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1,3-Di(*tert*-butyl)-2,4-di(*tert*-butylamido)-2,4-dimethylcyclodisilazane: A Chelating Ancillary Diamide Ligand for Transition Metals

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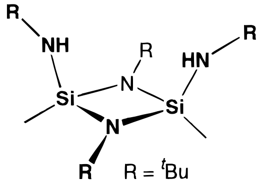
In the late 1980s Veith et al. reported the syntheses of the di(*tert*-butylamino)cyclodisilazane[1,2] [(MeSiN^{t}Bu)$_2$(N^{t}BuH)$_2$], **1a**, and some of its polycyclic main-group metal compounds.[3]



1a

In its dianionic form this molecule is an ideal chelating diamide, but because of its rather cumbersome purification steps, it never gained widespread acceptance as a ligand. We recently demonstrated that this heterocycle can also be used for the synthesis of group 4 metal[4] complexes and have sought an easier route to **1a** than that published previously. Contrary to these earlier reports we were able to separate both isomers by fractional crystallization, thus significantly simplifying the isolation of this molecule. Here we report the improved synthesis of **1a** and the single-crystal X-ray structures of its *trans* isomer **1b** and of *cis*-[(MeSiN^{t}Bu)$_2$(N^{t}BuLi·THF)$_2$], a convenient starting material for complexes of this ligand.

Experimental Section

All operations described were performed in standard Schlenk glassware under a protective atmosphere of purified nitrogen or argon. The solvents were thoroughly dried and freed of dissolved molecular oxygen by distillation from sodium or potassium benzophenone ketyl immediately before use. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Varian VXR-300 spectrometer. Peaks are referenced relative to C_6D_5H (7.15 ppm), C_6D_6 (128.0 ppm), and TMS (0.0 ppm), respectively. Melting points were obtained on a Mel-Temp apparatus; they are uncorrected. Elemental analyses were performed by Desert Analytics Laboratory, Tucson, AZ. Methyltrichlorosilane, *tert*-butylamine, *n*-butyllithium (2.5 M in hexanes), and *tert*-butyllithium (1.7 M in pentane) were obtained from Aldrich and used as received. Di(*tert*-butylamino)(chloro)methylsilane was prepared according to a published procedure.[5]

Synthesis of *cis/trans*-1,3-di(*tert*-butyl)-2,4-di(*tert*-butylamino)-2,4-dimethylcyclodisilazane. To 63 g (280 mmol) of di(*tert*-butylamino)(chloro)methylsilane in 400 mL of hexanes was added dropwise at 0 °C 170 mL of a 1.7 M *tert*-butyllithium solution. After about 35 mL of the butyllithium solution had been added, a white precipitate of LiCl formed. When the addition was complete, the solution was refluxed for 4 h, allowed to cool, and filtered through a medium-porosity frit. Most of the solvent was distilled off at ambient pressure, and the liquid residue was transferred to a 100 mL flask. It was then vacuum-distilled on a short-path distillation column (200×10^{-3} Torr, 90 °C) and collected as a colorless, syrupy liquid. After 24 h the liquid hardened to a white solid which consisted of a 3:1 cis/trans mixture. Yield: 33 g, 64%.

Separation of Cis and Trans Isomers by Fractional Crystallization. The solid from the previous step was dissolved in a volume of hexanes equal to its mass and stored at 4 °C for 3 days. This yielded 6.8 g of block-shaped crystals of **1b**. The supernatant was transferred to another flask, reduced to ca. 50% of its original volume, and stored at −12 °C for several days. This produced 19.7 g, 52.9 mmol, of needle-shaped crystals of slightly impure **1a** (ca. 4% trans content).

***cis*-1,3-di(*tert*-butyl)-2,4-di(*tert*-butylamino)-2, 4-dimethylcyclodisilazane, 1a.** Mp: −5 °C (mp for 2:1 cis/trans mixture: 58 °C). ^{1}H NMR (300 MHz, benzene-d_6, 21 °C): $\delta = 1.366$ (s, 18H; N^{t}Bu), 1.242 (s, 18H; N^{t}Bu), 0.361 (s, 6H, SiMe). ^{13}C NMR (75 MHz, benzene-d_6, 21 °C): $\delta = 50.26$ (s, NCMe$_3$), 49.55 (s, NCMe$_3$), 34.29 (q, NC*Me*$_3$), 33.70 (q, NC*Me*$_3$), 4.93 (q, SiMe). ^{29}Si{^{1}H} NMR (59.6 MHz, benzene-d_6, 21 °C): $\delta = -35.4$.

***trans*-1,3-di(*tert*-butyl)-2,4-di(*tert*-butylamino)-2,4-dimethylcyclodisilazane, 1b.** Mp: 77 °C. ^{1}H NMR (300 MHz, benzene-d_6, 21 °C): $\delta = 1.384$ (s, 18H; N^{t}Bu), 1.261 (s, 18H; N^{t}Bu), 0.349 (s, 3H, SiMe). ^{13}C NMR (75 MHz, benzene-d_6, 21 °C): $\delta = 50.24$ (s, NCMe$_3$), 49.69 (s, NCMe$_3$), 34.28 (q, NC*Me*$_3$), 33.52 (q, NC*Me*$_3$), 4.33 (q, SiMe). ^{29}Si{^{1}H} NMR (59.6 MHz, benzene-d_6, 21 °C): $\delta = -33.8$.

***cis*-[(MeSiN^{t}Bu)$_2$(N^{t}BuLi·THF)$_2$].** A 250 mL three-neck flask equipped with stirbar, dropping funnel, and two gas inlets was charged with 11.2 g (0.0301 mol) of **1a** and 60 mL of THF and cooled to −78 °C. Exactly 25 mL of 2.5 M *n*-butyllithium was then added dropwise to this solution. Upon reaching room temperature the light-yellow solution was refluxed for 3 h and then reduced to 30 mL in vacuo. After several days at −12 °C, 9.6 g of large, colorless crystals of *cis*-[(MeSiN^{t}Bu)$_2$(N^{t}BuLi·THF)$_2$] was isolated. The supernatant was concentrated to 15 mL and stored at −12 °C for 2 days to afford an additional 3.4 g of **2**. Overall yield: 13.0 g, 82%.

Mp: 96 °C (dec). ^{1}H NMR (300 MHz, benzene-d_6, 21 °C): $\delta = 3.680$ (t, 8H, OCH$_2$), 1.466 (s, 18 H; N^{t}Bu), 1.408 (s, 18H, N^{t}Bu), 1.320 (q, 8H, CH$_2$), 0.902 (s, Si−Me). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6, 21 °C): $\delta = 68.80$ (s, OCH$_2$), 51.25 (s, NCMe$_3$), 51.06 (s, NCMe$_3$), 38.61 (s, NC*Me*$_3$), 34.22 (s, NC*Me*$_3$), 25.43 (s, OCH$_2$*C*H$_2$), 5.77 (s, SiMe). ^{29}Si{^{1}H} NMR (59.6 MHz, benzene-d_6, 21 °C): $\delta = -25.5$. Anal. Calcd for $C_{26}H_{58}N_4Li_2O_2Si_2$: C, 59.07; H, 11.06; N, 10.59. Found: C, 58.71; H, 10.73; N, 10.81.

X-ray Diffraction Studies. For **1b** (**2**), a data set, $4.8° < 2\theta < 60.1°$ (3.2−50.0°), $-11 \le h \le 11$, $-22 \le k \le 22$, $-8 \le l \le 11$ ($-14 \le h \le 13$, $-24 \le k \le 24$, $-11 \le l \le 22$) of 7520 (15 520) reflections in 1271 frames was collected at 193 (233) K with a Siemens SMART CCD diffractometer using ω scans of 0.3° per frame. Of these

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(1) For representative articles and reviews on cyclodisilazanes, see: (a) Pflugmacher, A.; Dahmen, H. *Z. Anorg. Allg.Chem.* **1957**, *290*, 184. (b) Lienhard, K.; Rochow, E. G. *Angew. Chem.* **1963**, *75*, 638. (c) Fink, W. *Helv. Chim. Acta* **1966**, *49*, 1408. (d) Zhinkin, D. Y.; Varezhkin, Y. M.; Morgunova, M. M. *Usp. Khim.* **1980**, *49*, 2314. (e) Klingebiel, U. in *The Chemistry of Inorganic Homo- and Heterocycles*; Haiduc, I., Sowerby, D. B., Eds.; Academic Press: London, 1987; Vol. I .

(2) For a more recent article on bis(amido)cyclodisilazane complexes, see: Veith, M.; Rammo, A.; Hans, M. *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *93−94*, 197.

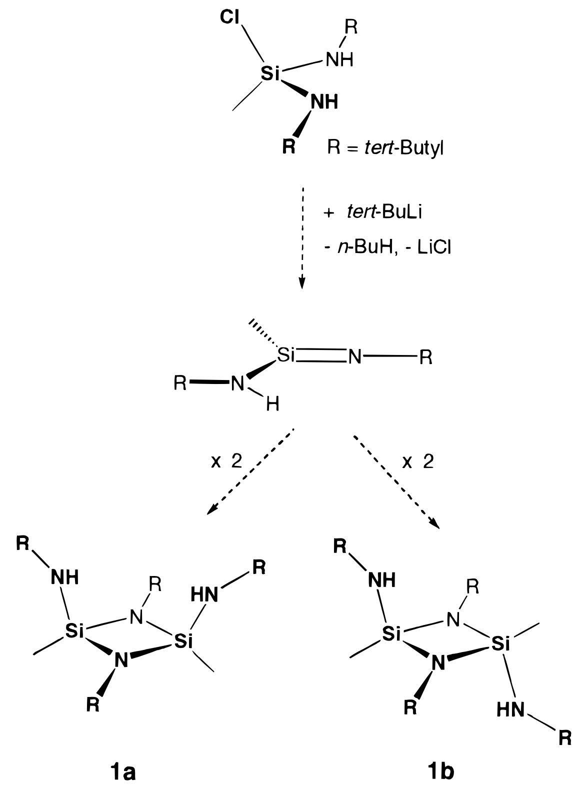
(3) (a) Veith, M.; Goffing, F.; Becker, S.; Huch, V. *J. Organomet. Chem.* **1991**, *406*, 105. (b) Veith, M.; Goffing, F.; Huch, V. *Chem. Ber.* **1988**, *121*, 943. (c) Veith, M.; Becker, S.; Huch, V. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1237. (d) Veith, M.; Goffing, F.; Huch, V. *Z. Naturforsch.* **1988**, *43b*, 846.

(4) Grocholl, L.; Huch, V.; Stahl, L.; Staples, R. J.; Steinhart, P.; Johnson, A. *Inorg. Chem.* **1997**, *36*, 4451.

(5) Transjö, L. *Acta Chem. Scand.* **1959**, *13*, 35.

S0020-1669(98)00114-1 CCC: $15.00

Scheme 1



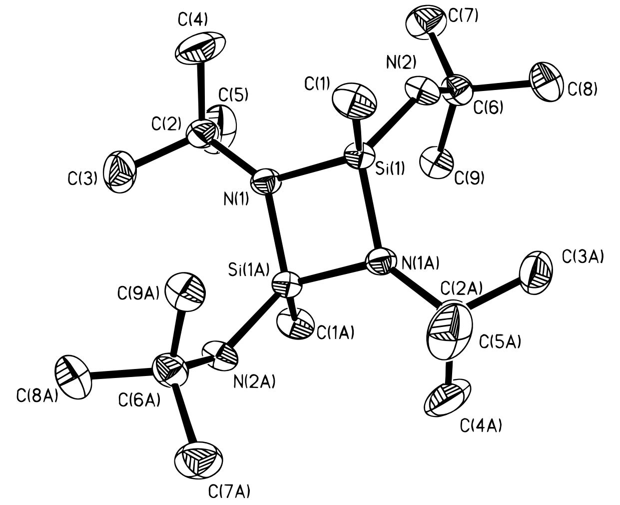


Figure 1. ORTEP drawing and numbering scheme for **1b**. The 50% thermal ellipsoids are shown.

Table 1. Crystal Data for **1b** and **2**

empirical formula	$C_{18}H_{44}N_4Si_2$	$C_{26}H_{58}Li_2N_4O_2Si_2$
fw	372.75	528.82
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
lattice constants		
a, Å	8.422(1)	10.550(2)
b, Å	16.997(4)	18.541(2)
c, Å	8.205(1)	17.524(2)
β, deg	98.44(1)	92.245(9)
V, Å^3	1161.8(4)	3425.2(7)
Z	2	4
ρ(calc), g cm^{-3}	1.066	1.026
λ, Å	0.710 73	0.710 73
T, K	193	233
μ, cm^{-1}	1.61	1.29
R(*F*)[a]	0.0459	0.0634
wR2[b]	0.1143	0.1753

[a] $R = \sum|F_o - F_c|/\sum|F_o|$. [b] $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o)^2 + (xP)^2 + yP]$ where $P = (F_o^2+2F_c^2)/3$. **1b**: $x = 0.0573$, $y = 0.4516$. **2**: $x = 0.0771$; $y = 2.0935$

Table 2. Selected Bond Lengths and Angles for **1b**

Bond Lengths (Å)			
Si(1)−N(1)	1.7397(13)	Si(1)−N(1A)	1.7374(12)
Si(1)−N(2)	1.7145(13)	Si(1)−C(1)	1.869(2)
Si(1)−Si(1A)	2.5417(8)	N(1)−C(2)	1.472(2)

Bond Angles (deg)			
N(1)−Si(1)−N(1A)	86.06(6)	N(1)−Si(1)−N(2)	119.41(6)
N(1A)-Si(1)−N(2)	120.00(6)	N(2)−Si(1)−C(1)	101.06(7)
N(1A)-Si(1)−C(1)	115.42(7)	N(1)−Si(1)−C(1)	115.81(7)
Si(1)−N(1)-Si(1A)	93.94(6)	Si(1)−N(1)−C(2)	132.45(10)
Si(1A)−N(1)−C(2)	133.17(10)		

reflections 3054 (5970) were considered unique and observed ($I > 2\sigma(I)$) and used in the refinement. The first 50 frames were re-collected at the end of data collection to monitor for decay. Cell parameters were retrieved with SMART[6] software and refined using SAINT[7] on all observed reflections. The data were reduced with SAINT, which corrects for Lp and decay, and were absorption corrected with XEMP. The structures were solved by direct methods with the SHELX-90[8] program and refined by least-squares methods on F^2 with SHELXL-93,[9] incorporated in SHELXTL-PC V 5.03.[10] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in their geometrically generated positions and refined assuming a riding model. A final difference map showed no rest-electron density greater than 0.268 e Å^{-3} (0.438 e Å^{-3}) or less than − 0.367 e Å^{-3} (−0.251 e Å^{-3}).

Results and Discussion

Reaction of di(*tert*-butylamino)(chloro)methylsilane with *tert*-butyllithium in hexanes, Scheme 1, gave predominantly the cyclodisilazanes **1a/1b** and, in smaller amounts, the substitution product di(*tert*-butylamino)(*tert*-butyl)methylsilane and some unidentified oligomeric and polymeric silazanes. The separation of these products by vacuum distillation afforded spectroscopically pure **1a/1b** in 60% isolated yields, from which the desirable cis isomer, **1a**, was obtained by fractional crystallization in greater than 95% purity.

While the pure cis isomer is a liquid at room, cocrystals of **1a/1b** were of sufficient quality to allow at least the derivation of the unit-cell parameters and the identification of the unit-cell content as a 2:1 mixture of both isomers. Disorder problems prevented us from satisfactorily refining the structure, but we were able to ascertain that the N−H groups of the cis isomer in the cocrystal have an endo-exo orientation with respect to the cyclodisilazane ring.

For single crystals of pure **1b**, Figure 1, structure solution and refinement proceeded straightforwardly, and its crystal data and selected bond distances and angles are listed in Tables 1 and 2, respectively. This cyclodisilazane is a molecular solid, whose C_i point symmetry demands that the cyclodisilazane ring and the two *tert*-butyl substituents be perfectly planar. The crystallographically nonequivalent silicon−nitrogen bonds of the ring, Si(1)−N(1) and Si(1)−N(1A), are identical in lengths and slightly longer than the exocyclic Si−N bonds. Both silicon atoms have distorted tetrahedral coordination environments that

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(6) *SMART V 4.043 Software for the CCD Detector System*; Siemens Analytical Instruments Division: Madison, WI, 1995.

(7) *SAINT V 4.035 Software for the CCD Detector System*; Siemens Analytical Instruments Division: Madison, WI, 1995.

(8) Sheldrick, G. M. *SHELXS-90, Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1986.

(9) Sheldrick, G. M. *SHELXL-93, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1993.

(10) *SHELXTL 5.03 (PC−Version), Program library for Structure Solution and Molecular Graphics*; Siemens Analytical Instruments Division: Madison, WI, 1995.

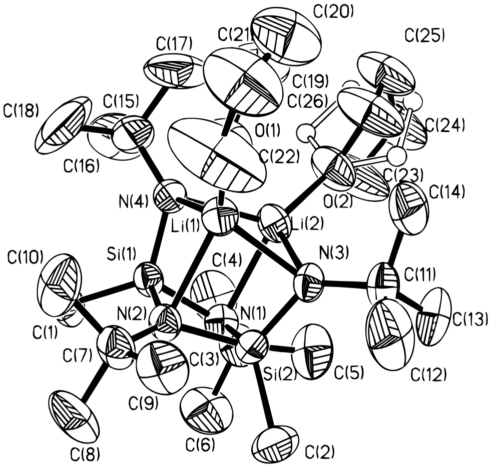

Figure 2. Perspective ORTEP view, showing the 50% thermal ellipsoids and numbering scheme for **2**. One of the tetrahydrofuran molecules adopts two conformations in the crystal; the minor one of these is shown in outline only.

range from a rather acute intraannular N(1)−Si−N(1A) angle of 86° to a comparatively obtuse extraannular N(2)−Si−N(1A) angle of 120°. Interestingly, the N−H groups of this isomer have an exo-exo orientation.

Although dilithiation of an isomeric mixture of **1a/b** with *n*-butyllithium in hexanes had been reported to proceed readily,[3b] it proved troublesome for pure **1a**, often resulting in very low yields. Treatment of the cyclodisilazane with 2 equiv of *n*-butyllithium in refluxing THF, however, afforded the dilithio salt, **2**, in good yields. This highly crystalline solid is an ideal starting material for metal complexes of this ligand.

An ORTEP drawing of **2** is shown in Figure 2, and its crystal data and selected bond distances and angles are collected in Tables 1 and 3, respectively. The crystal structure consists of approximately C_{2v}-symmetric heterocubes whose monomeric nature is in contrast to the *intermolecular* Li···N interactions of the dimeric unsolvated derivative.[3b] The distorted molecular cage has dissimilar edge lengths and intracube angles, which range from 1.670 to 2.255 Å, and from 85.70 to 107.32°, respectively. Although the endocyclic silicon−nitrogen bonds are slightly longer than those in pristine **1b**, the exocyclic Si−N bonds are shortened, presumably through inductive effects exerted by the lithium atoms. There are two distinct sets of lithium−nitrogen bonds, namely, four nearly equal lithium−amide bonds of the (Li−N)$_2$ moiety and two slightly longer, 0.1 Å, N−Li donor bonds. One of the more conspicuous features of this structure is the extremely short distance between the lithium atoms, which are within 0.1 Å of the sum of their covalent radii. Although these atoms are undoubtedly not bonded, their proximity does suggest that this ligand might find applications in the syntheses of metal−metal-bonded bimetallic species.

Table 3. Selected Bond Lengths and Angles for **2**

Bond Lengths (Å)			
Si(1)−N(4)	1.670(2)	Si(1)−N(2)	1.764(2)
Si(1)−N(1)	1.764(2)	Si(2)−N(3)	1.674(2)
Si(2)−N(2)	1.764(2)	Si(2)−N(1)	1.758(2)
Li(1)−O(1)	1.983(5)	Li(1)−N(4)	2.149(5)
Li(1)−N(3)	2.120(5)	Li(1)−N(2)	2.255(5)
Li(2)−O(2)	1.993(5)	Li(2)−N(4)	2.128(5)
Li(2)−N(3)	2.160(5)	Li(2)−N(1)	2.235(5)

Bond Angles (deg)			
N(2)−Si(1)−N(1)	85.70(10)	N(2)−Si(2)−N(1)	85.85(10)
N(4)−Li(1)−N(3)	103.7(2)	N(4)−Li(2)−N(3)	103.1(2)
Si(2)−N(1)−Si(1)	92.54(10)	Li(2)−N(4)−Li(1)	72.4(2)
Si(2)−N(2)−Si(1)	92.34(10)	Li(2)−N(3)−Li(1)	72.4(2)

Cyclodimerizations of dialkylamino(chloro)methylsilanes thus offer a convenient entry into substituted cyclodisilazanes. Its generality makes this synthetic procedure useful for a wide variety of bis(alkylamino)cyclodisilazanes, starting from the appropriate alkyltrichlorosilanes and alkylamines,[5] although the substituent-dependent ratio of cis and trans isomers does, of course, impose practical limits on the nature of the organic groups.

Acknowledgment. We thank the University of North Dakota and North Dakota EPSCoR for financial support.

Supporting Information Available: X-ray crystallographic files, in CIF format, for complexes **1b** and **2** are available on the Internet only. Access information is given on any current masthead page.

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