Synthesis and Structures of Monomeric Divalent Germanium and Tin Compounds Containing a Bulky Diketiminato Ligand†

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Received October 11, 2000

Reaction of the β-diketiminato lithium salt Li(OEt$_2$)[HC(CMeNAr)$_2$] (Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$) with GeCl$_2$·(dioxane) and SnCl$_2$ in diethyl ether provided the monomeric complexes [HC(CMeNAr)$_2$]MCl (M = Ge (**2**), Sn (**3**), respectively) with a three-coordinated metal center. The reductive dehalogenation reactions of **3** with C$_8$K and LiAlH$_4$ afforded [HC(CMeNAr)$_2$]$_2$Sn (**7**) and [HC(CMeNAr)$_2$]AlH$_2$, respectively. The metathesis reactions of **3** with *t*-BuLi, AgSO$_3$CF$_3$, and NaN$_3$ resulted in the formation of [HC(CMeNAr)$_2$]Sn(*t*-Bu) (**4**), [HC(CMeNAr)$_2$]Sn(OSO$_2$CF$_3$) (**5**), and [HC(CMeNAr)$_2$]SnN$_3$ (**6**), respectively. Compounds **2**, **3**, **5**, and **7** were characterized by single-crystal X-ray structural analysis. The structures indicate that the β-diketiminato backbone is essentially planar and the metal centers reside in distorted-tetrahedral environments with one vertex occupied by a lone pair of electrons. The bond angles at the metal center are in the range 85.2(8)−106.8(2)°, and the most acute angle is associated with the bite of the chelating ligand.

Introduction

There is widespread interest in the chemistry of divalent derivatives of the heavier group 14 elements, due to their carbene-like properties. Stable tin(II) compounds of formula (SnR$_2$)$_{1,2}$ and (RSnX^1)$_{1,2}$ (R = bulky ligand, X^1 = halide) are well-characterized.[1] In contrast, derivatives of tin(II) of the type Sn(X^2)R, where X^2 is a small ligand other than halide, have received much less attention. To the best of our knowledge, only few such compounds are known, including Sn(C$_7$H$_7$)[C$_6$H$_3$-2,6-(CH$_2$NMe$_2$)$_2$],[1e] [(*n*-Pr)$_2$ATI]SnN$_3$ (where [(*n*-Pr)$_2$ATI]$^-$ = *N*-(*n*-propyl)-2-(*n*-propylamino)troponiminate),[1l] Sn[B(C$_6$F$_5$)$_4$]Cp,[2] and [Sn(SO$_3$CF$_3$){N(SiMe$_3$)$_2$}]$_2$.[3] The anionic chelating β-diketiminato ligand [HC(CRNR′)$_2$]$^-$ (R = Me, Ph; R′ = SiMe$_3$, aryl), where steric flexibility is afforded by variation of the substituents on the ligand backbone, can be used as a spectator ligand. Such ligands already have been employed in transition-metal chemistry.[4] Recently the coordination chemistry of such ligands with main-group elements has drawn attention.[5] We have prepared the first monomeric aluminum(I) compound, [{HC(CMeNAr)$_2$}Al] (Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$), by taking advantage of such a ligand.[6] Herein we report on the preparation of compounds of divalent heavier group 14 elements using such a ligand, LGeCl (**2**) and LSnCl (**3**) (L = HC(CMeNAr)$_2$), and the resulting derivatives LSn(*t*-Bu) (**4**), LSn(OSO$_2$CF$_3$) (**5**), LSnN$_3$ (**6**), and L$_2$Sn (**7**). Compounds **2**, **3**, **5**, and **7** have been characterized by single-crystal X-ray structural analysis.

Experimental Section

General Considerations. All manipulations were carried out using standard Schlenk techniques or in a glovebox under

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† Dedicated to Professor Rolf Appel on the occasion of his 80th birthday.

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10.1021/om000871h CCC: $20.00

a nitrogen atmosphere. Diethyl ether was freshly distilled from Na and *n*-pentane from $LiAlH_4$ prior to use. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. A Bruker AM 200 instrument was used to record ^1H NMR (200.1 MHz), ^{119}Sn NMR (186.5 MHz), and ^{19}F NMR (188.3 MHz) spectra, with reference to TMS, $SnMe_4$, and $BF_3(OEt_2)$, respectively. Mass spectra were obtained on a Finnigan Mat 8230 instrument. The compounds $[HC(CMeNAr)_2]H$[7] and $GeCl_2$·(dioxane)[8] were prepared by literature procedures. Other chemicals were purchased from Aldrich and used as received.

LLi(OEt$_2$) (1). A solution of MeLi (13.0 mL, 1.6 M in diethyl ether, 20.0 mmol) was added dropwise to a stirred solution of $[HC(CMeNAr)_2]H$ (8.36 g, 20.0 mmol) in *n*-hexane (40 mL) at −78 °C. The reaction mixture was warmed to room temperature and was stirred for 3 h. After filtration, storage of the filtrate in a −32 °C freezer for 2 days afforded colorless crystals of **1** (8.91 g, 90%). ^1H NMR (C_6D_6): δ 0.49 (t, 6 H, $O(CH_2\mathit{Me})_2$), 1.16 (d, 12 H, CH*Me*$_2$), 1.22 (d, 12 H, CH*Me*$_2$), 1.88 (s, 6 H, *Me*), 2.70−2.82 (q, 4 H, $O(C\mathit{H}_2Me)_2$), 3.22−3.45 (sept, 4 H, C*H*Me$_2$), 4.98 (s, 1 H, γ-C*H*), 7.00−7.10 (m, 6 H, 2,6-*i*-$Pr_2C_6\mathit{H}_3$).

LGeCl (2). A solution of **1** (0.498 g, 1.0 mmol) in diethyl ether (20 mL) was added dropwise to a stirred suspension of $GeCl_2$·(dioxane) (0.27 g, 1.0 mmol) in diethyl ether (10 mL) at −78 °C. The reaction mixture was warmed to room temperature and was stirred for another 6 h. After removal of all the volatiles, the residue was extracted with *n*-hexane (20 mL). Storage of the extract in a −32 °C freezer for 3 days afforded colorless crystals of **2** (0.33 g, 63%). Mp: 197−199 °C. Anal. Calcd for $C_{29}H_{41}ClGeN_2$ (525.68): C, 66.21; H, 7.79; Cl, 6.75; N, 5.32. Found: C, 66.01; H, 7.97; Cl, 6.99; N, 5.22. EI-MS (70 eV): *m*/*e* (%) 526 (M^+, 65), 491 ($[M - Cl]^+$, 100). ^1H NMR (C_6D_6): δ 1.01 (d, 6 H, CH*Me*$_2$), 1.19 (d, 6 H, CH*Me*$_2$), 1.20 (d, 6 H, CH*Me*$_2$), 1.46 (d, 6 H, CH*Me*$_2$), 1.60 (s, 6 H, *Me*), 3.05−3.20 (sept, 2 H, C*H*Me$_2$), 3.80−4.00 (sept, 2 H, CH*Me*$_2$), 5.14 (s, 1 H, γ-C*H*), 7.00−7.10 (m, 6 H, 2,6-*i*-$Pr_2C_6\mathit{H}_3$).

LSnCl (3). A solution of **1** (0.498 g, 1.0 mmol) in diethyl ether (15 mL) was added dropwise to a stirred suspension of $SnCl_2$ (0.19 g, 1.0 mmol) in diethyl ether (10 mL) at −50 °C. The reaction mixture was warmed to room temperature and was stirred for 12 h. The precipitate was filtered, and the solvent was partially reduced (ca. 10 mL). Storage of the remaining solution in a −32 °C freezer for 2 days afforded yellow crystals of **3** (0.42 g, 73%). Mp: 207−211 °C. Recrystallization from *n*-hexane (15 mL) in a −10 °C freezer for 2 days afforded crystals suitable for X-ray diffraction analysis. Anal. Calcd for $C_{29}H_{41}ClN_2Sn$ (571.78): C, 60.91; H, 7.23; Cl, 6.20; N, 4.90. Found: C, 60.33; H, 7.12; Cl, 6.32; N, 4.98. EI-MS (70 eV): *m*/*e* 572 (M^+). ^1H NMR (C_6D_6): δ 1.03 (d, 6 H, CH*Me*$_2$), 1.16 (d, 6 H, CH*Me*$_2$), 1.19 (d, 6 H, CH*Me*$_2$), 1.42 (d, 6 H, CH*Me*$_2$), 1.61 (s, 6 H, *Me*), 3.00−3.20 (sept, 2 H, C*H*Me$_2$), 3.85−3.98 (sept, 2 H, C*H*Me$_2$), 5.05 (s, 1 H, γ-C*H*), 7.06 (m, 6 H, 2,6-*i*-$Pr_2C_6\mathit{H}_3$). ^{119}Sn NMR (C_6D_6): δ −224.

LSn(*t*-Bu) (4). A solution of *t*-BuLi in *n*-hexane (0.4 mL, 1.6 M) was added dropwise to a stirred solution of **3** (0.35 g, 0.62 mmol) in *n*-hexane (20 mL) at −78 °C. The reaction mixture was warmed to room temperature and was stirred for an additional 3 h. The precipitate was filtered, and the solvent was partially removed (ca. 10 mL) from the red filtrate. Storage of the remaining solution in a −10 °C freezer for 5 days afforded red crystals of **4** (0.32 g, 85%). Mp: 188−190 °C. Anal. Calcd for $C_{33}H_{50}N_2Sn$ (593.47): C, 66.79; H, 8.49; N, 4.72. Found: C, 66.58; H, 8.55; N, 4.55. EI-MS (70 eV): *m*/*e* 537 $[M - t\text{-}Bu]^+$. ^1H NMR (C_6D_6): δ 0.88 (s, 9 H, *t*-Bu), 1.12 (d, 6 H, CH*Me*$_2$), 1.14 (d, 6 H, CH*Me*$_2$), 1.32 (d, 6 H, CH*Me*$_2$), 1.40 (d, 6 H, CH*Me*$_2$), 1.61 (s, 6 H, *Me*), 3.30−3.42 (sept, 2 H, C*H*Me$_2$), 3.72−3.82 (sept, 2 H, C*H*Me$_2$), 4.82 (s, 1 H, γ-C*H*), 6.95−7.11 (m, 6 H, 2,6-*i*-$Pr_2C_6\mathit{H}_3$). ^{119}Sn NMR (C_6D_6): δ 259.

LSn(OSO$_2$CF$_3$) (5). A solution of **3** (0.572 g, 1.0 mmol) in toluene (20 mL) was added to a stirred suspension of $AgSO_3CF_3$ (0.239 g, 1.0 mmol) in toluene (10 mL) at −78 °C. The reaction mixture was warmed to room temperature and was stirred for 1 h. The precipitate was filtered, and the solvent was partially removed (ca. 15 mL) under reduced pressure from the pale yellow filtrate. Storage of the remaining solution in a −10 °C freezer for 2 days afforded colorless crystals of **5** suitable for X-ray diffraction analyses (0.55 g, 80%). Mp: 150 °C dec. EI-MS (70 eV): *m*/*e* 686 [M^+]. ^1H NMR (C_6D_6): δ 1.16 (d, 12 H, CH*Me*$_2$), 1.20 (d, 12 H, CH*Me*$_2$), 1.62 (s, 6 H, *Me*), 3.21−3.38 (sept, 4 H, C*H*Me$_2$), 5.31 (s, 1 H, γ-C*H*), 6.95−7.09 (m, 6 H, 2,6-*i*-$Pr_2C_6\mathit{H}_3$). ^{119}Sn NMR (C_6D_6): δ −239. ^{19}F NMR (C_6D_6): δ 85.28.

LSnN$_3$ (6). A solution of **3** (1.14 g, 2.0 mmol) in THF (20 mL) was added to a stirred suspension of NaN_3 (0.13 g, 2,0 mmol) in THF (10 mL) at room temperature. The reaction mixture was stirred for 3 days. After the solvent was removed, the residue was extracted with toluene (20 mL). Storage of the extract in a −32 °C freezer for 2 days afforded slightly yellow crystals of **6** (1.05 g, 90%). Mp: 205−212 °C. Anal. Calcd for $C_{29}H_{41}N_5Sn$ (578.38): C, 60.22; H, 7.15; N, 12.11. Found: C, 60.11; H, 7.04; N, 12.25. EI-MS (70 eV): *m*/*e* (%) 537 (100) $[M - N_3]^+$. ^1H NMR (C_6D_6): δ 1.02 (d, 6 H, CH*Me*$_2$), 1.15 (d, 6 H, CH*Me*$_2$), 1.21 (d, 6 H, CH*Me*$_2$), 1.49 (d, 6 H, CH*Me*$_2$), 1.66 (s, 6 H, *Me*), 2.90−3.15 (sept, 2 H, C*H*Me$_2$), 3.70−3.82 (sept, 2 H, C*H*Me$_2$), 4.93 (s, 1 H, γ-C*H*), 6.99−7.14 (m, 6 H, 2,6-*i*-$Pr_2C_6\mathit{H}_3$). ^{119}Sn NMR (C_6D_6): δ −237.

L$_2$Sn (7). A solution of **3** (1.14 g, 2.0 mmol) in *n*-hexane (30 mL) was added to C_8K (excess) at room temperature. The reaction mixture was stirred for 3 days. After filtration (of the tin, graphite, and potassium chloride) and partial removal of the solvent from the filtrate (ca. 15 mL), storage of the filtrate in a −32 °C freezer for 7 days afforded colorless crystals of **7** (0.19 g, 10%). Mp: 232−237 °C. Anal. Calcd for $C_{58}H_{82}N_4Sn$ (954.97): C, 73.02; H, 8.66; N, 5.87. Found: C, 72.96; H, 8.58; N, 5.95. EI-MS (70 eV): *m*/*e* 537 $[M - L]^+$. ^1H NMR (C_6D_6): δ 0.88−1.58 (m, 60 H, *Me* and CH*Me*$_2$), 2.80−3.40 (m, 8 H, C*H*Me$_2$), 4.25 (s, 1 H, γ-C*H*), 4.77 (s, 1 H, γ-C*H*), 6.99−7.03 (m, 12 H, 2,6-*i*-$Pr_2C_6\mathit{H}_3$). ^{119}Sn NMR (C_6D_6): δ −246.

X-ray Crystallography. Single crystals of **2**, **3**, **5**, and **7** were taken from the flask under nitrogen gas and mounted on a glass fiber in rapidly cooled perfluoropolyether.[9] Diffraction data were collected on a Stoe-Siemens-Huber four-circle diffractometer coupled to a Siemens CCD area detector at 200(2) K with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The structures were solved by direct methods (SHELXS-96[10]) and refined against F^2 using SHELXL-97.[11] All non-hydrogen atoms were refined anisotropically with similarity and rigid bond restraints. All hydrogen atoms were included in the refinement in geometrically ideal positions.

Crystallographic data for **2**, **3**, **5**, and **7** are given in Table 1.

Results and Discussion

Synthesis of Compounds 1−7. The β-diketiminato lithium salt $[HC(CMeNAr)_2]Li$ (Ar = 2,6-*i*-$Pr_2C_6H_3$) had been reported previously and used in situ without isolation and characterization.[5a,c] Therefore, the crystalline $[HC(CMeNAr)_2]Li(Et_2O)$ (**1**) was isolated and characterized spectroscopically. Reagent **1** is soluble in hydrocarbon solvents and stable under an inert atmo-

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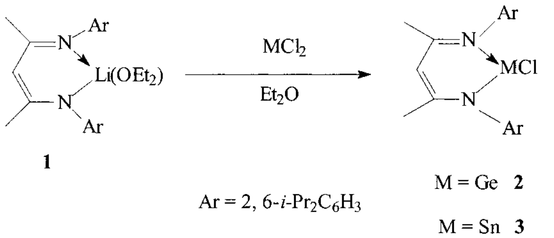
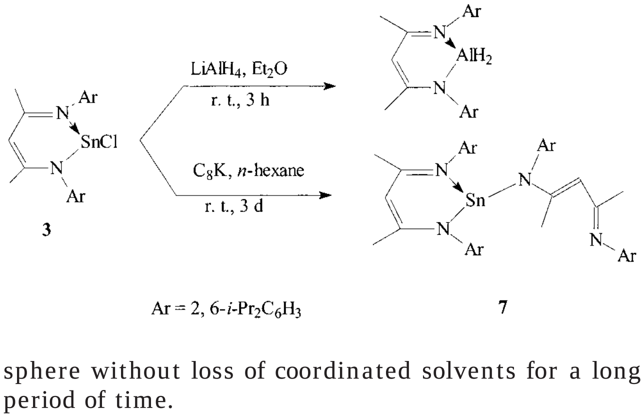
Table 1. Crystallographic Data for Compounds 2, 3, 5, and 7

	2	**3**	**5**	**7**
formula	$C_{29}H_{41}ClGeN_2$	$C_{29}H_{41}ClN_2Sn$	$C_{30}H_{41}F_3N_2O_3SSn{\cdot}C_7H_8$	$C_{58}H_{82}N_4Sn$
fw	525.28	571.78	777.53	953.97
color	colorless	pale yellow	colorless	colorless
cryst syst	triclinic	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_12_12_1$
a (Å)	8.656(2)	10.437(2)	12.1397(12)	15.845(12)
b (Å)	11.571(3)	12.138(3)	13.063(19)	17.024 (3)
c (Å)	14.946(4)	12.419(4)	23.955(6)	22.820(3)
α (deg)	98.154(15)	89.80(3)	90.00	90
β deg)	99.438(14)	72.327(12)	92.597(12)	90
γ (deg)	104.47(2)	71.147(14)	90	90
V (Å^3)	1403.2(6)	1410.8(6)	3795.0(11)	6155.5(15)
Z	2	2	4	4
d_{calcd} (g cm^{-3})	1.244	1.346	1.361	1.029
μ (mm^{-1})	1.205	1.019	0.779	0.449
F(000)	556	592	1608	2032
cryst size (mm)	0.80 × 0.20 × 0.20	1.00 × 0.40 × 0.40	1.00 × 0.50 × 0.20	0.60 × 0.50 × 0.40
2θ range (deg)	3.66−22.52	3.57−25.04	3.54−25.03	3.51−25.03
index range	$-9 \le h \le 9$, $-12 \le k \le 12$, $-10 \le l \le 16$	$-11 \le h \le 12$, $-14 \le k \le 14$, $-13 \le l \le 14$	$-14 \le h \le 14$, $-15 \le k \le 15$, $-27 \le l \le 28$	$-3 \le h \le 18$, $-20 \le k \le 20$, $-27 \le l \le 27$
no.of rflns collected	3821	6610	8959	7396
no. of indep rflns	3677 (R(int) = 0.0399)	4981 (R(int) = 0.0572)	6687 (R(int) = 0.0253)	6878 (R(int) = 0.0294)
R1, wR2 ($I > 2(\sigma)I$)	0.0380, 0.1051	0.0354, 0.0978	0.0410, 0.1081	0.0545, 0.1682
R1, wR2 (all data)	0.0408, 0.1086	0.0360, 0.0989	0.0454, 0.1132	0.0622, 0.1834
goodness of fit, F^2	1.065	1.061	1.050	1.143
no. of data/restaints/params	3675/0/308	4980/0/308	6687/396/417	6872/0/588
largest diff peak, e Å^{-3}	0.537 to −0.540	1.697 to −0.921	1.373 to −1.070	1.378 to −0.647

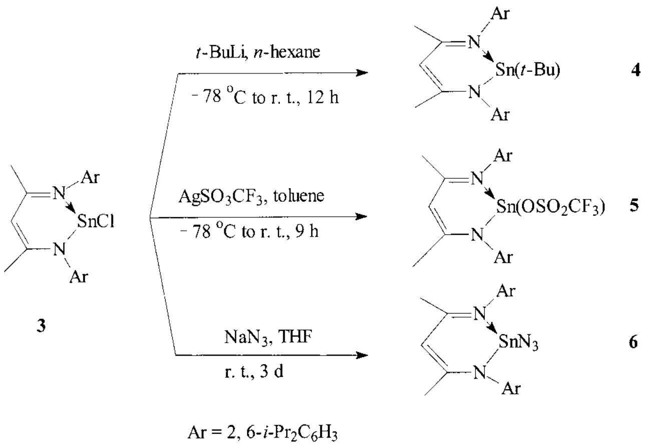
Scheme 1



Scheme 2



Scheme 3



sphere without loss of coordinated solvents for a long period of time.

The β-diketiminato Sn(II) chloride (**3**) was easily obtained in high yield by the reaction of **1** with 1 equiv of $SnCl_2$ in diethyl ether (Scheme 1). However, attempts to prepare di-β-diketiminato complexes by using 2 equiv of **1** were unsuccessful, even under more drastic conditions.

The reduction of complex **3** with C_8K unexpectedly resulted in the formation of L_2Sn (**7**) in low yield and a significant amount of tin metal (Scheme 2). No other reduced species could be isolated. Organotin(IV) hydrides generally can be prepared by the reduction of the corresponding chlorides with $LiAlH_4$.[12] However, treatment of **3** with $LiAlH_4$ in diethyl ether at room temperature did not give LSnH but, rather, the known aluminum hydride $LAlH_2$[13] (Scheme 2). Further attempts to prepare LSnH by reduction of **3** with various other reducing agents, including $NaBH_4$, KBH_4, KH, and NaH, were not successful.

Furthermore, we examined the substitution reactions of **3** with selected nucleophiles in order to prepare other tin(II) derivatives. Treatment of **3** with *t*-BuLi, $AgSO_3CF_3$, and NaN_3 resulted in the formation of **4**−**6,** respectively (Scheme 3). The addition of *t*-BuLi to **3** in *n*-hexane at low temperature proceeded smoothly to provide **4** in high yield. The triflate anion (SO_3CF_3) has long served as an excellent leaving group in nucleophilic displacement reactions.[14] Organotin triflates may act as a precursor for further reactions. $LSn(OSO_2CF_3)$ (**5**) was prepared in toluene in high yield as colorless

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crystals which are soluble in common organic solvents, such as *n*-hexane and toluene. Metal and nonmetal species containing the azide functionality are of interest as starting materials, and the tin(IV) azides are well-known.[15] However, to our knowledge, the sole example of a tin(II) azide, $[(n\text{-Pr})_2\text{ATI}]\text{SnN}_3$, was reported only recently.[11] The azide compound **6** was readily prepared as slightly yellow crystals by the reaction of **3** with NaN_3 in THF at room temperature in high yield.

Compound **2**, the germanium analogue of **3**, was prepared from **1** and $GeCl_2$·(dioxane) for comparison (Scheme 1). The solid-state structural data of **2** and **3** were obtained by single-crystal X-ray analysis.

Compounds **1**−**7** were fully characterized by elemental analyses, EI-MS, and multinuclear NMR. In the ^{1}H NMR spectra, the resonances of methyl groups of the aryl substituents, which appear as doublets in the range δ 1.01−1.58, could be distinguished due to their different environments. However, ^{1}H NMR signals of **7** overlapped in the range δ 0.88−3.44 because of the multiple chemical environments of their protons as shown in the solid-state structure. The ^{119}Sn NMR spectra of **3**−**7** are comparable with those of tin(II) poly(1-pyrazolyl)borates, in which the metal centers reside in a similar environment. ^{119}Sn NMR spectroscopy seems to be a useful probe for the determination of the coordination of tin(II) in the poly(1-pyrazolyl)borates, whose ^{119}Sn chemical shifts vary with coordination number: −730 to −950 ppm for six-coordinate tin, −650 to −730 ppm for four-coordinate tin, and −270 to −350 ppm for three-coordinate tin.[16] For compounds **3**, **5**, and **7**, in which the tin is three-coordinate in the solid state, the ^{119}Sn NMR chemical shifts are in the range −224 to −246 ppm. Although the coordination number of the metal center in the solution may be different from that in the solid state, when these chemical shifts are compared with those of the tin(II) poly(1-pyrazolyl)borates, the tin atoms in compounds **3**, **5**, and **7**, as well as that in **6** (^{119}Sn NMR: −237 ppm), probably are three-coordinate in solution as well. The ^{119}Sn NMR resonance of the *tert*-butyl derivative **4** is found at low field (259 ppm), suggesting that the tin atom in **4** may be two-coordinate in solution. All the EI-MS spectra of **2**, **3**, and **5** give the corresponding molecular ion peak M^+.

X-ray Diffraction Analyses for 2, 3, 5, and 7. The solid-state structures of compounds **2**, **3**, **5**, and **7** as determined by single-crystal X-ray diffraction are shown in Figures 1−4. Selected bond lengths and angles are listed in Table 2; additional bond distances and angles are included in the Supporting Information. The X-ray single-crystal structures of **2**, **3**, **5**, and **7** show that all compounds are monomeric. The metal centers adopt similar three-coordinated sites and reside in distorted-tetrahedral environments with one vertex occupied by a lone pair of electrons.

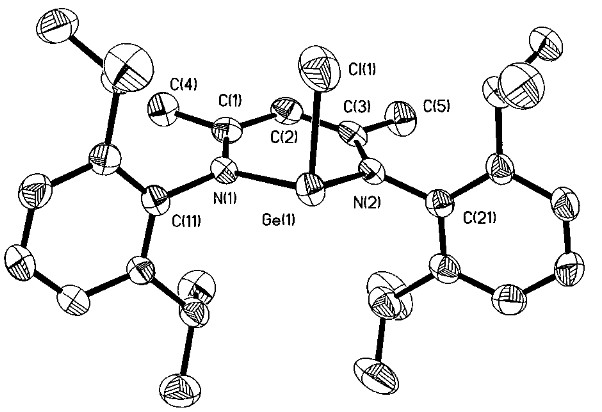

Figure 1. Thermal ellipsoid plot (50%) of **2**. H atoms are not shown. Important structural data are given in Table 1.

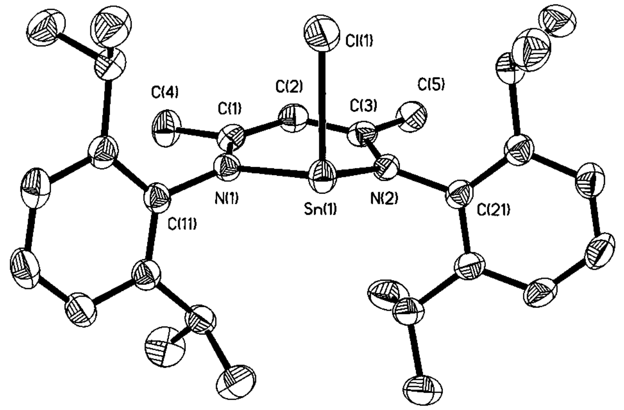

Figure 2. Thermal ellipsoid plot (50%) of **3**. H atoms are not shown. Important structural data are given in Table 1.

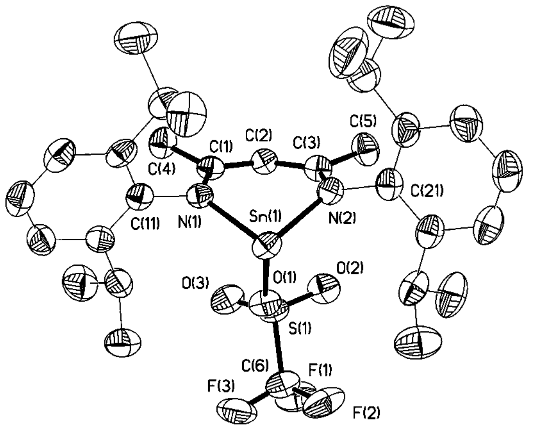

Figure 3. Thermal ellipsoid plot (50%) of **5**. H atoms are not shown. Important structural data are given in Table 1.

The structural features of these divalent compounds **2**, **3**, **5**, and **7** are different from those of the comparable tetravalent $SnCl(Me)_2[CH(CPhNSiMe_3)_2]$ (**8**) and $SnCl(Me)_2[CH(CPhNH)_2]$ (**9**), in which similar ligands are coordinated to tin.[17] In compounds **2**, **3**, **5**, and **7**, the backbone of the chelating ligand is essentially planar and the metal atom is always out of the plane (0.56 Å in **2**, 0.66 Å in **3**, 0.65 Å in **5**, and 0.24 Å in **7**). In compound **8** the central C (0.086 Å) and the Sn atom (0.76 Å) are out of the NC−CN plane. In compound **9**, the skeletal atoms, including Sn, are almost coplanar. Furthermore, the difference of the two bond lengths of the metal center to the chelating nitrogen atoms in the **2**, **3**, **5**, and **7** ranges from 0.003 to 0.019 Å. However, the comparable differences in **8** and in **9** (0.201 Å in **8** and 0.109 Å in **9**) are significantly longer. Obviously,

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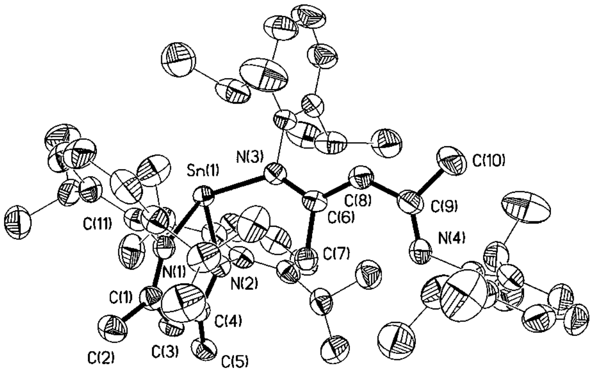

Figure 4. Thermal ellipsoid plot (50%) of **7**. H atoms are not shown. Important structural data are given in Table 1.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Compounds 2, 3, 5, and 7

bond distance		bond angle	
	Complex **2**		
Ge(1)−N(1)	1.988(2)	N(1)−Ge(1)−N(2)	90.89(10)
Ge(1)−N(2)	1.997(3)	N(1)−Ge(1)−Cl(1)	95.00(8)
Ge(1)−Cl(1)	2.295(12)	N(2)−Ge(1)−Cl(1)	95.60(8)
	Compound **3**		
Sn(1)−N(1)	2.185(2)	N(1)−Sn(1)−N(2)	85.21(8)
Sn(1)−N(2)	2.180(2)	N(1)−Sn(1)−Cl(1)	90.97(6)
Sn(1)−Cl(1)	2.473(9)	N(2)−Sn(1)−Cl(1)	93.47(6)
	Compound **5**		
Sn(1)−N(1)	2.142(3)	N(1)−Sn(1)−N(2)	87.78(10)
Sn(1)−N(2)	2.139(3)	N(1)−Sn(1)−O(1)	87.39(10)
Sn(1)−O(1)	2.254(2)	N(2)−Sn(1)−O(1)	90.62(10)
	Compound **7**		
Sn(1)−N(1)	2.235(6)	N(1)−Sn(1)−N(2)	85.2(2)
Sn(1)−N(2)	2.251(6)	N(1)−Sn(1)−N(3)	102.7(2)
Sn(1)−N(3)	2.166(6)	N(2)−Sn(1)−N(3)	106.8(2)

the larger ionic radius of M(II) (Sn(II) 1.12 Å) compared to that of M(IV) (Sn(IV) 0.71 Å) results in longer $M^{II}-N$ bond lengths, which are less influenced by the substituents at the metal center. We have recently shown by ab initio calculation on a comparable Al analogue that delocalization of electrons does not play an important role in this system.[6]

Figures 1 and 2 provide the molecular geometries for **2** and **3**, respectively, and show that the two complexes have similar structural features. However, the bond angle of N(1)−Ge(1)−N(2) (90.89(10)°**)** in **2** is larger than the corresponding angle in **3** (N(1)−Sn(1)−N(2) = 85.21(8)°), and the bond length of N−Ge (1.998(2) and 1.997(3) Å) in **2** is slightly shorter than the corresponding N−Sn bond length in **3** (2.185(2) and 2.180(2) Å), as expected. This indicates that the ionic interactions of the central metal atom with the ligand decrease from Ge to Sn due to the difference of the atomic radii (Ge(II) 0.93 Å, Sn(II) 1.12 Å).

The observed M−N bond lengths in **2**, **3**, **5**, and **7** are in the normal range (1.910−2.042 Å for Ge−N single bonds[18] and 2.121−2.397 Å for Sn−N[13]), but the bond length of Ge(1)−Cl(1) (2.295(12) Å) in **2** is 0.092 Å longer than that found in Ge(Cl)(C_6H_3-2,6-Trip$_2$) (2.203(10) Å)[1k] and the Sn(1)−Cl(1) bond length (2.473(9) Å) is 0.257 Å longer than that in Sn(Cl)[$C_6H_3(NMe_2)_2$-2,6] (2.216(5) Å).[1i]

A noteworthy feature of metal triflates is the diversity of bonding systems, ranging from ionic to mono-, bi-, or tridentate terminal or bridging modes.[3] For tin(II) triflate, the weakly coordinating ionic compound Sn(CF_3SO_3)[HB{3,5-(CF_3)$_2$Pz}$_3$] (**10**) was reported by Dias[19] and the bidentate compound [Sn(η^2-CF_3SO_3){N(SiMe$_3$)$_2$}]$_2$ (**11**) by Lappert.[3] In compound **5**, (Figure 3), the triflate group is monodentate. The Sn(1)−O(1) distance (2.254(2) Å) in **5** is shorter than those in **10** (2.507(3) Å)[19] and **11** (2.291(4) and 2.489(4) Å).[3] This closer contact of the triflate moiety with the metal center in **5** than is the case in **10** and **11** probably is caused by the differences of the coordinating environment of the metal center.

The structure of **7** shows that one ligand is chelated to tin, while the other is monodentate. This is a result of the steric demand of the two ligands. In compound **7**, the Sn−N bond distances of the chelating nitrogen atoms (2.233(6) and 2.251(6) Å) are longer than that of the monodentate ligand (2.166(6) Å), as well as those in **3** and **5** (2.139(3)−2.185(2) Å). This finding suggests that the chelating ligand in **7** is not as close to the Sn atom as are those in **3** and **5**.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supporting Information Available: Figures giving ORTEP diagrams and tables giving full details of the crystallographic data and data collection parameters, atom coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen coordinates for **2**, **3**, **5**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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