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Hydrostannylation of Ketones and Alkynes with LSnH [L = HC(CMeNAr)$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$]

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The reactions of the stable β-diketiminate tin(II) hydride LSnH [L = HC(CMeNAr)$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$] with different ketones (Ph$_2$CO, 2-Py$_2$CO, *cy*Pr$_2$CO, and 2-C$_4$H$_3$SCOCF$_3$) generated a variety of tin(II) alkoxides (**1**−**4**) in high yield. The activated terminal alkynes (HC≡CCO$_2$R, R = Me, Et) react with LSnH to yield the tin(II) substituted terminal alkenes (**5**−**6**) instead of dihydrogen elimination although the Sn−H and C−H bonds are differently polarized. Furthermore, LSnH reacts with disubstituted alkyne (RO$_2$CC≡CCO$_2$R, R = Et, *t*Bu) in toluene at room temperature to form the stannylene substituted internal alkenes (**7**−**8**). Compounds **1**−**8** were characterized by microanalysis and multinuclear NMR spectroscopy. Moreover compounds **3**, **4**, **5**, and **7** were characterized by X-ray crystallography, and the resulting structures confirmed the monomeric nature, in which the tin centers reside in a trigonal-pyramidal environment.

Introduction

Metal hydrides and their complexes are considered valuable synthons in chemistry. It was demonstrated that main group and transition metal hydrides are important intermediates in industrial processes and also function as catalysts.[1] In recent years the chemistry of stable heteroleptic metal hydrides has attracted much attention because of their versatile reactivity.[2] In comparison with main group hydrides the chemistry of transition metal hydrides is well documented.[3] Organometallic hydrides of group 14 play an important role in various metathesis reactions, and therefore the reactivity of hydrides like R$_3$SiH, R$_3$GeH, and R$_3$SnH is well studied.[4] In recent years the parent SnH$_2$ has been prepared and characterized in an argon matrix.[5] At elevated temperature SnH$_2$ changed to an insoluble solid of unknown structure. The terphenyl and β-diketiminate ligands have been used for the preparation of substituted tin(II) hydrides. The terphenyl derivatives show dimeric structures in the solid state,[6] while the β-diketiminate moiety exhibits a terminal tin(II) hydride with very weak intermolecular interaction.[7] Until recently the reactions of organotin hydrides were based mainly on tin(IV) precursors. Di- and triorganotin hydrides of composition R$_2$SnH$_2$ and R$_3$SnH with formal oxidation state of Sn(IV) show a rich variety of chemical transformations.[8] The preferred reagent of this class of compounds is the

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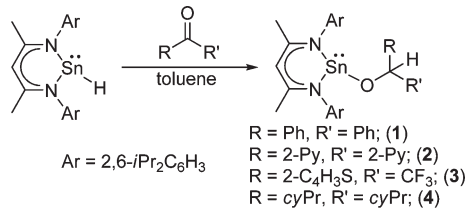
Scheme 1. Preparation of Compounds **1**, **2**, **3**, and **4**



tributyltin hydride, and it is widely used as a reducing agent in organic and inorganic chemistry.[9] In a preliminary publication we have shown some reactions of tin(II) hydride with unsaturated molecules.[10] There we describe the reaction of LSnH [L = $HC(CMeNAr)_2$, Ar = 2,6-$iPr_2C_6H_3$] with carbon dioxide, 2-benzoyl pyridine, 2,2,2-trifluoro acetophenone, ferrocene carbaldehyde, $MeC{\equiv}CO_2Et$, $MeO_2CC{\equiv}CCO_2Me$, and dicyclohexyl carbodiimide. LSnH reacts with alkynes under the formation of vinylated stannylenes. So far we used no terminal alkynes, which might either eliminate dihydrogen or undergo nucleophilic addition reaction to the triple bond. Herein, we describe the hydrostannylation reactions of a variety of ketones and alkynes with LSnH, although Albertin et al. reported on the reactivity of tin(IV) trihydride with terminal alkynes and carbon dioxide.[11]

Results and Discussion

LSnH was synthesized from the corresponding tin(II) chloride, LSnCl[12] with potassium triisobutylborohydride ($K[HB(iBu)_3]$) in toluene at −10 °C. The ^{1}H NMR spectrum of LSnH shows a low field singlet (δ 13.96 ppm) corresponding to the proton of the Sn-bound hydrogen. The ketone group and its transformation to other functional groups is very important in organic chemistry.[13] In the literature there are numerous reports on hydrostannation reaction of ketones using tin(IV) hydride.[14]

Treatment of LSnH with benzophenone, di(2-pyridyl)ketone, 2,2,2-trifluoroacetothiophene, and dicyclopropylketone leads quantitatively to the stannylene alkoxides **1**, **2**, **3**, and **4**, respectively, with a Sn(II)−O-C framework that is formed by nucleophilic hydride addition to the respective carbon of the carbonyl group (Scheme 1). Compounds **1**−**4** were monitored by their ^{1}H NMR spectra. Sharp resonances in the ^{1}H NMR of **1**−**4** gave the initial indication that the products have been formed in high yield.

The ^{1}H NMR spectra of **1** and **2** exhibit each an upfield shifted singlet (δ 6.28, 6.59 ppm) for the quaternary *CH* proton, when compared with that of LSnOC(O)*H*, (δ 8.97 ppm).[10] For the ^{1}H NMR spectra of LSnOC(O)*H*, (δ 8.97 ppm)[10] and LSnOC*H*Ph(2-Py) (δ 6.28 ppm)[10] we compared the *CH* resonances with that of LSn*H* (δ 13.96 ppm). This indicates the conversion of the tin(II)-hydride to the corresponding tin(II)-alkoxide. The ^{119}Sn NMR exhibits resonances at −256 ppm and −324 ppm for compounds **1** and **2**. The two values are different because of the non identical electronic nature of the phenyl rings when compared with those of the 2-pyridyl rings. In the EI mass spectra the molecular ion peaks were observed at m/z 719 and 722 as the base peaks for **1** and **2**.

Compound **3** has one CF_3 group and displays an interesting NMR spectrum. The ^{1}H NMR spectrum of **3** exhibits a quartet (δ 5.45 ppm) which corresponds to the quaternary C*H* proton and its coupling with the three F-atoms of the CF_3 group ($^3J(^{19}F-^1H)$ = 7 Hz). The ^{19}F NMR resonance arises as a doublet (δ −77.39 ppm) with the same coupling constant of 6.99 Hz and is flanked by Sn satellite lines ($^4J(^{119}Sn-^1H)$ = 42 Hz). The four isopropyl groups of **3** show four different resonances, and even the two methyl groups in the backbone exhibit two different signals in the ^{1}H NMR spectrum.

At room temperature there is no reaction observable when LSnH is treated with dicyclopropylketone in toluene. However, after refluxing this mixture for 12 h compound **4** is formed in high yield. Compound **4** is composed of two cyclopropyl rings, and to our surprise they were not decomposed during the reaction. The ^{1}H NMR spectrum of **4** exhibits a triplet (δ 2.47 ppm), which can be assigned to the quaternary C*H* proton which is coupled by two C−H protons from the two cyclopropyl rings with a coupling constant of 7.3 Hz. In the ^{1}H NMR spectrum of compound **4** the quaternary proton resonance arises upfield (δ 2.47 ppm), when compared with the corresponding proton signal in compounds **1**−**3** (δ 6.28, 6.59, 5.45 ppm). This is mainly due to the different electronic nature of the two cyclopropyl rings in compound **4**. The other protons of the cyclopropyl rings show the expected resonances. The two quaternary C*H* protons of the two cyclopropyl rings exhibit a multiplet each at 0.75 ppm. The four CH_2 groups of the two cyclopropyl rings are not identical, they show four multiplets (δ 0.21, 0.02, −0.07, −0.25 ppm). Each multiplet is not consistent with each methylene group. It has been found that each multiplet corresponds to one proton from each of the two cyclopropyl rings.

Single crystals of **3** and **4** suitable for X-ray structural analysis were obtained from *n*-hexane solutions. Both **3** and **4** crystallize in the triclinic space group $P\bar{1}$ (Table 1). The molecular structures of **3** and **4** are shown in Figures 1 and 2. The asymmetric unit of **3** and **4** contains one formula unit of the compound, and two of the molecules in each unit cell. As predicted on the basis of the ^{1}H NMR spectrum and the EI mass spectrum, compounds **3** and **4** contain a Sn(II)−O−CH core. The three coordinate tin atom is surrounded by two N atoms of the β-diketiminato ligand, and an exocyclic O atom. The Sn−O bond lengths (2.046 Å and 2.024 Å) are comparable with those of compound $[LAl(Me)O]_2Sn$ (1.9597 Å).[15] The O−C bond distances of **3** and **4** are in a narrow range of each other (1.418 Å and 1.431 Å). Furthermore compounds **1**−**4** were characterized by elemental analysis, except

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Table 1. Crystallographic Data for the Structural Analyses of Compounds **3**, **4**, **5**, and **7**

	3	**4**	**5**	**7**
empirical formula	$C_{35}H_{45}F_3N_2OSSn$	$C_{36}H_{52}N_2OSn$	$C_{33}H_{46}N_2O_2Sn$	$C_{37}H_{52}N_2O_4Sn$
CCDC-No.	730402	730399	730401	730400
T [K]	133(2)	133(2)	133(2)	133(2)
crystal system	triclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P21/c$
a [Å]	8.8197(18)	9.0024(18)	11.067(2)	14.806(3)
b [Å]	12.061(2)	12.105(2)	12.259(3)	12.705(3)
c [Å]	16.556(3)	16.135(3)	13.922(3)	19.471(4)
α [deg]	81.07(3)	76.66(3)	115.84(3)	90
β [deg]	77.65(3)	76.23(3)	93.10(3)	102.38(3)
γ [deg]	87.01(3)	84.38(3)	108.12(3)	90
V [Å^3]	1699.2(5)	1660.0(5)	1575.4(6)	3577.6(12)
Z	2	2	2	4
D_{calcd} [g cm^{-3}]	1.402	1.295	1.310	1.314
μ [mm^{-1}]	0.859	0.799	0.841	0.753
F(000)	740	680	648	1480
θ range [deg]	1.71−26.99	2.33−27.12	1.67−26.96	1.41−26.97
reflections collected/unique	16245/7340 [R(int) = 0.0384]	14776/7075 [R(int) = 0.0762]	14660/6731 [R(int) = 0.0322]	22711/7419 [R(int) = 0.1288]
data/restraints/parameters	7340/0/401	7075/0/379	6731/0/358	7419/0/413
$R1$, $wR2$ [$I > 2\sigma(I)$][a]	0.0488, 0.1348	0.0504, 0.1040	0.0317, 0.0557	0.0686, 0.0835
$R1$, $wR2$ (all data) [a]	0.0595, 0.1401	0.0797, 0.1104	0.0429, 0.0576	0.1449, 0.0999
GoF	1.044	0.884	1.052	0.983
$\Delta\rho$(max), $\Delta\rho$(min) [e Å^{-3}]	1.932, −1.712	2.206, −1.035	0.493, −1.147	1.274, −0.889

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{0.5}$.

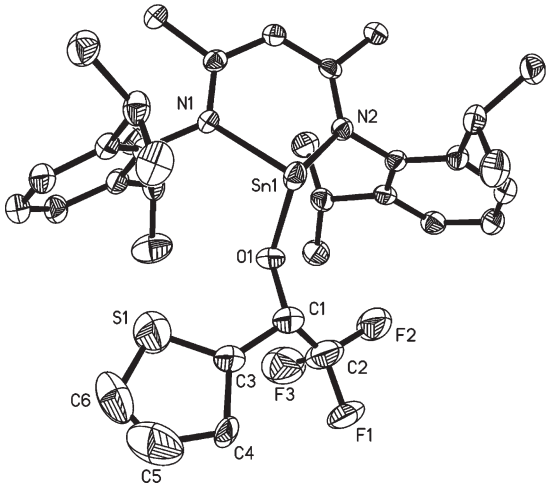


Figure 1. Molecular structure of **3**. Selected bond lengths [Å] and angles [deg]; anisotropic displacement parameters are depicted at the 50% probability level, and all restrained refined hydrogen atoms are omitted for clarity: Sn1−O1 2.046(3), Sn1−N1 2.194(3), O1−C1 1.418(6); N1−Sn1−N2 83.30(11), N1−Sn1−O1 93.04(12), Sn1−O1−C1 114.5(4).

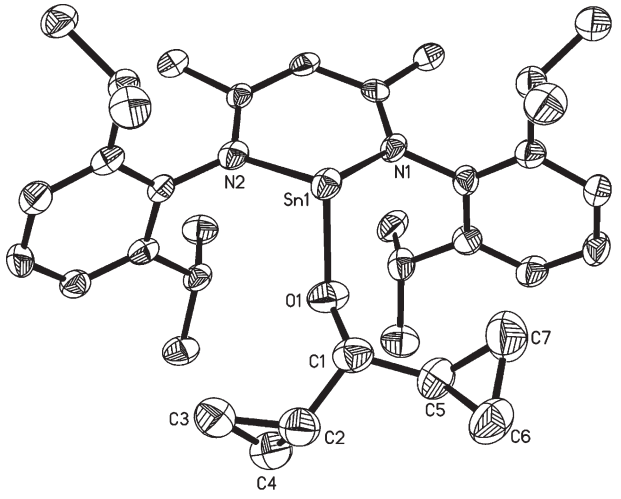
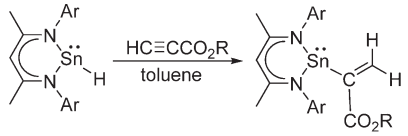


Figure 2. Molecular structure of **4**. Selected bond lengths [Å] and angles [deg]; anisotropic displacement parameters are depicted at the 50% probability level, and all restrained refined hydrogen atoms are omitted for clarity: Sn1−O1 2.024(3), Sn1−N1 2.199(4), O1−C1 1.431(6); N1−Sn1−N2 82.79(14), N1−Sn1−O1 95.80(13), Sn1−O1−C1 117.5(3).

"carbon" in compounds **1** and **4**; all the data are in good agreement with the calculated one. This error may be due to the unwanted impurities, although these are in the accepted experimental range.

The hydrostannation of alkynes is well-known since nearly 50 years ago, and follows a polar or a free radical pathway depending on substituents, catalyst, solvent, and conditions.[16] In contrast to this result the present hydrostannylation reaction of alkynes with LSnH proceeds without any catalyst. LSnH reacts with $HC{\equiv}CCO_2Me$ and $HC{\equiv}CCO_2Et$

Scheme 2. Preparation of Compounds **5** and **6**



Ar = 2,6-*i*Pr$_2$C$_6$H$_3$ R = Me; (**5**) R = Et; (**6**)

respectively at room temperature to form the vinyl stannylenes **5** and **6** (Scheme 2).

5 and **6** are obtained by the 1,2-addition of stannylene hydride LSnH to the terminal alkynes, and the result is the transfer of the hydrogen atom and stannylene to the carbon carbon triple bond (Scheme 2), rather than the elimination

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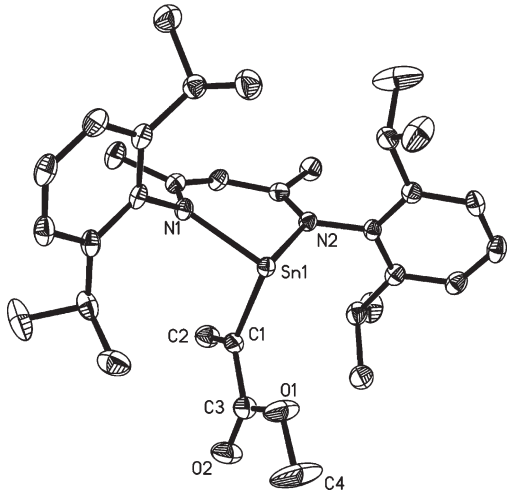
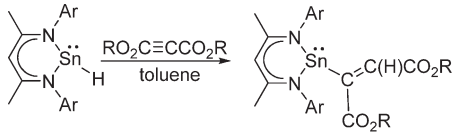


Figure 3. Molecular structure of **5**. Selected bond lengths [Å] and angles [deg]; anisotropic displacement parameters are depicted at the 50% probability level, and all restrained refined hydrogen atoms are omitted for clarity: Sn1−C1 2.241(2), Sn1−N1 2.202(2), C1−C3 1.488(3); N1−Sn1−N2 85.64(7), N1−Sn1−C1 93.06(8), Sn1−C1−C3 116.79(17).

Scheme 3. Preparation of Compounds **7** and **8**



of H_2 although the Sn−H and C−H bonds are differently polarized.

5 and **6** are yellow solids soluble in benzene, THF, *n*-hexane, and *n*-pentane and show no decomposition on exposure to air. **5** and **6** were characterized by multinuclear NMR and IR spectroscopy, EI mass spectrometry, and elemental analysis. Furthermore **5** was characterized by X-ray structural analysis (Figure 3). The ^{1}H NMR spectrum of **6** exhibits two broad resonances (δ 6.25 and 5.85 ppm) which correspond to the two alkenyl protons. Moreover, the ^{1}H NMR spectrum shows a quartet and a triplet resonance (δ 4.07 and 0.87 ppm) corresponding to the two different types of C*H* protons of the ethyl moieties. Compound **5** crystallizes in the triclinic space group $P\bar{1}$, with one monomer in the asymmetric unit, and with two molecules in each unit cell. Single crystals were obtained from a saturated *n*-hexane solution at −32 °C after 2 days (Table 1). The coordination polyhedron around the tin atom features a distorted tetrahedral geometry with a stereochemically active lone pair.

Furthermore we were interested in the selectivity of the addition across the carbon carbon triple bond. Therefore we selected the disubstituted alkynes, diethyl acetylenedicarboxylate and ditertiarybutyl acetylenedicarboxylate. LSnH reacts with dialkyl acetylenedicarboxylate, ($RO_2CC{\equiv}CCO_2R$, R = Et, *t*Bu) in toluene at room temperature to form the two isomers with *E*- and *Z*- stannylene substituted alkene in a different ratio (1.00:0.69 for **7** and 1.00:1.52 for **8**) (Scheme 3). The ^{1}H NMR spectra of **7** and **8** exhibit two singlets which are arranged between the tin satellites with two different coupling constants. The ^{119}Sn NMR resonances arise at δ −130 and −211 ppm, for *E*- and *Z*-isomers of **7** and the resonance at δ −123 and −205 ppm for *E*- and *Z*- isomers of **8**.

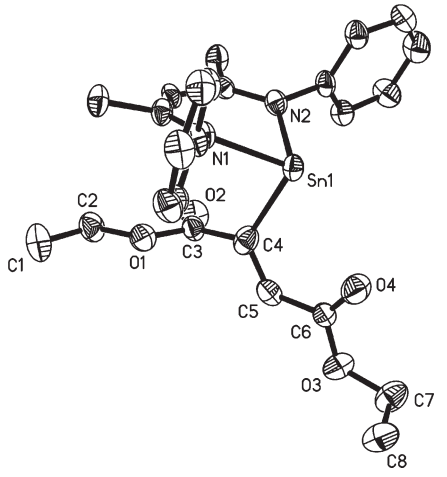


Figure 4. Molecular structure of **7**. Selected bond lengths [Å] and angles [deg]; anisotropic displacement parameters are depicted at the 50% probability level. Isopropyl groups and all restrained refined hydrogen atoms are omitted for clarity: Sn1−N1 2.207(5), Sn1−C4 2.330(8), C4−C5 1.331(9); N1−Sn1−N2 85.19(17), N1−Sn1−C4 92.3(2), Sn1−C4−C5 121.5(5).

The colors of **7** and **8** are yellow and red, respectively, in the solid state and in solution. **7** and **8** are soluble in benzene, THF, *n*-hexane, and *n*-pentane and show no decomposition on exposure to air.

7 crystallizes in the monoclinic space group $P2_1/c$, with one monomer in the asymmetric unit from saturated *n*-hexane solution at −32 °C after 1 day (Figure 4). In the crystalline state we were only able to isolate the *Z*-isomer.

Summary and Conclusion

Tin(II)-alkoxides have been prepared by the reaction of a tin(II)-hydride with a variety of ketones resulting in compounds containing the Sn(II)−O−CH core. Furthermore tin(II)-hydride reacts with terminal and internal alkynes generating the vinyl substituted stannylene, rather than under elimination of dihydrogen in the case of terminal alkynes. Compounds **1**−**8** represent a unique new class of stannylene compounds with an electron lone pair on tin(II) that is primed for complexation reaction with transition metal fragments. Moreover it is interesting to mention that most of the compounds are stable in air and moisture and highly soluble in common organic solvents.

Experimental Section

General Considerations. All manipulations were performed in a dry and oxygen-free atmosphere (N_2 or Ar) by using Schlenk-line and glovebox techniques. Solvents were purified with the M-Braun solvent drying system. Compound LSnH was prepared by literature procedure.[10] Other chemicals were purchased commercially and used as received.^{1}H, ^{13}C, ^{19}F, and ^{119}Sn NMR spectra were recorded on a Bruker 500 MHz instrument and referenced to the deuterated solvent in the case of the ^{1}H and ^{13}C NMR spectra. ^{19}F NMR spectra were referenced to $CFCl_3$ 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. Mass spectra were obtained on a Finnigan Mat 8230 instrument. Melting points were measured in a sealed glass tube with a Büchi melting point B 540 instrument and are not corrected.

Synthesis of [{HC(CMeNAr)$_2$}SnOCHPh$_2$] (Ar = 2,6-*i*Pr$_2$-C$_6$H$_3$) (1). A solution of Ph_2CO (0.180 g, 1.00 mmol in 5 mL of toluene) was added by cannula to a solution of LSnH (0.54 g, 1.00 mmol in toluene 20 mL) at room temperature. After 12 h all volatiles were removed from the solution in vacuo, and the remaining residue was extracted with *n*-hexane (25 mL) and concentrated to about 15 mL and stored in a −30 °C freezer. After 4 days yellow crystals of **1** are formed. Yield (0.590 g, 82%); mp 76 °C; ^{1}H NMR (500 MHz, C_6D_6): δ 6.86−7.70 (m, 16H, Ar-*H*), 5.97 (s, 1H, C*H*), 4.80 (s, 1H, γ-C*H*), 3.67 (sept, ^3J(H−H) = 6.50 Hz, 2H, C*H*(CH$_3$)$_2$), 3.15 (sept, ^3J(H−H) = 6.50 Hz, 2H, C*H*(CH$_3$)$_2$), 1.57 (s, 6H, CH_3), 1.19 (d, ^3J(H−H) = 6.50 Hz, 6H, CH(CH_3)$_2$), 1.14 (d, ^3J(H−H) = 6.50 Hz, 6H, CH(CH_3)$_2$), 1.12 (d, ^3J(H−H) = 6.50 Hz, 6H, CH(CH_3)$_2$), 1.07 (d, ^3J(H−H) = 6.50 Hz, 6H, CH(CH_3)$_2$); ^{13}C{^{1}H} NMR (125.77 MHz, C_6D_6): δ 165.22 (*C*N), 148.76−123.54 (Ar-*C*), 97.78 (γ-C), 78.87 (H*C*), 31.92, 28.58, 28.46, 26.32, 24.75, 24.71, 24.65, 24.46, 23.48, 23.42, 23.01 ppm; ^{119}Sn{^{1}H} NMR (186.46 MHz): δ −218 ppm; EI-MS (70 eV): *m*/*z* (%): 719 (100) [M]$^+$; elemental analysis (%) anal. calcd for $C_{42}H_{52}N_2OSn$ (719.59): C, 70.10; H, 7.28; N, 3.89. Found: C, 72.71; H, 7.53; N, 3.32.

Synthesis of [{HC(CMeNAr)$_2$}SnOCH(2-Py)$_2$] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (2). A solution of (2-Py)$_2$CO (0.185 g, 1.00 mmol in 5 mL of toluene) was added by cannula to a solution of LSnH (0.54 g, 1.00 mmol in toluene 20 mL) at room temperature. After overnight stirring all volatiles were removed from the solution in vacuo, and the remaining residue was extracted with *n*-hexane (25 mL). The solvent from the solution was completely removed and compound **2** was obtained as a powder. Yield (0.560 g, 78%); mp 160 °C; ^{1}H NMR (500 MHz, C_6D_6): δ 6.38−7.60 (m, 14H, Ar-*H*), 6.59 (s, 1H, C*H*), 4.85 (s, 1H, γ-C*H*), 3.93 (sept, ^3J(H−H) = 6.85 Hz, 2H, C*H*(CH$_3$)$_2$), 3.55 (sept, ^3J(H−H) = 6.85 Hz, 2H, C*H*(CH$_3$)$_2$), 1.72 (s, 6H, CH_3), 1.44 (d, ^3J(H−H) = 6.85 Hz, 6H, CH(CH_3)$_2$), 1.23 (d, ^3J(H−H) = 6.85 Hz, 6H, CH(CH_3)$_2$), 1.17 (d, ^3J(H−H) = 6.85 Hz, 6H, CH(CH_3)$_2$), 0.90 (d, ^3J(H−H) = 6.85 Hz, 6H, CH(CH_3)$_2$) ppm; ^{13}C{^{1}H} NMR (125.77 MHz, C_6D_6): δ 165.33, 164.43 (*C*N), 146.64−121.16 (Ar-*C*), 95.36 (γ-*C*), 79.86 (*C*H), 28.60, 28.44, 26.60, 24.88, 24.84, 24.60, 23.67 ppm; ^{119}Sn{^{1}H} NMR (186.46 MHz): δ −324 ppm; EI-MS (70 eV): *m*/*z* (%): 722 (100) [M]$^+$; elemental analysis (%) anal. calcd for $C_{40}H_{50}N_4OSn$ (722.30): C, 66.58; H, 6.98; N, 7.76. Found: C, 66.74; H, 6.94; N, 7.67.

Synthesis of [{HC(CMeNAr)$_2$}SnOCH(2-C$_4$H$_3$S)CF$_3$] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (3). A solution of 2,2,2-trifluoroacetothiophene (0.180 g, 1.00 mmol in 5 mL of toluene) was added by cannula to a solution of LSnH (0.54 g, 1.00 mmol in toluene 20 mL) at room temperature. After 12 h all volatiles were removed from the solution in vacuo, and the remaining residue was extracted with *n*-hexane (25 mL). The resulting solution was concentrated and stored in a freezer, after 3 days yellow crystals of **3** are formed which are suitable for X-ray structural analysis. Yield (0.610 g, 85%); mp 158 °C; ^{1}H NMR (500 MHz, C_6D_6): δ 7.03−7.20 (m, 6H, Ar-*H*), 6.81 (m, 2H, C$_4H_3$S), 6.64 (m, 1H, C$_4H_3$S), 5.44 (q, ^3J(F−H) = 6.99 Hz, 1H, C*H*), 4.87 (s, 1H, γ-C*H*), 3.78 (sept, ^3J(H−H) = 6.50 Hz, 1H, C*H*(CH$_3$)$_2$), 3.61 (sept, ^3J(H−H) = 6.50 Hz, 1H, C*H*(CH$_3$)$_2$), 3.30 (sept, ^3J(H−H) = 6.50 Hz, 1H, C*H*(CH$_3$)$_2$), 3.09 (sept, ^3J(H−H) = 6.50 Hz, 1H, C*H*(CH$_3$)$_2$), 1.57 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 1.42 (d, ^3J(H−H) = 6.50 Hz, 3H, CH(CH_3)$_2$), 1.37 (d, ^3J(H−H) = 6.50 Hz, 3H, CH(CH_3)$_2$), 1.24 (d, ^3J(H−H) = 6.50 Hz, 3H, CH(CH_3)$_2$), 1.21 (d, ^3J(H−H) = 6.50 Hz, 3H, CH(CH_3)$_2$), 1.19−1.12 (m, 12H, CH(CH_3)$_2$) ppm; ^{19}F NMR (188.29 MHz): δ −77.39 (d, ^3J(F−H) = 6.99 Hz, 3F, CF_3) ppm; ^{119}Sn{^{1}H} NMR (186.46 MHz): δ −262 ppm; EI-MS (70 eV): *m*/*z* (%): 718 (100) [M]$^+$; elemental analysis (%) anal. calcd for $C_{35}H_{45}F_3N_2OSSn$ (718.22): C, 58.59; H, 6.32; N, 3.90; S, 4.47. Found: C, 58.57; H, 6.52; N, 3.84; S, 4.81.

Synthesis of [{HC(CMeNAr)$_2$}SnOCH(C$_3$H$_5$)$_2$] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (4). A solution of dicyclopropylketone (0.110 g, 1.00 mmol in 5 mL of toluene) was added by cannula to a solution of LSnH (0.54 g, 1.00 mmol in toluene 20 mL) at room temperature. After that the solution was heated under reflux for 12 h. Then all volatiles were removed from the solution in vacuo, and the remaining residue was extracted with *n*-hexane (25 mL). The solution was concentrated and stored in a freezer, after 4 days yellow crystals of **4** are formed which are suitable for X-ray structural analysis. Yield (0.480 g, 74%); mp 169 °C; ^{1}H NMR (500 MHz, C_6D_6): δ 7.06−7.20 (m, 6 H, Ar-*H*), 4.71 (s, 1H, γ-C*H*), 3.81 (sept, 2H, C*H*(CH$_3$)$_2$), 3.24 (sept, 2H, C*H*(CH$_3$)$_2$), 2.47 (q, ^3J(H−H) = 7.3 Hz, 1H, C*H*), 1.58 (s, 6H, CH_3), 1.52 (s, 6H, CH_3), 1.28 (d, 6H, CH(CH_3)$_2$), 1.24 (d, 6H, CH(CH_3)$_2$), 1.14 (d, 6H, CH(CH_3)$_2$), 0.75 (m, 2H, C*H*), 0.21 (m, 2H, CH_2), 0.02 (m, 2H, CH_2), −0.07 (m, 2H, CH_2), −0.25 (m, 2H, CH_2) ppm; ^{119}Sn{^{1}H} NMR (186.46 MHz): δ −190.50 ppm; EI-MS (70 eV): *m*/*z* (%): 648 (100) [M]$^+$; elemental analysis (%) anal. calcd for $C_{36}H_{52}N_2OSn$ (648.31): C, 66.78; H, 8.09; N, 4.33. Found: C, 65.19; H, 8.00; N, 4.13.

Synthesis of [{HC(CMeNAr)$_2$}SnC(CO$_2$Me)CH$_2$] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (5). A solution of methyl propiolate (0.085 g, 1.00 mmol in 5 mL of toluene) was added drop by drop by cannula to a solution of LSnH (0.540 g, 1.00 mmol in toluene 15 mL) at room temperature. After 0.5 h under constant stirring at ambient temperature all volatiles were removed from the solution in vacuo, and the remaining residue was extracted with *n*-hexane (15 mL) and concentrated to about 5 mL and stored in a −30 °C freezer. Yellow crystals of **5** suitable for X-ray diffraction analysis are formed after 2 days. Yield: 0.435 g (70%); mp 170 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.08−7.14 (m, 6H, Ar-*H*), 6.45 (br, 1H, C=CH_2), 6.15 (br, 1H, C=CH_2), 4.81 (s, 1H, γ-C*H*), 3.67 (sept, 2H, C*H*(CH$_3$)$_2$), 3.42 (s, 3H, CH_3), 3.40 (sept, 2H, C*H*(CH$_3$)$_2$), 1.60 (s, 6H, CH_3), 1.27 (m, 12H, CH(CH_3)$_2$), 1.16 (m, 12H, CH(CH_3)$_2$) ppm; ^{119}Sn{^{1}H} NMR (186.46 MHz): δ −93.28 ppm. EI-MS: *m*/*z* (%) 622 (100) [M]$^+$. Elemental analysis (%) anal. calcd for $C_{33}H_{46}N_2O_2Sn$ (622.26): C, 63.78; H, 7.46; N, 4.51. Found: C, 63.80; H, 7.84; N, 4.47.

Synthesis of [{HC(CMeNAr)$_2$}SnC(CO$_2$Et)CH$_2$] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (6). A solution of ethyl propiolate (0.100 g, 1.00 mmol in 5 mL of toluene) was added drop by drop by cannula to a solution of LSnH (0.490 g, 1.00 mmol in toluene 15 mL) at room temperature. After 0.5 h under constant stirring at ambient temperature the yellow solution remains unchanged. All volatiles were removed from the solution in vacuo, and the remaining residue was extracted with *n*-hexane (15 mL) and concentrated to about 5 mL and stored in a −30 °C freezer. Yellow crystals of **6** are formed after 1 week. Yield: 0.460 g (72%); mp 168 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.10−7.20 (m, 6H, Ar-*H*), 6.70 (br, 1H, C=CH_2), 6.10 (br, 1H, C=CH_2), 4.82 (s, 1H, γ-C*H*), 4.08 (q, 2H, CH_2), 3.67 (sept, 2H, C*H*(CH$_3$)$_2$), 3.42 (sept, 2H, C*H*(CH$_3$)$_2$), 1.62 (s, 6H, CH_3), 1.28 (m, 12H, CH(CH_3)$_2$), 1.18 (m, 12H, CH(CH_3)$_2$), 1.03 (t, 3H, CH$_2$CH_3) ppm; ^{119}Sn{^{1}H} NMR (186.46 MHz): δ −89.02 ppm. EI-MS: *m*/*z* (%) 636 (100) [M]$^+$. Elemental analysis (%) anal. calcd for $C_{34}H_{48}N_2O_2Sn$ (636.27): C, 64.26; H, 7.61; N, 4.41. Found: C, 63.98; H, 7.92; N, 4.38.

Synthesis of [{HC(CMeNAr)$_2$}SnC(CO$_2$Et)CHCO$_2$Et] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (7). A solution of diethyl acetylenedicarboxylate (0.170 g, 1.00 mmol in 5 mL of toluene) was added drop by drop by cannula to a solution of LSnH (0.540 g, 1.00 mmol in toluene 15 mL) at room temperature. After 6 h under constant stirring at ambient temperature the yellow solution turned red. All volatiles were removed from the solution in vacuo, and the remaining residue was extracted with *n*-hexane (15 mL) and concentrated to about 5 mL and stored in a −30 °C freezer. Red crystals of **7** suitable for X-ray diffraction analysis are formed after 1 day. Yield: 0.480 g (68%); mp 138 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.05−7.16 (m, 6H, Ar-*H*), 6.93 (s, C*H*), 6.26 (s, C*H*), 4.87 (s, γ-C*H*), 4.85 (s, γ-C*H*), 4.22 (q, CH_2), 4.03 (q, CH_2), 3.98 (q, CH_2), 3.88 (m, C*H*(CH$_3$)$_2$), 3.84 (q, CH_2), 3.28

(m, C*H*(CH_3)$_2$), 1.65 (s, CH_3), 1.64 (s, CH_3), 1.35 (t, CH_3), 1.32−1.12 (m, CH(CH_3)$_2$), 1.06 (t, CH_3), 0.95 (t, CH_3), 0.87 (t, CH_3), 0.82 (t, CH_3) ppm; ^{119}Sn{^{1}H} NMR (186.46 MHz): δ −130.36, −211.20 ppm; EI-MS: *m*/*z* (%) 708 (100) [M^+]. Anal. calcd for $C_{37}H_{52}N_2O_4Sn$ (708.29): C, 62.81; H, 7.41; N, 3.96. Found: C, 60.63; H, 7.41; N, 3.64.

Synthesis of [{HC(CMeNAr)$_2$}SnC(CO$_2$*t*Bu)CHCO$_2$*t*Bu] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (8). A solution of ditertiarybutyl acetylenedicarboxylate (0.225 g, 1.00 mmol in 5 mL toluene) was added drop by drop by cannula to a solution of LSnH (0.540 g, 1.00 mmol in toluene 15 mL) at room temperature. After overnight constant stirring at ambient temperature, all the volatiles were removed from the solution in vacuo, and the remaining residue was extracted with *n*-hexane (25 mL). Complete evaporation of the filtrate resulted in a red power of the title compound **8**. Yield: 0.490 g (64%); mp 179 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.06−7.15 (m, 6H, Ar-*H*), 6.93 (s, C*H*), 6.18 (s, C*H*), 4.92 (s, γ-C*H*), 4.90 (s, γ-C*H*), 3.82 (m, 2H, C*H*(CH$_3$)$_2$), 3.36 (sept, 2H, C*H*(CH$_3$)$_2$), 1.72 (s, 6H, CH_3), 1.65 (s, 9H, C(CH_3)$_3$), 1.37−1.15 (m, 24H, CH(CH_3)$_2$), 1.25 (s, 9H, C(CH_3)$_3$) ppm. ^{119}Sn{^{1}H} NMR (186.46 MHz): δ −123.27 and −205.75 ppm; EI-MS: *m*/*z* (%) 707 (100) [M-*t*Bu]$^+$. Anal. calcd for $C_{41}H_{60}N_2O_4Sn$ (764.36): C, 64.49; H, 7.92; N, 3.67. Found: C, 64.38; H, 8.08; N, 3.59.

Crystallographic details for compounds 3, 4, 5, and 7. Suitable crystals of **3**, **4**, **5**, and **7** were mounted on a glass fiber, and data was collected on an IPDS II Stoe image-plate diffractometer (graphite monochromated Mo Kα radiation, λ = 0.71073 Å) at 133(2) K. The data was integrated with X-Area. The structures were solved by Direct Methods (SHELXS-97)[17] and refined by full-matrix least-squares methods against F^2 (SHELXL-97).[17] All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic data are presented in Table 1.

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Supporting Information Available: X-ray data for **3**, **4**, **5**, and **7** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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