New Silyl-Substituted Tin-Nitrogen Heterocubanes: Fourfold Metal-Coordinated Nitrogen and Exceptional Chemical and NMR Properties

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Dedicated to Prof. Schmutzler on the occasion of his 65th birthday

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The synthesis of new silyl-substituted tin-nitrogen heterocubanes and the structural analysis of $[Me_3SiNSn]_4$ is described. A sharp signal in the ^{14}N NMR spectrum and a septet in the ^{119}Sn NMR spectrum are among the interesting properties of this new type of compound with nitrogen surrounded by four (hemi)metals.

Introduction

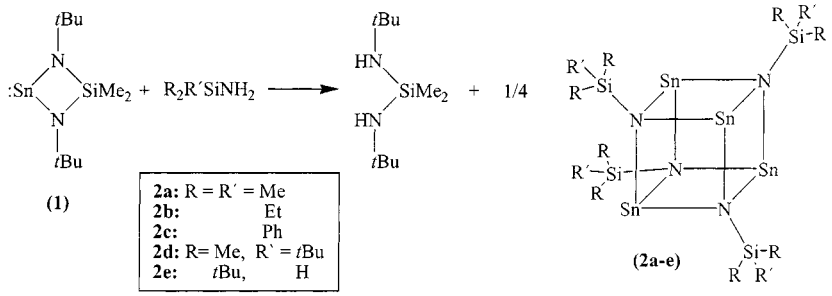
Iminostannylenes of the type $[SnNR]_4$ have been known for about twenty years and were prepared and examined with varying substituents (e.g. R = *t*Bu,[1] *i*Pr, NMe_2,[2] 2,6-$iPr_2C_6H_3$, $BMes_2$,[3] C_6H_{11}, 2-$CH_2C_5H_4N$,[4] Ph[5]).[6] The main structural feature of these compounds is a Sn_4N_4 cage which represents a distorted heterocubane or two interpenetrating tetrahedrons (Sn_4 or N_4), with the R ligands at the nitrogen atoms.

Results and Discussion

From the reaction of the cyclic diazastannylene **1** with primary silylamines (Scheme 1) it was possible to extend the spectrum of substituents to give a new class with silicon, which is the most electropositive element bonded to the nitrogen atom up to now. In addition, the nitrogen carries four electropositive ligands (three metals, one hemimetal) which is unusual for this element. To the best of our knowledge, only three compounds have been characterized by crystal structure analysis where nitrogen is surrounded by four tin(IV) atoms[7] or two silicon and two germanium(II) atoms.[8]

Because of the high condensation tendency of trimethylsilylamine,[9] it had to be synthesised and reacted in situ with **1** to obtain directly **2a**. With other silylamines, we obtained a seconorcubane-like cage $Sn_3H_2(NSiRR'_2)_4$ as an intermediate in the synthesis of **2b–e**, which is analogous to the reaction observed with *tert*-butylamine.[1a] At high temperatures and with reduced pressure (240 °C, 0.01 Torr) it can be transformed to the corresponding cubane-like cage.

The X-ray structure analysis of **2a** reveals, to a good approximation, a $\bar{4}3m$ (T_d) molecular symmetry, but the molecule has only one crystallographic mirror plane passing through Sn(1)−Sn(2)−N(1)−N(2). At the four corners of the distorted Sn_4N_4 cube the Me_3Si groups are located in a staggered form towards the divalent tin atoms (Figure 1). Compound **2a** is the first compound known to us where a nitrogen atom is surrounded by three tin atoms and one silicon atom. The Sn−N bonds in **2a** are slightly shorter than those in the *tert*-butyl-derivative $[tBuNSn]_4$, whereas the Si−N bonds are exceptionally short. The average distance is only about 173 pm whereas 179−183 pm is expected for quaternary nitrogen; only a few exceptions are known.[10]



Scheme 1. General synthesis for $[R'R_2Si–NSu]_4$ (**2a**–**2e**)

Because of this special coordination environment the nitrogen shows unusual NMR properties which are not usually found for (metal)organic compounds. The four electropositive elements surround the ^{14}N nucleus so symmetric-

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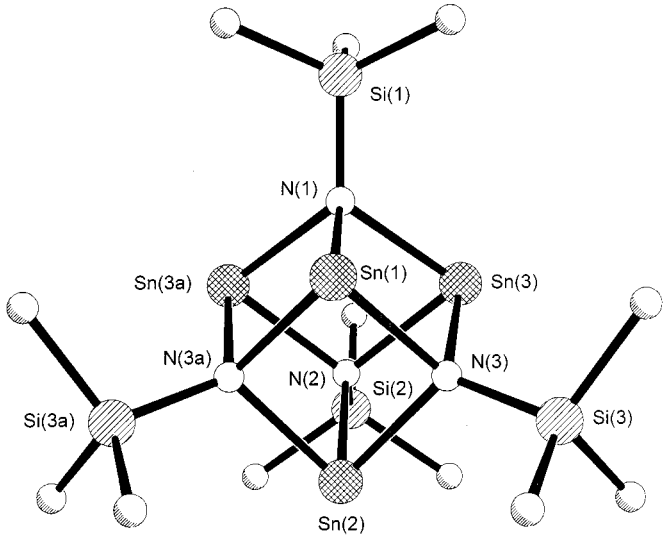

Figure 1. X-ray structure of **2a**; carbon atoms are not labelled; selected distances (average) [pm] and angles [°]: Sn−N 219.6(4), Sn−Sn 329.5(1), Si−N 172.7(4); N−Sn−N 82.3(2), Sn−N−Sn 97.2(2)

ally that its quadrupole moment does not affect the measurability of a ^{14}N NMR spectrum in a negative way. It is possible to get good ^{14}N signals with a half-height width of 8 Hz for the compounds **2a−e**; these signals are accompanied by Sn satellites (integration: approximately 35% of the signal, as expected[11] for three Sn atoms).[12] In addition to that the three ^{14}N nuclei ($I = 1$) around each ^{119}Sn atom split the tin resonance into a septet with an intensity ratio of 1:3:6:7:6:3:1 (Figure 2). The small satellite signals marked with stars are ^{117}Sn satellites with $^{2}J(^{117}Sn,^{119}Sn) = 57$ Hz, as proved by simulation[13] of the spectrum.

The tests on the reactivity of **2b** showed a remarkable stability of the Sn−N and Si−N bonds. No reaction could be observed with $AlCl_3$, $SnCl_4$, $ZnCl_2$, CuCl, Me_3SnCl, Ph_3SnCl, Me_3SiN_3, LiOMe, NaO*t*Bu, *t*BuOH, LiOH or NH_3, even under drastic conditions with some of them. This is probably due to the special bonding situation of the nitrogen with the neighbouring atoms.

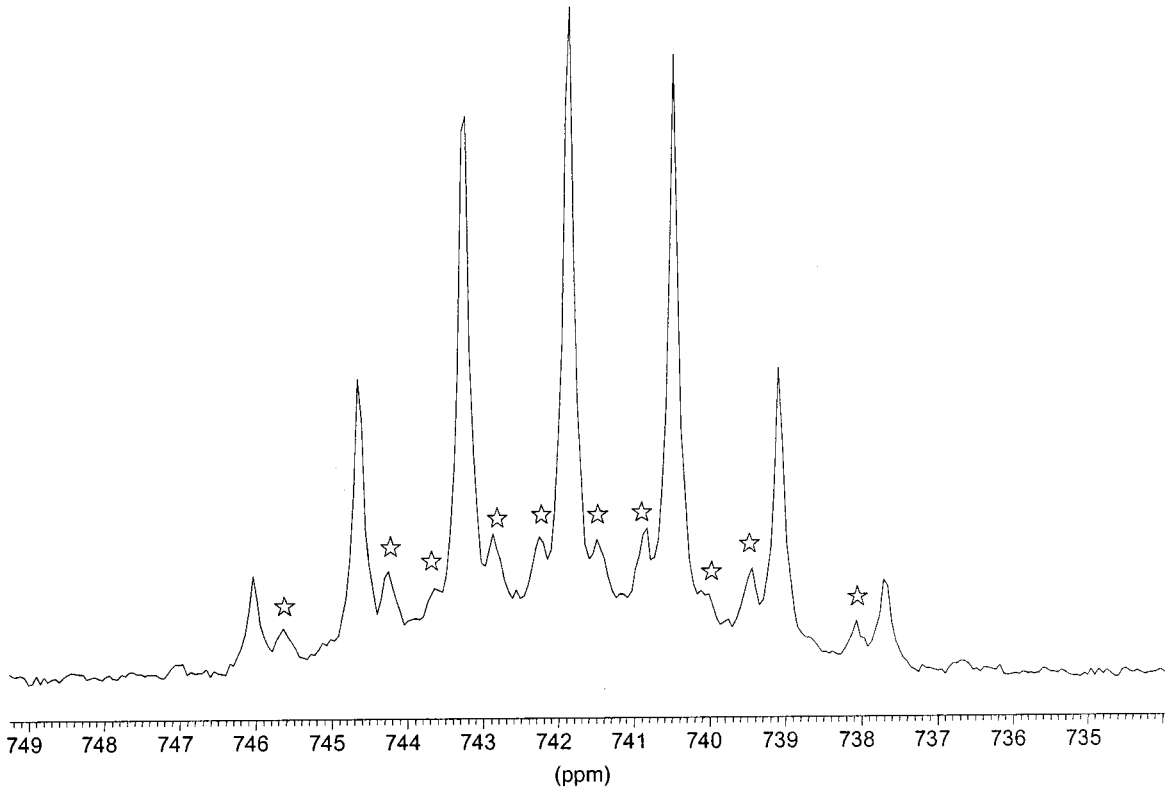

Figure 2. ^{119}Sn NMR spectrum of **2d**; couplings to three ^{14}N nuclei ($I = 1$) are responsible for the extraordinary splitting of the ^{119}Sn signal into a septet with a coupling constant of $^{1}J(^{14}N,^{119}Sn) = 103.8$ Hz, the signal intensities are in the ratio 1:3:6:7:6:3:1; the peaks marked with stars are ^{117}Sn satellite signals with $^{2}J(^{117}Sn, ^{119}Sn) = 57$ Hz

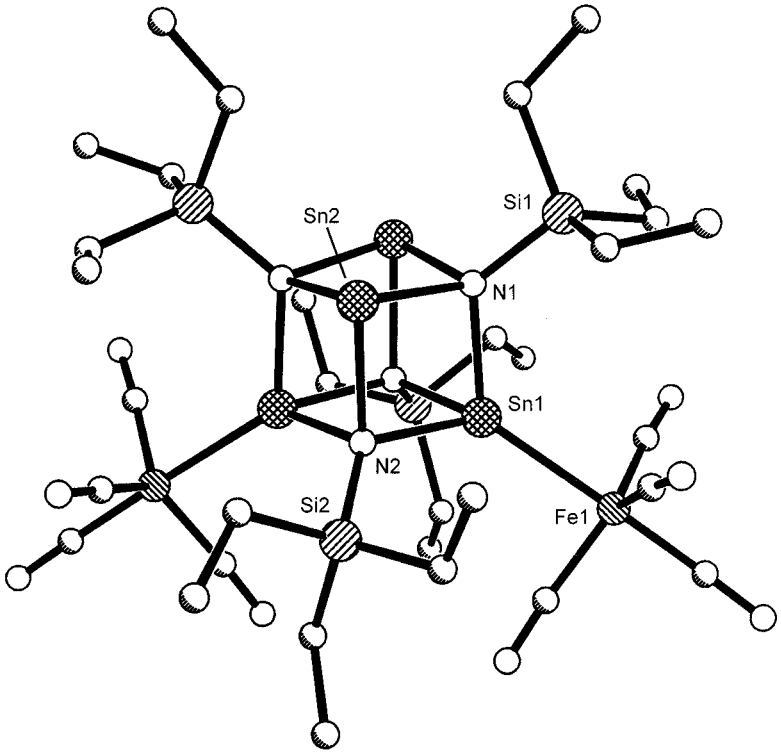

Figure 3. X-ray structure of **3**; carbon and oxygen atoms are not labelled; selected distances [pm] and angles [°]: Sn(1)−N (av.) 215.2(3), Sn(2)−N 224.4(3), Sn(1)−Sn(1a) 321.5(1), Sn(1/1a)−Sn(2/2a) (av.) 327.4(1), Sn(2)−Sn(2a) 332.6(1), Sn(1)−Fe(1) 248.4(1); N−Sn(1)−N (av.) 85.2(1), N−Sn(2)−N (av.) 81.5(1), Sn−N(1)−Sn (av.) 97.1(1), Sn−N(2)−Sn (av.) 95.4(1)

However, it was possible to make use of the Lewis base properties of two of the tin atoms. The reaction of $Fe_2(CO)_9$ with **2b** gave the molecule $[Et_3SiNSn]_4[Fe(CO)_4]_2$ **(3)**. A similar molecule, $[t\text{BuNSn}]_4[Cr(CO)_5]_2$,[14] is known. The structure of **3** (Figure 3) shows a crystallographic twofold axis (C_2) orthogonal to the cube faces Sn(1)−N(2)−Sn(1a)−N(2a) and Sn(2)−N(1)−Sn(2a)−N(1a). The Sn_4N_4 core is close to a C_{2v} (mm2) symmetry. The Sn(1)−N and Sn(1)−Sn(1a) contacts are considerably shorter than in **2a**. The reason for this is the shift of electron density from tin to iron and with that the Et_3Si groups make way for the iron carbonyls, as shown by the larger angles at Sn(1) and the different Si−N−Sn angles.

Experimental Section

General: All substances were handled under an atmosphere of dry nitrogen and solvents were dried and stored over sodium.

$[Me_3SiNSn]_4$ (2a): Me_3SiCl (11 g, 0.1 mol) in 50 mL hexane was added dropwise at −50 °C to liquid ammonia (50 mL). The ammonia was then removed in vacuo at the same temperature. The cold solution was decanted from the NH_4Cl precipitate, added to a solution of **1**[15] (3.2 g, 10 mmol) in hexane (10 mL) and was then allowed to warm to room temperature. After removing all volatile substances the crude product was purified by sublimation (0.01 Torr, 200 °C). m.p. 238 °C, 72% yield. − ^{1}H NMR (200.13 MHz, C_6D_6): δ = 0.26 (s).

$[R_2R'SiNSn]$ (2b−e): A solution of **1** (2.4 g, 7.5 mmol) was added dropwise to a solution of the silylamine (10 mmol; **b**: Et_3SiNH_2, **c**: Ph_3SiNH_2, **d**: $Me_2t\text{BuNH}_2$,[17] **e**: $t\text{Bu}_2\text{HSiNH}_2$[16]) in 10 mL toluene. After stirring for two hours it was refluxed for one hour. The volatile substances were removed in vacuum and the seconorcubane-like intermediate was pyrolysed in vacuo at 0.01 Torr and 250 °C. The formed silylamine was cold trapped and the product sublimed. − ^{1}H NMR (200.13 MHz, C_6D_6/C_7D_8) **2b**: δ = 0.86 (q), 1.15 (t); **2c**: δ = 7.05−7.25 (m), 7.58−7.63 (m); **2d**: δ = 0.26 (s), 1.10 (s); **2e**: δ = 1.24 (s), 4.30 [s, $^3J(^1\text{H}, ^{117/119}\text{Sn})$ = 18 Hz].

$[Et_3SiNSn]_4[Fe(CO)_4]_2$ (3): $Fe_2(CO)_9$ (0.76 g, 2.1 mmol) and **2b** (0.40 g, 0.40 mmol) were heated to 65 °C in toluene (10 mL) for 2 hours (the colour changed from orange to green) and then to 100 °C for 6 hours. Toluene and $Fe(CO)_5$ were then removed in vacuum. The mixture of crude product and $Fe_3(CO)_{12}$ was diluted with hexane, filtered and concentrated to obtain crystals of the product (82% yield) which were recrystallized from toluene. − ^{1}H NMR (200.13 MHz, C_6D_6): δ = 1.09/1.86 (broad signals).

All compounds gave correct elemental analyses. A molecular weight determination of **2b** in benzene (cryoscopy) gave a mass of 997.8 g·mol^{-1} (calcd. 992.0 g·mol^{-1}).

X-ray Crystallography

2a: Stoe AED2 diffractometer, Mo-K_α radiation (λ = 71.073 pm), 298 K, crystal size 1.0 × 0.7 × 0.5 mm, monoclinic, space group *C2/m* with a = 2646.8(5) pm, b = 1216.0(2) pm, c = 1097.8(2) pm, β = 110.79(3)°, V = 3303106 pm^3, Z = 4; ρ = 1.841 Mg m^{-3}; μ = 3.15 mm^{-1}, 1.65° ≤ θ ≤ 27.51°, −12 ≤ h ≤ 34, −14 ≤ k ≤ 15, −14 ≤ l ≤ 13, 7583 reflections measured, 3980 independent, empirical absorption correction (min. 0.537, max. 0.998), *R1* = 0.0388, *wR2* = 0.1094, GOF 1.354, no restraints, 133 parameters, remaining electron density max. 1.042 × 10^{-6}, min. −0.796 × 10^{-6} e·pm^{-3}.

3: Stoe IPDS diffractometer, Mo-K_α radiation (λ = 71.073 pm), 220 K, crystal size 0.8 × 0.5 × 0.3 mm, monoclinic, space group

*C*2/*c* with $a = 1775.0(4)$ pm, $b = 1998.7(4)$ pm, $c = 1792.9(4)$ pm, $\beta = 100.00(3)°$, $V = 6264106$ pm^3, $Z = 4$; $\rho = 1.603$ Mg·m^{-3}; $\mu = 2.14$ mm^{-1}, $2.34° \leq \theta \leq 23.95°$, $-20 \leq h \leq 20$, $-22 \leq k \leq 22$, $-20 \leq l \leq 20$, 19455 measured reflections, 4731 independent, *R1* = 0.0323, *wR2* = 0.0909, GOF 1.111, no restraints, 291 parameters, remaining electron density max. 0.907×10^{-6}, min. -0.485×10^{-6} e pm^{-3}.

The structures described in this paper were solved with the heavy-atom method and refined towards F^2 for all observed reflections (solution and refinement with SHELXS97, hydrogen atoms were calculated in ideal tetrahedral geometry and optimised).

Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-142230 (**2a**) and -142231 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[12] ^{14}N NMR (14.462 MHz) **2a**: δ = −329; **2b**: δ = −324; **2c**: δ = −322; **2d**: δ = −327. − ^{119}Sn NMR [74.631 MHz, $^1J(^{14}N,^{119}Sn)$ in Hz] **2a**: δ = 782/100.6; **2b**: δ = 753/102.2; **2c**: δ = 565/103.5; **2d**: δ = 741/103.8; **2e**: δ = 594/106.9; **3**: δ = 489, 520. − ^{29}Si NMR [39.761 MHz, $^2J(^{29}Si,^{117/119}Sn)$ in Hz] **2a**: δ = 4.17/29.4; **2b**: δ = 7.50/16.4; **2c**: δ = −15.1/17.7; **2d**: δ = 8.22/17.6; **2e**: δ = 11.9/15.5.
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