allow the tin metal center to readily carry out electrophilic attack at the 8-position. A similar situation occurs in the cyclopalladation of benzo[*h*]quinoline.[27] However, the cyclostannation of the HO-tbn ligand was found to occur quite readily at the 8-position. A mixture of HO-tbn (2 equiv) and $Sn(NMe_2)_4$ in benzene was found to convert to the bis-cyclometalated compound $[Sn(O\text{-}tbn\text{-}H)_2(HNMe_2)_2]$ (**12**) over hours (Scheme VI). The intermediate bis(amido) complex $[Sn(O\text{-}tbn)_2(NMe_2)_2]$ was observed by ^1H NMR spectroscopy but was not isolated. In the ^1H NMR spectrum of **12**, two singlets at δ 1.63 and 1.96 ppm in the ratio of 3:2 can be assigned to the *Bu*ᵗ and $HNMe_2$ protons, respectively. The aromatic region has five aromatic signals of equal intensity, which can be resolved, and their pattern is consistent with metalation of the naphthalene ring. The

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[27] Deeming, A. J.; Rothwell, I. P. *J. Chem. Soc., Dalton Trans.* **1980**, 1974.

Table VIII. Crystal Data and Data Collection Parameters

	1	2	6	7	10	11	12
formula	$Sn_2Cl_4O_2C_{42}H_{30}$	$SnO_2N_2C_{40}H_{38}$	$SnO_2NC_{42}H_{55}$	$Sn_2O_8N_2C_{60}H_{70}$	$Sn_2O_4C_{36}H_{40}$	$SnO_2N_2C_{42}H_{42}$	$SnO_2N_2C_{32}H_{42}$
fw	945.90	697.45	724.60	1184.62	774.10	725.51	605.39
space group	$P2_1/n$	$C2$ (No. 5)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a, Å	11.680 (1)	18.223 (1)	20.878 (3)	10.701 (2)	24.101 (2)	9.175 (1)	10.3832 (9)
b, Å	26.909 (3)	7.644 (2)	7.024 (1)	11.208 (1)	9.972 (1)	9.3158 (9)	9.075 (1)
c, Å	12.884 (1)	13.709 (1)	27.150 (3)	23.322 (2)	19.678 (1)	12.033 (2)	17.255 (2)
α, deg	90	90	90	91.386 (9)	90	76.20 (1)	90
β, deg	110.720 (8)	121.440 (7)	95.37 (1)	98.05 (1)	135.489 (8)	68.03 (1)	112.600 (8)
γ, deg	90	90	90	92.62 (1)	90	67.65 (1)	90
V, Å^3	3787 (1)	1629.2 (8)	3963 (2)	2765 (1)	3315 (1)	876.5 (2)	1501.1 (6)
Z	4	2	4	2	4	1	2
d_{calc}, g cm^{-3}	1.659	1.422	1.214	1.423	1.551	1.374	1.339
cryst dimens, mm	0.60 × 0.51 × 0.39	0.47 × 0.20 × 0.11	0.50 × 0.32 × 0.25	0.38 × 0.34 × 0.22	0.30 × 0.22 × 0.15	0.22 × 0.20 × 0.17	0.26 × 0.24 × 0.11
temp, °C	20	22	20	20	20	20	20
radiation (λ, Å)	Mo K*α* (0.710 73)	Mo K*α* (0.710 73)	Mo K*α* (0.710 73)	Mo K*α* (0.710 73)	Mo K*α* (0.710 73)	Mo K*α* (0.710 73)	Mo K*α* (0.710 73)
monochromator	graphite	graphite	graphite	graphite	graphite	graphite	graphite
linear abs coef, cm^{-1}	16.43	8.22	6.77	9.59	15.47	7.66	8.81
abs corr appl	empirical[a]	empirical[a]	empirical[a]	empirical[a]	empirical[a]	empirical[a]	empirical[a]
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
scan method	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
h, *k*, *l* limits	−12 to 11, 0 to 28, 0 to 13	0 to 19, 0 to 8, −14 to 12	−22 to 22, 0 to 7, 0 to 29	−11 to 11, −12 to 12, 0 to 25	0 to 25, 0 to 10, −21 to 14	−8 to 9, −9 to 10, 0 to 12	−11 to 10, −9 to 0, 0 to 18
2*θ* range, deg	4.00–45.00	4.00–45.00	4.00–45.00	4.00–45.00	4.00–45.00	4.00–45.00	4.00–45.00
scan width, deg	0.54 + 0.35 tan *θ*	0.67 + 0.35 tan *θ*	1.01 + 0.35 tan *θ*	0.60 + 0.35 tan *θ*	0.65 + 0.35 tan *θ*	0.52 + 0.35 tan *θ*	0.50 + 0.35 tan *θ*
take-off angle, deg	2.80	1.90	3.15	3.15	3.15	3.15	3.15
programs used	Enraf-Nonius SDP	Enraf-Nonius SDP	Enraf-Nonius SDP	Enraf-Nonius SDP	Enraf-Nonius SDP	Enraf-Nonius SDP	Enraf-Nonius SDP
F_{000}	1864.0	716.0	1520.0	1216.0	1552.0	374.0	628.0
p-factor used in weighting	0.04	0.07	0.040	0.040	0.040	0.040	0.040
no. of data collcd	5050	1156	5691	7204	2305	2273	2137
no. of unique data	5050	1156	5691	7204	2305	2273	2137
data with $I > 3.0\sigma(I)$	4132	1131	3046	5354	1850	2094	1395
no. of variables	421	203	415	649	190	223	169
largest shift/esd in final cycle	0.02	0.14	0.11	0.06	0.00	0.40	0.00
R	0.026	0.049	0.040	0.028	0.028	0.033	0.032
R_w	0.038	0.070	0.045	0.034	0.036	0.040	0.040
goodness of fit	1.302	1.669	1.092	0.979	1.265	0.923	1.254

[a] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *A39*, 158.

site of metalation was confirmed by a single-crystal X-ray diffraction analysis of 12 (Figure 8; Table VII). The molecular structure of 12 is closely related to that of 11 (Figure 7). There is a crystallographically imposed inversion center for the octahedral $SnO_2C_2N_2$ core.

Experimental Section

All operations were carried out under a dry nitrogen atmosphere in a Vacuum Atmospheres dri-lab glovebox or by standard Schlenk techniques. Hydrocarbon solvents were dried by distillation from sodium benzophenone under a nitrogen atmosphere. $Sn(NMe_2)_4$ was synthesized by a published procedures,[28] while $SnCl_4$, $HOC_6H_3Ph_2$-2,6, 2-phenylphenol, $HOCH_2Ph$, $HOCMe_2Ph$, and $HOCPh_2$ were purchased from Aldrich Chemical Co. Li($OC_6H_3Ph_2$-2,6) was prepared by the reaction of 2,6-diphenylphenol with *n*-butyllithium in hexane. The phenol $HOC_6H_2Bu^t_2$-2,4-Ph-6 was prepared by the reaction of isobutylene with a benzene solution of 2-phenylphenol with a few drops of H_2SO_4 to catalyze the reaction. ^1H and ^{13}C NMR spectra were recorded on a Varian Associates Gemini-200 spectrometer and GE QE 300 MHz spectrometer. Mass spectrometric measurements were performed on a Finnegan 4000 mass spectrometer.

Preparation of $[Sn(OC_6H_3Ph\text{-}C_6H_4)Cl_2]_2$ (1). To a solution of lithium 2,6-diphenylphenoxide (4.53 g, 18.0 mmol) in toluene (40 mL) was syringed neat tin tetrachloride (2.23 g, 8.5 mmol). The resulting yellow slurry was stirred for 4 h, and the solvent was removed under vacuum. The solid was washed with hexane (3 × 20 mL) to remove free phenol formed during the reaction, and the product was extracted from LiCl with benzene (4 × 15 mL). Crystals were formed by slowly cooling a hot saturated benzene solution. (Yield = 4.02 g, 75%.) These crystals of the benzene solvate proved satisfactory for an X-ray diffraction study but gave poor microanalytical results. Recrystallization of 1 from toluene produced a toluene adduct which gave satisfactory microanalytical data. Anal. Calcd for $Sn_2Cl_4O_2C_{36}H_{24}\cdot C_6H_6$: C, 53.33; H, 3.20; Cl, 14.99. Found: C, 52.85; H, 3.53; Cl, 13.09. Anal. Calcd for $Sn_2Cl_4O_2C_{36}H_{24}\cdot C_7H_8$: C, 53.80; H, 3.36; Cl, 14.77. Found: C, 54.50; H, 3.40; Cl, 14.77. ^1H NMR (C_6D_6, 300 MHz): δ 7.95 (d), 7.56 (t), 7.49 (t), 7.33 (d), 7.27 (d), 7.24 (d), 7.2–6.8 (m), and 6.40 (t).

Preparation of $[Sn(OC_6H_3Ph\text{-}C_6H_4)_2(HNMe_2)_2]$ (2). To a solution of $Sn(NMe_2)_4$ (1.000 g, 3.39 mmol) in benzene (10 mL) was added a solution of 2,6-diphenylphenol (1.753 g, 7.17 mmol) dissolved in benzene (15 mL). The resulting bright yellow solution was dried under vacuum after $^1/_2$ h of stirring. The bis(phenoxide) bis(amide) and the tris(phenoxide) mono(amide) product were observed by ^1H NMR spectroscopy. Product 2 was formed upon heating (50 °C) the reaction mixture in benzene for 24 h. Crystals of 2 were formed by slowly cooling the hot solution. The crystals were isolated and washed with hexane. (Yield = 1.51 g, 64%.) Anal. Calcd for $SnO_2N_2C_{40}H_{38}$ (2): C, 68.88; H, 5.48; N, 4.01. Found: C, 68.75; H, 5.28; N, 4.01. ^1H NMR (C_6D_6, 300 MHz): δ 7.78 (d), 7.67 (d), 7.55 (d, *o*-H, $^3J(^{119}Sn-^1H)$ = 53 Hz), 7.29 (t), 7.25–7.15 (m), 6.97 (t), 6.88 (t), 1.88 (br, Sn–N*H*Me$_2$), 1.49 (s,

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(28) Jones, K.; Lappert, M. F. *J. Chem. Soc.* **1965**, 1944.

Sn–NH*Me*$_2$). ^{13}C NMR (CDCl$_3$, 200 MHz): δ 146.6, 141.1, 135.4, 130.2, 130.0, 129.7, 129.3, 129.2, 128.8, 128.3, 127.8, 127.6, 126.1, 125.4, 120.6, 117.2, 38.1 (Sn–NH*Me*$_2$).

Preparation of [Me$_3$Sn(OC$_6$H$_3$Ph$_2$-2,6)] (3). To a slurry of Me$_3$SnCl (2.48 g, 12.4 mmol) in toluene (70 mL) was added LiOC$_6$H$_3$Ph-2,6 (3.13 g, 12.4 mmol). The reaction mixture was refluxed overnight and allowed to cool. The solvent was removed under vacuum, and the product (**3**) was extracted from LiCl by hexane (3 × 30 mL). The product (**3**) formed clear needle-shaped crystals upon cooling a hot saturated hexane solution. (Yield = 4.549, 89%.) Anal. Calcd for $SnOC_{21}H_{22}$ (**3**): C, 61.65; H, 5.42. Found: C, 61.14; H, 5.47. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 7.78 (d), 7.36 (d), 7.30 (t), 7.18 (d), 6.96 (t), –0.31 (s, Sn–*Me*, $^2J(^{119}$Sn–^{1}H) = 58 Hz). ^{13}C NMR (C$_6$D$_6$, 200 MHz): δ 140.8, 134.7, 130.5, 130.0, 129.9, 128.0, 126.6, 120.0, –4.2 (Sn–*Me*, $^1J(^{119}$Sn–^{13}C) = 373 Hz).

Preparation of [Me$_2$Sn(OC$_6$H$_3$Ph$_2$-2,6)$_2$] (4). **4** was prepared in a manner similar to that for **3** but using Me$_2$SnCl$_2$ (3.85 g, 17.6 mmol) and 2 equiv of LiOC$_6$H$_3$Ph$_2$-2,6 (9.06 g, 35.9 mmol). (Yield = 7.54 g, 67%.) Anal. Calcd for $SnO_2C_{38}H_{32}$ (**4**): C, 71.38; H, 5.04. Found: C, 70.17; H, 5.24. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 7.52 (d), 7.18 (d), 7.13 (t), 7.01 (d), 6.83 (t), –0.84 (s, Sn–*Me*, $^2J(^{119}$Sn–^{1}H) = 66 Hz).

Preparation of [Sn(OC$_6$H$_2$Bu$^t{}_2$-C$_6$H$_4$)(HNMe$_2$)] (6). To a solution of Sn(NMe$_2$)$_4$ (0.500 g, 1.69 mmol) in benzene (10 mL) was added to a solution of HOC$_6$H$_2$Bu$^t{}_2$-2,4-Ph-6 (0.959 g, 3.39 mmol) in benzene (10 mL). After 20 min of stirring, the solvent of the resulting solution was removed under vacuum to yield a yellow glass. The product (**5**) was taken and dissolved benzene (10 mL), and the solution was heated (80 °C). After 7 h clear crystals formed at the solvent level and were isolated and washed with hexane. More product was isolated upon extended heating. ^{1}H NMR for Sn(OC$_6$H$_2$Bu$^+{}_2$-2,4-Ph-6)$_2$(NMe$_2$)$_2$ (**5**) (CDCl$_3$, 200 MHz): δ 7.7–6.9 (m), 2.02 (s, N*Me*, $^3J(^{119}$Sn–^{1}H) = 75 Hz), 1.81 (s, Bu^t), 1.32 (s, Bu^t). Anal. Calcd for $SnO_2NC_{42}H_{55}$ (**6**): C, 69.62; H, 7.65; N, 1.93. Found: C, 68.56; H, 7.75; N, 2.33. ^{1}H NMR (CDCl$_3$, 200 MHz): δ 7.82 (d, *o*-H, $^3J(^{119}$Sn–^{1}H) = 63 Hz), 7.78 (d), 7.48 (t), 7.44 (s), 7.33 (s), 7.21 (t), 3.4 (s, Sn–N*H*Me$_2$), 2.50 (s, Sn–NH*Me*$_2$), 1.48 (s, C*Me*$_3$), 1.35 (s, C*Me*$_3$).

Preparation of [Sn$_2$(OCH$_2$Ph)$_8$(NHMe$_2$)$_2$] (7). To a stirred solution of Sn(NMe$_2$)$_4$ (0.500 g, 1.69 mmol) in benzene (10 mL) was slowly added a solution of HOCH$_2$Ph (0.734 g, 6.79 mmol) in benzene (15 mL). The resulting clear solution was evaporated under vacuum to a white powder and was washed with hexane. The product (**7**) was recrystallized from hot toluene and the crystals were washed with hexane (2 × 10 mL). (Yield = 0.69 g, 69%.) Anal. Calcd for $Sn_2O_8N_2C_{60}H_{70}$ (**7**); C, 60.84; H, 5.96; N, 2.36. Found: C, 58.58; H, 5.64; N, 2.56%. ^{1}H NMR (CDCl$_3$): δ 7.75 (d); 7.4–7.1 (m); 5.68 (septet, *N*HMe$_2$); 5.5–4.8 (m, OC*H*$_2$Ph); 1.84 (d,-NH*Me*$_2$, $^3J(^{119}$Sn-^{1}H) = 37 Hz). ^{13}C NMR (CDCl$_3$): δ 145.3, 144.9, 141.1, 130.8, 128.7, 128.5, 128.1, 127.7, 127.1, 126.8, (aromatic carbons) 69.1, 68.1, 67.8, (*C*H$_2$Ph), (NH*Me*$_2$) 39.7.

Preparation of [Sn(OCMe$_2$Ph)$_4$] (8) and [Sn(OCMe$_2$-C$_6$H$_4$)$_2$]$_2$ (10). To a solution of Sn(NMe$_2$)$_4$ (1.083 g, 3.67 mmol) in benzene (10 mL) was added a solution of HOCMe$_2$Ph (2.001 g, 14.69 mmol) in benzene (10 mL). The resulting clear solution was evaporated under vacuum to afford the product (**8**) as a clear liquid. Purification of liquid **8**, especially its separation from 2-phenylpropan-2-ol was found to be difficult, and satisfactory microanalytical data were not obtained. This crude product was heated neat at 100 °C for 4 days to yield crystals of the bis-cyclometalated product (**10**). The crystals were isolated and washed with hexane. (Yield = 0.47 g, 74%.) Data for $SnO_4C_{36}H_{44}$ (**8**), are as follows. ^{1}H NMR (C$_6$D$_6$): δ 7.4–7.2 (m); 1.67 (s, C*H*$_3$). ^{13}C NMR (C$_6$D$_6$): δ 151.1, 129.0, 128.8, 125.8, 125.2, 78.1 (O*C*Me$_2$Ph) and 34.6 (OC*Me*$_2$Ph). Data for **10** are as follows. Anal. Calcd for $Sn_2O_4C_{36}H_{40}$ (**10**): C, 55.86; H, 5.21. Found: C, 56.24; H, 5.58. ^{1}H NMR (C$_6$D$_6$): δ 8.10 (d, *o-H*, $^3J($Sn^{119}–^{1}H) = 75 Hz); 7.4–6.7 (m); 2.03 (s), 1.95 (s), 1.74, and 1.54 (s, OC*Me*$_2$Ph). ^{13}C NMR (CDCl$_3$): δ 160.1, 155.6, 135.2, 134.9, 133.2, 132.5, 131.1, 130.1, 127.6, 126.5, 125.2, 124.4, 79.5, 77.0, 35.2, 34.9, 34.4.

Preparation of [Sn(OCPh$_3$)$_2$(NMe$_2$)$_2$] (9) and [Sn(OCPh$_2$C$_6$H$_4$)$_2$(NHMe$_2$)$_2$] (11). To a solution of Sn(NMe$_2$)$_4$ (1.002 g, 3.39 mmol) in benzene (10 mL) was slowly added solid HOCPh$_3$ (1.755 g, 6.74 mmol). The solution was stirred overnight, and the solvent was removed under vacuum to leave a white powder of **9**. The product can be recrystallized by cooling a saturated toluene solution. When the tin bis(alkoxide) bis(amide) product (**9**) is heated for 24 h in benzene (10 mL), clear crystals of **11** grow above the solvent level. The crystals were washed with hexane. More product was precipitated from solution by adding hexane to the supernatant. Further heating of **9** at elevated temperatures causes loss of amine ligands and is believed to produce an insoluble dimer. (Yield = 1.65 g, 65%.) Data for Sn(OCPh$_3$)$_2$(NMe$_2$)$_2$ (**9**) are as follows. ^{1}H NMR (CDCl$_3$): δ 7.4–7.1 (m); 2.14 (s, N*Me*$_2$, $^3J(^{119}$Sn–^{1}H) = 69 Hz). ^{13}C NMR (CDCl$_3$): δ 149.2, 129.1, 128.0, 127.1, 86.3 (O*C*Ph$_2$), 41.8 (N*Me*$_2$). Data for **11** are as follows. Anal. Calcd for Sn(OCPh$_2$C$_6$H$_4$)$_2$(NHMe$_2$)$_2$ (**11**): C, 69.53; H, 5.83; N, 3.86. Found: C, 70.12; H, 5.88; N, 3.75. ^{1}H NMR (CDCl$_3$): δ 8.10 (m, *o-H*, $^3J(^{119}$Sn–^{1}H = 68 Hz); 7.3–7.1 (m); 2.08 (s, NH*Me*$_2$); 1.9 (s, N*H*Me$_2$). ^{13}C NMR (CDCl$_3$): δ 155.8, 152.6, 136.2, 134.0, 129.8, 129.4, 128.9, 128.1, 127.3, 126.8, 83.8 (O*C*Ph$_2$C$_6$H$_4$), 38.1 (NH*Me*$_2$).

Preparation of [Sn(O-tbn-H)$_2$(NHMe$_2$)$_2$] (12). To a solution of Sn(NMe$_2$)$_4$ (2.00 g, 6.78 mmol) in benzene (15 mL) was added a solution of 2-*tert*-butyl-1-naphthol (2.71 g, 13.5 mmol) in benzene (20 mL). Allowing this mixture to remain in solution at room temperature for 3 days or heating the solution for 4 h produced the bis-cyclometalated product (**12**). The product was recrystallized from a saturated solution of toluene and washed with hexane. More product may be precipitated by adding hexane to the supernatant. Anal. Calcd for Sn(O-tbn-H)$_2$(NHMe$_2$)$_2$ (**12**): C, 63.47; H, 6.94; N, 4.63. Found: C, 63.98; H, 7.04; N, 3.96. ^{1}H NMR (CDCl$_3$): δ 8.02 (d, *o-H*, $^3J(^{119}$Sn–^{1}H) = 74 Hz); 7.80 (d); 7.6–7.45 (m); 7.12 (d); 1.96 (s, NH*Me*$_2$); 1.7 (s, N*H*Me$_2$); 1.63 (s, C*Me*$_3$). ^{13}C NMR (CDCl$_3$): δ 158.8, 135.1, 133.1, 132.0, 130.4, 129.1, 128.9, 127.3, 125.9, 113.5, 37.4, 35.2, 30.0.

Crystallographic Studies. The crystal data and data collection parameters are listed in Table VIII. Further details of the crystallographic studies can be found in the supplementary material.

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Registry No. 1, 118599-57-8; **2**, 118599-58-9; **3**, 118599-55-6; **4**, 118599-56-7; **5**, 138694-77-6; **6**, 138694-80-1; **7**, 138694-81-2; **8**, 138694-78-7; **9**, 138694-79-8; **10**, 138694-82-3; **11**, 138694-83-4; **12**, 138694-84-5; SnCl$_4$, 7646-78-8; Sn(NMe$_2$)$_4$, 1066-77-9; Me$_3$SnCl, 1066-45-1; Me$_2$SnCl$_2$, 753-73-1; lithium 2,6-diphenylphenoxide, 116643-01-7.

Supplementary Material Available: Tables of crystallographic data, thermal parameters, full bond distances and angles, and hydrogen positions (91 pages); listings of observed and calculated structure factors (129 pages). Ordering information is given on any current masthead page.