

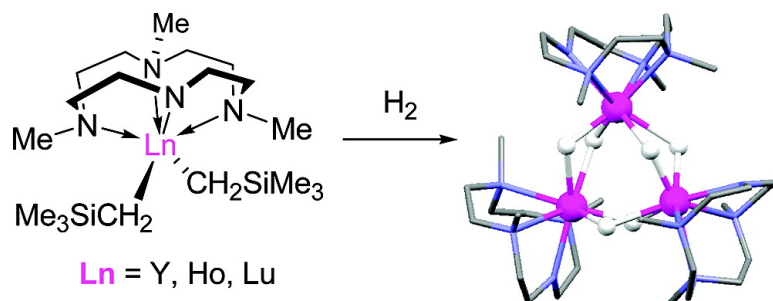
Communication

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 by a Cyclen-Derived [NNNN] Macrocyclic Ancillary Ligand**

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Rare-Earth Metal Alkyl and Hydride Complexes Stabilized by a Cyclen-Derived [NNNN] Macrocyclic Ancillary Ligand

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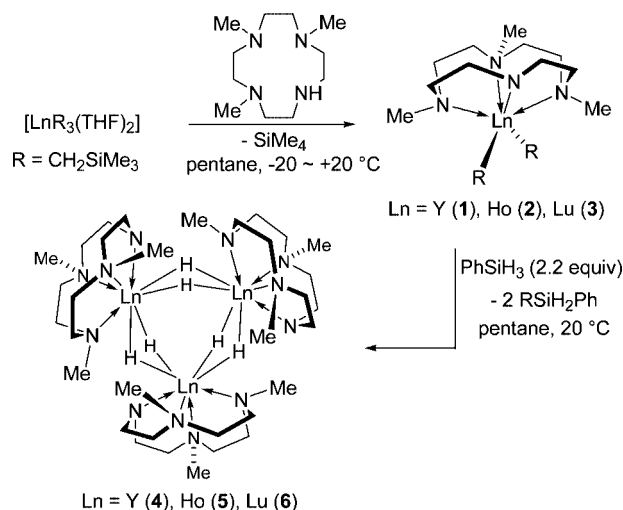
The design of inert ancillary ligands for large, Lewis acidic f-block metal centers often requires the incorporation of a facially coordinating donor set with sufficient steric bulk.^{1,2} Examples include ligands derived from 1,4,7-triazacyclononane (TACN),^{2a-d} 6-amino-6-methyl-1,4-diazepine,^{2c} or crown ethers³ that were used to support rare-earth metal alkyls and alkyl cations. The 12-membered cyclen-derived macrocyclic ligand DOTA (1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetato)^{4a} is known to form inert lanthanide complexes with square antiprismatic coordination geometry, applied as contrast agents in magnetic resonance imaging (MRI).^{4b} We report here that a monoanionic [NNNN] ligand, Me₃TACD (Me₃TACDH = 1,4,7-trimethyl-1,4,7,10-tetraazacyclododecane⁵), provides a macrocyclic ancillary ligand capable of stabilizing Lewis base free rare-earth metal alkyl and hydride fragments and that the hydride complex catalyzes the hydrosilylation of olefins.

Reaction of the tris(alkyl) complex, [Ln(CH₂SiMe₃)₃(THF)₂] with an equimolar amount of Me₃TACDH in pentane afforded the corresponding dialkyl complexes [Ln(Me₃TACD)(CH₂SiMe₃)₂] (Ln = Y, **1**; Ho, **2**; Lu, **3**) in moderate to good isolated yields with concomitant formation of tetramethylsilane (Scheme 1).

The coordination geometry of the yttrium center in **1** is best regarded as “a twisted square antiprism with two vacancies” with the twist angle of ca. 36° (Figure 1).⁶ In order to fill the vacant sites, both Y–C–Si angles are bent sharply (Y1–C10–Si1 117.22(14)° and Y1–C20–Si2 118.67(13)°),⁷ and as a result, two SiMe₃ methyl groups, C11 and C21, are oriented toward the vacancies, although these interactions are not tight enough to be considered as γ-agostic. The yttrium–amide nitrogen distance Y–N1 of 2.23 Å is shorter than the other three yttrium–amine nitrogen bonds of av. 2.55 Å. The amide nitrogen atom has a significant sp² character, as indicated by the sum of the angles around the nitrogen (359.1°) as well as by the bond distances between the carbon atoms and the amide nitrogen (1.435(3)–1.441(3) Å) that are shorter than those for the amine nitrogen (1.475(3)–1.494(3) Å). Thus, the Me₃TACD ligand formally acts as a monoanionic, 10-electron donor in the dialkyl complex **1**. Moreover, the ligand is highly distorted due to the sp² amide nitrogen atom and the resulting coplanar orientation of the five atoms (C–C–N(sp²)-C–C) around the amide nitrogen.

In contrast to the dissymmetric structure observed in the solid state, the ¹H NMR spectrum of **1** in C₆D₆ at ambient temperature showed eight resonances assignable to ring protons, consistent with the complex having C_s symmetry on the NMR time scale. This observation is also supported by the ¹³C{¹H} NMR spectrum that

Scheme 1



only shows four signals attributable to the TACD ring carbons, indicating that the yttrium complex **1** is fluxional and a rapid exchange process between two enantiomers is occurring (Figure 2).⁸ The exchange is probably due to the ring flipping of the TACD macrocycle and the twisting of the alkyl groups via a transition state with a pseudomirror plane.⁹

The alkyl complexes **1–3** were found to react with dihydrogen or PhSiH₃ at room temperature to give the dihydride complexes

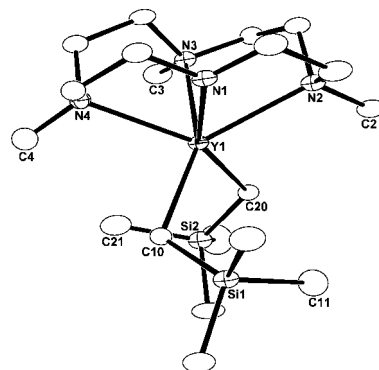


Figure 1. Molecular structure of **1** with thermal ellipsoids at the 30% probability level. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y1–N1 2.227(2), Y1–N2 2.567(2), Y1–N3 2.546(2), Y1–N4 2.527(2), Y1–C10 2.447(3), Y1–C20 2.493(3); N1–Y1–N3 90.32(8), N1–Y1–N2 67.49(8), N1–Y1–N4 72.80(8), N2–Y1–N4 124.97(8), C10–Y1–C20 93.17(10), Y1–C10–Si1 117.22(14), Y1–C20–Si2 118.67(13).

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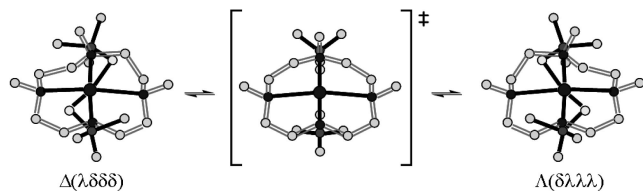


Figure 2. Interconversion between enantiomers of **1**.

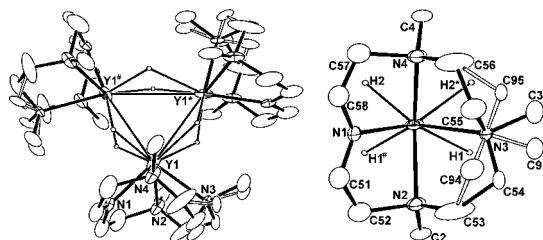


Figure 3. ORTEP drawings of the trimer form (left) and the monomeric unit (right) of **4** with thermal ellipsoids at the 30% probability level. H atoms except for the bridging hydrides are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y1–Y1 3.516(1), Y1–N1 2.335(5), Y1–N2 2.587(5), Y1–N3 2.482(5), Y1–N4 2.589(5), Y1–H1 2.29(6), Y1–H2 2.08(7); N1–Y1–N3 89.06(18), N1–Y1–N2 69.6(2), N1–Y1–N4 69.8(2), N2–Y1–N4 122.51(18), H1–Y1–H2 115(3), Y1[#]–Y1–Y1* 60.0, N1–Y1–H1 149.30(16), N1–Y1–H2 87.6(2).

[Ln(Me₃TACD)H₂]₃ (Y, **4**; Ho, **5**; Lu, **6**) which were isolated in 65–75% yields. In the ¹H NMR spectrum of the yttrium and lutetium complex, the hydride resonance was recorded at δ 6.37 (m) and 9.81 (s) ppm, respectively. The X-ray diffraction study of **4** revealed a trinuclear structure [Y(Me₃TACD)(μ-H)₂]₃ with an interatomic Y–Y distance of 3.5164(9) Å (Figure 3). Complex **4** represents a rare example for trinuclear lanthanide hydrides,¹⁰ and its structure was well reproduced using DFT methods (see Supporting Information). A slightly longer Y–Y distance of 3.55 Å and six almost equivalent Y–H bonds (2.19 and 2.23 Å) were calculated. An NBO analysis of the density indicates that the cohesion of the structure is due to the Y–H bonds. At the second order perturbation theory, Y–Y interactions were found (50 kcal·mol⁻¹), accounting for the increase in stability of **4**. The calculated ¹H NMR chemical shift of δ 6.15 ppm is also in good agreement with the experiment.

Each eight-coordinate yttrium center bonded to four nitrogen atoms of the Me₃TACD ligand and four bridging hydrides adopts a square antiprism coordination geometry. The three vectors joining the amide nitrogen with the opposite amine in each mononuclear unit are arranged in a head-to-tail fashion to form a regular triangle, most likely due to reduction of the steric hindrance between the adjacent NMe groups on TACD macrocycles. The hydride **4** is obtained as a single isomer. This is consistent with the ¹H and ¹³C NMR spectra, indicating a set of eight and four signals, respectively, attributable to only one kind of the TACD ring.

When hydride complexes **4** and **6** were dissolved in C₆D₆, neither formation of the mixed-metal hydride complexes nor exchange of the hydrides between the two complexes was observed, suggesting that the trinuclear framework remains intact in solution. The catalytic activity of the hydride complex **4** in situ generated from **1** in olefin hydrosilylation, nonetheless, is relatively high.^{11a} 1-Hexene was hydrosilylated with PhSiH₃ at 60 °C in the presence of **4** ([Y]₀/[PhSiH₃]₀/[alkene]₀ = 1:43:40 in C₆D₆) with regioselective formation of (*n*-Hex)₂PhSiH₂ (85%, 7 h) and formation of up to 10% of (*n*-Hex)₂PhSiH at longer reaction times (15–19 h).

Hydrosilylation of 1,5-hexadiene with PhSiH₃ (C₆D₆, 60 °C, 100% conversion within 17 h) gave 90–95% of 1,6-bis(phenylsilyl)hexane with 5–10% of phenylsilylcycloheptane. Notably, no (phenylsilylmethyl)cyclopentane was formed, commonly observed in hydrosilylation of 1,5-hexadiene catalyzed by single-site lanthanide catalysts as a result of intramolecular insertion.^{11b} We assume that the hydrosilylation occurs at the intact trimer.

In conclusion, the Me₃TACD ligand has been introduced as a monoanionic ancillary environment for the stabilization of rare-earth metal alkyl and hydride with properties distinct from other monoanionic ligands such as cyclopentadienyl ligands.

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Supporting Information Available: Detailed experimental and computational procedures, spectral data, and crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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