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Syntheses and Structures of a Series of Very Low Coordinate Barium Compounds: $\mathrm{Ba[N(SiMe_3)_2]_2(THF)_2}$, $\mathrm{\{Ba[N(SiMe_3)_2]_2(THF)\}_2}$, and $\mathrm{\{Ba[N(SiMe_3)_2]_2\}_2}$

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Barium hexamethyldisilazide tetrahydrofuranate, $\mathrm{Ba[N(SiMe_3)_2]_2(THF)_2}$ (**1**), is synthesized from barium granules and 1,1,1,3,3,3-hexamethyldisilazane at 25 °C in THF. Gaseous ammonia is a necessary catalyst. In the solid state, the compound is a monomer containing a tetrahedral four-coordinate barium center. Crystal data (−157 °C): a = 17.952 (3) Å, b = 20.740 (3) Å, c = 17.652 (3) Å with Z = 8 in the space group *Pbca*. One of the coordinated THF molecules is removed from **1** by stripping a toluene solution of **1** to dryness in vacuo, yielding $\mathrm{\{Ba[N(SiMe_3)_2]_2(THF)\}_2}$ (**2**). In the solid state, **2** is a dimer containing two bridging and two terminal hexamethyldisilamido groups. The four-coordinate, tetrahedral geometry at each barium is completed by terminal THF molecules. Crystal data (−155 °C): a = 20.356 (3) Å, b = 15.632 (2) Å, c = 16.952 (3) Å with Z = 4 in space group *Pnab*. The solvent-free compound $\mathrm{\{Ba[N(SiMe_3)_2]_2\}_2}$ (**3**) is obtained by sublimation of **1**. This compound is a dimer in the solid state, with three-coordinate barium centers. Crystal data (−172 °C): a = 11.154 (6) Å, b = 12.262 (6) Å, c = 9.834 (4) Å, α = 95.87 (2)°, β = 106.74 (2)°, γ = 115.13 (2)° with Z = 1 in the space group $P\bar{1}$.

Introduction

In an endeavor to incorporate additional metals into alkoxide precursors for oxide materials,[1,2] we have looked to metal amides as possible reaction partners for existing metal–alkoxide–alcoholates (eq 1). A source of barium was of interest, particularly

$$\mathrm{M}_n(\mathrm{OR})_m(\mathrm{HOR})_2 + \mathrm{Ba(NR'_2)_2} \rightarrow \mathrm{BaM}_n(\mathrm{OR})_{m+2} + 2\mathrm{HNR'_2} \tag{1}$$

with respect to its integration into compound oxides such as the well-known high-T_c superconductor $\mathrm{YBa_2Cu_3O_7}$. No molecular amide of barium is known.[3]

The bulky bis(trimethylsilyl)amido ligand, $\mathrm{N(SiMe_3)_2^-}$, has been exploited for a variety of metal complexes, particularly to stabilize metals of low coordination number.[3] While many group IA and IIA bis(trimethylsilyl)amido compounds are known, the chemistry of silylamido compounds of the heavier alkaline-earth metals is wholly undeveloped. Because of the anticipated broad synthetic utility of an anhydrous and hydrocarbon-soluble source of $\mathrm{Ba^{2+}}$, we have studied the $\mathrm{N(SiMe_3)_2}$ moiety as a partner anion to $\mathrm{Ba^{2+}}$. It was also our choice to employ a halide-free synthetic procedure, in order to avoid possible production of so-called "ate" compounds (e.g., eq 2).[2] We therefore studied the *redox* approach shown

$$\mathrm{BaCl_2 + 2LiN(SiMe_3)_2 \rightarrow LiBaCl[N(SiMe_3)_2]_2} \tag{2}$$

$$\mathrm{Ba + 2HN(SiMe_3)_2 \xrightarrow{?} Ba[N(SiMe_3)_2]_2 + H_2} \tag{3}$$

in eq 3. The results of this work, reported here, reveal interesting characteristics of the Lewis acidity of $\mathrm{Ba[N(SiMe_3)_2]_2}$ and of the steric "shielding" power of the $\mathrm{N(SiMe_3)_2}$ group. Most surprising, however, are the kinetic problems associated with the heterogeneous aspect of eq 3. We describe here a potentially general approach for overcoming this difficulty.

Experimental Section

Manipulations of all reactants and products were carried out under an argon atmosphere or in vacuo, with rigorous exclusion of air and moisture. All solvents were dried and distilled prior to use and stored under dry dinitrogen or argon. Barium granules were obtained from Alfa Products and 1,1,1,3,3,3-hexamethyldisilazane was purchased from Aldrich Chemical Co. NMR spectra (^{1}H, ^{13}C{^{1}H}) were recorded on a Bruker AM-500 spectrometer with chemical shifts referenced to resonances of the solvent. Infrared spectra were recorded on a Nicolet 510P FT-IR spectrometer as Nujol mulls between KBr plates. All compounds are very sensitive to air; this effect increases as metal coordination number decreases. As a result, completely satisfactory combustion analyses could not be attained, even with glovebox handling.

Syntheses. $\mathrm{Ba[N(SiMe_3)_2]_2(THF)_2}$ (1). In a drybox, 1.0 g of barium granules (7.28 mmol) was weighed into a Schlenk tube. The tube was removed from the drybox and charged with 6 mL of $\mathrm{HN(SiMe_3)_2}$ (28.44 mmol) and 6 mL of THF. Gaseous $\mathrm{NH_3}$ was bubbled into the reaction mixture for approximately 5 min. The evolution of bubbles indicated that barium was reacting. The solution was stirred for 18 h, and then $\mathrm{NH_3}$ was introduced again for approximately 5 min. The treatment with $\mathrm{NH_3}$ was repeated several times in order to ensure that all the barium had reacted. The resulting murky solution was stripped of solvent in vacuo, leaving a viscous oil. The addition of 20 mL of pentane and 2 mL of THF to this oil yielded a yellowish solution, which was filtered away from the residual solids and stripped to dryness. The product was recrystallized from cold pentane, and a colorless crystalline solid was obtained in 60% yield. Anal. Calcd for $\mathrm{BaSi_4O_2N_2C_{20}H_{52}}$: C, 39.88; H, 8.70; N, 4.65. Found: C, 38.66; H, 8.55; N, 4.32. ^{1}H NMR (toluene-d_8): δ 3.52 (m, 8 H), 1.40 (m, 8 H), 0.28 (s, 36 H). ^{13}C{^{1}H} NMR (toluene-d_8): δ 68.62 (s), 25.46 (s), 5.60 (s). Infrared (cm^{-1}): 1240 (st), 1088 (vs), 1036 (st), 874 (st), 822 (vs), 754 (st), 658 (st), 604 (st).

Table I. Crystallographic Data for $\mathrm{Ba[N(SiMe_3)_2]_2(THF)_2}$

chem formula	$\mathrm{C_{20}H_{52}N_2O_2Si_4Ba}$	fw	602.33
space group	*Pbca*	T, °C	−157
a, Å	17.952 (3)	λ, Å	0.71069
b, Å	20.740 (3)	ρ_{calcd}, g cm^{-3}	1.217
c, Å	17.652 (3)	μ(Mo Kα), cm^{-1}	13.6
V, Å^3	6572.32	R	0.0526
Z	8	R_w	0.0529

$\mathrm{\{Ba[N(SiMe_3)_2]_2(THF)\}_2}$ (2). A 250-mg sample of $\mathrm{\{Ba[N(SiMe_3)_2]_2(THF)_2\}}$ (**1**) was redissolved in 10 mL of toluene (the solvent used here must have a higher boiling point than does THF). The solution was stirred for 15 min and then stripped to dryness in vacuo yielding a colorless oil. The product was crystallized by addition of pentane and slowly concentrating the solution in vacuo. Complete removal of pentane gave a quantitative yield of a white powder, which was shown by NMR spectroscopy to have the stoichiometry $\mathrm{Ba[N(SiMe_3)_2]_2(THF)}$. Anal. Calcd for $\mathrm{BaSi_4ON_2C_{16}H_{44}}$: C, 36.24; H, 8.36; N, 5.28. Found: C, 33.78; H, 7.53; N, 4.47. ^{1}H NMR (toluene-d_8): δ 3.49 (m, 4 H), 1.38 (m, 4 H), 0.26 (2, 36 H). ^{13}C{^{1}H} NMR (toluene-d_8): δ 68.61 (s), 25.35 (s), 5.52 (s). Infrared (cm^{-1}): 1546 (br, w), 1248 (vs), 1185 (w), 1077 (sh), 1047 (vs), 990 (st), 931 (w), 876 (st), 822 (vs), 760 (med), 750 (med), 662 (st), 608 (w), 581 (st).

$\mathrm{\{Ba[N(SiMe_3)_2]_2\}_2}$ (3). A sample of solid $\mathrm{Ba[N(SiMe_3)_2]_2(THF)_2}$ (**1**) was placed into a vessel equipped with a cold finger. A fine white powder as well as colorless crystals were sublimed onto the cold finger by using heat from an infrared lamp under a vacuum of approximately 50 mTorr. ^{1}H NMR confirmed that this material contained no coordinated THF. Mp: 186–188 °C. Anal. Calcd for $\mathrm{BaSi_4N_2C_{12}H_{36}}$: C, 31.46; H, 7.92; N, 6.11. Found: C, 28.17; H, 7.13; N, 5.32. ^{1}H NMR (toluene-d_8): δ 0.19 (s). ^{13}C{^{1}H} NMR (toluene-d_8): δ 5.39 (s). Infrared (cm^{-1}): 1592 (br, w), 1246 (st), 1237 (st), 1053 (vs), 1038 (st), 880 (st), 860 (st), 824 (vs), 762 (st), 723 (med), 662 (st), 608 (med), 581 (st), 556 (st).

X-ray Diffraction Studies. For each of compounds **1**–**3**, a suitable crystal was chosen and transferred to the goniostat by using standard inert-atmosphere handling techniques. Data were collected (6° < 2θ < 45°) in the usual manner[4] using a continuous θ–2θ scan with fixed

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Table II. Fractional Coordinates[a] and Isotropic Thermal Parameters[b] for $Ba[N(SiMe_3)_2]_2(THF)_2$

	x	y	z	$10B_{iso}$, Å^2
Ba(1)	1881.2 (3)	1046.1 (2)	1926.5 (3)	21
N(2)	1366 (4)	−44 (3)	2409 (4)	24
Si(3)	1963 (1)	−661 (1)	2301 (1)	26
C(4)	2829 (5)	−351 (4)	1817 (6)	35
C(5)	2276 (6)	−1054 (5)	3209 (6)	44
C(6)	1625 (5)	−1340 (4)	1681 (5)	35
Si(7)	484 (1)	−34 (1)	2733 (1)	30
C(8)	374 (7)	−313 (5)	3740 (6)	54
C(9)	−177 (6)	−517 (6)	2149 (7)	53
C(10)	133 (6)	822 (4)	2717 (6)	39
N(11)	1015 (4)	1718 (3)	1053 (4)	22
Si(12)	808 (1)	1319 (1)	253 (1)	22
C(13)	1402 (5)	560 (4)	198 (5)	30
C(14)	−184 (5)	1038 (5)	202 (5)	37
C(15)	1007 (6)	1778 (5)	−639 (5)	38
Si(16)	755 (1)	2438 (1)	1399 (1)	25
C(17)	−276 (5)	2507 (5)	1605 (6)	36
C(18)	1013 (5)	3151 (4)	790 (5)	35
C(19)	1237 (6)	2577 (4)	2335 (5)	38
O(20)	3212 (3)	1278 (3)	1210 (3)	31
C(21)	3636 (6)	1019 (5)	600 (6)	40
C(22)	4016 (9)	1566 (6)	251 (8)	79
C(23)	4084 (6)	2061 (5)	852 (6)	46
C(24)	3406 (7)	1947 (5)	1318 (7)	49
O(25)	2470 (4)	1379 (3)	3290 (4)	51
C(26)	2647 (8)	1934 (6)	3689 (6)	64
C(27)	2781 (6)	1778 (5)	4490 (5)	40
C(28)	2589 (7)	1079 (5)	4561 (6)	47
C(29)	2715 (11)	849 (7)	3753 (9)	94

[a] Fractional coordinates are times 10^4. [b] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

Table III. Selected Bond Distances (Å) and Angles (deg) for $Ba[N(SiMe_3)_2]_2(THF)_2$

Ba(1)–O(20)	2.745 (6)	O(20)–C(24)	1.442 (11)
Ba(1)–O(25)	2.717 (6)	O(25)–C(26)	1.388 (12)
Ba(1)–N(2)	2.587 (6)	O(25)–C(29)	1.438 (15)
Ba(1)–N(11)	2.596 (6)	C(21)–C(22)	1.460 (15)
Si(3)–N(2)	1.680 (7)	C(22)–C(23)	1.482 (15)
Si(7)–N(2)	1.684 (7)	C(23)–C(24)	1.487 (15)
Si(12)–N(11)	1.677 (7)	C(26)–C(27)	1.470 (14)
Si(16)–N(11)	1.680 (7)	C(27)–C(28)	1.497 (14)
O(20)–C(21)	1.424 (11)	C(28)–C(29)	1.521 (18)

O(20)–Ba(1)–O(25)	91.44 (22)	Ba(1)–O(25)–C(26)	138.6 (6)
O(20)–Ba(1)–N(2)	128.04 (19)	Ba(1)–O(25)–C(29)	115.4 (7)
O(20)–Ba(1)–N(11)	98.83 (19)	C(26)–O(25)–C(29)	106.0 (9)
O(25)–Ba(1)–N(2)	93.96 (21)	Ba(1)–N(2)–Si(3)	113.6 (3)
O(25)–Ba(1)–N(11)	128.54 (21)	Ba(1)–N(2)–Si(7)	115.9 (3)
N(2)–Ba(1)–N(11)	116.77 (21)	Si(3)–N(2)–Si(7)	130.4 (4)
Ba(1)–O(20)–C(21)	138.4 (5)	Ba(1)–N(11)–Si(12)	111.6 (3)
Ba(1)–O(20)–C(24)	108.6 (5)	Ba(1)–N(11)–Si(16)	115.3 (3)
C(21)–O(20)–C(24)	109.5 (7)	Si(12)–N(11)–Si(16)	133.0 (4)

Table IV. Crystal Data for $\{Ba[N(SiMe_3)_2]_2(THF)\}_2$

chem formula	$C_{32}H_8N_4O_2Si_8Ba_2$	fw	1060.44
space group	*Pnab*	T, °C	−155
a, Å	20.356 (3)	λ, Å	0.71069
b, Å	15.632 (2)	ρ_{calcd}, g cm^{-3}	1.306
c, Å	16.952 (3)	μ(Mo Kα), cm^{-1}	16.5
V, Å^3	5394.18	R	0.0745
Z	4	R_w	0.0696

Table V. Fractional Coordinates[a] and Isotropic Thermal Parameters[b] for $\{Ba[N(SiMe_3)_2]_2(THF)\}_2$

	x	y	z	$10B_{iso}$, Å^2
Ba(1)	1853.4 (3)	2506 (1)	998.0 (4)	27
N(2)	2500*	3692 (9)	0*	29
Si(3)	3133 (2)	4203 (2)	469 (2)	29
C(4)	3918 (7)	3605 (12)	375 (8)	60
C(5)	3010 (6)	4290 (10)	1551 (7)	40
C(6)	3325 (9)	5306 (12)	110 (12)	83
N(7)	2500*	1253 (9)	0*	32
Si(8)	2906 (2)	684 (3)	712 (2)	46
C(9)	2345 (9)	304 (10)	1499 (8)	57
C(10)	3522 (8)	1382 (12)	1221 (8)	60
C(11)	3386 (12)	−286 (12)	400 (11)	86
N(12)	672 (5)	2741 (8)	1543 (6)	43
Si(13)	487 (2)	3651 (4)	2036 (2)	55
C(14)	1219 (10)	4354 (19)	2018 (12)	136
C(15)	−210 (11)	4274 (12)	1615 (13)	89
C(16)	282 (10)	3525 (17)	3125 (11)	104
Si(17)	109 (2)	1988 (4)	1309 (2)	50
C(18)	−477 (7)	2311 (12)	515 (9)	69
C(19)	551 (9)	1044 (14)	923 (12)	80
C(20)	−406 (7)	1591 (14)	2159 (9)	72
O(21)	2237 (4)	2274 (5)	2553 (5)	33
C(22)	2825 (6)	2342 (11)	3027 (8)	50
C(23)	2607 (9)	2511 (16)	3825 (9)	91
C(24)	1891 (7)	2432 (11)	3861 (7)	50
C(25)	1730 (6)	1993 (10)	3097 (7)	40

[a] Fractional coordinates are times 10^4. Parameters marked by an asterisk were not varied. [b] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

Table VI. Selected Bond Distances (Å) and Angles (deg) for $\{Ba[N(SiMe_3)_2]_2(THF)\}_2$

Ba(1)–O(21)	2.773 (8)	Si(17)–N(12)	1.690 (12)
Ba(1)–N(2)	2.834 (9)	O(21)–C(22)	1.446 (14)
Ba(1)–N(7)	2.903 (10)	O(21)–C(25)	1.452 (14)
Ba(1)–N(12)	2.602 (9)	C(22)–C(23)	1.448 (21)
Si(3)–N(2)	1.712 (7)	C(23)–C(24)	1.464 (23)
Si(8)–N(7)	1.713 (8)	C(24)–C(25)	1.501 (18)
Si(13)–N(12)	1.693 (13)		

O(21)–Ba(1)–N(2)	121.48 (18)	Ba(1)–N(2)–Si(3)	112.18 (21)
O(21)–Ba(1)–N(7)	109.75 (20)	Ba(1)–N(2)–Si(3)	103.45 (22)
O(21)–Ba(1)–N(12)	86.64 (26)	Si(3)–N(2)–Si(3)	124.4 (9)
N(2)–Ba(1)–N(7)	83.3 (3)	Ba(1)–N(7)–Ba(1)′	95.2 (4)
N(2)–Ba(1)–N(12)	123.3 (3)	Ba(1)–N(7)–Si(8)	99.13 (22)
N(7)–Ba(1)–N(12)	136.1 (3)	Ba(1)–N(7)–Si(8)	122.87 (24)
Ba(1)–O(21)–C(22)	138.8 (7)	Si(8)–N(7)–Si(8)	117.3 (9)
Ba(1)–O(21)–C(25)	116.3 (6)	Ba(1)–N(12)–Si(13)	119.9 (6)
C(22)–O(21)–C(25)	104.9 (9)	Ba(1)–N(12)–Si(17)	116.4 (6)
Ba(1)–N(2)–Ba(1)′	98.3 (4)	Si(13)–N(12)–Si(17)	123.4 (6)

backgrounds. Data were reduced to a unique set of intensities and associated σ values, and the structures were solved by a combination of direct methods (MULTAN78) and Fourier techniques.

$Ba[N(SiMe_3)_2]_2(THF)_2$ (1). A crystal of **1** was cooled to −157 °C for characterization and data collection (Table I). A systematic search of a limited hemisphere of reciprocal space revealed intensities with orthorhombic symmetry. Following complete intensity data collection, a more careful inspection revealed systematic absences that uniquely determined space group *Pbca*. Because of the lack of well-defined faces, no attempt was made to correct for absorption. The Ba position was determined from an E map. The remaining non-hydrogen atoms were obtained from subsequent iterations of least-squares refinement and difference Fourier calculations. Only a few of the hydrogens were evident. All hydrogens were included in fixed calculated positions to improve the refinement of the non-hydrogen atoms. Hydrogen thermal parameters were fixed at 1 plus the isotropic thermal parameter of the atom to which they were bonded. The final difference map had one peak of 1.4 e/Å^3 in the vicinity of C(28) and C(29), which may be due to a slight disorder in this THF ligand since it also seemed to have the largest thermal parameters. All other residual peaks were 0.7 e/Å^3 or less. Results of the refinement are shown in Tables II and III and Figure 1. Further details are available as supplementary material.

$\{Ba[N(SiMe_3)_2]_2(THF)\}_2$ (2). A crystal of **2** was cooled to −155 °C for characterization and data collection (Table IV). A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences uniquely corresponding to the orthorhombic space group *Pnab*. Subsequent solution and refinement of the structure confirmed this choice.

There were considerable difficulties in phasing, and more than 12 cycles were required before the molecule was completely defined. A difference Fourier synthesis revealed the location of some, but not all, hydrogen atoms. All hydrogen atom positions were therefore located in idealized geometries with d(C–H) = 0.95 Å and were held fixed in the final cycles of refinement. The molecule lies on a crystallographic 2-fold axis. Results of the refinement are shown in Tables V and VI and Figure

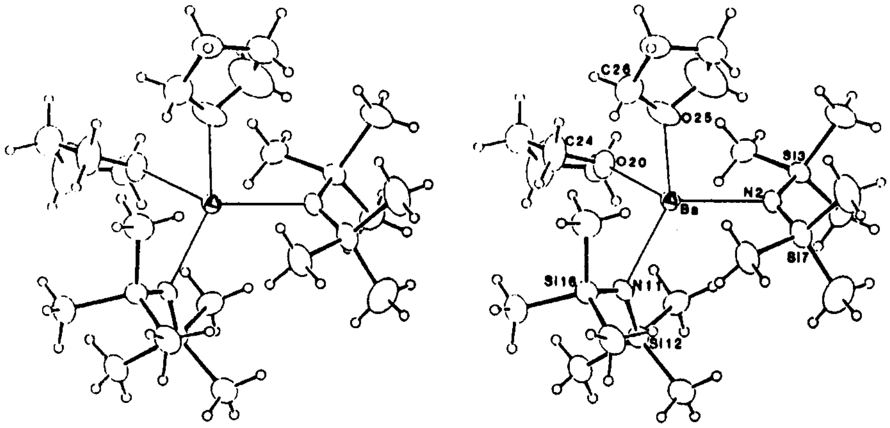

Figure 1. Stereo ORTEP drawing (50% probability) of $Ba[N(SiMe_3)_2]_2(THF)_2$, showing selected atom labeling.

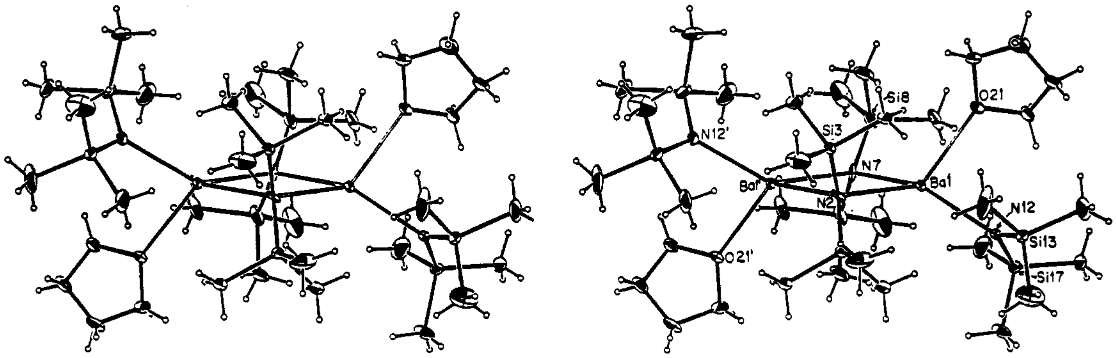

Figure 2. Stereo ORTEP drawing of $\{Ba[N(SiMe_3)_2]_2(THF)\}_2$, showing selected atom labeling. A crystallographic 2-fold axis of symmetry passes through N(2) and N(7).

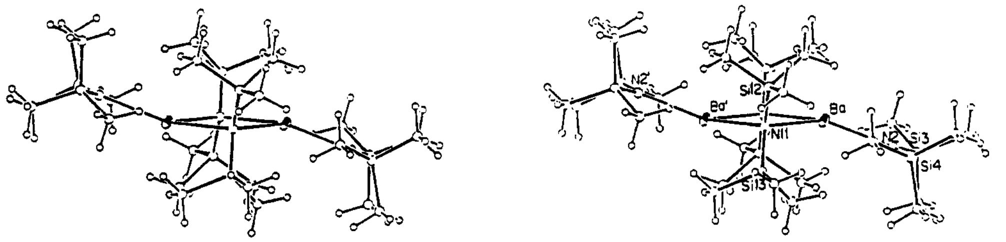

Figure 3. Stereo ORTEP drawing of $\{Ba[N(SiMe_3)_2]_2\}_2$, showing selected atom labeling. A center of inversion is located between the two barium atoms.

Table VII. Crystallographic Data for $\{Ba[N(SiMe_3)_2]_2\}_2$

chem formula	$C_{24}H_{72}N_4Si_8Ba_2$	Z	1
space group	$P\bar{1}$	fw	916.23
a, Å	11.154 (6)	T, °C	−172
b, Å	12.262 (6)	λ, Å	0.71069
c, Å	9.834 (4)	ρ_{calcd}, g cm^{-3}	1.351
α, deg	95.87 (2)	μ(Mo K_α), cm^{-1}	19.6
β, deg	106.74 (2)	R	0.0263
γ, deg	115.13 (2)	R_w	0.0283
V, $Å_3$	1126.22		

2. Further details are available as supplementary material.

$\{Ba[N(SiMe_3)_2]_2\}_2$ (3). A crystal of compound **3** was cooled to −172 °C for characterization and data collection (Table VII). The sample was exceedingly air sensitive and tended to decompose rapidly in spite of the glovebag handling. The crystal mounted was nearly equidimensional and was covered by a layer of decomposed material. In spite of the visible decomposition, the diffraction properties were excellent. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with no symmetry or systematic absences, indicating a triclinic space group. Subsequent solution and refinement of the structure confirmed the centrosymmetric choice, $P\bar{1}$. All hydrogen atoms were clearly visible in a difference Fourier synthesis phased on the non-hydrogen parameters and were refined isotropically.

Because of the poor surface condition of the crystal, no attempt was made to perform an absorption correction. A final difference Fourier analysis was featureless, with the largest peak being 0.89 e/Å^3 at the metal site. The results of the refinement are shown in Tables VIII and IX and Figure 3. Further details are available as supplementary material.

Table VIII. Fractional Coordinates[a] and Isotropic Thermal Parameters[b] for $\{Ba[N(SiMe_3)_2]_2\}_2$

	x	y	z	$10B_{iso}$, Å^2
Ba(1)	439.1 (2)	8573.0 (2)	692.4 (2)	15
N(2)	651 (3)	7070 (3)	2281 (4)	16
Si(3)	−876 (1)	5807 (1)	2078 (1)	16
Si(4)	2319 (1)	7471 (1)	3409 (1)	16
C(5)	−2379 (5)	5768 (5)	551 (6)	23
C(6)	−1353 (6)	5818 (6)	3758 (6)	33
C(7)	−950 (6)	4258 (4)	1536 (6)	27
C(8)	2805 (6)	6187 (5)	3410 (6)	26
C(9)	3637 (5)	8647 (5)	2767 (5)	22
C(10)	2720 (6)	8180 (5)	5378 (5)	27
N(11)	−1926 (3)	8892 (3)	−651 (4)	15
Si(12)	−2669 (1)	7927 (1)	−2370 (1)	16
Si(13)	−2645 (1)	9008 (1)	634 (1)	16
C(14)	−2899 (5)	8733 (5)	−3888 (5)	23
C(15)	−1462 (5)	7305 (5)	−2687 (6)	22
C(16)	−4435 (5)	6519 (5)	−2874 (6)	27
C(17)	−2868 (6)	10443 (5)	872 (6)	23
C(18)	−1403 (5)	9180 (5)	2513 (5)	23
C(19)	−4434 (6)	7711 (5)	347 (7)	30

[a] Fractional coordinaes are times 10^4. [b] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

Table IX. Selected Bond Distances (Å) and Angles (deg) for $\{Ba[N(SiMe_3)_2]_2\}_2$

Ba(1)···Ba(1)	4.2640 (10)	Si(4)–N(2)	1.690 (4)
Ba(1)–N(2)	2.576 (3)	Si(12)–N(11)	1.702 (4)
Ba(1)–N(11)	2.798 (3)	Si(13)–N(11)	1.704 (3)
Ba(1)–N(11)	2.846 (4)	N(11)···N(11)	3.700 (12)
Si(3)–N(2)	1.685 (3)		
N(2)–Ba(1)–N(11)	129.09 (10)	Ba(1)–N(11)–Ba(1)	98.11 (10)
N(2)–Ba(1)–N(11)′	140.54 (10)	Ba(1)–N(11)–Si(12)	110.85 (15)
N(11)–Ba(1)–N(11)′	81.89 (10)	Ba(1)–N(11)–Si(12)	103.04 (15)
Ba(1)–N(2)–Si(3)	116.72 (17)	Ba(1)–N(11)–Si(13)	101.84 (15)
Ba(1)–N(2)–Si(4)	115.76 (16)	Ba(1)–N(11)–Si(13)	107.31 (15)
Si(3)–N(2)–Si(4)	127.52 (20)	Si(12)–N(11)–Si(13)	131.08 (20)

Results

Syntheses and Spectral Data. Reaction of barium granules with $HN(SiMe_3)_2$ in THF can be initiated by heating, but yields are variable, and the reaction of considerable amounts of barium takes many days. In our hands, the reaction is irreproduceable under these conditions. Use of an ultrasonic gun to attempt activation of the barium metal appears to have little effect. Likewise, addition of catalytic amounts of $HgCl_2$ or I_2, or a good Lewis base such as $Me_2NC_2H_4NMe_2$, does not increase the reactivity of the barium. The method of choice would appear to be that described above, where gaseous NH_3 is initially bubbled into the reaction mixture and quickly reacts with the barium metal. It is presumed that the $HN(SiMe_3)_2$ is too sterically crowded to oxidize the metal surface efficiently, while preliminary reaction of NH_3 to form a transient barium ammide is much more rapid. An amount of solid purple-gray precipitate generated in the reaction may contain insoluble $Ba(NH_2)_2$. This is easily separated from the product by filtration.

The colorless crystalline $Ba[N(SiMe_3)_2]_2(THF)_2$ (**1**) is readily soluble in pentane, benzene, or toluene. The solid is also rather robust toward loss of coordinated THF (no THF loss upon prolonged pumping under dynamic vacuum at 25 °C), except when dissolved in a higher boiling solvent, which is subsequently removed in vacuo. Using toluene, this procedure yields compound **2**, having one less THF per barium atom. The ^1H NMR spectrum of **1** reveals a single resonance for all methyl groups at δ 0.28 and resonances for coordinated THF at δ 3.52 and 1.40. Integration establishes the number of coordinated THF molecules in **1** as two per formula unit (each resonance integrates 2:9 vs the methyl singlet). Similarly, the $^{13}C\{^1H\}$ NMR spectrum reveals a single methyl group resonance at δ 5.60 and THF resonances at δ 68.62 and 25.46. The NMR spectra remain essentially unchanged down to −80 °C in toluene-d_8.

The colorless crystalline compound, $\{Ba[N(SiMe_3)_2]_2(THF)\}_2$ (**2**), is similar in appearance to compound **1** and exhibits similar solubility. The ^1H NMR spectrum of **2** also reveals only one resonance for all methyl groups, in this case at δ 0.26. Resonances for the coordinated THF molecules at δ 3.49 and 1.38 each integrate 1:9 vs the methyl singlet. The $^{13}C\{^1H\}$ NMR spectrum is consistent with the proton NMR spectrum, revealing a single methyl resonance at δ 5.52 and THF resonances at δ 68.61 and 25.35. The NMR spectra do not appear to "freeze-out" terminal and bridging hexamethyldisilazide environments (which are observed in the solid-state structure (vide infra)) in the temperature range +25 to −90 °C in toluene-d_8.

The sublimed, THF-free compound, $Ba[N(SiMe_3)_2]_2$ (**3**), is also readily soluble in toluene. Consistent with the previously described THF adducts, compound **3** displays a single methyl group environment at all temperatures studied. The ^1H NMR resonance for the methyl protons is shifted yet further upfield to δ 0.19. Similarly, the $^{13}C\{^1H\}$ NMR resonance appears at δ 5.39. Its melting point was determined to be 186–188 °C and represents a true melting point, whereas THF loss from **1** and **2** would prevent reversible melting behavior.

Solid-State Structures. $\mathbf{Ba[N(SiMe_3)_2]_2(THF)_2}$ **(1).** Compound **1** crystallizes as a monomer in the solid state, giving barium a four-coordinate environment (Figure 1). While the geometry at barium is nearly tetrahedral, the steric requirements of the silylamide ligands result in a range of angles at the barium center from 91.44 to 128.54°, where the smallest angle is that which includes both THF oxygens. The Ba–N bond distances (2.596 (6) and 2.587 (6) Å) do not differ significantly. Distances from THF oxygens to the barium center are 2.745 (6) and 2.717 (6) Å.

$\mathbf{\{Ba[N(SiMe_3)_2]_2(THF)\}_2}$ **(2).** The compound of empirical formula $Ba[N(SiMe_3)_2]_2(THF)$ exists as a dimer in the solid state (Figure 2). The molecule possesses a crystallographic C_2 axis passing through N(2) and N(7), the nitrogens of the two bridging amides. The X-ray structure reveals four-coordinate barium centers, each surrounded by one terminal and two bridging hexamethyldisilamido ligands and one molecule of THF. The geometry at barium is only crudely tetrahedral, with angles ranging from 83.3 (3) to 136.1 (3)°. The smallest angle is due to the N–Ba–N angle within the ring. Other distortions derive from a considerable flattening of the BaN_3 moiety (sum of angles: 342.7°) in a manner which serves to crowd the smaller THF ligand and minimize repulsion *between* the bulky silylamide ligands. The THF oxygen is coplanar with its three attached groups, as is also the case for the THF groups in **1**. The bond length from barium to nitrogen of terminal amides (Ba–N(12) = 2.602 (9) Å) is shorter than those to *bridging* nitrogen atoms (Ba–N(2) = 2.834 (9) Å, Ba–N(7) = 2.903 (10) Å). The asymmetry (0.07 Å or 7σ) of the Ba–(μ-N) distances is small yet statistically significant and must arise from repulsions between bulky silylamide groups. This same repulsion causes the NSi_2 plane of the bridging amides to be nearly orthogonal to the $Ba_2(\mu\text{-}N)_2$ plane.

$\mathbf{\{Ba[N(SiMe_3)_2]_2\}_2}$ **(3).** The metal coordination number of 3 in this dimer (Figure 3) is unprecedentedly low for barium. The molecule is situated on an inversion center, located at the midpoint between barium atoms. Similar to the bis(tetrahydrofuran) dimer discussed previously, the molecule contains two (asymmetrically bound) bridging silylamide groups and two terminal silylamide groups. The geometry at barium is not rigorously planar; the sum of angles at Ba is 351.5° and the angle Ba···Ba–N(2) is 158.3°. Again, this is likely a feature of the steric requirements of the bridging silylamide groups (both NSi_2 planes are orthogonal to the $Ba_2(\mu\text{-}N)_2$ plane), as is the asymmetry in Ba–(μ-N) distances (Ba–N(11) = 2.846 (4) and 2.798 (3) Å). Note that the difference in these two bond distances (ca. 0.05 Å) is less dramatic than was observed in the structure of compound **2**, but in this case corresponds to about 14σ. Atom N(2) is rigorously planar, and the terminal Ba–N(2) distance (2.576 (3)Å) is notably shorter than the distances from barium to bridging nitrogen atoms in this molecule. The shorter Ba–N bond lengths in this structure compared to the THF-containing analogue, **2**, are accompanied by a more acute angle within the central ring (N(11)–Ba–N(11)′ = 81.89°). Also rather noticeable in comparing the stereoviews of **2** (Figure 2) and **3** (Figure 3), is the *eclipsing* of the bridging NSi_2 planes in **3** whereas they are somewhat staggered in **2**. Accompanying this difference, there are also dissimilarities in the twist of the terminal NSi_2 planes of **2** and **3**.

Discussion

In spite of the tendency of large metals to adopt high coordination numbers and, for MX_2 species, a polymeric structure, the bulky amide $N(SiMe_3)_2$ is sufficient to give a (soluble) molecular species when M = Ba. A particularly simple synthetic method suffices, although some initial difficulties are encountered.

We judged that the absence and/or the irreproducibility of the reaction of $HN(SiMe_3)_2$ with bulk barium metal resulted from the marginal rate of reaction of a bulky amine at the metal surface. We hoped that a smaller and more polar amine might react faster to form a metal amide and H_2. Then, provided that the resulting amido group is a stronger Bronsted base than $N(SiMe_3)_2^-$, a kinetically facile *homogeneous* amido group exchange (eq 4)

$$L_nBa\text{-}B + H\text{-}b \rightarrow L_nBa\text{-}b + HB \qquad (4)$$

B = strongly basic group (e.g., NH_2)

b = less basic group (e.g., $N(SiMe_3)_2$)

should take place to generate the desired product. The envisioned reaction is a non-metal catalyzed version of eq 3, where we have chosen NH_3 as the catalyst. This synthetic strategy has broad potential for heterogeneous reactions beginning with metallic elements.

Perhaps the most interesting feature of the structure described here are the unusually low coordination numbers for a divalent cation as large[5] as Ba^{2+}. This again demonstrates the ability of the bis(trimethylsilyl)amido ligand to provide sufficient steric bulk as to stabilize low coordination numbers. The *variability* of the barium coordination number is also noteworthy. The systematic loss of THF along a series of *isolable* members is also presumably driven by the steric bulk of the $N(SiMe_3)_2$ group.

Another interesting feature is the trend shown by NMR spectroscopy as the number of coordinated THF molecules changes. The chemical shifts of the coordinated THF are shifted upfield compared to free THF in toluene-d_8 (δ 3.55, 1.46). The dimeric compound **2** has its THF resonances farther upfield than those of the bis(THF) monomer, **1**. Resonances for the methyl groups also show an upfield shift as one goes to fewer coordinated THF molecules. This is evident in both the ^1H and $^{13}C\{^1H\}$ NMR spectra.

A brief comparison of these structures to those of other divalent metal amido compounds is noteworthy. The chemistry of divalent metal bis(trimethylsilyl)amides includes monomers (M = Zn),[6] monomer/dimer equilibria involving $M_2(NR_2)_2(\mu\text{-}NR_2)_2$ (M = Mn, Fe, Co, Ni),[7-9] and formation of 1:1 mononuclear adducts with THF (Mn, Fe).[8] Chromium(II) forms a bis(THF) adduct.[10] The influence of still larger silyl groups has also been investigated.[11,12] In contrast to **3**, the metal is planar in $Cr_2(N^iPr_2)_4$[13] and in $\{M[N(SiMe_3)_2]_2\}_2$, M = Mn, Co.[8]

While the larger barium atom acquires three-coordination by dimerizing in compound **3**, the lighter group IIA atom, beryllium, is monomeric in $Be[N(SiMe_3)_2]_2$.[14]

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Supplementary Material Available: For compounds **1–3**, tables of crystallographic data, fractional coordinates, and isotropic and anisotropic thermal parameters and labeled figures (11 pages); listings of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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Reactivity of Palladium(II) Complexes with Bidentate Bis(phosphine) Ligands toward the Octahydrotriborate(1–) Anion and Dependence of the Reaction upon Halide Arrangement: Molecular Structure of the *trans*-(bis(diphenylphosphino)hexane)palladium(II) Dichloride Dimer

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The reactivity of the palladium(II) bis(phosphine) complexes, $(Ph_2P(CH_2)_nPPh_2)PdCl_2$ (n = 1–6), toward the octahydrotriborate(1–) anion, $[B_3H_8]^-$, has been investigated. For n = 1–4, the metallaborane $(Ph_2P(CH_2)_nPPh_2)Pd(B_3H_7)$ is produced, although the yield depends upon the organic chain length of the phosphino ligand and is maximized when n = 2. Our observation that no reaction occurs between the $[B_3H_8]^-$ anion and (bis(diphenylphosphino)pentane)- or (bis(diphenylphosphino)hexane)-palladium(II) dichloride leads us to examine the structure of these starting materials. Unlike $(Ph_2P(CH_2)_nPPh_2)PdCl_2$ for n = 1–4, which are cis monomers, complexes with n = 5 or 6 are dimeric with a trans arrangement of chloro substituents; the molecular structure of *trans*-$[(Ph_2P(CH_2)_6PPh_2)PdCl_2]_2$ is presented: triclinic, $P\bar{1}$; a = 9.448 (2), b = 11.772 (2), c = 16.983 (3) Å; α = 74.18 (2), β = 87.14 (2), γ = 77.59 (2)°; V = 1774.9 (9) Å^3, Z = 2; R_F = 5.17%. A detailed comparison of this structure with those of related complexes is made.

The versatility of the triborane ligand with respect to bonding to metal fragments has been recognized for some years.[1-5] As the octahydrotriborate(1–) anion, $[B_3H_8]^-$, the triborane ligand tends to coordinate through terminal hydrogen atoms to generate M–H–B bridging interactions, e.g. $Cr(CO)_4B_3H_8$,[6] $Mn(CO)_3B_3H_8$,[7] and $(\mu\text{-}Br)Mn_2(CO)_6B_3H_8$.[8] On the other hand, in situ loss of a proton formally produces the "borallyl" $[B_3H_7]^{2-}$ ligand (not isolated as a free entity), as confirmed structurally in the complexes $(Me_2PhP)_2PtB_3H_7$,[9,10] $(Ph_3P)_2(CO)HIrB_3H_7$,[11,12] and $(dppf)PdB_3H_7$[13] (dppf – 1,1′-bis(diphenylphosphino)ferrocene). The preferred coordination mode of the triborane ligand is sensitive to the bonding capability of the metal fragment,[4] and clearly, as the $[B_3H_8]^-$ anion reacts with a given metal complex, it responds to the presence (or absence) of potential leaving groups present.

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