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Synthesis and Spectroscopic Properties of Bis(trimethylsilyl)amides of the Alkaline-Earth Metals Magnesium, Calcium, Strontium, and Barium

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Alkaline-earth-metal bis[bis(trimethylsilyl)amides] of magnesium, calcium, strontium, and barium have been isolated in high yield from bis[bis(trimethylsilyl)amido]tin(II) by utilizing the transmetalation reaction in common organic solvents. When this reaction is performed in 1,2-dimethoxyethane, an ether adduct with two DME molecules is formed for each metal. The alkaline-earth-metal diamides without complexating reagents appear to be dimeric in benzene and toluene. Only the magnesium bis[bis(trimethylsilyl)amide] shows a temperature-dependent equilibrium with a high percentage of monomeric units at high temperatures. In the gaseous phase, this compound as well as the calcium derivative appears to be monomeric; the strontium and the barium amides show fragmentation patterns in the mass spectrum for dimeric species. The dimeric appearance of the ether-free amides is confirmed by the $^{13}C\{^1H\}$ NMR and $^{29}Si\{^1H\}$ NMR measurements, where two signals can be observed for two chemically different trimethylsilyl groups, as well as by the IR spectra and the cryoscopically (in benzene) determined molecular weights.

Introduction

There has only been little research on the synthesis and the properties of the bis[bis(trimethylsilyl)amides] of the alkaline-earth metals. The beryllium and magnesium derivatives have been well-known a good 20 years, whereas the compounds of the heavier alkaline-earth metals are still unknown.

Bürger, Forker, and Goubeau[1] isolated the beryllium bis[bis(trimethylsilyl)amide] (I) in moderate yield after utilizing the metathesis reaction (eq 1). This compound is distillable at 110 °C and 3 mbar and is monomeric in organic solvents; the structure determination by electron diffraction at 100 °C confirms the monomeric structure with a linear N–Be–N moiety in the gaseous phase.[2] The NMR spectroscopic characterization by Nöth and Schlosser[3] confirms the monomeric constitution in solution.

$$BeCl_2{\cdot}O(C_2H_5)_2 + 2NaN(SiMe_3)_2 \xrightarrow[\substack{-O(C_2H_5)_2}]{-2NaCl} \underset{I}{Be[N(SiMe_3)_2]_2} \quad (1)$$

Magnesium bis[bis(trimethylsilyl)amide] (II) has been prepared by the metalation reaction of hexamethyldisilazane with dialkylmagnesium (eq 2). The adduct formed in ether loses its ligand at 110 °C and 0.4 mbar;[4] however, in hexane derivative II has been isolated directly in good yield.[5] Wannagat and co-worker[4] found the amide to have a monomeric constitution by cryoscopic molecular weight studies in benzene and in the vapor phase.

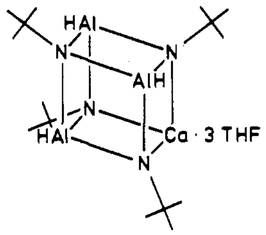
$$MgR_2 + 2HN(SiMe_3)_2 \xrightarrow[-2RH]{} \underset{II}{Mg[N(SiMe_3)_2]_2} \quad (2)$$

$$R = C_2H_5, C_4H_9$$

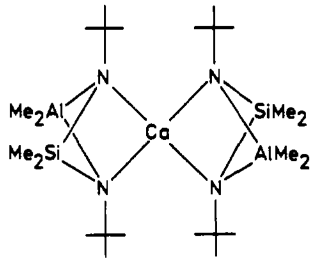
It is surprising that no data exist for the heavier alkaline-earth-metal homologues, even though in the neighboring main groups the bis(trimethylsilyl)amides are well characterized.[6] The only exception appears to be boron, because the bis(trimethylsilyl)amino group is sterically too demanding, so that only the chlorobis[bis(trimethylsilyl)amino]borane is isolable.[7,8] On the other hand, the tris[bis(trimethylsilyl)amino] derivatives of aluminum,[9] gallium,[10–12] indium,[10,11] and thallium[13] are found to be monomeric in solution and the solid state.

In addition, the bis[bis(trimethylsilyl)amides] of the second transition-metal group, namely of zinc(II),[14,15] cadmium(II),[14] and mercury(II),[14,16] are distillable liquids under reduced pressure and are monomeric. These derivatives are valuable ligands in organotransition-metal chemistry.[6]

We report here the preparation and characterization of the missing derivatives of the second main-group metals. Only very few calcium diamides are known and well investigated thus far. Sanderson and co-worker[17] reacted several amines in liquid ammonia with calcium metal; however, the resulting highly air-sensitive compounds were not characterized. Nevertheless, there are some polycyclic mixed-metal amides, containing the metals aluminum and calcium. Cucinella and co-worker[18] reacted calcium aluminate $Ca(AlH_4)_2$ with primary amines and isolated the polycyclic (*N*-alkylimino) derivative III. Veith[19] recently published the cage compound IV, which resulted from a metalation reaction of a secondary amine with calcium metal.



III



IV

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Table I. NMR Data for Benzene-d_6 Solutions of Bis[bis(trimethylsilyl)amides] of the Alkaline-Earth Metals Magnesium, Calcium, Strontium, and Barium at 30 °C[a]

	1a	**1b**	**1c**	**1d**
		^{1}H		
δ(SiMe$_3$)	0.27	0.30	0.30	0.33
$^2J_{SiH}$	6.0	6.2	6.0	6.0
δ(OCH$_3$) (DME)	3.07	3.05	3.08	3.08
δ(CH$_2$) (DME)	3.07	2.92	3.13	3.09
		^{13}C{^{1}H}		
δ(SiMe$_3$)	6.40	5.63	5.99	5.95
$^1J_{SiC}$	53.1	52.3	51.8	51.0
δ(OCH$_3$) (DME)	59.2[b]	59.75	59.45	59.16
δ(CH$_2$) (DME)	71.5[b]	70.97	70.73	70.59
		^{29}Si{^{1}H}		
δ(SiMe$_3$)	−8.55	−15.11	−16.49	−18.06

[a] Chemical shifts in ppm; coupling constants in Hz. [b] Line width of approximately 25 Hz.

Experimental Section

All operations were carried out under an oxygen-free argon atmosphere by using standard Schlenk techniques. All solvents were rigorously dried and distilled under argon by standard methods. The deuterated solvents were degassed by three consecutive freeze–pump–thaw cycles and saturated with argon prior to use. The compound bis[bis(trimethylsilyl)amido]tin(II) was obtained by a reported procedures.[20] The magnesium was activated according to literature procedures;[21] the alkaline-earth metals calcium, strontium, and barium were used for the transmetalations after distillation as described.[22] The ^{1}H NMR spectra were recorded on Bruker WP60 and Bruker AM200 spectrometers, (C_6D_5H at 7.15 ppm for spectra in benzene-d_6). ^{13}C{^{1}H} and ^{29}Si{^{1}H} NMR spectra were obtained on a Bruker AM200 spectrometer (50.323 and 39.761 MHz for ^{13}C and ^{29}Si NMR experiments, respectively). The mass spectrometric measurements were performed on a Varian MAT711 instrument. The substance PFK was used to reference the high-resolution mass peaks of single molecular ions. The IR spectra were recorded on Perkin-Elmer 283 and 684 spectrophotometers. The listing of the bands around 2900 and 1400 cm^{-1} was omitted due to overlapping with the CH stretching frequencies of Nujol. The melting points were measured under argon in sealed capillaries and are uncorrected values. The elemental analyses were performed by the Microanalytic Laboratory Pascher in Remagen-Bandorf, Germany.

Synthesis of Magnesium Bis[bis(trimethylsilyl)amide]–2-Dimethoxyethane (1a). A suspension of 0.89 g of magnesium powder (36 mmol) in 50 mL of DME was cooled to 0 °C. A 11.3-g amount of bis[bis(trimethylsilyl)amido]tin(II) (26.3 mmol) was added dropwise to the stirred suspension. After the addition was complete, the reaction mixture was warmed to room temperature and stirred for an additional 3 h. The metals (excess of magnesium and tin) were allowed to settle without stirring, and the orange solution was decanted. All volatile material was removed in vacuum at room temperature and the residue was crystallized from a solvent mixture of *n*-pentane/DME in the ratio of approximately 5:2 at −60 °C. Bright yellow crystals could be isolated: yield 5.8 g (11 mmol), 42%; mp 56 °C dec. NMR data are listed in Table I. IR (in Nujol between KBr windows): 1243 vs, 1195 m, 1125 s, 1110 sh, 1085 vs, 1058 s, 998 vs, 960 s, 938 s, 870 vs, 835 vs, 780 m, 750 s, 733 w, 700 m, 663 s, 615 m, 608 m, 490 m, 472 w, 395 w, 365 cm^{-1} w. MS (355 K, 20 eV, amu): *m/e* 344 (17.6%; [M − 2DME]$^+$), 329 (100%; [M − 2DME − Me]$^+$).

Synthesis of Calcium Bis[bis(trimethylsilyl)amide]–2-Dimethoxyethane (1b). A 1.8-g sample of distilled calcium metal (45 mmol) and 12.2 g of bis[bis(trimethylsilyl)amido]tin(II) (28 mmol) were combined at room temperature in 70 mL of DME, and the mixture was stirred for approximately 10 h, giving a yellow solution. After the metals (excess of calcium and tin) were allowed to settle, the solution was decanted. The solvent was removed, giving a colorless solid that could be crystallized from *n*-hexane or a mixture of diethyl ether and *n*-hexane in a ratio 1:5 at −60 °C: yield 8.2 g (15.2 mmol), 54%; dec pt above 110 °C. Molecular weight: found, 518 (by freezing point depression in benzene); calcd, 541. NMR data are listed in Table I. IR (in Nujol between KBr windows): 1255 vs, 1240 sh, 1185 w, 1110 m, 1060 vs, 1030 sh, 995 sh, 935 m, 870 s, 830 vs, 750 s, 665 s, 608 s, 595 s, 390 w, 365 cm^{-1} m. MS (370 K, 70 eV, amu): *m/e* 360 (3.2%; [M − 2DME]$^+$), 345 (10.4%; [M − 2DME − Me]$^+$), 161 (5.2%; HNSi$_2$Me$_6$), 146 (100%; HNSi$_2$Me$_5$), 90 (3.5%; DME). High-resolution MS (*m/e*): found, 360.1580 ([M − 2DME]$^+$); calcd, 360.1580.

Synthesis of Strontium Bis[bis(trimethylsilyl)amide]–2-Dimethoxyethane (1c). An 8.48-g sample of strontium metal (96.8 mmol) and 37.3 g of bis[bis(trimethylsilyl)amido]tin(II) (85 mmol) were stirred together in 150 mL of DME for nearly 15 h. The metal was allowed to settle, and the yellow solution was decanted and the residue washed with 50 mL of DME. Combining of all the DME fractions and removing the volatile material gave a colorless residue, which was crystallized from a mixture of DME and *n*-hexane in a ratio of 1:4: yield 44.5 g (75.7 mmol), 89%; mp 114 °C dec. Molecular weight: found, 436 (by freezing point depression in benzene); calcd, 588. NMR data are listed in Table I. IR (in Nujol between KBr windows): 1305 m, 1245 vs, 1212 w, 1190 m, 1105 s, 1065 vs, 1033 vs, 1022 sh, 990 w, 980 w, 930 m, 880 s, 855 s, 825 vs, 760 s, 745 s, 690 w, 653 s, 603 m, 583 m, 560 w, 360 cm^{-1} m. MS (375 K, 70 eV, amu): *m/e* 656 (4.2%; Sr$_2$N$_3$Si$_6$Me$_{18}$), 408 (4.3%; [M − 2DME]$^+$), 393 (9.5%; [M − 2DME − Me]$^+$), 248 (13.4%; SrNSi$_2$Me$_6$), 146 (100%; HNSi$_2$Me$_5$), 90 (7.1%; DME). High-resolution MS (*m/e*): found, 408.1005 ([M − 2DME]$^+$); calcd, 408.1010.

Synthesis of Barium Bis[bis(trimethylsilyl)amide]–2-Dimethoxyethane (1d). The reaction of 25 g of barium metal (182 mmol) with 70 g of bis[bis(trimethylsilyl)amido]tin(II) (159 mmol) was performed analogously to that of the strontium derivative. A greenish compound can be isolated, in which the ether content is slightly higher (2.2 DME molecules per barium atom) according to the integration of the ^{1}H NMR spectrum. Further exposure to a vacuum of about 10^{-2} mbar does not lead to a further loss of ligand. Yield: 85.1 g (130 mmol), 81%; mp 76 °C dec. NMR data are listed in Table I. IR (in Nujol between KBr windows): 1303 s, 1245 vs, 1210 sh, 1187 s, 1110 vs, 1060 vs, 1020 vs, 975 s, 930 m, 910 m, 875 s, 835 vs, 750 vs, 683 m, 655 vs, 603 s, 580 s, 550 w, 355 cm^{-1} m. MS (335 K, 70 eV, amu): *m/e* 298 (1.1%; BaNSi$_2$Me$_6$), 161 (8.6%; HNSi$_2$Me$_6$), 146 (100%; HNSi$_2$Me$_5$), 90 (8.6%; DME).

Synthesis of Calcium Bis[bis(trimethylsilyl)amide]–2-Tetrahydrofuran (2). A 1-g amount of calcium metal (25 mmol) and 10.2 g of bis[bis(trimethylsilyl)amido]tin(II) (23.2 mmol) were combined in 75 mL of THF. During the first few hours the solution turned deep red; the reaction was finished when the solution color changed to reddish brown. The solution was decanted, and the volatile material was removed and the residue crystallized from *n*-hexane at 0 °C as colorless crystals: yield 7.1 g (14.1 mmol), 61%; mp 181 °C. Molecular weight: found, 494 (by freezing point depression in benzene); calcd, 505. ^{1}H NMR (C_6D_6): δ 0.33 (SiMe$_3$; $^2J_{SiH}$ = 6.0 Hz), 1.30 (m) and 3.59 (m) (THF). ^{13}C{^{1}H} NMR (C_6D_6): δ 5.87 (SiMe$_3$; $^1J_{SiC}$ = 52.1 Hz), 24.98 and 69.71 (THF). ^{29}Si{^{1}H} NMR (C_6D_6): δ −14.73. IR (in Nujol between KBr windows): 1317 w, 1300 w, 1240 vs, 1050 vs, 1030 sh, 870 vs, 820 vs, 758 s, 745 s, 660 s, 605 s, 590 s, 380 w, 363 cm^{-1} m. MS (360 K, 20 eV, amu): *m/e* 560 (6.1%; Ca$_2$N$_3$Si$_6$Me$_{18}$), 400 (1.7%; Ca$_2$N$_2$Si$_4$Me$_{12}$), 360 (10.4%; [M − 2THF]$^+$), 345 (25.4%; [M − 2THF − Me]$^+$), 273 (11.3%; CaNSi$_3$Me$_9$), 161 (7.1%; HNSi$_2$Me$_6$), 146 (100%; HNSi$_2$Me$_5$), 72 (7.7%; THF). High-resolution MS (*m/e*): found, 360.1581 ([M − 2THF]$^+$); calcd, 360.1580.

Synthesis of Magnesium Bis[bis(trimethylsilyl)amide] (3a). In 40 mL of benzene, 0.96 g of magnesium powder (40 mmol) and 9 g of bis[bis(trimethylsilyl)amido]tin(II) (20.5 mmol) were combined, and the solution was stirred at room temperature for approximately 15 h. Then the solution was decanted, and the volatile material was removed under vacuum at room temperature. The residue was crystallized from *n*-pentane at −60 °C as light tan crystals: yield 4.5 g (13 mmol), 64%; mp 122–123 °C dec. Molecular weight: found, 517 (by freezing point depression in benzene); calcd for the monomer, 344. NMR data of the dimer are listed in Table II. NMR data of the monomeric unit: ^{1}H NMR (C_6D_6), δ 0.15 (broad); ^{13}C{^{1}H} NMR (C_6D_6), δ 5.64 ($^1J_{SiC}$ = 52.3 Hz); ^{29}Si{^{1}H} NMR (C_6D_6), δ −12.58. The IR spectrum is identical with the published one.[4] MS (325 K, 20 eV, amu): *m/e* 344 (9.3%; M$^+$), 329 (57.5%; M$^+$ − Me), 161 (5.9%; HNSi$_2$Me$_6$), 146 (100%; HNSi$_2$Me$_5$).

Synthesis of Dimeric Calcium Bis[bis(trimethylsilyl)amide] ((3b)$_2$). A 2-g amount of calcium metal and 10.4 g of bis[bis(trimethylsilyl)amido]tin(II) (23.7 mmol) were combined in 50 mL of toluene, and the solution was stirred at room temperature for approximately 5 days. All solid material (calcium, tin) was separated. At −60 °C reddish brown crystals could be obtained from this solution. The mother liquor was

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Table II. NMR Data for the Dimeric Bis[bis(trimethylsilyl)amide] Derivatives of Magnesium, Calcium, Strontium, and Barium[a]

	$(\mathbf{3a})_2$	$(\mathbf{3b})_2$	$(\mathbf{3c})_2$	$(\mathbf{3d})_2$
		^{1}H		
temp, K	302[b]	210[c]	210[c]	300[c]
$\delta_b(SiMe_3)$	0.45	0.21	0.12	0.14
$\delta_t(SiMe_3)$	0.38	0.33	0.33	0.14
$\Delta\delta$[e]	0.07	0.12	0.21	0.00
		$^{13}C\{^1H\}$		
temp, K	302[b]	302[b]	210[c]	280[c]
$\delta_b(SiMe_3)$	8.12	6.94	6.31	5.42
$^1J_{SiC}$	53[d]	51.4	51.8	52.1
$\delta_t(SiMe_3)$	7.14	6.48	6.14	5.39
$^1J_{SiC}$	53[d]	52.2	52.0	52.1
$\Delta\delta$[e]	0.98	0.46	0.17	0.03
		$^{29}Si\{^1H\}$		
temp, K	302[b]	302[b]	210[c]	210[c]
$\delta_b(SiMe_3)$	−3.29	−6.54	−10.58	−18.32
$\delta_t(SiMe_3)$	−11.57	−13.25	−14.95	−18.32
$\Delta\delta$[e]	8.28	6.71	4.37	0.00

[a] Chemical shifts in ppm; coupling constants in Hz; the upper value is attached to the bridging bis(trimethylsilyl)amido group with the 4-fold-coordinated nitrogen atom (subscript b), the lower value to that of the terminal triple-coordinated nitrogen (subscript t). [b] Solvent: benzene-d_6. [c] Solvent: toluene-d_8. [d] Due to broadening of the signals, a more accurate value cannot be given. [e] $\Delta\delta = |\delta_b - \delta_t|$.

concentrated, and at −60 °C another crop of crystals was isolated. The slightly orange-brown crystal fractions were combined and dried when vacuum at 10^{-2} mbar: yield 7 g (9.7 mmol), 82%; dec at above 120 °C. Molecular weight: found, 691 (by freezing point depression in benzene); calcd, 722. NMR and IR data are listed in Tables II and III, respectively. MS (400 K, 70 eV, amu): *m/e* 360 (0.3%; M^+), 345 (1.0%; M^+ − Me), 161 (5.0%; $HNSi_2Me_6$), 146 (100%; $HNSi_2Me_5$). Anal. Found (calcd for $CaN_2Si_4C_{12}H_{36}$): C, 40.53 (39.94); H, 10.24 (10.06); N, 7.65 (7.76); Si, 30.7 (31.13); Ca, 10.8 (11.11).

Synthesis of Dimeric Strontium Bis[bis(trimethylsilyl)amide] ((3c)$_2$). A 3.4-g sample of strontium (38.8 mmol) and 16 g of bis[bis(trimethylsilyl)amido]tin(II) (36 mmol) were combined in toluene, and the solution was stirred for 6 days at room temperature. The reaction solution turned orange-brown. After separation of the metal (excess of strontium and tin), storage of the filtrate at −20 °C led to the formation of colorless crystals. After reduction of the volume of the mother liquor, a second batch of crystals was isolated. These two crystal fractions were combined and dried at 10^{-2} mbar. Yield: 12.1 g (14.8 mmol), 82%; mp 163–164 °C dec. Molecular weight: found, 794 (by freezing point depression in benzene); calcd, 817. NMR and IR data are listed in Tables II and III, respectively. MS (685 K, 20 eV, amu): *m/e* 801 (1.3%; $Sr_2N_4Si_8Me_{23}$), 656 (45.3%; $Sr_2N_3Si_6Me_{18}$), 408 (45.1%; M^+), 393 (69.4%; M^+ − Me), 146 (100%; $HNSi_2Me_5$). High-resolution MS (*m/e*): found, 801.1792 ($Sr_2N_4Si_8C_{23}H_{69}$); calcd, 801.1786. Anal. Found (calcd for $SrN_2Si_4C_{12}H_{36}$): C, 34.84 (35.29); H, 8.97 (8.89); N, 6.80 (6.86); Si, 27.9 (27.51); Sr, 21.6 (21.45).

Synthesis of Dimeric Barium Bis[bis(trimethylsilyl)amide] ((3d)$_2$). A 6.6-g amount of barium (48 mmol) and 16.9 g of bis[bis(trimethylsilyl)amido]tin(II) (38 mmol) were stirred together in toluene at room temperature. After a few minutes the solution turned red-brown. After 3 days the dark red solution was decanted from the metal (barium, tin), and all volatile materials were removed in vacuum at room temperature. The waxy residue was dissolved in *n*-pentane and crystallized to yield orange crystals (due to the poor solubility a large amount of solvent was necessary): yield 11 g (12 mmol), 63%; dec pt above 150 °C. Molecular weight: found, 827 (by freezing point depression in benzene); calcd, 916. NMR and IR data are listed in Tables II and III, respectively. MS (420 K, 70 eV, amu): *m/e* 756 (12.1%; $Ba_2N_3Si_6Me_{18}$), 458 (3.2%; M^+), 443 (21.0%; M^+ − Me), 371 (18.0%; $BaNSi_3Me_9$), 298 (100%; $BaNSi_2Me_6$), 146 (62.2%; $HNSi_2Me_5$). High-resolution MS (*m/e*): found 458.1004 (M^+), calcd 458.1006; found 756.1033 ($Ba_2N_3Si_6C_{18}H_{54}$), calcd 756.1035. Anal. Found (calcd for $BaN_2Si_4C_{12}H_{36}$): C, 31.42 (31.46); H, 7.55 (7.92); N, 5.45 (6.12); Si, 22.4 (24.52); Ba, 28.8 (29.98). These deviations from the calculated values may be a consequence of in situ decomposition during analysis; the samples were spectroscopically pure.

Synthesis of Calcium Bis[bis(trimethylsilyl)amide]–Dimethoxyethane (4). A 0.45-g sample of calcium bis[bis(trimethylsilyl)amide]-2-dimethoxyethane (**1b**) (0.83 mmol) was heated to 150 °C under vacuum, so that all volatile materials were removed. A white solid sublimed onto the colder part of the flask. The white material is **4**: yield 0.09 g (0.2 mmol), 24%; mp 144 °C dec. ^{1}H NMR (C_6D_6): δ 0.32 ($SiMe_3$; $^2J_{SiH}$ = 6.1 Hz), 2.96 (OCH_3) and 2.62 (CH_2) (DME). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 5.62 ($SiMe_3$), 70.25 (CH_2) and 60.29 (OCH_3) (DME). The MS spectrum (380 K, 70 eV, amu) is closely identical with that of compound **1b**: *m/e* 360 (3.5%; M^+), 345 (11.1%; M^+ − Me), 161 (5.3%; $HNSi_2Me_6$), 146 (100%; $HNSi_2Me_5$), 90 (2.8%; DME).

Results and Discussion

Preparation. The metal–hydrogen exchange reaction is not applicable for the preparation of calcium, strontium, and barium bis[bis(trimethylsilyl)amides]. Even in liquid ammonia the alkaline-earth metals do not react with the added hexamethyldisilazane. The addition of a fluoren crystal to this ammonia solution also fails to generate the desired product via difluorenylcalcium[23] as an intermediate followed by the metalation of hexamethyldisilazane.

The transmetalation with bis[bis(trimethylsilyl)amido]tin(II) is a viable synthetic reaction giving halogen-free products. A distillation of calcium, strontium, and barium was undertaken according to literature procedures[22] to raise the reactivity of the alkaline-earth metals. The tin(II) compound reacts with the purified alkaline-earth metal in common organic solvents to yield the alkaline-earth-metal bis[bis(trimethylsilyl)amides] and tin metal. When 1,2-dimethoxyethane (DME) is chosen as a solvent, the ether adduct **1** can be isolated in moderate to good yields (eq 3). For the synthesis of the calcium bis[bis(trimethylsilyl)amide],

$$\begin{gathered} M + Sn[N(SiMe_3)_2]_2 \xrightarrow{DME} M[N(SiMe_3)_2]_2{\cdot}2DME + Sn \\ M = Mg\ (\mathbf{1a}),\ Ca\ (\mathbf{1b}), \\ Sr\ (\mathbf{1c}),\ Ba\ (\mathbf{1d}) \end{gathered} \tag{3}$$

THF was also used as a solvent for this transmetalation reaction (eq 4). Surprisingly, in both cases two complexed ether molecules

$$Ca + Sn[N(SiMe_3)_2]_2 \xrightarrow{THF} \underset{\mathbf{2}}{Ca[N(SiMe_3)_2]_2{\cdot}2THF} + Sn \tag{4}$$

are coordinated to the calcium atom, so that the metal has the coordination number 6 for the DME adduct **1b** but the coordination number 4 for the THF complex **2**. The measurement of the freezing point depression in benzene for these two complexes results in the expected values for a monomeric unit. The ether bases of the homologue derivatives **1a,c,d** are less strongly bonded; therefore, depressed molecular weights are found by freezing point depression in benzene.

No side reactions were observed in DME or in THF. The removal of the complexating ether under vacuum with heating leads to the decomposition of all compounds **1** and **2**. For example, the calcium derivative **1b** looses one DME base at 150 °C and 10^{-2} mbar to yield calcium bis[bis(trimethylsilyl)amide]–dimethoxyethane (**4**) in a poor yield. The major decomposition products of this thermolysis reaction are hexamethyldisilazane and *N,N'*-bis(trimethylsilyl)-2,2,4,4-tetramethyl-1,3,2,4-diazadisiletidine, $[Me_3Si{-}N{-}SiMe_2]_2$. However, when the metal–metal exchange is performed in a noncomplexating solvent such as toluene or benzene, the dimeric alkaline-earth-metal diamides are obtained according to eq 5. The determination of the freezing

$$\begin{gathered} 2M + 2Sn[N(SiMe_3)_2]_2 \rightarrow \{M[N(SiMe_3)_2]_2\}_2 + 2Sn \\ M = Mg\ ((\mathbf{3a})_2), \\ Ca\ ((\mathbf{3b})_2), \\ Sr\ ((\mathbf{3c})_2), \\ Ba\ ((\mathbf{3d})_2) \end{gathered} \tag{5}$$

point depression in benzene gives a molecular weight of 517 for the magnesium bis[bis(trimethylsilyl)amide] (**3a**); 688 is calculated for a dimer. The NMR spectroscopic results show this deviation originates from the presence of a monomer, dimer equilibrium in solution. For the calcium, strontium, and barium derivatives (**3b–d**)$_2$, the cryoscopically determined molecular weights are in

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[23] The formation of difluorenylcalcium in liquid ammonia is already investigated: Pascault, J.-P.; Golé, J. *J. Chim. Phys. Phys. Chim. Biol.* **1971**, *68*, 449.

Table III. IR Data for the Ether-Free Alkaline-Earth-Metal Bis[bis(trimethylsilyl)amides] in Nujol between CsBr Windows

Be[a] (I)	Mg[b] (II, **3a**)	Ca (**3b**)	Sr (**3c**)		Ba (**3d**)	
monomer	dimer	dimer	polymer	dimer[c]	polymer	assgnt
1445 w						$\delta_{as}(CH_3)$
1405 w						
1252 w	1255 vs	1248 vs	1250 vs	1250 vs	1250 vs	$\delta_s(CH_3)$
		1240 vs	1240 vs	1240 vs	1238 vs	
958 vs	970 s	1010 vs	1020 vs	1030 vs	1040 vs	$\nu_{as}(SiNSi)$
	955 s	920 vs		970 vs		
	882 vs	870 vs	875 vs	875 vs	880 s	$\rho_{as,s}(CH_3)$
863 vs	850 vs	855 s	860 s	865 s	860 s	
835 vs	835 sh	830 vs	820 vs	820 vs	825 vs	
755 m	775 m	762 s	762 s	760 s	760 m	
	765 m	755 sh	750 sh	750 sh	750 sh	
	725 w	725 w	725 m	725 sh	725 w	
678 m	670 s	660 s	660 s		660 s	$\nu_{as}(SiC_3)$
618 m	625 sh	600 sh	608 s	605 m	605 m	$\nu_s(SiC_3)$
548 s	600 m	592 m	592 s	583 s	580 m	$\nu_s(SiNSi)$
			558 m		555 m	
	465 m	410 m	390 m		378 w	$\nu_{as}(MN_2)$
351 w		365 w	360 w		358 w	$\delta,\rho(SiC_3)$
323 w		355 m				

[a] The BeN_2 vibrations are located at 1325 (ν_{as}) and 402 cm^{-1} (δ) according to the literature.[1] [b] Published[4] and measured IR data are very similar. [c] Benzene solution in a KBr cell.

agreement with the calculated values for dimers in benzene solution.

These metal bis[bis(trimethylsilyl)amides] $(3)_2$ are nearly insoluble in *n*-hexane, but they can be recrystallized from toluene with the exception of the barium derivative $(\mathbf{3d})_2$. All of these compounds are nearly colorless or yellow and form only slightly yellow solutions in benzene or ether; however, $(\mathbf{3d})_2$ yields deep red solutions with aromatic solvents like benzene and toluene, most probably due to the formation of a charge-transfer complex. The solvolysis in DME or THF yields the formerly described ether adducts **1** and **2**, respectively. All these alkaline-earth-metal diamides are extremely sensitive toward air and moisture; the calcium derivatives are more heat sensitive than the lighter and heavier homologue compounds.

Mass Spectrometric Experiments. The adducts **1** and **2** show the mass peak for the complexed ether. Furthermore, the parent ion signal for a monomeric unit can easily be observed. The mass distribution of the compounds $(3)_2$ is very similar. The heaviest recorded cation can be associated with the M^+ peak of a monomeric uncomplexed molecule in the case of the magnesium and calcium derivatives. The heavier homologues show the highest masses 801 and 756 amu for the empirical formula $Sr_2N_4Si_8C_{23}H_{69}$ and $Ba_2N_3Si_6C_{18}H_{54}$, respectively. This can be confirmed by a high-resolution mass detection referenced to PFK. The calcium compound $(\mathbf{3b})_2$ represents with the highest observed mass of 360 amu only the monomeric unit in the vapor phase. This could be due to decomposition as a result of the heat sensitivity of the compound, evidenced by the extremely low intensity of the parent ion peak of **3b**. However, the THF adduct **2** shows a surprisingly high stability, so that a high-resolution determination of the ether-free M^+ peak at *m*/*e* 360.1580 was successful. In addition, derivative **2** clearly shows masses of a dimeric species that forms during the removal of the THF ligand. Besides the fragmentation of all these alkaline-earth-metal diamides, an intense signal at 161 amu has to be associated with the parention of hexamethyldisilazane. In agreement with Wannagat,[4] this result can only be explained by hydrogen abstraction from the trimethylsilyl group.

NMR Spectroscopic Results. The alkaline-earth-metal diamides **1** are characterized by NMR spectroscopic data (Table I). The chemical shifts of the trimethylsilyl groups show values around 0.3 and 6 ppm in the ^1H and $^{13}C\{^1H\}$ NMR measurements, respectively, without characteristic differences between the homologue compounds. However, the $^{29}Si\{^1H\}$ NMR data display an obvious trend with the chemical shifts moving to a higher field on going from the lighter to the heavier metals. This fact is consistent with the expectation that the ionic character of the metal–nitrogen bond increases in the same direction and consequently leads to a higher shielding of the silicon atom due to an increasing $(p_N-d_{Si})_\pi$ back-bonding. In addition $^1J_{SiC}$ decreases slightly from 53.1 Hz for the magnesium compound **1a** to 51.0 Hz for the barium derivative **1d**.

Only one resonance can be observed in solution for the complexed metal bis[bis(trimethylsilyl)amides] (**1**). Structurally investigated alkaline-earth-metal derivatives (ML_2) show a tendency to bend on going from calcium to barium. Thus, the monomeric calcium difluoride is bent in the vapor phase, whereas only the heavier strontium and barium dichlorides as well as the barium diiodide are bent.[24] The pentamethylcyclopentadienide sandwich complexes, studied by electron diffraction[25] in the gaseous phase and by X-ray diffraction[26] in the solid state, are also bent with an angle around 150° with the exception of the magnesium compound, which is linear. Furthermore, the europium bis[bis(trimethylsilyl)amide]-2-dimethoxyethane has a non-octahedral coordination with 134.5° for the N–Eu–N angle.[27] The influence of the smaller coordination number at the metal center is only of minor significance, since the NMR parameters of the THF complex **2** are only slightly different from those of compound **1b**.

At low temperatures the dimeric derivatives $(3)_2$ clearly show two different signals for the trimethylsilyl groups, dependent on the coordination number of the nitrogen atom. For the terminal amido ligand with the three-coordinate nitrogen atom, the NMR resonances are observed at high field compared to that of the $SiMe_3$ moiety bonded to the bridging four-coordinate nitrogen (Table II). The charge located on the amido ligand increases from magnesium to barium, as indicated by the increasing high-field shift of the ^{29}Si and ^{13}C nuclei, as it was found analogously for the ether adducts **1**. The increasing ionicity of these metal–amide bonds leads to a decreasing shift separation ($\Delta\delta$ values, Table II) between the bridging and the terminal ligand for these derivatives. Thus, the observed shift differences $\Delta\delta$ between the bridging

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(24) (a) Wharton, L.; Berg, R. A.; Klemperer, W. *J. Chem. Phys.* **1963**, *39*, 2023. (b) White, D.; Calder, G. V.; Hemple, S.; Mann, D. E. *J. Chem. Phys.* **1973**, *59*, 6645. (c) Guido, M.; Gigli, G. *J. Chem. Phys.* **1976**, *65*, 1397. (d) Kasparov, V. V.; Ezhov, Y. S.; Rambidi, N. G. *Zh. Strukt. Khim.* **1979**, *20*, 341; *Chem. Abstr.* **1979**, *91*, 30924a.

(25) (a) Andersen, R. A.; Boncella, J. M.; Burns, C. J.; Blom, R.; Haaland, A.; Volden, H. V. *J. Organomet. Chem.* **1986**, *312*, C49. (b) Andersen, R. A.; Blom, R.; Boncella, J. M.; Burns, C. J.; Volden, H. V. *Acta Chem. Scand.* **1987**, *A41*, 24. (c) Andersen, R. A.; Blom, R.; Burns, C. J.; Volden, H. V. *J. Chem. Soc., Chem. Commun.* **1987**, 768. (d) Blom, R.; Faegri, K.; Volden, H. V. *Organometallics* **1990**, *9*, 372.

(26) Williams, R. A.; Hanusa, T. P.; Huffman, J. C. *Organometallics* **1990**, *9*, 1128.

(27) Tilley, T. D.; Zalkin, A.; Andersen, R. A.; Templeton, D. H. *Inorg. Chem.* **1981**, *20*, 551.

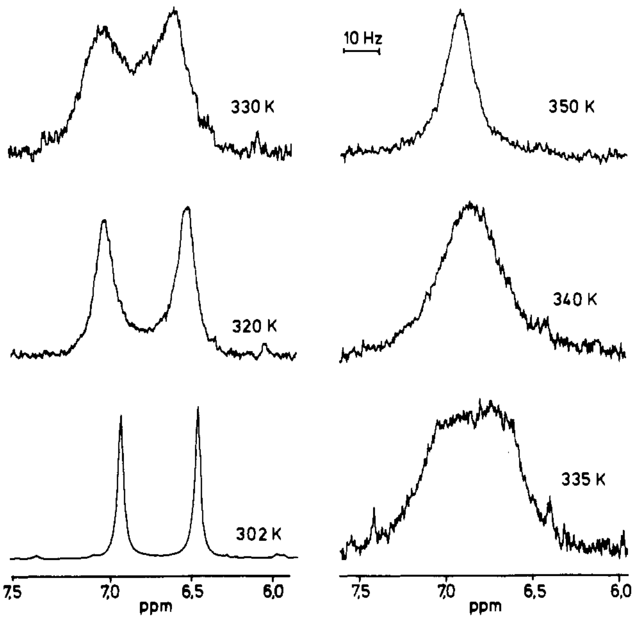
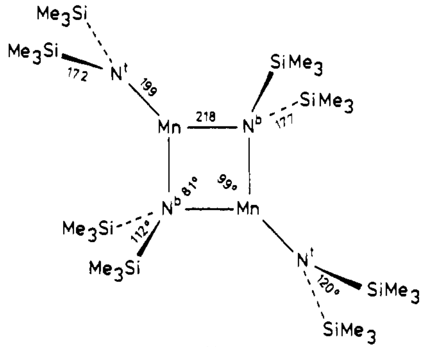


Figure 1. Temperature-dependent $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectra of the dimeric calcium bis[bis(trimethylsilyl)amide] ($(\mathbf{3b})_2$) in benzene-d_6 at 50.323 MHz.

($\delta_b(\mathrm{SiMe_3})$) and the terminal bis(trimethylsilyl)amido groups ($\delta_t(\mathrm{SiMe_3})$) decrease from 8.3 to 0.0 ppm and from 0.98 to 0.03 ppm in the $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ and $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectra, respectively.

The greater shielding of the terminal amido ligand results from the more effective $(p_N\text{–}d_{Si})_\pi$ back-bonding of the anionic charge from the planar sp^2-hybridized nitrogen to the silicon atoms. The bridging nitrogen atom is of distorted tetrahedral geometry, which consequently leads to a weakening of the π back-bonding. In a completely ionic case, π back-bonding is expected to be maximal and nearly independent of whether the amido ligand is bridging or terminal. Hence, the shift difference $\Delta\delta$ should be small. In fact, this is observed for the dimeric barium bis[bis(trimethylsilyl)amide] $(\mathbf{3d})_2$.

The formation of a four-membered ring with two metal(II) centers and two nitrogen atoms, as described here, is for example verified by X-ray structure determination of the dimeric manganese bis[bis(trimethylsilyl)amide] (V)[28] (in the structure bond distances (pm) are given at the top and bond angles are at the bottom); the stronger $(p_N\text{–}d_{Si})_\pi$ back-donation of anionic charge within the planar terminal amido ligand is obviously realized, since the N^t–Si bond is about 5 pm shorter than that in the bridging amido ligand.



V

Fluxional Behavior. The dimeric alkaline-earth-metal bis[bis(trimethylsilyl)amides] $(\mathbf{3a–c})_2$ show at raised temperatures singlets with average values for the chemical shifts. No temperature dependence could be observed for the barium bis[bis(trimethylsilyl)amide] ($(\mathbf{3d})_2$); in toluene-d_8 two signals can be observed in the $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectrum, whereas in benzene-d_6 only one singlet at 5.41 ppm could be recorded. From the Eyring equation,[29] values for the energy barrier of this exchange reaction can be estimated. In the case of magnesium bis[bis(trimethylsilyl)amide] (**3a**), a second dynamic process complicates this situation. Here, the temperature-dependent monomer–dimer equilibrium leads to a less accurate estimation of the energy for the transition state, since the Gutowsky–Holm equation is limited to a two-site exchange process only. Furthermore, compound $(\mathbf{3a})_2$ decomposes in toluene at higher temperatures, so that we used benzene as solvent for these high-temperature measurements.

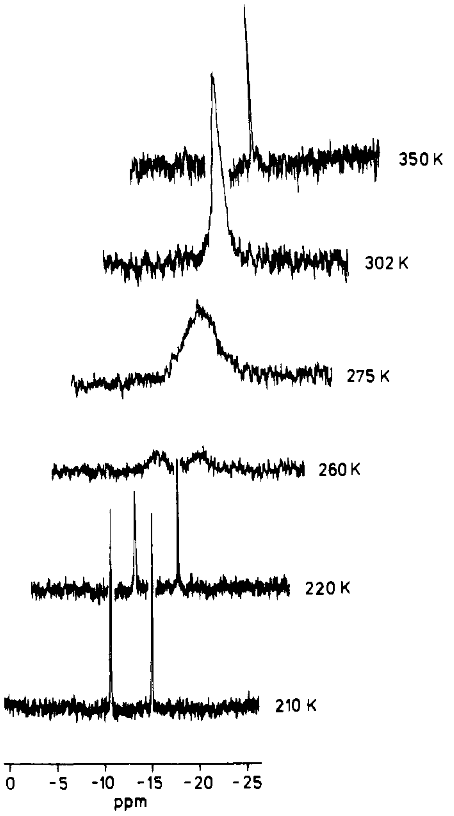
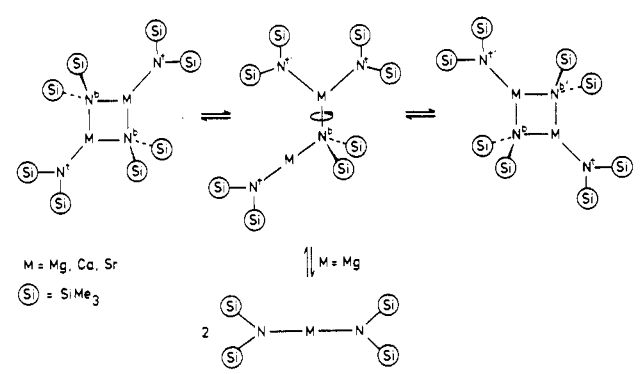


Figure 2. Temperature-dependent $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR spectra of the dimeric strontium bis[bis(trimethylsilyl)amide] ($(\mathbf{3c})_2$) in benzene-d_6 above 280 K and in toluene-d_8 below 280 K at 39.761 MHz (see text).

Scheme I



With these limitations, the energy barriers $\Delta G^\ddagger$ for the exchange processes decrease drastically from the magnesium derivative $(\mathbf{3a})_2$ with an approximate value of about 80 kJ·mol^{-1} to 72 kJ·mol^{-1} for the calcium to finally 53 kJ·mol^{-1} for strontium compound $(\mathbf{3c})_2$. The coalescence temperature is independent from the concentration of these diamides as well as from the matter whether

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[28] (a) Bradley, D. C.; Hursthouse, M. B.; Malik, K. M. A.; Möseler, R. *Transition Met. Chem.* **1978**, *3*, 253. (b) For a review on two coordination of transition-metal amides, see: Power, P. P. *Comments Inorg. Chem.* **1989**, *8*, 177.

[29] Günther, H. *NMR-Spektroskopie*; Georg Thieme Verlag: Stuttgart, Germany, 1983; p 222.

benzene or toluene is chosen as a solvent. Figure 1 displays the $^{13}C\{^1H\}$ NMR spectra of calcium bis[bis(trimethylsilyl)amide] (**3b**)$_2$ in toluene-d_8; Figure 2 shows the temperature-dependent $^{29}Si\{^1H\}$ NMR spectra of strontium bis[bis(trimethylsilyl)amide] ((**3c**)$_2$), where all the spectra above 280 K were obtained from a benzene-d_6 solution, whereas the spectra at lower temperatures were recorded in a toluene-d_8 solution. In both cases the downfield signals of the bridging bis(trimethylsilyl)amido ligand broaden at lower temperatures before the highfield signals do. We propose Scheme I as a mechanistic description of the dynamic intramolecular exchange process of the terminal (superscript t) and the bridging (superscript b) amido groups. This reaction is explained herein by a rotation around a M–N^b bond after cleavage of another appropriate M–N^b bond. The following bond formation closes the four-membered ring again, where one of the nitrogen atoms (N$^{b\prime}$) was terminal (N^t) before the rotation occurred. Due to the equality of the four bondings, forming the M_2N_2 ring system, the bond cleavage and consecutive formation with previous rotation led to equivalent trimethylsilyl groups in the temporal average at high temperatures and therefore to singlets in the NMR spectra. A monomeric species could only be observed for the magnesium derivative **3a** (Scheme I).

IR Spectroscopic Characterization. The alkaline-earth-metal bis[bis(trimethylsilyl)amides] are IR spectroscopically investigated as Nujol suspensions between KBr or CsBr windows. Due to the additional stretching frequencies caused by the complexed ether bases, compounds **1** and **2** give rather unintelligible IR spectra. Therefore, a discussion in detail is limited here to the base-free derivatives **3** (Table III).

Wannagat[30] published the ν_{as} stretching frequencies for the NSiN moiety of the alkaline-metal bis(trimethylsilyl)amides with values from 1035 cm^{-1} for the sodium amide to around 1100 cm^{-1} for the rubidium and cesium derivatives. Going from the magnesium bis[bis(trimethylsilyl)amide] ((**3a**)$_2$) to the heavier homologues, a similar trend can be observed. However, the appearance of a single ν_{as}(SiNSi) frequency for the Nujol suspensions of the strontium and barium derivatives **3c** and **3d** is remarkable, which is only in the case of **3d** consistent with the investigations in solution. The dimeric calcium compound (**3b**)$_2$ shows two bands at 1010 and 920 cm^{-1} for ν_{as}(SiNSi) of the terminal and the bridging amido ligand, respectively. Therefore, a benzene solution of strontium bis[bis(trimethylsilyl)amide] ((**3c**)$_2$) was investigated by IR spectroscopy. In this solution two SiNSi stretching frequencies at 1030 and 970 cm^{-1} could be observed (Table III). The planar bis(trimethylsilyl)amido group is observed at higher energies due to the fact that the $(p_N-d_{Si})_\pi$ back-bonding leads to a strengthening of the N–Si bond. In summary, these results are in accord with the NMR experiments, where only the barium derivative **3d** has been found to be the most ionic. The strontium compound **3c** appears to be mostly ionic in the Nujol suspension due to the observation of a single ν_{as}(SiNSi) band at 1020 cm^{-1}. However, in solution discrete dimers can be detected by NMR and IR spectroscopy.

The metal–nitrogen vibration decreases in energy with increasing mass of the metal atom (Table III). These values fit very well to the corresponding IR spectroscopic data on related compounds. Thus the vibration of the metal–nitrogen bond for the calcium derivative (**3b**)$_2$ is observed around 410 cm^{-1}, which is in harmony with the measurements of gallium tris[bis(trimethylsilyl)amide];[11] corresponding comparisons can be made successfully for compounds **3c** and **3d** with their neighbors of the third main group.[11,13a]

Conclusion

Bis[bis(trimethylsilyl)amides of the alkaline-earth metals are preparable in acceptable yield by transmetalation of the corresponding tin(II) compound. The derivatives synthesized in benzene or toluene are dimeric, whereas the isolated compounds from DME or THF crystallize as the diether complexes. The dimeric ether-free compounds are characterized by the four-membered M_2N_2 ring, where each metal center is also bonded to a terminal amido ligand. It could be shown that the planar terminal nitrogen back-donates the anionic charge more effectively to the trimethylsilyl group than the bridging nitrogen does. Nevertheless, in the NMR experiments at higher temperatures dynamic processes lead to the chemical exchange of bridging and terminal ligands. Only barium bis[bis(trimethylsilyl)amide] ((**3d**)$_2$) shows no temperature dependence in the NMR spectra.

All the bis[bis(trimethylsilyl)amide] derivatives of magnesium, calcium, strontium, and barium are extremely sensitive toward moisture and air and are partially heat sensitive. It is expected that these compounds can be useful adducts for the widely unknown organometallic chemistry of the heavier alkaline-earth metals, as the derivatives of the alkaline metals and of the dications of the second-transition-metal group have already proved to be.

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[30] Wannagat, U. *Pure Appl. Chem.* **1969**, *19*, 329.