efficient and gave a mixture of $(SF_5)_2NCF_3$ and $SF_5N(CF_3)N(CF_3)SF_5$, which could not be separated from the unreacted starting material.

The compound $SF_5N(Br)CF_3$ reacted readily with ethylene upon warming to room temperature to give $SF_5N(CF_3)CH_2CH_2Br$ in over 85% yield:

$$SF_5N(Br)CF_3 + C_2H_4 \rightarrow SF_5N(CF_3)CH_2CH_2Br \quad (18)$$

On the other hand, a temperature of 170 °C was required for its reaction with hexafluoropropylene. The addition product, which was isolated in 53% yield, was found to be largely one of two possible isomers:

$$SF_5N(Br)CF_3 + CF_3CF{=}CF_2 \rightarrow SF_5N(CF_3)CF_2CF(CF_3)Br + SF_5N(CF_3)CF(CF_3)CF_2Br \quad 99.5{:}0.5 \quad (19)$$

In fact, the second isomer was observed only with the enhanced sensitivity and signal averaging obtained from an NMR spectrometer operating at 470.6 MHz. The distribution of isomers is as expected based on the results of other addition reactions of hexafluoropropylene.[1,42] Generally attack is favored at the CF_2 position not only because it is sterically advantageous but also because a more stable anionic or radical intermediate (depending on the mechanism) is formed.[42a] The results outlined above point to a rather surprising thermal and photolytic stability for the bromoamine $SF_5N(Br)CF_3$.

As with the tellurium chemistry,[1] the reaction of $SF_5N(Br)CF_3$ with carbon monoxide failed to give the carbamoyl bromide $SF_5N(CF_3)C(O)Br$ but gave SF_5Br and $CF_3N{=}C{=}O$ instead:

$$SF_5N(Br)CF_3 + CO \rightarrow [SF_5N(CF_3)C(O)Br] \rightarrow SF_5Br + CF_3N{=}C{=}O \quad (20)$$

Attempts failed to prepare the first pentafluorochalcogen iodides by this reaction pathway, and a different route was observed when the reaction was repeated with the *N*-iodoamines (prepared in situ):

$$Hg[N(CF_3)EF_5]_2\ (E = S, Te) + 2ICl + 2CO \rightarrow 2[EF_5N(CF_3)C(O)I] + HgCl_2 \rightarrow 2EF_5N{=}CF_2 + 2IC(O)F \quad (21)$$

It is quite possible that the carbamoyl iodide was never formed and that the IC(O)F resulted from the reaction of IF (IF_5) with CO.[18] Nevertheless, we saw no evidence for the formation of a pentafluorochalcogen iodide under these conditions.

Conclusion. This investigation has demonstrated the utility of the mercurials $Hg[N(CF_3)SF_5]_2$ and $Hg[N(CF_3)TeF_5]_2$ for incorporating the $SF_5N(CF_3)$– and $TeF_5N(CF_3)$– groups into a variety of materials. The group electronegativities of $SF_5N(CF_3)$– and $TeF_5N(CF_3)$–, although not discernible from one another, clearly lie between the values for $(CF_3)_2N$– and $(SF_5)_2N$–. The structural investigation of $Hg[N(CF_3)TeF_5]_2$ provides yet another example of the ability of highly electron-withdrawing, bulky substituents to flatten the geometry about an otherwise pyramidal amine.

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Registry No. $Hg[N(CF_3)TeF_5]_2$, 98720-67-3; $Hg[N(CF_3)SF_5]_2$, 2375-55-5; HgF_2, 7783-39-3; $SF_5N{=}CCl_2$, 1801-00-9; $SF_5N(F)CF_3$, 4101-60-4; $SF_5N(Cl)CF_3$, 2194-08-3; $SF_5N(Br)CF_3$, 112043-76-2; $SF_5N(I)CF_3$, 112043-77-3; $SF_5N(CH_3)CF_3$, 112043-78-4; CH_3I, 74-88-4; $TeF_5N(CH_3)CF_3$, 112043-79-5; $(SF_5)_2NCF_3$, 112043-80-8; $SF_5(CF_3)NN(CF_3)SF_5$, 2375-56-6; $SF_5N(CF_3)CH_2CH_2Br$, 112043-81-9; C_2H_4, 74-85-1; C_3F_6, 116-15-4; $SF_5N(CF_3)CF_2CF(CF_3)Br$, 112043-82-0; $SF_5N(CF_3)CF(CF_3)CF_2Br$, 112043-83-1; SF_5Br, 15607-89-3; $CF_3N{=}C{=}O$, 460-49-1; $SF_5N{=}CF_2$, 2375-32-8; FC(O)I, 1495-48-3; COF_2, 353-50-4; $TeF_5N{=}CF_2$, 98720-68-4; F_2, 7782-41-4; Cl_2, 7782-50-5; Br_2, 7726-95-6; ICl, 7790-99-0; CO, 630-08-0.

Supplementary Material Available: Anisotropic thermal parameters (Table S-I) (1 page); structure factors (Table S-II) (5 pages). Ordering information is given on any current masthead page.

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Synthesis and X-ray Crystal Structure of the Divalent [Bis(trimethylsilyl)amido]samarium Complexes $[(Me_3Si)_2N]_2Sm(THF)_2$ and $\{[(Me_3Si)_2N]Sm(\mu\text{-}I)(DME)(THF)\}_2$

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$SmI_2(THF)_2$ reacts with 2 equiv of $NaN(SiMe_3)_2$ in THF to form $[(Me_3Si)_2N]_2Sm(THF)_2$, which crystallizes from hexane in space group $P2_1/c$ with unit cell dimensions $a = 8.690$ (5) Å, $b = 19.721$ (5) Å, $c = 19.870$ (5) Å, $\beta = 97.78$ (5)°, and $Z = 4$ for $D_{calcd} = 1.21$ g cm^{-3}. Least-squares refinement on the basis of 2041 unique observed reflections converged to a final $R = 0.040$. The THF oxygen atoms and the $N(SiMe_3)_2$ nitrogen atoms form a distorted tetrahedron around the Sm atom with average Sm–O and Sm–N distances of 2.59 (1) and 2.43 (1) Å, respectively. $[(Me_3Si)_2N]_2Sm(THF)_2$ reacts with 1 equiv of $SmI_2(THF)_2$ in a THF/DME mixture to form $\{[(Me_3Si)_2N]Sm(\mu\text{-}I)(DME)(THF)\}_2$, which crystallizes from a THF/DME mixture in space group $C2/c$ with unit cell dimensions $a = 28.580$ (4) Å, $b = 8.7679$ (14) Å, $c = 20.247$ (3) Å, $\beta = 90.224$ (11)°, and $Z = 4$ (dimers) for $D_{calcd} = 1.57$ g cm^{-3}. Least-squares refinement on the basis of 2617 unique observed reflections converged to a final $R = 0.042$. The THF oxygen atom, the silylamide nitrogen atom, the two bridging iodide ligands, and the two DME oxygen atoms describe an irregular six-coordinate geometry around samarium. The Sm–N distance is 2.455 (7) Å; the Sm–I distances are 3.3414 (9) and 3.3553 (9) Å.

Introduction

As part of our study of the remarkable organometallic chemistry of Sm(II), we have used the pentamethylcyclopentadienyl ligand extensively.[2-8] Traditionally, cyclopentadienyl ligands have been important in organolanthanide chemistry because they meet the electrostatic and steric requirements necessary to form thermally

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stable, isolable complexes.[9,10] As monoanions that can formally occupy three coordination positions, C_5R_5 ligands (R = H or alkyl) provide the steric bulk needed to sterically saturate the coordination environment of the large lanthanide ions without a large buildup of negative charge on the complex. For Sm(II), the C_5Me_5 ligand has been particularly important in providing soluble complexes. $[(C_5H_5)_2Sm(THF)]_n$[11] and $[(MeC_5H_4)_2Sm(THF)]_n$[12] are insoluble in solvents with which they do not react, whereas $(C_5Me_5)_2Sm(THF)_2$[13] and $(C_5Me_5)_2Sm$[14] are soluble in arenes.

The electronic nature of the C_5Me_5 ligand is likely to be less important than the steric and charge characteristics in *trivalent* lanthanide complexes, since the 4f orbitals have a limited radial extension.[9,15-17] Orbital overlap is likely to be small, and effects transmitted by covalent interaction will be weaker than those in transition-metal complexes. For divalent lanthanide complexes, the effect of the electronic characteristics of the ligand remains to be determined. The unusual bent structures of $(C_5Me_5)_2Sm$,[14] $(C_5Me_5)_2Eu$,[4] and $(C_5Me_5)_2Yb$[18] indicate that the principles of steric saturation which work well for trivalent complexes may not always be directly applicable to divalent species.[19]

To probe the effects of different ligands in soluble Sm(II) complexes, we have prepared bis(trimethylsilyl)amido analogues of two important classes of pentamethylcyclopentadienyl Sm(II) complexes, namely, $(C_5Me_5)_2Sm(THF)_2$ and $[(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$.[7] The $(Me_3Si)_2N$ ligand has been used previously to form interesting complexes of a variety of metals[20,21] including complexes of both trivalent[22-26] and divalent[27-30] lanthanides. These studies have shown that this ligand is attractive for use in the study of Sm(II) chemistry because it provides the steric, electrostatic, and solubility characteristics required for our purposes.

Table I. Crystal and Data Collection Parameters for $[(Me_3Si)_2N]_2Sm(THF)_2$ (**1**) and $\{[(Me_3Si)_2N]Sm(\mu\text{-}I)(DME)(THF)\}_2$ (**2**)

	1	**2**
formula	$C_{20}H_{52}N_2O_2Si_4Sm$	$C_{28}H_{72}I_2N_2O_6Si_4Sm_2$
mol wt	615.34	1199.74
space group	$P2_1/c$	$C2/c$
a, Å	8.690 (5)	28.580 (4)
b, Å	19.721 (5)	8.768 (1)
c, Å	19.870 (5)	20.247 (3)
β, deg	97.78 (5)	90.22 (1)
cell vol, Å^3	3374	5074
Z	4	4
D_{calcd}, g/cm^3	1.21	1.57
temp, °C	24	22
λ(Mo Kα), Å	0.71073; graphite monochromator	0.71073; graphite monochromator
μ, cm^{-1}	19.2	36.3
min–max transmissn coeff	0.67–0.75	0.113–0.175
type of scan	θ–2θ	θ–2θ
scan width, deg	0.80 + 0.20 tan θ	−1.2 in 2θ from Kα_1 to +1.2 from Kα_2
scan speed, deg/min	variable	4–16
2θ range, deg	2–44	4–45
no. of reflcns measd	4041	3333
no. of obsd reflcns	2041	2617
no. of params	262	199
$R(F)$	0.040	0.042
$R_w(F)$	0.046	0.059
GOF	0.87	1.85
max Δ/σ in final cycle	0.05	0.08

Experimental Section

The complexes described in this paper are air- and moisture-sensitive. Therefore, all syntheses and subsequent manipulations were conducted under nitrogen by using Schlenk, vacuum-line and glovebox (Vacuum Atmospheres HE-553 Dri-Lab) techniques. Solvents and $SmI_2(THF)_2$ were prepared as previously described.[7] Sodium bis(trimethylsilyl)amide (1 M in THF, Aldrich) was used as received. Infrared and ^1H NMR spectra and complexometric analyses were obtained as previously described.[7,31] ^{13}C NMR spectra were obtained on a Bruker 250-MHz or a General Electric GN 500-MHz NMR spectrometer.

$[(Me_3Si)_2N]_2Sm(THF)_2$ (1). In the glovebox, a 1 M THF solution of sodium bis(trimethylsilyl)amide (9.5 mL, 9.5 mmol) was stirred into a solution of $SmI_2(THF)_2$ (2.60 g, 4.74 mmol) in 10 mL of THF. The solution was stirred for 4 h and the THF was removed by rotary evaporation, leaving a purple solid. The solid was dissolved in hexane and filtered to remove NaI. Rotary evaporation of the hexane yielded **1** (2.68 g, 92%). Crystals suitable for X-ray analysis were grown from a concentrated hexane solution at −34 °C. Anal. Calcd for $C_{20}H_{52}N_2O_2Si_4Sm$: Sm, 24.4. Found: Sm, 24.4. ^1H NMR (C_6D_6): δ 4.53 (s, 12 H, $SiMe_3$), −0.40 (s, 6 H, $SiMe_3$). ^{13}C NMR (C_6D_6): δ 146.4 (t, J_{CH} = 141 Hz, THF), 27.0 (q, J_{CH} = 115 Hz, Me_3Si), 25.8 (t, J_{CH} = 136 Hz, THF). IR (KBr): 2950 s, 2900 s, 1445 w, 1250 s, 1240 s, 1060 vbr s, 870 s, 830 br s, 760 s, 660 m cm^{-1}. Magnetic susceptibility: $\chi_M^{297\,K} = 5000 \times 10^{-6}$ cgsu; $\mu_{eff}^{297\,K} = 3.45\ \mu_B$.

$\{[(Me_3Si)_2N]Sm(\mu\text{-}I)(DME)(THF)\}_2$ (2). In the glovebox, $SmI_2(THF)_2$ (365 mg, 0.666 mmol) and **1** (410 mg, 0.667 mmol) were dissolved together in a THF/DME (50:50) mixture and stirred overnight. The solvent was removed slowly by intermittent rotary evaporation (stopping frequently to warm the solution in order to avoid precipitating $SmI_2(THF)_2$) to yield black **2** (0.79 g, 98%). Crystals suitable for X-ray analysis were grown by slowly cooling a hot saturated THF/DME solution of **2** to ambient glovebox temperature. Anal. Calcd for $C_{28}H_{72}I_2N_2O_6Si_4Sm_2$: Sm, 25.1. Found: Sm, 24.9. ^1H NMR (C_4D_8O): δ 7.80 (s, 6 H, $SiMe_3$), 3.34 (s, 10 H, DME), 2.66 (s, 12 H, $SiMe_3$). The ^1H NMR spectrum of a DME-free sample of **2** prepared by stripping a THF solution of **2** to dryness and redissolving the resulting solid in

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Table II. Fractional Coordinates for $[((CH_3)_3Si)_2N]_2Sm(THF)_2$

atom	*x*	*y*	*z*
Sm	0.18952 (9)	−0.26404 (3)	0.56182 (4)
Si(1)	0.0496 (5)	−0.4121 (2)	0.6344 (2)
Si(2)	0.3608 (5)	−0.3588 (2)	0.6999 (2)
Si(3)	0.0665 (6)	−0.1307 (2)	0.6550 (2)
Si(4)	0.3519 (6)	−0.1018 (2)	0.5882 (3)
N(1)	0.202 (1)	−0.3584 (5)	0.6419 (5)
N(2)	0.205 (1)	−0.1499 (4)	0.6074 (5)
O(1)	−0.001 (1)	−0.2342 (6)	0.4543 (5)
O(2)	0.346 (1)	−0.3290 (6)	0.4790 (5)
C(1)	0.101 (2)	−0.5046 (7)	0.6195 (9)
C(2)	−0.063 (2)	−0.4137 (9)	0.7102 (9)
C(3)	−0.097 (2)	−0.3866 (8)	0.5586 (8)
C(4)	0.473 (2)	−0.4429 (8)	0.704 (1)
C(5)	0.318 (2)	−0.340 (1)	0.7900 (8)
C(6)	0.501 (2)	−0.2902 (8)	0.675 (1)
C(7)	−0.048 (2)	−0.0494 (8)	0.630 (1)
C(8)	0.143 (2)	−0.124 (1)	0.7509 (8)
C(9)	−0.083 (2)	−0.2034 (8)	0.6472 (9)
C(10)	0.463 (2)	−0.1498 (8)	0.5258 (9)
C(11)	0.292 (3)	−0.0178 (9)	0.548 (2)
C(12)	0.510 (2)	−0.085 (1)	0.665 (1)
C(13)	0.349 (4)	−0.401 (1)	0.484 (1)
C(14)	0.437 (4)	−0.425 (1)	0.436 (1)
C(15)	0.496 (3)	−0.370 (1)	0.400 (1)
C(16)	0.427 (3)	−0.309 (1)	0.425 (1)
C(17)	−0.048 (3)	−0.275 (1)	0.395 (1)
C(18)	−0.156 (3)	−0.233 (1)	0.351 (1)
C(19)	−0.168 (3)	−0.167 (1)	0.384 (1)
C(20)	−0.056 (4)	−0.165 (1)	0.440 (1)

Table III. Fractional Coordinates for $\{[((CH_3)_3Si)_2N]Sm(\mu\text{-}I)(DME)(THF)\}_2$

atom	*x*	*y*	*z*
Sm(1)	0.33242 (2)	0.26508 (5)	0.54027 (2)
I(1)	0.23132 (2)	0.44791 (9)	0.56432 (4)
Si(1)	0.4089 (1)	0.4252 (4)	0.6630 (1)
Si(2)	0.4332 (1)	0.1125 (4)	0.6144 (2)
N(1)	0.3997 (3)	0.2700 (8)	0.6160 (3)
O(1)	0.2961 (2)	0.0881 (9)	0.6289 (3)
O(2)	0.1103 (3)	0.2547 (12)	0.5645 (4)
O(3)	0.1416 (3)	−0.0236 (11)	0.5198 (4)
C(1)	0.1110 (6)	0.3317 (26)	0.6253 (7)
C(2)	0.0813 (8)	0.1339 (37)	0.5606 (15)
C(3)	0.1005 (7)	−0.0021 (26)	0.5614 (12)
C(4)	0.1645 (6)	−0.1645 (16)	0.5288 (8)
C(5)	0.2992 (6)	0.1294 (21)	0.6950 (6)
C(6)	0.2628 (9)	−0.0300 (27)	0.6228 (8)
C(7)	0.2470 (8)	−0.0772 (24)	0.6832 (8)
C(8)	0.2726 (9)	−0.0048 (29)	0.7286 (7)
C(9)	0.3571 (4)	0.5550 (14)	0.6569 (7)
C(10)	0.4623 (5)	0.5414 (15)	0.6367 (8)
C(11)	0.4157 (6)	0.3806 (19)	0.7536 (6)
C(12)	0.4071 (5)	−0.0301 (14)	0.5556 (7)
C(13)	0.4956 (5)	0.1449 (23)	0.5864 (10)
C(14)	0.4343 (9)	0.0014 (20)	0.6978 (8)

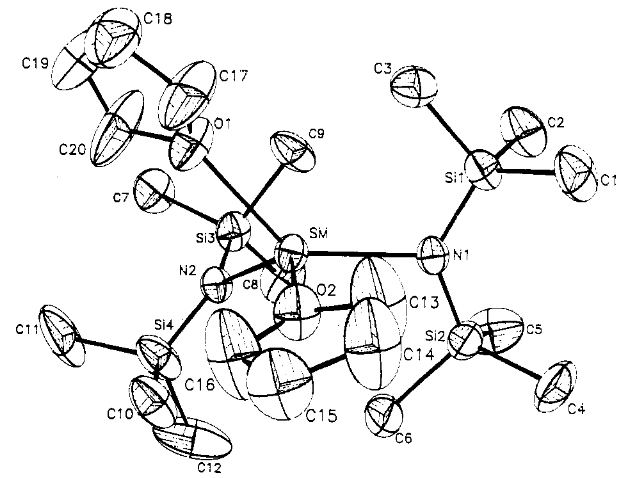

Figure 1. ORTEP diagram of $[(Me_3Si)_2N]_2Sm(THF)_2$ (**1**).

C_4D_8O showed resonances at δ 7.83 (s, 6 H) and 2.72 (s, 12 H). ^{13}C NMR (C_4D_8O): δ 75.9 (t, J_{CH} = 137 Hz, $CH_3O\mathit{C}H_2\mathit{C}H_2OCH_3$), 62.6 (q, J_{CH} = 139 Hz, $\mathit{C}H_3OCH_2CH_2O\mathit{C}H_3$), 32.3 (q, J_{CH} = 112 Hz, Me_3Si), 31.4 (q, J_{CH} = 117 Hz, Me_3Si). IR (KBr): 2960 s, 2900 s, 2840 m, 1455 m, 1240 s, 1190 w, 1060 vbr s, 860 s, 830 s, 750 m, 655 m cm^{-1}. Magnetic susceptibility: $\chi_M{}^{297\,K} = 4840 \times 10^{-6}$ cgsu; $\mu_{eff}{}^{297\,K} = 3.4\ \mu_B$.

X-ray Crystallography of $[(Me_3Si)_2N]_2Sm(THF)_2$. A single crystal measuring 0.22 × 0.15 × 0.15 mm was sealed under N_2 in a thin-walled glass capillary. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections ($\theta > 15°$) accurately centered on the diffractometer are given in Table I. Data were collected on an Enraf-Nonius CAD-4 Diffractometer by the θ–2θ scan technique. This method has been previously described.[32] A summary of data collection parameters is given in Table I. The intensities were corrected for Lorentz, polarization, and absorption effects. For the latter, an empirical method similar to that of Churchill was employed.[33]

Calculations were carried out with the SHELX system of computer programs.[34] Neutral-atom scattering factors for Sm, N, Si, and C were taken from Cromer and Waber[35] and the scattering for samarium was corrected for the real and imaginary components of anomalous dispersion by using the table of Cromer and Liberman.[36] Scattering factors for H were from ref 37.

The space group was uniquely determined as $P2_1/c$ from systematic absences. The position of the samarium atom was revealed by inspection of a Patterson map, and the remaining non-hydrogen atoms were located on a subsequent difference Fourier map. Hydrogen atoms were not located. All non-hydrogen atoms were refined with anisotropic thermal parameters.

The final agreement factors were $R = 0.040$ and $R_w = 0.046$. A final difference Fourier map showed no feature greater than 0.8 e/Å^3. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table II.

X-ray Crystallography of $\{[(Me_3Si)_2N]Sm(\mu\text{-}I)(DME)(THF)\}_2$. General procedures for data collection and reduction have been described previously.[38] A crystal measuring 0.2 mm × 0.4 mm × 0.7 mm was sealed under N_2 in a glass capillary and mounted on a Nicolet R3m/V diffractometer. Lattice parameters were determined at 22 °C from the angular settings of 25 computer-centered reflections with $25° \leq 2\theta \leq 35°$. Data were collected by the θ-2θ scan technique in bisecting geometry. The p factor[39] in the expression for the standard deviation of the observed intensities was given a value of 0.05. Relevant crystal and data collection parameters are given in Table I. During the data collection, the intensities of three standard reflections displayed only random fluctuations within ±3%. An empirical absorption correction was applied. Systematic absences (hkl, $h + k$ odd; $h0l$, l odd) established the space group as $C2/c$ (No. 15). Patterson and difference Fourier techniques were used to locate all non-hydrogen atoms, which were refined with anisotropic thermal parameters by use of full-matrix least-squares methods. No hydrogen atoms were located. Atomic scattering factors were taken from ref 35. A final difference map contained no recognizable features; its largest peak was of height 0.2 e Å^{-3} at a distance of 1.51 Å from the samarium atom. Fractional coordinates are given in Table III.

Results

$[(Me_3Si)_2N]_2Sm(THF)_2$ (1). The reaction of 2 equiv of $NaN(SiMe_3)_2$ with $SmI_2(THF)_2$ in THF provides a straightforward synthesis of $[(Me_3Si)_2N]_2Sm(THF)_2$ according to eq 1. Removal

$$SmI_2 + 2NaN(SiMe_3)_2 \rightarrow [(Me_3Si)_2N]_2Sm(THF)_2 + 2NaI \tag{1}$$

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Table IV. Selected Distances (Å) and Angles (deg) for $[((CH_3)_3Si)_2N]_2Sm(THF)_2$

	Distances		
Sm–N(1)	2.442 (9)	Sm–N(2)	2.424 (9)
Sm–O(1)	2.586 (9)	Sm–O(2)	2.607 (9)
	Angles		
N(1)–Sm–N(2)	118.0 (3)	O(1)–Sm–O(2)	85.4 (4)
N(2)–Sm–O(1)	95.5 (4)	N(1)–Si(1)–C(2)	115.0 (7)
N(2)–Sm–O(2)	133.2 (4)	N(1)–Si(1)–C(3)	109.7 (6)
N(1)–Si(1)–C(1)	114.6 (7)	N(1)–Si(2)–C(5)	113.2 (7)
N(1)–Si(2)–C(4)	113.5 (7)	N(1)–Si(2)–C(6)	108.3 (6)
N(2)–Si(3)–C(7)	115.7 (7)	N(2)–Si(3)–C(8)	113.2 (7)
N(2)–Si(4)–C(10)	109.3 (6)	N(2)–Si(3)–C(9)	108.3 (6)
Sm–N(1)–Si(1)	117.2 (5)	N(2)–Si(4)–C(11)	114.8 (8)
Sm–N(2)–Si(4)	116.6 (5)	N(2)–Si(4)–C(12)	113.2 (9)
Sm–O(1)–C(17)	129 (1)	Sm–N(1)–Si(2)	114.2 (5)
Sm–O(2)–C(16)	134 (1)	Sm–N(2)–Si(3)	114.4 (5)
N(1)–Sm–O(1)	132.7 (4)	Sm–O(1)–C(20)	122 (1)
N(1)–Sm–O(2)	93.3 (3)	Sm–O(2)–C(13)	117 (1)

of solvent and extraction of the resulting solid with hexane provides a convenient way to separate the byproduct NaI from the alkane-soluble **1**. The purple color of **1** is consistent with a Sm(II) species,[10] and the complexometric metal analysis agreed with the formula. The complex was definitively identified by X-ray crystallography (see below).

The ^1H NMR spectrum of **1** shows two $(Me_3Si)_2N$ resonances at δ 4.53 and -0.40 in a ratio of 2:1, respectively. This contrasts with the single resonance observed at δ 0.41 ppm for $[(Me_3Si)_2N]_2Yb(OEt_2)$[29] (**3**) and at δ 0.24 ppm for $[(Me_3Si)_2N]Yb[\mu\text{-}N(SiMe_3)_2]_2Na$[29] (**4**). As described below, the X-ray crystal structure supports the existence of two types of carbon atoms (in a 2:1 ratio) in the solid-state structure of **1**. It is surprising to see this in solution, however. In the ^{13}C NMR spectrum of **1**, only a single methyl carbon signal is resolved even at 125.8 MHz.

Complex **1** crystallizes from hexane as a bis(tetrahydrofuran) adduct, $[(Me_3Si)_2N]_2Sm(THF)_2$, as shown in Figure 1. Selected bond distances and angles are given in Table IV. The two nitrogen donor atoms and the two oxygen donor atoms describe a distorted tetrahedral geometry around the samarium atom. As expected, the O(1)–Sm–O(2) angle between the two smaller ligands, 85.4 (4)°, is less than the N(1)–Sm–N(2) angle between the two large $(Me_3Si)_2N$ groups, 118.0 (3)°. The Sm–N distances in **1**, 2.424 (9) and 2.442 (9) Å, can be conveniently compared with those in divalent europium bis(trimethylsilyl)amide complexes[27,29] since the adjacent elements Sm and Eu differ only by 0.01–0.02 Å in ionic radius.[40,41] The Eu–N distance of 2.446 (3) Å for the nonbridging $(Me_3Si)_2N$ ligand in formally three-coordinate $[(Me_3Si)_2N]Eu[\mu\text{-}N(SiMe_3)_2]_2Na$ (**5**)[29] is similar to the Sm–N length in **1**. The Eu–N distance in formally six-coordinate $[(Me_3Si)_2N]_2Eu(MeOCH_2CH_2OMe)_2$ (**6**),[27] 2.530 (4) Å, is longer. All of these distances are larger than the Eu–N distance of 2.259 Å in trivalent $[(Me_3Si)_2N]_3Eu$[25] as would be expected for the larger divalent ions. Direct comparisons of these distances are difficult to make given that the exact coordination number in these complexes is difficult to define (see below).

In addition to the four donor atom samarium interactions described above, four carbon atoms, C(3), C(6), C(9), and C(10), also appear to be oriented toward the metal center. These four atoms describe a tetrahedron that interpenetrates the O(1), O(2), N(1), and N(2) tetrahedron. The Sm–C distances for these four carbon atoms, 3.32 (1), 3.32 (1), 3.42 (1) and 3.46 (1) Å, are significantly shorter than any of the other eight Sm–C distances, which range from 4.727 (8) to 4.958 (9) Å, and they are less than the sum of the van der Waals radii of a methyl group and samarium.[42,43]

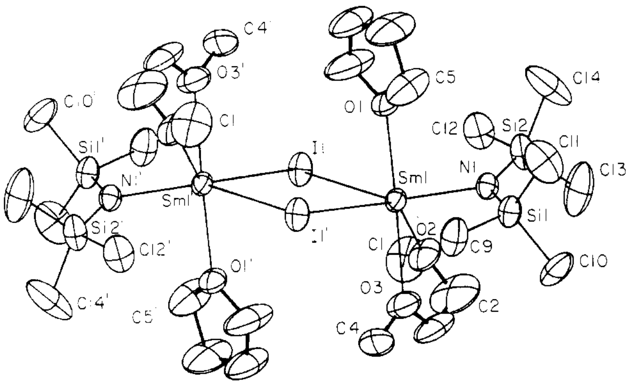

Figure 2. ORTEP diagram of $\{[(Me_3Si)_2N]Sm(\mu\text{-}I)(DME)(THF)\}_2$ (**2**).

Ln–C distances shorter than the sum of their van der Waals radii are a hallmark of divalent lanthanide bis(trimethylsilyl)amide complexes.[28-30] In **5**, four carbon atoms have Eu–C distances of this type with a Eu–C range of 2.97–3.44 Å. The ytterbium analogue of **5** also has close contacts of this type.[29] These distances were attributed to a Ln(δ+)–C(δ–) interaction or an interaction between the metal and the electron pair of a CH bond of the methyl group. The possibility that this was a crystal packing effect was also considered, since no evidence for such an interaction was observed in the ^1H NMR spectrum of the diamagnetic Yb analogue **4**. Crystal packing is unlikely to explain the short Sm–C distances in **1**, since in solution two ^1H NMR $(Me_3Si)_2N$ signals are observed.

Associated with the short Ln–C distances in these silylamido complexes are variations in N–Si–C angles. In **5**, the N–Si–C angles of the carbon atoms oriented toward Eu were found to be smaller (110 ± 1° average) than the N–Si–C angles involving the other carbon atoms (114 ± 2°).[29] A similar situation was found for the Yb analogue of **5**. Two sets of N–Si–C angles are also found in **1**. The N–Si–C angles for C(3), C(6), C(9), and C(10), which are oriented toward Sm, range from 108.3 (6) to 109.7 (6)° whereas the other N–Si–C angles range from 113.2 (9) to 115.7 (7)°.

$\{[(Me_3Si)_2N]Sm(\mu\text{-}I)(DME)(THF)\}_2$ (2). The reaction of complex **1** with an equivalent amount of $SmI_2(THF)_2$ in THF/DME gives a quantitative yield of the mixed iodide amide complex **2** according to eq 2. The reaction is reversible under

$$[(Me_3Si)_2N]_2Sm(THF)_2 + SmI_2(THF)_2 \xrightarrow[THF]{DME} \{[(Me_3Si)_2N]Sm(\mu\text{-}I)(DME)(THF)\}_2 \quad (2)$$

the appropriate conditions. For example, cooling a THF solution of **2** to −34 °C precipitates some $SmI_2(THF)_2$, leaving a solution containing $[(Me_3Si)_2N]_2Sm(THF)_2$.

The ^1H NMR spectrum of **2**, like that of **1**, contains two $(Me_3Si)_2N$ resonances in a 2:1 ratio. The relative positions of the large and small resonances, 2.66 and 7.80 ppm, respectively, are reversed compared to those in **1**. These resonances shift upfield and broaden at higher temperatures but do not coalesce at 50 °C. Two ^{13}C NMR resonances are observed for the Me_3Si groups in **2** and are found to be close in shift: 32.3 and 31.4 ppm. The similarity of these shifts may explain why only one signal was resolved for **1**.

The mixed amide iodide complex is isolated from THF/DME as a THF/DME solvate as shown in Figure 2. The molecule contains a crystallographic inversion center. Bond distances and angles are given in Table V.

The coordination geometry around each samarium atom is not regular. The six primary donor atoms around Sm, i.e., N(1), O(1), O(2), O(3), I(1) and I(1′) do not describe either a regular octahedral or regular trigonal-prismatic geometry. N(1), O(2), and

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(43) One can also compare these distances to the shortest Sm–C(THF) distances which range from 3.49 to 3.74 Å for Sm–C(13), Sm–C(16), Sm–C(17), Sm–C(20).

Table V. Selected Bond Distances (Å) and Angles (deg) for $\{[((CH_3)_3Si)_2N]Sm(\mu\text{-}I)(DME)(THF)\}_2$

	Distances		
Sm(1)–I(1)	3.3414 (9)	Sm(1)–O(1)	2.592 (6)
Sm(1)–I(1′)	3.3553 (9)	Sm(1)–O(3)	2.679 (8)
Sm(1)–N(1)	2.455 (7)	Sm(1)–O(2)	2.691 (8)
	Angles		
N(1)–Sm(1)–O(1)	83.9 (2)	N(1)–Si(2)–C(13)	114.8 (7)
N(1)–Sm(1)–O(3)	92.9 (3)	N(1)–Si(2)–C(14)	113.6 (7)
N(1)–Sm(1)–O(2)	90.9 (3)	Si(1)–N(1)–Sm(1)	119.2 (4)
O(1)–Sm(1)–O(3)	159.0 (3)	Si(2)–N(1)–Sm(1)	114.7 (4)
O(1)–Sm(1)–O(2)	138.9 (3)	C(5)–O(1)–Sm(1)	119.1 (8)
O(3)–Sm(1)–O(2)	61.7 (3)	C(6)–O(1)–Sm(1)	130.6 (8)
N(1)–Si(1)–C(9)	109.5 (5)	C(2)–O(2)–Sm(1)	106.2 (11)
N(1)–Si(1)–C(11)	113.5 (6)	C(1)–O(2)–Sm(1)	135.7 (9)
N(1)–Si(1)–C(10)	113.4 (5)	C(4)–O(3)–Sm(1)	132.1 (9)
N(1)–Si(2)–C(12)	109.5 (5)	C(3)–O(3)–Sm(1)	112.2 (10)
I(1)–Sm(1)–I(1′)	83.8 (1)	I(1)–Sm(1)–O(3)	84.3 (3)
I(1)–Sm(1)–N(1)	125.2 (2)	I(1′)–Sm(1)–O(1)	83.4 (2)
I(1′)–Sm(1)–N(1)	145.7 (2)	I(1′)–Sm(1)–O(2)	78.3 (3)
I(1)–Sm(1)–O(1)	80.6 (2)	I(1′)–Sm(1)–O(3)	109.6 (3)
I(1)–Sm(1)–O(2)	132.4 (2)		

O(3) form a plane that is parallel to the O(1), I(1), and I(1′) plane within 10°, but these triangles are not eclipsed as in a trigonal prism and the other angles in the molecule fail to give octahedral geometry around Sm. The primary coordination sphere can perhaps be best viewed as a distorted trigonal bipyramid in which the two DME oxygen atoms occupy a single axial site. The "equatorial" ligands N(1), I(1), and I(1′) are planar to within 0.23 Å, and the average of the L–Sm–L angles for these ligands, 118°, is close to the 120° for a regular trigonal bipyramid. However, the individual angles differ greatly: 83.8 (1), 125.2 (2)°, and 145.7 (2)°. The O(1)–Sm–(equatorial ligand) angles of 80.6 (2), 83.4 (2), and 83.9(2)° are a little less than the 90° expected; the angles beween the midpoint of the O(2)–O(3) vector and the equatorial ligands are a little larger than 90°: 93.1, 94.0, and 108.7°.

In addition to this primary coordination sphere, C(9) and C(12) appear to be oriented toward the Sm atom. The Sm(1)–C(9) and Sm(1)–C(12) distances of 3.54 (1) and 3.37 (1) Å are much shorter than the other Sm–C(Me_3Si) distances in **2** (4.84–5.03 Å) and are in the range observed in **1** for Sm–C lengths less than the sum of the van der Waals radii. As in **1**, the N–Si–C angles for C(9) and C(12), 109.5 (5)° each, are smaller than the 113.4 (5)–114.8 (7)° N–Si–C angles for the other carbon atoms. Including C(9) and C(12) in the coordination sphere would give a distorted pentagonal-bipyramidal geometry (with DME again occupying a single axial site). C(9) and C(12) are within 0.20 Å of the Sm(1), I(1), I(1′), and N(1) plane. In considering these Sm–C distances, it should be noted that the C(5) carbon atom of THF is also in this range: Sm–C(5) is 3.49 (1) Å.[43]

The Sm–I and Sm–I′ distances, 3.3414 (9) and 3.3553 (9) Å, are similar. These distances are longer than the 3.242 (1) Å average Sm–(μ-I) distance in divalent $[Sm(\mu\text{-}I)_2(NCCMe_3)_2]_n$, which contains six-coordinate Sm(II).[44] On the basis of trivalent organolanthanide structural chemistry,[45] this might be expected if complex **2** had a samarium center with a coordination number larger than six. However, the eight-coordinate complex *trans*-$SmI_2[O(CH_2CH_2OMe)_2]_2$[46] has a similar Sm–I length, 3.260 (1) Å, whereas its cis isomer, i.e., *cis*-$SmI_2[O(CH_2CH_2OMe)_2]_2$,[44] has a 3.332 (1) Å Sm–I length, similar to that in **2**! The Sm–N distance of 2.455 (7) Å is comparable to that in **1** as is the Sm–O(THF) distance of 2.592 (6) Å. The Sm–O(DME) distances of 2.679 (8) and 2.691 (8) Å are longer and are more in the range of the Eu–O(DME) distances of 2.634 (4) and 2.756 (4) Å in **6** and the average Sm–O(diglyme) distances of 2.68 and 2.70 Å in *cis*- and *trans*-$SmI_2[O(CH_2CH_2OMe)_2]_2$, respectively.

Discussion

The synthesis of complexes **1** and **2** provides bis(trimethylsilyl)amido complexes of Sm(II) that parallel the pentamethylcyclopentadienyl derivatives $(C_5Me_5)_2Sm(THF)_2$ and $[(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$. Complex **1** is considerably more soluble than $(C_5Me_5)_2Sm(THF)_2$ in alkanes. In contrast, **2** and $[(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$ have similar solubilities; i.e., they are insoluble in alkanes and arenes, but both are soluble in ethers. The latter two complexes also have the parallel property that they tend to ligand redistribute to $SmI_2(THF)_2$ and the corresponding SmL_2 complex.

One main difference between **1** and **2** and their C_5Me_5 analogues is that formation of a tris ligand species, i.e., $[(Me_3Si)_2N]_3Sm$(**7**),[22] is possible. In contrast, $(C_5Me_5)_3$ is thought to be too sterically crowded to exist.[47] Preliminary reaction studies suggest that formation of **7** will be an important factor in the chemistry of **1** and **2**. Hence, both **1** and **2** react with CO as do $(C_5Me_5)_2Sm(THF)_2$[6] and $[(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$,[48] but **7** is the product that is readily isolated instead of a reduced CO complex such as the ketenecarboxylate complex, $[(C_5Me_5)_4Sm_2(O_2CCCO)(THF)]_2$, found in the $(C_5Me_5)_2Sm(THF)_2$ reaction.[6]

Conclusion

The synthesis of **1** and **2** provides new soluble complexes of Sm(II). The X-ray study fully establishes the structures of **1** and **2** and demonstrates that, like divalent Eu and Yb bis(trimethylsilyl)amide complexes,[28-30] long range metal–methyl contacts are present in divalent Sm complexes. With these complexes in hand, their importance to the development of Sm(II) chemistry can be determined.

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Registry No. **1**, 112068-81-2; **2**, 112044-19-6; $SmI_2(THF)_2$, 94138-28-0.

Supplementary Material Available: Tables of bond distances and angles and anisotropic thermal parameters (5 pages); tables of observed and calculated structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

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