A Chiral Triamidostannate: Its Structure and Properties as a Nucleophile†

Harald Memmler, Uta Kauper, Lutz H. Gade,* and Dietmar Stalke

Institut für Anorganische Chemie der Universität Würzburg, Am Hubland,
D-97074 Würzburg, Germany

Joseph W. Lauher

Department of Chemistry, State University of New York, Stony Brook, New York 11794

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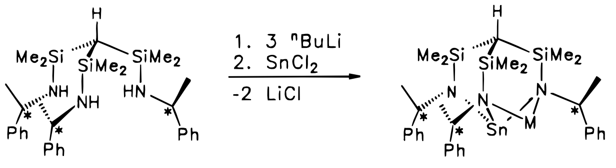
*Summary: The first enantiomerically pure chiral triamidostannate, HC{SiMe₂N[(S)-CH(Me)Ph]}₃SnLi(THF) (**2**), has been synthesized and structurally characterized; the crystal structure of the derived Sn−Ni heterobimetallic complex [Li(THF)₄][HC{SiMe₂N[(S)-CH(Me)Ph]}₃-Sn−Ni(CO)₃] (**5**) is reported.*

The versatility of organotin compounds in organic synthesis has recently fueled the development of chiral stannanes with the aim of effecting enantioselective transformations using these reagents.[1] Whereas all the reported species of this type are derivatives of tetravalent tin,[2] there has so far been no example of an enantiomerically pure chiral tin(II) compound in the literature. The anionic stannates(II), in particular, are valuable metal nucleophiles[3,4] which may be transformed to the corresponding stannanes by simple nucleophilic substitution or addition reactions.[5]

The facile accessibility of triamidostannates containing a tripodal amido ligand[6] along with the possibility of generating enantiomerically pure C_3-chiral tripod ligands provided the motivation for the the synthesis of a chiral stannate and a study of its properties as a metal nucleophile. Lithiation of the previously reported triamine $HC\{SiMe_2NH[(S)\text{-}CH(Me)Ph]\}_3$[7] with 3 molar equiv of *n*-BuLi and subsequent reaction with $SnCl_2$ gave the chiral stannate **1** in almost quantitative yield as evidenced by NMR spectroscopy (Scheme 1).

Scheme 1



M = Li **1**
M = Li(THF) **2**

Using THF as the reaction medium for the lithiation or addition of THF to **1** led to the isolation of the monosolvated species **2**. The ^{1}H, ^{13}C, and ^{29}Si NMR resonances of the stannate unit in both **1** and **2** indicate the reduction of its potentially 3-fold symmetry due to direct coordination of the cation to the tripodal triamidostannte anion.[8] The mode of coordination of the Li^+ or $Li(THF)^+$ cation was established by a single-crystal X-ray structure analysis of **2** (Figure 1).[9] This revealed its position as bridging between two amido N atoms, a situation which leads to a remarkable distortion of the stannate cage.

The Li atom “ties” the two amido functions involved together, generating an N-donor arrangement which deviates from the otherwise more or less undistorted trigonal-monopyramidal arrangement of the N_3Sn unit (N(1)−Sn−N(3) = 82.6(2)° but N(1)−Sn−N(2) = 99.2(2)° and N(2)−Sn−N(3) = 102.0°). Another structural consequence of the direct bonding of the amidostannate to the cation is the rotation of the $SiMe_2$ groups at Si(1) and Si(3) to an almost eclipsed arrangement, which

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† We dedicate this paper to Professor Max Herberhold on the occasion of his 60th birthday.

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[1] (a) Marshall, J. A. *Chem. Rev.* **1996**, *96*, 31. Yamamoto, Y., Ed. Organotin Compounds in Organic Synthesis. *Tetrahedron* **1987**, *45*, 909. (b) Omae, I. *Organotin Chemistry*; Elsevier: Amsterdam, 1989.

[2] Nozaki, H. In *Organometallics in Synthesis-A Manual*; Schlosser, M., Ed.; Wiley: New York, 1994; p 535.

[3] Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987.

[4] Studies of solid-state structures: (a) Reed, D.; Stalke, D.; Wright, D. S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1459. (b) Veith, M.; Ruloff, C.; Huch, V.; Töllner, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1381. (c) Hitchcock, P. B.; Lappert, M. F.; Lawless, G. A.; Royo, B. *J. Chem. Soc., Chem. Commun.* **1993**, 554. (d) Steiner, A.; Stalke, D. *J. Chem. Soc., Chem. Commun.* **1993**, 1702. (e) Steiner, A.; Stalke, D. *Inorg. Chem.* **1995**, *34*, 4846.

[5] Fieser, M. *Reagents for Organic Synthesis*; Wiley-Interscience: New York, 1990; Vol. 15.

[6] (a) Hellmann, K. W.; Steinert, P.; Gade, L. H. *Inorg. Chem.* **1994**, *33*, 3859. (b) Hellmann, K. W.; Gade, L. H.; Gevert, O.; Steinert, P.; Lauher, J. W. *Inorg. Chem.* **1995**, *34*, 4069.

[7] Memmler, H.; Gade, L. H.; Lauher, J. W. *Inorg. Chem.* **1994**, *33*, 3064.

[8] Preparation of **1** and **2**: To a solution of $HC\{SiMe_2NH[(S)\text{-}CH(Me)Ph]\}_3$[7] (1.35 g, 2.49 mmol) in 30 mL of diethyl ether which was cooled to −50 °C was added 3 mL of a 2.5 M solution of *n*-BuLi in hexanes, and the reaction mixture was warmed to ambient temperature within a period of 1 h. After recooling to −50 °C solid $SnCl_2$ (0.50 g, 2.63 mmol) was added; the reaction mixture was then warmed to room temperature and stirred for another 1 h. Removal of the solvent *in vacuo* and extraction with pentane yielded a solution of the crude product which was concentrated to 15 mL and left to crystallize at −20 °C. **1** was obtained as a colorless solid in 47% yield. Crystallization from a mixture of pentane−THF (1:1) afforded the solvated species **2** (yield 39%). Data for **1** are as follows. ^{1}H NMR (C_6D_6, 295 K): δ −0.92 (s, $HC(Si...)_3$), −0.71, 0.08, 0.30, 0.37, 0.40, 0.43 (s, $Si(CH_3)_2$), 1.36, 1.49, 1.90 (d, $^3J_{HH}$ = 6.9, 6.7, 6.7 Hz, $HCCH_3$), 4.32, 4.42, 4.96 (q, $HCCH_3$), 6.75−7.74 (m, C_6H_5). $^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): δ 4.5, 5.1, 5.4, 6.0, 7.1, 7.2 ($Si(CH_3)_2$), 9.8 ($HC(Si...)_3$), 24.1, 24.8, 27.8 ($HCCH_3$), 55.8, 56.4, 57.8 ($HCCH_3$), 124.2−131.2 ($C^{2,6}$,C^4, $C^{3,5}$ of C_6H_5), 150.0, 150.7, 154.0 (C^1 of C_6H_5). $^7Li\{^1H\}$ NMR (C_6D_6, 295 K): δ −0.25. $^{29}Si\{^1H\}$ NMR (C_6D_6, 295 K): δ −1.9, −1.0, 0.5. Anal. Calcd for $C_{31}H_{46}LiN_3Si_3Sn$: C, 55.42; H, 6.91; N, 6.26. Found: C, 55.30; H, 7.11; N, 6.02. Data for **2** are as follows. ^{1}H NMR (C_6D_6, 295 K): δ −0.90 (s, $HC(Si...)_3$), −0.22, 0.10, 0.14, 0.28, 0.51, 0.54 (s, $Si(CH_3)_2$), 1.15 (m, CH_2CH_2O), 1.52, 1.61, 2.02 (d, $^3J_{HH}$ = 6.7, 6.8, 6.8 Hz, $HCCH_3$), 3.22 (m, CH_2CH_2O), 4.35, 4.56, 5.05 (q, $HCCH_3$), 6.77−7.79 (m, C_6H_5). Anal. Calcd for $C_{35}H_{54}LiN_3OSi_3Sn$: C, 56.60; H, 7.33; N, 5.66. Found: C, 56.22; H, 7.05; N, 5.78.

[9] Crystal data for **2**: $C_{35}H_{54}LiN_3OSi_3Sn$, M_r = 742.72, orthorhombic, space group $P2_12_12_1$, a = 8.2893(2) Å, b = 20.8243(4) Å, c = 21.9993(4) Å, V = 3797.5(2) Å^3, T = 23 °C, Z = 4, D_c = 1.299 g cm^{-3}, $F(000)$ = 1552, μ(Mo Kα) = 0.796 mm^{-1}. R = 0.032 and R_w = 0.038 with $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{0.5}$.

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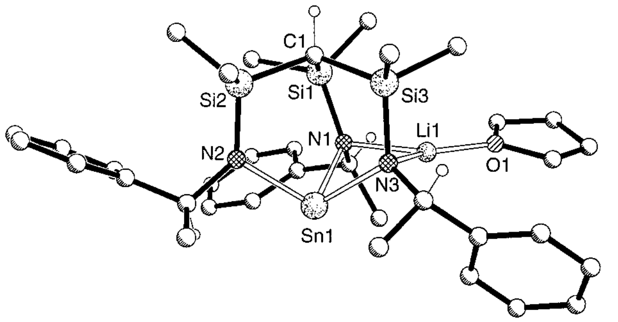


Figure 1. Molecular structure of **2**. Principal bond lengths (Å) and interbond angles (deg): Sn(1)−N(1) = 2.215(6), Sn-(1)−N(2) = 2.118(7), Sn(1)−N(3) = 2.190(6), N(1)−Li(1) = 2.09(2), N(3)−Li(1) = 2.06(2), O(1)−Li(1) = 1.95(1); N(1)−Sn−N(3) = 82.6(2), N(1)−Sn−N(2) = 99.2(2), N(2)−Sn−N(3) = 102.0(3), Sn(1)−N(3)−Li(1) = 85.4(5), Sn(1)−N(1)−Li(1) = 83.9(5).

has previously not been observed in tripodal amido complexes containing a trisilylmethane backbone due to steric repulsion of the methyl groups.

While the signal patterns in the NMR spectra of **1** and **2** indicate closely related structures and are consistent with a retention in solution of the structural arrangement established for the solid, both compounds differ significantly with respect to dynamic behavior in solution. The coordinated THF ligand appears to "lock" the Li cation in its position between the two N atoms, thus conferring structural rigidity upon the molecule on the NMR time scale. On the other hand, the nonsolvated compound **1** displays remarkable dynamic behavior. As ^{1}H-EXSY studies have revealed, the Li atom appears to "rotate" around the N_3Sn unit, generating an effective 3-fold molecular symmetry in the fast-exchange limit. This intramolecular motion is reminiscent of the dynamic behavior reported by Veith and coworkers for a tetraamidoindate,[10] although it appears to occur much more rapidly in the latter case.

In order to assess the properties of **1** and **2** as metal nucleophiles, their reactivity toward CH_3I, Me_3SnCl, and $Ni(CO)_4$ (and thus the displacement of both anionic and neutral "nucleofuges") was studied (Scheme 2).[11] All three reactions yielded products possessing molecular

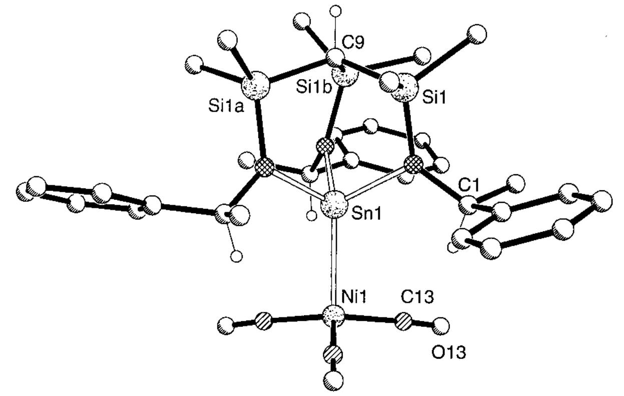
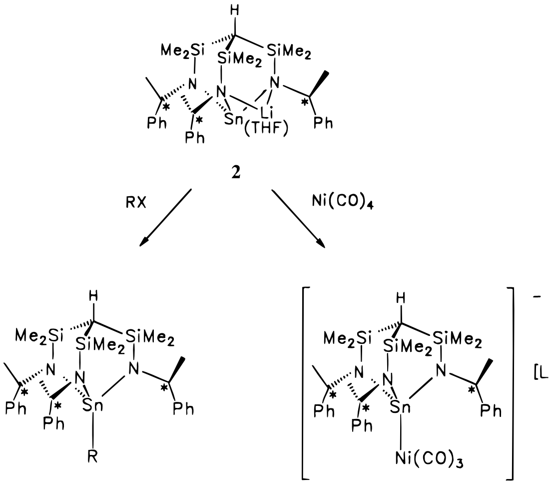


Figure 2. Structure of the $HC(Me_2SiNC(H)MeC_6H_5)_3$-$SnNi(CO)_3$ anion in the solid-state structure of **5**. The $Li(THF)_4$ cation is omitted for clarity. Selected bond lengths (Å) and interbond angles (deg): Sn(1)−N(1) = 2.086(6), Sn-(1)−Ni(1) -= 2.492(2), Si(1)−N(1) = 1.720(7), N(1)−C(1) = 1.46(1), Ni(1)−C(13) = 1.77(1); N(1)−Sn−N(1a) = 99.1(2), C(13)−Ni(1)−C(13a) = 116.0(2).

Scheme 2



$R = CH_3$ **3**
$R = Sn(CH_3)_3$ **4**

C_3 symmetry. In view of the highly crystalline nature of the Sn−Ni heterobimetallic complex **5**, the latter was chosen for an X-ray crystallographic study (Figure 2).[12]

Although the anionic complex $[(Ph_3Sn)Ni(CO)_3]^-$ was first reported by Kruck *et al.* in 1969,[13] there has been no report of a crystal structure of an $[(R_3Sn)Ni(CO)_3]^-$ anion to date. Crystals of **5** were found to be extremely air- and moisture-sensitive, instantaneously turning opaque when isolated due to loss of lattice solvent. Therefore, the flask as well as the flushing argon were cooled to ca. −80 °C during crystal selection. Crystals were handled and transferred to the diffractometer at about −80 °C, and data were collected at −120 °C.[14] The trisilylmethane and triamidostannate units are part of

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(10) Veith, M.; Zimmer, M.; Müller-Becker, S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1731.

(11) Data for **3** are as follows. ^{1}H NMR (C_6D_6, 295 K): δ −0.77 (s, HC(Si...)$_3$), −0.61 (s, $SnCH_3$), 0.37, 0.39 (s, $Si(CH_3)_2$), 1.24 (d, $^3J_{HH}$ = 6.6 Hz, $HCCH_3$), 4.36 (q, $HCCH_3$), 7.04−7.38 (m, C_6H_5). $^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): δ −24.4 ($SnCH_3$, $^2J_{SnH}$ = 73 Hz), 5.4, 6.1 ($Si(CH_3)_2$), 7.8 (HC(Si...)$_3$), 26.0 ($HCCH_3$), 53.9 ($HCCH_3$), 126.6, 127.6, 128.3 ($C^{2,6}$,C^4, $C^{3,5}$ of C_6H_5), 148.9 (C^1 of C_6H_5). $^{29}Si\{^1H\}$ NMR (C_6D_6, 295 K): δ 5.3. $^{119}Sn\{^1H\}$ NMR (C_6D_6, 295 K): δ −41.2 Anal. Calcd for $C_{32}H_{49}N_3Si_3Sn$: C, 56.53; H, 7.27; N, 6.18. Found: C, 56.32; H, 7.36; N, 5.97. Data for **4** are as follows. ^{1}H NMR (C_6D_6, 295 K): δ −0.79 (s, HC(Si...)$_3$), −0.27 (s, $SnCH_3$, $^2J_{SnH}$ = 54 Hz, $^3J_{SnH}$ = 26 Hz), 0.31, 0.38 (s, $Si(CH_3)_2$), 1.55 (d, $^3J_{HH}$ = 6.6, $HCCH_3$), 4.52 (q, $HCCH_3$), 7.10−7.61 (m, C_6H_5). $^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): δ −6.2 ($SnCH_3$), 6.5, 6.6 ($Si(CH_3)_2$), 8.8 (HC(Si...)$_3$), 27.0 ($HCCH_3$), 55.9 ($HCCH_3$), 126.7, 127.7, 128.4 ($C^{2,6}$,C^4, $C^{3,5}$ of C_6H_5), 148.9 (C^1 of C_6H_5). $^{29}Si\{^1H\}$ NMR (C_6D_6, 295 K): δ 4.5. $^{119}Sn\{^1H\}$ NMR (C_6D_6, 295 K): δ −50.2 (N_3Sn), −94.9 ($SnCH_3$). Anal. Calcd for $C_{34}H_{55}N_3Si_3Sn_2$: C, 49.37; H, 6.70; N, 5.08. Found: C, 49.21; H, 6.78; N, 4.89. Data for **5** are as follows. ^{1}H NMR (d_6-DMSO, 295 K): δ −1.09 (s, HC(Si...)$_3$), −0.30, −0.00 (s, $Si(CH_3)_2$), 1.66 (d, $^3J_{HH}$ = 6.8 Hz, $HCCH_3$), 1.84 (m, CH_2CH_2O), 3.70 (m, CH_2CH_2O), 4.76 (q, $HCCH_3$), 7.18−7.61 (m, C_6H_5). $^{13}C\{^1H\}$ NMR (d_6-DMSO, 295 K): δ 6.8, 7.3 ($Si(CH_3)_2$), 11.1 (HC(Si...)$_3$), 25.1 (CH_2CH_2O), 25.5 ($HCCH_3$), 55.2 ($HCCH_3$), 67.9 (CH_2CH_2O), 124.9, 127.0, 127.4 ($C^{2,6}$,C^4, $C^{3,5}$ of C_6H_5), 150.0 (C^1 of C_6H_5), 201.7 (CO). $^7Li\{^1H\}$ NMR (d_6-DMSO, 295 K): δ 1.1. $^{29}Si\{^1H\}$ NMR (d_6-DMSO, 295 K): δ 2.0. $^{119}Sn\{^1H\}$ NMR (d_6-DMSO, 295 K): δ 195.5. IR (toluene): ν(CO) 1987 (s, br), 1964 (sh) cm^{-1}. Due to facile loss of THF upon isolation a correct elemental analysis could not be obtained.

(12) Crystal data for **5**: $C_{54}H_{86}LiN_3O_8Si_3NiSn$, M_r = 1173.87, cubic, space group $P2_13$, a = 1.8298(2) Å, V = 6126.2(12) Å^3, T = −153 °C, Z = 4, D_c = 1.273 g cm^{-3}, $F(000)$ = 2472, μ(Mo Kα) = 0.823 mm^{-1}. R1($F > 4\sigma(F)$) = 0.048 and wR2 = 0.141 (all data) with $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{0.5}$ (Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467. Sheldrick, G. M. SHELXL-96, Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1996).

(13) Kruck, T.; Herber, B. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 679.

(14) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615.

a [2.2.2]bicyclooctane-related cage with one of the bridgehead positions being occupied by the Sn−Ni(CO)$_3$ fragment. The Sn(1)−Ni(1) vector is aligned along the 3-fold crystallographic axis imposing exact C_3 symmetry upon the anion. The lithium atom of the Li(THF)$_4^+$ cation is also located on the 3-fold axis, whereas the oxygen atom and the center of the opposite CH$_2$−CH$_2$ bond of one THF molecule are close to it. This imposes a 3-fold disorder upon this single THF molecule with site occupation factors of 0.33 each. The approximately tetrahedral coordination sphere of the lithium cation is completed by another THF molecule on a general position, resulting in three additional coordinated solvent molecules. The Sn−Ni bond length of 2.492(2) Å lies within the previously observed range found for Sn−M heterobimetallics (M = 3d transition metal).[15] The coordination of the Lewis acidic Ni(CO)$_3$ fragment to the Lewis basic stannate effects a significant contraction of the Sn−N distances (Sn(1)−N(1) = 2.086(6) Å) in comparison to **2** (average Sn−N = 2.174(6) Å). The stannate ligand is readily displaced from the nickel by better donors such as phosphines and isocyanides.

In conclusion, we have provided a facile access to the first example of an enantiomerically pure chiral stannate and have established its nature as a metal nucleophile. The reactivity of this species is currently being investigated.

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Supporting Information Available: Text giving preparative procedures for compounds **3**−**5** and tables of crystal data, fractional coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates and figures giving additional views of **2** and **5** (21 pages). Ordering information is given on any current masthead page.

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[15] Holt, M. S.; Wilson, W. L.; Nelson, J. H. *Chem. Rev.* **1989**, *89*, 11.