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Communications

Rare Earth Azatrane Chemistry: Facile Cleavage of THF To Give a Y_2Li_3O Cluster

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Triamidoamine $[N(CH_2CH_2NR)_3]^{3-}$ ligands have several attractive features for the coordination chemist: the chelate effect confers considerable stability on their complexes, which are potentially C_3 symmetric and hence chiral, and sterically constrained pockets which are suitable for coordination or activation of small molecules may be formed around the metal ion. The sterically demanding (trimethylsilyl)amide $[N(CH_2CH_2NSiMe_3)_3]^{3-}$ (abbreviated here as $[N'_3N]^{3-}$) has been particularly thoroughly investigated, and complexes with main group,[1] transition,[2] and actinide[3] metals have been reported, with metals in oxidation states +3 and +4. The lanthanides with their stable +3 oxidation state should be ideal candidates for formation of tris(amino) aminate(3−) complexes; however, Verkade recently reported that $[Li_3[N'_3N](THF)_2]$ was the only compound isolated when $LaCl_3$ and $Li_3[N'_3N]$ were heated to reflux for 70 h in THF.[4] In this Communication we report the reaction of YCl_3 with $Li_3[N'_3N]$ in THF to give a remarkable Li_3Y_2 cluster containing one conventional $Y[N'_3N]$ fragment, as well as an encapsulated oxide ion, two enolate ligands, and a modified $[N'_3N]$ ligand, all derived from a facile cleavage of THF.

Addition of a THF solution of $Li_3[N'_3N]$ to a THF suspension of $LnCl_3$ under rigorously anhydrous and anaerobic conditions at 0 °C led to immediate formation of a clear colorless solution for Ln = Y. In the case of Ln = La, complete reaction was only effected by heating to reflux for 30 min. Removal of THF *in vacuo* gave an off-white solid from which product could be extracted with toluene and subsequently crystallized as air- and moisture-sensitive colorless prisms from petroleum ether.[5] The ^1H NMR spectrum of these prisms in C_6D_6 was extremely complex, but spectra recorded for samples prepared on several different occasions were indistinguishable and did not alter with time, demonstrating that the complexity was not due to varying degrees of decomposition. Elemental analysis showed that the product was not a simple $Ln[N'_3N]$ complex, and so an X-ray diffraction study of the Y complex (**1**) was undertaken in order fully to characterize this compound. Elemental analysis and NMR spectroscopy indicate that the Y and La complexes are analogous.

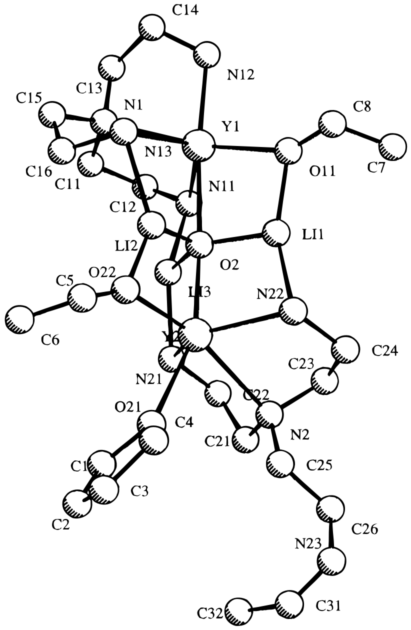

Figure 1. PLUTO plot of **1** omitting $SiMe_3$ groups for clarity. Selected bond lengths (Å) and angles (deg): Y(1)−N(1) 2.51(3), Y(1)−N(11) 2.43(3), Y(1)−N(12) 2.28(3), Y(1)−N(13) 2.35(2), Y(2)−N(2) 2.53(2), Y(2)−N(21) 2.32(3), Y(2)−N(22) 2.35(3), Y(1)−O(2) 2.43(2), Y(2)−O(2) 2.15(2), Y(1)−O(11) 2.26(2), Y(2)−O(22) 2.25(2), Li(1)−O(2) 1.81(8), Li(2)−O(2) 1.72(9), Li(3)−O(2) 1.92(7), Li(1)−O(11) 1.90(8), Li(2)−O(22) 1.81(9); Y(1)−O(2)−Y(2) 179(1), N(1)−Y(1)−N(11) 72.1(9), N(1)−Y(1)−N(12) 73.2(9), N(1)−Y(1)−N(13) 71.1(9), Li(1)−O(2)−Li(2) 110(4), Li(1)−O(2)−Li(3) 128(3), Li(2)−O(2)−Li(3) 123(4).

The X-ray diffraction study[6] showed **1** to be $[\{N(CH_2CH_2SiMe_3)_3\}Y(\mu_5\text{-}O)Li_3(\mu_2\text{-}OCHCH_2)_2Y(THF)\{N(CH_2CH_2SiMe_3)_2CH_2CH_2N[SiMe_3](CHCH_2)\}]$.[6] A PLUTO plot of the complex is shown in Figure 1, omitting $SiMe_3$ groups for clarity, and a

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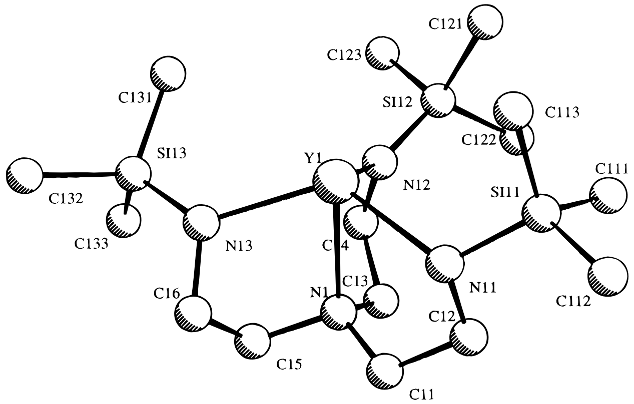

Figure 2. PLUTO plot of the Y(**1**)[N′$_3$N] fragment of **1**.

view of the Y(1)[N′$_3$N] fragment is shown in Figure 2. The refinement of the structure was hampered by the presence of disordered solvent with partial occupancy; however, this structure is fully consistent with analytical results. The complexity of **1** was surprising, and yet we have reproducibly prepared it several times using different batches of starting materials, with a typical isolated yield of close to 70%.[5] The encapsulated oxide O(2), the enolate ligands, and the vinyl group on N(23) must all be derived from THF cleavage. It is well-known that *n*-BuLi reacts with THF to give ethylene and the lithium enolate of acetaldehyde,[7] but although many organolanthanide complexes are highly reactive toward C−H bonds,[8] and ring opening of THF by a phosphido lanthanide complex to give an alkoxy species has been reported,[9] cleavage of THF by an organolanthanide to give a lanthanide enolate requires quite forcing conditions.[10] Li$_3$[N′$_3$N] is stable in THF at elevated temperature, and lanthanide tris(dialkylamides) Ln(NR$_2$)$_3$ (R = SiMe$_3$, ^{i}Pr) are also unreactive with THF. The mechanism of the cleavage of THF is not clear: the high isolated yield of **1** indicates that it cannot be due to a straightforward stoichiometric deprotonation of THF by [N′$_3$N]$^{3-}$, and no H$_3$[N′$_3$N] has been observed by ^{1}H NMR of the crude reaction mixture (the methylene protons of H$_3$[N′$_3$N] show distinctive resonances in the NMR spectrum). The reaction is carried out with a 1:1 Li$_3$[N′$_3$N]:LnCl$_3$ ratio, and as the final reaction mixture is a clear, virtually colorless solution in THF, it is apparent that all the insoluble LnCl$_3$ must be consumed during the reaction. Three moles of LiCl is produced for each mole of **1**; the fate of the other 3 mol of Cl$^-$ has not been determined, but it is likely that chlorinated organic compounds are formed. These would easily be removed either *in vacuo* or during recrystallization. **1** does not react further with THF: there is no change in the ^{1}H NMR spectrum of a sample in THF-d_8 on heating to 78 °C for several hours.

Y(1) is coordinated by the [N′$_3$N] ligand as expected (see Figure 2), with Y(1) lying 0.72 Å above the plane defined by N(11), N(12), and N(13). This may be compared with the average out-of-plane distance of 0.860 Å for the similarly sized U^{4+} in U[N′$_3$N](C$_5$Me$_5$).[3] N(12) lies just 0.058 Å out of the plane defined by Y(1), Si(12), and C(14); however, the other amino nitrogens show greater deviation from planarity, N(13) and N(11) being respectively 0.226 and 0.465 Å out of the planes defined by the surrounding Y, C, and Si atoms. The [Y$_2$Li$_3$O]$^{7+}$ structural unit is novel; coordination about the oxide ion is distorted trigonal bipyramidal, with the oxide ion lying just 0.009 Å out of the plane defined by Li(1), Li(2), and Li(3), and the Y(1)−O(2)−Y(2) angle being 179(1)°. Linear Ln−O−Ln bridges in lanthanide complexes of the type [Cp$_2$Ln(THF)]$_2$(μ-O) are well documented. Allowing for the differences in ionic radii, the Y−O distances in **1** are somewhat longer than those reported for Ln = Lu,[9] where the bridge is unsymmetrical with Lu−O distances of 2.003(3) and 2.295(8) Å; for Sm[11] or Yb,[12] the bridge is symmetrical with Ln−O distances of 2.094(1) and 2.01(5) Å, respectively.

In conclusion, we have prepared and characterized the first complex of a rare earth element with a tris(amino) aminate(3−) ligand and have observed a facile cleavage of THF which is unprecedented in rare earth or lithium amide chemistry. We are currently investigating the reactions of later lanthanides with Li$_3$[N′$_3$N], which appear to be much more straightforward.

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Supporting Information Available: Tables of experimental details, positional parameters, thermal parameters, and intramolecular bond lengths and angles for **1** (32 pages). Ordering information is given on any current masthead page.

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(5) Reaction of YCl$_3$ with Li$_3$N$_3$N: To a dispersion of YCl$_3$ (1.12 g, 5.75 mmol) in THF (25 cm^3) at room temperature was added, with stirring, Li$_3$[N′$_3$N] (89.0 cm^3 of a 0.064 M solution in THF, 5.70 mmol). When addition of Li$_3$[N′$_3$N] was complete, all the YCl$_3$ had dissolved to give a clear, pare yellow solution, which was stirred for a further 16 h at room temperature. Solvent was removed *in vacuo*, and product was extracted into toluene (120 cm^3) to yield a clear pale yellow solution. This was separated from LiCl by decantation and evaporated to dryness *in vacuo*. The resulting pale brown solid was dissolved in petroleum ether (35 cm^3). Product was deposited as clear, colorless prisms on cooling to −10 °C. These were washed with petroleum ether and dried *in vacuo*. Yield = 2.34 g (69%). Anal. Calcd for C$_{40}$H$_{95}$Li$_3$N$_8$O$_4$Si$_6$Y$_2$: C, 42.92; H, 8.55; N, 10.01. Found: C, 42.56; H, 9.10; N, 10.17. ^{7}Li NMR: δ 4.54 (br, 2Li), 5.40 (br, 1Li).

(6) Crystal data: C$_{40}$H$_{95}$Li$_3$N$_8$O$_4$Si$_6$Y$_2$, triclinic, $P1$ (No. 2), $Z = 2$, a = 15.90(1) Å, b = 17.59(2) Å, c = 13.32(2) Å, α = 104.27(8), β = 94.25(9)°, γ = 109.84(7)°, V = 3343(6) Å^3, D_c = 1.173 g cm^{-3}, μ(Mo Kα) = 18.81 cm^{-1}, T = −120 °C, $2\theta_{max}$ = 50°, 2509 observed reflections ($I > 5\sigma(I)$), 313 refined parameters, R = 0.097, R_w = 0.131. Structure solution was by direct methods (SHELXS). Y and Si atoms were refined anisotropically; all other non-hydrogen atoms were refined isotropically. Hydrogen atom positions were calculated and were not refined. Refinement was hampered by the presence of disordered solvent with partial occupancy.

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