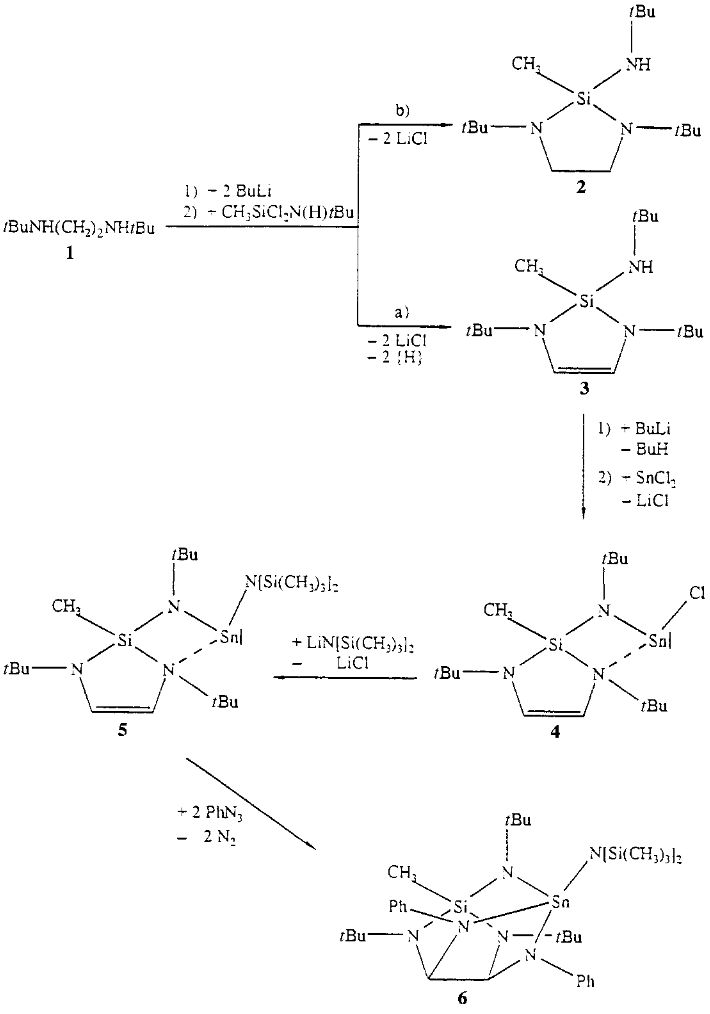
A Tricyclic, Organometallic Cage Molecule with a Tetraaminoethane Unit**

Michael Veith,* Bernhard Schillo, and Volker Huch

Dedicated to Professor Peter Jutzi
on the occasion of his 60th birthday

Organyl nitrenes, accessible by the thermal decomposition of organyl azides, are known to react readily with both carbon π bonds and carbene analogues of type R_2E (E = Ge, Sn),[1, 2] yielding respectively cycloaminopropanes[3] and germa- and stannazenes.[4] Both types of product are reactive and are generally stable only under certain conditions (low temperature or sterically demanding ligands). Therefore, stannazenes with insufficient steric protection are known to react further with the organyl azide to form the corresponding stannatetrazoles.[5] It seemed to us an attractive idea to combine within a single molecule both a reactive π bond and a stannylene unit, so as to trigger further reactions through steric immobilization of the two reaction centers, thereby leading perhaps to novel, otherwise inaccessible interatomic linkages. The strategy presented herein should also be transferable to other systems.

We selected the compound **5**, which contains both reaction centers and, as shown in Scheme 1, can be constructed by a multistep reaction sequence. In **5** the π system and the stannylene moiety are held together at a defined distance through the $-N(t\text{Bu})Si(Me)[t\text{BuN}-]_2$ group. In the synthesis of **5** the following should be noted: a) The ethylenediamine derivative **1** must undergo reaction with butyllithium and $Cl_2Si(Me)N(H)t\text{Bu}$ in concentrated solution in order to obtain the 1,3-diaza-2-silacyclopentene **3**. b) If the reaction is carried out in a more dilute solution, the cyclopentane **2** is formed.[6] The cause of the hydrogen abstraction from the ethylene moiety in the formation of **3** is unclear; similar behavior has been observed in other analogous reactions of ethylenediamines.[7] Both spectroscopic data and X-ray crystallography confirm the presence of a C=C bond in **3** (Figure 1).



Scheme 1. a) Concentrated solution; b) dilute solution.

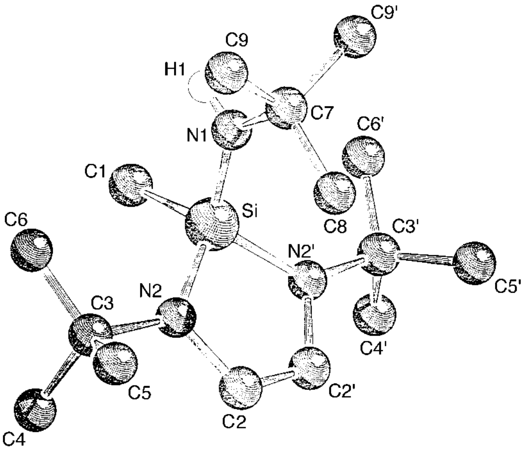


Figure 1. Ball-and-stick representation of the structure of **3** in the crystal.[8] Important bond lengths [Å] and angles [°]: Si–N1 1.679(6), Si–N2 1.721(4), N2–C2 1.402(5), C2–C2′ 1.310(9); N1-Si-N2 116.3(2), N2-Si-N2′ 92.1(3), C2-N2-Si 109.4(3), C2′-C2-N2 114.6(2).

Compound **3** can be converted by a classical reaction sequence into the tin(II) compound **4**, which is in turn converted into **5** through a $Cl/N(SiMe_3)_2$ exchange. We were able to obtain single crystals of **4**, and its crystal structure has been determined. As can be seen from Figure 2, the tin(II) atom is bonded to three different ligands—quadruply (N1) and triply coordinated nitrogen atoms (N2) and a chlorine atom. Two enantiomers of the compound crystallize together in a centrosymmetric crystal structure (with chirality centers at Si and N1 as well as at the Sn atom[6]). The bond lengths and angles in **4** are within the expected range.[8] The NMR spectra of **4** and **5** in solution show that the chirality centers in both compounds are clearly not stable towards intramolecular Lewis acid–base reactions in either compound. This can be explained by the two nitrogen atoms of the enediamine moiety competing with each another for coordination to the metal atom (see the number of ^{1}H, ^{13}C, and ^{15}N signals (Experimental Section)). Moreover, the crystal structure

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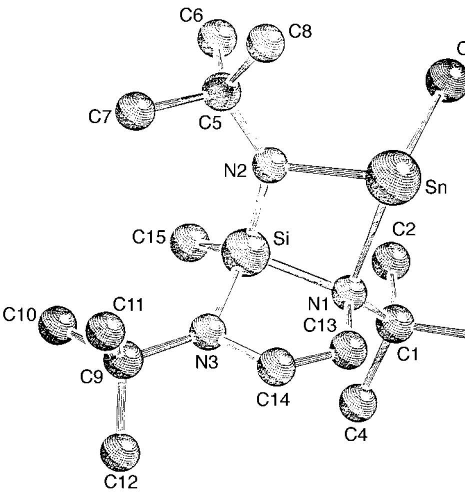

Figure 2. Ball-and-stick representation of the structure of **4** in the crystal.[8] Important bond lengths [Å] and angles [°]: Sn–N2 2.084(4), Sn–N1 2.369(4), Sn–Cl 2.510(3), Si–N2 1.677(4), Si–N1 1.818(4), Si–N3 1.736(4), N1–C13 1.449(6), N3–C14 1.382(7), C13–C14 1.313(8); Si-N1-Sn 89.7(2), Si-N2-Sn 104.2(2), C13-N1-Si 102.8(3), N3-Si-N1 93.3(2), C13-N1-Sn 97.5(3).

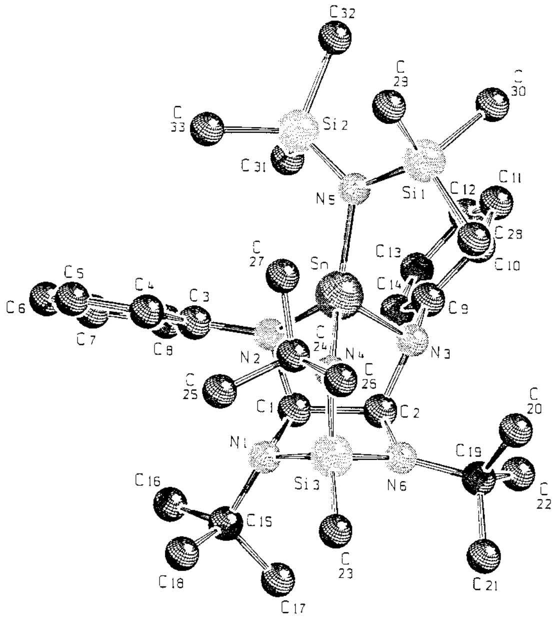

Figure 3. Ball-and-stick representation of the structure of **6** in the crystal.[8] Important bond lengths [Å] and angles [°]: Sn–N2 2.049(3), Sn–N3 2.065(3), Sn–N4 2.060(3), Si3–N1 1.744(4), Si3–N4 1.754(3), Si3–N6 1.713(3), C1–C2 1.609(5), N2–C1 1.486(5), N1–C1 1.476(5), N3–C2 1.476(5), N6–C2 1.452(4); N2-Sn-N3 80.82(12), C1-N2-Sn 102.3(2), C2-N3-Sn 100.5(2), Si3-N4-Sn 107.81(14), C1-N1-Si3 102.2(2), C2-N6-Si3 106.7(2).

analysis of **4** shows the tin atom to be pushed closer to the C=C bond (the distance from the Sn atom to the midpoint of the C=C bond is 3.309 Å).

On reaction of **5** with phenyl azide (1 equiv) at ambient temperature, only half an equivalent of **5** undergoes reaction, with evolution of nitrogen. Even at −50 °C it is not possible to control the addition of the azide or "nitrene" so that only one of the two centers reacts. What is more, no intermediate species could be detected spectroscopically. The reaction proceeds almost quantitatively to **6**, which was fully characterized by NMR spectroscopy and X-ray crystallography (Figure 3). The basic framework of **6** is made up of a tetraaminoethane skeleton in which two pairs of nitrogen atoms are linked through the (Me)Si or [$(Me_3Si)_2N$]Sn centers to form two five-membered rings with a common (H)C–C(H) edge. The Si and Sn atoms are linked through a *t*BuN group, forming the polycyclic cage including two CN_2SiSnN rings which are present in chair conformations.

To account for the formation of **6** various mechanisms are possible. The phenylnitrene moieties undergo a formal double insertion between the carbenoid tin atom and the activated C=C bond. The labile centers react with one another as was envisaged in our strategy. Of the bonds in the polycyclic structure **6**, the relatively long C1–C2 bond (1.609(5) Å) and the short Sn–N5 bond (2.026(3) Å) are particularly striking. Similarly noteworthy is the fact that the sum of the angles at N1–N4 deviates distinctly from 360°, which is extremely unusual for nitrogen atoms coordinated to the heavy elements of Group 14. In the nine-atom cage in **6**, five atoms (nitrogen) are tricoordinated and the other four tetracoordinated.

The acetylenetetraamine unit (the bisaminal of glyoxal) is generated in the described synthesis by a metal-mediated addition of two phenylnitrenes to an enediamine. The two phenylnitrene moieties add stereospecifically to "the same side" of the C=C bond, and the *R*,*S* isomer (relative to the chiral carbon atoms) is exclusively obtained. The reaction may prove to be of preparative use, as 1,1,2,2-tetraaminoethanes have hitherto only been prepared with cyclic N-C_n-N-frameworks.[9–15]

Experimental Section

3: To a solution of **1** (29.04 g, 168.5 mmol) in hexane (30 mL) was added dropwise a solution of *n*BuLi in hexane(140 mL, 339 mmol), and the mixture was heated under reflux for 45 min. The solvent was removed by distillation, and the residue was taken up in THF (150 mL). $MeSiCl_2NHtBu$ (31.37 g, 168.5 mmol) was added slowly dropwise at ambient temperature with cooling in a water bath. After the mixture was stirred for 14 h the solvent was condensed off, the residue was taken up in hexane (50 mL), and the filtrate was fractionally distilled. This gave 19.75 g (41 %) of a colorless liquid which crystallized at 7–9 °C. B.p.: 31–34 °C/10^{-3} torr; correct elemental analysis; NMR (200 MHz, [D_6]benzene, 296 K, TMS): ^1H NMR: $\delta = 0.30$ (s, 3H, SiMe), 1.17 (s, 9H, N*t*Bu), 1.30 (s, 18H, N*t*Bu), 5.73 (s, 2H, CH); ^{13}C NMR: $\delta = 4.38$ (s, SiMe), 30.45 (s, NC(CH_3)$_3$), 32.50 (s, NC(CH_3)$_3$), 48.77 (s, NC(CH_3)$_3$), 50.79 (s, NC(CH_3)$_3$), 110.49 (s, CH); ^{15}N NMR: $\delta = -301.9$ (s, N*t*Bu), −295.1 (s, N*t*Bu); ^{29}Si NMR: $\delta = -30.72$ (s, SiMe).

4: A solution of *n*BuLi in hexane (5.4 mL, 13 mmol) was added dropwise at −78 °C to a solution of **3** (3.71 g, 13 mmol) in diethyl ether (25 mL), and the mixture was heated under reflux for 1 h. The solvent was then removed and the yellow residue taken up in benzene (75 mL) and added to a solution of $SnCl_2$ (2.480 g, 13.1 mmol) in benzene (25 mL). After being stirred for 12 h the mixture was filtered, and the solvent was condensed in a cold trap. The yellow-brown oil left behind was then distilled at 110 °C in a Kugelrohr apparatus under a dynamic vacuum. The oil obtained crystallized within 12 h. Recrystallization from hexane gave 3.61 g (63 %) of a colorless solid. Correct elemental analysis; NMR ([D_8]toluene): ^1H NMR: $\delta = 0.57$ (s, 3H, SiMe), 1.08 (s, 18H, N*t*Bu), 1.30 (s, 9H, N*t*Bu), 5.61 (s, 2H, CH) $^5J(^1H, ^{117/119}Sn) = 8.3$ Hz; ^{13}C NMR: $\delta = 9.65$ (s, SiMe), 29.72 (s, NC(CH_3)$_3$), 35.88 (s, NC(CH_3)$_3$), 52.52 (s, NC(CH_3)$_3$), 54.95 (s, NC(CH_3)$_3$), 117.00 (s, CH); ^{15}N NMR: $\delta = -286.9$ (s, N*t*Bu), −255.0 (s, N*t*Bu); ^{29}Si NMR: $\delta = -12.39$ (s, SiMe, $^2J(^{29}Si, ^{117/119}Sn) = 16$ Hz); ^{119}Sn NMR: $\delta = 42.4$ (s, SnCl, $b_{1/2} = 293$ Hz).

5: To a solution of **4** (2.97 g, 6.8 mmol) in benzene (20 mL) was added dropwise a solution of $LiN(SiMe_3)_2$ (1.14 g, 6.8 mmol) in benzene (30 mL). After being stirred for 14 h the mixture was filtered, and the solvent was condensed off. The yellow-brown oil obtained crystallized after 12 h. Recrystallization from hexane gave 2.37 g (62 %) of light yellow crystals. Correct elemental analysis; ^{1}H NMR: $\delta = 0.50$ (s, 18 H, $N(SiMe_3)_2$), 0.71 (s, 3 H, SiMe), 1.13 (s, 18 H, N*t*Bu), 1.28 (s, 9 H, N*t*Bu), 5.67 (s, 2 H, CH) $^{5}J(^{1}H, ^{117/119}Sn) = 5.6$ Hz; ^{13}C NMR: $\delta = 7.59$ (s, $N(SiMe_3)_2$), 9.21 (s, SiMe), 29.71 (s, $NC(CH_3)_3$), 35.50 (s, $NC(CH_3)_3$), 52.26 (s, $NC(CH_3)_3$), 54.74 (s, $NC(CH_3)_3$), 118.15 (s, *C*H); ^{15}N NMR: $\delta = -289.8$ (s, N*t*Bu); ^{29}Si NMR: $\delta = -15.70$ (s, SiMe, $^{2}J(^{29}Si, ^{117/119}Sn) = 20.6$ Hz), -0.77 (s, $N(SiMe_3)_2$, $^{2}J(^{29}Si, ^{117/119}Sn) = 54.4/19.2$ Hz); ^{119}Sn NMR: $\delta = 205.2$ (s, NSnN, $b_{1/2} = 774$ Hz).

6: To a solution of **5** (0.258 g, 0.459 mmol) in benzene (20 mL) was added dropwise phenyl azide (0.109 g,0.919 mmol). The solution rapidly turned red with the evolution of gas. After the mixture was stirred for 2 h the solvent was removed, and the residue recrystallized from hexane to give 0.27 g (78 %) of light yellow crystals. Correct elemental analysis; ^{1}H NMR: $\delta = 0.14$ (s, 18 H, $N(SiMe_3)_2$), 0.77 (s, 3 H, SiMe), 1.17 (s, 18 H, N*t*Bu), 1.56 (s, 9 H, N*t*Bu), 5.42 (s, 2 H, CH, $^{3}J(^{1}H, ^{117/119}Sn) = 57.8/60.4$ Hz), 6.85 – 7.26 (m, 10 H, C_6H_5); ^{13}C NMR: $\delta = 4.97$ (s, $N(SiMe_3)_2$, $^{3}J(^{13}C, ^{117/119}Sn) = 28.0$ Hz), 8.89 (s, SiMe, $^{3}J(^{13}C, ^{117/119}Sn) = 15.9$ Hz), 31.95 (s, $NC(CH_3)_3$), 36.92 (s, $NC(CH_3)_3$, $^{3}J(^{13}C, ^{117/119}Sn) = 15.3$ Hz), 52.48 (s, $NC(CH_3)_3$), 54.95 (s, $NC(CH_3)_3$, $^{2}J(^{13}C, ^{117/119}Sn) = 14.4$ Hz), 79.37 (s, CH, $^{2}J(^{13}C, ^{117/119}Sn) = 15.9$ Hz), 121.20 (s, NC_6H_5, $^{5}J(^{13}C, ^{117/119}Sn) = 4.7$ Hz), 125.57 (s, NC_6H_5, $^{4}J(^{13}C, ^{117/119}Sn) = 12.3$ Hz), 128.49 (s, NC_6H_5), 152.29 (s, NC_6H_5, $^{2}J(^{13}C, ^{117/119}Sn) = 8.3$ Hz); ^{15}N NMR: $\delta = -270.3$ (s, N*t*Bu), -294.9 (s, N*t*Bu), -336.2 (s, NC_6H_5); ^{29}Si NMR: $\delta = -8.33$ (s, SiMe, $^{2}J(^{29}Si, ^{117/119}Sn) = 22.4$ Hz), 8.37 (s, $N(SiMe_3)_2$, $^{2}J(^{29}Si, ^{117/119}Sn) = 28.0/7.4$ Hz); ^{119}Sn NMR: $\delta = -175.3$ (s, NSnN).

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[8] Crystal structure analyses: **3**: $C_{15}H_{33}N_3Si$, $M_r = 283.53$, orthorhombic, space group *Pnma*, $a = 938.8(6)$, $b = 1693.0(14)$, $c = 1132.4(9)$ pm, $V = 1800(2) \times 10^6$ pm^3, $Z = 4$, $\rho_{calcd} = 1.046$ g cm^{-3}, $F(000) = 632$, Stoe-AED2 four circle diffractometer, $T = 193(2)$ K, $2.16 \leq \theta \leq 19.99°$, 775 symmetry-independent reflections, no restrictions, 76 parameters; solved by direct methods (SHELXS86), refinement (SHELXL-93) with anisotropic temperature factors for all non-hydrogen atoms, hydrogen atoms located geometrically, $R_1 = 0.0557$, $wR_2 = 0.1442$. **4**: $C_{15}H_{32}ClN_3SiSn$, $M_r = 436.67$, monoclinic, space group $P2_1/n$, $a = 1125.7(12)$, $b = 1441.6(14)$, $c = 1273.7(11)$ pm, $\beta = 96.10(8)°$, $V = 2055(4) \times 10^6$ pm^3, $Z = 4$, $\rho_{calcd} = 1.411$ g cm^{-3}, $F(000) = 896$, Stoe-AED2 four circle diffractometer, $T = 293(2)$ K, $2.14 \leq \theta \leq 24.00°$, 3230 symmetry-independent reflections, no restrictions, 194 parameters; for solution and refinement see details given for **3**, $R1 = 0.0395$, $wR2 = 0.0986$. **6**: $C_{33}H_{60}N_6Si_3Sn$, $M_r = 743.83$, monoclinic, space group $P2_1/c$, $a = 1856.4(4)$, $b = 1045.9(2)$, $c = 2196.3(4)$ pm, $\beta = 93.15(3)°$, $V = 4258(2) \times 10^6$ pm^3, $Z = 4$, $\rho_{calcd} = 1.160$ g cm^{-3}, $F(000) = 1568$, Stoe-AED2 four circle diffractometer, $T = 293(2)$ K, $2.69 \leq \theta \leq 28.38°$, 10050 symmetry-independent reflections($R_{int} = 0.0504$), no restrictions, 388 parameters for solution and refinement see details given for **3**, $R1 = 0.0600$, $wR2 = 0.1831$. Crystallographic data (excluding structure factors) of the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-103341, 103342, and 103343. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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N,N-Phthaloylamino Acids as Chiral Auxiliaries in Asymmetric Mannich-Type Reactions[**]

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Herbert Waldmann[*]

Dedicated to Professor Janos Rétey
on the occasion of his 65th birthday

The Mannich reaction is one of the most important methods of organic synthesis. It provides a powerful tool for instance for the construction of β-amino ketones and β-amino acids that are versatile building blocks in the preparation of biologically important compounds[1] and their analogues (for example β-peptides[2]). Therefore, the development of methods that allow this transformation to be carried out asymmetrically is of great importance to organic synthesis, and diastereo-[3] and enantioselective[3a, 4] Mannich-type processes have attracted considerable attention. Herein we report that a very high level of stereoselectivity (diastereomeric ratio of

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