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Synthesis of Monomeric Divalent Tin(II) Compounds with Terminal Chloride, Amide, and Triflate Substituents

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Dedicated to Professor George B. Kauffman on the occasion of his 80th birthday

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Monomeric three-coordinate (amidinato)tin chloride [PhC(N*t*Bu)$_2$SnCl] (**1**) was prepared by the reaction of *N*,*N*′-di-*tert*-butylcarbodiimide, phenyllithium and $SnCl_2$. The metathesis reaction of **1** with $AgSO_3CF_3$ and $(Me_3Si)_2NLi$ afforded the formation of PhC(N*t*Bu)$_2$SnOTf (Tf = CF_3SO_2) (**2**) and PhC(N*t*Bu)$_2$SnN(SiMe$_3$)$_2$ (**3**). The reductive dehalogenation of **1** with L-selectride resulted in the formation of the four-coordinate homoleptic tin compound Ph_2C_2(N*t*Bu)$_4$Sn (**4**). Compounds **1**, **2**, **3**, and **4** were characterized by single-crystal structural analysis. Furthermore, **1** was treated with $Fe_2(CO)_9$ to afford the Lewis acid–base adduct **5**.

Introduction

There is widespread interest in the chemistry of divalent derivatives of the heavier group 14 elements, because of their carbene-like properties.[1] In contrast to carbenes and silylenes, the germylenes and stannylenes are less reactive due to the larger energy gap between the s- and p-orbitals.[2] The germanium analogue of Arduengo's carbene (*t*BuNCHCHN*t*Bu)Ge was obtained by Herrmann et al. in 1992,[3] and presently Ge^{II} chemistry is rich and diversified with different types of germylene derivatives,[4] which have been reviewed periodically.[5] On the contrary, the tin analogue of the "Arduengo-type carbene" is relatively scant despite the well-known inert pair effect, which proposes that divalent group 14 species should become more stable upon descending the group.[6a] Russell et al. recently reported the synthesis and structural elucidation of five tin analogues of N-heterocyclic carbene.[6b] Nonetheless, there has been considerable interest over the past three decades in the chemistry of dialkyl- and diaryl-Sn^{II} compounds following the pioneering studies by Lappert and co-workers.[7] Stable tin(II) compounds of formula $(SnR_2)_{1,2}$ and $(RSnX^1)_{1,2}$ (R = bulky ligand, X^1 = halide) are well characterized and are an abundant class of compounds.[8] 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. This is surprising, because these tin(II) derivatives can act as good precursors for polymerization and other catalytic reactions. For example, Gibson et al. showed that tin(II) compounds performed the role of initiator for the living polymerization of *rac*-lactide to heterolactic-enriched polylactide.[9a] It is also noteworthy that simple Sn^{II} halides are important promoters for Pt-catalyzed hydroformylation.[9b] Moreover, owing to their low toxicity Sn^{II} compounds are preferred over other metal ions for medical and pharmaceutical applications, for example tin(II) chlorides are important in nuclear medicine as an essential component in diagnostic agents used to visualize blood, heart, lung, kidney, and bone.[9c,9d] In recent years several compounds including Sn(C_7H_7)[2,6-(CH_2NMe_2)$_2C_6H_3$],[8e] [(*n*Pr)$_2$ATI]SnN_3 {[(*n*Pr)$_2$ATI] = *N*-(*n*-propyl)-2-(*n*-propylamino)troponiminate},[8l] Sn[B(C_6F_5)$_4$]Cp,[10] [Sn(SO_3CF_3)-{N(SiMe$_3$)$_2$}]$_2$,[11] (2,6-Trip$_2C_6H_3$)SnX [Trip = 2,4,6-*i*Pr$_3C_6H_2$; X = Me, N(SiMe$_3$)$_2$], and [{HC(CMeNAr)$_2$}-SnX] [Ar = 2,6-*i*Pr$_2C_6H_3$; X = Cl, I, N(SiMe$_3$)$_2$, Me, F, OTf][12] have been isolated. There is plenty of room for new discoveries in tin(II) chemistry, and we believe that base-stabilized heteroleptic stannylenes are particularly attractive in extending the heavier group 14 analogues of carbene.

In order to explore the chemistry of three-coordinate tin, it was necessary to design a ligand with the following properties: (1) easy to synthesize and modify, (2) coordinates strongly to tin preferably as a bidentate ligand, (3) provides the opportunity to fine-tune the ligand by altering substituents. A ligand that fits these criteria is the four-membered monoanionic amidinato ligand. It has already been employed as an ancillary ligand in various catalytic conversions, for example oligomerization[13] or polymerization[14]

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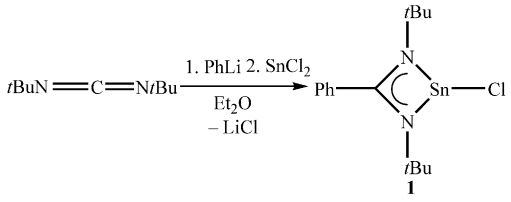
of olefins or of cyclic esters.[15] The steric and electronic properties of the amidinato ligand are readily modulated through variation of the substituents on the carbon and nitrogen atoms. Because of the geometric constraints of the NCN ligand backbone, amidinates have small N–M–N bite angles. They have a rich coordination geometry in which both chelating and bridging coordination modes can be achieved. The balance between chelating and bridging coordination is critically governed by the substitution pattern of the amidinato ligand. Large substituents on the carbon atom induce a convergent orientation of the lone pairs (favoring chelation), whereas small substituents lead to a more parallel orientation of the lone pairs (enabling bridging).[16] Such ligands have already been utilized in main-group and transition-metal chemistry.[17] The substituents on the amidinate nitrogen atoms can be used for fine-tuning the steric requirement of the ligand, influencing the coordination geometry of the metal center. The 2,6-diisopropylphenyl group has turned out to be very efficient in this respect, and has been used successfully in the development of stabilization of low-valent metal oxidation states.[18] We have found that the *t*Bu group is also very effective for that purpose. Recently, we have prepared a few heteroleptic silylenes [LSiX: X = Cl, O*t*Bu, NMe_2, P*i*Pr$_2$; L = PhC(N*t*Bu)$_2$][19] and *gauche*-bent silicon(I) and germanium(I) dimers {[PhC(N*t*Bu)$_2$]$_2$Si$_2$, [PhC(N*t*Bu)$_2$]$_2$Ge$_2$} by taking advantage of such a ligand.[20] Herein we report the preparation of a compound with a divalent heavier group 14 element, LSnCl (**1**) [L = PhC(N*t*Bu)$_2$], and the resulting derivatives, LSn(OSO_2CF_3) (**2**), LSnN($SiMe_3$)$_2$ (**3**) and L_2Sn (**4**). Furthermore, **1** was treated with $Fe_2(CO)_9$ to afford LSnCl→$Fe(CO)_4$ (**5**), a Lewis acid–base adduct.

Results and Discussion

The reaction of *tert*-butylcarbodiimide (*t*BuN=C=N*t*Bu) with 1 equiv. of PhLi in diethyl ether followed by treatment with $SnCl_2$ afforded [PhC(N*t*Bu)$_2$]SnCl (**1**; Scheme 1). Compound **1** was obtained as a colorless crystalline solid in 75% yield, and its structure was confirmed by NMR spectroscopy, EI mass spectrometry, and elemental analysis.



Scheme 1. Preparation of **1**.

The ^{1}H NMR spectrum of **1** shows a singlet at δ = 1.02 ppm for the 18 protons of two *t*Bu groups and another multiplet for five aromatic protons (δ = 7.48–7.56 ppm). Compound **1** resonates at δ = 29.6 ppm in the ^{119}Sn NMR spectrum. The molecular ion peak is observed with the highest relative intensity in the EI mass spectrum at *m*/*z* = 385.5.

Maintaining a toluene solution of **1** at –32 °C overnight resulted in colorless single crystals suitable for X-ray structural analysis. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ (Figure 1). Compared to the similar structures [{cy$_2$NC(NAr)$_2$}SnCl] (cy = cyclohexyl), [{(*cis*-$Me_2C_5H_8$-N)C(NAr)$_2$}SnCl][21] and [{*t*BuC(NAr)$_2$}SnCl][15d] (Ar = 2,6-diisopropylphenyl) the structure of **1** is very similar showing a distorted trigonal-pyramidal geometry indicating a stereochemically active lone pair. The bond lengths and angles are in the same range, but the N–Sn–Cl angles (92.3 and 94.2°) in **1** have slightly smaller values than in the other structures (94.4–99.8°). The tin atom is 0.20 Å above the plane of the amidinato ligand. In the other three structures this value is smaller (0.03–0.12 Å).

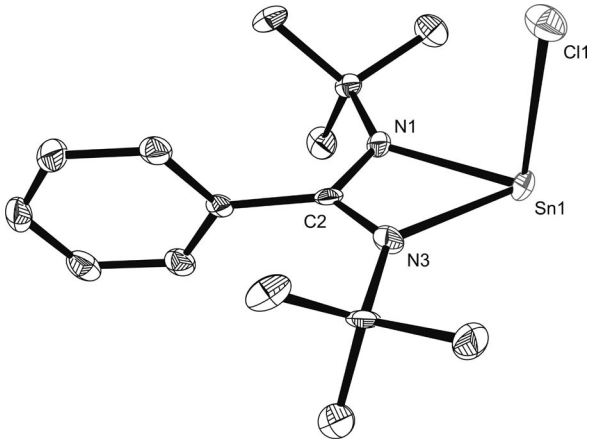
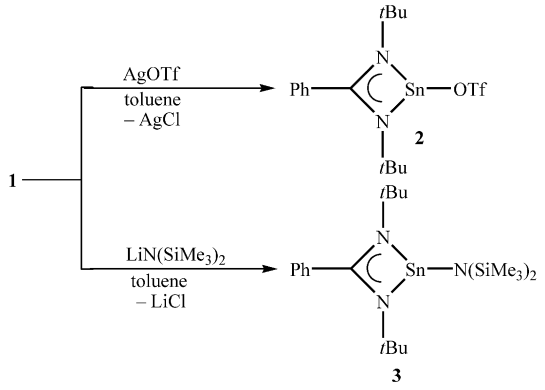


Figure 1. Molecular structure of **1**. Anisotropic displacement parameters are depicted at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Sn1–N1 2.177(3), Sn1–N3 2.192(3), Sn1–Cl1 2.4831(9); N1–Sn1–N3 60.5(1), N1–Sn1–Cl1 92.28(7), N3–Sn1–Cl1 94.16(8).

With the objective of preparing tin(II) derivatives we performed substitution reactions of **1** with selected nucleophiles. It is well known that the triflate anion ($CF_3SO_3^-$) has long served as an excellent leaving group in nucleophilic displacement reactions.[22] Organotin triflates may act as precursors for further reactions. Treatment of **1** with AgOTf in toluene at room temperature for 3 h afforded LSnOTf [L = PhC(N*t*Bu)$_2$] (**2**) in good yield (78%) (Scheme 2). Compound **2** (Figure 2) was characterized by ^{1}H, ^{13}C, ^{19}F and ^{119}Sn NMR spectroscopy, EI mass spectrometry and elemental analysis. In the ^{19}F NMR spectrum **2** exhibits a singlet resonance at δ = –73.6 ppm, whereas in the ^{119}Sn NMR spectrum it resonates at δ = –33.16 ppm. Colorless crystals of **2** were obtained from a toluene solution at room temperature after 1 d.

The structure of **2** was unequivocally established by X-ray crystallography. Compound **2** crystallizes in the monoclinic space group $P2_1/n$. Selected bond lengths and bond



Scheme 2. Preparation of **2** and **3**.

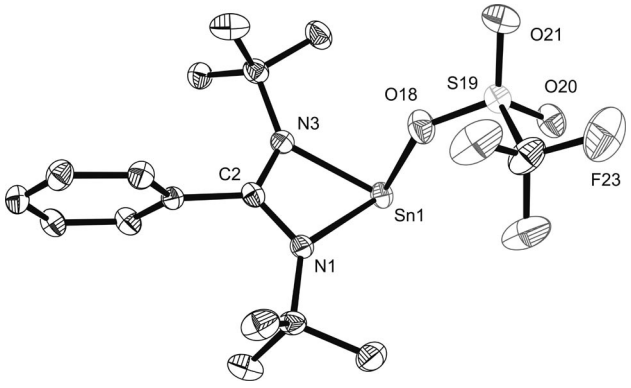


Figure 2. X-ray single-crystal structure of **2**. Anisotropic displacement parameters are depicted at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Sn1–N1 2.176(2), Sn1–N3 2.163(2), Sn1–O18 2.362(2); N1–Sn1–N3 60.88(8), N1–Sn1–O18 86.43(8), N3–Sn1–O18 83.09(8).

angles are given in the caption of Figure 2. The geometry of the amidinato ligand and the coordination of the tin atom are similar to what is found in structure **1**. However, the N–Sn–O bond angles are much smaller than the N–Sn–Cl angles in **1** (83.1 and 86.5 compared to 92.3 and 94.2°). The distance of the tin atom to the plane of the amidinato ligand is quite similar (0.23 Å compared to 0.20 Å in **1**). Similar compounds $[PhC(NSiMe_3)_2SnOCPh_3]$, $[PhC(NSiMe_2Ph)_2SnOCPh_3]$,[15c] $[tBuC(NAr)_2SnOiPr]$[15d] (Ar = 2,6-$iPr_2C_6H_3$) show smaller Sn–O bond lengths (2.006–2.040 Å compared to 2.362 Å in **2**), whereas the Sn–N bonds are longer (2.208–2.252 Å compared to 2.163 and 2.176 Å) and the N–Sn–O angles wider (87.3–94.8° compared to 83.1 and 86.5°).

Our interest in subvalent group 14 metal bis(trimethylsilyl)amides derives from work with the isoelectronic bis(trimethylsilyl)methyl derivatives and from earlier studies on many amides, including $SnMe_3(NMe_2)$.[23] The bis(trimethylsilyl)amido ligand was chosen because (1) its size often stabilizes complexes in which the metal atom has a low coordination number, (2) the numerous methyl groups provide for good hydrocarbon solubility. Compound $LSnN(SiMe_3)_2$ (**3**) was obtained in high yield from the reaction of **1** with 1 equiv. of $LiN(SiMe_3)_2$ in diethyl ether at room temperature (Scheme 2). Compound **3** (Figure 3) is a white solid, soluble in benzene, thf, toluene, and shows no decomposition on exposure to air for a short period of time. The (amidinato)tin amide is a very interesting compound, because it can act as a precursor for polymerization and hydrolysis reactions. Richeson and his team showed that (amidinato)tin(II) amide compounds are good catalysts for cyclotrimerization of phenyl isocyanate to triphenyl isocyanurates.[23d,23e] Compound **3** was characterized by ^1H, ^{13}C, ^{29}Si, and ^{119}Sn NMR spectroscopy, EI mass spectrometry, elemental and X-ray structural analysis. The ^1H NMR spectrum of compound **3** shows two singlets (δ = 1.27 and 0.25 ppm) corresponding to *t*Bu and $SiMe_3$ protons respectively, and one multiplet (δ = 7.33–7.45 ppm) for the Ph protons. The ^{119}Sn NMR spectrum of **3** exhibits a singlet at δ = –33.58 ppm. The ^{29}Si NMR shows a resonance at δ = 1.49 ppm. The molecular ion peak is observed with the highest relative intensity in the EI mass spectrum at *m*/*z* = 511.

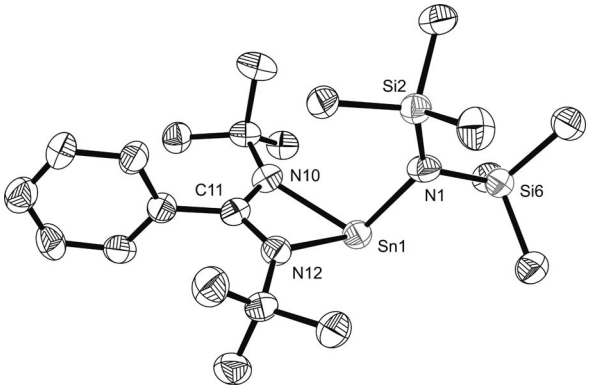
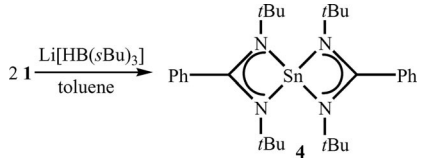


Figure 3. X-ray single-crystal structure of **3**. Anisotropic displacement parameters are depicted at 50% probability level. There are two molecules in the asymmetric unit. Molecule 1 is shown and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°] for molecule 1: Sn1–N1 2.116(6), Sn1–N10 2.216(6), Sn1–N12 2.227(6); N1–Sn1–N10 103.6(2), N1–Sn1–N12 105.0(2), N10–Sn1–N12 59.9(2); selected bond lengths [Å] and bond angles [°] for molecule 2 (not shown): Sn2–N1′ 2.134(5), Sn2–N10′ 2.191(7), Sn2–N12′ 2.214(6), N1′–Sn2–N10′ 102.1(3), N1′–Sn2–N12′ 106.4(2), N10′–Sn2–N12′ 59.3(2).

An X-ray diffraction study on a single crystal of **3** obtained from a toluene solution stored at –30 °C in a freezer for 1 d confirmed the features deduced from the spectroscopic data. Compound **3** crystallizes as a pseudomerohedral twin [twin fraction 0.473(2)] in the triclinic space group $P\bar{1}$ with two very similar molecules in the asymmetric unit. We find the typical geometry as shown by **1** and **2**. But here the mean bonds between the tin and amidinato nitrogen atoms (2.21 Å) are longer than the mean values in **1** and **2** (2.18 and 2.17 Å). But the value corresponds to those found in similar structures: $[tBuC(NSiMe_3)_2SnN(SiMe_3)_2]$,[21d] $[tBuC(Ncyclohexyl)_2SnN(SiMe_3)_2]$[23e] and $[tBuC(NAr)_2SnNMe_2]$[15d] (Ar = 2,6-$iPr_2C_6H_3$) (2.19–2.26 Å) as well as the

average value for the Sn–N (from monodentate amide) bond (2.13 Å in **3**) compared to the two other LSnN(SiMe$_3$)$_2$ structures (2.12 and 2.14 Å) and the N–Sn–NSiMe$_3$ bond angles (102.1–106.4° in **3** compared to 99.0–105.4°). In these structures the deviation of the tin atom from the plane of the amidinato ligand is larger (0.5 in **3** and 0.3–0.5 Å in the others) compared to **1** and **2**.

Organotin(II) hydrides generally can be prepared by the reduction of the corresponding chlorides with DIBAL, AlH$_3$·NMe$_3$ or by direct reaction with H$_2$.[24] Treatment of **1** with AlH$_3$·NMe$_3$ in toluene at room temperature does not lead to LSnH. However, recently we successfully synthesized L^{1}SnH [L^1 = HC(CMeNAr)$_2$; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$] in good yield and without impurity with the Li[HB(*s*Bu)$_3$] (commonly known as L-selectride) reagent.[25] Consequently, compound **1** was treated with 1 equiv. of L-selectride, and this resulted in the formation of L$_2$Sn (**4**) (Scheme 3). The propensity of the formation of homoleptic tin compound is due to the instability of the (amidinato)tin(II) hydride. Compound **4** was characterized by ^{1}H, ^{13}C, ^{119}Sn NMR spectroscopy, EI mass spectrometry, elemental and X-ray structural analysis. The ^{1}H NMR spectrum exhibits a singlet at δ = 1.12 ppm, which was attributed to 36 protons of *t*Bu groups, and a multiplet (δ = 7.30–7.34 ppm) assigned to ten protons. The ^{119}Sn NMR spectrum of **4** shows a resonance at δ = –285 ppm, which is upfield shifted, when compared with that of **1**. In the EI mass spectrum only peaks of smaller ions are observed. Further attempts to prepare the Sn–H compound with NaBH$_4$, KH or NaH failed.



Scheme 3. Preparation of **4**.

Maintaining a toluene solution of **4** at –30 °C in a freezer afforded temperature-sensitive colorless crystals suitable for X-ray analysis. Compound **4** (Figure 4) crystallizes as a nonmerohedral twin [twin fraction 0.0252(9)] in the monoclinic space group *C*2/*c* with half a molecule and a solvent toluene molecule in the asymmetric unit. The coordination geometry around Sn1 can be viewed as distorted sawhorse-like, with N1 and N1# in the axial positions and N2 and N2# residing in the equatorial plane. Accordingly, the axial Sn–N(1) bond is longer [2.394(1) Å] than the Sn–N(2) bond [2.195(1) Å]. There are several known structures with two coordinating amidinato ligands to Sn^{II},[26] for example [(PhCNSiMe$_3$N*t*Bu)$_2$Sn].[27] All have a more or less distorted sawhorse-like coordination with two longer (2.32–2.44 Å) and two shorter bonds (2.15–2.27 Å), but the "axial" angle varies tremendously (119.6–148.8°) showing the highest value in **4**. Accordingly, also the angle between the planes of the amidinato ligands exhibits a broad range of variation (42.4–89.3°, 53.8° in **4**).

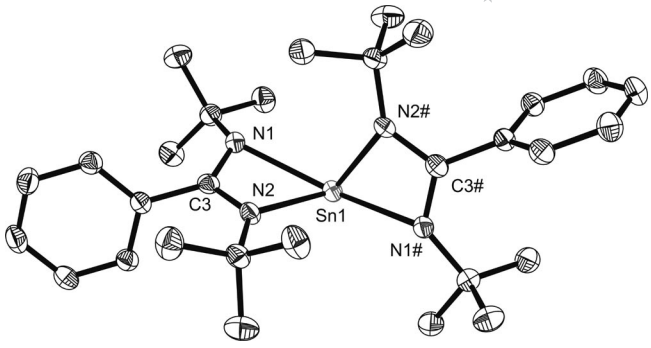
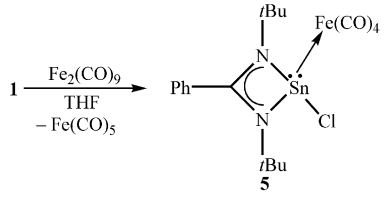


Figure 4. Molecular structure of **4**. Anisotropic displacement parameters are depicted at 50% probability level. Hydrogen atoms are omitted for clarity. Symmetry-related atoms are denoted with #. Selected bond lengths [Å] and bond angles [°] Sn1–N2 2.195(1), Sn1–N1 2.394(1); N2–Sn1–N2# 98.12(8), N2–Sn1–N1 57.75(5), N2#–Sn1–N1 103.97(5), N1–Sn1–N1# 154.24(7).

The aptitude of silylene, germylene and stannylene to act as a σ-donor and π-acceptor already established them as preeminent ligands for the synthesis of transition-metal complexes with potential application in homogeneous catalysis.[28] After the successful isolation of chlorostannylene, we have been intrigued by the question as to whether such tricoordinate stannylenes can act as ligands to stabilize metal complexes. Therefore, [PhC(N*t*Bu)$_2$]SnCl and nonacarbonyldiiron [Fe$_2$(CO)$_9$] were selected as probes to investigate their reaction behavior. The synthetic procedure of **5** (Scheme 4) is similar to that of {[PhC(N*t*Bu)$_2$]-Si*O*t*Bu}Fe(CO)$_4$.[28b]



Scheme 4. Preparation of **5**.

Treatment of **1** with 1.2 equiv. of nonacarbonyldiiron in thf for 40 h afforded complex **5**. The solvent was then removed in vacuo, and the residue was extracted with toluene. The insoluble solid was filtered off, and the filtrate was concentrated to yield a red-brown solid. Complex **5** was characterized by NMR spectroscopy, EI mass spectrometry and elemental analysis. In the ^{119}Sn NMR spectrum **5** exhibits a sharp resonance (δ = 255 ppm), which indicates the coordination of the Fe to the tin atom resulting in a downfield chemical shift (^{119}Sn of **1**: δ = 29.6 ppm). This downfield chemical shift suggests the removal of electron density from the tin atom upon product formation. A similar kind of downfield chemical shift was observed for the *t*Bu protons of the amidinato ligand, which resonate at δ = 1.41 ppm, when compared to those of **1** (δ = 1.02 ppm). In the EI mass spectrum the molecular ion appears as the most abun-

dant peak with highest relative intensity at *m*/*z* = 553. All these data corroborate the formation of **5**. Here it is worth mentioning that **5** can be an efficient precursor for the synthesis of amidinato-stabilized tin(II) hydroxide as we have shown recently that reaction of $L^1Sn(NMe_2)Fe(CO)_4$ [L^1 = $HC(CMeNAr)_2$; Ar = 2,6-*i*$Pr_2C_6H_3$] with H_2O gave the first example of a monomeric tin(II) hydroxide complex of composition $LSn(OH)Fe(CO)_4$.[29]

Conclusion

We have prepared monomeric tin(II) chloride stabilized by a bulky amidinato ligand. By taking advantage of nucleophilic substitution reactions using AgOTf or $(Me_3Si)_2NLi$, we synthesized a divalent tin(II) monomer with different substituents. These compounds can act as good precursors for catalysis and polymerization reactions. We are currently exploring their chemistry.

Experimental Section

General: All manipulations were performed under dry and oxygen-free N_2 by using standard Schlenk techniques or inside an MBraun MB 150-GI glove box. All solvents were distilled from Na/benzophenone prior to use. Chemicals were purchased commercially and used as received. ^1H, ^{13}C, ^{19}C and ^{119}Sn NMR spectra were recorded with a Bruker Avance DRX 500 MHz instrument and referenced to the deuterated solvent in the case of the ^1H and ^{13}C NMR spectra. ^{19}F and ^{29}Si NMR spectra were referenced to $BF_3{\cdot}Et_2O$ and $SiMe_4$, and those of ^{119}Sn NMR to $SnMe_4$. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. EI mass spectra were measured with a Finnigan Mat 8230 or a Varian MAT CH5 instrument. Melting points were measured in sealed glass tubes with a Buchi melting point B 450 instrument.

Preparation of Compound 1: PhLi (6.86 mL, 13.72 mmol, 1.8 M in diethyl ether) was added to a solution of *t*BuN=C=N*t*Bu (2.12 g, 13.72 mmol) in diethyl ether (80 mL) in a 200 mL Schlenk flask at –78 °C. The solution was warmed to ambient temperature and stirred for 4 h. The solution was added drop by drop to a stirred suspension of $SnCl_2$ (3.18 g, 13.72 mmol) in diethyl ether (20 mL) at –78 °C. The reaction mixture was warmed to room temperature and stirred for 24 h. The precipitate was filtered off, and, after removal of all volatiles in vacuo, the residue was extracted with toluene (20 mL). Storage of the extract at –32 °C in a freezer for 1 d afforded colorless crystals of **1**. M.p. 135–140 °C. $C_{15}H_{23}ClN_2Sn$ (385.52): calcd. C 46.73, H 6.01, N 7.27; found C 46.96, H 6.33, N 7.56. ^1H NMR (200 MHz, [D$_8$]thf, 25 °C): δ = 1.02 (s, 18 H, *t*Bu), 7.41–7.48 (m, 5 H, *Ph*) ppm. $^{13}C\{^1H\}$NMR (125.75 MHz, [D$_8$]thf, 25 °C): δ = 31.8 (C*Me*$_3$), 54.2 (*C*Me$_3$), 128.6, 128.9, 129.1, 129.9, 130.6, 135.6 (*Ph*), 173.3 (N*C*N) ppm. ^{119}Sn NMR (111.92 Hz, [D$_8$]-thf, 25 °C): δ = 29.6 ppm. EI-MS: *m*/*z* (%) = 385.5 (100) [M$^+$].

Preparation of Compound 2: A solution of **1** (0.385 g, 1.0 mmol) in toluene (20 mL) was added to a stirred suspension of $AgSO_3CF_3$ (0.257 g, 1.0 mmol) in toluene (10 mL) at room temperature and was stirred for 4 h. The precipitate was filtered off, and the solvent was partially removed (ca. 15 mL) under reduced pressure. Storage of the remaining solution in a freezer at –32 °C for 2 d afforded colorless crystals of **2** suitable for X-ray diffraction analyses (0.55 g, 80%). M.p. 135–140 °C. $C_{16}H_{23}F_3N_2O_3SSn$ (500.04): calcd. C 38.50, H 4.64, N 5.61; found C 38.96, H 4.75, N 6.01. ^1H NMR (200 MHz, [D$_8$]thf, 25 °C): δ = 1.08 (s, 18 H, *t*Bu), 7.41–7.48 (m, 5 H, *Ph*) ppm. $^{13}C\{^1H\}$NMR (125.75 MHz, [D$_8$]thf, 25 °C): δ = 32.7 (C*Me*$_3$), 53.0 (*C*Me$_3$), 127.3, 127.5, 128.0, 128.4, 128.7, 129.3 (*Ph*), 168.0 (N*C*N) ppm. ^{119}Sn NMR (111.92 Hz, [D$_8$]thf, 25 °C): δ = –33.16 ppm. ^{19}F NMR (188.3 Hz, [D$_8$]thf, 25 °C): δ = –73.6 ppm. EI-MS: *m*/*z* (%) = 500 (100) [M$^+$].

Preparation of Compound 3: Compound **1** and $LiN(SiMe_3)_2$ were placed in a 100 mL Schlenk flask, and diethyl ether (40 mL) was added at room temperature. The reaction mixture was stirred overnight. A precipitate was formed and filtered off. The solvent was partially removed in vacuo. Storage of the remaining solution in a freezer at –30 °C overnight resulted in colorless crystals of **3** suitable for X ray analysis. M.p.120–125 °C. $C_{21}H_{41}N_3Si_2Sn$ (511.19): calcd. C 49.41, H 8.10, N 8.23; found C 48.96, H 8.33, N 7.56. ^1H NMR (200 MHz, [D$_8$]thf, 25 °C): δ = 0:25 (s, 18 H, *TMS*), 1.27 (s, 18 H, *t*Bu), 7.33–7.43 (m, 5 H, *Ph*) ppm. $^{13}C\{^1H\}$NMR (125.75 MHz, [D$_8$]thf, 25 °C): δ = 25.3 (Si*Me*$_3$), 32.9 (C*Me*$_3$), 53.7 (*C*Me$_3$), 128.2, 128.3, 128.6, 129.1, 129.7, 130.1 (*Ph*), 169.3 (N*C*N) ppm. ^{119}Sn NMR (111.92 Hz, [D$_8$]thf, 25 °C): δ = –33.58 ppm. ^{29}Si NMR (59.63 Hz, [D$_8$]thf, 25 °C): δ = 1.49 ppm. EI-MS: *m*/*z* (%) = 511 (100) [M$^+$].

Preparation of Compound 4: A solution of $Li[HB(sBu)_3]$ in thf (2.00 mL, 1 M in thf) was slowly added drop by drop to a stirred solution of **1** (1.050 g, 2 mmol) in toluene (30 mL) at –10 °C. The reaction mixture was warmed to room temperature and then stirred for an additional 1 h. After removal of all the volatiles, the residue was extracted with toluene (30 mL), concentrated to 10 mL, and stored in a freezer at –30 °C. Colorless crystals of **4** were formed after 1 d. M.p. 135–140 °C. $C_{30}H_{46}N_2Sn$ (581.42): calcd. C 65.11, H 8.38, N 5.06; found C 64.96, H 8.33, N 5.56. ^1H NMR (200 MHz, [D$_8$]thf, 25 °C): δ = 1.08 (s, 36 H, *t*Bu), 7.41–7.48 (m, 10 H, *Ph*) ppm. $^{13}C\{^1H\}$NMR (125.75 MHz, [D$_8$]thf, 25 °C): δ = 31.8 (C*Me*$_3$), 54.2 (*C*Me$_3$), 128.6, 128.9, 129.1, 129.9, 130.6, 135.6 (*Ph*), 173.3 (N*C*N) ppm. ^{119}Sn NMR (111.92 Hz, [D$_8$]thf, 25 °C): δ = –285 ppm. EI-MS: *m*/*z* (%) = 581 (100) [M$^+$].

Preparation of Compound 5: thf (30 mL) was added to a mixture of **1** (0.4 g, 1.03 mmol) and nonacarbonyldiiron (0.45 g, 1.23 mmol) at ambient temperature under N_2. After stirring for 40 h, the initially light-orange solution became darker to ultimately afford a garnet-brown solution. The solvent was then removed in vacuo, and the residue was extracted with toluene (30 mL). The insoluble solid was filtered off. The garnet-brown filtrate was concentrated and stored at –30 °C to yield a red-brown solid of **5** (0.52 g, 61%). M.p. 182–189 °C. $C_{19}H_{23}ClFeN_2O_4Sn$ (553.40): calcd. C 41.24, H 4.19, N 5.06; found C 43.51, H 5.33, N 4.85. ^1H NMR (200 MHz, [D$_8$]thf, 25 °C): δ = 1.41 (s, 18 H, *t*Bu), 7.56–7.82 (m, 5 H, Ph) ppm. $^{13}C\{^1H\}$NMR (125.75 MHz, [D$_8$]thf, 25 °C): δ = 31.3 (C*Me*$_3$), 54.9 (*C*Me$_3$), 127.8, 128.2, 128.3, 129.2, 130.0, 130.7 (*Ph*), 171.1 (N*C*N), 220.5 (*C*O) ppm. ^{119}Sn NMR (111.92 Hz, [D$_8$]thf, 25 °C): δ = 255 ppm. EI-MS: *m*/*z* (%) = 553 (100) [M$^+$].

Crystal Structure Determination: The data for structures **1**, **2**, **3**, and **4** were collected with a Bruker three-circle diffractometer equipped with a SMART 6000 CCD detector and a mirror-system-monochromated Cu-K_α source. The data were integrated with SAINT, and a semi-empirical absorption correction with SADABS was applied.[30,31] The structures were solved by direct methods (SHELXS-97)[32] and refined against all data by full-matrix least-

Table 1. Crystallographic data for the X-ray structural analyses of compounds **1**, **2**, **3** and **4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{15}H_{23}ClN_2Sn$	$C_{16}H_{23}F_3N_2O_3SSn$	$C_{21}H_{41}N_3Si_2Sn$	$C_{44}H_{62}N_4Sn$
Formula mass	385.49	499.14	510.44	765.67
T [K]	100(2)	100(2)	100(2)	100(2)
Crystal system	triclinic	monoclinic	triclinic	monoclinic
CCDC no.	780255	780256	780257	780258
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$C2/c$
a [Å]	6.0640(10)	9.737(2)	11.317(2)	10.179(2)
b [Å]	10.309(2)	21.101(3)	17.526(4)	16.519(3)
c [Å]	13.705(2)	10.218(2)	13.602(3)	24.900(4)
α [°]	85.4310(10)	90	90.03(3)	90
β [°]	80.1550(10)	106.09(2)	104.50(3)	98.06(2)
γ [°]	84.060(2)	90	89.98(3)	90
V [Å^3]	837.9(2)	2017.2(6)	2611.9(9)	4145.5(13)
Z	2	4	4	4
$\rho_{calcd.}$ [Mg m^{-3}]	1.528	1.643	1.298	1.226
μ [mm^{-1}]	13.498	11.457	8.725	5.140
F(000)	388	1000	1064	1616
Reflections collected	8315	16964	46091	27483
R(int)	0.0383	0.0404	0.0505	0.0384
Data/restraints/parameters	2337/175/219	3140/0/241	10192/0/513	3516/57/230
GooF	1.129	1.034	1.163	1.057
R_1, $wR_2[I > 2\sigma(I)]$[a]	R_1 = 0.0236, wR_2 = 0.0583	R_1 = 0.0252, wR_2 = 0.0666	R_1 = 0.0476, wR_2 = 0.1259	R_1 = 0.0205, wR_2 = 0.0502
R_1, wR_2 (all data)[b]	R_1 = 0.0237, wR_2 = 0.0583	R_1 = 0.0263, wR_2 = 0.0684	R_1 = 0.0501, wR_2 = 0.1295	R_1 = 0.0211, wR_2 = 0.0504
Largest difference peak/hole [e Å^{-3}]	0.650/–0.693	0.851/–0.620	1.573/–2.389	0.376/–0.252

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$.

squares methods on F^2 (SHELXL-97).[33] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions by using a riding model with their U_{iso} values constrained to 1.5·U_{equ} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. In compound **1** one *t*Bu group was modelled in two conformations [occupancy of the minor component was refined to 0.40(1)]. The disordered group was refined with distance restraints and restraints for the anisotropic displacement parameters. The structure of **3** was refined as a pseudomerohedral twin [twin fraction 0.473(2)] in space group $P\bar{1}$ with two molecules in the asymmetric unit. Also a refinement in space group $P2_1/c$ with a disordered model was possible, but showed the following features: systematic absence violations, high residual density peak of 0.75 e Å^{-3}, higher $R1$ and $wR2$ values, higher standard uncertainties for bond lengths and angles, strange proposed weighting scheme high K (mean F_o^2/F_c^2) for the reflections with the lowest intensities. Compound **4** crystallizes as a nonmerohedral twin [twin fraction 0.0252(9)] in the monoclinic space group $C2/c$. The twin law is a twofold rotation about the real axis 001. Crystallographic data for the X-ray structural analyses of compounds **1**, **2**, **3**, and **4** are given in Table 1. CCDC-780255 (for **1**), -780256 (for **2**), -780257 (for **3**) and -780258 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

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