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[11] The cyclic voltammetric measurements were carried out in CH_2Cl_2 at $-20\,^\circ C$ with Bu_4NPF_6 (0.1M) as supporting electrolyte and calibrated against cobaltocenium/cobaltocene ($E_{ox} = -1.04\,V_{SCE}$; SCE = saturated calomel electrode). The scan speed was $100\,\mathrm{mV\,s^{-1}}$; working electrode: Pt button; reference electrode: Pt wire.

[12] A differential scanning calorimetry (DSC) measurement carried out at up to 250 °C gave no indication of topochemical solid-state polymerization.

[13] The oligomeric mixture is readily soluble in *n*-pentane and shows molecular masses of up to $M = 9200$ (molecular mass of the icosomer (20mer) of **3d**) in the matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrum.

[14] Broadened ^{1}H NMR ring-proton signals have also been observed by Watanabe et al. with ferroceno[1.1]ruthenophane. This finding was attributed to a rapid equilibrium between the *syn* conformers (*syn*-A and *syn*-B) in solution which proceeds through a *twist* form. A similar equilibrium is also possibly present in the case of the ferrocenophane **6**: a) M. Watanabe, A. Nagasawa, I. Motoyama, T. Takayama, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2127–2136; b) U. T. Mueller-Westerhoff, *Angew. Chem.* **1986**, *98*, 700–716; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 702–718.

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New Building Blocks in Amide Chemistry—*N*-Lithiobis(trimethylstannyl)amine and *N*-Lithiotrimethylstannyl(trimethylsilyl)amine[**]

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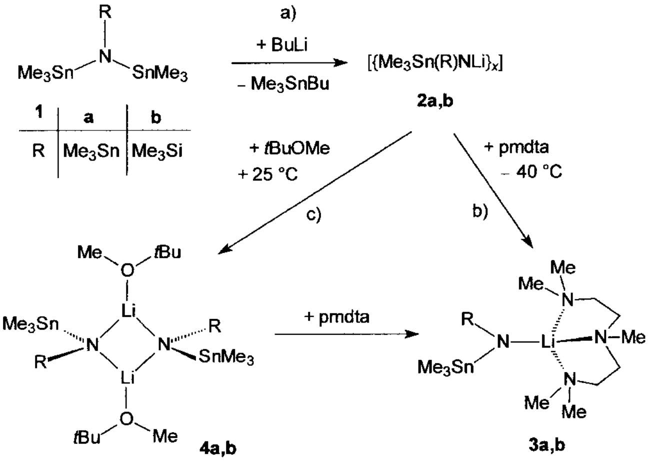
The enormous synthetic utility of *N*-lithiosilylamines, in particular of *N*-lithiobis(trimethylsilyl)amine, [$LiN(SiMe_3)_2$],[1] has been well documented.[2] In contrast, related tin derivatives have remained unknown so far, and *N*-lithiostannylamines in general have received scant attention,[3] probably because of the greatly enhanced reactivity of the Sn–N bond[4] when compared with Si–N bonds. However, this enhanced reactivity is desirable in metal amides for further transformations, and therefore, selective smooth syntheses of such amides bearing one or two trimethylstannyl groups at the nitrogen atom are an attractive goal. We have now succeeded in obtaining pure *N*-lithiobis(trimethylstannyl)-amine, [$LiN(SnMe_3)_2$] (**2a**), and *N*-lithiotrimethylsilyl(trimethylstannyl)amine, [$LiN(SiMe_3)SnMe_3$] (**2b**), for the first time from the 1:1 reaction of tris(trimethylstannyl)amine, $(Me_3Sn)_3N$ (**1a**),[5] and trimethylsilylbis(trimethylstannyl)-amine, $(Me_3Sn)_2NSiMe_3$ (**1b**),[6] respectively, with butyllithium (Scheme 1). The low solubility of **2a**,**b** points to a mixture of oligomers ($x \approx \infty$ in Scheme 1).



Scheme 1. Synthesis of **2a**,**b**, **3a**,**b**, and **4a**,**b**. $x = 1, 2$.

The reaction of **1a** or **1b**, dissolved in hexane, with BuLi in hexane (Scheme 1a) afforded colorless, extremely air- and moisture-sensitive powders that could be isolated and stored

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for prolonged time under argon atmosphere. After addition of *N,N',N''*-pentamethyldiethylenetriamine ($(Me_2NCH_2CH_2)_2$-NMe; pmdta) to a suspension of **2a** in hexane at −40 °C, crystalline $[(Me_3Sn)_2NLi(pmdta)]$ (**3a**) was isolated (Scheme 1b). When **2a** was dissolved in *t*BuOMe, in the absence of pmdta, the dimer $[\{(Me_3Sn)_2NLi(t\text{BuOMe})\}_2]$ (**4a**) was obtained as a crystalline product (Scheme 1c). Compound **2b**, dissolved in *t*BuOMe (Scheme 1c), gave the analogous dimer $[\{Me_3Sn(Me_3Si)NLi(t\text{BuOMe})\}_2]$ (**4b**), and treatment of **4b**, dissolved in *t*BuOMe, with pmdta, afforded the mononuclear species $[Me_3Sn(Me_3Si)NLi(pmdta)]$ (**3b**) in good yield.

The solid-state molecular structures of **3a**[7] and **4a**[8] are shown in Figures 1 and 2, respectively. The sterically demanding stannyl group has a special influence on the bonding properties in these metal amides. The bond length Li1–N1 (1.92(1) Å) in **3a** is the shortest so far for a bond to a tetracoordinate Li atom (e.g. *d*(Li–N) = 1.98(2) Å in $[(Me_3Si)_2NLi(pmdta)]$[9, 10]). The Sn1–N1 (1.994(5) Å) and Sn2–N2 (1.995(5) Å) distances in **3a** are the shortest Sn–N single bonds observed as yet (see e.g. **1a**: *d*(Sn–N) = 2.037(6) Å (av)[11]). In spite of this, the Sn-N-Sn angle (115.5(2)°) is smaller than in any known structure of bis(trimethylstannyl)amine derivatives containing a three-coordinate nitrogen atom. In contrast, the silicon analogue of **3a**, $[(Me_3Si)_2NLi(pmdta)]$, displays a wide Si-N-Si angle (125.3(2)°).[9, 10] Although this wide angle may be caused by repulsive interactions of the silyl groups, the different electronic properties of the Si–N and Sn–N bonds need to be taken into consideration when discussing the molecular structures of these compounds. The nitrogen atom in **3a** resides in a trigonal-planar environment.

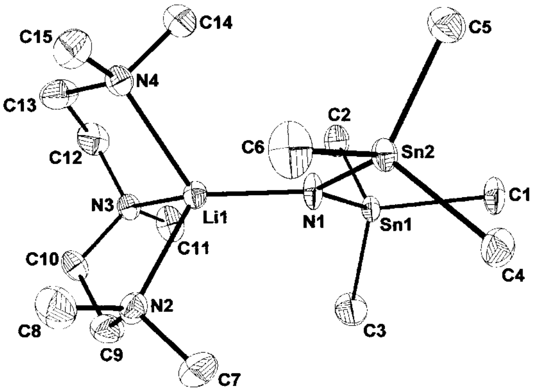


Figure 1. Molecular structure of $[(Me_3Sn)_2NLi(pmdta)]$ (**3a**; ORTEP, thermal ellipsoids represent a 25 % probability). Selected bond lengths [Å] and angles [°]: Li1-N1 1.92(1), Sn1-N1 1.994(5), Sn2-N1 1.995(5), Li1-N2 2.15(1), Li-N3 2.18(1), Li1-N4 2.22(1), Sn1-C1 2.179(7), Sn1-C2 2.145(8), Sn1-C3 2.145(9), Sn2-C4 2.148(7), Sn2-C5 2.162(8), Sn2-C6 2.157(8); Sn1-N1-Sn2 115.5(2), Sn1-N1-Li1 123.8(4), Sn2-N1-Li1 120.6(4), N1-Li1- N2 116.1(5), N1-Li1-N3 129.4(6), N1-Li1-N4 120.2(6),C2-Sn1-C3 108.2(4), C1-Sn1-C2 103.7(3), N1-Sn1-C1 115.8(3).

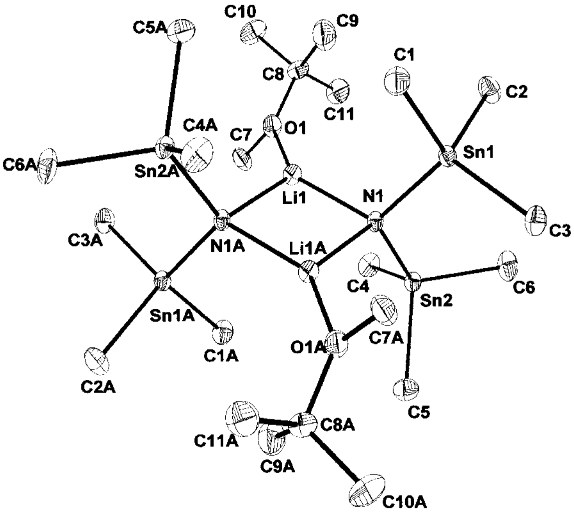


Figure 2. Molecular structure of $[\{(Me_3Sn)_2NLi(t\text{BuOMe})\}_2]$ (**4a**; ORTEP, thermal ellipsoids represent a 25 % probability). Selected bond lengths [Å] and angles [°]: Li1-N1 2.001(5), Li1A-N1 2.022(5), Sn1-N1 2.032(2), Sn2-N1 2.032(2), Li1-O1 1.987(6), O1-C8 1.437(5), Sn1-C1 2.153(3), Sn1-C2 2.164(3), Sn1-C3 2.160(3), Sn2-C6 2.167(3); Sn1-N1-Sn2 111.0(1), Sn1-N1-Li1 115.4(2), Sn2-N1-Li1 120.2(2), N1-Li1-N1A 103.9(2), Li1-N1-Li1A 76.1(2), N1-Sn1-C1 107.4(1), N1-Sn2-C6 114.4(1).

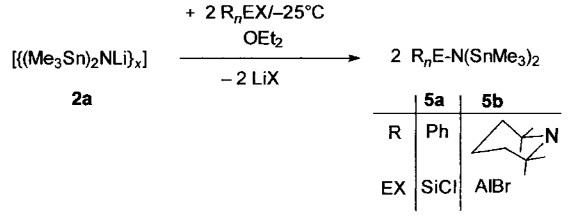
In the dimer **4a**, the lithium atoms are three-coordinate, and the N_2Li_2 ring is planar. The Li–N distances are longer than those in **3a**, but slightly shorter than those in the dimer $[\{(Me_3Si)_2NLi(Et_2O)\}_2]$.[12] The planes around the lithium and the oxygen atoms in **4a** form an angle of about 40°. The N-Li-N angle of 103.9(2)° as well as the Li-N-Li angle of 76.1(2)° are similar to that in the corresponding bis(silyl) derivative. However, the small Sn-N-Sn angle (111.0(1)°) in **4a** (which is even smaller than in **3a**) is again remarkably different from the Si-N-Si angle (121.9(4)°).

The relationship between solid-state structures of lithium amides[13] and their state of association in solution[14] can be assessed best by studying ^{6}Li- and ^{15}N-labeled material. Therefore, the reactions of ^{15}N-labeled (ca. 12 %) **1a** and **1b** with ^{6}Li-labeled (99 %) MeLi in *t*BuOMe were carried out and studied by ^{6}Li, ^{15}N, and ^{119}Sn NMR spectroscopy. After complete reaction of **1a** with MeLi in *t*BuOMe, **4a** was formed as a single species together with Me_4Sn. The dimer **4a** was identified by the typical pattern in the ^{15}N NMR spectrum (coupling of ^{15}N nucleus with two equivalent ^{6}Li nuclei) and by the intensities of the ^{15}N satellites in the ^{6}Li NMR spectrum (according to the degree of ^{15}N labeling). Furthermore, the ^{119}Sn NMR spectrum of **4a** shows a single resonance, accompanied by ^{15}N satellites and ^{117}Sn satellites with correct intensities. Therefore, the structure of the dimer **4a** at low temperature is retained in solution. When pmdta was added to the solution of **4a** in *t*BuOMe, the presence of mainly two species, **3a** and **4a**, and a minor unidentified compound, became apparent.

The monomeric structure of **3a** (−40 °C) follows from the 1:1:1 triplet ($^1J(^{15}N,^6Li) = 7.5$ Hz) in the ^{15}N NMR spectrum. This confirms that only one ^{6}Li atom is linked to the central nitrogen atom. The ^{6}Li NMR spectrum (−40 °C) displays a singlet, which is accompanied by satellite signals with coupling constants of $^1J(^{15}N,^6Li) \approx 7.5$ Hz and $^2J(^{119/117}Sn,^6Li) \approx 7.5$ Hz. The monomer **3a** exhibits a broad ^{119}Sn NMR signal at room temperature which splits below −20 °C into two broadened signals of equal intensity. Again there are ^{15}N satellites, as well as ^{119}Sn (AB spin system) and ^{117}Sn satellites (AX spin system), indicating that the two ^{119}Sn NMR signals belong to tin atoms in the same molecule. Apparently there is restricted rotation about the $Li–N(SnMe_3)_2$ bond ($\Delta G^{\neq} = 43.1 \pm 1.0$ kJ mol^{-1}), a feature observed here for the first time.

Thus, the molecular structure in solution must be very similar to that "frozen" in the solid state. Similar findings can be deduced fom the NMR data available for **3b** and **4b**; in this case additional data arises from the presence of the ^{29}Si isotope. The low-temperature NMR spectra are further complicated by the presence of two isomers in the case of **4b** and two rotamers in the case of **3b**.[15]

The application of the new building blocks has been documented with two extreme examples. The reactions of the bulky substituted silicon and aluminum halides with **2a** [Eq. (1)] proceed under mild conditions (–25 °C) providing



(1)

the products in good yield. These reactions can be carried out with crude **2a**, isolated as a powdery substrate, redissolved in Et_2O. The reaction of the halides with **1a** instead of **2a** was unsuccessful even at elevated temperatures. To our knowledge there is no other convenient route for the introduction of the distannylamine moiety.[15]

Experimental Section

N-lithiobis(trimethylstannyl)amine **2a**, $[(Me_3Sn)_2NLi(pmdta)]$ (**3a**), and $[(Me_3Sn)_2NLi(MeO\mathit{t}Bu]_2$ (**4a**): A solution of **1a** (2.53 g, 5 mmol) in hexane (20 mL) was cooled at –50 °C, and BuLi (3.1 mL, 1.6 M in hexane) was added dropwise over 15 min under vigorous stirring. After the reaction mixture had been allowed to slowly attain ambient temperature (15 h), the white precipitate was filtered off, and volatile material was removed in vacuo (10^{-3} Torr, 4 h). The colorless, extremely air- and moisture-sensitive powder **2a** was suspended in hexane (20 mL), cooled at –40 °C, and pmdta (1.0 mL, 0.87 g, 5.0 mmol) was added. The colorless liquid was cooled in a freezer at –78 °C for 30 days, from which **3a** (1.80 g, 69 %; m.p. >128 °C (decomp)) crystallized as colorless prisms. Dissolution of **2a** in *t*BuOMe (15 mL), followed by storage of the solution at –20 °C for 10 days gave crystals of the dimer **4a** (1.66 g, 76 %; m.p. >260 °C (decomp)). The compounds **2b**, **3b**, and **4b** could be obtained in the same way.[15]

3a: ^{1}H, ^{13}C, ^{6}Li, ^{15}N, and ^{119}Sn NMR (C_6D_6 or [D$_8$]toluene): $\delta(^1H) = 0.37$ (s, $^2J(^{119}Sn,^1H) = 48.8$ Hz, 18 H; $SnMe_3$), 1.68–1.72 (br s, 15 H; NMe and NMe_2), 2.01–2.18 (br s, 8 H; CH_2); $\delta(^{13}C) = -0.2$ ($^1J(^{119}Sn,^{13}C) = 297.3$ Hz, $SnMe_3$), 46.2 (NMe_2), 53.7 (NMe), 57.1, 58.4 (CH_2); at –40 °C: $\delta(^6Li) = 2.7$ ($^1J(^{15}N,^6Li) = 7.5$, $^2J(^{119}Sn,^6Li) = 7.5$ Hz); $\delta(^{15}N) = -359.6$ (1:1:1 t, $^1J(^{15}N,^6Li) = 7.5$ Hz); $\delta(^{119}Sn) = 49.3$ (br s, $^1J(^{119}Sn,^{15}N) = 148$, $^2J(^{119}Sn,^{117}Sn) = 470$ Hz), 54.4 (br s, $^1J(^{119}Sn,^{15}N) = 146$, $^2J(^{119}Sn,^{117}Sn) = 470$ Hz).

4a: ^{1}H, ^{13}C, ^{6}Li, ^{15}N, and ^{119}Sn NMR ([D$_8$]toluene): $\delta(^1H) = -0.69$ (s, $^2J(^{119}Sn,^1H) = 49.2$ Hz, 36 H; $SnMe_3$), 1.02 (s, 18 H; *t*Bu), 3.05 (s, 6 H; Me); $\delta(^{13}C) = -1.83$ ($^1J(^{119}Sn,^{13}C) = 320.6$ Hz, $SnMe_3$), 27.2 ($(CH_3)_3$), 50.2 (OMe), 75.0 (OC); at –40 °C: $\delta(^6Li) = 3.1$ ($^1J(^{15}N,^6Li) = 4.5$ Hz); $\delta^{15}N = -366.2$ (1:2:3:2:1 q, $^1J(^{15}N,^6Li) = 4.5$ Hz), $\delta(^{119}Sn) = 63.0$ (br s, $^1J(^{119}Sn,^{15}N) = 143.5$, $^2J(^{119}Sn,^{117}Sn) = 467$ Hz).

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[7] a) Crystal structure analysis: Siemens/Bruker P4 diffractometer, CCD area detector with Siemens LT 2 device; $Mo_{K\alpha}$ radiation, $\lambda = 0.71063$ Å, graphite monochromator; single crystals, coated with perfluoroether oil, were mounted on a glass fiber. Crystal data were determined and intensity data recorded at 193 K. The data reduction was carried out by using the program SAINT, the structure solution by the Patterson method, and the refinement by using the SHELXTL system;[16] final refinement was performed by using the SHELX-97 programs.[17] All atoms except the hydrogen atoms are described with anisotropic temperature factors, all hydrogen positions were geometrically placed (d(C–H) = 0.96 Å) and refined by using the riding model and fixed U_{ij}. b) Crystal structure data of **3a**: $M_r = 521.84$; colorless rhombs; size 0.20 × 0.20 × 0.30 mm, monoclinic; space group $P2(1)/n$, $Z = 4$, $a = 9.671(1)$, $b = 15.367(3)$, $c = 17.007$ Å, $\beta = 101.73(1)°$, $V = 2474.82(5)$ Å^3, $\rho_{calcd} = 1.401$ Mg m^{-3}, $\mu = 2.020$ mm^{-1}, $F(000) = 1048$. Data collection: 10248 reflections in $-10 \leq h \leq 10$, $-17 \leq k \leq 12$, $-18 \leq l \leq 18$, 2θ range 13.64–46.50°; 3078 independent reflections; $R_{int} = 0.0366$, 2331 reflections with $F_o > 4\sigma(F_o)$, semiempirical absorption correction, max/min transmission: 1.000/0.787; GOOF = 1.117; 210 variables, $R = 0.040$, $wR^2 = 0.0919$, largest difference peak: 0.921 e Å^{-3}. c) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-159571 (**3a**) and CCDC-159570 (**4a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[8] Crystal structure data of **4a**: General data see ref. [7a]. Crystal data: $M_r = 436.68$; colorless prism; size 0.20 × 0.20 × 0.20 mm, monoclinic; space group $P2(1)/n$, $Z = 4$, $a = 9.912(2)$, $b = 17.966(4)$, $c = 10.925(3)$ Å, $\beta = 112.12(1)°$, $V = 1802.4(7)$ Å^3, $\rho_{calcd} = 1.609$ Mg m^{-3}, $\mu = 2.756$ mm^{-1}, $F(000) = 856$. Data collection: 8637 reflections in $-10 \leq h \leq 11$, $-21 \leq k \leq 21$, $-12 \leq l \leq 12$, 2θ range = 13.64–49.42°; 2709 independent reflections; $R_{int} = 0.0271$, 2412 reflections with $F_o > 4\sigma(F_o)$, semiempirical absorption correction, max/min transmission: 0.6087/0.6087; GOOF = 1.109, 196 variables, $R = 0.0262$, $wR^2 = 0.0580$, largest difference peak: 0.605 e Å^{-3}.[7c]

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