

Formation of Novel T-Shaped NNN Ligands via Rare-Earth Metal-Mediated Si–H Activation

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S Supporting Information

ABSTRACT: Reactions of silylamides [Ln{N-(SiHMe₂)₂}₃(thf)₂] with sterically crowded terphenylamine DmpNH₂ (Dmp = 2,6-Mes₂C₆H₃ with Mes = 2,4,6-Me₃C₆H₂) afforded via a template reaction the formation of a new tridentate ligand, and derived complexes of composition [LnN{SiMe₂N(Dmp)}₂] (Ln = Ce, Pr) were obtained. Usage of the even more bulky amine Ar^{*}NH₂ (Ar^{*} = 2,6-Trip₂C₆H₃ with Trip = 2,4,6-*i*Pr₃C₆H₂) yielded the free protonated ligand NH{SiMe₂NH(Ar^{*})}₂.

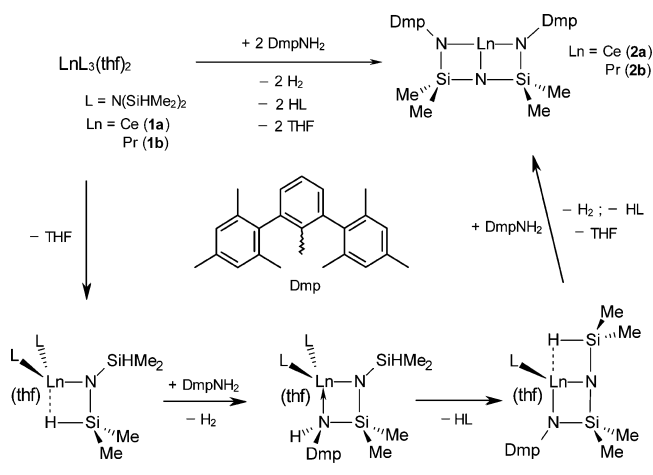
The formation of macrocycles and chelating ligands promoted by lanthanide(III) cations is well established and, in particular, investigated for Schiff-base-type condensations.¹ Although other metals, in particular alkaline-earth and transition metals, are also qualified to promote template reactions,^{2,3} the use of lanthanides partly benefits from a number of advantages such as low cost and toxicity. Moreover, because of their different ionic radii, fine control of the reaction outcome is possible because the character and size of the formed ligand essentially depends on the size of the cation.⁴ Lanthanide complexes with multidentate ligands exhibit some very interesting properties and possible applications, such as polymerization catalysts,⁵ contrast enhancing agents in magnetic resonance imaging,⁶ luminescent biolabels and materials,⁷ ionic liquid crystals,⁸ and extracting agents for lanthanide actinide separation.⁹ In the following, we report the synthesis of novel tripodal nitrogen donor ligands via Si–H activation promoted by rare-earth metal ions.¹⁰

As part of a project on the preparation of well-defined cerium(III) complexes, which might be used for cerium-catalyzed α -hydroxylation of β -diketo compounds with molecular oxygen,¹¹ we have examined reactions between the silylamide [Ce{N(SiHMe₂)₂}₃(thf)₂] (**1a**) and sterically crowded 4-arylpent-3-en-2-ones. Therefore, the solvent-free reaction of **1a** with ketimine DmpNHC(Me)C(H)C(Me)O (Dmp = 2,6-Mes₂C₆H₃ with Mes, 2,4,6-Me₃C₆H₂) afforded as a byproduct in very small yield the novel complex [CeN{SiMe₂N(Dmp)}₂] (**2a**) as air-sensitive orange crystals. The formation of **2a** can be explained either by the presence of DmpNH₂ impurities in the ketimine or generation of the latter by unintentional hydrolysis during the reaction. Compound **2a** and its homologous praseodymium complex [PrN{SiMe₂N(Dmp)}₂] (**2b**) can be synthesized in a more rational way and in

much better yield by the reaction of 2 equiv of the amine DmpNH₂ with the corresponding lanthanide silylamides Ln{N-(SiHMe₂)₂}₃(thf)₂ [Ln = Ce (**1a**) or Pr (**1b**)].¹² The starting materials were melted together at 100 °C for 2 days and afterward treated with *n*-heptane. The obtained precipitates were extracted into tetrahydrofuran (THF/thf), and the THF extracts were stored at –20 °C to afford complexes [LnN{SiMe₂N(Dmp)}₂] [Ln = Ce (**2a**), Pr (**2b**)] as orange (**2a**) or pale-yellow (**2b**) crystalline materials in 74% and 62% yield, respectively.

A plausible mechanism for the formation of **2a** and **2b** is depicted in Scheme 1. It first involves dissociation of one

Scheme 1. Proposed Reaction Path for the Formation of 2a and 2b



coordinated THF molecule from the starting material **1a**. An additional agostic Ln...Si–H interaction may be formed that provides some electronic compensation for loss of the electron density close to the Lewis acidic metal center. Similar interactions have been observed before in a number of structurally characterized lanthanide disilazanes.^{13,14} The weakened Si–H bond is activated and reacts with the amine DmpNH₂ under elimination of H₂. In a further step, tetramethyldisilazane is eliminated, and the whole sequence is repeated once more.

While metal-mediated activation of both SiH groups and generation of a trianionic tris(amido) ligand are novel features in

Received: November 27, 2013

Published: January 23, 2014



tetramethyldisilazane chemistry, formation of the dianionic bis(amido) ligand $[\text{SiMe}_2\text{N}(\text{SiHMe}_2)_2]$ via elimination of H_2SiMe_2 has been observed previously by different groups.¹⁵ In one of these papers, Buffet and Okuda^{15b} reported functionalization of the cyclic polyamine 1,4,7-trimethyl-1,4,7,10-tetraazacyclododecane $[(\text{Me}_3\text{TACD})\text{H}]$ with a pendant $\text{SiMe}_2\text{N}(\text{SiHMe}_2)$ group via H_2 elimination from $\text{KN}(\text{SiHMe}_2)_2$ and $(\text{Me}_3\text{TACD})\text{H}$. Similar attempts to prepare derivatives of the protonated ligand $\text{HN}\{\text{SiMe}_2\text{N}(\text{Dmp})\text{H}\}_2$ in a different way either via silylation of the amine with a catalytic amount of potassium or sodium hydride as previously described for a number of compounds with Si–N bonds¹⁶ or by reaction of the aluminum silylamide $\text{Al}\{\text{N}(\text{SiHMe}_2)_2\}_3$ ¹⁷ with the amine under the same reaction conditions as those described above were not successful and afforded the unreacted starting materials only.

In further experiments, the reaction of the bulkier amine Ar^*NH_2 ($\text{Ar}^* = 2,6\text{-Trip}_2\text{C}_6\text{H}_3$ with Trip, 2,4,6-*i*-Pr₃C₆H₂) with lanthanide silylamides $\text{Ln}\{\text{N}(\text{SiHMe}_2)_2\}_3(\text{thf})_2$ was examined. Instead of the expected metal derivative, formation of the free protonated ligand $\text{NH}\{\text{SiMe}_2\text{NH}(\text{Ar}^*)\}_2$ (**3**) was observed. The propensity of very bulky terphenyl-substituted ligand systems for unexpected demetalation reactions has been noted before.¹⁸

In the solid-state structure of the tris(amine) **3** (Figure 1), the Si1–N2–Si2 angle at the central nitrogen atom is widened to

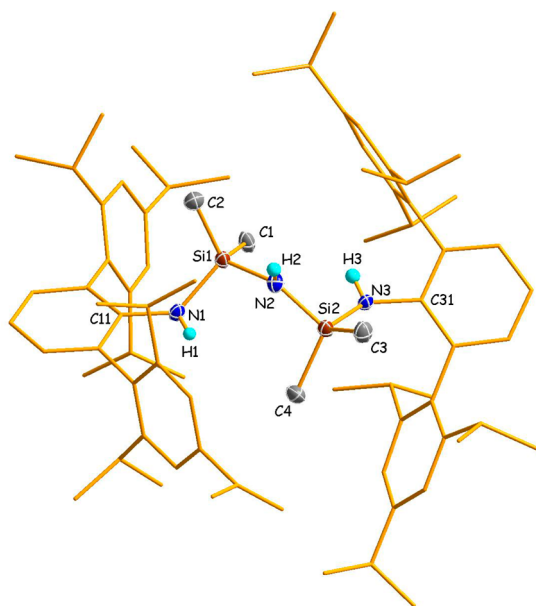


Figure 1. Molecular structure of **3**·1.5THF with thermal ellipsoids set to 30% probability. Most hydrogen atoms and cocrystallized solvent molecules have been omitted, and Ar* substituents are shown as lines for clarity. Selected bond lengths (Å) and angles (deg): N1–C11 1.404(2), Si1–N1 1.7477(18), N1–H1 0.74(2), Si2–N2 1.715(2), Si1–N2 1.7216(19), N2–H2 0.76(2), N3–C31 1.407(2), Si2–N3 1.7477(18), N3–H3 0.78(2), Si1–C1 1.847(2), Si1–C2 1.849(2), Si2–C3 1.847(2), Si2–C4 1.848(2); Si1–N2–Si2 136.76(15), C11–N1–Si1 132.90(15), C31–N3–Si2 133.25(15), N1–Si1–N2 104.78(9), N2–Si2–N3 104.57(9).

136.76(15)°. While N2 shows a strictly planar environment, as reflected by the angle sum of 359.9°, there is slight pyramidalization at the outer nitrogen atoms [$\Sigma^\circ(\text{N1}) = 348.6^\circ$ and $\Sigma^\circ(\text{N3}) = 351.1^\circ$].

Complexes **2a** and **2b** cocrystallize with different solvent molecules located in cavities of the structure. **2b** contains three

units of THF, whereas **2a** was isolated from either *n*-heptane or THF with 1 and 1.5 formula units of solvent, respectively. Because of their very similar features, only the solid-state structure of the cerium complex **2a**·1.5THF will be discussed in detail in the following. In all three structures, there are no significant interactions between the cocrystallized solvent molecules and metal atoms. The later show an exceptional anchor-like coordination by three nitrogen atoms of the chelating amido ligand (Figure 2). Steric and electronic saturation of the

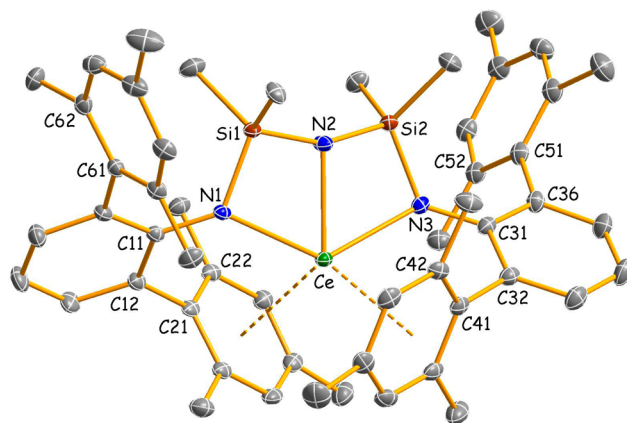


Figure 2. Molecular structure of **2a**·1.5THF with thermal ellipsoids set to 30% probability. Hydrogen atoms and cocrystallized solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for **2a**·1.5THF and **2b**·3THF (in brackets): M–N1 2.456(2) {2.4240(18)}, M–N2 2.292(2) {2.280(2)}, M–N3 2.422(2) {2.4260(18)}, M···C21 2.953(3) {2.956(2)}, M···C22 3.035(3) {3.159(3)}, M···C23 3.189(3) {3.307(3)}, M···C24 3.325(3) {3.287(3)}, M···C25 3.211(3) {3.069(3)}, M···C26 3.034(3) {2.942(2)}, M···C41 2.945(3) {2.939(2)}, M···C42 2.980(3) {2.961(2)}, M···C43 3.137(3) {3.075(3)}, M···C44 3.361(3) {3.227(2)}, M···C45 3.332(3) {3.218(2)}, M···C46 3.148(3) {3.083(2)}, M···X5 2.764 {2.763}, M···X4 2.781 {2.727}; N1–M–N2 65.82(8) {66.41(6)}, N1–M–N3 131.57(7) {132.72(7)}, N2–M–N3 65.85(8) {66.32(7)}, N1–Si1–N2 97.92(12) {97.26(10)}, N2–Si2–N3 96.77(12) {97.28(10)}, Si1–N2–Si2 156.74(16) {157.75(14)}, X4···M···X5 127.9 {127.3}. X5 and X4 define the centroids of the coordinated C21, C22, C23, C25, and C26 (for **2a**), C21, C22, C24, C25, and C26 (for **2b**), and C41, C42, C43, and C46 (for **2a** and **2b**) arene carbon atoms.

metal atom is achieved by additional Ce··· π interactions to two pending mesityl rings of the terphenyl groups. On the basis of the observed shortest metal···centroid distances, a η^5/η^4 - π coordination is formally assigned involving the carbon atoms (C21 \rightarrow C23, C25, C26)/ (C41 \rightarrow C43, C46) with Ce···C and Ce···centroid distances in the ranges of 2.945(3)–3.211(3) and 2.764/2.781 Å, respectively.

Taking into account the additional π contacts, a formal coordination number (cn) of 9 is calculated. However, if the observed average Ce–N distance of 2.390(2) Å is compared with the corresponding distances in other cerium amides {cn = 3, $[\text{Ce}\{\text{N}(\text{SiMe}_2)_2\}_3]^{19a} = 2.320(3)$ Å and $[\text{Ce}(\text{Tmp})_3]$ (Tmp = 2,2,6,6-tetramethylpiperidinate)^{19b} = 2.323(7) Å; cn = 4, $[\text{Ce}(\text{Tmp})_3(\text{thf})]^{19c} = 2.361(2)$ Å and $[\text{Ce}(\text{NCy}_2)_3(\text{thf})]^{19d} = 2.317(2)$ Å; cn = 5, $[\text{Ce}\{\text{N}(\text{SiHMe}_2)_2\}_3(\text{thf})_2] = 2.388(3)$ Å, see the Supporting Information (SI); cn = 6, $[\text{Ce}\{\text{N}(\text{Si}t\text{BuMe}_2)(2\text{-C}_5\text{H}_3\text{N-6-Me})\}_3]^{19e} = 2.437$ Å}, a lower effective cn of approximately 5 may be estimated for complex **2a** (and **2b**),

assuming that every π -bonded arene ring occupies only one coordination site.

Notably, the Ce–N distances to the central nitrogen atom N2 and the outer nitrogen atoms N1 and N3 are rather different with 2.292 and 2.456/2.422 Å, respectively. The distinct values reflect the different substitutions of the donor atoms. Therefore, the nitrogen atom N2 embedded between the two electropositive silicon atoms shows a stronger negative polarization, which allows a stronger electrostatic interaction with the cerium atom, whereas the aryl/silyl-substituted donor atoms N1 and N3 are less negatively charged. This view is supported by DFT calculations, including natural bond orbital and natural population analysis (NPA) on the model anion $[\text{N}\{\text{SiMe}_2\text{NPh}\}_2]^{3-}$ and the model complex $[\text{PrN}\{\text{SiMe}_2\text{NMph}\}_2]$ (**2b_M**; Mph = 2-MesC₆H₄; for details, see the SI). In the former, the different nucleophilicities of the nitrogen donor atoms is reflected by NPA charges of –1.768 on N2 and –1.061 on N1/N3. In the model system **2b_M**, the high NPA charges of +2.656 on Pr, –1.393 on N1/N3, and –1.901 on N2 and the low Wiberg bond orders²⁰ of 0.128 (2 \times)/0.194 for the Pr–N1(N3)/Pr–N2 bonds are in accordance with the mainly ionic character of these bonds. For the Pr \cdots C bonding to the 12 carbon atoms of the mesityl rings, a total Wiberg bond order of 0.151 is calculated. The Coulomb contributions for the metal– π -arene interactions are reflected by the high positive NPA charge on praseodymium on the one side and the negatively charged carbon atoms on the π -bonded mesityl arene rings of the Mph substituents (average total charges: C₆H₄Mes, –0.066; Mes, –0.074) on the other side.

In summary, lanthanide-induced Si–H activation has allowed functionalization of the silylamide $[\text{N}(\text{SiHMe}_2)_2]^-$ with two different bulky anilines to give tripodal ligands of the composition $[\text{N}\{\text{SiMe}_2\text{NAr}\}_2]^{3-}$. Future work will focus on extending the scope of this reaction to other amines and on exploring the coordination chemistry of these novel ligands.

■ ASSOCIATED CONTENT

📄 Supporting Information

Details of syntheses and characterization for compounds **2a**, **2b**, and **3**, including X-ray data in CIF format for **1a**, **1b**, **2a**·1.5THF, **2b**·3THF, **2a**·*n*-heptane, and **3**, and computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was performed within the Collaborative Research Centre (SFB 706; Selective Catalytic Oxidations Using Molecular Oxygen; Stuttgart) and funded by the German Research Foundation.

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