Organometallics **1996,** *15,* 5769−5771 5769

$[Si(HNCH_2CH_2)_2(NCH_2CH_2)N]_2$: A Novel Product of Hydrogen Elimination from $HSi(HNCH_2CH_2)_3N$

Yanjian Wan and John G. Verkade*

Gilman Hall, Department of Chemistry, Iowa State University, Ames, Iowa 50011

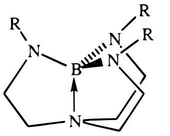
Received August 26, 1996⊗

Summary: Rather than oligomers, the title dimer is formed in high yield by dehydrogenation of $HSi(HNCH_2CH_2)_3N$ *under a variety of conditions ranging from 77% by pyrolysis at 200 °C to 95% by dimerization in liquid ammonia in the presence of a catalytic amount of* $NaNH_2$*. The structure of the dimer was confirmed by X-ray crystallographic studies.*

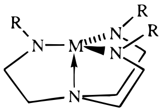
Introduction

Owing to the current interest in group 13 and 14 nitrides as ceramic materials and semiconductors,[1−6] the amide chemistry of the first three members of group 13 and silicon in group 14 has undergone intense scrutiny during the last decade. Because comparatively few of these investigations have utilized highly symmetrical amide ligand systems,[7] we have undertaken to examine symmetrical tripodal tetraamines such as **1**−**5**. As examples in group 13 we have synthesized monomeric **6**−**11**[8,9] in which boron is tetrahedral but aluminum and gallium display the relatively rare trigonal pyramidal coordination geometry.[10] When not excessively encumbered sterically by substituents on the equatorial nitrogens, aluminum and gallium form dimers such as **12**−**14** which arise from the formation of two N→M coordinate bonds.[9]

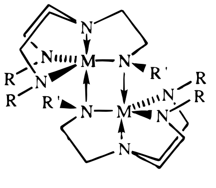
R = H, **1**; Me, **2**; *iso*-Pr, **3**; SiMe$_3$, **4**; SiMe$_2$-*tert*-Bu, **5**



	R
6	Me
7	SiMe$_3$

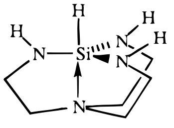


	M	R
8	Al	SiMe$_3$
9	Al	SiMe$_2$-*tert*-Bu
10	Ga	SiMe$_3$
11	Ga	SiMe$_2$-*tert*-Bu

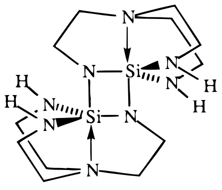


	M	R	R'
12	Al	Me	Me
13	Al	SiMe$_3$	H
14	Ga	Me	Me

We now show that azasilatrane **15**[11,12] readily undergoes thermolytic or base catalyzed dehydrocyclodimerization to give the dehydrocyclodimer **16** in high yield. The structure of **16** determined by X-ray means is also described. To our knowledge, this is the first example of a dehydrocyclodimerization reaction involving a five-coordinate aminosilane.



15



16

Experimental Section

All reactions were carried out under dry nitrogen with the strict exclusion of moisture by the use of vacuum line and Schlenk techniques. Solvents such as toluene, benzene, tetrahydrofuran (THF), and diethyl ether were distilled from sodium/benzophenone under nitrogen prior to use. Deuterated benzene was dried over and distilled from CaH_2 under an argon atmosphere. Tris(dimethylamino)silane was purchased from Huls America, Inc. (Piscataway, NJ), and used without further purification. tren [$(H_2NCH_2CH_2)_3N$] was distilled at 85 °C/15 × 10^{-3} mmHg from $LiAlH_4$ after being received as a kindly supplied research sample from the Hampshire Chemical Co. Compound **15** was synthesized according to a modification[13] of a procedure we reported earlier.[12]

^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Varian VXR 300 spectrometer with deuterated solvents and an internal lock. ^1H (299.949 MHz) and ^{13}C (75.429 MHz) spectra were referenced to the residual proton signal of a deuterated solvent (7.15 ppm for benzene-d_6 and 128.0 ppm for benzene-d_6, respectively). ^{29}Si (59.591 MHz) spectra were referenced to a 20% volume solution of Me_4Si in benzene-d_6 as an external standard. Mass spectra were obtained on a Finnigan 4000 low-resolution (70 eV, EI) or a Kratos MS-50 high-resolution instrument. The masses are reported for the most abundant isotope available.

⊗ Abstract published in *Advance ACS Abstracts,* December 1, 1996.

[1] Paine, R. T.; Narula, C. K. *Chem. Rev.* **1990**, *90*, 73.

[2] Wade, T.; Park, J.; Garza, E. G.; Ross, C. B.; Smith, D. M.; Crooks, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 9457.

[3] Jones, C.; Koutsantonis, G. A.; Raston, C. L. *Polyhedron* **1993**, *12*, 1829.

[4] (a) Almond, M. J.; Jenkins, C. E.; Rice, D. A.; Hagen, K. *J. Organomet. Chem.* **1992**, *439*, 251. (b) Almond, M. J.; Jenkins, C. E.; Rice, D. A. *Ibid.* **1993**, *443*, 137.

[5] Cowley, A. H.; Jones, R. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1208.

[6] Riedel, R.; Schaible, S.; Klingebiel, V.; Noltemeyer, M.; Werner, E. *Z. Anorg. Allg. Chem.* **1991**, *603*, 119.

[7] (a) Moise, F.; Pennington, W. T.; Robinson, G. H. *J. Coord. Chem.* **1991**, *24*, 93. (b) Atwood, D. A.; Atwood, V. O.; Cowley, A. H.; Atwood, J. L.; Roman, E. *Inorg. Chem.* **1992**, *31*, 3871. (c) Atwood, J. L.; Bott, S. G.; Jones, C.; Raston, C. L. *Inorg. Chem.* **1991**, *30*, 4868. (d) Coutsolelos, A.; Guilard, R.; Boukhirs, A.; Lecomte, C. *J. Chem. Soc., Dalton Trans.* **1986**, 1779.

[8] Pinkas, J.; Gaul, B.; Verkade, J. G. *J. Am. Chem. Soc.* **1993**, *115*, 3925.

[9] Pinkas, J.; Wang, T.; Jacobson, R. A.; Verkade, J. G. *Inorg. Chem.* **1994**, *33*, 4202.

[10] Emig, N.; Réau, R.; Krautscheid, H.; Fenske, D.; Bertrand, G. *J. Am. Chem. Soc.* **1996**, *118*, 5822 and references therein.

[11] Lukevics, E.; Zelchan, G. I.; Solomennikova, I. I.; Liepin'sh, E. E.; Yankovska, I. S.; Mazheika, I. B. *J. Gen. Chem. U.S.S.R. (Engl. Transl.)* **1977**, *47*, 98.

[12] Gudat, D.; Verkade, J. G. *Organometallics*, **1989**, *8*, 2772.

[13] Wan, Y.; Verkade, J. G. *J. Am. Chem. Soc.* **1995**, *117*, 141.

Preparation of 16. Method A. Compound **15** (1.579 g, 9.180 mmol) was introduced into a Schlenk tube equipped with a stirring bar. Upon heating of the tube, the contents melted at ca. 85 °C. Further heating to 200 °C while stirring the clear mixture led to its solidification after 38 h. During heating, a very slow release of gas bubbles (presumably H_2) was observed. After being cooled to room temperature, the solid was crushed to a powder. Unreacted starting material **15** was extracted with 3 × 10 mL of diethyl ether. After removal of ether under vacuum, the solid residue was kept at 55 °C/10 × 10^{-3} mmHg giving additional unreacted starting material **15** (0.17 g) by sublimation. Recrystallization of the solid residue from hot toluene afforded pure **16** in 77.5% yield. Clear crystals of **16** suitable for X-ray diffraction were grown by slowly cooling a saturated solution of **16** in toluene in a refrigerator. Compound **16** dissolves well in nonpolar solvents such as benzene or toluene but only slightly in chloroform or ether. Although stable in a drybox for a year, **16** decomposed in air within 30 min to give a white powder and $N(CH_2CH_2NH_2)_3$, which was identified by ^1H NMR spectroscopy.[12] Characterization of **16**: ^1H NMR (C_6D_6) 3.09 (t, 4 H, $\mathrm{Si_2NC}\mathit{H}_2\mathrm{CH_2}$, $^3J = 5.7$ Hz), 2.87 (m, 8 H, $\mathrm{SiNC}\mathit{H}_2\mathrm{CH_2}$), 2.29 (t, 4 H, $\mathrm{Si_2NCH_2C}\mathit{H}_2$), 2.23 (m, 8 H, $\mathrm{SiNCH_2C}\mathit{H}_2$), 1.02 (s, 4 H, NH); ^{13}C NMR (C_6D_6) 53.82 (2C, $\mathrm{Si_2NCH_2}\mathit{C}\mathrm{H_2}$), 51.55 (4C, $\mathrm{SiHNCH_2}\mathit{C}\mathrm{H_2}$), 38.48 (2C, $\mathrm{Si_2N}\mathit{C}\mathrm{H_2CH_2}$), 38.23 (4C, $\mathrm{SiHN}\mathit{C}\mathrm{H_2CH_2}$); ^{29}Si NMR (C_6D_6) −76.26; LR MS (70 eV, EI) *m/z* (relative intensity, proposed ion) 340.1 (42.8, M^+), 310.2 (19.6, $M^+ - CH_2NH_2$), 298.2 (100.0, $M^+ - CH_2CH_2N$), 269.1 (16.2), 226.1 (4.49), 171.1 (56.5, $M/2 + H^+$); HRMS for $C_{12}H_{28}N_8Si_2$ (M^+) calcd 340.19755, found 340.19791; HRMS for $C_{10}H_{24}N_7Si_2$ ($M^+ - CH_2CH_2N$) calcd 298.16318, found 298.16451. Anal. Calcd for $C_{12}H_{28}N_8Si_2$: C, 42.35; H, 8.24; N, 32.94. Found: C, 42.73; H, 8.63; N, 32.23.

Method B. Compound **15** (2.10 g, 12.1 mmol) was mixed with KH powder (3 mg, 0.07 mmol) in a Schlenk tube equipped with a stirring bar. The mixture was slowly heated in an oil bath to 85 °C (the melting point of **15**) whereupon a rapid release of a gas was observed. After the oil bath was kept at 90 °C for ca. 10 min, the reaction was complete as indicated by the solidification of the reaction mixture. After purification as described above, 0.25 g of unconsumed **15** was recovered and crystalline **16** was obtained in 86% yield. Active KH was detected in the toluene used for recrystallization as indicated by the release of gas bubbles when it was exposed to moisture.

Method C. To a mixture of **15** (1.0 g, 5.7 mmol) and KH (3 mg, 0.07 mmol) was added 30 mL of THF. The solution was stirred at room temperature for 36 h. After removal of the THF under vacuum, the solid residue was extracted with 4 × 10 mL of toluene. Evaporation of the solvent afforded **16** in 88% yield.

Method D. Into a mixture of 0.50 g (2.9 mmol) of **15** and 0.02 g (0.5 mmol) of $NaNH_2$ was condensed ~25 mL of anhydrous ammonia distilled from sodium. The solution was stirred at −35° for 4 h, and then it was allowed to warm slowly to room temperature while evaporating the NH_3. Extraction of the residue with 4 × 8 mL portions of benzene followed by removal of the benzene under vacuum afforded **16** in 95% yield.

Crystal Structure Determination of 16. A clear crystal of **16** (dimensions 0.3 × 0.3 × 0.5 mm) grown from toluene was mounted in a glass capillary which was then placed on the CAD4 diffractometer for data collection at −50 ± 10 °C. Pertinent data collection and reduction information is given in Table 1. Lorentz and polarization corrections as well as a 2.4% correction based on a decay in the standard reflections were applied. An absorption correction based on a series of ψ-scans was applied. The agreement factor for the average of the observed reflections was 1.4% (based on *F*).

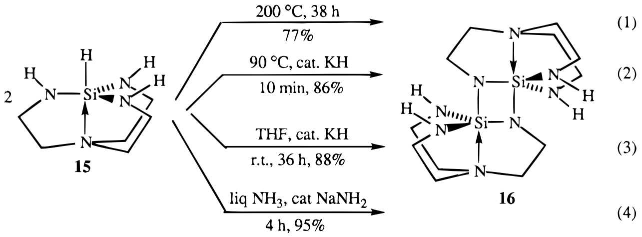
Table 1. Crystallographic Data for 16

formula	$Si_2N_8C_{12}H_{28}$
fw	340.58
a (Å)	6.962(2)
b (Å)	10.449(2)
c (Å)	11.253(3)
α (deg)	90.0
β (deg)	98.15(2)
γ (deg)	90.0
V (Å^3)	810.3(6)
Z	2
space group	$P2_1/n$
T (°C)	−50(1)
λ (Å)	0.710 73
d_{calc} (g/cm^3)	1.39
μ (cm^{-1})	2.2
transm coeff	0.999/0.931
R (F_o, %)	5.2
R_2 (F_o, %)	3.5

Axial photographs indicated that the lattice was monoclinic. The space group $P2_1/n$ was chosen on the basis of the systematic absences. The crystal structure was solved by direct methods.[14] All methylene hydrogens were generated with ideal positions with C−H distances equal to 0.96 Å and with isotropic thermal parameters fixed at a factor of 1.0 times the accompanying carbon atom. These were subsequently refined as riding hydrogen atoms. The amine hydrogens from N(2) and N(3) were found in a difference-Fourier map and were refined isotropically. The X-ray data collection and structure solution were carried out at the Iowa State Molecular Structure Laboratory. Refinement calculations were performed on a Digital Equipment Corp. MicroVAX II computer using the CAD4-SDP programs.[15,16] Positional parameters are listed in the Supporting Information.

Discussion

Despite the apparent opportunity for **15** to polymerize on loss of H_2, the formation of the dehydrocyclodimer **16** occurs in excellent yield under a variety of conditions:



Numerous examples of dehydrocyclodimerization reactions involving tetracoordinate aminosilanes have been reported[17] and catalytic dehydrocyclodimerization is believed to begin with deprotonation of an NH bond to form an amide.[17,18] The amide intermediate in our case would be **17**, which we had characterized earlier as the stable derivative **18**.[12] Here the N→Si transannular bond is retained, as was shown by ^{29}Si NMR spectroscopy. Whether this bond persists in the postulated intermediate **17** (wherein there is negative charge

---

(14) SHELXS-86: Sheldrick, G. M. Institut für Anorganische Chemie der Universität, Göttingen, FRG.

(15) Enraf-Nonius Structure Determination Package; Enraf-Nonius: Delft, Holland.

(16) Neutral-atom scattering factors and anomalous scattering corrections were taken from: *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV.

(17) (a) Andrianov, V. M.; Kopylov, V. M.; Khananashvili, L. M.; Nesterova, T. V. *Dokl. Akad. Nauk SSR* **1967**, *176*, 85. (b) Andrianov, V. M.; Shkol'nik, M. I.; Syrtsova, Zh. S.; Petrov, K. I.; Kopylov, V. M.; Zaitseva, M. G.; Koroleva, E. A. *Dokl. Akad. Nauk SSR* **1975**, *223*, 347. (c) Andrianov, V. M.; Shkol'nik, M. I.; Kopylov, V. M.; Prikhod'ko, P. L. *Dokl. Akad. Nauk SSR* **1975**, *227*, 352. (d) Breed, L. W.; Wiley, J. C., Jr. *Inorg. Chem.* **1972**, *11*, 1634.

(18) Klingebiel, U.; Bentman, D.; Meller, A. J. *J. Organomet. Chem.* **1978**, *144*, 381.

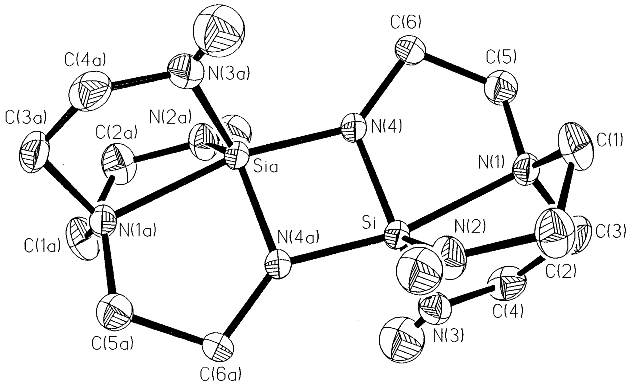
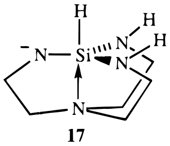
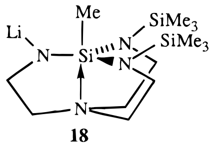


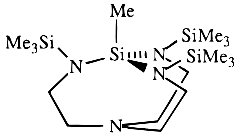
Figure 1. Computer drawing of **16**. Ellipsoids are drawn at the 50% probability level.



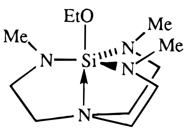
17



18

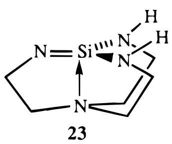


19

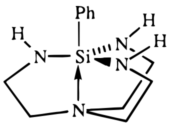


20

accumulation on the silicon) or during the subsequent attack of **17** on another molecule of **15** (at which point intermolecular steric interactions may stretch this bond) is not known. It may be pointed out in this regard, however, that steric interactions among the methyl and Me_3Si groups in **19** does lead to a lengthening of this bond by about 0.6 Å compared with **20**.[12] One plausible pathway for the base-catalyzed formation of **16** is shown in Scheme 1 for the case of KH as the catalyst. Whether or not transannular interactions occur in intermediates **21** and **22** is speculative. A similar mechanism was put forth earlier[17] for silazane formation from amino-functionalized silyl hydrides. A second mechanism postulated for similar reactions involves a silaimine intermediate formed by β-elimination.[18] In our reaction such an intermediate would resemble **23** which would then dimerize in "head-to-tail" fashion to **16**. A pathway involving a silaimine has also been postulated in the reaction of lithium silylamides with chlorosilanes to give cyclodisilazanes, but an attempt to trap the silaimine intermediate was unsuccessful.[19]

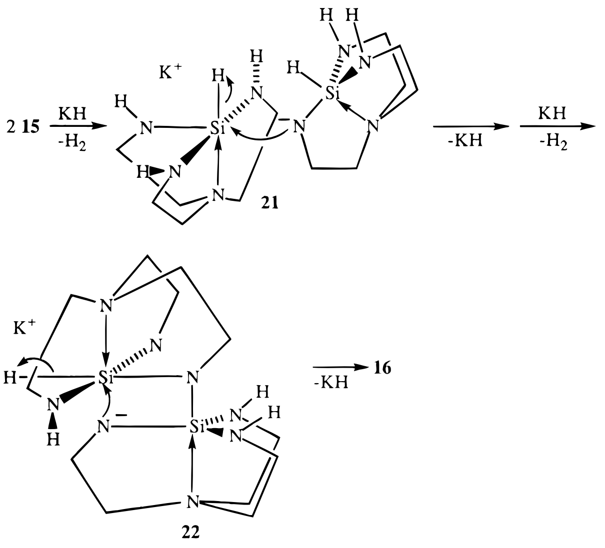


23



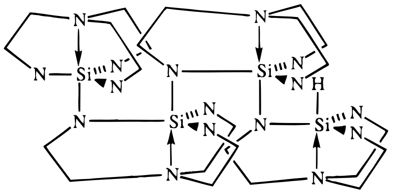
24

Scheme 1



The transannular Si←N bonds in **16** are 2.139(2) Å which compares very favorably with that in **20** (2.135(2) Å[12]) and **24** (2.132(2) Å[20]). The equatorial Si−N bond lengths in **16** are within 3σ of one another with an average of 2.137(2) Å. The presence of the four-membered ring distorts the N(4)−Si(a)−N(1a) angle from linearity to 166.94(7)°, but the geometry around N(4) is approximately as planar as it is in **20**. Thus the sum of the bond angles around N(4) in **16** is 356.5°, while in **20** the average of the three sums of these angles is 352.6°.[12]

It would appear that the primary reason for the termination of reactions 1−4 in the dimeric product **16** in the high yields observed here is steric in origin. Thus if the second and third condensations were to occur intermolecularly with a third and fourth molecule of **15**, the tetramer would resemble the structure depicted as **25** wherein the amino hydrogens have been omitted for clarity. In this structure the five-coordinate silicon stereochemistry (enforced by the normal transannular Si←N bond) is seen to constrain the cages to interpenetrate with substantial concommitant contacts of the protons on the CH_2CH_2 groups.



25

Acknowledgment. The authors thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for grant support of this research. We thank Dr. V. Young for the crystal structure determination.

Supporting Information Available: Text describing X-ray procedures, tables of crystal data, bond distances, bond angles, positional parameters, and general displacement parameters, and ORTEP diagrams (9 pages). Ordering information is given on any current masthead page.

OM960736Y

---

(19) Wiseman, G. H.; Wheeler, D. R.; Seyferth, D. *Organometallics* **1986**, *5*, 146.

(20) Macharshvili, A.; Shklover, V. E.; Struchkhov, Yu. T.; Lapsina, A.; Zelchan, G.; Lukevic, E. *J. Organomet. Chem.* **1988**, *349*, 23.