The First Oligomeric Samarium(II) Silylamide: Coordinative Saturation through Agostic Sm···SiH Interactions

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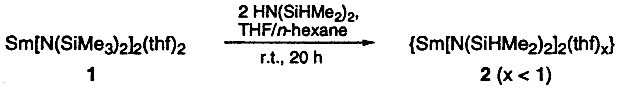
$Sm[N(SiMe_3)_2]_2(thf)_2$ reacts with 1,1,3,3-tetramethyldisilazane by a transsilylamination reaction to form the hexane-soluble $Sm[N(SiHMe_2)_2]_2(thf)_x$ in high yield. An X-ray diffraction study reveals a novel trinuclear complex of composition $Sm\{[\mu\text{-}N(SiHMe_2)_2]_2Sm[N(SiHMe_2)_2](thf)\}_2$ featuring a bent array of metal centers. Multiple metal···SiH β-agostic interactions sterically and electronically saturate the samarium(II) centers implying a new coordination mode of the bridging amide ligands.

Introduction

Sterically encumbered amide ligands are known to stabilize the lower oxidation states of transition metals efficiently.[1][2] However, complexes of strong reductants such as $Sm^{(II)}$ (E_0 = −1.55 V) display an intrinsic instability in the presence of β-H atoms and functional groups.[3] Donor ligand coordination and ate complex formation usually add to complex stability by counteracting oligonuclear aggregation and subsequent disproportionation reactions.[2][4] Recently, we introduced the bis(dimethylsilyl)amide ligand, $N(SiHMe_2)_2$, into organolanthanide chemistry which imparts (i) increased complex stability relative to the similarly sized $N\mathit{i}Pr_2$ ligand, and (ii) enhanced steric flexibility relative to the commonly employed $N(SiMe_3)_2$ ligand.[5] In addition, the Si−H moiety proved to be an excellent spectroscopic probe prone to unique agostic, "Ln···SiH", interactions.[6] This paper describes how the Si−H functionality can also provide a stabilizing environment in samarium(II) chemistry.

Results and Discussion

When $SmI_2(thf)_2$[7] was allowed to react with 1.95 equivalents of $Li[N(SiHMe_2)_2]$, in THF at ambient temperature, the color of the suspension turned from dark green to black. Evaporation of the solvent gave a residue whose IR spectrum showed the presence of samarium-bonded $N(SiHMe_2)_2$ ligands. However, tractable $Sm^{(II)}$ species soluble in *n*-hexane or toluene could not be isolated.



Scheme 1. Synthesis of complex **2**

In order to exclude any ate complex formation or alkali metal salt contamination, we performed a transsilylamination reaction, using $Sm[N(SiMe_3)_2]_2(thf)_2$[4a] (**1**) and $HN(SiHMe_2)_2$ as reagents (Scheme 1). A similar transsilylamination reaction was recently used to form $Na[N(SiHMe_2)_2]$ by exploiting the difference in the pK_a values of the parent silylamines [pK_a(THF): 25.8 $HN(SiMe_3)_2$), 22.6 $HN(SiHMe_2)_2$].[8] Following this procedure, the compound $Sm[N(SiHMe_2)_2]_2(thf)_x$ (**2**) was obtained in almost quantitative yield. IR spectroscopy confirmed the coordination of the bis(dimethylsilyl)amide ligand by the appearance of a very strong SiH stretching vibration at 2040 cm^{-1} (free silylamine: 2118 cm^{-1}). Additionally, a broad lower energy shoulder at approximately 1936 cm^{-1}, indicative of agostic interactions, was observed. The ^1H NMR spectrum of **2**, measured in $[D_8]$tetrahydrofuran, showed two resonances at δ = −2.47 and −12.18 in a ratio of 6:1, respectively, as would be expected for an intact $N(SiHMe_2)_2$ ligand. Recrystallization of compound **2** from *n*-hexane/THF (4:1) solutions at −35°C yielded black, rhombic single crystals (**2a**). Both the crude reaction product **2** and the crystals **2a** gave similar ^1H NMR spectra in $[D_6]$benzene displaying at least five resonances. Although a variable-temperature ^1H NMR spectroscopic study showed the coalescence of some signals at −60°C, which is in agreement with the presence of differently coordinated amide ligands, the resonances ranging from δ = 14 to −40 proved of little diagnostic value.

An X-ray crystallographic study of **2a** revealed an unprecedented, trinuclear molecular structure of composition $Sm\{[\mu\text{-}N(SiHMe_2)_2]_2Sm[N(SiHMe_2)_2](thf)\}_2$. As shown in Figure 1, three samarium(II) atoms are arranged in a bent fashion ("Sm···Sm···Sm" 130°). In contrast, the structurally related heteroleptic complexes $Yb\{[\mu\text{-}DAC]Yb[N(SiMe_3)_2]\}_2$ (DAC = deprotonated 4,13-diaza-18-crown-6)[3c] and $Mn\{[\mu\text{-}NHC_6H_3\mathit{i}Pr_2\text{-}2,6]_2Mn\text{-}[N(SiMe_3)_2]\}_2$[9] show almost linear arrays of metal centers ["M···M···M" 176.9(1)° and 170.3(1)°, respectively]. The central Sm(1) is formally four-coordinate − the nitrogen atoms of the bridging amide ligands producing a distorted tetrahedral SmN_4 core coordination ["N−Sm(1)−N"

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84.00(7)−143.83(7)°]. The formal four-coordination of the terminal samarium atoms, which are approximately related by a C_2 axis through Sm(1), is completed by terminal amide and THF donor ligands.

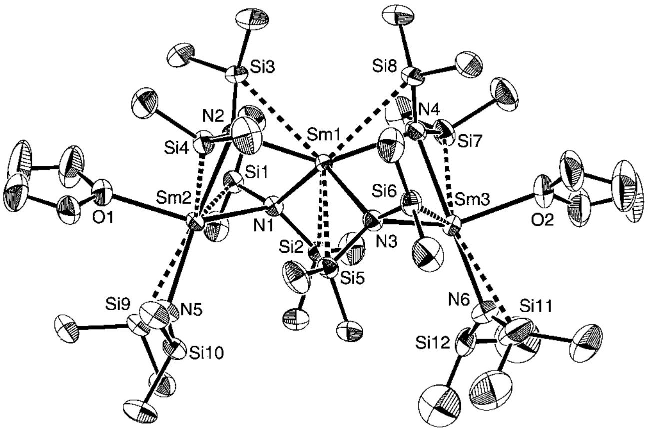
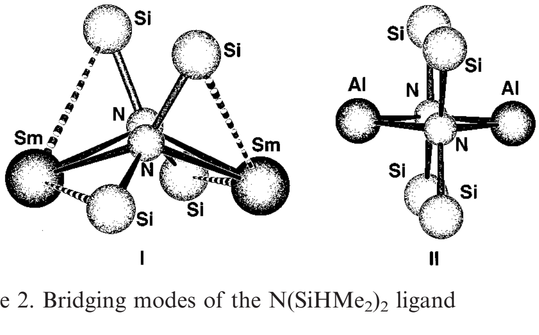


Figure 1. Molecular structure of **2a** (PLATON, 50% probability level). Hydrogen atoms and one part of the disordered Si(12)Me$_2$ group are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sm(1)−Sm(2) 3.6920(2), Sm(1)−Sm(3) 3.6999(3), Sm···Si 3.2317(9)-3.342(1); N−Sm(2)−N 81.09(7)-146.27(7), N−Sm(2)−O(1) 88.35(8)-136.76(7), N−Sm(3)−N 82.48(7)−152.8(1), N−Sm(3)−O(2) 89.5(1)-134.61(9), Sm(1)−N(1)−Si(1) 132.7(1), Sm(1)−N(1)−Si(2) 96.04(9), Sm(1)−N(2)−Si(3) 94.7(1), Sm(1)−N(2)−Si(4) 128.0(1), Sm(1)−N(3)−Si(5) 96.10(9), Sm(1)−N(3)−Si(6) 130.5(1), Sm(1)−N(4)−Si(7) 127.7(1), Sm(1)−N(4)−Si(8) 95.0(1), Sm(2)−N(1)−Si(1) 92.1(1), Sm(2)−N(1)−Si(2) 122.4(1), Sm(2)−N(2)−Si(3) 127.9(1), Sm(2)−N(2)−Si(4) 93.7(1), Sm(2)−N(5)−Si(9) 100.5(1), Sm(2)−N(5)−Si(10) 130.8(1), Sm(3)−N(3)−Si(5) 122.3(1), Sm(3)−N(3)−Si(6) 92.9(1), Sm(3)−N(4)−Si(7) 94.5(1), Sm(3)−N(4)−Si(8) 127.6(1), Sm(3)−N(6)−Si(11) 106.8(2).

The coordination mode of the bridging amide ligands is asymmetric since the N atoms are located closer to the central Sm(1) atom [av. Sm(1)−N 2.633 Å]. The remaining Sm−N bond lengths associated with the bridging amide ligands range from 2.664(2) to 2.723(2) Å and are the longest Sm−N σ-bonds observed so far. In comparison, the bridging Sm−N bond lengths in MSm[N(SiMe$_3$)$_2$]$_3$ average 2.560(6) Å (M = Na) and 2.529(3) Å (M = K), respectively,[2] while the Sm−N bond lengths in Sm[HB(3,5-Me$_2$pz)$_3$]$_2$ (pz = pyrazolyl) are 2.617(4) Å.[10] The two terminal amide ligands are *cis*-orientated and have Sm−N lengths [av. 2.470 Å] comparable with those of the formally four-coordinate complex **1** [av. 2.433 Å]. The Sm−O distances average 2.552 Å and are in the expected range {**1**, av. 2.596 Å; Sm[N(SiMe$_3$)(C$_6$H$_3$*i*Pr$_2$-2,6)]$_2$(thf)$_2$, av. 2.550 Å}.[4]



I

II

Figure 2. Bridging modes of the N(SiHMe$_2$)$_2$ ligand

A closer examination of the bridging silylamide ligands reveals a novel coordination mode featuring "SiNSi moieties" tilted towards the metal centers (**I** in Figure 2). This asymmetric ligand coordination is confirmed by the Sm−N−Si angles, which vary between 92.1(1) and 132.7(1)°. Apparently, coordinatively unsaturated and electron-deficient Sm^{II} centers favor the formation of close Sm···SiH β-agostic interactions involving all of the SiHMe$_2$ groups. The resulting Sm−Si (av. 3.273 Å) and Sm−H contacts (av. 2.75 Å) are remarkably short. In contrast, the shortest Sm−Si distance in **1** showing Sm···SiCH$_3$ contacts is 3.467 Å.[4a] The two terminal amide ligands in complex **2a** also show close Sm···SiH contacts. Taking the Sm···SiH β-agostic interactions into account a coordination number of 8 and 7 can be assigned to the central and terminal Sm atoms, respectively. The complex {Me$_2$Al[(μ-N(SiHMe$_2$)$_2$]}$_2$ displays an unperturbated geometry (**II** in Figure 2) due to minimum attractive Al···SiH interactions [Al−N−Si 111.5(1)°].[11]

Conclusions

We have reported the first homotrinuclear samarium(II) amide featuring an unusual oligomeric structure. Considering the solid-state structures of mononuclear, solvated Sm[N(SiMe$_3$)$_2$]$_2$(thf)$_2$ (**1**) and dinuclear, unsolvated {Yb[N(SiMe$_3$)$_2$]$_2$}$_2$,[12] on one hand this novel structural motif might be attributable to the decreased steric bulk of N(SiHMe$_2$)$_2$,[5] which favors aggregation. On the other hand β-agostic Sm···SiH interactions seem to be markedly stronger than Sm(Yb)···SiCH$_3$ γ-agostic interactions as evidenced by the displacement of donor (THF) molecules. The toleration of SiH functionalities might have implications for the use of Sm$^{(II)}$ reagents in organic synthesis. We are currently investigating the feasibility of ligand exchange reactions of Sm[N(SiHMe$_2$)$_2$]$_2$(thf)$_x$ (**2**) with bulky protic subtrates.

Experimental Section

General: All manipulations were performed in a argon-filled glovebox (MBraun MB150B-G-II). Solvent pretreatment and physical characterizations were conducted as described previously.[5] SmI$_2$(thf)$_2$,[7] Li[N(SiHMe$_2$)$_2$][8] and **1**[4a] were synthesized according to known procedures.

Sm^{II} Silylamide 2 (2a): A solution of 1,1,3,3-tetramethyldisilazane (0.587 g, 4.40 mmol) in THF (5 mL) was added to a solution of **1** (1.231 g, 2.00 mmol) in THF (15 mL) and stirred at ambient temperature for 20 h, whereupon the color of the solution turned from purple to black. Evaporation of the THF afforded a black powder **2** (yield > 95%) which completely dissolved in *n*-hexane and gave crystals of **2a** after recrystallization from *n*-hexane/THF. − IR (Nujol): $\tilde{\nu}$ = 2040 s, 1936 m sh, 1243 vs, 1039 vs, 954 vs, 893 vs, 836 vs, 785 s, 762 s, 680 m, 626 m, 599 w cm^{-1}. − ^{1}H NMR (270.16 MHz, [D$_8$]THF): δ = −2.47 (s, 6 H), −12.18 (s, 1 H). − ^{13}C (67.93 MHz, [D$_8$]THF): δ = 14.7. − MS (CI); *m/z* (%): 547 {2, Sm[N(SiHMe$_2$)$_2$]}, 532 [3, {Sm[N(SiHMe$_2$)$_2$]$_3$ − Me}$^+$], 415 {21, Sm[N(SiHMe$_2$)$_2$]$_2$}. − C$_{32}$H$_{100}$N$_6$O$_2$Si$_{12}$Sm$_3$·C$_6$H$_{14}$ (1475.47): calcd. C 30.93, H 7.79, N 5.70; found (**2**) C 29.5, H 7.4, N 5.6; found (**2a**) C 29.7, H 7.6, N 5.6.

X-ray Crystal Structure Analysis of 2a: $C_{32}H_{100}N_6O_2Si_{12}Sm_3$, M = 1389.35; monoclinic, space group $P2_1/c$, a = 11.4620(7), b = 28.873(2), c = 22.064(1) Å, β = 96.605(6), V = 7253.4(8) Å^3, T = 173(1) K, Z = 4, F(000) = 2816, D_c = 1.272 g cm^{-3}, μ = 2.62 mm^{-1}. 122106 (17029 unique) Bragg reflections with sinΘ/λ_{max} = 0.66 Å^{-1} were collected on an image plate system from STOE IPDS[13] with a rotating anode generator (Nonius FR591; Mo-K_α, λ = 0.71073 Å). 12806 independent reflections. Full-matrix least-squares refinement of 537 parameters against 11255 observed reflections reflections (sinΘ/λ_{max} = 0.6 Å^{-1}) converged to $R1$ = 0.023, $wR2$ = 0.061, residual electron density: +0.95/-0.46 eÅ^{-3}.[14] The terminal Si(12)Me_2 moiety was described by a disordering model with two split Si positions. One of the resulting $SiMe_2$ groups (occupation factor 0.43) displays an additional Sm···SiH β-agostic interaction. The positions of the agostic hydrogen atoms in the nondisordered $SiHMe_2$ groups were refined. Furthermore, disordered *n*-hexane molecules were located in a potential solvent accessible area of 243 Å^3. However, the BYPASS method[15] was applied to account for the disordered solvent contribution to the structure factor in the final refinements. Structure graphics were performed with the programs PLATON[16] and SCHAKAL.[17] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-118713. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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