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# Selective Assembly of Trinuclear Rare-Earth Alkyl Hydrido Clusters Supported by Amidopyridinate Ligands

Dmitrii M. Lyubov,[†] Christian Döring,[‡] Georgii K. Fukin,[†] Anton V. Cherkasov,[†] Andrei S. Shavyrin,[†] Rhett Kempe,[*,‡] and Alexander A. Trifonov[*,†]

*G.A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of SciencesTropinina 49, GSP-445, 603950 Nizhny Novgorod, Russia, and Lehrstuhl Anorganische Chemie II, Universität Bayreuth, 95440 Bayreuth, Germany*

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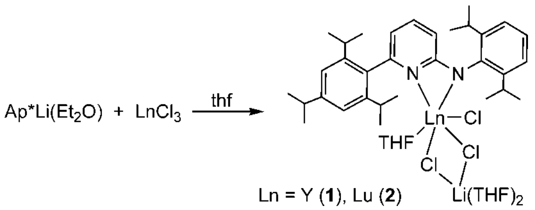
*Summary: The reactions of the bis(alkyl) complexes [Ap*Ln(CH$_2$SiMe$_3$)$_2$(thf)] (Ln = Y, Lu) with both PhSiH$_3$ and H$_2$ result in selective assembly of the novel trinuclear rare-earth alkyl hydrido clusters [(Ap*Ln)$_3$($\mu_2$-H)$_3$($\mu_3$-H)$_2$(CH$_2$SiMe$_3$)(thf)$_2$]. Both cluster compounds are single-component ethylene polymerization catalysts.*

Rare-earth-metal hydrides possess an intriguing variety of unique structural and chemical properties.[1] The rapid development of this area, stimulated by the promising catalytic activity of hydrido complexes, has resulted in considerable contributions to organolanthanide chemistry.[2] Until recently rare-earth-metal hydrides were represented exclusively by sandwich-[1] and half-sandwich-type (“constrained geometry”)[3] monohydride complexes, and very few classes of their non-cyclopentadienyl analogues are known.[4] Assembly of the anionic trinuclear tetrahydride lanthanide species {[Cp$_2$LnH]$_3$H}{Li(THF)$_4$} was reported by Evans in the early 1980s.[1b–d] The first “mono(cyclopentadienyl) dihydrido” complexes were reported in 2001, and their stoichiometric and catalytic chemistry was developed by Hou and co-workers.[5] The synthesis of rare-earth polyhydrido species in coordination environments alternative to that of cyclopentadienyl still remains a challenge.[4] Sterically demanding amidopyridinato ligands[6] were successfully used as a suitable coordination environment for the stabilization of monomeric lanthanide species, and our work has been aimed at the synthesis of related polyhydrido complexes. Herein we report on the selective formation, structure, and properties of trinuclear rare-earth alkyl hydrido clusters.

**Scheme 1. Synthesis of 1 and 2**



Bulky (2,6-diisopropylphenyl)[6-(2,4,6-triisopropylphenyl)pyridin-2-yl]amine (Ap*-H) was used as the ligand precursor for the preparation of the aminopyridinato dichloride, dialkyl, and alkyl hydrido complexes of yttrium and lutetium. Reactions of anhydrous LnCl$_3$ (Ln = Y, Lu) with an equimolar amount of Ap*Li(Et$_2$O)[6b] in THF at 20 °C afforded the ate complexes [Ap*LnCl(thf)($\mu$-Cl)$_2$Li(thf)$_2$] (Ln = Y (**1**), Lu (**2**)) (Scheme 1), which were isolated after recrystallization from THF–hexane mixtures as pale yellow crystals in 78 and 85% yields,

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* To whom correspondence should be addressed. A.A.T.: e-mail, trif@iomc.ras.ru; fax, (+7)8314621497. R.K.: e-mail, kempe@uni-bayreuth.de; fax, (+49)921552157.

[†] G.A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences.

[‡] Universität Bayreuth.

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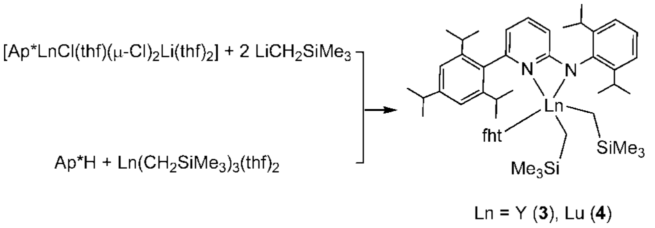
**Scheme 2. Synthesis of 3 and 4**



respectively. Complex **1** has been characterized by an X-ray diffraction study, which revealed its monomeric structure (see the Supporting Information).

Alkylation of complexes **1** and **2** with 2 equiv of $LiCH_2SiMe_3$ in hexane at 0 °C allowed synthesis of the salt-free dialkyl complexes $[Ap^*Ln(CH_2SiMe_3)_2(thf)]$ (Ln = Y (**3**), Lu (**4**)), which were obtained after recrystallization from pentane (**3**) or hexane (**4**) at −20 °C in 68 and 75% yields, respectively (Scheme 2). Complexes **3**[6c] and **4** were also synthesized through alkane elimination from trialkyl complexes and parent aminopyridine in hexane at 0 °C.

Crystallization of **3** and **4** by slow cooling of their concentrated pentane or hexane solutions to −20 °C resulted in single crystals of solvates containing one molecule of solvent per one molecule of complex. X-ray crystal structure investigations have revealed that **3** and **4** are isostructural monomeric complexes (Figure 1). The coordination sphere of the metal atom consists of two nitrogen atoms of the bidentate amidopyridinate ligand, two carbon atoms of the alkyl groups, and one oxygen atom of the THF molecule, resulting in a formal coordination number of 5.

The Y−C bond lengths in complex **3** are slightly longer compared to the appropriate distances in five-coordinated dialkyl yttrium compounds[7a–c] and are very close to the values reported for a related five-coordinated complex supported by a bulky amidinate ligand (2.374(4), 2.384(4) Å).[7d] In complex **4**, which is a rather rare example of a five-coordinated dialkyl lutetium complex, the Lu−C bond lengths are close to the distances previously reported for an analogue containing an anilido−pyridine−imine ligand (2.329(6), 2.349(6) Å).[7e] Complex **4**, despite the low coordination number of its central metal atom, is surprisingly stable at room temperature in $C_6D_6$ solution: no evidence of decomposition has been observed over 1 month. The stability of complex **3** is somewhat lower: under similar conditions over 1 week, ∼10% of the compound was decomposed. In the $^1H$ NMR spectrum of complex **4** at 20 °C the hydrogen atoms of methylene groups attached to the lutetium atom appear as a singlet at −0.63 ppm; in the $^{13}C\{^1H\}$ NMR spectrum the appropriate carbons give rise to a singlet at 46.1 ppm.

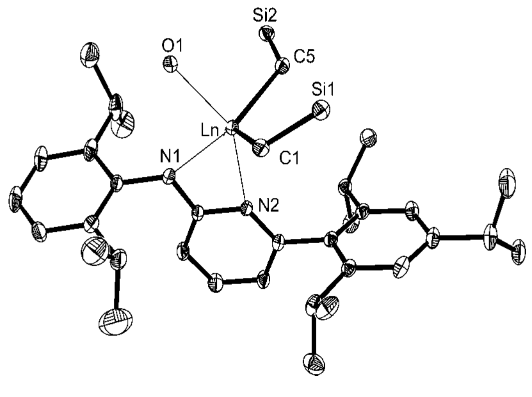
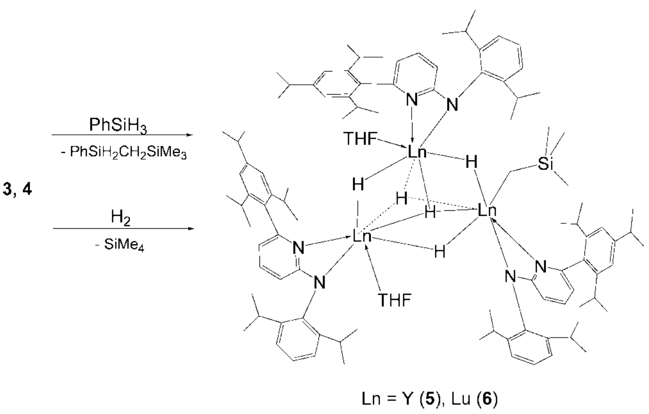


**Figure 1.** ORTEP drawing of **3** and **4** with 30% thermal ellipsoids. The Me groups of $Me_3Si$ and $CH_2$ groups of THF are omitted. Selected bond lengths (Å) and angles (deg): for **3**, M−N(1) = 2.316(4), M−N(2) = 2.415(4), M−C(1) = 2.370(5), M−C(5) = 2.383(5), M−O = 2.337(3), C−Ln−C = 113.20(19), N−Ln−N = 57.33(14); for **4**, M−N(1) = 2.272(2), M−N(2) = 2.371(2), M−C(1) = 2.320(3), M−C(5) = 2.332(3), M−O = 2.2907(19), C−Ln−C = 113.10(9), N−Ln−N = 58.44(7).

**Scheme 3. Synthesis of 5 and 6**



The most common synthetic route to lanthanide hydrido complexes is σ-bond metathesis reaction of parent alkyls under treatment with dihydrogen[2c,f] or phenylsilane.[8] Hou and coworkers have demonstrated that hydrogenolysis of the cyclopentadienyl-supported dialkyl complexes $Cp'Ln(CH_2SiMe_3)_2(thf)$ ($Cp' = C_5Me_4SiMe_3$, Ln = Sc, Y, Gd, Dy, Ho, Er, Tm) affords the tetranuclear polyhydrido clusters $[Cp'Ln(\mu\text{-}H)_2]_4(thf)_n$, while the reaction with $PhSiH_3$ in the case of lutetium results in the formation of the dimeric alkyl hydrido complex $[Cp'Lu(\mu\text{-}H)(CH_2SiMe_3(thf)]_2$.[5] We have found that the reactions of **3** and **4** with both $PhSiH_3$ (1:2 molar ratio, 0 °C) and $H_2$ (5 atm, 15 °C, 24 h) smoothly occur in hexane under the aforementioned conditions and result in formation of the unusual trinuclear alkyl hydrido clusters $[(Ap^*Ln)_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)_2(CH_2SiMe_3)(thf)_2]$ (Ln = Y (**5**), Lu (**6**)), which were isolated after recrystallization from hexane at −20 ° C in 58 and 64% yields, respectively (Scheme 3). Surprisingly, all attempts to remove the remaining alkyl group and to obtain polyhydrido clusters consisting of $Ap^*LnH_2$ units failed: the use of a 10-fold molar excess of $PhSiH_3$ or an increase in the reaction time with $H_2$ afforded only complexes **5** and **6**. Until recently very few examples of dimeric alkyl hydrido rare -earth complexes have been described,[5c,8,9] and to the best of our knowledge complexes **5** and **6** present the first examples of alkyl hydrido clusters.

Complexes **5** and **6** crystallize from hexane as solvates with one molecule of the solvent per unit. Exposure of complexes **5** and **6** at room temperature to dynamic vacuum (1 h) allowed us to remove hexane and to obtain nonsolvated compounds. Complexes **5** and **6** are extremely air- and moisture-sensitive crystalline solids; they are highly soluble in hexane and pentane. Complexes **5** and **6** can be kept in the solid state or in $C_6D_6$ solutions under dry argon or in sealed evacuated tubes at 20 °C for several weeks without decomposition. Clear yellow single-crystal samples of **5** suitable for an X-ray crystal structure determination were obtained by slowly cooling its hexane

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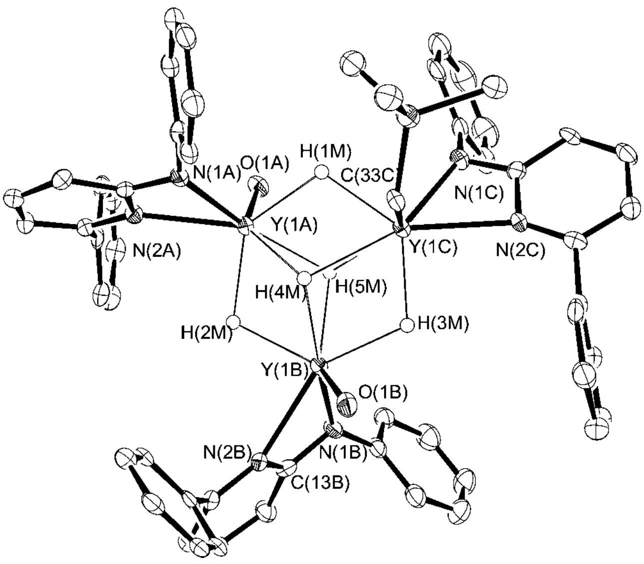

**Figure 2.** ORTEP drawing of **5** with 30% thermal ellipsoids. The *i*-Pr groups of Ap* and the $CH_2$ groups of THF are omitted. Selected bond lengths (Å) and angles (deg): Y(1A)−N(1A) = 2.323(2), Y(1A)−O(1A) = 2.3496(19), Y(1A)−N(2A) = 2.459(2), Y(1A)−Y(1B) = 3.4408(4), Y(1A)−Y(1C) = 3.5158(4), Y(1B)−N(1B) = 2.307(2), Y(1B)−O(1B) = 2.3510(19), Y(1B)−N(2B) = 2.477(2), Y(1B)−Y(1C) = 3.5058(4), Y(1C)−N(1C) = 2.331(2), Y(1C)−C(33C) = 2.402(3), Y(1C)−N(2C) = 2.503(2), Y(1B)−Y(1A)−Y(1C) = 60.512(8), N(1A)−Y(1A)−N(2A) = 56.70(8), N(1B)−Y(1B)−N(2B) = 56.64(7), N(1C)−Y(1C)−N(2C) = 56.40(7).

solution to −20 °C. X-ray single-crystal structure analysis has shown that **5** adopts a trimeric structure (Figure 2), where three Ap*Y fragments are bound by three $\mu_2$-H and two $\mu_3$-H ligands, while the alkyl group remains terminal. The coordination sphere of two yttrium atoms is determined by two nitrogen atoms of Ap* ligands, four hydrido ligands, and the oxygen atom of the coordinated THF molecule. In the coordination environment of the third yttrium atom there is no THF molecule, but it is covalently bound to the $CH_2SiMe_3$ group. The hexanuclear $Y_3H_3$ core is nearly planar (the maximum deviation from the $Y_3H_3$ plane is 0.132 Å), and the two remaining hydrogen ligands are situated above and below this plane (1.023 and 1.089 Å). The Y−($\mu_2$-H) distances are 2.08−2.16 Å, whereas the Y−($\mu_3$-H) distances are in the range of 2.19−2.42 Å. The Y−Y distances in complex **5** (3.5158(4), 3.4408(4), and 3.5058(4) Å) are noticeably shorter compared to the related distances in dimeric hydrides supported by bulky guanidinate ligands (3.6522(5)[10] and 3.6825(5) Å[4b]). The Y−C bond in **5** (2.402(5) Å) is slightly elongated compared to that in the starting dialkyl derivative **3**.

The Ap* ligands appear as complex sets of signals in the $^1H$ NMR spectra ($C_7D_8$, −80 to −60 °C); however, the fact that the para protons of the pyridyl fragments give rise to three signals (**5**, 6.67, 6.78, and 6.83 ppm (dd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 7.2 Hz); **6**:, 6.62, 6.73, and 6.78 ppm (dd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 7.2 Hz)) reflects that their nonequivalence resulted from the unsymmetric structures of **5** and **6**. Three slightly broadened singlets (9.08, 12.25, and 12.37 ppm) with an integral intensity ratio of 3:1:1 in the $^1H$ NMR spectrum of **6** correspond to the hydrido ligands. Apparently the signal at 9.08 ppm is due to $\mu_2$-hydrido ligands, while the signals at 12.25 and 12.37 ppm correspond to the $\mu_3$-hydrido ligands situated in the apical positions of the trigonal bipyramid $Lu_3(\mu_3\text{-}H)_2$. The signals of the hydrido ligands of **6** are substantially shifted to low field compared to the positions of respective signals of the reported cyclopentadienyl polyhydrido clusters (8.81 ppm),[5c] which corresponds to the tendency observed in the series of yttrium hydrides supported by cyclopentadienyl, cyclopentadienylamido, amidinate, and guanidinate ligands.[4b] In the $^1H$ NMR spectra of **5** the $\mu_2$-hydrido ligands appear as a triplet of doublets at 5.66 ppm with intensity corresponding to three protons. The multiplicity of this signal results from the coupling of each hydrido ligand with two neighboring yttrium nuclei ($^1J_{YH}$ = 20.8 Hz) and with the third yttrium atom ($^1J_{YH}$ = 5.8 Hz) situated across the planar $Y_3H_3$ core. Unfortunately, the signals corresponding to the $\mu_3$-hydrido ligands cannot be assigned unambiguously, since they overlap with signals of aromatic protons. Nevertheless, the existence of cross-peaks in the COSY spectrum of **5** between the triplet of doublets at 5.66 ppm and the multiplet between 6.9 and 7.3 ppm gives evidence of the location of these signals in the area 6.9−7.3 ppm. The protons of the methylene group attached to the metal atom are nonequivalent in both **5** and **6** and appear in the $^1H$ NMR spectra at 293 K as a set of two doublets (at −1.10 and −0.03 ppm ($^2J_{HH}$ = 9.0 Hz) for **5** and at −1.35 and −0.42 ppm ($^2J_{HH}$ = 9.7 Hz) for **6**). Thus, the $^1H$ NMR spectra of **5** and **6** prove that the trimeric structures of these compounds are retained in solutions in noncoordinating solvents.

Complexes **5** and **6** catalyze ethylene polymerization (20 °C, ethylene pressure 0.5 atm) but are inactive in styrene poly merization. The ethylene polymerization activity of complex **5** was found to be 560 g $mmol^{-1}$ $bar^{-1}$ $h^{-1}$, but the catalyst was deactivated in 3 h. The lutetium complex **6** was less active (168 g $mmol^{-1}$ $bar^{-1}$ $h^{-1}$) but did not demonstrate loss of the reaction rate over 1 day.

In summary, it was found that the reactions of dialkyl complexes $[Ap^*Ln(CH_2SiMe_3)_2(thf)]$ (Ln = Y, Lu) with both $PhSiH_3$ and $H_2$ result in selective assembly of the novel trinuclear rare-earth alkyl hydrido clusters $[(Ap^*Ln)_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)_2(CH_2SiMe_3)(thf)_2]$. The yttrium complex has been structurally characterized. Both compounds show moderate activity in ethylene polymerization. Further studies on the synthesis and reactivity of this novel family of alkyl hydrido clusters are currently in progress.

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**Supporting Information Available:** Text, tables, figures, and CIF files giving detailed information on the synthesis and characterization of the lanthanide complexes described here and crystallographic details of the structures determined by X-ray crystal structure analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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