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Facile Access of Stable Divalent Tin Compounds with Terminal Methyl, Amide, Fluoride, and Iodide Substituents

Anukul Jana, Herbert W. Roesky,* Carola Schulzke, Alexander Döring, Tobias Beck, Aritra Pal, and Regine Herbst-Irmer

Institut für Anorganische Chemie, Universität Göttingen, Tammannstrasse 4, 37077 Göttingen, Germany

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The stable β-diketiminate tin(II) complexes LSnX [L = HC(CMeNAr)$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$] with terminal methyl, amide, fluoride, and iodide (X = Me, N(SiMe$_3$)$_2$, F, I) are described. LSnMe (**2**) is synthesized by salt metathesis reaction of LSnCl (**1**) with MeLi and can be isolated in the form of yellow crystals in 88% yield. Compound LSnN(SiMe$_3$)$_2$ (**3**) was obtained by treatment of LH with 2 equiv of KN(SiMe$_3$)$_2$ in THF followed by adding 1 equiv of SnCl$_2$. Reaction of **2** and **3** respectively with Me$_3$SnF in toluene provided the tin(II)fluoride LSnF (**4**) with a terminal fluorine as colorless crystals in 85% yield. **4** is highly soluble in common organic solvents. The reaction of LLi(OEt$_2$) with 1 equiv of SnI$_2$ in diethyl ether afforded the LSnI (**5**). Compounds **2**, **3**, **4**, and **5** were characterized by microanalysis, multinuclear NMR spectroscopy, and X-ray structural analysis. Single crystal X-ray structural analyses indicate that all the compounds (**2**, **3**, **4**, **5**) are monomeric and the tin center resides in a trigonal-pyramidal environment.

Introduction

There has been considerable interest over the past three decades in the chemistry of dialkyl and diaryl Sn(II) compounds.[1−5] But remarkably little is known about the chemistry of simpler heteroleptic derivatives such as L′Sn(II)R (L′ = chelating ligand or bulky aryl ligand, and R a small substituent). Recently our group reported the synthesis and structure of LSn(II)H [L = HC(CMeNAr)$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$].[6] Now we are interested in the synthesis of heteroleptic Sn(II) derivatives containing a Me, F, and I substituent, respectively. The methyl derivative LSn(II)Me (**2**) is synthesized by the nucleophilic substitution reaction of LSn(II)Cl with MeLi. Power and Eichler reported on the reaction of 2,6-Trip$_2$H$_3$C$_6$Sn(II)Cl (Trip = C$_6$H$_2$-2,4,6-iPr$_3$) with MeLi. They obtained 2,6-Trip$_2$H$_3$C$_6$Sn(II)−Sn(IV)(Me)$_2$-C$_6$H$_3$-2,6-Trip$_2$ instead of 2,6-Trip$_2$H$_3$C$_6$Sn(II)Me.[7] Moreover it is mentioned that the dimethylstannylene (SnMe$_2$) is a transient species at room temperature, which is generated in situ under special experimental conditions from a variety of substrates, and some aspects of its chemistry in solution and gas phase have been reported.[8−10] The organometallic fluorides of the heavier group 14 elements are important because of their industrial applications, synthetic methodology, and theoretical implications.[11−13] To the best of our knowledge there are only two organotin(II)fluorides known in literature[14] although there are reports on a number of organotin(IV)fluorides.[15] Herein we report on the preparation

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* To whom correspondence should be addressed. E-mail: hroesky@gwdg.de. Fax: +49-551-393373.

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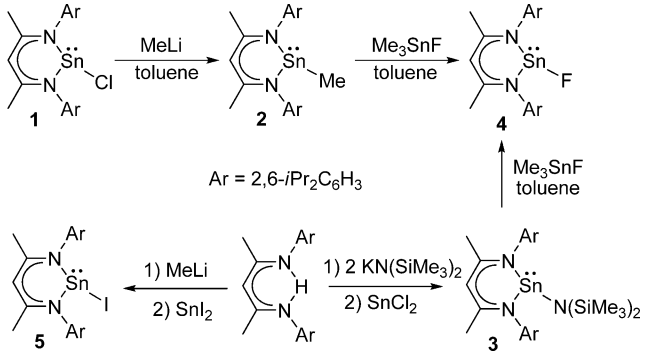
10.1021/ic8015639 CCC: $40.75

Scheme 1



and characterization of the monomeric LSn(II)Me (**2**), LSn(II)N(SiMe$_3$)$_2$ (**3**), LSn(II)F (**4**), and LSn(II)I (**5**).

Results and Discussion

Generally organotin(IV) fluorides are prepared by the substitution of chloride with KF in the presence of a phase transfer catalyst. Therefore the known compound [HC(CMeNAr)$_2$SnCl] (Ar = 2,6-iPr$_2$C$_6$H$_3$) (**1**) was used as a precursor.[16] Compound **1** is soluble in common organic solvents. A complete reaction of **1** with Me$_3$SnF in toluene even after refluxing for several days was not observed. Consequently we changed the method for the preparation of compound **4**. It is well-known that Me$_4$Sn and Cl$_4$Sn depending on the molecular ratio and temperature show metathesis and give in high yield Me$_3$SnCl, Me$_2$SnCl$_2$, and MeSnCl$_3$ respectively.[17] The question was whether it is possible to apply this type of reaction to Me-Sn(II) and F−Sn(IV) species. It was therefore reasonable to prepare LSn(II)Me (**2**) from LSn(II)Cl with MeLi. Furthermore we prepared LSn(II)N(SiMe$_3$)$_2$ and studied the reaction with Me$_3$SnF.

Treatment of **1** with MeLi in diethyl ether at −78 °C then allowed the solution to reach ambient temperature and, kept for 3 h at this temperature, afforded the corresponding methyl derivative [HC(CMeNAr)$_2$SnMe] (Ar = 2,6-iPr$_2$C$_6$H$_3$) (**2**) in high yield (88%) (Scheme 1). Yellow crystals of **2** suitable for single crystal X-ray analysis were obtained from a n-hexane solution at −30 °C after 2 days. Compound **2** is thermally stable. No decomposition was observed at temperatures below its melting point (170 °C) under an inert atmosphere. EI-MS of **2** gave the corresponding monomeric molecular ion peak M$^+$. The ^{1}H NMR spectrum of **2** consists of a triplet resonance (0.59 ppm) for Sn−CH_3 with the coupling constant 33.07 Hz. Also the ^{119}Sn NMR spectrum exhibits a singlet resonance (δ = 192.65 ppm), which is very much different from the parent compound [HC(CMeNAr)$_2$SnCl] (Ar = 2,6-iPr$_2$C$_6$H$_3$) (**1**), where the tin shows a resonance at δ = −224 ppm. This change was expected because of the different electronic nature of the substituents on the tin atoms. The other resonances of the ^{1}H NMR spectrum and elemental analyses are in accordance with **2** as formulated.

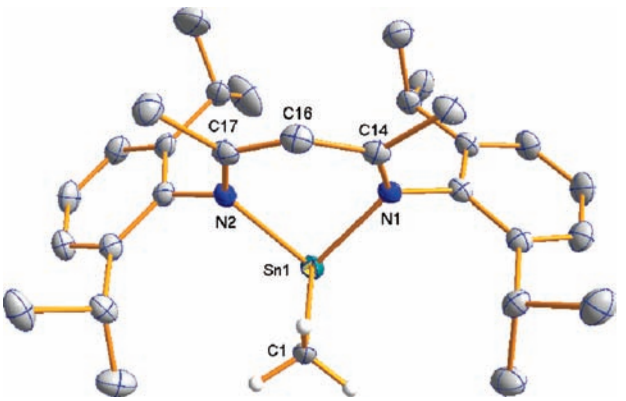


Figure 1. Molecular structure of **2**. Selected bond lengths [Å] and angles [deg]; anisotropic displacement parameters are depicted at the 50% probability level, and all restrained refined hydrogen atoms are omitted for clarity except Sn−Me hydrogens: Sn1−C1 2.253(2), Sn1−N1 2.2091(18), N1−C14 1.331(3); N1−Sn1−C1 92.95(8), N2−Sn1−C1 92.69(9), N1−Sn1−N2 84.69(7).

The yellow compound **2** was also characterized by single crystal X-ray structural analysis. The molecular structure is depicted in Figure 1 and reveals the monomeric feature in the solid state. The Sn−N and Sn−C bond lengths are comparable to those found in literature.[16]

The well-defined compound LSn(II)N(SiMe$_3$)$_2$ (**3**) was obtained in high yield from the reaction of LH with 2 equiv of KN(SiMe$_3$)$_2$ followed by the reaction with 1 equiv of SnCl$_2$ at room temperature in tetrahydrofuran (THF, Scheme 1).

Compound **3** is a yellow solid soluble in benzene, THF, n-hexane, and n-pentane and shows no decomposition on exposure to air for a short period of time. **3** was characterized by ^{1}H, ^{13}C, ^{29}Si, and ^{119}Sn NMR spectroscopy, EI mass spectrometry, elemental, and X-ray structural analysis. The ^{1}H NMR spectrum of compound **3** shows a singlet at 5.01 ppm for the γ-CH proton, two septets (3.73 and 3.16 ppm) corresponding to the CH protons of the iPr moieties, and singlets at 0.46 and 0.24 ppm for the two nonequivalent SiMe$_3$ groups. The ^{119}Sn NMR **3** of exhibits a singlet at 134.54 ppm. The most abundant ion peak in the EI mass spectrum appeared at m/z 537.

Maintaining a n-hexane solution of **3** for 1 day at 0 °C resulted in slightly yellow single crystals suitable for X-ray structural analysis. Compound **3** crystallizes in the orthorhombic space group P_{nma}, with half a molecule in the asymmetric unit. The coordination environment of the central Sn atom exhibits a distorted tetrahedral geometry (see Supporting Information). The LSn(II)NMe$_2$ compound has already been reported, and the ^{119}Sn NMR exhibits a singlet at −172.44 ppm.[18]

Treatment of **2** with Me$_3$SnF in toluene at room temperature, after refluxing the suspension for 3 h afforded the corresponding fluoride HC(CMeNAr)$_2$SnF (Ar = 2,6-

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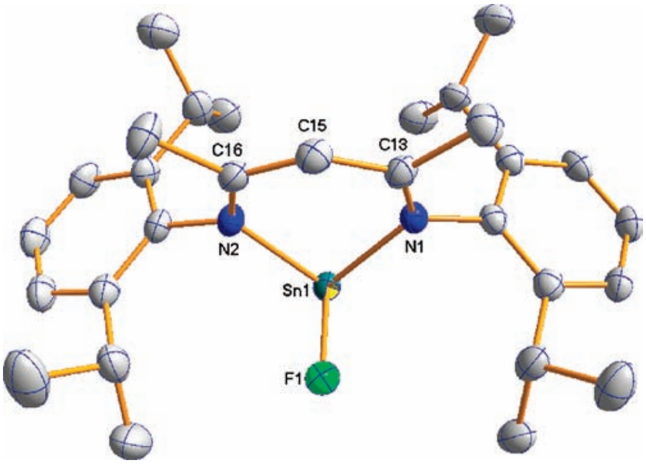

Figure 2. Molecular structure of **4**. Selected bond lengths [Å] and angles [deg]; anisotropic displacement parameters are depicted at the 50% probability level, and all restrained refined hydrogen atoms are omitted for clarity: Sn1−F1 1.988(2), Sn1−N1 2.178(3), N1−C13 1.333(4); N1−Sn1−F1 90.26(9), N2−Sn1−F1 90.20(9), N1−Sn1−N2 86.22(10).

i$Pr_2C_6H_3$) (**4**) in high yield (85%, Scheme 1). Compound **4** is thermally stable. No decomposition was observed at temperatures below the corresponding melting point (130 °C) under an inert atmosphere. Compound **4** is also obtained by treating **3** with Me_3SnF under the same conditions (Scheme 1).

Compound **4** is a white solid that is soluble in benzene, toluene, *n*-hexane, and THF, in contrast to the fluorinating agent Me_3SnF, which is only slightly soluble in these solvents. **4** was characterized by ^1H, ^{13}C, ^{19}F, ^{119}Sn NMR spectroscopy, EI mass spectrometry, elemental analysis, and X-ray structural analysis. The ^1H NMR spectrum of compound **3** shows a singlet (δ = 4.99 ppm) for the γ-CH protons and two septets (δ = 3.84 and 3.09 ppm) corresponding to the two different types of C*H* protons of the *i*Pr moieties. Also, the complete disappearance of the resonance arising from Sn−CH_3 (δ = 0.59 ppm) in **2** and the resonance arising from Sn−N(Si(CH_3)$_3$)$_2$ (δ = 0.46 and 0.24 ppm) in **3** clearly indicates the formation of compound **4**. The ^{19}F NMR spectrum of **4** shows a singlet at −125.29 ppm. Also the ^{119}Sn NMR spectrum exhibits a doublet resonance (δ = −371.52 ppm). This value is very much different from the precursor **2** (δ = 192.65 ppm), but this was expected when compared with that of compound **1** (δ = 224 ppm). The Sn−F coupling constant of $J(^{119}Sn-^{19}F) = 3100$ Hz is quite large when compared with the previously reported Sn−F coupling constant.[14] EI-MS of **4** gave the corresponding monomeric molecular ion peak M^+.

The molecular structure of **4** has been determined by single crystal X-ray diffraction analysis (Figure 2) which demonstrates that the complex exists as a monomer. Colorless crystals of **4** suitable for single crystal X-ray analysis were obtained from a *n*-hexane solution at −30 °C after 1 day. Compound **4** crystallizes in the monoclinic space group $P2_1/c$, with one monomer in the asymmetric unit. The coordination polyhedron around the tin atom features a distorted tetrahedral geometry with one lone pair. The sum of angles around the tin atom is 266.68°. The terminal Sn−F bond distance (1.988 Å) in **4** is quite short when compared with that of the bridging one of Sn−F−Sn (2.156 Å).[14] The Sn−N bond lengths in **2** and **4** are similar.

The reaction of the β-diketiminato lithium salt LLi(OEt_2) with SnI_2 in diethyl ether provided the monomeric complex LSn(II)I (**5**), (Scheme 1). Maintaing a diethyl ether solution of **5** for 1 day at −32 °C resulted in colorless crystals suitable for X-ray structural analysis. Compound **5** crystallizes in the triclinic space group $P\bar{1}$, with one monomer in the asymmetric unit. The coordination environment of the central Sn atom exhibits a distorted tetrahedral geometry. (See Supporting Information). In the ^{119}Sn NMR spectrum the resonance arises at δ = −107.33 ppm, which is very different from that of the terphenyl iodide 2,6-$Trip_2C_6H_3$Sn(II)I (δ = 1140 ppm).[19] The different chemical shifts might be due to the different coordination environment around both the Sn(II) atoms.

Summary and Conclusion

In this contribution we report the syntheses and characterization of four novel well-defined monomeric tin(II) compounds supported by the bulky β-diketiminate ligand. The synthetic strategy takes advantage of the recently synthesized stable HC(CMeNAr)$_2$SnCl (Ar = 2,6-*i*$Pr_2C_6H_3$) (**1**) precursor. By using the concept of nucleophilic displacement reaction with MeLi and Me_3SnF respectively afforded the monomeric organotin(II) fluoride compound in high yield which is highly soluble in common organic solvents. The latter is the first example of a divalent monomeric organotin fluoride compound.

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.[16] Other chemicals were purchased commercially and used as received. ^1H, ^{13}C, ^{19}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 ^1H and ^{13}C NMR spectra. ^{19}F and ^{29}Si NMR spectra were referenced to $BF_3 \cdot Et_2O$ and TMS, 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-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 HC(CMeNAr)$_2$Sn(II)Me (Ar = 2,6-*i*$Pr_2C_6H_3$) (2). A solution of MeLi in diethyl ether (0.63 mL, 1.6 M) was added drop by drop to a stirred solution of **1** (0.570 g, 1 mmol) in diethyl ether (25 mL) at −78 °C. The reaction mixture was warmed to room temperature and was stirred for an additional 3 h. After removal of all the volatiles, the residue was extracted with *n*-hexane (20 mL), and the remaining solution concentrated to about 10 mL

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Table 1. Crystallographic Data for the Structural Analyses of Compounds **2** and **4**

	2	**4**
empirical formula	$C_{30}H_{44}N_2Sn$	$C_{29}H_{41}FN_2Sn$
CCDC No.	697820	697821
T [K]	133(2)	133(2)
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a [Å]	8.6420(17)	9.0047(18)
b [Å]	11.638(2)	9.6328(19)
c [Å]	14.986(3)	32.308(6)
α [deg]	98.08(3)	90
β [deg]	98.62(3)	89.92(3)
γ [deg]	105.76(3)	90
V [Å^3]	1407.9(5)	2802.4(9)
Z	2	4
D_{calcd} [g cm^{-3}]	1.301	1.316
μ [mm^{-1}]	0.926	0.936
F(000)	576	1152
θ range [deg]	1.85−27.14	1.26−25.63
reflections collected	13371	20990
independent reflections	6051	5251
data/restraints/parameters	6051/0/312	5251/0/311
$R1$, $wR2$ [$I > 2\sigma(I)$]^a	0.0295, 0.0606	0.0350, 0.0827
$R1$, $wR2$ (all data)^a	0.0412, 0.0636	0.0506, 0.0874
GoF	0.998	0.960
$\Delta\rho$(max), $\Delta\rho$(min) [e Å^{-3}]	0.628, −0.705	0.640, −1.230

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2)^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds **2** and **4**

	Compound **2**		
Sn(1)−N(1)	2.2091(18)	C(14)−C(16)	1.404(4)
Sn(1)−N(2)	2.218(2)	C(16)−C(17)	1.407(3)
Sn(1)−C(1)	2.253(2)	C(14)−C(15)	1.517(3)
N(1)−C(14)	1.331(3)	C(17)−C(18)	1.511(3)
N(2)−C(17)	1.4338(3)		
N(1)−Sn(1)−N(2)	84.69(7)	Sn(1)−N(1)−C(14)	122.26(16)
N(1)−Sn(1)−C(1)	92.95(8)	Sn(1)−N(2)−C(17)	123.21(16)
N(2)−Sn(1)−C(1)	92.69(9)		
	Compound **4**		
Sn(1)−F(1)	1.988(2)	C(13)−C(15)	1.399(5)
Sn(1)−N(1)	2.178(3)	C(15)−C(16)	1.391(5)
Sn(1)−N(2)	2.178(3)	C(13)−C(14)	1.506(5)
N(1)−C(13)	1.333(4)	C(16)−C(17)	1.514(4)
N(2)−C(16)	1.335(4)		
F(1)−Sn(1)−N(1)	90.20(9)	Sn(1)−N(1)−C(13)	119.6(3)
F(1)−Sn(1)−N(2)	90.26(9)	Sn(1)−N(2)−C(16)	124.7(2)
N(1)−Sn(1)−N(2)	86.22(10)		

and stored in a −30 °C freezer. Yellow crystals of **2** suitable for X-ray diffraction analysis are formed after 2 days. Yield: 0.485 g (88%); mp 170 °C. ^{1}H NMR (500 MHz, C_6D_6): δ = 7.10−7.15 (m, 6H, Ar-*H*), 4.86 (s, 1H, γ-C*H*), 3.59 (sept, 2H, C*H*(CH_3)$_2$), 3.37 (sept, 2H, C*H*(CH_3)$_2$), 1.60 (s, 6H, C*H*$_3$), 1.35 (d, 6H, CH(C*H*$_3$)$_2$), 1.22 (d, 6H, CH(C*H*$_3$)$_2$), 1.19 (d, 12H, CH(C*H*$_3$)$_2$), 0.59 (t, 3H, Sn−C*H*$_3$) ppm. ^{13}C {^{1}H} NMR (125.75 MHz, C_6D_6): δ = 165.81 (*C*N), 144.90, 143.28, 126.69, 124.45 (Ar-*C*), 97.94 (γ-C), 29.02 (*C*HMe$_2$), 27.68 (CH*Me*$_2$), 24.89 (CH*Me*$_2$), 23.95 (*Me*), 16.24 (Sn-*C*H$_3$) ppm; ^{119}Sn {^{1}H} NMR (186.50 MHz, C_6D_6): δ = 192.65 ppm. EI-MS: *m*/*z* (%) 537 (100) [M$^+$ − Me]. Anal. Calcd for $C_{30}H_{44}N_2Sn$ (552.25): C, 65.35; H, 8.04; N, 5.08. Found C, 64.96; H, 8.64; N, 5.09.

Synthesis of [HC(CMeNAr)$_2$Sn(II)N(SiMe$_3$)$_2$] (Ar = 2,6-*i*Pr$_2$-C$_6$H$_3$) (3). A solution of LH (0.418 g, 1 mmol) in THF (15 mL) was added drop by drop to a stirred suspension of KN(SiMe$_3$)$_2$ (0.400 g, 2 mmol) in THF (10 mL) at room temperature, and stirring was continued overnight. The resulting solution was added drop by drop to a stirred suspension of SnCl$_2$ (0.190 g, 1 mmol) in THF (20 mL) at room temperature under stirring for another 24 h. After removal of all the volatiles, the residue was extracted with *n*-hexane (30 mL), concentrated to about 5 mL, and finally stored in a 0 °C freezer. Yellow crystals of LSnN(SiMe$_3$)$_2$ suitable for X-ray diffraction analysis are formed after 1 day. Yield (0.570 g, 82%), mp 202 °C. ^{1}H NMR (300 MHz, C_6D_6): δ = 6.98−7.21 (m, 6H, Ar-*H*), 5.01 (s, 1H, γ-C*H*), 3.73 (sept, 2H, C*H*(CH_3)$_2$), 3.16 (sept, 2H, C*H*(CH_3)$_2$), 1.52 (s, 6H, C*H*$_3$), 1.45 (d, 6H, CH(C*H*$_3$)$_2$), 1.22 (q, 12H, CH(C*H*$_3$)$_2$), 1.13 (d, 6H, CH(C*H*$_3$)$_2$), 0.46 (s, 9H, Si(C*H*$_3$)$_3$), 0.24 (s, 9H, Si(C*H*$_3$)$_3$) ppm; ^{13}C {^{1}H} NMR (75.47 Hz, C_6D_6): δ = 167.25 (*C*N), 145.38, 144.00, 128.09, 124.72 (Ar-*C*), 102.23 (γ-C), 28.77 (*C*HMe$_2$), 26.55 (CH*Me*$_2$), 25.80 (CH*Me*$_2$), 23.40 (*Me*), 7.98 (Si*Me*$_3$), 6.55 (Si*Me*$_3$) ppm; ^{29}Si{^{1}H} NMR (99.36 Hz, C_6D_6): δ = 0.61 (*Si*Me$_3$), −4.70 (*Si*Me$_3$) ppm; ^{119}Sn {^{1}H} NMR (112.00 Hz, C_6D_6): δ = −134.54 ppm. EI-MS (70 eV): *m*/*z* (%): 682 (100) [M − Me]$^+$. Anal. Calcd for $C_{35}H_{59}N_3SnSi_2$(697): C, 60.33; H, 8.54; N, 6.03. Found C, 60.20; H, 8.49; N, 5.88.

Synthesis of HC(CMeNAr)$_2$Sn(II)F (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (4). Method A: A solution of **2** (0.550 g, 1 mmol) in toluene (20 mL) was added to a stirred suspension of Me$_3$SnF (0.200 g, 1.1 mmol) in toluene (10 mL), and the reaction mixture was refluxed for 3 h. After removal of all the volatiles the residue was extracted with *n*-hexane (30 mL), and the resulting solution was concentrated to about 10 mL and stored in a −30 °C freezer. Colorless crystals of **4** suitable for X-ray diffraction analysis are formed after 1 day. Yield: 0.470 g (85%).

Method B: A solution of **3** (0.700 g, 1 mmol) in toluene (20 mL) was added to a stirred suspension of Me$_3$SnF (0.200 g, 1.1 mmol) in toluene (10 mL), and the reaction mixture was refluxed for 3 h. After removal of all the volatiles the residue was extracted with *n*-hexane (30 mL), and the resulting solution was concentrated to about 10 mL and stored in a −30 °C freezer. Colorless crystals of **4** suitable for X-ray diffraction analysis are formed after 1 day. Yield: 0.390 g (70%); mp 130 °C. ^{1}H NMR (500 MHz, C_6D_6): δ = 7.04−7.17 (m, 6H, Ar-*H*), 4.99 (s, 1H, γ-C*H*), 3.84 (sept, 2H, C*H*(CH_3)$_2$), 3.09 (sept, 2H, C*H*(CH_3)$_2$), 1.63 (s, 6H, C*H*$_3$), 1.41 (d, 6H, CH(C*H*$_3$)$_2$), 1.18 (q, 12H, CH(C*H*$_3$)$_2$), 1.09 (d, 6H, CH(C*H*$_3$)$_2$), ppm. ^{13}C {^{1}H} NMR (125.75 MHz, C_6D_6): δ = 165.14 (*C*N), 145.71, 142.75, 141.55, 127.42, 125.18, 123.91 (Ar-*C*), 98.75 (γ-*C*), 28.85 (*C*HMe$_2$), 27.70 (CH*Me*$_2$), 26.70 (CH*Me*$_2$), 24.99 (*Me*), ppm; ^{19}F {^{1}H} NMR (188.31 MHz, C_6D_6): δ = −125.29 ppm ($J\,^{19}$F-^{119}Sn = 3100 Hz); ^{119}Sn {^{1}H} NMR (186.50 MHz, C_6D_6): δ = −371.52 ppm. EI-MS: *m*/*z* (%) 521 (100) [M$^+$ − F. Me]. Anal. Calcd for $C_{29}H_{41}FN_2Sn$ (556.23): C, 62.72; H, 7.44; N, 5.04. Found C, 62.38; H, 8.67; N, 5.00.

Synthesis of {HC(CMeNAr)$_2$}Sn(II)I (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (5). A solution of LLi(OEt$_2$) (0.498 g, 1 mmol) in diethyl ether (20 mL) was added drop by drop to a stirred suspension of SnI$_2$ (0.375 g, 1 mmol) in diethyl ether (10 mL) at −78 °C. The reaction mixture was warmed to room temperature, and stirring was continued for another 12 h. The precipitate was filtered, and the solvent was partially reduced (ca. 20 mL). Storage of the remaining solution in a −32 °C freezer overnight afforded colorless crystals of **5** suitable for X-ray diffraction analyses. Yield (0.510 g, 77%); mp 197 °C. ^{1}H NMR (300 MHz, C_6D_6): δ = 7.01−7.15 (m, 6H, Ar-*H*), 5.20 (s, 1H, γ-C*H*), 4.05 (sept, 2H, C*H*(CH_3)$_2$), 3.09 (sept, 2H, C*H*(CH_3)$_2$), 1.59 (s, 6H, C*H*$_3$), 1.42 (d, 6H, CH(C*H*$_3$)$_2$), 1.17 (q, 12H, CH(C*H*$_3$)$_2$), 1.06 (d, 6H, CH(C*H*$_3$)$_2$) ppm; ^{13}C {^{1}H} NMR (75.47 Hz, C_6D_6): δ = 167.11 (*C*N), 146.46, 143.23, 141.40, 125.74, 124.07(Ar-*C*), 102.79 (γ-*C*), 29.39 (*C*HMe$_2$), 29.25 (CH*Me*$_2$), 28.15 (CH*Me*$_2$), 24.71 (CH*Me*$_2$), 23.90 (*Me*) ppm; ^{119}Sn {^{1}H} NMR (112.00 Hz, C_6D_6): δ = −107.33 ppm. EI-MS (70 eV): *m*/*z* (%):

663 (100) $[M]^+$. Anal. Calcd for $C_{29}H_{41}IN_2Sn$(664): C, 52.51; H, 6.23; N, 4.22. Found C, 51.55; H, 5.78; N, 4.06.

Crystallographic Details for Compounds 2 and 4. Suitable crystals of **2** and **4** were mounted on a glass fiber and data was collected on an IPDS II Stoe image-plate diffractometer (graphite monochromated Mo Kα radiation, $\lambda = 0.71073$ Å) at 133(2) K. The data was integrated with X-Area. The structures were solved by Direct Methods (SHELXS-97)[20] and refined by full-matrix least-squares methods against F^2 (SHELXL-97).[20] All non-hydrogen atoms were refined with anisotropic displacement parameters. One of the eight isopropyl groups in both **2** and **4** was found to be disordered. The hydrogen atoms were refined isotropically on calculated positions using a riding model. Crystallographic data are presented in Table 1, and selected bond distances and angles in Table 2.

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Supporting Information Available: X-ray data for **2**, **3**, **4**, and **5** (CIF) and tables of crystallographic and structural refinement data of **3** and **5** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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