5302 *Inorg. Chem.* **1994,** *33,* 5302−5308

Lanthanide and Yttrium Complexes of Deprotonated 4,13-Diaza-18-crown-6 (DAC): Synthesis and Structural Characterization of Y[DAC][N(SiMe$_3$)$_2$] and the Novel Trinuclear Ytterbium(II) Complex {Yb[N(SiMe$_3$)$_2$][μ-DAC]}$_2$Yb

Lawrence Lee, David J. Berg,* and Gordon W. Bushnell

Department of Chemistry, University of Victoria, Victoria, British Columbia, Canada V8W 2Y2

Received March 31, 1994⊗

The ability of a deprotonated diazacrown ether, 4,13-diaza-18-crown-6 (DAC), to allow isolation of soluble lanthanide and yttrium complexes was investigated. Reaction of H$_2$DAC with Ln[N(SiMe$_3$)$_2$]$_3$ provided soluble complexes, Ln[DAC][N(SiMe$_3$)$_2$] (Ln = Y (**1a**), Ce (**1b**)). A single crystal X-ray diffraction study of **1a** revealed a seven-coordinate monomer in which the six donors of the DAC ligand adopt a basketlike conformation around the yttrium atom. [Crystal data: monoclinic space group $P2_1/n$, $a = 9.471(1)$ Å, $b = 28.786(3)$ Å, $c = 10.567(3)$ Å, $\beta = 114.45(1)°$, $V = 2622.5$ Å^3, $Z = 4$, $R = 0.010$, $R_w = 0.124$.] Reaction of H$_2$DAC with divalent Yb[N(SiMe$_3$)$_2$]$_2$[OEt$_2$]$_2$ in 2:3 stoichiometry provided the novel trinuclear cluster {[(Me$_3$Si)$_2$N]Yb(μ-DAC)}$_2$Yb (**2**). The crystal structure of **2** shows a linear (Me$_3$Si)N−Yb--Yb--Yb−N(SiMe$_3$)$_2$ arrangement with two DAC amido-N groups bridging between pairs of adjacent Yb centers. The DAC ligand is folded back such that the four ether donors interact with an outer Yb atom (seven-coordinate). The central four-coordinate Yb exhibits distorted tetrahedral coordination. [Crystal data: monoclinic space group $P2_1/n$, $a = 19.982(3)$ Å, $b = 17.870(2)$ Å, $c = 16.933(3)$ Å, $\beta = 113.56(1)°$, $V = 5542$ Å^3, $Z = 4$, $R = 0.087$, $R_w = 0.104$.] Reaction of H$_2$DAC with Yb[N(SiMe$_3$)$_2$]$_2$[OEt$_2$]$_2$ in 1:2 stoichiometry produced the dinuclear complex {Yb[N(SiMe$_3$)$_2$]}$_2${μ-DAC} (**3**). Divalent Sm[N(SiMe$_3$)$_2$]$_2$[THF]$_2$ reacts with H$_2$DAC to yield *trivalent* Sm[DAC][N(SiMe$_3$)$_2$] (**4**) in good yield. Experimental evidence suggests that this product is formed by the unusual Sm(II) reduction of a DAC N−H bond.

Introduction

The coordination chemistry of the lanthanides with crown ethers and their N-substituted analogs (azacrowns) has been extensively studied.[1] Perhaps it is somewhat surprising therefore that no attempts appear to have been made to utilize deprotonated azacrowns as ancillary ligands in nonaqueous or organolanthanide chemistry. Indeed, the only examples[2] of deprotonated azacrown ligands in organometallic chemistry are the aluminum alkyl complexes prepared by Robinson[3] and Gokel and Richey.[4]

Deprotonated azacrowns are intriguing as ancillary ligands because they provide a flexible donor array which has the potential to fill one hemisphere of the lanthanide coordination sphere. This coordination mode should prevent formation of polymeric products and provide an alternative to bis(pentamethylcyclopentadienyl) ligation. With these ideas in mind, we decided to investigate the reaction chemistry of 4,13-diaza-18-crown-6 (H$_2$DAC)[5] with both trivalent and divalent lanthanide silylamides. The results of this study are presented herein.

Experimental Section

General Procedures. All manipulations were carried out under an argon atmosphere, with the rigorous exclusion of oxygen and water, using standard glovebox (Braun MB150-GII) or Schlenk techniques, except as noted in the text. Tetrahydrofuran (THF), diethyl ether, hexane, and toluene were dried by distillation from sodium benzophenone ketyl under argon immediately prior to use. 4,13-Diaza-18-crown-6 (H$_2$DAC) was prepared according to a literature procedure[6] from 1,2-bis(2-iodoethoxy)ethane[7] and 1,8-diamino-3,6-dioxaoctane[6] in 30% yield after recrystallization from hexane. Anhydrous metal trichlorides (Ce and Y) were prepared from the hydrated salts by prolonged reflux in neat SOCl$_2$ followed by vacuum distillation and drying at 150 °C (10^{-2} Torr) for 16−20 h. Anhydrous SmI$_2$ was prepared from Sm powder and CH$_2$I$_2$ in THF solution.[8] THF of solvation was removed by heating at 150 °C for 16 h. Ytterbium diiodide was prepared from Yb metal chips and NH$_4$I in liquid ammonia.[9] Hexamethyldisilazane was purchased from Aldrich and

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* Author to whom correspondence should be addressed.

⊗ Abstract published in *Advance ACS Abstracts,* September 15, 1994.

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dried by distillation from sodium metal. Lanthanide silylamides, $Ln[N(SiMe_3)_2]_3$ (Ln = Ce, Y),[10] $Sm[N(SiMe_3)_2]_2[THF]_2$,[11] and $Yb[N(SiMe_3)_2]_2[OEt_2]_2$[9] were prepared as reported in the literature.

^1H and ^{13}C spectra were recorded on a Bruker WM-250 MHz or a Bruker AMX-360 MHz spectrometer. Spectra were recorded in C_6D_6 or C_7D_8 solvent, previously distilled from sodium under argon, using 5 mm tubes fitted with a Teflon valve (Brunfeldt). Mass spectra were recorded on a Kratos Concept H spectrometer using an electron impact source (70 eV). Melting points were recorded using a Reichert hot stage and are not corrected. Elemental analyses were performed by Canadian Microanalytical, Delta, BC, Canada. Analytical results were generally low in C despite repeated recrystallizations and clean NMR spectra. We have observed this problem many times in lanthanide complexes containing silicon.

$Y[DAC][N(SiMe_3)_2]$ (1a). In the glovebox, H_2DAC (1.00 g, 3.81 mmol) and $Y[N(SiMe_3)_2]_3$ (2.16 g, 3.81 mmol) were dissolved in 50 mL of toluene. The solution was stirred vigorously overnight. Removal of the solvent under reduced pressure produced a white powder. Recrystallization from a toluene−hexane mixture produced colorless crystals of **1a**. Yield: 1.54 g (79.4%). Mp: 148−149 °C dec. MS (EI): *m/z* 508 (M^+), 494 ($M^+ - CH_3$), 466 ($M^+ - C_2H_3O$), 348 ($M^+ - N(SiMe_3)_2$), 305 ($M^+ - N(SiMe_3)_2 - C_2H_3O$). Anal. Calcd for $C_{18}H_{42}N_3O_4Si_2Y$: C, 42.42; H, 8.31; N, 8.25. Found: C, 41.56; H, 8.37; N, 8.01.

$Ce[DAC][N(SiMe_3)_2]$ (1b). Reaction of H_2DAC (0.250 g, 0.953 mmol) with $Ce[N(SiMe_3)_2]_3$ (0.591 g, 0.953 mmol) according to the procedure outlined for **1a** afforded **1b** as a microcrystalline powder. Yield: 0.36 g (67%). Mp: 140 °C dec. MS (EI): *m/z* 560 (M^+), 545 ($M^+ - CH_3$), 517 ($M^+ - C_2H_3O$), 399 ($M^+ - N(SiMe_3)_2$), 356 ($M^+ - N(SiMe_3)_2 - C_2H_3O$). Anal. Calcd for $C_{18}H_{42}N_3O_4Si_2Ce$: C, 38.55; H, 7.55; N, 7.49. Found: C, 37.71; H, 6.78; N, 7.26.

Attempted Preparation of $Y[DAC][OC_6H_3tBu_2]$ (II). In the glovebox, complex **1a** (0.10 g, 0.20 mmol) was dissolved in 250 mL of toluene in a 500 mL Erlenmeyer flask fitted with a dropping funnel. A solution of freshly sublimed 2,6-di-*tert*-butylphenol (0.041 g, 0.20 mmol) in 100 mL of toluene was placed in the dropping funnel and slowly added to the vigorously stirred solution of **1a** over 6 h. At the end of this period, the solvent was removed from the clear, colorless reaction mixture to produce an oily white solid. Examination of this material by ^1H NMR (C_6D_6) showed free H_2DAC and $Y[OC_6H_3tBu_2]_3$ [δ 7.25 (d, 6H, *m*-aryl C*H*, $^3J_{HH}$ = 7.8 Hz), 6.82 (t, 3H, *p*-aryl C*H*, $^3J_{HH}$ = 7.8 Hz), 1.51 (s, 54H, C*Me*$_3$)] as major components of the complex mixture. Reaction of **1a** with *tert*-butyl alcohol was carried out in an analogous fashion. In this case, white precipitate formed immediately, while the toluene supernatant contained free H_2DAC by ^1H NMR.

$Yb\{(\mu\text{-}DAC)Yb[N(SiMe_3)_2]\}_2$ (2). In the glovebox, H_2DAC (0.250 g, 0.953 mmol) and $Yb[N(SiMe_3)_2]_2[OEt_2]_2$ (0.812 g, 1.43 mmol) were dissolved in 50 mL of toluene. The deep red solution was stirred vigorously overnight. Removal of the solvent under reduced pressure produced a red-brown powder. Recrystallization from a toluene−hexane mixture produced ruby red crystals of **2** (0.52 g, 80%). Mp: 170 °C dec. Anal. Calcd for $C_{36}H_{84}N_6O_8Si_4Yb_3$: C, 31.78; H, 6.22; N, 6.18. Found: C, 31.50; H, 5.99; N, 6.13.

$\{Yb[N(SiMe_3)_2]\}_2\{\mu\text{-}DAC\}$ (3). This complex was prepared as described for **2** above using a 1:2 ratio of H_2DAC (0.250 g, 0.950 mmol) and $Yb[N(SiMe_3)_2]_2[OEt_2]_2$ (1.08 g, 1.91 mmol). Black crystals of **3** were obtained by recrystallization from a toluene−hexane mixture at −30 °C. Yield: 0.15 g (17%). Mp: 170 °C. Anal. Calcd for $C_{24}H_{60}N_4O_4Si_4Yb_2$: C, 31.08; H, 6.53; N, 6.04. Found: C, 30.19; H, 6.26; N, 5.89.

Interconversion of 2 and 3. A solution of **2** (0.030 g, 0.022 mmol) in 10 mL of toluene was added to a stirred solution of $Yb[N(SiMe_3)_2]_2[OEt_2]_2$ (0.013 g, 0.022 mmol) in 10 mL of toluene dropwise. The red colored solution quickly faded to a clear black. The solvent was removed under reduced pressure and the residue completely redissolved in C_6D_6. The ^1H NMR of this solution was identical with that of pure **3**.

Table 1. Summary of Crystallographic Data for $Y[DAC][N(SiMe_3)_2]$ (**1a**) and $\{[(Me_3Si)_2N]Yb(\mu\text{-}DAC)\}_2Yb$ (**2**)

	$Y[DAC]$-$[N(SiMe_3)_2]$	$\{[(Me_3Si)_2N]$-$Yb(\mu\text{-}DAC)\}_2Yb$
empirical formula	$C_{18}H_{42}N_3O_4Si_2Y$	$C_{36}H_{84}N_6O_8Si_4Yb_3$
fw	509.6	1360.6
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a (Å)	9.471(1)	19.982(3)
b (Å)	28.786(3)	17.870(2)
c (Å)	10.567(3)	16.933(3)
α (deg)	90	90
β (deg)	114.45(1)	113.56(1)
γ (deg)	90	90
V (Å^3)	2622.5	5542
Z	4	4
ϱ(calcd) (g cm^{-3})	1.291	1.630
μ (cm^{-1})	42.81	103.45
radiation, λ (Å)	Cu Kα, 1.542	Cu Kα, 1.542
T	ambient	ambient
$2\theta_{max}$ (deg)	60	50
no. of obsd reflcns	3682	4980
no. of unique reflcns	2311	2473
R^a	0.010	0.087
$R_w{}^b$	0.124	0.104

^{a} $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$.

A solution of **3** (0.030 g, 0.032 mmol) was dissolved in 10 mL of toluene and added to a stirred solution of H_2DAC (0.003 g, 0.01 mmol) in 2 mL of toluene. The solution rapidly changed color from black to ruby red. After the solution was stirred for 2 h, the solvent was removed and the residue completely redissolved in C_6D_6. The ^1H NMR of this solution was identical with that reported for pure **2** with the exception that resonances due to a small amount of free H_2DAC were present.

$Sm[DAC][N(SiMe_3)_2]$ (4). Reaction of H_2DAC (0.125 g, 0.447 mmol) and *divalent* $Sm[N(SiMe_3)_2]_2[THF]_2$ (0.293 g, 0.447 mmol) in 50 mL of toluene resulted in an initial purple solution which faded to green and finally yellow after stirring for 2.5 h. This yellow solution was evaporated to dryness and recrystallized from a toluene−hexane mixture at −30 °C. Bright yellow crystals of **4** were isolated by filtration and dried under vacuum. Yield: 0.214 g (78.7%). Mp: 175 °C dec. MS (EI): *m/z* 572 (M^+), 557 ($M^+ - CH_3$), 529 ($M^+ - C_2H_3O$), 411 ($M^+ - N(SiMe_3)_2$), 368 ($M^+ - N(SiMe_3)_2 - C_2H_3O$). Anal. Calcd for $C_{18}H_{42}N_3O_4Si_2Sm$: C, 37.86; H, 7.41; N, 7.35. Found: C, 37.42; H, 7.36; N, 7.15.

X-ray Crystallographic Studies. Crystallographic data for **1a** and **2** are summarized in Table 1. Crystals of **1a** (0.9 × 0.5 × 0.4 mm) and **2** (0.8 × 0.2 × 0.15 mm) were loaded into glass capillaries in the glovebox and subsequently examined by photographic methods using Weissenberg and precession cameras. The space groups of **1a** and **2** were uniquely determined by the systematic absences. The crystals were transferred to a Nonius CAD4F diffractometer equipped with Ni-filtered Cu Kα radiation. The unit cell of **1a** was refined using 25 reflections in the 2θ range 52−71,° while that of **2** was refined using 25 reflections in the 2θ range 38−92°. Experimental densities were not obtained because of the air sensitivity of both compounds. Three standard reflections, measured periodically during data collection (for **1a**, 4,14,2, 6,6,0, 0,12,4; for **2**, −17,2,12, −10,4,14, −6,15,6), showed a decline in combined intensity to 50 and 79% of their original value, for **1a** and **2**, respectively. Intensity measurements were collected over one-quarter of the sphere for both compounds. After the usual data reduction procedures, including an absorption correction according to a measured Ψ scan, the structures were solved using SHELX76, SHELXS, and the Patterson function (**2**) or direct methods (**1a**).[12] The refinements minimized $\sum w((|F_o| - |F_c|)^2)$ and proceeded normally using SHELX76. The structure of **1a** was refined anisotropically for all heavy atoms, while that of **2** was refined isotropically for C, N, and O and anisotropically for Yb and Si. Criteria for inclusion of reflections were $I > 4\sigma(I)$ and $I > 3\sigma(I)$ for **1a** and **2**, respectively. The weighting scheme was determined by counting statistics using $w = 1/(\sigma^2(F) +$

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Table 2. NMR Data[a] for Lanthanide DAC Complexes

	$^1H^b$		^{13}C			
	DAC	$N(SiMe_3)_2$	C_a	C_b	C_c	$N(SiMe_3)_2$
1a	3.65 (m, 4H, C_cH) 3.55 (m, 8H, C_bH and C_cH) 3.27 (m, 4H, C_aH) 3.19 (m, 4H, C_aH) 3.02 (m, 4H, C_bH)	0.38 (s, 18H)	55.6	66.8	73.3	5.3
1b[c]	26.0 (s, 4H, $\nu_{1/2}$ = 32 Hz) 19.7 (s, 4H, 28 Hz) 6.3 (s, 4H, 35 Hz) −3.0 (s, 4H, 26 Hz) −9.2 (s, 4H, 24 Hz) −17.7 (s, 4H, 22 Hz)	1.4 (s, 18H, 16 Hz)				
2	3.76 (m, 4H, C_bH) 3.60 (m, 4H, C_cH) 3.17 (m, 8H, C_bH and C_cH) 3.02 (m, 4H, C_bH) 2.79 (m, 4H, C_aH)	0.39 (s, 18H)	54.6	67.6	70.9	6.4
3	3.36 (t, 8H, C_bH, $^3J_{HH}$ = 4.7 Hz) 3.01 (t, 8H, C_aH, $^3J_{HH}$ = 4.7 Hz) 2.87 (s, 8H, C_cH)	0.37 (s, 18H)	55.1	68.2	73.2	6.1
4[c]	5.7 (m, 4H, $\nu_{1/2}$ = 23 Hz) 4.5 (br d, 4H, 22 Hz) 3.4 (m, 4H, 16 Hz) 1.9 (m, 4H, 21 Hz) −1.5 (m, 4H, 18 Hz) −4.3 (m, 4H, 21 Hz)	1.1 (s, 18H, 6 Hz)				

[a] Spectra recorded at 250 MHz in d_6-benzene or d_8-toluene at 296 K. Assignment letters refer to the carbon atoms of the unique $NC_aH_2C_bH_2OC_cH_2$ portion of the DAC ligand (the remaining carbons are related to these by the molecular symmetry). [b] Assignments for the diamagnetic complexes **1a**, **2**, and **3** were made on the basis of $^1H-^{13}C$ COSY experiments. Exo and endo proton assignments have not been made. No assignments are possible for the paramagnetic complexes **1b** and **4**. [c] ^{13}C NMR spectra were not observable due to paramagnetism.

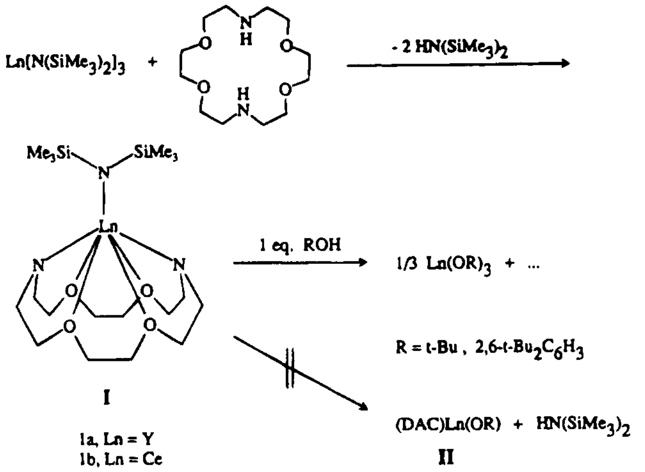
$0.001F^2$). Convergence was satisfactory for both compounds: max shift/esd = 0.005 for **1a** and 0.0874 for **2**. A total of 253 parameters (28 atoms × 9 parameters per atom + scale) were refined in two blocks for **1a**. For **2**, 264 parameters (7 × 9 parameters per anisotropic atom + 50 × 4 parameters per isotropic atom + scale) were refined in two blocks. The quality of the data for **1a** was poor due to the rapid decomposition of the crystal in the X-ray beam (the crystal turned dark amber during data collection), and a rapid scan rate was required. No intermolecular contacts shorter than 3.5 Å were observed in either structure. The structural perspective plots were drawn using ORTEP.[13]

Compound **1b** was also investigated by X-ray diffraction, but the structure was badly disordered in the macrocyclic ring. Crystal data: monoclinic space group $P2_1/n$, a = 9.557(1) Å, b = 56.897(8) Å, c = 10.777(2) Å, β = 114.37(1)°, V = 5338.0 Å^3, Z = 4 (8 molecules per cell since the asymmetric unit contains 2 independent molecules). Samarium complex **4** had a Weissenberg pattern similar to that for **1b** in both intensity and position of the diffraction spots.

Results and Discussion

Trivalent Lanthanide Complexes. The reaction of 4,13-diaza-18-crown-6 (H_2DAC) with 1 equiv of $Ln[N(SiMe_3)_2]_3$ produced crystalline $Ln[DAC][N(SiMe_3)_2]$ (**1a**, Ln = Y; **1b**, Ln = Ce) by the protonolysis reaction shown in Scheme 1. Complexes **1a,b** are moderately soluble in hexane and very soluble in diethyl ether, THF, and toluene. NMR spectroscopic data for these complexes and the Sm analog **4**, prepared by an alternate route (*vide infra*), are collected in Table 2. The ^1H NMR spectrum of all three complexes shows six DAC multiplets in addition to the silylamide singlet. This fact, coupled with the observation of only three DAC resonances in the ^{13}C NMR spectrum of **1a**, is consistent with a monomeric structure of C_{2v} symmetry as shown in **I**. Complexes **1a**, **1b**, and **4** give molecular ions in their mass spectrum consistent with a monomeric structure. In order to confirm structure **I**, **1a** was investigated by X-ray diffraction.

Scheme 1



An ORTEP plot of **1a** is given in Figure 1. Fractional atomic coordinates are given in Table 3, and selected bond distances and angles are collected in Table 4. The structure of **1a** is monomeric as suggested by NMR and mass spectroscopy; the nearest intermolecular contacts are >3.5 Å. The bonding geometry around Y may be regarded as consisting of primary trigonal planar coordination of the three amido N atoms (sum of the N−Y−N angles around Y is 359.7°) with secondary coordination of the four ether O atoms above and below the YN_3 plane. The four ether O atoms and the silylamide N atom form a distorted square pyramid about the Y atom. The DAC N−Y distances are equal within experimental error at 2.29(2) Å and marginally shorter than the Y−N(3) (silylamide) distance (2.338(11) Å). The observed Y−N distances fall within the 2.24−2.40 Å range predicted from several other lanthanide silylamides.[14,15] The Y−O distances span a considerable range from 2.457(12) to 2.590(12) Å. The wide range is probably a

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(13) Johnson, C. K. *ORTEPII*; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

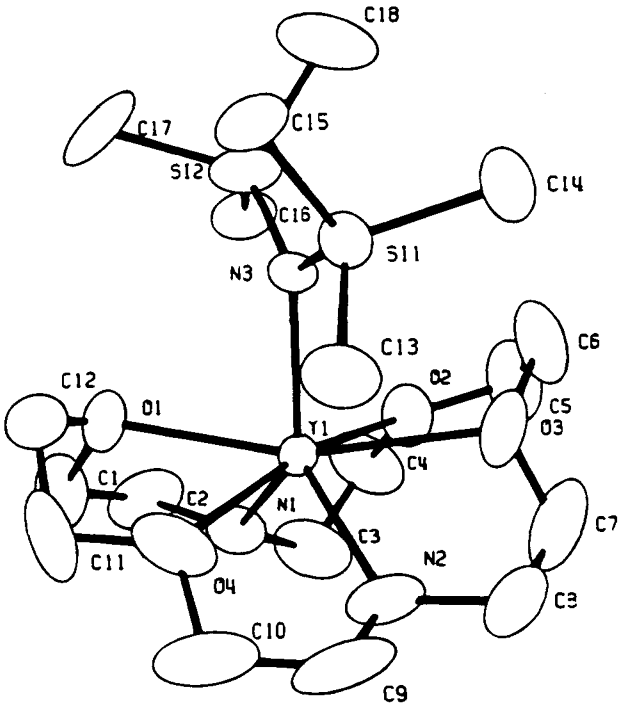

Figure 1. ORTEP plot of Y[DAC][N(SiMe$_3$)$_2$] (**1a**).

reflection of packing effects in the solid state. As expected, the silylamide N is planar (sum of angles at N(3) = 360°).

The cerium complex **1b** was also investigated by X-ray crystallography since preliminary photographic work showed that **1b** and **1a** were not isostructural. Unfortunately, the diffraction study revealed two independent monomers in the unit cell, one of which was severely disordered. The well-behaved molecule showed the same gross structural features as **1a**. Preliminary photographic work indicated that **4** was isostructural with **1b** but, since the latter was similar to **1a** in molecular detail, a full structure determination was not carried out. Cell constants for **1b** are given in the Experimental Section (*vide supra*).

Attempts to convert **1a** into alkoxide **II** (Scheme 1) were carried out in an effort to prepare suitable precursors to lanthanide alkyl complexes. Lanthanide alkoxides have been widely used as precursors to alkyls because clean elimination of insoluble LiOR is often observed during metathesis with LiR.[16] However, direct alcoholysis with 1 equiv of 2,6-di-*tert*-butylphenol or the less acidic *tert*-butyl alcohol could not be controlled even under conditions of high dilution and slow addition of the alcohol. This may indicate that differentiation between the DAC and N(SiMe$_3$)$_2$ groups is not possible or that product **II** undergoes facile ligand redistribution to give Ln(OR)$_3$- and DAC-containing products.

Table 3. Fractional Atomic Coordinates[a] and Equivalent Isotropic Temperature Factors[b] for Y[DAC][N(SiMe$_3$)$_2$] (**1a**) (Estimated Standard Deviations in Parentheses)

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
Y(1)	22619(12)	34734(4)	−759(11)	504(5)
Si(1)	11.3(5)	397.9(2)	−331.5(4)	7.8(2)
Si(2)	346.9(6)	416.9(2)	−220.1(6)	10.4(3)
O(1)	413(2)	304.6(4)	−72(2)	11.1(8)
O(2)	359(2)	411.0(4)	177(2)	11.7(8)
O(3)	71(2)	411.8(6)	33(2)	12.3(8)
O(4)	131(2)	272.7(4)	−124.8(14)	13.0(7)
N(1)	438.7(14)	322.4(5)	180.8(13)	8.1(6)
N(2)	21(2)	320.0(7)	31(2)	11.8(9)
N(3)	194.9(13)	391.0(4)	−204.1(11)	6.4(5)
C(1)	527(3)	278.6(8)	43(3)	14(2)
C(2)	576(2)	309.4(11)	173(2)	13.8(13)
C(3)	474(3)	347.7(8)	309(2)	14.0(13)
C(4)	500(2)	396.0(7)	303(2)	13.1(11)
C(5)	287(3)	453.2(8)	190(3)	16(2)
C(6)	158(3)	458.7(8)	66(3)	13.9(14)
C(7)	9(4)	399.1(14)	122(3)	17(2)
C(8)	−80(3)	354.7(12)	68(3)	15(2)
C(9)	−65(3)	281.3(11)	−26(2)	16(2)
C(10)	36(4)	245.7(10)	−75(3)	18(2)
C(11)	227(4)	242.4(8)	−167(3)	17(2)
C(12)	335(4)	276.3(8)	−194(2)	15(2)
C(13)	−120(2)	348.6(6)	328(2)	11.3(10)
C(14)	−85(2)	455.9(7)	−316(2)	12.1(11)
C(15)	1(3)	393.9(7)	−520(2)	11.4(11)
C(16)	520(2)	421.9(6)	−47(2)	10.3(9)
C(17)	419(3)	383.3(10)	−335(2)	16(2)
C(18)	312(3)	477.1(9)	−288(3)	19(2)

[a] $\times 10^n$, where $n = 5$ for Y and $n = 3$ for Si, O, N, and C. [b] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*(a_ia_j)$ Å$^2 \times 10^n$, where $n = 4$ for Y and $n = 2$ for Si, O, N, and C.

Table 4. Selected Distances (Å) and Angles (deg) for Y[DAC][N(SiMe$_3$)$_2$] (**1a**)[a]

Distances			
Y(1)−O(1)	2.467(11)	Y(1)−N(2)	2.29(2)
Y(1)−O(2)	2.590(12)	Y(1)−N(3)	2.338(11)
Y(1)−O(3)	2.514(12)	N(3)−Si(1)	1.714(11)
Y(1)−O(4)	2.457(12)	N(3)−Si(2)	1.692(12)
Y(1)−N(1)	2.283(12)		
Angles			
O(1)−Y(1)−O(2)	112.2(5)	O(3)−Y(1)−N(1)	116.9(5)
O(1)−Y(1)−O(3)	162.1(5)	O(3)−Y(1)−N(2)	67.8(6)
O(1)−Y(1)−O(4)	65.2(5)	O(3)−Y(1)−N(3)	83.5(5)
O(1)−Y(1)−N(1)	67.0(5)	O(4)−Y(1)−N(1)	99.9(4)
O(1)−Y(1)−N(2)	129.5(6)	O(4)−Y(1)−N(2)	68.0(7)
O(1)−Y(1)−N(3)	82.3(4)	O(4)−Y(1)−N(3)	97.9(4)
O(2)−Y(1)−O(3)	59.2(2)	N(1)−Y(1)−N(2)	104.2(5)
O(2)−Y(1)−O(4)	163.8(4)	N(1)−Y(1)−N(3)	133.3(4)
O(2)−Y(1)−N(1)	65.7(4)	N(2)−Y(1)−N(3)	122.5(5)
O(2)−Y(1)−N(2)	107.2(6)	Y(1)−N(3)−Si(1)	118.4(6)
O(2)−Y(1)−N(3)	97.6(4)	Y(1)−N(3)−Si(2)	121.7(6)
O(3)−Y(1)−O(4)	127.7(5)	Si(1)−N(3)−Si(2)	119.9(7)

[a] Estimated standard deviation in parentheses.

Divalent Lanthanide Complexes. In view of difficulties in preparing the trivalent alkoxide precursor **II**, we turned our attention to preparation of the divalent complexes Ln[DAC] (Ln = Yb, Sm) as potential precursors to trivalent alkyls by redox reactions with reducible group 12 metal alkyls. Reaction of Yb[N(SiMe$_3$)$_2$]$_2${OEt$_2$}$_2$ with 1 equiv of H$_2$DAC resulted in isolation of a ruby red compound analyzing as Yb$_3$(DAC)$_2$[N(SiMe$_3$)$_2$]$_2$ (**2**) in moderate yield. Repeating the reaction using a 3:2 ratio of Yb−H$_2$DAC gave an 80% isolated yield of crystalline **2** (Scheme 2). The ^{1}H NMR spectrum (Table 2) clearly showed **2** to be diamagnetic with a 1:1 ratio of DAC to N(SiMe$_3$)$_2$. The presence of only three DAC resonances in the ^{13}C NMR indicated a single type of DAC ligand was present.

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(14) The Ln−N(SiMe$_3$)$_2$ bond distances for a variety of structurally characterized lanthanide silylamides[15] were corrected for differences in metal ionic radius, oxidation state, and coordination number according to: Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

(15) (a) Bradley, D. C.; Ghotra, J. S.; Hart, F. A.; Hursthouse, M. B.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1977**, 1166. (b) Aspinall, H. C.; Bradley, D. C.; Hursthouse, M. B.; Sales, K. D.; Walker, N. P. C. *J. Chem. Soc., Dalton Trans.* **1985**, 1585. (c) Aspinall, H. C.; Bradley, D. C.; Hursthouse, M. B.; Sales, K. D.; Walker, N. P. C.; Hussain, B. *J. Chem. Soc., Dalton Trans.* **1989**, 623. (d) Heeres, H. J.; Meetsma, A.; Teuben, J. H.; Rogers, R. D. *Organometallics* **1989**, *8*, 2637. (e) Aspinall, H. C.; Moore, S. R.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1992**, 153. (f) Allen, M.; Aspinall, H. C.; Moore, S. R.; Hursthouse, M. B.; Karvalov, A. I. *Polyhedron* **1992**, *11*, 409.

(16) Mehrotra, R. C.; Singh, A.; Tripathi, U. M. *Chem. Rev.* **1991**, *91*, 1287 and references herein.

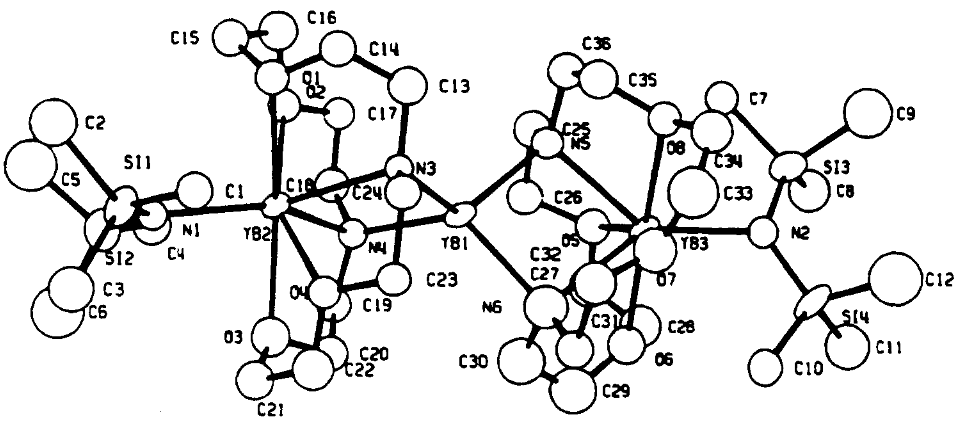
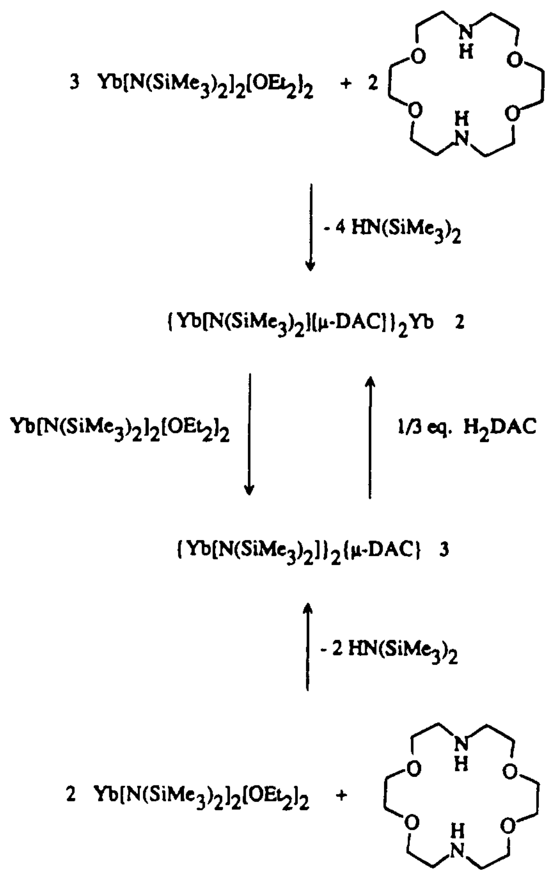


Figure 2. ORTEP plot of $\{Yb[N(SiMe_3)_2][\mu\text{-DAC}]\}_2Yb$ (**2**).

Scheme 2



Since an unambiguous structural assignment was not possible from NMR data alone, a single crystal X-ray diffraction study was carried out.

An ORTEP plot of **2** is given in Figure 2. Fractional atomic coordinates are given in Table 5, while selected bond distances and angles are collected in Table 6. The structure of **2** consists of a trinuclear Yb cluster. The three Yb atoms and two terminal silylamide N atoms are in a linear arrangement (nonbonding angles: Yb(2)−Yb(1)−Yb(3), 176.9(1)°; N(1)−Yb(2)−Yb(1), 172.4(7)°; N(2)−Yb(3)−Yb(1), 176.9(7)°). Central Yb(1) has a distorted tetrahedral geometry in which the N−Yb(1)−N angles for N belonging to the same DAC unit are compressed (90.4(12) and 93.1(10)°) while the N−Yb(1)−N angles for N belonging to different DAC units are opened (115.5(9)−122.0-(12)°). The dihedral angle between the N(3)−Yb(1)−N(4) and N(5)−Yb(1)−N(6) planes is 89.5°. The Yb(1)−N distances range from 2.34(3) to 2.41(3) Å, considerably shorter than the 2.50(3) to 2.61(3) Å range observed between these same N atoms and the outer metal atoms, Yb(2) and Yb(3). In light of the highly asymmetric Yb−N−Yb bridging, it is reasonable to regard the structure as containing a central YbN_4^{2-} core bonded to two outer $Yb[N(SiMe_2)_2]^+$ cations through the DAC O and N lone pairs as shown schematically in Figure 3.

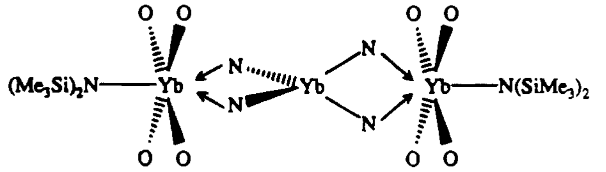


Figure 3. Schematic drawing of the core geometry for **2**.

The outer Yb atoms are seven-coordinate. The Yb−N(silylamide) distances are equivalent within experimental error at 2.44(3) Å and agree well with the value of 2.46(2) Å predicted from structure **1a**.[17] The outer Yb atoms lay within the planes defined by their three surrounding N atoms (displacement of 0.04 Å for both Yb(2) and Yb(3)). The Yb(2/3)−O distances vary from 2.49(2) to 2.57(3) Å, which is shorter than the expected distance of 2.63(2) Å predicted from **1a**.[17] Overall the molecule has approximate (not crystallographic) C_{2v} symmetry. A more detailed discussion of bond length variations is not warranted on the basis of the generally poor quality of this structure.

Complex **2** was isolated as the only Yb-containing product at all Yb:H_2DAC ratios below 1.5:1; excess H_2DAC was recovered, as well as **2**, at lower ratios. Increasing the ratio to 2:1 resulted in formation of black crystals of $\{Yb[N(SiMe_3)_2]\}_2\{\mu\text{-DAC}\}$ (**3**) (Scheme 2). The ^1H NMR spectrum of **3** shows only three DAC resonances suggesting a symmetrical structure. Attempts to obtain a crystal structure of this compound were frustrated by extensive disorder of the C_2H_4 bridges of the DAC ligand. However, we were able to confirm the general structure suggested by NMR and illustrated schematically in Figure 4.

Interconversion of **2** and **3** was demonstrated by NMR as shown in Scheme 2. No evidence for Yb[DAC] was observed in any of these reactions. Surprisingly, no reaction was observed between **2** and HgR_2 (R = Ph, CH_2Ph, *t*-Bu). Presumably **2** is too sterically crowded for reduction of HgR_2 to occur. The less crowded complex **3** does react with these reagents, but no trivalent products have been cleanly isolated from the rather complex product mixture.

Reaction of $Sm[N(SiMe_3)_2]_2[THF]_2$ with H_2DAC did not follow the same course as the Yb analogue. On addition of 1 equiv of H_2DAC, the purple $Sm[N(SiMe_3)_2]_2[THF]_2$ solution

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[17] Corrections of +0.12 and −0.06 Å were applied to the Y^{3+} distances of **1a** in order to make comparisons to the 7- and 4-coordinate Yb^{2+} centers of **2**.[14]

Table 5. Fractional Atomic Coordinates[a] and Equivalent Isotropic Temperature Factors[b] for $\{[(Me_3Si)_2N]Yb(\mu\text{-DAC})\}_2Yb$ (**2**) (Estimated Standard Deviations in Parentheses)

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
Yb(1)	474.4(13)	1535.0(10)	2518.3(14)	54.8(10)
Yb(2)	−1239.9(10)	14507.2(12)	2688.3(11)	52.2(11)
Yb(3)	2202.6(11)	1454.4(11)	2359.0(13)	56.4(11)
Si(1)	−2654(7)	713(7)	3246(8)	77(7)
Si(2)	−3061(8)	1955(8)	2027(10)	95(8)
Si(3)	3954(8)	2157(7)	2771(9)	90(8)
Si(4)	3639(8)	691(7)	1847(9)	90(9)
O(1)	−80.6(14)	172.8(13)	431(2)	8.4(9)′
O(2)	−85(2)	284.9(14)	318(2)	8.4(9)′
O(3)	−178(2)	107(2)	114(2)	11.3(11)′
O(4)	−103.9(14)	17.4(12)	241(2)	7.0(8)′
O(5)	175(2)	265(2)	153(2)	9.7(10)′
O(6)	163(2)	138(2)	71(2)	11.0(10)′
O(7)	217(2)	17(2)	300(3)	13.7(13)′
O(8)	274.7(14)	134.7(14)	400(2)	8.4(9)′
N(1)	−246(2)	136.3(14)	266(2)	6.4(9)′
N(2)	341(2)	143(2)	233(2)	7.4(10)′
N(3)	7.1(14)	103.3(14)	353(2)	5.1(8)′
N(4)	−64(2)	219(2)	178(2)	6.6(9)′
N(5)	157(2)	229(2)	302(2)	7.2(10)′
N(6)	95(2)	78(2)	174(3)	13(2)′
C(1)	−185(2)	7(2)	391(3)	8.9(14)′
C(2)	−298(3)	115(3)	408(4)	15(2)′
C(3)	−334(3)	−1(3)	265(4)	13(2)′
C(4)	−264(3)	266(2)	158(3)	12(2)′
C(5)	−354(3)	257(3)	252(4)	19(3)′
C(6)	−378(4)	159(3)	112(5)	20(3)′
C(7)	353(2)	282(2)	332(3)	8.8(14)′
C(8)	418(3)	275(3)	200(4)	14(2)′
C(9)	491(3)	192(3)	371(4)	18(3)′
C(10)	288(2)	−5(2)	147(3)	9(2)′
C(11)	389(3)	96(3)	98(4)	16(2)′
C(12)	447(4)	11(4)	262(4)	20(3)′
C(13)	44(2)	145(2)	438(3)	10(2)′
C(14)	−8(2)	150(2)	485(3)	8.9(13)′
C(15)	−110(2)	249(2)	437(3)	10(2)′
C(16)	−63(3)	306(3)	411(3)	12(2)′
C(17)	−35(2)	320(2)	283(3)	7.7(14)′
C(18)	−69(2)	303(2)	190(3)	9(2)′
C(19)	−109(2)	205(2)	83(3)	8.9(14)′
C(20)	−127(2)	123(2)	74(3)	9(2)′
C(21)	−203(3)	32(3)	108(3)	10(2)′
C(22)	−141(3)	−20(3)	164(3)	12(2)′
C(23)	−34(2)	−21(2)	290(3)	7.2(13)′
C(24)	4(2)	24(2)	376(3)	8.1(13)′
C(25)	149(3)	309(2)	268(3)	11(2)′
C(26)	118(3)	305(2)	170(3)	10(2)′
C(27)	150(3)	271(3)	57(4)	14(2)′
C(28)	187(3)	215(3)	39(4)	14(2)′
C(29)	92(4)	107(3)	27(4)	16(3)′
C(30)	53(3)	102(3)	76(5)	16(2)′
C(31)	106(2)	3(2)	170(3)	10(2)′
C(32)	147(3)	−13(3)	276(4)	12(2)′
C(33)	270(3)	4(3)	388(5)	18(3)′
C(34)	311(3)	62(3)	432(3)	12(2)′
C(35)	224(3)	161(3)	437(3)	11(2)′
C(36)	199(2)	235(2)	401(3)	10(2)′

[a] $\times 10^n$, where $n = 4$ for Yb and Si and $n = 3$ for O, N, and C. [b] $U_{eq} = {}^1/_3\Sigma_i\Sigma_j U_{ij}a_i{}^*a_j{}^*(a_ia_j)$ Å^2 × 10^n, where $n = 3$ for Yb and Si $n = 2$ for O, N, and C. Primed values indicate that U_{iso} is given as $T = \exp[-(8\pi^2 U_{iso}(\sin^2\theta)/\lambda^2)]$.

Table 6. Selected Distances (Å) and Angles (deg) for $\{[Me_3Si)_2N]Yb(\mu\text{-DAC})\}_2Yb$ (**2**)[a]

Distances

Yb(1)−N(3)	2.34(3)	Yb(3)−N(2)	2.44(3)
Yb(1)−N(4)	2.38(3)	Yb(3)−N(5)	2.50(3)
Yb(1)−N(5)	2.41(3)	Yb(3)−N(6)	2.59(4)
Yb(1)−N(6)	2.34(5)	Yb(3)−O(5)	2.52(3)
Yb(2)−N(1)	2.43(3)	Yb(3)−O(6)	2.57(3)
Yb(2)−N(3)	2.57(3)	Yb(3)−O(7)	2.56(3)
Yb(2)−N(4)	2.61(3)	Yb(3)−O(8)	2.56(3)
Yb(2)−O(1)	2.56(3)	N(1)−Si(1)	1.67(3)
Yb(2)−O(2)	2.56(3)	N(1)−Si(2)	1.63(3)
Yb(2)−O(3)	2.52(3)	N(2)−Si(3)	1.67(3)
Yb(2)−O(4)	2.49(2)	N(2)−Si(4)	1.70(3)

Angles

N(3)−Yb(1)−N(4)	93.1(10)	N(1)−Yb(2)−N(4)	137.0(9)
N(3)−Yb(1)−N(5)	118.9(10)	N(3)−Yb(2)−N(4)	82.8(9)
N(3)−Yb(1)−N(6)	122.0(12)	Yb(2)−N(1)−Si(1)	122(2)
N(4)−Yb(1)−N(5)	115.5(9)	Yb(2)−N(1)−Si(2)	114(2)
N(4)−Yb(1)−N(6)	119.4(13)	Si(1)−N(1)−Si(2)	124(2)
N(5)−Yb(1)−N(6)	90.4(12)	O(5)−Yb(3)−O(6)	62.3(9)
Yb(1)−N(3)−Yb(2)	92.3(9)	O(5)−Yb(3)−O(7)	159.0(11)
Yb(1)−N(4)−Yb(2)	90.6(10)	O(5)−Yb(3)−O(8)	124.8(9)
Yb(1)−N(5)−Yb(3)	93.4(10)	O(5)−Yb(3)−N(2)	98.5(1)
Yb(1)−N(6)−Yb(3)	92.7(14)	O(5)−Yb(3)−N(5)	66.7(10)
O(1)−Yb(2)−O(2)	64.9(8)	O(5)−Yb(3)−N(6)	95.2(11)
O(1)−Yb(2)−O(3)	169.2(9)	O(6)−Yb(3)−O(7)	109.7(11)
O(1)−Yb(2)−O(4)	109.7(8)	O(6)−Yb(3)−O(8)	172.5(9)
O(1)−Yb(2)−N(1)	86.9(9)	O(6)−Yb(3)−N(2)	89.4(10)
O(1)−Yb(2)−N(3)	67.9(9)	O(6)−Yb(3)−N(5)	115.8(9)
O(1)−Yb(2)−N(4)	121.6(8)	O(6)−Yb(3)−N(6)	66.1(12)
O(2)−Yb(2)−O(3)	125.3(10)	O(7)−Yb(3)−O(8)	62.9(10)
O(2)−Yb(2)−O(4)	155.0(8)	O(7)−Yb(3)−N(2)	100.9(11)
O(2)−Yb(2)−N(1)	106.4(9)	O(7)−Yb(3)−N(5)	104.0(11)
O(2)−Yb(2)−N(3)	90.8(8)	O(7)−Yb(3)−N(6)	64.4(12)
O(2)−Yb(2)−N(4)	66.4(10)	O(8)−Yb(3)−N(2)	91.6(10)
O(3)−Yb(2)−O(4)	62.8(9)	O(8)−Yb(3)−N(5)	68.2(9)
O(3)−Yb(2)−N(1)	86.4(11)	O(8)−Yb(3)−N(6)	109.2(12)
O(3)−Yb(2)−N(3)	112.9(10)	N(2)−Yb(3)−N(5)	135.1(10)
O(3)−Yb(2)−N(4)	68.7(10)	N(2)−Yb(3)−N(6)	141.9(12)
O(4)−Yb(2)−N(1)	97.5(8)	N(5)−Yb(3)−N(6)	82.9(12)
O(4)−Yb(2)−N(3)	65.4(8)	Yb(3)−N(2)−Si(3)	117(2)
O(4)−Yb(2)−N(4)	101.0(9)	Yb(3)−N(2)−Si(4)	119(2)
N(1)−Yb(2)−N(3)	140.1(9)	Si(3)−N(2)−Si(4)	125(2)

[a] Estimated standard deviation in parentheses.

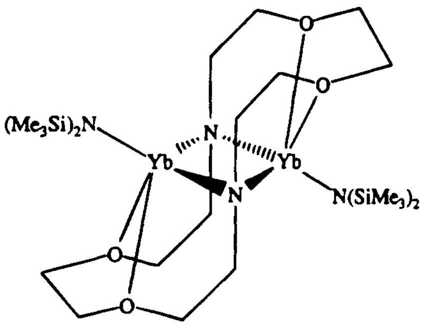

Figure 4. Schematic drawing of **3**.

rapidly turned dark green. After being stirred for 2−3 h, the reaction mixture slowly turned yellow. Bright yellow crystals of *trivalent* $Sm[DAC][N(SiMe_3)_2]$ (**4**) were isolated in 79% yield. The identity of **4** was established from NMR (Table 2) and mass spectral data, and as mentioned earlier, crystals of **4** proved to be isostructural with **1b**. It is reasonable to assume that the dark green intermediate is a Sm(II) complex since intense colors are typical of divalent Sm.[18] Two reasonable pathways for the formation of **4** are shown in Scheme 3. Path A involves rapid protonolysis of $Sm[N(SiMe_3)_2]_2[THF]_2$ to form Sm[DAC] and $HN(SiMe_3)_2$ followed by slow reduction of $HN(SiMe_3)_2$ to form **4**. Alternately, path B involves initial protonolysis to give an $HDAC^-$ complex followed by slow reduction of the remaining DAC N−H bond.

Attempts to follow the reaction by ^1H NMR spectroscopy were complicated by the low solubility of H_2DAC and the intermediate green complex in d_8-toluene. Nevertheless, our evidence would seem to support path B for several reasons.

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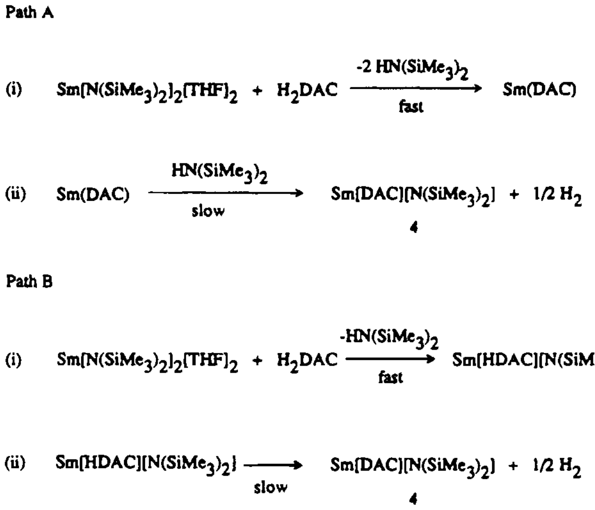
(18) Examples are the intensely purple $Sm[N(SiMe_3)_2]_2[THF]_2$ and the pale yellow $Sm[N(SiMe_3)_2]_3$ as well as the deep green SmI_2 compared with pale yellow SmI_3.

Scheme 3



Path A

(i) $Sm[N(SiMe_3)_2]_2[THF]_2 + H_2DAC \xrightarrow[fast]{-2\,HN(SiMe_3)_2} Sm(DAC)$

(ii) $Sm(DAC) \xrightarrow[slow]{HN(SiMe_3)_2} Sm[DAC][N(SiMe_3)_2] + 1/2\,H_2$ **4**

Path B

(i) $Sm[N(SiMe_3)_2]_2[THF]_2 + H_2DAC \xrightarrow[fast]{-HN(SiMe_3)_2} Sm[HDAC][N(SiMe_3)_2]$

(ii) $Sm[HDAC][N(SiMe_3)_2] \xrightarrow[slow]{} Sm[DAC][N(SiMe_3)_2] + 1/2\,H_2$ **4**

First, it is clear from the ^1H NMR that $HN(SiMe_3)_2$ appears within 10 min of mixing (the first spectrum acquired) and does not change in integrated intensity relative to d_8-toluene throughout the experiment. Second, product peaks do not appear until ca. 2 h after mixing, yet removal of the solvent under vacuum after 15 min results in a greenish powder which slowly converts to **4** in the *solid state*. This would seem to rule out reduction of $HN(SiMe_3)_2$ since this noncoordinating base should be removed with the solvent. Third, the reaction proceeds at a much more rapid rate in d_8-THF than in d_8-toluene; product peaks are evident after 15 min in d_8-THF. If reduction of $HN(SiMe_3)_2$ was involved, addition of a large excess of a more strongly coordinating base such as THF should prevent the second step of path A from occurring. In addition we observed no reaction between $Sm[N(SiMe_3)_2]_2$ and either $HN(SiMe_3)_2$ or $HNEt_2$ by ^1H NMR at 60 °C (24 h); decomposition of $Sm[N(SiMe_3)_2]_2$ to uncharacterized products was observed at higher temperatures. We have not been able to assign the resonances due to the intermediate green compound or H_2. Assignment of a H_2 resonance is obviously difficult given its small relative intensity. The low solubility of the intermediate may indicate a more complicated structure than that depicted in path B but the general features of this route are consistent with the experimental observations.

Reduction of an amine N−H bond by Sm(II) to form an amide would appear to be without precedence. Although Sm(II) is a well-known reducing agent in organic chemistry,[19] most examples involve reduction of carbonyl functions to give radical anions. The most closely related example in organosamarium chemistry involves the reduction of 2,3,5,6-tetramethylphenol by $Cp^*{}_2Sm(THF)_2$ to give $Cp^*{}_2Sm(O\text{-}2,3,5,6\text{-}Me_4C_6H)$.[20] Reduction of amine N−H bonds to metal amides and hydrogen is of course well-known for zerovalent group 1 metals in the presence of catalytic amounts of transition metal salts.[21]

In summary, this work demonstrates that deprotonated 4,13-diaza-18-crown-6 can function as a suitable ligand for the preparation of monomeric complexes of the trivalent lanthanides. Interesting polymetallic complexes are isolated with Yb(II), while Sm(II) reduces an NH bond of the ligand to give a trivalent product. Work is continuing to assess the utility of this and other macrocyclic ligands in the organometallic and coordination chemistry of the f-elements.

Acknowledgment. We thank Mrs. C. Greenwood for assistance in recording the NMR spectra, Mrs. Kathy Beveridge for help with the X-ray structural studies, and Dr. D. McGillivray and Mr. L. Shallig for recording the mass spectra. L.L. thanks Mr. Gord Cross and Mrs. Alison Ingham for helpful discussions regarding preparation of the macrocycle. This research was supported by the NSERC (Canada) and a University of Victoria Internal Research Grant (to D.J.B.).

Supplementary Material Available: Full tables of distances, angles, and anisotropic thermal parameters (Tables S1−S3) for **1a**, and full tables of distance, angles, and anisotropic thermal parameters (Tables S4−6) for **2** (11 pages). Ordering information is given on any current masthead page.

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