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Bis(trimethylsilyl)methylamine from Cyanides[1]

Jean-Paul Picard,* Stephane Grelier, Thierry Constantieux, and Jacques Dunoguès

Laboratoire de Chimie Organique et Organométallique (URA 35 CNRS),
Université Bordeaux I, 33405 Talence, France

Jesus Maria Aizpurua and Claudio Palomo

Departamento de Química Orgánica, Facultad de Química, Universidad del País Vasco,
Ado 1072, 20080 San Sebastián, Spain

Michel Pétraud and Bernard Barbe

Centre d'Etude Structurale et d'Analyse des Molécules Organiques (CESAMO),
Université Bordeaux I, 33405 Talence, France

Ludovico Lunazzi

Dipartimento di Chimica Organica "A. Mangini", Università di Bologna, 40136 Bologna, Italy

Jean-Michel Léger

Laboratorie de Chimie Analytique (SDI 6315 CNRS), Faculté des Sciences Pharmaceutiques,
Université Bordeaux II, 3 ter. Place de la Victoire, 33076 Bordeaux, France

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An efficient preparative method for bis(trimethylsilyl)methylamine (BSMA), 1, starting from various cyanides or isocyanides and using reductive silylation reaction is described. The intermediacy of the previously known *N*,*N*-bis(trimethylsilyl)[bis(trimethylsilyl)methyl]amine, 2, has been demonstrated, and its structure as a single rotamer was confirmed. Rotation around the C–N bond has been shown to be prevented for temperatures up to 180 °C. The same structure and properties were found for new silylmethyl derivatives **3a** and **3b**. Results have been interpreted in terms of radical anion process, (iso)cyanotrimethylsilane being apparently the common intermediate. Also involved was a 1–4 internal hydrogen radical migration, occurring in an intermediate radical anion.

Introduction

The chemistry of α-silyl functional compounds, SiCZ (Z being a heteroatomic functionality), is now well developed[2,3] and illustrated, for instance, by the use of halomethylsilanes in Peterson olefination reactions.[4–6] Among these, monosilylmethylamines, $\equiv SiCH_2NH_2$, and their derivatives have received increased attention since they were shown to present great synthetic (for example, as precursors of pyrrolidine derivatives[7,8]) and biologic potential (for some of them[9–11]).

We are currently interested in bis(silyl)methylamine derivatives, $\equiv Si_2CHN<$, and have recently shown bis(trimethylsilyl)methylamine (BSMA), 1, to be a good synthon for organic synthesis. For example, original imines, phthalimides, 2-aza 1,3-dienes, azetidinones, oxa- and carbacephems, and pyrrole derivatives have been efficiently prepared.[12–15]

In order to develop such a chemistry, we have made efforts to set up synthetic methods for BSMA and have already reported amination of bis(trimethylsilyl)chloromethane to be effective:[15]

$$CH_2Cl_2 \rightarrow (Me_3Si)_2CHCl \rightarrow (Me_3Si)_2CHNH_2 \quad (1)$$

However, considering its structure, we thought the formation of BSMA from a cyanide or isocyanide moiety (Σ-(CN)) through reductive silylation may be possible, a reaction which has been demonstrated to be very efficient when applied to a large variety of unsaturated functionalities,[16] including nitrile derivatives.[17]

$$\Sigma\text{-(CN)} \rightarrow (Me_3Si)_2CHN(SiMe_3)_2 \rightarrow 1$$

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[1] This work is taken in part from the Thesis of S.G., University Bordeaux I, 1991.

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[7] Imai, N.; Terao, T.; Achiwa, K. *J. Synthetic Org. Chem.* **1985**, *43*, 862.

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[13] Palomo, C.; Aizpurua, J. M.; Garcia, J. M.; Picard, J.-P.; Dunoguès, J. *Tetrahedron Lett.* **1990**, *31*, 1921.

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[15] Palomo, C.; Aizpurua, J. M.; Garcia, J. M.; Legido, M. *J. Chem. Soc., Chem. Commun.* **1991**, 524.

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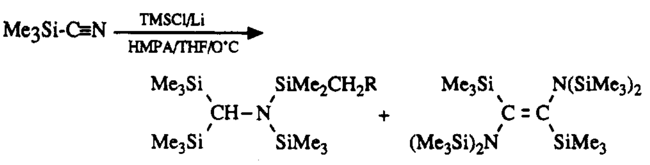
Scheme I. Reductive Silylation of Cyanotrimethylsilane



(2) R = H ; (3) R = SiMe3 (4)

Table I. Influence of the Quality of Lithium

Na, %	2 + 3 yield, %	2/3 ratio, %
0.01	60	65/35
1	80	17/83

This paper deals with reductive silylation of various cyano derivatives and shows that this reaction provides effectively an excellent access to 1. A preliminary account of part of this work has been published.[18]

Results

Reductive Silylation Reactions. To test our intended methodology, we first considered the reductive silylation of cyanotrimethylsilane, in THF solution at 0–5 °C, with lithium and chlorotrimethylsilane (TMSCl) in the presence of hexamethylphosphoramide (HMPA).[19] *N,N*-Disilyl derivatives **2** and **3** were formed in addition to trace amounts of enediamine **4** (Scheme I).

Factors expected to have marked influence on the course of the reaction were examined. In all cases, yield of **4** remained low (constant around 5%). On the contrary, as shown in Table I and using standard conditions as defined below (Table II, entry 5), an increase of the sodium content in lithium increased the **2** + **3** yield slightly and inverted the **2**/**3** ratio.

The ratio of reactants was also very significant. To convert 1 equiv of cyanotrimethylsilane into compound **2** or **3**, the stoichiometry would require 4 equiv of lithium, 4 equiv of TMSCl, and 4 equiv of HMPA (to form the HMPA/LiCl complex[20]). Keeping the HMPA/Li ratio equal to 1 and using different TMSCl/Li ratios induced noticeable changes in the results of the reaction, as shown in Table II.

Contrary to the observation made by West[21] in the course of the reductive silylation of bis(trimethylsilyl)acetylene, an increase in the yield of the more silylated compound (here **3**) is associated with an increase of the quantity of the reactants. With the conditions thus defined (Table II, entry 5), various cyanides and isocyanides were submitted to the reductive silylation reaction (Table III).

Table II. Influence of the Ratio of Reactants

entry	Li, equiv	TMSCl, equiv	2 + 3 yield, %	2/3 ratio, %
1	6	4	30	60/40
2	4	4	25	75/25
3	4	20	40	63/37
4	8	20	60	30/70
5	8	40	80	17/83

Table III. Reductive Silylation of (Iso)cyanides

entry	substrate	2 + 3 yield, %	2/3 ratio, %
1	$Me_3SiC{\equiv}N$	80	17/83
2	$EtMe_2SiC{\equiv}N$	85	22/78
3	$t\text{-}BuMe_2SiC{\equiv}N$	57	58/42
4	$Me_2NC{\equiv}N$	78	25/75
5	$t\text{-}OctN{=}C$	65	65/35
6	$t\text{-}BuN{=}C$	80	98/2

Results from cyanosilanes (Table III, entries 2 and 3) clearly indicated that the formation of **2** and **3** proceeded through the loss of the original trialkylsilyl moiety. This was confirmed by the quantitative formation of ethyl- and *tert*-butylpentamethyldisilanes. Assuming the cyanide group to be responsible for the compounds' reactivity,[22] dimethylcyanamide was tested (Table III, entry 4) on the basis of the ability of cyanamides to free the cyano group (behaving in such instance as a pseudohalogen) in the presence, for example, of Grignard[23] or lithium reagents.[24] Results as good as from cyanotrimethylsilane were obtained.

On the other hand, it was reported that isonitriles were able to transfer their isonitrile group (to form a nitrile) when treated with an organolithium reagent.[25,26] This also occurred in our case from *tert*-octyl- and *tert*-butylisonitriles (Table III, entries 5 and 6) as **2** + **3** mixtures were obtained along with quantitative yields of *tert*-octyl- and *tert*-butyltrimethylsilanes, respectively.

Preparation of BSMA. Treatment of a methanolic solution of **2** and/or **3** by 1 equiv of TMSCl gave quantitative yields of the hydrochloride of BSMA, **5**, along with the corresponding methoxysilanes (Scheme II). When an excess of TMSCl was used, the corresponding siloxanes were formed instead, with evolution of methyl chloride.[27]

Neutralization of **5** afforded the desired amine **1** in good to excellent overall yields (65–80%).

Identification of the Products. Compound **2** has been previously obtained by Calas et al.,[28] who explained the number of peaks (three) in the ^1H, ^{13}C, and ^{29}Si NMR spectra of its trimethylsilyl groups, by a hindered rotation around the C–N bond, resulting in a stable conformation with one N–Si bond eclipsing the C–H bond, as shown below. This excluded the staggered rotamer A. A similar phenomenon was observed recently with *N,N*-disilylisopropylamine, $Me_2CHN(SiH_3)_2$, even in the gaseous state.[29]

The more careful ^1H, ^{13}C, and ^{29}Si NMR study we have made has confirmed this hypothesis and has allowed

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(16) Calas, R.; Dunoguès, J. *J. Organomet. Chem. Lib.* **1976**, *2*, 227.

(17) Picard, J.-P.; Aizpurua, J.-M.; Elyusufi, A.; Kowalski, J. *J. Organomet. Chem.* **1990**, *391*, 13.

(18) Picard, J.-P.; Grelier, S.; Dunoguès, J.; Aizpurua, J.-M.; Palomo, C. *J. Organomet. Chem.* **1991**, *419*, C1.

(19) Due to the suspected toxicity of this material, the use of various chemicals proposed as substitutes for HMPA was checked: either they gave very poor yields (1,3-dimethyl-2-imidazolidinone "DMEU" and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidone "DMPU") or they react themselves (DMF, TMU, for example).

(20) De Bolster, M. W. G.; Groeneveld, L. *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 477.

(21) Quass, L. C.; West, R.; Husk, G. R. *J. Organomet. Chem.* **1970**, *21*, 65.

(22) LiCN has been tested: under the same reaction conditions, the 2 + 3 mixture was obtained in a 40% overall yield.

(23) Kharasch, M. S.; Reinmuth, O. *Grignard Reactions of Non Metallic substances*; Prentice Hall: New York, 1954; p 777.

(24) Ambrose, R. J.; Hergenrother, W. L. *Macromolecules* **1972**, *5*, 275.

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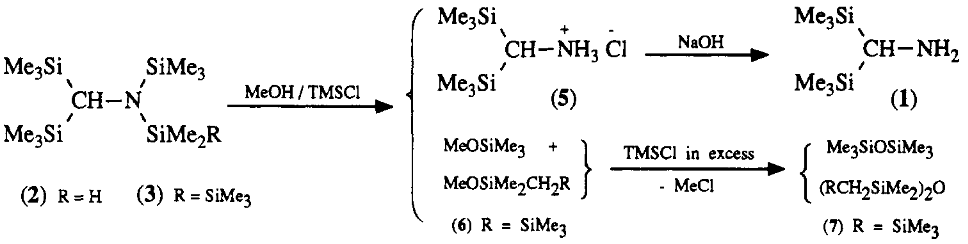
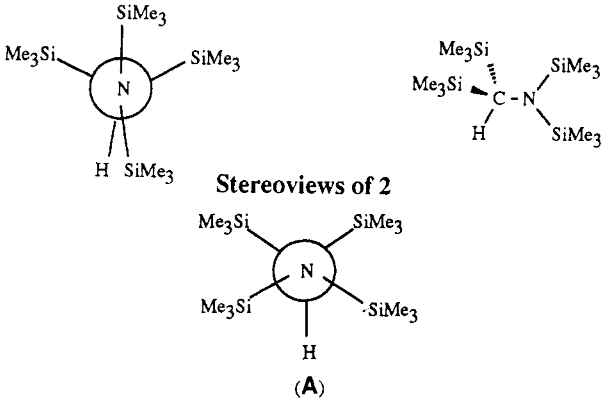
(29) Anderson, D. G.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1989**, 779.

Scheme II. Preparation of BSMA, 1

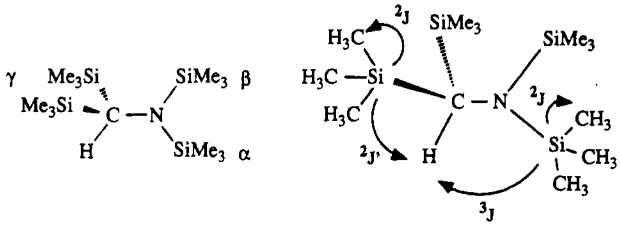




Stereoviews of 2

(A)

Table IV. ^{29}Si Chemical Shifts and $^nJ(^1\text{H}-^{29}\text{Si})$ Coupling Constants in 2



Me$_3$Si group	δ (ppm)	^2J (Hz)	$^2J'$ (Hz)	^3J (Hz)
α	4.45	6.3		7.1
β	7.54	6.4		11.5
γ	2.37	6.3	12.6	

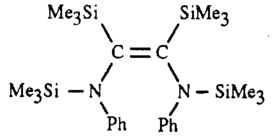
complete assignment of signals. First, all observed signals were matched for each type of nucleus using 2D ^{13}C–^{1}H and ^{29}Si–^{1}H correlation methods, demonstrating that two equivalent Me$_3$Si groups were linked to the carbon atom and two other magnetically inequivalent groups were attached to the nitrogen atom. The measurement of $^nJ(^1\text{H}-^{29}\text{Si})$ coupling constants and the involvement of a Karplus-type relation, as previously proposed in the case of silylated cyclopropane derivatives,[30] then allowed unambiguous assignment of the latter (Table IV). Moreover, NMR spectra recorded at variable temperatures have not shown any change up to 180 °C.[31] This was quite surprising as rotation was observed above 80 °C with symmetrical tetrakis(trimethylsilyl)ethane.[32]

Elemental analysis led to the formula $C_{16}H_{45}NSi_5$ for **3**. High-resolution mass spectrometric analysis confirmed it and cleanly showed the typical Me$_3$SiCH$_2$SiMe$_2$– fragment to be present in the molecule, excluding the isomeric formula (Me$_3$Si)$_3$CN(SiMe$_3$)$_2$. Careful GC analysis showed two very close peaks of almost equal intensities. Corresponding mass (from GC/MS) and infrared (from GC/FTIR) spectra were very similar. This, together with the large number of NMR signals, led us to consider **3** as a mixture of two rotamers, **3a** and **3b**, in which the framework was the same as in **2** and one trimethylsilyl group linked to nitrogen was replaced by the silylmethylsilyl moiety. Complete assignment of their ^{1}H, ^{13}C, and ^{29}Si NMR spectra was made possible by using values recorded for **2** and (^{1}H–^{13}C) and (^{1}H–^{2}19Si) correlations. Results are collected in Tables V and VI.

In order to assign the silyl groups of both rotamers **3a** and **3b**, [$^nJ(^{29}\text{Si}-^1\text{H})$] coupling constants were measured. A heteronuclear J-resolved 2D analysis via a nonrefocusing INEPT pulse sequence in ^{29}Si NMR was used.[33] The F_2 slice from the 2D map (Figure 2) led to an INEPT spectrum for each inequivalent silyl group. The INEPT spectrum was calculated using a new method[33] (Figures 1 and 2).

The minor compound **4**, a solid, has been studied by X-ray diffraction (Figure 3 and Table VII). The double bond is E and planar (in contrast with the previously described compound **4′** where the double bond is Z and twisted[34]), the nitrogen atoms are nearly planar, and the silazanyl groups are in a plane almost perpendicular to that of the double bond. The double bond is shorter than usual, and the silicon–sp^2-carbon bonds are longer as are the C–N bonds (Table VII).

(4')



Interpretation of the Results. Because of the heterogeneous character of the reductive silylation reaction medium, it was difficult to perform any mechanistic study. However, on the basis of our experience in similar reactions and of the observations made while performing this study, an interpretation of our results could be drawn (Scheme III). This scheme calls for the following comments:

(i) Reductive silylation generally involves a radical anion process where an electron is transferred from the metal onto the substrate.[35] The reaction then progresses successively through silylation of the anionic species and capture of an electron by radicals to form anions which are silylated to give neutral molecules.

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(30) Grignon-Dubois, M.; Laguerre, M. *Actual. Chim.* **1983** (12), 21. Grignon-Dubois, M.; Laguerre, M.; Barbe, B.; Pétraud, M. *Organometallics* **1984**, *3*, 359.

(31) Experiment run by Prof. L. Lunazzi, University of Bologna, Italy.

(32) Brownstein, S.; Dunoguès, J.; Lindsay, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1977**, *99*, 2073.

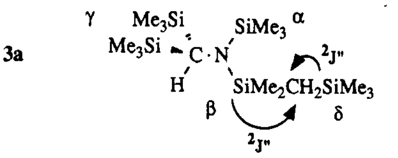
(33) Gouron, V.; Jousseaume, B.; Ratier, M.; Lartigue, J.-C.; Pétraud, M. *Magn. Reson. Chem.* **1990**, *28*, 755. Pétraud, M. Private communication.

(34) Efendene, B. Thesis, Bordeaux 1, 1983.

(35) See, for instance, ref 16 and particularly: Dunoguès, J.; Calas, R.; Bolourtchian, M.; Biran, C.; Duffaut, N. *J. Organomet. Chem.* **1973**, *57*, 55.

Table V. ^{29}Si Chemical Shifts and $^nJ(^1H-^{29}Si)$ Coupling Constants in 3a

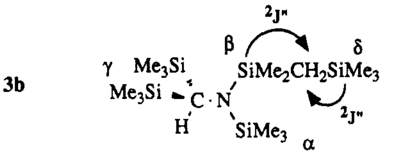
3a



MeSi group	δ (ppm)	^2J (Hz)	$^2J'$ (Hz)	$^2J''$ (Hz)	^3J (Hz)
α	3.60	6.3			11.3
β	6.52	6.2		9.3	7.0
γ	1.88	6.4	12.6		
δ	−1.12	6.5		9.2	

Table VI. ^{29}Si Chemical Shifts and $^nJ(^1H-^{29}Si)$ Coupling Constants in 3b

3b

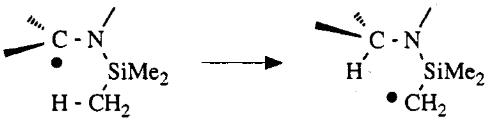


MeSi group	δ (ppm)	^2J (Hz)	$^2J'$ (Hz)	$^2J''$ (Hz)	^3J (Hz)
α	6.27	6.3			6.8
β	3.84	6.3		9.5	11.9
γ	1.88	6.4	12.6		
δ	−1.06	6.5		9.2	

(ii) Step a: $Me_3Si(CN)$ (i.e., silylcyanide and/or isocyanide isomer[36–38]) appears to be the common intermediate, whatever the starting material could be (Scheme IV). Ingold has already shown that reaction as loss of radical $\Sigma^{\bullet}$ from radical r_1 can easily occur to form isocyanosilane.[39]

(iii) Steps b–d: following a similar sequence of reactions, this silyl cyanide could lead to the iminoyl radical **R** (Scheme V) which would give either intermediate imine **M** (step c) after reductive silylation or enediamine **4** (step d) through dimerization and reductive silylation.

(iv) Step e: capture of one electron by **M** would form the corresponding radical anion **AR** (Scheme III). This could be silylated to make the tetrasilylated radical **R′**, a radical the great stability of which was demonstrated by Ingold[39,40] and recently confirmed by Walton.[41] Formation of **2** from **R′** would involve trapping of a hydrogen from the reaction medium, an unlikely event owing to the stability of **R′**. Moreover, formation of **3** from **R′** would involve its rearrangement to the isomeric primary radical by hydrogen–electron exchange:[42]



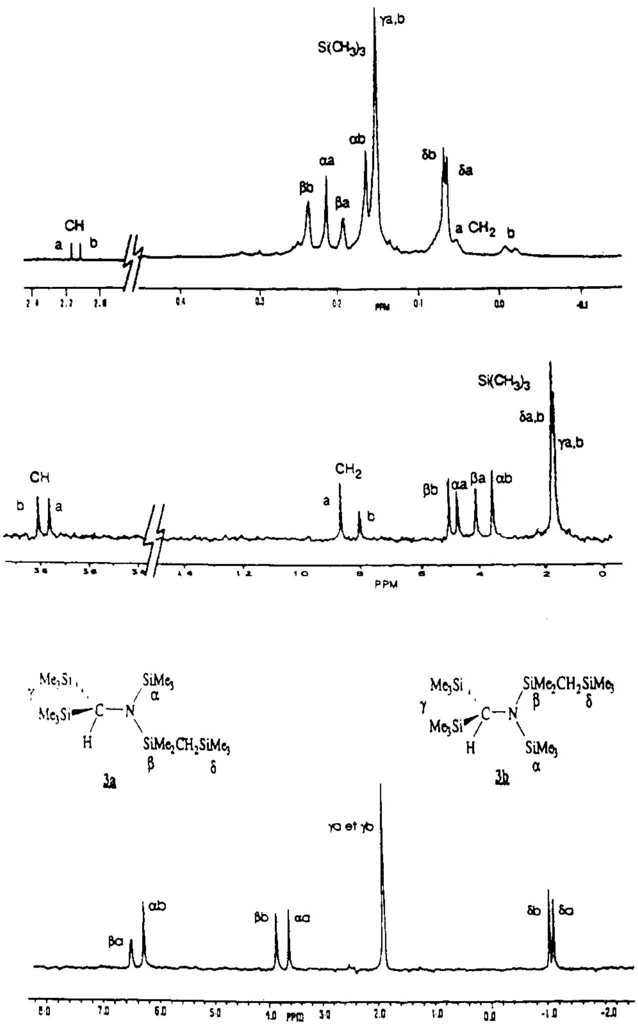
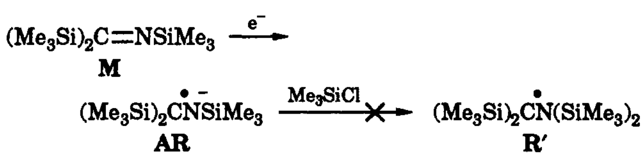


Figure 1. ^1H, ^{13}C, and ^{29}Si NMR spectra of **3** (**3a** + **3b** mixture).

In addition, if such rearrangement had occurred from **R′**, further reduction and silylation should have led only to **3a**. For this reason also, **R′** appeared not to be an intermediate in these reactions:



$$\underset{\mathbf{M}}{(Me_3Si)_2C{=}NSiMe_3} \xrightarrow{e^-}$$

$$\underset{\mathbf{AR}}{(Me_3Si)_2\overset{\bullet}{C}\overset{-}{N}SiMe_3} \not\xrightarrow{Me_3SiCl} \underset{\mathbf{R'}}{(Me_3Si)_2\overset{\bullet}{C}N(SiMe_3)_2}$$

(v) Steps f and g: occurrence of the same hydrogen transfer taking place on the less hindered radical-anion **AR** seems more likely (Scheme VI). This would give the isomeric radical-anion **AR′** (under its two rotameric forms **AR′a** and **AR′b**). Then, a silylation–reduction–silylation sequence would yield the observed products. Hydrogen abstraction from the reaction medium by intermediate silylmethyl radicals would yield **2**.

Conclusions

Reductive silylation of various (iso)cyanides, followed by desilylation, provides an alternative efficient preparative method for BSMA. Moreover, dimethylcyanamide, an industrial product, constitutes an attractive starting material, owing to its low cost.

The structure of *N*,*N*-bis(trimethylsilyl)[bis(trimethylsilyl)methyl]amine, **2**, as a single rotamer, has been

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[36] See ref 4, p 15.

[37] Bury, A. Private communication. Cited by: Bither, T. A.; Knoth, W. H.; Lindsey, R. V., Jr.; Sharkey, W. H. *J. Am. Chem. Soc.* **1958**, *80*, 41.

[38] Müller, R.; Neef, H. *J. Prakt. Chem.* **1971**, *313*, 754.

[39] Kaba, R.; Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 6202.

[40] Brunton, G.; Taylor, J. F.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 4880.

[41] As well as being long-lived, this radical was shown to survive to heat (180 °C). We are indebted to Dr. J. Walton, University of St. Andrews, Scotland (G.B.), for having performed this experiment.

[42] A similar rearrangement involving anionic species has been proposed in the case of insaturated substrates. See: Wrocynski, R. J.; Baum, M. W.; Kost, D.; Mislow, K.; Vick, S. C.; Seyferth, D. *J. Organomet. Chem.* **1979**, *170*, C29.

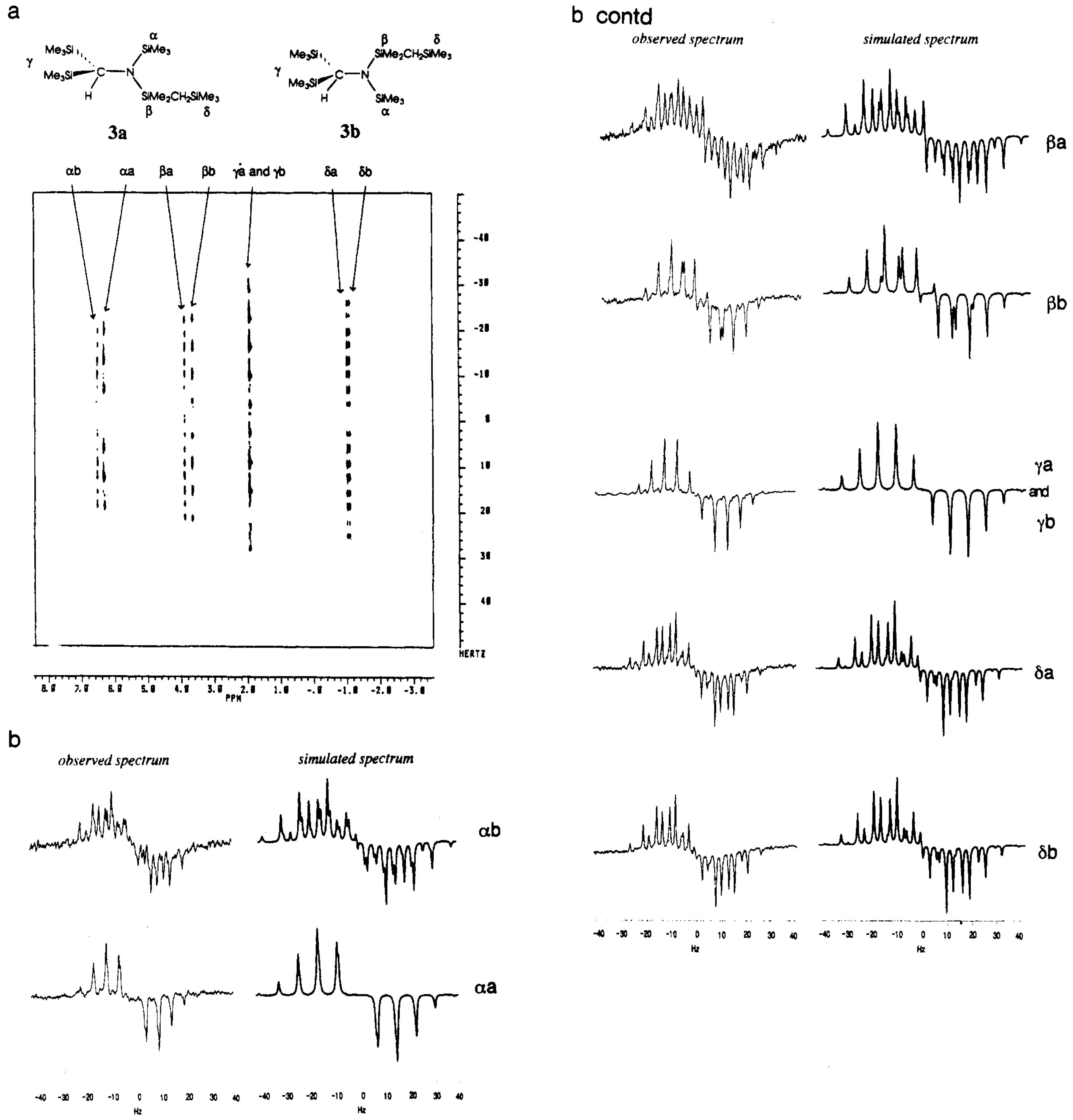


Figure 2. (a) [^{29}Si–^{n}J(^{29}Si–H)]-Resolved 2D NMR spectrum of **3** (**3a** + **3b** mixture). (b) Slices from the observed and simulated INEPT spectra for each silicon atom from the 2D map.

confirmed. Rotation around the C–N bond has not been observed at temperatures up to 180 °C. The same structure and properties were encountered with new silylmethyl derivatives **3a** and **3b**.

Results of the reductive silylation have been interpreted in terms of a reaction involving radical anion intermediates, (iso)cyanotrimethylsilane being apparently the common intermediate. Also involved was an internal 1–4 hydrogen radical migration, converting the tertiary **AR** radical anion into the primary one, **AR′**.

Experimental Section

General Details. Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrometer. A Nicolet Model 20 SXC GC instrument connected to a Carlo-Erba Model GC 6000 Vega chromatograph (PTE, 25-m × 0.25-mm capillary column) was used for FTIR studies. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 250 and ^{29}Si, ^{15}N, and 2D NMR spectra on a Bruker AC 200. Shifts, in $CDCl_3$, were referenced with respect to internal Me_4Si for ^{1}H, ^{13}C, and ^{29}Si and to internal CH_3NO_2 for ^{15}N. To record mass spectra, a VG Micromass 16F (70 eV) mass spectrometer, coupled with an Intersmat IGC 121M (BP1, 25-m × 0.25-mm capillary column) chromatograph, was used. Elemental analyses were performed at Laboratoire Central de Microanalyse du C.N.R.S. (B.P. 22, 69390 Vernaison, France). GC analyses were carried out using a Perkin-Elmer IGC 15 model apparatus equipped with a column packed with Silicon OV-101 (5%) on Chromosorb P. All yields, determined by GC analysis, have been corrected for detector response, under the conditions of the analysis, using weight samples of pure products.

Materials. All reductive silylations were carried out under an argon atmosphere. Trimethylcyanosilane (Fluka), dimeth-

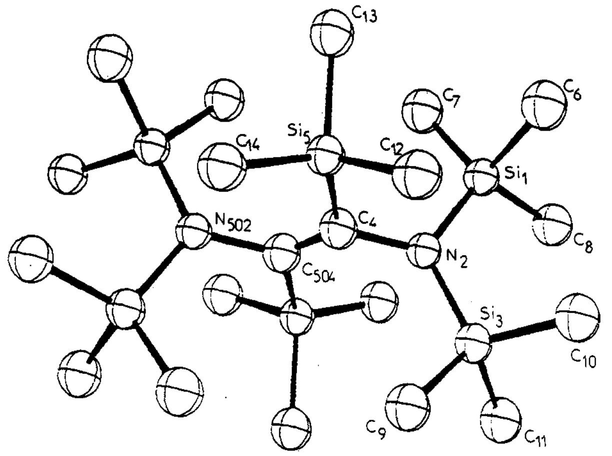
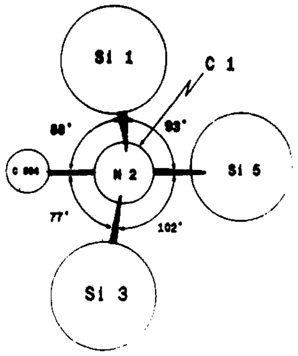


Figure 3. ORTEP drawing of compound 4 showing atoms numbering scheme. The spheres are at 30% probability level. (Hydrogen atoms have been omitted for the purpose of clarity.)

Table VII. Selected Bond Lengths (Å) and Bond Angles (deg) for 4

bond or param	value	similar bond or param value		
Bond Lengths (Å)				
C(4)–C(504)	1.29	1.368^a	1.36^b	
Si(5)–C(4)	1.946	1.915^a	1.853^c	1.929^b
C(4)–N(2)	1.51		1.42^b	1.468^b
Bond Angles (deg)				
C(504)C(4)Si(5)	124.6	124.10^a		
C(504)C(4)N(2)	121.4			
N(2)C(4)Si(5)	113.9			
C(4)N(2)Si(1)	119.0			
Si(1)N(2)Si(3)	118.4			
sum of angles at C(4)	359.9			
sum of angles at N(2)	358.8	360^d		
Dihedral angles (deg)				
Si(505)C(504)C(4)N(2)	~1	-5^b	29.5^a	
N(502)C(504)C(4)Si(5)	~-1	7^b		

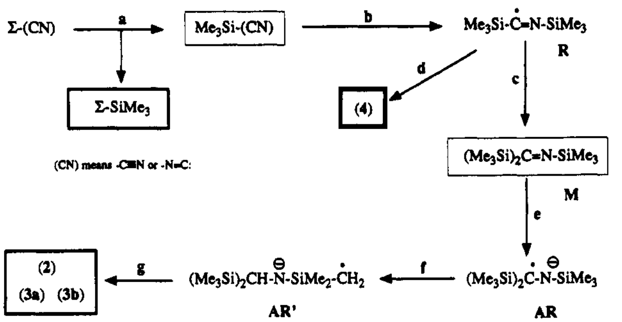
Dihedral Angles around C(1)–N(2) Bond



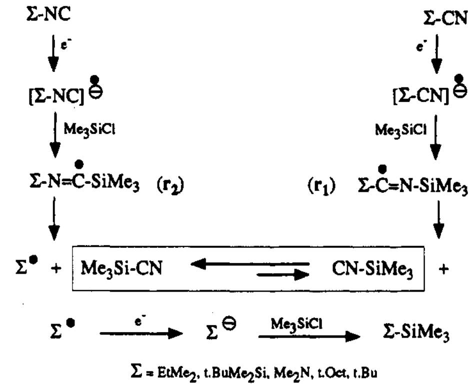
[a] Sakurai, H.; Nakadaira, Y.; Tobita, H.; Ito, T.; Toriumi, K.; Ito, H. *J. Am. Chem. Soc.* **1982**, *104*, 300. [b] Efendene, B. Thesis, University Bordeaux I, 1983. [c] Bažant, V.; Chvalovský, V.; Rathouský, J. *Organosilicon Compounds*; Academic Press: New York, 1965; Vol. 1, p 172. [d] Glidewell, C.; Rankin, D. W. H.; Robiette, A. G.; Sheldrick, G. M. *J. Mol. Struct.* **1969**, *4*, 215.

ylcyanamide, *tert*-octyl and *tert*-butyl isocyanides (Aldrich), and reagent-grade solvents (HMPA, THF, methanol) were all used without purification. Ethyl- and *tert*-butyldimethylcyanosilanes were prepared following described procedures.[43,44] Trimethylchlorosilane (kindly supplied by Rhône-Poulenc Co.) was distilled from magnesium powder prior to use and kept under argon.

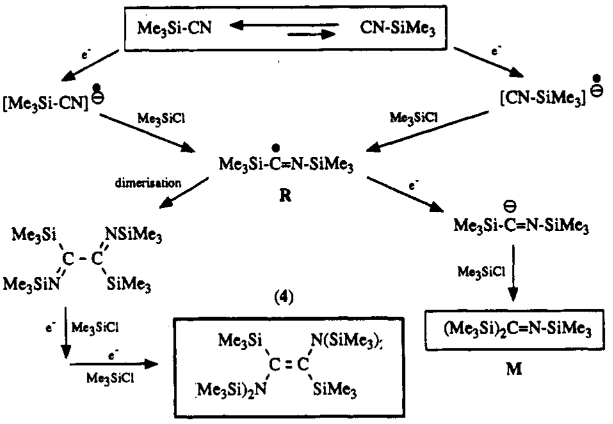
Scheme III. Proposed Mechanism for the Reductive Silylation of (Iso)nitriles



Scheme IV



Scheme V



Lithium wire (Aldrich) was cut into small pieces (5-mm length) and then washed with petroleum ether and THF just prior to use.

Reductive Silylation: Standard Procedure. In a 2-L three-neck round-bottomed flask kept at 0 °C and equipped with a pressure-equalizing dropping funnel, a condenser, a thermometer, and a mechanical stirrer were introduced trimethylchlorosilane (4 mol, 504 mL), THF (250 mL), lithium (0.8 mol, 5.6 g), and substrate (0.1 mol). Then a mixture of HMPA (1 mol, 180 mL) and dry THF (50 mL) was added dropwise slowly through the funnel so that the temperature of the mixture remained between 0 and 5 °C. The color of the reaction medium changed from red-orange to green-blue, and finally a milky lavender mixture was obtained after 10 h of stirring. Low-boiling materials (THF and excess of trimethylchlorosilane) were evaporated, and the residue was extracted with pentane (4 × 50 mL), washed with water, neutralized, dried over Na_2SO_4, and obtained as a yellow oil after evaporation of the solvent.

***N*,*N*-Bis(trimethylsilyl)[bis(trimethylsilyl)methyl]-amine, 2,** was separated by distillation from the crude reaction mixture as a white waxy solid: bp 90 °C (0.05 mmHg); ^{1}H NMR δ 0.15 (s, 18 H, γ $SiMe_3$), 0.17 (s, 9 H, α $SiMe_3$), 0.23 (s, 9 H, β

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(43) Becu, C.; Anteunis, M. *Bull. Soc. Chim. Belg.* **1987**, *96*, 115.
(44) Gassman, P. G.; Haberman, L. M. *J. Org. Chem.* **1986**, *51*, 5010.

Scheme VI

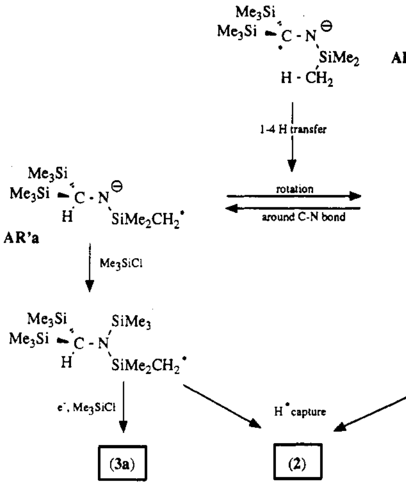

Table VIII. Crystal Data for 4

formula	$Si_6C_{20}H_{54}N_2$	Z	4
formula wt	490	D_X, g·cm^{-3}	1.06
scan technique	$\omega/2\theta$	μ, cm^{-1}	24.9
symmetry	monoclinic	$N_{\mathrm{unique,nonzero}}$	1863
space grp	$C2/c$	N_{used} $F \geq 3\sigma(F)$	1133
$a(\sigma)$, Å	17.642(6)	no. of variables	235
$b(\sigma)$, Å	9.136(2)	R factor	0.070
$c(\sigma)$, Å	19.367(5)	R_w factor	0.090
$\beta(\sigma)$, deg	99.23(2)	S	2.700
V, Å^3	3081.1		

Table IX. Atomic Parameters for 4

	X	Y	Z	B_{eq}
Si(1)	0.8673(2)	0.4438(2)	0.1065(1)	5.3(1)
N(2)	0.8202(6)	0.2756(6)	0.0859(3)	4.5(3)
Si(3)	0.8435(2)	0.1281(2)	0.1428(1)	5.1(1)
C(4)	0.7490(6)	0.2725(8)	0.0313(4)	5.8(4)
Si(5)	0.3575(2)	0.3449(2)	0.0644(1)	5.2(1)
C(6)	0.8337(7)	0.5492(9)	0.1786(5)	7.7(6)
C(7)	0.8574(6)	0.5697(9)	0.0301(5)	7.1(5)
C(8)	0.9731(6)	0.4169(10)	0.1388(5)	7.0(5)
C(9)	0.7680(6)	−0.0161(9)	0.1298(4)	6.5(5)
C(10)	0.8571(5)	0.1872(9)	0.2366(4)	6.8(5)
C(11)	0.9357(6)	0.0338(10)	0.1362(5)	7.2(6)
C(12)	0.6654(7)	0.3122(10)	0.1593(5)	7.2(6)
C(13)	0.6495(6)	0.5489(9)	0.0503(5)	6.8(5)
C(14)	0.6622(6)	0.2624(10)	0.0284(5)	6.9(6)

SiMe$_3$), 2.27 (s, 1 H), no change was observed at temperatures up to 180 °C; ^{13}C NMR δ 1.4 (γ), 3.4 (α), 4.6 (β), 38.3; ^{15}N NMR δ −368.7 (^1J(N–Si) coupling constants: 14.1 and 12.1); ^{29}Si NMR shifts and (H–Si) coupling constants are given in Table IV; MS (70 eV) m/z 319 (2.4), 246 (89.6), 216 (11.9), 172 (24.2), 73 (100). Anal. Calcd for $C_{13}H_{37}NSi_4$: C, 48.87; H, 11.68; N, 4.39. Found: C, 48.39; H, 11.76; N, 4.42.

***N*-(Trimethylsilyl)-*N*-[[(trimethylsilyl)methyl]dimethylsilyl][bis(trimethylsilyl)methyl]amine, 3,** was separated, after **2**, as a viscous liquid, by distillation from the crude reaction mixture: bp 120 °C (0.05 mmHg); MS (70 eV) m/z 391 (1.2), 318 (100), 172 (15.7), 145 (45.3), 73 (77.9); precise mass measurement on peak m/e 145 was made: found 145.359, calcd for $Me_3SiCH_2SiMe_2$ 145.374; ^{15}N NMR δ −365.1 (^1J(N–Si) coupling constants: 12.4 and 12.4 Hz), −365.4 (14.5 and 11.1 Hz). Anal. Calcd for $C_{16}H_{46}NSi_5$: C, 48.03; H, 11.57; N, 3.57. Found: C, 49.29; H, 11.58; N, 3.10. Although **3a** + **3b** mixture gave two peaks on capillary column GC analysis, we were not able to separate each compound in a pure state. However, detailed ^{1}H, ^{13}C, and ^{29}Si NMR analysis allowed the complete assignment of spectra (Figures 1 and 2). **3a**: ^{1}H NMR δ −0.05 (s, 2 H), 0.06 (s, 9 H, δ SiMe$_3$), 0.15 (s, 18 H, γ SiMe$_3$), 0.19 (s, 6 H, β SiMe$_3$), 0.21 (s, 9 H, α SiMe$_3$), 2.16 (s, 1 H); ^{13}C NMR δ 1.5 (γ), 1.6 (δ), 4.1 (β), 4.7 (α), 8.6, 38.3; ^{29}Si NMR shifts and (H–Si) coupling constants are given in Table V. **3b**: ^{1}H NMR δ −0.01 (s, 2 H), 0.063 (s, 9 H, δ SiMe$_3$), 0.15 (s, 18 H, γ SiMe$_3$), 0.16 (s, 9 H, α SiMe$_3$), 0.23 (s, 6 H, β SiMe$_2$), 2.11 (s, 1 H); ^{13}C NMR δ 1.5 (γ), 1.6 (δ), 3.6 (α), 5.0 (β), 7.9, 38.1; ^{29}Si NMR shifts and (H–Si) coupling constants are given in Table VI.

(*E*)-Hexakis(trimethylsilyl)-1,4-diazabut-2-ene, 4, was collected from the tail of the distillation and recrystallized from ethanol: mp 288 °C (capillary); ^{1}H NMR δ 0.28 (s, 36 H), 0.31 (s, 18 H); ^{13}C NMR δ 4.2, 5.57, 161.9; ^{29}Si δ −10.44 (^2J(H–Si) = 6.4 Hz), 3.95 (^2J(H–Si) = 6.3Hz); MS (70 eV) m/z 490 (1.5), 417 (90.9), 257 (12), 230 (64.7), 73 (100). Anal. Calcd for $C_{20}H_{54}N_2Si_6$: C, 48.91; H, 11.08; N, 5.7; Si, 34.31. Found: C, 48.85; H, 10.95; N, 5.78; Si, 34.23.

X-ray Crystal Structure Analysis of 4. Transparent colorless crystals were obtained at room temperature from ethanol. X-ray diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer (λ Cu Kα), and experimental data are set out in Table VIII. Crystal data were as follows: monoclinic space group $C2/c$, a = 17.642 Å, b = 9.136 Å, c = 19.367 Å, β = 99.23°, Z = 4. A total of 1863 independent reflexions were measured, 1133 of which were observed. The final reliability factor is 0.070. The unit set volume is 3081.1 Å^3 and the density 1.059 (Table VIII). The structure was solved by direct methods using MULTAN 78[45] and refined by a block-diagonal least-squares method with anisotropic thermal parameters for non-hydrogen atoms and isotropic parameters for hydrogen. The scattering factors for non-hydrogen atoms were taken from *International Tables for X-ray Crystallography*.[46] For hydrogen, the values given by Stewart et al.[47] were used. All calculations were performed on a Mini 6-92 CII-Honeywell Bull computer using unpublished programs.[48] Atomic parameters of each crystal are given in Table IX. Molecule 4 and the atom numbering scheme are shown in Figure 3.

Protolysis of 2 and 3. Into a 100-mL two-neck round-bottomed flask kept at 0 °C and equipped with a pressure-equalizing dropping funnel, a condenser, and a magnetic stirring bar was introduced compound **2**, **3**, or a mixture of both and methanol (20 mL/0.05 mol). Trimethylchlorosilane (15 mL/0.05 mol) then was added dropwise with stirring. After the addition was complete, the reaction mixture was stirred at room temperature for 15 min. Evaporation of low-boiling materials (methanol, methoxysilane, and excess of trimethylchlorosilane) under reduced pressure left a quantitative yield (from **2**) of the hydrochloride of BSMA, **5**, as a white solid. When **3** or a **2** + **3** mixture was used, **5** was accompanied with either the methoxysilane **6** or the corresponding siloxane **7**, depending upon the excess of trimethylchlorosilane used. Salt **5** was separated from **6** (or **7**) by dissolving it in water, and **6** (or **7**) was extracted with ether and identified.

[Bis(trimethylsilyl)methyl]ammonium chloride, 5: mp 191 °C (from pentane); ^{1}H NMR δ 0.26 (s, 18 H), 1.97 (s, 1 H), 8.1 (m, 3 H, D$_2$O exchangeable); ^{13}C NMR δ −0.7 (CH$_3$), 32.1 (CH); ^{29}Si NMR δ 3.64 (^2J(H$_C$–Si) = 6.4 Hz, 9 H) (^3J(H$_N$–Si) = 3.4 Hz, 3 H); MS (70 eV) m/z 211 (0.2), 103 (13.4), 88 (43.5), 73 (100). Anal. Calcd for $C_7H_{22}NSi_2Cl$: C, 39.68; H, 10.46; N, 6.61; Si, 26.51; Cl, 16.73. Found: C, 40.01; H, 10.53; N, 6.41; Si, 23.69; Cl, 16.65.

(Methoxydimethylsilyl)(trimethylsilyl)methane, 6: bp 89 °C (25 mmHg); IR ν 1057 cm^{-1} (SiO); ^{1}H NMR δ 0.00 (s, 9 H, CSiMe$_3$), 0.07 (s, 6 H, OSiMe$_2$), −0.17 (s, 2 H, CH$_2$), 3.35 (s, 3 H, OMe); ^{13}C NMR δ 0.5 (SiMe$_3$), 1.0 (SiMe$_2$), 4.1 (CH$_2$), 49.9 (OMe); MS (70 eV) m/z 161 (100), 131 (71.8), 89 (9.1), 73 (19.3). Anal. Calcd for $C_7H_{20}NSi_2O$: C, 47.66; H, 11.43; Si, 31.84. Found: C, 47.85; H, 11.59; Si, 29.96.

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(45) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. MULTAN 80: A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data; University of York, England, 1980.

(46) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.23.

(47) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(48) From Laboratoire de Christallographie, Université Bordeaux I, 33405 Talence, France.

1,3-Bis[(trimethylsilyl)methyl]tetramethyldisiloxane, 7: bp 130 °C (25 mmHg); IR ν 1053 cm^{-1} (SiO); ^{1}H NMR δ 0.08 (s, 18 H, CSiMe$_3$), 0.12 (s, 12 H, OSiMe$_2$), -0.14 (s, 2 H, CH$_2$); ^{13}C NMR δ 1.2 (SiMe$_3$), 3.3 (SiMe$_2$), 6.7 (CH$_2$); ^{29}Si NMR δ -1.09 (^2J(H-Si) = 6.56 Hz, 9 H) (^3J(H-Si) = 8.75 Hz, 3 H), 6.03 (OSiMe$_2$); MS (70 eV) *m/z* 291 (70.1), 219 (10.1), 203 (98.9), 145 (29.4), 73 (100). Anal. Calcd for $C_{12}H_{34}Si_4O$: C, 46.99; H, 11.17; Si, 36.62. Found: C, 47.31; H, 11.22; Si, 35.92.

Neutralization of Hydrochloride 5, Obtention of BSMA, 1. A 20% sodium hydroxide solution was slowly added, with stirring, to hydrochloride 5 dissolved in iced water (10 mL/0.05 mol). Extraction with ether (4 × 20 mL), washing with brine, drying over NaOH, and careful solvent evaporation gave, after distillation, a 98% yield of BSMA. For preparative purposes, protolysis performed directly on the crude product of the reductive silylation reaction, followed by neutralization of the salt, afforded BSMA in overall yields ranging from 60 to 75%, depending on the starting material used.

[Bis(trimethylsilyl)methyl]amine, 1 (BSMA): bp 70 °C (25 mmHg); IR ν 3300 cm^{-1} (NH$_2$); ^{1}H NMR δ 0.01 (s, 18 H, SiMe$_3$), 1.56 (s, 1 H, CH), 1.0 (concentration dependent and deuterium exchangeable, s, 2 H, NH$_2$); ^{13}C NMR δ -1.8 (SiMe$_3$), 31.4 (CH); ^{29}Si NMR δ 2.11 (^2J(H-Si) = 6.34 Hz, 9 H) (^3J(H-Si) = 8.34 Hz, 1 H); MS (70 eV) *m/z* 175 (1.9), 160 (14.6), 102 (84.9), 74 (100). Anal. Calcd for $C_7H_{21}NSi_2O$: C, 47.93; H, 12.07; N, 7.98; Si, 32.02. Found: C, 47.83; H, 11.84; N, 7.40; Si, 30.49.

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Supplementary Material Available: Tables of anisotropic thermal parameters for the non-hydrogen atoms and positional parameters for the hydrogen atoms of 4 (2 pages). Ordering information is given on any current masthead page.

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