Inorg. Chem. **2009**, *48*, 2273−2276

Inorganic Chemistry
Article

Preparation and Structural Characterization of Molecular Al−O−Sn(II) and Al−O−Sn(IV) Compounds

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Received November 10, 2008

Reaction of the organoaluminum hydroxide LAl(Me)OH (**1**) with different stoichiometric ratios of the homoleptic Sn(II) amide, $Sn[N(SiMe_3)_2]_2$, produced the bimetallic and trimetallic oxygen bridged aluminum−tin compounds LAl(Me)(μ-O)$Sn[N(SiMe_3)_2]$ (**2**) and [LAl(Me)(μ-O)]$_2$Sn (**3**), respectively. The former compound exhibits an Al−O−Sn(II)−N core and the latter an Al−O−Sn(II)−O−Al skeleton. In addition, we obtained the [LAl(Me)-(μ-O)$SnPh_3$] (**5**) with Al−O−Sn(IV) core by the reaction of [L(Me)Al−O−$Mg(THF)_2N(SiMe_3)_2$] (**4**) with Ph_3SnOH in a 1:1 molar ratio.

Introduction

The most important mineral of tin is an oxide, SnO_2, commonly known as *cassiterite* or *tin-stone*.[1a] Likewise, the lighter group element silicon exists as SiO_2, but the heavier element lead appears as a sulfide, *galena* PbS.[1b] The naturally occurring combined metal oxides of tin are extremely rare, and mixed metal sulfide minerals are more common, for example, *stannite*, *mohite*, *teallite*, and so forth.[1a] There has been a continuously growing interest in the synthesis of oxides of group 14 elements containing metals from different groups of the periodic table. In this regard, zeolites[2] and aluminosilicates[3] that contain Al−O−Si moieties have found various applications, for example, as ion exchanger, catalysts, catalyst supports, and molecular sieves.[4−13] Recently, we reported on molecular $(SnO)_6$ trapped in $[(SnO)_6(R_2Si_2O_3)_2]$ (R = (2,6-iPr$_2$C$_6$H$_3$NSiMe$_3$)) as structural model for metal modified silicates.[14]

However, molecular compounds containing the Al−O−Sn moieties are not well documented. The reported Al and Sn mixed metallic alkoxides and oxides are dominated by Sn(IV) compounds.[15,16] Sn(II) and aluminum mixed metallic alkoxides and oxoalkoxides are rarely known.[17−19] To the best

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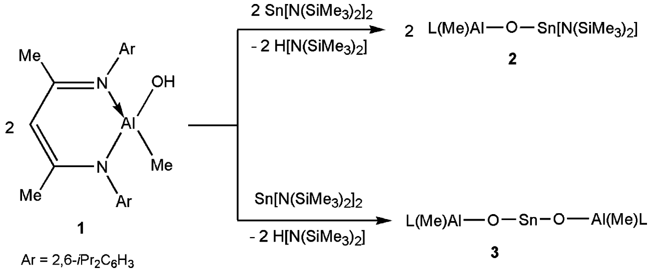
of our knowledge only four compounds $(t\text{BuO})_4\text{AlSnCl}$,[20] $[(i\text{PrO})_5\text{Cl}_2\text{Al}_2]_2\text{O}_2\text{Sn}_4\text{Cl}_2$,[20] $[(i\text{PrO})_4\text{AlSn}_2\text{Cl}_3]_x$,[20] and $(t\text{BuN})_3(t\text{BuAlO})\text{Sn}_4$[21] have been structurally characterized, and no pure mixed metallic oxide of Al and Sn(II) is known. In fact no other low valent group 14 metals have been combined with Al in the form of mixed metal oxide, that is, compounds containing a M(II)−O−Al moiety are unknown (M = Ge, Sn, Pb).[22] Incorporation of the oxide ion between Al and Sn(II) moieties is a synthetic challenge because of the unavailability of suitable reactive species containing oxides of either Al or Sn reagents. Moreover, there is no direct control over metal nuclearity and on the composition of the resulting product. In 1994 Oliver et al. reported the dimeric structure of $[(\text{Me}_2\text{Al})(\mu\text{-OSnPh}_3)]_2$ formed from the reaction of Me_3Al with $[\text{Ph}_3\text{Sn}]_2\text{O}$.[23]

Results and Discussion

Herein, we report a rational synthesis of a heterobimetallic Al and Sn(II) oxide-amide, $\text{LAl(Me)}(\mu\text{-O})\text{Sn}[\text{N}(\text{SiMe}_3)_2]$ (**2**), and the homoleptic oxide complex, $[\text{LAl(Me)}(\mu\text{-O})]_2\text{Sn}$ (**3**), as a new modification of Sn(II) oxide based on the aluminum hydroxide LAl(Me)OH (**1**)[24–26] (L = $[\text{HC}\{(\text{CMe})(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\}_2]$). The current discussion also includes an unprecedented monomeric heterobimetallic oxygen bridged compound, $[\text{LAl(Me)}(\mu\text{-O})\text{SnPh}_3]$ (**5**), with an Al−O−Sn(IV) core which was obtained from the reaction of Ph_3SnOH with $[\text{L(Me)Al−O−Mg(THF)}_2\text{N}(\text{SiMe}_3)_2]$ (**4**).

The reaction between LAl(Me)OH (**1**) and $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$[27] proceeds in a very controlled manner. Thus, treatment of $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ with 1 equiv of **1** leads to the formation of **2**, a compound with an Al−O−Sn(II)−N framework. Formation of **2** proceeds with the elimination of 1 equiv of $\text{H}[\text{N}(\text{SiMe}_3)_2]$ (Scheme 1). When $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ is treated with 2 equiv of **1**, it affords compound **3**, with an Al−O−Sn(II)−O−Al framework that proceeds with the elimination of 2 equiv of $\text{HN}(\text{SiMe}_3)_2$ (Scheme 1). Formation of **2** and **3** was monitored by ^{1}H NMR spectroscopy. Sharp resonances in the ^{1}H NMR of **2** and **3** gave the initial indication of the diamagnetic nature of these compounds in solution. The ^{1}H NMR spectrum of **2** exhibits the Al-*Me* (−0.72 ppm) and the Si*Me*$_3$ protons of $\text{Sn}[\text{N}(\text{Si}Me_3)_2]$ (0.34 ppm). In the ^{1}H NMR spectrum of **3**, the Al-*Me* proton resonance was detected (−0.80 ppm), and the complete disappearance of the proton resonance of $\text{Sn}[\text{N}(\text{Si}Me_3)_2]$ was observed. This indicates the complete conversion of the tin amide to the corresponding tin−aluminum oxide. The EI mass spectrum of **2** reveals ions corresponding to the free ligand, L, and its fragments while that of **3** exhibits the molecular ion peak at *m*/*z* 1070 albeit in low intensity. The base peak for **3** was found at *m*/*z* 1055 corresponding to $[\text{M}^+ - \text{Me}]$. The ^{29}Si NMR spectrum of **2** reveals a resonance at −1.16 ppm typical of $[\text{N}(\text{SiMe}_3)_2]$ attached to the Sn(II) center.[27] The ^{119}Sn NMR for **2** shows a resonance at 433 ppm which is consistent with a dicoordinate Sn(II) atom. The Sn(II) atom in **3** resonates more upfield (137 ppm) compared to **2**. However, **2** and **3** exhibit very upfield chemical shifts for the tin atoms compared to $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ (768 ppm).[27] The upfield chemical shifts might be due to the bonding situation. **2** exhibits one (O−Al) group bound to the Sn(II), whereas compound **3** shows two (O−Al) bonds connected to Sn(II). The literature data for alkoxides, however, exhibit (O−C) bonds at the Sn(II) center and therefore another sequence of atoms is shown there.[28]

Scheme 1. Synthesis of Heterometallic Al−O−Sn(II) Compounds



The reaction of $[\text{L(Me)Al−O−Mg(THF)}_2\text{N}(\text{SiMe}_3)_2]$[29] (**4**) with triphenyltin hydroxide in toluene and tetrahydrofuran (THF) solution at room temperature unexpectedly results in the formation of $[\text{LAl(Me)}(\mu\text{-O})\text{SnPh}_3]$ (**5**) (Scheme 2). The Al-*Me* resonance in the ^{1}H NMR of **5** is slightly downfield shifted (−0.66 ppm) compared to those of **2** and **3**.

The ^{119}Sn NMR of **5** shows a resonance (−110 ppm) typical for a Sn(IV) atom bonded to three phenyl groups and a bridging oxygen atom.[30] The molecular ion peak for **5** was observed at *m*/*z* 826 with very low intensity; the base peak was found at *m*/*z* 811 ($[\text{M}^+ - \text{Me}]$).

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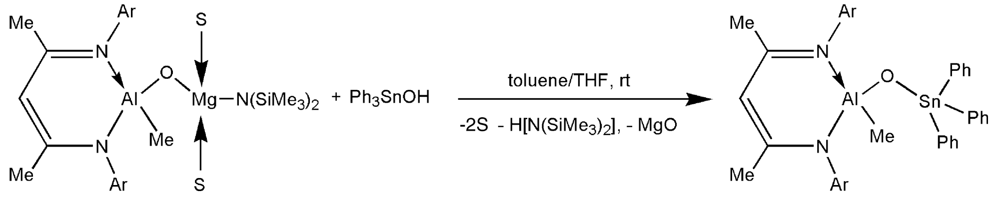
Scheme 2. Synthesis of the Heterobimetallic Al−O−Sn(IV) Compound **5**



4

5

Ar = 2,6-*i*Pr$_2$C$_6$H$_3$; S = THF; Ph = C$_6$H$_5$

Table 1. Crystallographic Data for **3**·0.5 *n*-hexane and **5**

compound	**3**·0.5 *n*-hexane	**5**
empirical formula	$C_{63}H_{95}Al_2N_4O_2Sn$	$C_{48}H_{59}AlN_2OSn$
CCDC No.	664532	664533
fw (g·mol^{-1})	1113.08	825.64
T (K)	100(2)	100(2)
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	8.977(1)	11.460(1)
b (Å)	18.074(2)	11.513(1)
c (Å)	20.414(2)	16.750(2)
α (deg)	74.81(2)	84.520(1)
β (deg)	82.50(2)	84.950(1)
γ (deg)	79.19(2)	81.884(1)
V (Å^3)	3128.3(4)	2171.7(3)
Z	2	2
μ_{calc}[Mo Kα] (mm^{-1})	0.479	0.645
2θ range (deg)	4.64−50.74	4.50−50.74
measured reflections	38089	34307
independent reflections	11406 (R_{int} = 0.0322)	7961 (R_{int} = 0.0338)
parameters	672	489
GOF	1.023	1.053
$R1$, $wR2$ [$I > 2\sigma(I)$][a,b]	0.0324, 0.0776	0.0238, 0.0543
g_1, g_2[c]	0.0424, 1.5589	0.0227, 1.056

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2}$. [c] $w = [\sigma^2(F_o^2) + (g_1P)^2 + g_2P]^{-1}$, $P = 1/3[\max(F_o^2,0) + 2F_c^2]$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds **3** and **5**

Compound **3**			
Al(1)−N(1)	1.9228(18)	Sn(1)−O(2)	1.9680(14)
Al(2)−N(3)	1.9124(19)	O(2)−Al(2)	1.7199(16)
Al(1)−O(1)	1.7173(16)	O(1)−Sn(1)	1.9597(15)
Al(1)−C(1)	1.951(2)		
N(1)−Al(1)−N(2)	95.15(8)	O(1)−Sn(1)−O(2)	99.47(6)
N(3)−Al(2)−N(4)	95.62(8)	Sn(1)−O(2)−Al(2)	134.59(9)
Al(1)−O(1)−Sn(1)	137.58(9)		
Compound **5**			
Al(1)−N(1)	1.9222(16)	Sn(1)−O(1)	1.9428(12)
Al(1)−N(2)	1.9094(16)	Sn(1)−C(31)	2.1356(19)
Al(1)−O(1)	1.7181(13)	Al(1)−C(1)	1.944(2)
N(1)−Al(1)−N(2)	96.26(7)	C(1)−Al(1)−O(1)	114.50(8)
N(1)−Al(1)−C(1)	110.06(8)	O(1)−Sn(1)−C(31)	110.43(6)
Al(1)−O(1)−Sn(1)	136.90(8)		

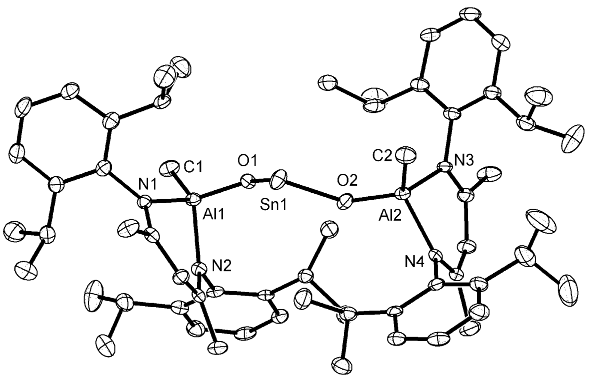


Figure 1. Molecular structure of [LAl(Me)(μ-O)]$_2$Sn (**3**). Anisotropic displacement parameters are drawn at a 50% probability level, and all hydrogen atoms were omitted for clarity.

Single crystals of **3** and **5** suitable for X-ray structural analysis were obtained from *n*-hexane and toluene/THF solutions, respectively. Both **3** and **5** crystallize in the triclinic space group $P\bar{1}$ (Table 1). The molecular structure of **3** is shown in Figure 1. Selected bond lengths and bond angles of compounds **3** and **5** are listed in Table 2.

The asymmetric unit of **3** contains one formula unit of the compound and half a molecule of *n*-hexane. As predicted, based on the ^{1}H NMR spectrum, compound **3** contains a V-shaped O−Sn(II)−O core. The two terminal LAl(Me) units are arranged in a *trans* manner (Figure 1). No Sn···Sn interactions were found in the solid state. The Al−O bond distance (1.719 Å) is comparable to that in its parent compound LAl(Me)OH (**1**)[25] (1.731(3) Å). The Sn−O bond distance of 1.960(2) Å and 1.968(2) Å is longer than that in Sn(OC$_6$H$_2$-4-Me-2,6*t*Bu$_2$)$_2$ (1.807 Å)[31] but shorter than those observed in [(*i*PrO)$_5$Cl$_2$Al$_2$]$_2$O$_2$Sn$_4$Cl$_2$ (**I**) (2.074(3) Å)[20] and considerably shorter than those found in [Ph$_2$SiO]$_8$[AlO(OH)]$_2$-[AlO$_2$]$_2$Sn·2C$_4$H$_8$O$_2$ (**II**) (2.159 Å), [Ph$_2$SiO]$_8$[AlO(OH)]$_2$-[AlO$_2$]$_2$Sn·2THF (**III**) (2.150 Å), [Ph$_2$SiO]$_8$[AlO$_2$]$_4$-Sn$_2$·2THF (**IV**) (2.154 Å),[32] (*t*BuO)$_4$AlSnCl (2.153 Å),[20] and (*t*Bu$_3$N)$_3$(Me$_3$AlO)Sn$_4$ (2.198 Å).[21] The Al(1)−O(1)−Sn(1) and Al(2)−O(2)−Sn(1) bond angles in **3** are 137.58(9)° and 134.59(9)°, respectively. The O(1)−Sn(1)−O(2) bond angle (99.47(6)°) is comparable to that found in (*t*BuCN)$_3$(*t*BuAlO)-Sn$_4$ (99.5−101.1°)[21] but wider than the angles observed in **II** (range 66.3−88.6°), **III** (range 68.6−85.8°), **IV** (range 69.6−84.3°),[32] **I** (range 67.3−94.5°),[20] and in Sn(OC$_6$H$_2$-4-Me-2,6*t*Bu$_2$)$_2$ (88.8(2)°).[31]

The molecular structure of **5** is shown in Figure 2. The metric parameters in **5** are not unusual. The tin atom resides in a slightly distorted tetrahedral environment comprising three phenyl groups and an oxygen atom. The Sn(1)−O(1) bond length in **5** (1.943(2) Å) is only slightly shorter than that in [(Me$_2$Al)(μ-OSnPh$_3$)]$_2$ (1.984(4) Å).[23] The Al(1)−O(1)−Sn(1) core in **5** is bent with an angle of 136.90(2)° that is similar to the Al−O−Sn angles in **3** (see above) but slightly wider than that found in [(Me$_2$Al)(μ-OSnPh$_3$)]$_2$ (131.3(2)°).[23]

Summary and Conclusion

Heterobimetallic and trimetallic oxygen bridged systems have been prepared by the reaction of an organoaluminum

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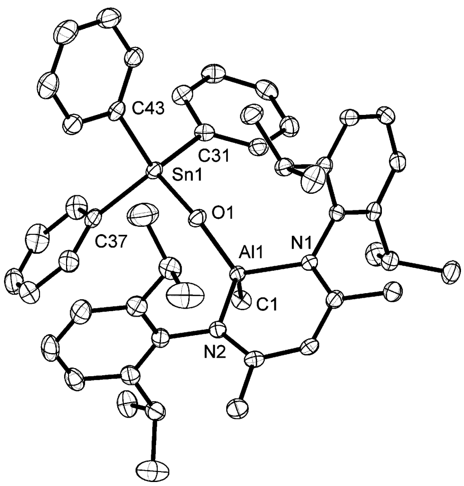

Figure 2. Molecular structure of [LAl(Me)(μ-O)SnPh$_3$] (**5**). Anisotropic displacement parameters are drawn at a 50% probability level, and all hydrogen atoms were omitted for clarity.

hydroxide **1** with a Sn(II) amide containing an Al−O−Sn(II)−N and an Al−O−Sn(II)−O−Al core respectively. Compound **5** was formed by the reaction of **4** with Ph$_3$SnOH. The latter is an unprecedented reaction product that contains an Al−O−Sn(IV) skeleton.

Experimental Section

All manipulations were performed under a dry and oxygen free atmosphere (N$_2$) using standard Schlenk techniques or inside a MBraun MB 150-GI glovebox. All solvents were distilled from Na/benzophenone prior to use. The starting material **1** was prepared using literature procedures.[25] Other chemicals were purchased commercially and used as received. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded on a Bruker Avance DRX 500 MHz instrument and referenced to the deuterated solvent in the case of the ^{1}H and ^{13}C NMR spectra. ^{119}Sn NMR spectra were referenced to Me$_4$Sn. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. EI-MS were measured on a Finnigan Mat 8230 or a Varian MAT CH5 instrument. Melting points were measured in sealed glass tubes with a Büchi melting point B 540 instrument and are not corrected.

Synthesis of LAl(Me)(μ-O)Sn[N(SiMe$_3$)$_2$] (2). LAl(Me)OH (0.47 g, 1.00 mmol) dissolved in toluene (20 mL) was added drop by drop at −40 °C to a solution of Sn[N(SiMe$_3$)$_2$]$_2$ (0.44 g, 1.00 mmol) in toluene (15 mL). The solution was allowed to warm to room temperature and stirred overnight. The color of the solution changed from orange to yellow; after removal of all the volatiles the residue was extracted with *n*-hexane (40 mL). Partial removal of the solvent and storage at room temperature for 2 days afforded crystalline **2**. Yield: (0.65 g, 86%). Mp 108−110 °C. Anal. Calcd for C$_{36}$H$_{62}$AlN$_3$OSi$_2$Sn (754.76): C, 57.29; H, 8.28; N, 5.57; found C, 57.32; H, 8.30; N, 5.53. ^{1}H NMR (200 MHz, C$_6$D$_6$, TMS): δ −0.72 (s, 3 H, Al*Me*), 0.34 (s, 18 H, SnN(Si*Me*$_3$)$_2$), 1.12 (d, $^{3}J_{\mathrm{HH}} = 6.8$ Hz, 6 H, CH*Me*$_2$), 1.25 (d, $^{3}J_{\mathrm{HH}} = 6.8$ Hz, 6 H, CH*Me*$_2$), 1.31 (d, $^{3}J_{\mathrm{HH}} = 6.8$ Hz, 12 H, CH*Me*$_2$), 1.58 (s, 6 H, C*Me*), 3.25 (sept, $^{3}J_{\mathrm{H-H}} = 6.8$ Hz, 2 H, C*H*Me$_2$), 3.83 (sept, $^{3}J_{\mathrm{H-H}} = 6.8$ Hz, 2 H, C*H*Me$_2$), 5.02 (s, 1 H, γ-C*H*), 7.09−7.12 (m, *Ar*) ppm. ^{29}Si NMR (99.4 MHz, C$_6$D$_6$, TMS): δ −1.16 ppm. ^{119}Sn NMR (186 MHz, C$_6$D$_6$, Me$_4$Sn): δ 433 ppm broad. IR (Nujol, cm^{-1}): 1531, 1386, 1319, 1257, 1190, 1178, 1108, 1056, 1023, 940, 876, 770, 757, 689, 543, 460.

Synthesis of [LAl(Me)(μ-O)]$_2$Sn (3). LAl(Me)OH (0.95 g, 2.00 mmol) dissolved in toluene (30 mL) was added drop by drop at 0 °C to a solution of Sn[N(SiMe$_3$)$_2$]$_2$ (0.44 g, 1.00 mmol) in toluene (15 mL). The solution was allowed to warm to room temperature and stirred overnight. The color of the solution changed from orange to yellow; after removal of all the volatiles the residue was extracted with *n*-hexane (60 mL). Partial removal of the solvent and storage at room temperature for 2 days afforded crystalline **3**. Yield: (0.76 g, 71%). Mp 210−212 °C. Anal. Calcd for C$_{60}$H$_{88}$Al$_2$N$_4$O$_2$Sn (1070.04): C, 67.35; H, 8.29; N, 5.24; found C, 67.33; H, 8.31; N, 5.28. ^{1}H NMR (200 MHz, C$_6$D$_6$, TMS): δ −0.80 (s, 3 H, Al*Me*), 1.13 (d, $^{3}J_{\mathrm{HH}} = 6.8$ Hz, 12 H, CH*Me*$_2$), 1.23 (d, $^{3}J_{\mathrm{HH}} = 6.8$ Hz, 12 H, CH*Me*$_2$), 1.32 (d, $^{3}J_{\mathrm{HH}} = 6.8$ Hz, 12 H, CH*Me*$_2$), 1.40 (d, $^{3}J_{\mathrm{HH}} = 6.8$ Hz, 12 H, CH*Me*$_2$), 1.64 (s, 12 H, C*Me*), 3.27 (sept, $^{3}J_{\mathrm{H-H}} = 6.8$ Hz, 4 H, C*H*Me$_2$), 3.95 (sept, $^{3}J_{\mathrm{H-H}} = 6.8$ Hz, 4 H, C*H*Me$_2$), 5.10 (s, 2 H, γ-C*H*), 7.07−7.12 (m, *Ar*) ppm. ^{119}Sn NMR (186 MHz, C$_6$D$_6$, Me$_4$Sn): δ 137 ppm broad. EI-MS (70 eV): *m*/*z* (%): 1070 (6) [M$^+$], 1055 (100) [M$^+$ − Me], 1039 (21) [M$^+$ − 2Me]. IR (Nujol, cm^{-1}): 1532, 1383, 1320, 1255, 1193, 1172, 1106, 1043, 938, 876, 770, 757, 689, 543, 456.

Synthesis of [LAl(Me)(μ-O)SnPh$_3$] (5). LAl(Me)(μ-O)Mg(THF)$_2$-N(SiMe$_3$)$_2$ (0.80 g, 1.00 mmol) dissolved in THF (10 mL) was added at room temperature to a stirred suspension of Ph$_3$SnOH (0.37 g, 1.00 mmol) in THF/toluene (30 mL). The mixture was stirred for 2 days. After removal of all volatiles the title compound was extracted with THF/toluene solution (20 mL). The solution was kept at −32 °C for 2 days to afford colorless crystals of **5**. The mother liquor when concentrated to 8 mL afforded another crop at −32 °C. Total yield: (0.50 g, 61%). Mp 168−171 °C. Anal. Calcd for C$_{48}$H$_{59}$AlN$_2$OSn (825.64): C, 69.76; H, 7.15; N, 3.39; found C, 68.87; H, 7.11; N, 3.33. ^{1}H NMR (500 MHz, C$_6$D$_6$, TMS): δ −0.66 (s, 3H, Al*Me*), 1.08 (d, $^{3}J_{\mathrm{HH}} = 6.8$ Hz, 12H, CH*Me*$_2$), 1.15 (d, $^{3}J_{\mathrm{HH}} = 6.8$ Hz, 6H, CH*Me*$_2$), 1.25 (d, $^{3}J_{\mathrm{HH}} = 6.8$ Hz, 6H, CH*Me*$_2$), 1.58 (s, 6H, C*Me*), 3.22 (sept, $^{3}J_{\mathrm{HH}} = 6.8$ Hz, 2H, C*H*Me$_2$), 3.70 (sept, $^{3}J_{\mathrm{HH}} = 6.8$ Hz, 2H, C*H*Me$_2$), 5.00 (s, 1H, γ-C*H*), 7.48−7.69 (m, 15H, *Ph*), 7.60−7.16 (m, *Ar*) ppm. ^{119}Sn NMR (186 MHz, C$_6$D$_6$, Me$_4$Sn): δ −110 ppm. EI-MS (70 eV): *m*/*z* (%): 826 (3) [M$^+$], 811 (100) [M$^+$ − Me].

Crystallographic details for 3 and 5. All data were collected from shock-cooled crystals on a Bruker SMART-APEX II diffractometer with a D8 goniometer at 100 K[33] (graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å). The data were integrated with SAINT,[34] and an empirical absorption correction (SADABS[35]) was applied. The structures were solved by direct methods (SHELXS[36]) and refined on F^2 using SHELXL.[37]

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft.

Supporting Information Available: X-ray data for **3** and **5** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC802151C

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