

Hydrido Complexes of Yttrium and Lutetium Supported by Bulky Guanidinato Ligands $[\text{Ln}(\mu\text{-H})\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\}_2]_2$ ($\text{Ln} = \text{Y}, \text{Lu}$): Synthesis, Structure, and Reactivity

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Keywords: Rare earths / Alkyl complexes / Hydrido complexes / Guanidinato ligands / Polymerization / Hydrosilylation

Lewis base free hydrido complexes of yttrium and lutetium supported by bulky cyclohexyl-substituted guanidinato ligands, $[\text{Ln}(\mu\text{-H})\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\}_2]_2$ ($\text{Ln} = \text{Y}, \text{Lu}$), were synthesized and characterized. Single-crystal X-ray diffraction studies revealed dimeric structures. ^1H NMR spectroscopy shows that complex $[\text{Y}(\mu\text{-H})\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\}_2]_2$ retains its dimeric structure in C_6D_6 solution. Scrambling of the hydrido complexes $[\text{Ln}(\mu\text{-H})\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\}_2]_2$ ($\text{Ln} = \text{Y}, \text{Lu}$) in C_6D_6 resulted in an equilibrium mixture containing the heterodimetallic species $[(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2]_2\text{Y}(\mu\text{-H})_2\text{Lu}\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\}_2]$, indicating the dissociation of dimers and the presence of monomeric species in solution. Both compounds initiate the polymerization of ethylene: the activity of the cyclohexyl-substituted yttrium complex, $[\text{Y}(\mu\text{-H})\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\}_2]_2$, is much lower than that of the isopropyl-substituted analogue, $[\text{Y}(\mu\text{-H})\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NiPr})_2\}_2]_2$,

while in the case of lutetium the activities of $[\text{Ln}(\mu\text{-H})\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NR})_2\}_2]_2$ ($\text{R} = i\text{Pr}, \text{Cy}$) are similar. Complexes $[\text{Ln}(\mu\text{-H})\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NR})_2\}_2]_2$ ($\text{Ln} = \text{Y}, \text{Lu}; \text{R} = i\text{Pr}, \text{Cy}$) were shown to catalyze efficiently the hydrosilylation of 1-nonene with PhSiH_3 (at a 1:1 substrates mol ratio) to give the terminal silane $\text{PhSiH}_2(n\text{-C}_9\text{H}_{19})$ exclusively. If the hydrosilylation reaction is carried out in the presence of a twofold molar excess of 1-nonene, double addition takes place and leads to the formation of tertiary silane $\text{PhSiH}(n\text{-C}_9\text{H}_{19})_2$, which was obtained in 96 % yield. The hydrido complexes $[\text{Ln}(\mu\text{-H})\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NiPr})_2\}_2]_2$ ($\text{Ln} = \text{Y}, \text{Lu}$) efficiently initiate the ring-opening polymerization of ϵ -caprolactone to give polymers with molar mass up to 80000.

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Introduction

Organolanthanide sandwich and half-sandwich-type hydrido complexes have played an important role in the development of organolanthanide chemistry^[1] since the discovery of the first hydride in the early 1980s.^[2] These compounds attract considerable attention due to their catalytic activity in a variety of olefin transformations^[3] and extremely high reactivity in stoichiometric reactions, which allows even C–F bond activation.^[4] However, despite the high

potential of such species, the study of these compounds has so far been limited almost to cyclopentadienyl derivatives,^[5] and their analogues in alternative coordination environments still remain poorly investigated.^[6] The large size and highly positive charge of the Ln^{III} ions, the Lewis acidity of lanthanides and therefore the high sensitivity of their derivatives to coordination unsaturation of the metal center make crucial the design of new ligand systems facilitating the synthesis of stable and isolable complexes. Moreover tuning the electronic and steric properties of the ancillary ligation can allow modification and control of the reactivity of the complexes. Tetrasubstituted guanidinato ligands have been recently employed for early- and late-transition metals^[7] and were shown to be the promising ligand system for the synthesis of lanthanide alkyl complexes.^[8] We employed the advantages of the $\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NiPr})_2\}$ coordination environment for the stabilization of lanthanide hydrides and synthesized a novel family of dimeric Lewis base free hydridolanthanide complexes, $[\text{Ln}(\mu\text{-H})\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NiPr})_2\}_2]_2$ ($\text{Ln} = \text{Y}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Yb}, \text{Lu}$).^[9] The samarium and yttrium derivatives have shown high catalytic activity in ethylene polymerization. To date, the number of known monomeric hydridolanthanide species is very limited,^[4,10] and the

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synthesis of structurally defined monomeric hydrido complexes still remains challenging. The fact that bulky cyclohexyl-substituted guanidinato ligands allowed the synthesis of neutral monomeric bis(guanidinato)lanthanide chlorides^[8d] encouraged us to test them for the synthesis of hydride species, in the expectation that the steric repulsion of the ligands can enable the existence of monomeric complexes. We report here on the synthesis and structure of hydridoyttrium and hydridolutetium complexes $[\text{Ln}(\mu\text{-H})\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\}_2]_2$ ($\text{Ln} = \text{Y}, \text{Lu}$) supported by bulkier cyclohexyl-substituted guanidinato ligands and their catalytic activity in the reactions of olefin polymerization and hydrosilylation.

Results and Discussion

The most efficient synthetic route to hydridolanthanide complexes is the σ -bond metathesis reaction of the parent alkyl compounds on treatment with dihydrogen^[3c,3d] or phenylsilane.^[11] For the synthesis of the hydridolanthanide derivatives supported by isopropyl-substituted guanidinato ligands, $[\text{Ln}(\mu\text{-H})\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NiPr})_2\}_2]_2$ ($\text{Ln} = \text{Y}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Yb}, \text{Lu}$),^[9] we successfully used the reaction of related alkyl complexes, $[\text{Ln}(\text{CH}_2\text{SiMe}_3)\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NiPr})_2\}_2]$, with PhSiH_3 in hexane at room temperature. The same synthetic approach was envisaged for the preparation of yttrium and lutetium analogues containing bulkier cyclohexyl-substituted guanidinato ligands. Previously, we had reported on the attempt to synthesize complex $[\text{Y}(\text{CH}_2\text{SiMe}_3)\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\}_2]$ by the alkylation reaction of chloridobis(guanidinato)yttrium complex $[\text{YCl}\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\}_2]\text{thf}$ with $\text{Li}(\text{CH}_2\text{SiMe}_3)$, which afforded an inseparable mixture of the alkyl compound and its decomposition products.^[8d] We have found that the reactions of *ate*-complexes $[\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\}_2\text{Ln}(\mu\text{-Cl})_2\text{-Li}(\text{thf})_2]$ ($\text{Ln} = \text{Y}$ (**1**), Lu (**2**))^[8d] with $\text{LiCH}_2\text{SiMe}_3$ occur in hexane at 0 °C cleanly and allow the synthesis of alkyl complexes $[\text{Ln}(\text{CH}_2\text{SiMe}_3)\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\}_2]$ ($\text{Ln} = \text{Y}$ (**3**), Lu (**4**)) (Scheme 1).

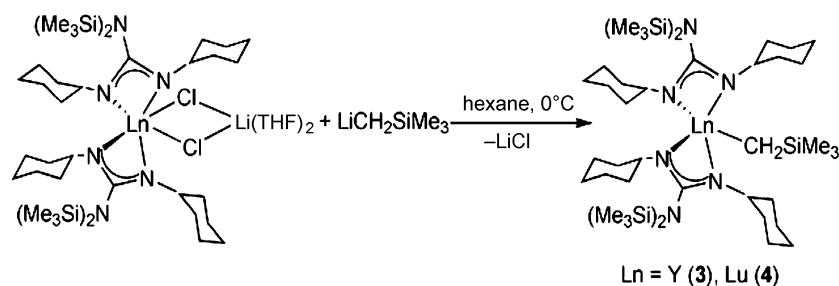
Yttrium derivative **3** was isolated as a colorless microcrystalline solid in 64% yield after separation of LiCl and recrystallization from hexane at -18 °C. Unfortunately in the case of lutetium the same handling procedure afforded a viscous colorless oil (90% yield), and all attempts to crystallize alkyl complex **4** failed. Compounds **3** and **4** are

highly moisture- and air-sensitive. They are fairly soluble in commonly used organic solvents (thf, toluene, hexane, pentane). Complexes **3** and **4** were characterized by ^1H , ^{13}C NMR and IR spectroscopy. For compound **3**, correct microanalysis data were obtained, while for the lutetium analogue **4** characterization was hampered by the difficulty of sample preparation; nevertheless, the lutetium metal microanalysis data correspond to the proposed formula. In an inert atmosphere, complexes **3** and **4** can be stored in the crystalline state at -20 °C without decomposition, while in the C_6D_6 solution at 20 °C they slowly decompose with elimination of Me_4Si . The decomposition is complete in three days. Complexes **3** and **4** do not contain coordinated thf molecules. In the ^1H NMR spectrum of complex **3** at 20 °C, the hydrogen atoms of the methylene group attached to the yttrium atom appear as a doublet at -0.19 ppm ($^2J_{\text{YH}} = 3.0$ Hz); in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum the appropriate carbon atoms give rise to a doublet at $\delta = 35.1$ ppm ($^2J_{\text{YC}} = 38.3$ Hz). In the case of lutetium derivative **4**, the singlet at $\delta = -0.49$ ppm in the ^1H NMR spectrum and the singlet at $\delta = 40.0$ ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum correspond to the methylene fragment CH_2Lu . The guanidinato ligands give the expected sets of signals in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra.

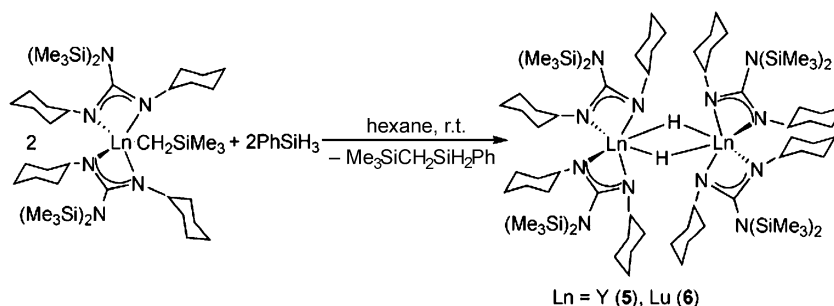
The σ -bond metathesis reactions of alkyl complexes **3** and **4** with phenylsilane were employed as a synthetic approach to bis(guanidinato)lanthanide hydrides. The reactions of **3** and **4** with equimolar amounts of PhSiH_3 were carried out in hexane at 0 °C and resulted in the formation of hydrido complexes $[\text{Ln}(\mu\text{-H})\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\}_2]_2$ [$\text{Ln} = \text{Y}$ (**5**), Lu (**6**)]. Concentration of the reaction mixture and cooling to -18 °C allowed isolation of complexes **5** and **6** as colorless crystalline solids in 76 and 64% yield, respectively (Scheme 2).

Hydrido complexes **5** and **6** are extremely air- and moisture-sensitive colorless crystalline solids. They are sparingly soluble in aromatic hydrocarbons and in hexane. Complexes **5** and **6** can be kept in the solid state in an inert atmosphere at 0 °C for several weeks without decomposition. The ^1H NMR samples of **5** and **6** in C_6D_6 do not show any traces of decomposition or solvent metalation for at least one week at 20 °C.

Clear, colorless single crystals of **5** and **6** suitable for structure determination by single-crystal X-ray diffraction were obtained by slow cooling of their hexane solutions



Scheme 1.



Scheme 2.

from 20 to -18°C . Complex **5** crystallizes as solvate with one molecule of hexane per asymmetric unit, while crystals of compound **6** do not contain the solvent molecules. The molecular structures of complexes **5** and **6** are depicted in Figure 1 and Figure 2 respectively.

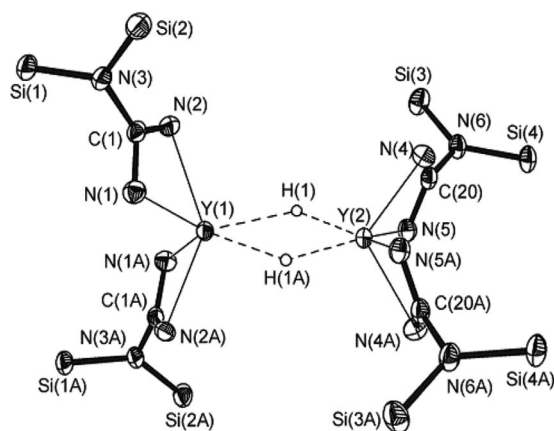


Figure 1. ORTEP diagram (30% probability thermal ellipsoids) of $[\text{Y}(\mu\text{-H})\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\}_2]_2$ (**5**). Methyl radicals of SiMe_3 groups and cyclohexyl fragments are omitted for clarity. Selected bond lengths [Å] and angles [$^\circ$]: $\text{Y}(1)\text{-N}(1)$ 2.332(3), $\text{Y}(2)\text{-N}(4)$ 2.337(3), $\text{Y}(1)\text{-N}(2)$ 2.404(3), $\text{Y}(2)\text{-N}(5)$ 2.406(3), $\text{C}(1)\text{-N}(2)$ 1.303(4), $\text{N}(4)\text{-C}(20)$ 1.327(4), $\text{C}(1)\text{-N}(1)$ 1.340(4), $\text{N}(5)\text{-C}(20)$ 1.312(4), $\text{C}(1)\text{-N}(3)$ 1.430(4), $\text{N}(6)\text{-C}(20)$ 1.447(4), $\text{Y}(1)\text{-H}(1)$ 2.25(4), $\text{Y}(2)\text{-H}(1)$ 1.95(4), $\text{Y}(1)\text{-Y}(2)$ 3.6522(5); $\text{C}(1)\#1\text{-Y}(1)\text{-C}(1)$ 121.53(13), $\text{C}(20)\text{-Y}(2)\text{-C}(20)\#1$ 120.76(14), $\text{N}(2)\text{-C}(1)\text{-N}(1)$ 115.3(3), $\text{N}(5)\text{-C}(20)\text{-N}(4)$ 116.1(3), $\text{Y}(1)\text{-H}(1)\text{-Y}(2)$ 120.4(2).

Single-crystal X-ray diffraction analysis has shown that complexes **5** and **6** have similar structures: they do not contain coordinated Lewis bases and adopt dimeric structures in which two μ -hydrido ligands bridge two metal atoms (Figure 1 and Figure 2). The coordination sphere of the metal centers is determined by the four nitrogen atoms of the two guanidinato ligands and by two bridging hydrido ligands. The formal coordination number of the metal atom is 6.

In the planar tetranuclear Y_2H_2 -core, the Y-H bond lengths are noticeably different: 1.95(4) and 2.25(4) Å, and they are surprisingly shorter than the related distances in the previously reported hydridoyttrium complex containing isopropyl-substituted guanidinato ligands, $[\text{Y}(\mu\text{-H})\{(\text{Me}_3\text{Si})_2\text{NC}(\text{N}i\text{Pr})_2\}_2]_2$ (**7**) [2.15(3) and 2.50(4) Å]. The $\text{Y}\cdots\text{Y}$ distance in **5** [3.6522(5) Å] is shorter than the $\text{Y}\cdots\text{Y}$ distance

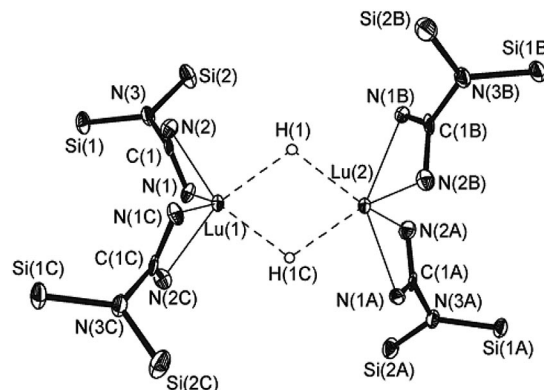
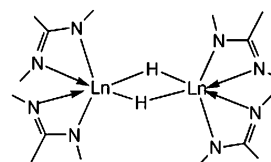


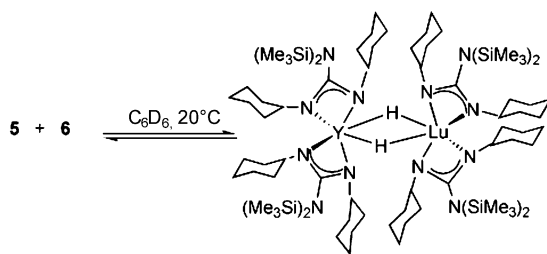
Figure 2. ORTEP diagram (30% probability thermal ellipsoids) of $[\text{Lu}(\mu\text{-H})\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\}_2]_2$ (**6**). Methyl radicals of SiMe_3 groups and cyclohexyl fragments are omitted for clarity. Selected bond lengths [Å] and angles [$^\circ$]: $\text{Lu}(1)\text{-N}(1)$ 2.348(6), $\text{Lu}(1)\text{-N}(2)$ 2.265(7), $\text{C}(1)\text{-N}(1)$ 1.304(12), $\text{C}(1)\text{-N}(2)$ 1.336(10), $\text{C}(1)\text{-N}(3)$ 1.444(11), $\text{Lu}(1)\text{-Lu}(1)\#2$ 3.5717(18), $\text{Lu}(1)\text{-H}(1)$ 2.24, $\text{Lu}(1)\text{-H}(1)\#2$ 2.2; $\text{C}(1)\#1\text{-Lu}(1)\text{-C}(1)$ 119.9(3), $\text{N}(2)\text{-C}(1)\text{-N}(1)$ 115.7(8), $\text{Lu}(1)\text{-H}(1)\text{-Lu}(1)\#1$ 105.0(3).

in complex **7** [3.6825(5) Å]. The dihedral angle between the $\text{C}(1)\text{Y}(1)\text{C}(1\text{A})$ and the $\text{C}(20)\text{Y}(2)\text{C}(20\text{A})$ planes in **5** is $90.9(3)^\circ$. The coordination mode and geometric parameters of the guanidinato ligands in complex **5** differ noticeably from those in compound **7**. All four chelating guanidinato ligands in **5** are bonded to the metal atom in a similar fashion: by one short and one long Y-N bond [**5**: 2.404(3), 2.332(3) and 2.406(3), 2.337(3) Å; **7**: 2.349(2), 2.365(2) Å]. The bonding situation within the NCN fragments of the guanidinato ligands in **5** shows evidence of a localized π system, since one C-N bond is short [1.303(4), 1.312(4) Å], while the second one is long [1.340(4), 1.327(4) Å]. The geometric parameters of the YNCN metallacycles in **5** are different from those observed in complex **7** and are consistent with a localized resonance structure depicted in Figure 3.

Figure 3. Localized resonance structure of **5**.

Unlike the Y...Y distances in complexes **5** and **7**, the Lu...Lu distances in **6** [3.572(2) Å] and [Lu(μ-H){(Me₃Si)₂NC(NiPr)₂}₂]₂ (**8**) [3.5767(3) Å] are similar. The values of the dihedral angles between two guanidinato ligands and the metal atom in complexes **6** and **8** are 90.0(4) and 86.8(3)°, respectively. The Lu–N distances in **6** [2.265(7), 2.348(6) Å] and **8** [2.304(2), 2.315(2) and 2.267(2), 2.371(2) Å] are comparable and reflect the asymmetric fashion of coordination of the guanidinato ligands.

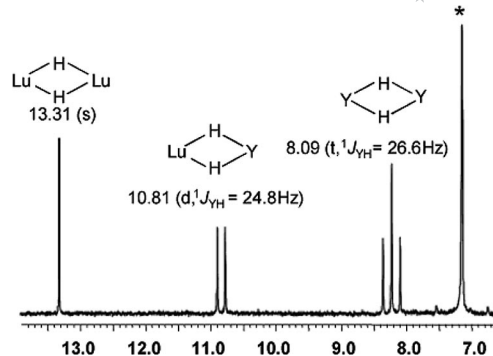
The retention of a dimeric structure in complex **5** in C₆D₆ solution is proved by NMR spectroscopy. The ¹H and ¹³C{¹H} NMR spectra of complex **5** (20 °C, C₆D₆) are consistent with a dimeric molecule with an internal mirror plane. The hydrido ligands appear in the ¹H NMR spectrum of **5** as a sharp, well-resolved triplet at δ = 8.09 ppm (¹J_{YH} = 26.6 Hz), which indicates that each hydrido ligand couples with two equivalent ⁸⁹Y nuclei. In the ¹H NMR spectrum of complex **6** the hydrido ligands give rise to a singlet at δ = 13.31 ppm. For both complexes **5** and **6** the signals corresponding to hydrido ligands are substantially shifted lowfield relative to the respective signals of the other reported Y and Lu hydrides.^[2,3c,3d,6a,6b,11–14] The ¹H NMR spectrum of complex **5** does not show any evidence of the presence of monomeric hydrido species. The dissociation of the dimeric hydrido complexes **5** and **6** and the existence of a monomer–dimer equilibrium on the chemical time scale was proved by scrambling these compounds in C₆D₆ solution. In approximately 24 h after mixing the compounds, an equilibrium mixture of homometallic complexes **5** and **6** and heterodimetallic complex [(Me₃Si)₂NC(NCy)₂]₂Y(μ-H)₂Lu{(Me₃Si)₂NC(NCy)₂}] was observed (Scheme 3).



Scheme 3.

The hydrido ligand of the heterodimetallic complex appears as a diagnostic doublet at δ = 10.81 ppm (¹J_{YH} = 24.8 Hz) (Figure 4). Formerly, similar behavior was described for hydridolanthanide complexes supported by a linked amido-cyclopentadienyl ligand.^[14c]

The catalytic tests of complexes **5** and **6** in ethylene polymerization were carried out under rigorously anaerobic conditions in a sealed glass manometric system (volume of toluene: 5 mL; catalyst concentration: 5.89 × 10^{−6} and 6.83 × 10^{−6} mol L^{−1}; temperature: 20 °C; ethylene pressure: −0.5 atm), which allows monitoring the polymerization process by consumption of the monomer. Catalyst efficiencies were estimated both by monomer conversion and by quenching the polymerization reaction after measured time

Figure 4. ¹H NMR spectrum of mixture of **5** and **6** (hydride region, C₆D₆, 20 °C) after 24 h. (* - C₆D₅H).

intervals and weighing the quantity of polyethylene produced. The ethylene polymerization activity of hydrido-yttrium complex **5** (65 gmmol^{−1} atm^{−1} h^{−1}) was found to be much lower than that of related complex **7** (442 gmmol^{−1} atm^{−1} h^{−1}). The catalytic activity of complex **6** (76 gmmol^{−1} atm^{−1} h^{−1}) is comparable to the activity of the isopropyl-substituted analogue, [Lu(μ-H){(Me₃Si)₂NC(NiPr)₂}₂]₂ (**8**)^[9a] (83 gmmol^{−1} atm^{−1} h^{−1}). Both complexes **5** and **6** are inactive in the polymerization of propylene or styrene.

Hydrosilylation of olefins by rare earth catalysts is a well-known process, and alkyl and hydrido complexes of the metallocene^[15] and post-metallocene^[16] type have shown high activity and selectivity in this reaction. The mechanism and energetics of the hydrosilylation catalytic cycle have been investigated.^[17] We have tested the activity of complexes **5**–**8** as catalysts of hydrosilylation of olefins with PhSiH₃. The catalytic tests were carried out at a 1:1 olefin/silane mol ratio in benzene or C₆D₆ solutions at 20 °C in the presence of 2 mol-% of complexes **5**–**8**. 1-Nonene was found to react with PhSiH₃ in the presence of complexes **5**–**8** to give only the anti-Markovnikov addition product PhSiH₂(*n*-C₉H₁₉) within 4–6 h in quantitative yields. Complexes **5**–**8** do not initiate either 1-nonene polymerization or PhSiH₃ dehydrogenative coupling, thus providing clear conversion of 1-nonene to PhSiH₂(*n*-C₉H₁₉). No reaction was observed for PhSiH₃ with cyclohexene, styrene, or norbornene under similar conditions. The steric bulk of the ligands apparently limits the reactivity of the catalysts such that only 1-nonene reacts at a measurable rate. Interestingly, if the reaction of PhSiH₃ was carried out with a twofold molar excess of 1-nonene in the presence of complexes **5**–**8** under similar conditions, the product of a double terminal addition, PhSiH(*n*-C₉H₁₉)₂, was isolated in high yields.

Rare earth hydrido complexes used as initiators for the ring-opening polymerization of cyclic esters are, to the best of our knowledge, rather limited.^[18] Yasuda has successfully used [SmH(C₅Me₅)₂]₂ for the homopolymerization of ε-caprolactone (ε-CL) as well as for the copolymerization of polar monomers such as ε-caprolactone (or methylmethacrylate) with ethylene. By using this highly active samarocene hydride, high molar mass polymers ($\bar{M}_n > 70\,000$) with the lowest molar mass distribution ever reported, ($\bar{M}_w/\bar{M}_n$

Table 1. Polymerization of ϵ -CL initiated by **7** or **8** in thf at 23 °C.

Run	Initiator	$[\text{H}^-]_0$ ^[a] [mmol L ⁻¹]	$[\epsilon\text{-CL}]_0$ [mmol L ⁻¹]	$[\epsilon\text{-CL}]_0/[\text{H}^-]_0$	Reaction time [min]	$(\bar{M}_n)_{\text{theo}}$ ^[b] [g mol ⁻¹]	$(\bar{M}_n)_{\text{SEC}}$ ^[c] [g mol ⁻¹]	$\bar{M}_w/\bar{M}_n$ ^[d,e]
1	7	21.5	631	29	15	3 300	7 850	2.5
2	7	19.1	1082	57	15	6 500	11 650	3.0
3	7	6.4	451	70	45	8 000	16 600	4.2
4	7	20.6	1984	96	15	10 950	17 600	2.2
5	7	6.5	1002	154	45	17 600	37 674	2.1
6	7	5.5	1804	328	45	37 400	79 000	2.0
7	8	0.5	25	50	15	5 700	13 200	2.6
8	8	5.4	451	84	45	9 600	18 050	2.3
9	8	0.5	42	84	15	9 600	13 100	3.5
10	8	7.9	1002	127	45	14 500	37 300	2.4
11	8	5.3	1804	320	45	36 500	69 900	1.8

[a] $[\text{H}^-]_0 = [1/2]_0 = [\textbf{7} \text{ or } \textbf{8}]_0$. [b] Calculated from ¹H NMR analysis. [c] Calculated for one growing polymer chain per metal atom with $(\bar{M}_n)_{\text{theo}} = ([\epsilon\text{-CL}]_0/[\text{H}^-]_0 \times 114 \times \text{conversion})$. [d] SEC values of precipitated polymer samples corrected with the coefficient 0.56. [e] Molar mass distribution calculated from SEC chromatogram traces.

<1.08), for such elevated mass values have been obtained in a living process.^[18c,18d] AB type block copolymerization of ϵ -CL with ethylene have also been observed in the presence of the organolanthanide hydride initiators $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_2\text{-2-Me}_3\text{Si-4-R})_2\text{LnH}]_2$ (Ln = Y, R = *t*BuMe₂Si; Ln = Sm, R = *t*Bu), $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_2\text{-2-Me}_3\text{Si})_2\text{SmH}]_2$, and $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2\text{SmH}]_2$.^[18c,18f]

Complexes **7** and **8** do indeed efficiently polymerize ϵ -caprolactone in thf within 15–45 min at room temperature. The reaction is almost immediate: for solutions with a high concentration of initiator (20 mmol L⁻¹), the polymerization is (visually) instantaneous, and a colorless gel is formed within less than 30 s, while lower initiator concentrations yield much less viscous solutions. In all experiments, quantitative monomer conversion is always obtained. Yet, if one supposes that the hydride species **7** or **8** are the real initiating species, the polymerization remains uncontrolled, regardless of the experimental conditions and the metallic hydride used. Molar masses obtained from size exclusion chromatography (SEC), $(\bar{M}_n)_{\text{SEC}}$, were always greater than the ones calculated from the $[\text{monomer}]_0/[\text{initiator}]_0$ ratio and monomer conversion, $(\bar{M}_n)_{\text{theo}}$, suggesting initiation by species other than **7** or **8**. A $[\{(\text{Me}_3\text{Si})_2\text{NC}(\text{N}i\text{Pr})_2\}_2]\text{Ln-O}(\text{CH}_2)_6\text{-O-Ln}\{[(\text{Me}_3\text{Si})_2\text{NC}(\text{N}i\text{Pr})_2\}_2]\}$ (Ln = Lu, Y) initiating species, potentially formed upon reduction of the carbonyl group of the first lactone monomer along with an oxygen–acyl bond cleavage, might well be generated in situ leading to a HO–PCL–O(CH₂)₆–O–PCL–OH polymer. Such a reduction of the carbonyl group of ϵ -caprolactone has been reported in the reaction of $[(\text{C}_5\text{Me}_5)_2\text{SmH}]_2$, from which the product recovered after hydrolysis was shown to be 1,6-hexanediol.^[18c] Initiation by such a dimetallic species would reduce by half the calculated molar mass, which would then be in agreement with the experimental molar mass values. Molar mass distribution values, $\bar{M}_w/\bar{M}_n$, are quite large, indicating the presence of side reactions such as transesterifications, the most common in polyester synthesis, involving intramolecular back-biting or intermolecular reshuffling. Yet these side reactions do not necessarily occur with a prolonged polymerization time, as the narrowest mo-

lar mass distribution was obtained over the longest reaction time of 45 min (Table 1, entry 11); neither do these side reactions occur as a result of a highly concentrated reaction medium, as the molar mass distribution increased upon dilution of the initiator (Table 1, entries 8–9).

The ¹H NMR spectrum of a precipitated polymer clearly shows a HO–PCL pattern with typical signals: δ = 4.03 (t, CH₂O), 3.60 (t, CH₂OH), 2.25 [t, C(O)CH₂], 1.61 (m, CH₂CH₂CH₂), 1.34 (m, CH₂CH₂CH₂) ppm. No signal corresponding to the expected HO–PCL–C(O)H ($\delta_{\text{C(O)H}}$ = 9.7 ppm), resulting from polymerization by a $[(\text{Lu/Y})(\mu\text{-H})\{(\text{Me}_3\text{Si})_2\text{NC}(\text{N}i\text{Pr})_2\}_2]_2$ complex along with an oxygen–acyl bond cleavage of the monomer, was ever observed, which indicates some modification of the initial hydrido complex **7** or **8** prior to initiation and propagation of the reaction. While one chain end could clearly be identified as –CH₂OH, the other extremity could not be identified without ambiguity. These results indicate that hydrides **7** and **8** lead to highly active initiating species; yet, the polymerization is not controlled.

Conclusions

Contrary to our expectations, replacement of isopropyl-substituted guanidinato ligands by bulkier cyclohexyl-containing analogues in the dimeric hydrido complexes $[\text{Ln}(\mu\text{-H})\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NR})_2\}_2]_2$ (Ln = Y, Lu) does not result in formation of monomeric hydrido species or a lengthening of the Ln–Ln distance. Nevertheless, the dissociation of dimeric hydrido complexes **5** and **6** and the existence of a monomer–dimer equilibrium on the chemical time scale was proved by scrambling equimolar amounts of **5** and **6** in C₆D₆ solution, which resulted in the formation of the heterodimetallic complex $[\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\}_2\text{Y}(\mu\text{-H})_2\text{-Lu}\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\}_2]$. Complexes **5** and **6** catalyze ethylene polymerization under mild conditions with moderate activity. 1-Nonene was found to react with PhSiH₃ in a 1:1 molar ratio in the presence of complexes **5–8** to give only the anti-Markovnikov addition product, PhSiH₂(*n*-C₉H₁₉).

The reaction of PhSiH_3 with a twofold molar excess of 1-nonene catalyzed by complexes **5–8** results in a double terminal addition $\text{PhSiH}(n\text{-C}_9\text{H}_{19})_2$. Complexes **7** and **8** efficiently polymerize ϵ -caprolactone in thf; however, the polymerization remains uncontrolled.

Experimental Section

All experiments were performed in evacuated tubes by using standard Schlenk techniques with rigorous exclusion of traces of moisture and air. The solvents thf, benzene, toluene, and hexane were purified by distillation from sodium/benzophenone ketyl and were condensed in vacuo prior to use. N,N' -diisopropylcarbodiimide and 1-nonene were purchased from Acros, dried with molecular sieves, and purified by distillation. N,N' -dicyclohexylcarbodiimide was purchased from Acros and used without any purification. Phenylsilane was dried with calcium hydride and condensed in vacuo prior to use. Anhydrous LnCl_3 [19] and $[\text{Li}(\text{Et}_2\text{O})\text{N}(\text{SiMe}_3)_2]$ [20] were prepared according to literature procedures. ϵ -Caprolactone (ϵ -CL, Lancaster) was dried first with CaH_2 (one week) and then over 4,4'- ϵ -caprolactone (ϵ -CL, Lancaster). All other commercially available chemicals were used after the appropriate purification. IR spectra were recorded as Nujol mulls with a FSM 1201 spectrophotometer. NMR spectra were recorded with Bruker DPX 200 and Bruker Avance DPX 400 spectrometers. Deuteriated benzene was dried with sodium benzophenone ketyl and vacuum-transferred. Chemical shifts for ^1H and ^{13}C NMR spectra were referenced internally to the residual solvent resonances and reported relative to tetramethylsilane. Lanthanide metal analyses were carried out by complexometric titration. Molar mass ($\bar{M}_n$) and molar mass distribution ($\bar{M}_w/\bar{M}_n$) determinations were performed by size exclusion chromatography (SEC) in thf at 20 °C (flow rate 1.0 mL min⁻¹) with a Jasco apparatus equipped with a refractive index detector and one Polymer Laboratory column with 5 μm particle size. The polymer samples were dissolved in thf (2 mg mL⁻¹). Average molar mass values were calculated from the linear polystyrene calibration curve by using the correction coefficient previously reported [$(\bar{M}_n)_{\text{exp}} = 0.56(\bar{M}_n)_{\text{SEC}}$] [21]. The monomer conversion was calculated from the ^1H NMR spectrum of the crude polymer sample by the integration (Int.) ratio $\text{Int.P}(\text{CL})/[\text{Int.P}(\text{CL}) + \text{Int.}(\text{CL})]$ by using the $\text{CH}_2\text{OC}(\text{O})$ methylene triplet ($\delta = 4.04$ ppm) peak.

Synthesis of $[\text{Y}(\text{CH}_2\text{SiMe}_3)\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\}_2]$ (3**):** To a solution of **1** (1.090 g, 1.04 mmol) in hexane (20 mL) was added a solution of $\text{Me}_3\text{SiCH}_2\text{Li}$ (0.098 g, 1.04 mmol) in hexane (10 mL) at 0 °C, and the reaction mixture was stirred for 1 h. The colorless solution was filtered and concentrated in vacuo to approximately 1/10 of its initial volume. Complex **3** was isolated as a colorless microcrystalline solid (0.70 g, 64%) from hexane by cooling. $\text{C}_{42}\text{H}_{91}\text{N}_6\text{Si}_5\text{Y}$ (909.52): calcd. C 55.46, H 10.08, Y 9.77; found C 55.33, H 10.31, Y 9.58. ^1H NMR (200 MHz, C_6D_6 , 20 °C): $\delta = 3.37$ (br.m, 4 H, CH, Cy), 1.15–1.91 (m, 40 H, CH_2 , Cy), 0.45 [s, 9 H, $\text{CH}_2\text{Si}(\text{CH}_3)_3$], 0.30 [s, 36 H, $\text{NSi}(\text{CH}_3)_3$], -0.19 (d, $^2J_{\text{Y-H}} = 3.0$ Hz, 2 H, YCH_2) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, C_6D_6 , 20 °C): $\delta = 168.3$ (CN_3), 55.2 (CH, Cy), 35.1 (d, $^1J_{\text{Y-C}} = 38.3$ Hz, YCH_2), 36.8, 33.2, 26.4, 26.1, 22.7 (CH_2 , Cy), 4.7 [$\text{CH}_2\text{Si}(\text{CH}_3)_3$], 2.4 [$\text{NSi}(\text{CH}_3)_3$] ppm. IR (Nujol, KBr): $\tilde{\nu} = 1635$ (s), 1310 (w), 1254 (s), 1195 (s), 1060 (m), 955 (s), 845 (s), 740 (s) cm⁻¹.

Synthesis of $[\text{Lu}(\text{CH}_2\text{SiMe}_3)\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\}_2]$ (4**):** To a solution of **2** (0.950 g, 0.84 mmol) in hexane (20 mL) was added a solution of $\text{Me}_3\text{SiCH}_2\text{Li}$ (0.079 g, 0.84 mmol) in hexane (10 mL) at

0 °C, and the reaction mixture was stirred for 1 h. The colorless solution was filtered. After removing all volatiles, complex **3** was isolated as a colorless viscous liquid (0.750 g, 90%). ^1H NMR (200 MHz, C_6D_6): $\delta = 3.55$ (m, 4 H, CH, Cy), 1.96–1.21 (m, 40 H, CH_2 , Cy), 0.42 [s, 9 H, $\text{CH}_2\text{Si}(\text{CH}_3)_3$], 0.27 [s, 36 H, $\text{NSi}(\text{CH}_3)_3$], -0.49 (s, 2 H, LuCH_2) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, C_6D_6): $\delta = 169.3$ (CN_3), 55.2 (CH, Cy), 40.0 (LuCH_2), 37.9, 32.0, 26.4, 26.2, 23.1 (CH_2 , Cy), 5.2 [$\text{CH}_2\text{Si}(\text{CH}_3)_3$], 2.6 [$\text{NSi}(\text{CH}_3)_3$] ppm. IR (Nujol, KBr): $\tilde{\nu} = 1630$ (s), 1300 (w), 1250 (s), 1200 (s), 1210 (m), 950 (s), 930 (m), 820 (s) cm⁻¹.

Synthesis of $[\text{Y}(\mu\text{-H})\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\}_2]_2$ (5**):** To a hexane solution of **3** (40 mL) in situ obtained from **1** (1.530 g, 1.46 mmol) and $\text{Me}_3\text{SiCH}_2\text{Li}$ (0.138 g, 1.46 mmol) was added a solution of PhSiH_3 (0.158 g, 1.46 mmol) in hexane (5 mL) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C and then concentrated in vacuo to approximately 1/4 of its initial volume. When crystallization started, the solution was cooled to -18 °C and kept at that temperature overnight. The mother liquor was decanted, the colorless solid was washed with cold hexane and dried in vacuo at room temperature for 45 min to give **5** as a colorless microcrystalline solid (0.914 g, 76%). $\text{C}_{76}\text{H}_{162}\text{N}_{12}\text{Si}_8\text{Y}_2$ (1646.68): calcd. C 55.43, H 9.91, Y 10.79; found C 55.07, H 10.32, Y 10.43. ^1H NMR (200 MHz, C_6D_6): $\delta = 8.09$ [t, $^1J_{\text{Y-H}} = 26.6$ Hz, 2 H, $\text{Y}(\mu\text{-H})_2\text{Y}$], 3.23 (m, 8 H, CH, Cy), 2.09–1.30 (m, 80 H, CH_2 , Cy), 0.31, 0.21 (s, together 72 H, SiMe_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, C_6D_6): $\delta = 168.8$ (CN_3), 55.0 (CH, Cy), 37.5, 36.9, 31.6, 26.1, 25.4, 25.0 (CH_2 , Cy), 2.7, 2.3 [$\text{N}[\text{Si}(\text{CH}_3)_3]_2$] ppm. IR (Nujol, KBr): $\tilde{\nu} = 1630$ (s), 1605 (m), 1320 (s), 1250 (s), 1205 (s), 1050 (s), 950 (s), 820 (s) cm⁻¹.

Synthesis of $[\text{Lu}(\mu\text{-H})\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\}_2]_2$ (6**):** A solution of PhSiH_3 (0.110 g, 1.02 mmol) in hexane (5 mL) was added at room temperature to a solution of **4** obtained in situ from **2** (1.153 g, 1.02 mmol) and $\text{Me}_3\text{SiCH}_2\text{Li}$ (0.096 g, 1.02 mmol) in hexane (40 mL) at 0 °C. The reaction mixture was stirred for 45 min and then concentrated in vacuo to approximately 1/4 of its initial volume. When crystallization started, the solution was cooled to -18 °C and kept at that temperature overnight. The mother liquor was decanted, the solid was washed with cold hexane and dried in vacuo at room temperature for 45 min to give **6** as a colorless microcrystalline solid (0.594 g, 64%). $\text{C}_{76}\text{H}_{162}\text{Lu}_2\text{N}_{12}\text{Si}_8$ (1818.70): calcd. C 50.19, H 8.98, Lu 19.24; found C 49.86, H 8.57, Lu 18.93. ^1H NMR (200 MHz, C_6D_6): $\delta = 13.31$ [s, 2 H, $\text{Lu}(\mu\text{-H})_2\text{Lu}$], 3.70 (m, 8 H, CH, Cy), 2.12–1.21 (m, 80 H, CH_2 , Cy), 0.37, 0.36 (s, together 72 H, SiMe_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, C_6D_6): $\delta = 168.9$ (CN_3), 55.3 (CH, Cy), 37.6, 36.7, 31.6, 26.3, 25.5, 25.4 (CH_2 , Cy), 3.2, 2.9 [$\text{N}[\text{Si}(\text{CH}_3)_3]_2$] ppm. IR (Nujol, KBr): $\tilde{\nu} = 1635$ (s), 1610 (m), 1305 (s), 1250 (s), 1070 (s), 955 (s), 835 (s) cm⁻¹.

Typical Ethylene Polymerization Procedure: Catalytic tests with ethylene (volume of toluene: 5 mL, catalyst concentration: 5.9×10^{-6} and 6.8×10^{-6} mol L⁻¹, temperature: 20 °C, monomer pressure: -0.5 atm) and propylene (volume of toluene: 5 mL, catalyst concentration: 5.9×10^{-6} and 6.1×10^{-6} mol L⁻¹, temperature: 0 °C, monomer pressure: -0.5 atm) were carried out under rigorously anaerobic conditions in a sealed glass manometric system. The reactions were monitored by monomer consumption. Catalyst efficiencies were estimated by both monomer absorption and by quenching the polymerization reaction after measured time intervals and weighing the quantity of polymer produced. The polymers were washed with dilute HCl and methanol and dried in vacuo to constant weight.

Typical ϵ -CL Polymerization Procedure: Compound **7** (9.6 mg, 6.41 μmol) or **8** was initially dissolved in thf (1.9 mL) before addition of ϵ -CL (0.1 mL, 0.9 mmol). The clear solution was then stirred over 15–45 min at 23 °C. The reaction was then quenched

with an acetic acid solution (0.1 mL, 1.45 mol, $14.5 \times 10^3 \text{ mol L}^{-1}$). The resulting mixture was dried, and the conversion determined by ^1H NMR spectroscopic analysis of the crude polymer sample. This nonfractionated polymer was dissolved in CH_2Cl_2 , purified upon precipitation in a large amount of cold pentane, and finally dried under dynamic vacuum. The recovered polymers were then characterized by ^1H and ^{13}C NMR spectroscopy and SEC.

Typical Hydrosilylation Procedure (PhSiH₃/1-Nonene = 1:1): To a solution of **7** (0.0418 g, 0.033 mmol) in hexane (3 mL), were added phenylsilane (0.280 g, 0.260 mmol) and 1-nonene (0.330 g, 0.260 mmol) (PhSiH₃/1-nonene = 1:1). The reaction mixture was stirred for 24 h and then treated with methanol (1 mL). The pale-yellow solution was filtered and concentrated in vacuo. The viscous liquid residue was dried in vacuo at 100 °C for 1 h. The product of reaction was purified by Kugelrohr distillation (180–210 °C, 10^{-2} bar). PhSiH₂(*n*-C₉H₁₉) (0.550 g) was isolated as a colorless liquid in 91% yield. C₁₅H₂₆Si (234.45): calcd. C 76.84, H 11.18, Si 11.98; found C 76.92, H 11.30, Si 11.79. ^1H NMR (200 MHz, CDCl₃): δ = 7.61 (m, 2 H, Ph), 7.42 (d, $^3J_{\text{H-H}}$ = 1.8 Hz, 2 H, Ph), 7.39 (d, $^3J_{\text{H-H}}$ = 1.5 Hz, 1 H, Ph), 4.34 (t, $^1J_{\text{Si-H}}$ = 3.8 Hz, 2 H, SiH₂), 1.31 (br.m, 14 H, CH₂), 0.93 (br.m, 5 H, CH₃, SiCH₃) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, CDCl₃): δ = 135.3 (Ph), 132.9 (Ph), 129.5 (Ph), 127.9 (Ph), 32.9, 31.9, 29.6, 29.4, 29.3, 25.2, 22.8 (CH₂), 14.2 (CH₃), 10.8 (SiCH₃) ppm. IR (Nujol, KBr): $\tilde{\nu}$ = 3070 (m), 3050 (m), 3015 (s), 2130 (s), 1950 (w), 1880 (w), 1813 (w), 1638 (w), 1589 (w), 1378 (m), 1300 (m), 1250 (s), 1169 (s), 1115 (s), 940 (m), 840 (s), 699 (m), 635 (s), 505 (w), 455 (m) cm⁻¹.

Typical Hydrosilylation Procedure (PhSiH₃/1-Nonene = 1:2): To a solution of **5** (0.0418 g, 0.032 mmol) in hexane (3 mL) were added phenylsilane (0.200 g, 1.85 mmol) and 1-nonene (0.470 g, 3.70 mmol) (PhSiH₃/1-nonene = 1:2). The reaction mixture was stirred for 24 h and then treated with methanol (1 mL). A pale-yellow solution was filtered and concentrated in vacuo. The viscous liquid residue was dried in vacuo at 80 °C for 2 h. After Kugelrohr distillation (180–210 °C, 10^{-2} bar) PhSiH(*n*-C₉H₁₉)₂ was obtained as a colorless liquid (0.610 g, 91%). C₂₄H₄₄Si (360.69): calcd. C 79.92, H 12.29, Si 7.79; found C 79.49, H 12.30, Si 7.74. ^1H NMR (200 MHz, CDCl₃): δ = 7.51 (m, 2 H, Ph), 7.36 (d, $^3J_{\text{H-H}}$ = 2.3 Hz, 2 H, Ph), 7.32 (d, $^3J_{\text{H-H}}$ = 1.5 Hz, 1 H, Ph), 4.23 (quint, $^1J_{\text{Si-H}}$ = 3.3 Hz, 1 H, SiH), 1.24 (br.m, 28 H, CH₂), 0.87 (br.m, 10 H, CH₃, SiCH₃) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, CDCl₃): δ = 136.2 (Ph), 134.7 (Ph), 129.1 (Ph), 127.8 (Ph), 33.3, 31.9, 29.5, 29.4, 29.3, 24.5, 22.7 (CH₂), 14.1 (CH₃), 11.9 (SiCH₃) ppm. IR (Nujol, KBr): $\tilde{\nu}$ = 3070 (m), 3049 (m), 3015 (s), 2109 (s), 1949 (w), 1876 (w), 1813 (w), 1759 (w), 1734 (w), 1589 (w), 1465 (s), 1425 (m), 1408 (m), 1378 (m), 1300 (m), 1260 (s), 1169 (s), 1115 (s), 1013 (m), 940 (m), 822 (s), 732 (s), 695 (s), 466 (m) cm⁻¹.

X-ray Crystallography: Low-temperature diffraction data were collected with Bruker-AXS Smart Apex I (for **5**) and Apex II (for **6**) diffractometers with graphite-monochromated Mo- K_α radiation (λ = 0.71073 Å). All structures were solved by direct methods and refined against F^2 on all data by full-matrix least-squares with SHELXTL.^[22] Absorption correction in **5** was applied by using SADABS.^[23] The crystals of complex **6** are twins. A double set of

Table 2. Crystallographic data and structure refinement details for **5** and **6**.

	5	6
Empirical formula	C ₈₂ H ₁₇₅ N ₁₂ Si ₈ Y ₂	C ₇₆ H ₁₆₂ Lu ₂ N ₁₂ Si ₈
Formula weight	1731.88	1818.84
<i>T</i> [K]	100(2)	100(2)
Space group	<i>Fdd2</i>	<i>I42d</i>
Crystal system	orthorhombic	tetragonal
Unit cell dimensions		
<i>a</i> [Å]	37.7477(18)	26.656(9)
<i>b</i> [Å]	38.30371(8)	26.656(9)
<i>c</i> [Å]	14.9435(7)	14.905(7)
α [°]	90	90
β [°]	90	90
γ [°]	90	90
Volume [Å ³]	21606.5(18)	10590(7)
<i>Z</i>	8	4
Density (calculated), [g cm ⁻³]	1.065	1.141
Absorption coefficient [mm ⁻¹]	1.198	1.983
<i>F</i> (000)	7528	3824
Crystal size [mm]	0.10 × 0.10 × 0.10	0.22 × 0.14 × 0.10
θ range for data collection, deg	26.00	27.00
Index ranges	−46 ≤ <i>h</i> ≤ 46 −47 ≤ <i>k</i> ≤ 47 −18 ≤ <i>l</i> ≤ 18	−23 ≤ <i>h</i> ≤ 24 0 ≤ <i>k</i> ≤ 33 0 ≤ <i>l</i> ≤ 19
Independent reflections	10487, <i>R</i> _{int} = 0.0668	5840
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]		3280
Completeness to θ	99.7	98.9
Data/restraints/parameters	10487/86/501	5840/0/223
Goodness-of-fit on <i>F</i> ²	0.993	0.877
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0550 <i>wR</i> ₂ = 0.1339	<i>R</i> ₁ = 0.0490 <i>wR</i> ₂ = 0.0926
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0832 <i>wR</i> ₂ = 0.1445	<i>R</i> ₁ = 0.1133 <i>wR</i> ₂ = 0.1080
Largest diff. peak and hole [e Å ⁻³]	0.648/−0.282	1.645/−2.568

data for twinning components was indexed by using CELL_NOW program incorporated in the APEX II software.^[24] The frames were integrated separately for each component and then reflections of two components were separately included in the refinement by HKLF 5 format [BASF = 0.116(9)]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms in **5** and **6** (except hydrido H atoms) were included in idealized positions, and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms [$U_{iso}(H) = 1.5U_{eq}$ for methyl carbon atoms and $1.2U_{eq}$ for other carbon atoms]. Hydrido hydrogen atoms in **5** and **6** were located from Fourier synthesis and refined isotropically in **5** and in riding motion approximation for **6**. Crystallographic data and structure refinement details are given in Table 2. CCDC-675002 and -675003 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This work has been supported by the Russian Foundation for Basic Research (Grant Nos. 08-03-00391-a, 06-03-32728-a, 07-03-12164-ofi), Program of the Presidium of the Russian Academy of Science (RAS), and RAS Chemistry and Material Science Division. A. T. thanks the Russian Foundation for Science Support.

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- Received: December 14, 2007
Published Online: March 10, 2008