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

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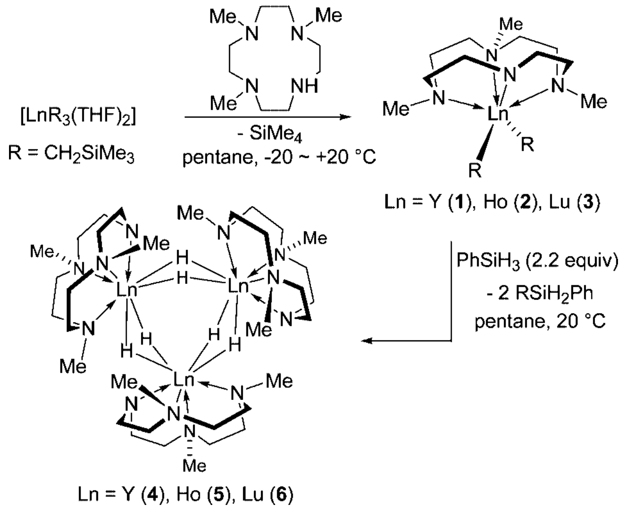
The design of inert ancillary ligands for large, Lewis acidic f-block metal centers often requires the incorporation of a facially coordinating donor set with sufficient steric bulk.[1,2] Examples include ligands derived from 1,4,7-triazacyclononane (TACN),[2a–d] 6-amino-6-methyl-1,4-diazepine,[2e] or crown ethers[3] 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, Me_3TACD (Me_3TACDH = 1,4,7-trimethyl-1,4,7,10-tetraazacyclododecane[5]), 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, $[Ln(CH_2SiMe_3)_3(THF)_2]$ with an equimolar amount of Me_3TACDH in pentane afforded the corresponding dialkyl complexes $[Ln(Me_3TACD)(CH_2SiMe_3)_2]$ (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 $SiMe_3$ 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 sp^2 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 Me_3TACD ligand formally acts as a monoanionic, 10-electron donor in the dialkyl complex **1**. Moreover, the ligand is highly distorted due to the sp^2 amide nitrogen atom and the resulting coplanar orientation of the five atoms (C−C−N(sp^2)−C−C) around the amide nitrogen.

In contrast to the dissymmetric structure observed in the solid state, the ^1H NMR spectrum of **1** in C_6D_6 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 $^{13}C\{^1H\}$ NMR spectrum that 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]

Scheme 1



The alkyl complexes **1**−**3** were found to react with dihydrogen or $PhSiH_3$ at room temperature to give the dihydride complexes

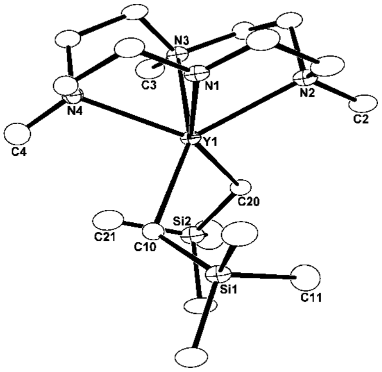


Figure 1. Molecular structure of **1** with thermal ellipsoids at the 30% probability level. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y1−N1 2.227(2), Y1−N2 2.567(2), Y1−N3 2.546(2), Y1−N4 2.527(2), Y1−C10 2.447(3), Y1−C20 2.493(3); N1−Y1−N3 90.32(8), N1−Y1−N2 67.49(8),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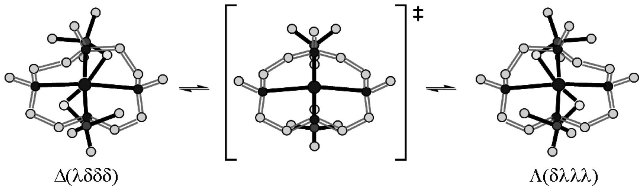

Figure 2. Interconversion between enantiomers of **1**.

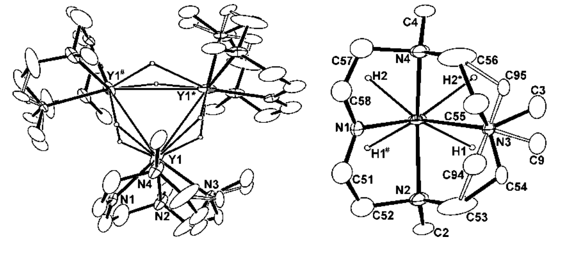

Figure 3. ORTEP drawings of the trimer form (left) and the monomeric unit (right) of **4** with thermal ellipsoids at the 30% probability level. H atoms except for the bridging hydrides are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y1−Y1 3.516(1), Y1−N1 2.335(5), Y1−N2 2.587(5), 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).

$[Ln(Me_3TACD)H_2]_3$ (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 $[Y(Me_3TACD)(\mu\text{-}H)_2]_3$ 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 $kcal\cdot mol^{-1}$), 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 Me_3TACD 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 ^{13}C 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 C_6D_6, 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 $PhSiH_3$ at 60 °C in the presence of **4** ($[Y]_0/[PhSiH_3]_0/[alkene]_0 = 1{:}43{:}40$ in C_6D_6) with regioselective formation of $(n\text{-}Hex)PhSiH_2$ (85%, 7 h) and formation of up to 10% of $(n\text{-}Hex)_2PhSiH$ at longer reaction times (15−19 h). Hydrosilylation of 1,5-hexadiene with $PhSiH_3$ (C_6D_6, 60 °C, 100% conversion within 17 h) gave 90−95% of 1,6-bis(phenylsilyl)hexane with 5−10% of phenylsilacycloheptane. 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 Me_3TACD 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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