Reaction of β-diketiminate tin(II) dimethylamide LSnNMe$_2$ [L = HC(CMeNAr)$_2$; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$] with ketones and alkynes†‡

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The reactions of stable β-diketiminate tin(II) dimethylamide LSnNMe$_2$ [L = HC(CMeNAr)$_2$; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$] (**1**) with ketones and activated terminal alkynes are described. **1** reacts with 2-benzoylpyridine and 2,2,2-trifluoroacetophenone to give the tin(II)-alkoxides LSnOCPh(2-Py)NMe$_2$ (**2**) and LSnOCPh(CF$_3$)NMe$_2$ (**3**), respectively, by nucleophilic addition of the dimethylamido group to the carbonyl moiety. Furthermore, the reaction of **1** with terminal alkynes (HCCCO$_2$R, R = Me, Et) forms tin(II)-alkynyl LSnCCCO$_2$R (R = Me, (**4**); R = Et, (**5**)) compounds under elimination of Me$_2$NH rather than undergoing a nucleophilic addition reaction at the carbon–carbon triple bond. Compounds **2–5** were characterized by microanalysis and multinuclear NMR spectroscopy. Moreover, **2** and **5** could be crystallized and their constitutions were confirmed by X-ray structural analysis. **2** and **5** are monomers in the solid state and the metal atom shows a distorted trigonal-pyramidal coordination sphere.

Introduction

The chemistry of compounds with low valent group 14 elements, namely carbenes, silylenes, germylenes, stannylenes, and plumbylenes has received considerable attention in recent years, due to some special properties and reactivities.[1] Recently we showed that "H"-transfer was successful to a variety of unsaturated compounds by using germanium(II) hydride, LGeH[2] and tin(II) hydride, LSnH,[3] respectively, at room temperature without adding any catalyst [L = HC(CMeNAr)$_2$; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$]. Now we became interested in transferring the "NMe$_2$" residue to unsaturated organic molecules to synthesize the nitrogen containing compounds. The latter play an important role in many biologically active systems as well as in organic targets, new materials, and fine chemicals.[4] Here we selected the stable tin(II) amido compound LSnNMe$_2$ (**1**)[5] as a starting material.

Results and discussion

After the preparation of the monomeric β-diketiminate stabilised heteroleptic tin(II) chloride LSnCl[6] it turned out to be the right starting material for the preparation of stannylenes LSnX with small terminal substituents X = H,[3a,7] Me,[8] F.[8] Hetero-bimetallic compounds with direct metal–metal bonds are accessible in nucleophilic substitution reactions.[9] In 2006 Gibson and co-workers reported the synthesis of LSnNMe$_2$ (**1**) and studied the mechanistic properties of single-site β-diketiminate tin(II) initiators for polymerization of *rac*-lactide.[5] Herein we describe the preparation of LSnNMe$_2$ (**1**) using diethyl ether as a solvent instead of toluene and obtained **1** in excellent yield by the reaction of LSnCl with LiNMe$_2$ in a 1 : 1 ratio. The spectroscopic data match with previously reported values.[5] It is worth mentioning that recently we reported the synthesis of LGeNH$_2$ by the reaction of L^{1}Ge [L^1 = HC{(C=CH$_2$)(CMe)(NAr)$_2$; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$] with NH$_3$.[10]

The insertion reaction of carbonyl compounds into the metal–nitrogen bond has been known for lanthanides and for transition metal complexes.[11] However, the insertion of the carbon–oxygen bond into the metal–nitrogen bond has not been well studied with main group compounds. This may be due to the poor reactivity of compounds with nitrogen bonds, although last year our group reported the addition of dimethylaminobismuth to aldehydes, ketones, alkenes, and alkynes.[12] Lappert and co-workers described the addition of aminostannanes to a variety of alkynes and alkenes and also aminosilylation and aminophosphination reactions with highly electrophilic substrates.[13] Recently, Hartwig and co-workers reported transammination of alkenes and vinylarenes by rhodium(I) amides.[14] The insertion of an alkyne into a molybdenum–amide bond has also been described.[15]

The carbonyl group and its transformation to other functional groups is very important in organic chemistry.[16] Up to now there are no reports in the literature of reactions with tin(IV) amide and carbonyl compounds.

Treatment of **1** with 2-benzoylpyridine and 2,2,2-trifluoroacetophenone leads almost quantitatively to the stannylene alkoxides **2** and **3**, respectively (Scheme 1) with formation of the Sn–O–CNMe$_2$ core. The ^{1}H NMR spectrum of **2** exhibits a singlet (δ 4.92 ppm) which can be assigned to the γ-C*H* proton and a singlet resonance at δ 1.83 ppm for the N*Me*$_2$ group. The four isopropyl groups of **2** are exhibiting four different resonances, and even the two methyl groups in the backbone show two different signals in the proton NMR spectrum. The ^{119}Sn NMR resonance of **2** arises at δ −328 ppm. **2** crystallizes in the triclinic space group $P\bar{1}$ with one monomer in the asymmetric unit (Fig. 1).

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‡ CCDC reference numbers 743154 and 743155 for **2** and **5** respectively. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c002849e

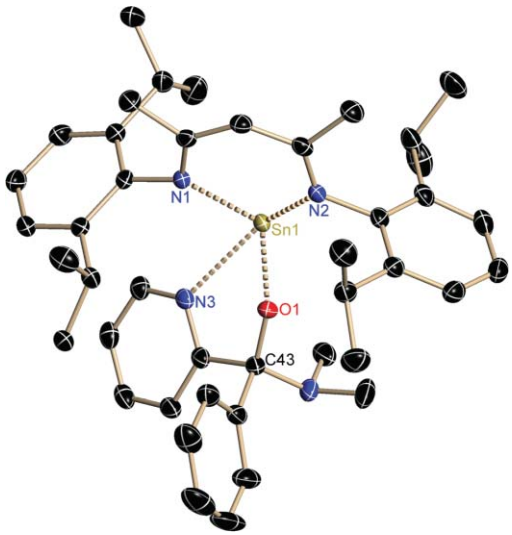
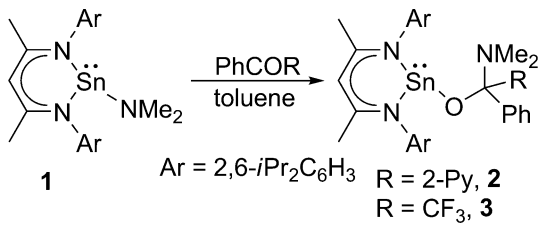


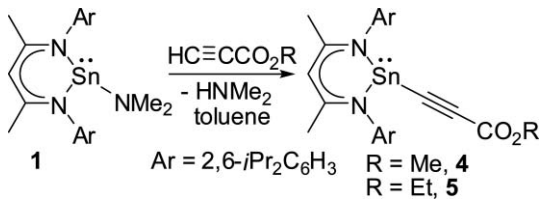
Fig. 1 Molecular structure of **2**. Anisotropic displacement parameters are depicted at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sn1–O1 2.0505(11), Sn1–N1 2.2538(13), Sn1–N3 2.5580(14), O1–C43 1.3907(19); N1–Sn1–N2 83.14(5), N1–Sn1–O1 102.50(5), Sn1–O1–C43 125.03(10).



Scheme 1 Preparation of compounds **2** and **3**.

Compound **3** has one CF_3 group and the ^{1}H NMR spectrum exhibits a quartet (δ 5.15 ppm) which corresponds to the quaternary C*H* proton. The ^{19}F NMR resonance arises as a singlet (δ –69.74 ppm) and is flanked by ^{119}Sn satellite lines ($^4J(^{119}\text{Sn},^{19}\text{F}) =$ 129 Hz). The ^{119}Sn NMR resonance of **3** arises as a quartet at δ –232 ppm with the same coupling constant of $^4J(^{119}\text{Sn},^{19}\text{F}) =$ 129 Hz. The two ^{119}Sn NMR values of **2** and **3** are different due to the contrasting substituents of R.

After the successful reaction of **1** with ketones, we subsequently treated **1** with alkynes. Compound **1** reacts with HC≡CCO_2Me and HC≡CCO_2Et, at room temperature in quantitative yield to the alkynyl linked stannylenes **4** and **5**, respectively, with a Sn(II)–C≡C framework that is formed by elimination of Me_2NH due to the different polarized Sn–NMe_2 and C–H bonds (Scheme 2). The reactions of **4** and **5** were monitored by their ^{1}H NMR spectra. Sharp resonances in the ^{1}H NMR of **4** and **5** indicate that the products have been formed in high yield. In the course of the reaction there is no sign that some side products are formed by nucleophilic addition of LSnNMe_2 (**1**) to the carbon–carbon triple bond, which we observed exclusively in the case of LGeH[2] and LSnH[3] when they were reacted with terminal alkynes.



Scheme 2 Preparation of compounds **4** and **5**.

In the ^{1}H NMR spectra of **4** and **5**, the complete disappearance of the proton resonance of Sn–NMe_2 was observed. This indicates the total conversion of the tin amide to the corresponding tin-alkynyl compounds.

Compounds **4** and **5** are yellow solids soluble in benzene, THF, *n*-hexane, and *n*-pentane, respectively and show no decomposition on exposure to air. **4** and **5** were characterized by multinuclear NMR and IR spectroscopy, EI mass spectrometry, and elemental analysis. Furthermore, **5** could be characterized by single crystal X-ray structural analysis (Fig. 2). **5** crystallizes in the monoclinic space group $P2_1/n$ with one monomer in the asymmetric unit, and with four molecules in each unit cell. Single crystals were obtained after two days from a saturated *n*-hexane solution in a freezer at –30 °C (Table 1). The coordination polyhedron around the tin atom features a distorted tetrahedral geometry with a stereochemically active lone pair. The ^{1}H NMR spectrum of **5** shows a quartet and a triplet resonance (δ 3.92 and 0.92 ppm) corresponding to the two different types of C*H* protons of the ethyl moiety.

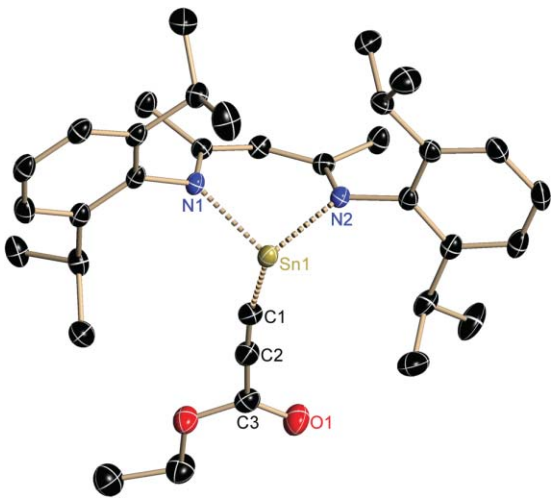


Fig. 2 Molecular structure of **5**. Anisotropic displacement parameters are depicted at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sn1–N1 2.1802(16), Sn1–C1 2.214(2), C1–C2 1.213(3); C2–C3 1.447(3), C3–O1 1.208(3), C3–O2 1.343(3); N1–Sn1–N2 86.33(6), N1–Sn1–C1 89.90(7), Sn1–C1–C2 168.83(19), C1–C2–C3 176.9(2).

Experimental section

General considerations

All manipulations were performed in a dry and oxygen-free atmosphere (N_2) by using Schlenk-line and glove-box techniques. Solvents were purified with the M-Braun solvent drying system. Compound LSnCl was prepared by literature procedure.[6] Other chemicals were purchased and used as received. ^{1}H, ^{19}F, and ^{119}Sn NMR spectra were recorded on a Bruker Avance DRX instrument and referenced to the deuterated solvent in the case of the ^{1}H

Table 1 Crystal data for complexes **2** and **5**

	2	**5**
Empirical formula	$C_{43}H_{56}N_4OSn$	$C_{34}H_{46}N_2O_2Sn$
CCDC-No.	743154	743155
Temperature	100(2) K	100(2) K
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a/Å	11.0083(9)	12.777(2)
b/Å	11.8819(10)	19.911(4)
c/Å	16.971(2)	13.186(2)
α (°)	96.9270(10)	90
β (°)	101.1180(10)	104.998(2)
γ (°)	113.0550(10)	90
V/Å^3	1956.3(3)	3240.2(10)
Z	2	4
ρ_c/Mg m^{-3}	1.296	1.298
μ/mm^{-1}	0.690	0.819
F(000)	800	1320
Crystal Size/mm	0.3/0.05/0.05	0.1/0.1/0.05
θ range [°]	2.08-26.02	1.90-26.73
Reflections	42763/7688	60564/6864
Collected/independent	[R(int) = 0.0233]	[R(int) = 0.0313]
Data/restraints/parameters	7688/0/454	6864/0/363
R_1, wR_2 [$I > 2\sigma(I)$][a]	0.0200/0.0474	0.0249/0.0564
R_1, wR_2 (all data)[a]	0.0232/0.0484	0.0307/0.0592
GoF	1.066	1.068
Residual density max./min./e Å^{-3}	0.326, –0.250	0.942, –0.706

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

NMR spectrum. ^{19}F and ^{119}Sn NMR spectra were referenced to $CFCl_3$ and $SnMe_4$. 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.

Synthesis of [{HC(CMeNAr)$_2$}SnNMe$_2$] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (1). A solution of LSnCl (0.498 g, 1.0 mmol) in diethyl ether (20 mL) was added drop by drop to a stirred suspension of $LiNMe_2$ (0.051 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 12 h. The precipitate was filtered off, and the solvent was partially reduced (*ca.* 20 mL). Storage of the remaining solution in a freezer at –30 °C overnight afforded yellow crystals. Yield: 0.533 g (92%). ^{1}H NMR (200 MHz, C_6D_6): δ 7.02–7.16 (m, 6H, Ar-*H*), 4.82 (s, 1H, γ-C*H*), 3.45 (sept, 2H, C*H*(CH$_3$)$_2$), 3.37 (sept, 2H, C*H*(CH$_3$)$_2$), 3.00 (s, 6H, N(C*H*$_3$)$_2$), 1.65 (s, 6H, C*H*$_3$), 1.27–1.35 (m, 18H, CH(C*H*$_3$)$_2$), 1.17 (d, 6H, CH(C*H*$_3$)$_2$) ppm. For comparison see ref. 5.

Synthesis of [{HC(CMeNAr)$_2$}SnOCPh(CF$_3$)nMe$_2$] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (2). A solution of 2-benzoylpyridine (0.180 g, 1.00 mmol in 5 mL toluene) was added by cannula to a solution of **1** (0.54 g, 1.00 mmol in toluene 20 mL) at room temperature. After 12 h all volatiles were removed *in vacuum*, and the remaining residue was extracted with *n*-hexane (25 mL) and concentrated to about 15 mL and stored in a freezer at –30 °C. Yellow crystals of **2** suitable for X-ray diffraction analysis are formed after four days. Yield: 0.670 g (88%); mp 176 °C. ^{1}H NMR (200 MHz, C_6D_6): δ 8.24 (d, 2H, *o*-Ph-*H*), 7.60 (d, 1H, *o*-Py-*H*), 7.33 (t, 2H, *m*-Ph-*H*), 7.03-7.16 (m, 6H, Ar-*H*), 6.83-6.79 (m, 2H, *p*-Ph-*H*, *p*-Py-*H*), 6.3 (m, 2H, *m*-Py-*H*), 4.95 (s, 1H, γ-C*H*), 4.21 (sept, 1H, C*H*(CH$_3$)$_2$), 3.79 (sept, 1H, C*H*(CH$_3$)$_2$), 3.66 (sept, 1H, C*H*(CH$_3$)$_2$), 3.32 (sept, 1H, C*H*(CH$_3$)$_2$), 1.86 (s, 6H, N(C*H*$_3$)$_2$), 1.79 (s, 3H, C*H*$_3$), 1.72 (s, 3H, C*H*$_3$), 1.56 (d, 6H, CH(C*H*$_3$)$_2$), 1.31–1.11 (m, 15H, CH(C*H*$_3$)$_2$), –0.12 (d, 3H, CH(C*H*$_3$)$_2$) ppm. ^{119}Sn {^{1}H} NMR (186.50 MHz, C_6D_6): δ –328 ppm. EI-MS: *m*/*z* (%) 537 (100) [M-OCPh(2-Py)NMe$_2$]$^+$. Found C, 67.79; H, 7.96; N, 7.24. Calcd. for $C_{43}H_{56}N_4OSn$ (764.35): C, 67.63; H, 7.39; N, 7.34.

Synthesis of [{HC(CMeNAr)$_2$}SnOC(NMe$_2$)PhCF$_3$] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (3). A solution of 2,2,2-trifluoroacetophenone (0.175 g, 1.00 mmol in 5 mL toluene) was added by cannula to a solution of **1** (0.54 g, 1.00 mmol in toluene 20 mL) at room temperature. After 12 h all volatiles were removed in vacuum, and the remaining residue was extracted with *n*-hexane (25 mL). The solvent was removed and compound **3** obtained as a powder. Yield: 0.550 g (73%); mp 178 °C. ^{1}H NMR (200 MHz, C_6D_6): δ 7.32 (d, 2H, *o*-Ph-*H*), 7.08–7.17 (m, 6H, Ar-*H*), 7.00 (m, 3H, *p*-Ph-*H*, *m*-Ph-*H*), 4.66 (s, 1H, γ-C*H*), 3.99 (sept, 2H, C*H*(CH$_3$)$_2$), 3.14 (sept, 2H, C*H*(CH$_3$)$_2$), 1.99 (s, 6H, N(C*H*$_3$)$_2$), 1.59 (s, 3H, CH(C*H*$_3$)$_2$), 1.55 (s, 3H, C*H*$_3$), 1.53 (s, 3H, C*H*$_3$), 1.51 (d, 3H, CH(C*H*$_3$)$_2$), 1.12–1.27 (m, 15H, CH(C*H*$_3$)$_2$), 1.14 (d, 6H, CH(C*H*$_3$)$_2$) ppm. ^{119}Sn {^{1}H} NMR (186.50 MHz, C_6D_6): δ –232 ppm. EI-MS: *m*/*z* (%) 537 (100) [M–OCPh(CF$_3$)NMe$_2$]$^+$. Found C, 61.55; H, 6.67; N, 5.47. Calcd. for $C_{39}H_{52}F_3N_3OSn$ (755.31): C, 62.08; H, 6.95; N, 5.57.

Synthesis of [{HC(CMeNAr)$_2$}SnCCCO$_2$Me] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (4). A solution of HCCCO$_2$Me (0.085 g, 1.00 mmol in 5 mL toluene) was added drop by drop by cannula to a solution of **1** (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 in vacuum, and the remaining residue was extracted with *n*-hexane (15 mL) and concentrated to about 5 mL and stored in a freezer at –30 °C. After two days yellow crystals of **4** are formed. Yield: 0.545 g (88%); mp 124 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 7.03–7.16 (m, 6H, Ar-*H*), 4.98 (s, 1H, γ-C*H*), 3.88 (sept, 2H, C*H*(CH$_3$)$_2$), 3.29 (s, 3H, CO$_2$CH$_3$), 3.23 (sept, 2H, C*H*(CH$_3$)$_2$), 1.58 (s, 6H, C*H*$_3$), 1.47 (d, 6H, CH(C*H*$_3$)$_2$), 1.36 (d, 6H, CH(C*H*$_3$)$_2$), 1.21 (d, 6H, CH(C*H*$_3$)$_2$), 1.08 (d, 6H, CH(C*H*$_3$)$_2$) ppm. ^{119}Sn {^{1}H} NMR (111.92 MHz, C_6D_6): δ –254.91 ppm. EI-MS: *m*/*z* (%) 620 (85) [M]$^+$, 562 (100) [M–Me–*i*Pr]$^+$. Found C, 63.28; H, 7.51; N, 4.73. Calcd. for $C_{33}H_{44}N_2O_2Sn$ (620.24): C, 63.99; H, 7.16; N, 4.52.

Synthesis of [{HC(CMeNAr)$_2$}SnCCCO$_2$Et] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (5). A solution of HCCCO$_2$Et (0.100 g, 1.00 mmol in 5 mL toluene) was added drop by drop by cannula to a solution of **1** (0.490 g, 1.00 mmol in toluene 15 mL) at room temperature. After 0.5 h under constant stirring at ambient temperature the red solution turned deep-red. All volatiles were removed in vacuum, and the remaining residue was extracted with *n*-hexane (15 mL) and concentrated to about 5 mL and stored in a freezer at –30 °C. Yellow crystals of **5** suitable for X-ray diffraction analysis are formed after two days. Yield: 0.495 g (78%); mp 164 °C. ^{1}H NMR (200 MHz, C_6D_6): δ 7.05–7.19 (m, 6H, Ar–H), 4.99 (s, 1H, γ-CH), 3.84–4.01 (m, 4H, C*H*(CH$_3$)$_2$, C*H*$_2$CH$_3$), 3.26 (sept, 2H, CH(C*H*$_3$)$_2$), 1.60 (s, 6H, C*H*$_3$), 1.51 (d, 6H, CH(C*H*$_3$)$_2$), 1.40 (d, 6H, CH(C*H*$_3$)$_2$), 1.23 (d, 6H, CH(C*H*$_3$)$_2$), 1.11 (d, 6H, CH(C*H*$_3$)$_2$), 0.92 (t, 3H, CH$_2$C*H*$_3$) ppm. ^{119}Sn NMR (186.50 MHz, C_6D_6): δ –252.97 ppm. EI-MS: *m*/*z* (%) 562 (100) [M-Et-*i*Pr]$^+$. Found C,

63.88; H, 6.98; N, 4.48. Calcd. for $C_{34}H_{46}N_2O_2Sn$ (634.26): C, 64.47; H, 7.32; N, 4.42.

Crystallographic details of 2 and 5. The data set of **2** was collected on a Bruker TXS-Mo rotating anode equipped with INCOATEC Helios mirror optics and the data set of **5** was collected on a INCOATEC Mo micro source equipped with INCOATEC quazar mirror optics (MoKα λ = 0.71073 Å).[17] The crystals were mounted in a shock-cooled oil drop at the tip of a fibre.[18] The data were integrated with SAINT V7.46A (**2**), and SAINT V7.60A (**5**),[19] and an empirical absorption correction SADABS-2008/2 (**2**, **5**) was applied.[20] The structures were solved by direct methods (SHELXS)[21] and refined on F^2 using the full-matrix least-squares method of SHELXL.[22] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were assigned ideal positions and refined using a riding model with U_{iso} constrained to 1.2 (1.5) times the U_{eq} value of the parent carbon atom. Crystallographic data are presented in Table 1.

Conclusion

In conclusion the results show that the tin(II)-alkoxides have been prepared by the reaction of **1** with ketones resulting in compounds containing the Sn(II)–O–CNMe$_2$ core. Furthermore, tin(II)-dimethylamide reacts with terminal alkynes generating the alkynyl substituted tin(II) compounds under elimination of dimethyl amine rather than the addition of **1** to the C≡C triple bond. **2–5** represent a class of compounds with low valent group 14 elements and an electron lone pair at tin(II) that is prone for complexation reaction with transition metal fragments or Lewis acids. Moreover, it is interesting to mention that all the compounds are stable in air and moisture and highly soluble in common organic solvents.

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