Synthesis and X-Ray Crystal Structure of a Stannaimine

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A stannaimine has been isolated for the first time; the tin atom is surrounded by three nitrogen atoms in a planar arrangement and the tin–nitrogen double bond is shortened by 10 pm compared with tin–nitrogen single bonds.

Only a few examples of stable compounds containing a double bond to tin atoms have been reported. For recent results regarding the $>$Sn=P– and $>$Sn=Sn$<$ sequences see ref. 1 and 2 and citations given there. Two stannenes with $>$Sn=C$<$ double bonds have been also described and one of them characterized by an X-ray structure determination (so far the only one for a compound with a double bond on tin).[3] Stannaimines, species containing a $>$Sn=N–unit, are extremely reactive and have been trapped in a variety of reactions. The reaction with stannylene has produced azadistanniridine in a [2 + 1]cycloaddition[4] and with azides [2 + 3]cycloadditions have led to the formation of stannatetrazoles[4–6] while the addition to the Si–N bond of trimethylsilylazide yielded an azidostannane.[6] Otherwise dimerization products of stannaimines as diazadistannetidines[4,5,7,8] or a hexaazadistannadispirodecane were isolated.[9]

We have prepared stable germaimines from highly sterically hindered diazagermylenes and azidosilanes or 2,6-disubstituted phenylazides.[10,11] The same type of reaction has now yielded bis[bis(trimethylsilyl)amino]-(2,6-diisopropylphenylimino)stannane **1**, the first stannaimine isolated in substance as shown in Scheme 1.†

Crystalline **1** is stable at −30 °C but rearranges in solution of hexane within 2 weeks to give **2** by intramolecular addition of the C–H bond of one of the isopropyl groups across the Sn=N bond.

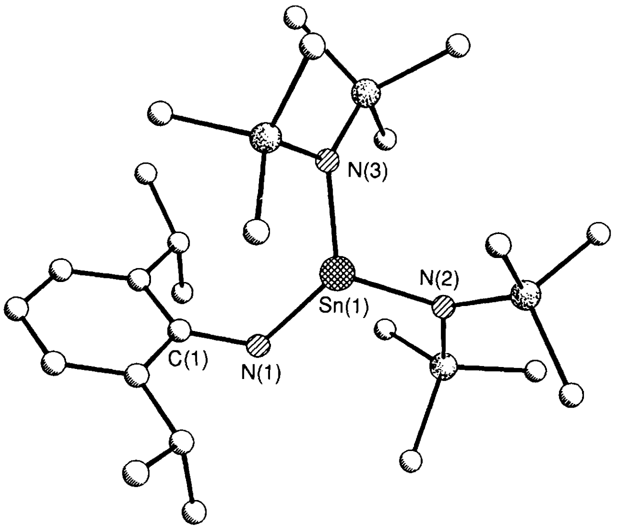
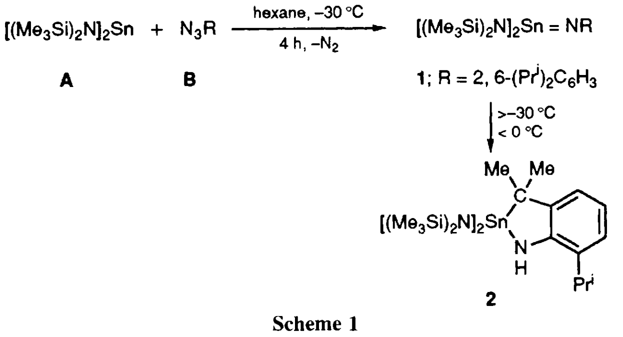


Fig. 1 Molecular structure of **1**; selected bond distances (pm) and angles (°): Sn(1)–N(1) 192.1(2), Sn(1)–N(2) 201.5(2), Sn(1)–N(3) 203.0(3), N(1)–C(1) 140.6(4); N(1)–Sn(1)–N(2) 114.3(1), N(1)–Sn(1)–N(3) 129.1(1), N(2)–Sn(1)–N(3) 115.8(1), C(1)–N(1)–Sn(1) 120.6(2).

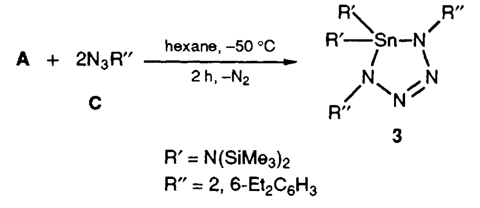


Scheme 1

The crystal structure analysis of **1**‡ shows a trigonal planar arrangement of the three N atoms around the tin atom. The two Sn–N single bond lengths 201.5(2) and 203.0(3) pm are slightly shortened compared to most Sn–N single bonds (205 pm),[12] the Sn=N (imino) bond length is further shortened by 10 pm and is 192.1(2) pm.

Our attempts to obtain stannaimines by the following reactions were unsuccessful: **A** did not react with 2,4,6-$(Bu^t)_3C_6H_2N_3$ in toluene at 111 °C and [2,6-$(Pr^i)_2C_6H_3$(Me$_3$Si)N]$_2$Sn and 2,4,6-$Me_3C_6H_2N_3$ were both recovered unchanged from boiling hexane (69 °C). On the other hand the reaction of **A** and 2,6-$Et_2C_6H_3N_3$ **C** at −50 °C (2 h) gave the corresponding stannatetrazole **3** by a [2 + 3]cycloaddition of a second mol of **C** across the Sn=N bond of the corresponding stannaimine formed as an intermediate (Scheme 2).§

Compounds **1**, **2** and **3** show spectroscopic data in accordance with the structures given.¶ The only intriguing value is



Scheme 2

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† *Preparative details*: Starting materials: **A**;[14] **B**: yellow oil, b.p. 48 °C/0.01 mbar (52%) analogue;[15] **C**: yellow oil, b.p. 42 °C/0.01 mbar (53%) analogue.[15] All reactions under dry nitrogen.

To 2.78 g (6.33 mmol) of bis[bis(trimethylsilyl)amino]stannane **A**, which was freshly distilled into a Schlenkbulb, was added 70 ml of degassed dry hexane. Then 1.29 g (6.33 mmol) of 2,6-diisopropylphenylazide **B** were added at −30 °C by a syringe through a septum. The solution was stirred at −30 °C for 4 h. Within 15 min the colour changed from light-orange to brown–red. Storing at −80 °C for 2 weeks gave crystals of **1**, from which the solution was decanted. The crystals were washed at −78 °C by recondensation of 10 ml of hexane *in vacuo*. The yield of vacuum-dried crystals at −30 °C was 2.2 g (3.6 mmol) (57%) of **1**. From the ^{1}H NMR spectrum the purity exceeded 90%. Dark-red single crystals were obtained, together with a poorly crystallized substance, by storing a solution of **1**, which was concentrated at −30 °C, at −80 °C. Crystallization at lower concentration led to crystals which were not suitable for a structure analysis.

For the preparation of **2**, 30 ml of hexane was condensed onto 1.1 g (1.8 mmol) of **1** *in vacuo* at −78 °C and the stirred solution was slowly warmed to ambient temperature. By removing part of the solvent under reduced pressure and storing at −25 °C, pale-yellow crystals of **2** were obtained (0.82 g, 1.33 mmol, 76%), m.p. 106 °C (air sensitive). Satisfactory elemental analyses were obtained.

‡ *Crystal data* for **1**: $C_{24}H_{53}N_3Si_4Sn$, triclinic, space group $P\bar{1}$, a = 909.0(3), b = 1067.9(3), c = 1765.6(6) pm, α = 86.68(3), β = 80.99(2), γ = 81.02(2)°, U = 1.6710(9) nm^3, Z = 2, D_c = 1.222 Mg m^{-3}, μ = 0.92 mm^{-1}, $F(000)$ = 648, crystal dimensions 0.2 × 0.4 × 0.6 mm, 7848 reflections measured in the range of $8<2\theta<55°$, 5892 unique and 5888 reflections used in the structural analysis. The data set was collected on a Siemens-Stoe AED diffractometer using Mo-Kα radiation (λ = 71.073 pm) at a temperature of 153 K. Semiempirical absorption correction was applied. The structure was solved by Patterson and Fourier methods. All non-hydrogen atoms were refined anisotropically, and a riding model starting from calculated positions was employed for the hydrogen atoms. 305 parameters were refined with a weighting scheme [$w^{-1} = \sigma^2F_o^2 + (0.0220\ P)^2 + 1.72\ P$, where $P = (F_o{}^2 + 2F_c{}^2)/3$]. The refinement converged with $wR2$ = 0.0690 for all data and $R1$ = 0.0322 for $F > 4\sigma(F)$ and final difference electron density maxima of 0.42 and minima of -0.54×10^{-6} e pm^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to the Authors, Issue No. 1.

§ *Selected spectroscopic data* for **3**: yellow crystals, m.p. 135–136 °C (decomp.), 38% yield. Satisfactory elemental analyses were obtained. MS [*m/z* (%)]: El 762 (3) [M$^+$], 146 (100). NMR: δ(^{1}H) 0.16 (s, 36H, SiMe$_3$), 1.32 (t, $^3J_{HH}$ 7.5 Hz, 12H, CH$_2$C*H*$_3$), 2.85 (q, 8H, C*H*$_2$CH$_3$), 6.88—6.98 (2H), 7.07–7.13 (4H) (2 × m, C$_6$H$_3$); δ(^{13}C) (* denotes C quart); 6.30 [$^1J_{SiC}$ 56 Hz, ^3J ($^{117/119}$Sn^{13}C) 12.6 Hz, SiMe$_3$], 15.91 (CH$_2$*C*H$_3$), 27.22 (*C*H$_2$CH$_3$), 126.92 (4C), 127.31 (2C), 143.08* (4C); 143.84* (2C) (C$_6$H$_3$).

¶ *Selected spectroscopic data*: **1**: NMR (in [^{2}H$_8$]toluene at −40 °C): δ(^{1}H) 0.29 (s, 36H, SiMe$_3$), 1.41 (d, $^3J_{HH}$ 6.8 Hz, 12H, CH(C*H*$_3$)$_2$, 3.69 [sept, 2H, C*H*(CH$_3$)$_2$], 7.05 (pseudo t, 2 × d at 7.04 + 7.06, $^3J_{HH}$ 7.6 Hz, 1H, C$_6$H$_3$), 7.25 (d, $^3J_{HH}$ 7.6 Hz, 2H, C$_6$H$_3$); δ(^{13}C) 4.53 (SiMe$_3$), 23.52 [CH(*C*H$_3$)$_2$], 29.63 [*C*H(CH$_3$)$_2$], 121.52 (1C), 122.36 (2C), 140.02 (2C), 153.01 (1C) (C$_6$H$_3$), δ(^{29}Si) 6.82 ($^1J_{SiC}$ 56 Hz, $^2J_{SiSn}$ 16 Hz); δ(^{119}Sn) −3.5 (rel. to Me$_4$Sn ext.).

2: MS [*m/z* (%)] El: 615(25) [M$^+$], 280(100) [SnN(SiMe$_3$)$_2{}^+$]. NMR (in CDCl$_3$): δ(^{1}H) 0.20 (s, 36H, SiMe$_3$), 1.26 (d, $^3J_{HH}$ 6.8 Hz, 6H, CH(C*H*$_3$)$_2$, 1.67 [s, ^3J($^{117/119}$SnH) 121.6/125.5 Hz], 2 pairs of satellites, 6H, C(CH$_3$)$_2$, 2.86 [sept, 1H, C*H*(CH$_3$)$_2$], 3.77 (s, 1H, NH), 6.61 (pseudo t, 2 × d at 6.60 + 6.62, $^3J_{HH}$ 7.6 Hz, 1H, C$_6$H$_3$), 6.97 (d, $^3J_{HH}$ 7.6 Hz, 2H, C$_6$H$_3$); δ(^{13}C) (* denotes C quart) 5.91 (SiMe$_3$), 22.39 [CH(*C*H$_3$)$_2$], 28.63 [*C*H(CH$_3$)$_2$], 29.34 [C(*C*H$_3$)$_2$], 43.87* [^1J ($^{117/119}$Sn^{13}C) 678.0/709.3 Hz, C(*C*H$_3$)$_2$], 115.35, 121.44, 122.84, 131.06*, 134.48*, 146.81* (C$_6$H$_3$); δ(^{29}Si) 4.90 ($^1J_{SiC}$ 55.6 $^2J_{SiSn}$ 10.2 Hz); δ(^{15}N) (rel. to CH$_3$NO$_2$ ext.) for NH: −303.4 [$^1J_{NH}$ 78 Hz, ^1J($^{117/119}$Sn^{15}N) 68/72 Hz]; δ(^{119}Sn) ([^{2}H$_8$]toluene rel. to Me$_4$Sn) −24.2.

the chemical shift of ^{119}Sn in compound **1** which is unexpectedly at -3.5 ppm higher field than Me_4Sn and only 21 ppm at lower field compared with **2**. However, it is well known that unusual bond systems give rise to unexpected shift values, *e.g.* in amino-iminoboranes, in which the $\delta(^{11}B)$ shifts nearly correspond to those of tetracoordinated boron.[13]

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