Post-Metallocene Hydridolanthanide Chemistry: $[Lu\{(Me_3Si)_2NC(NiPr)_2\}_2(\mu\text{-}H)]_2$ — A Novel Lanthanide Hydride in a Non-Cyclopentadienyl Coordination Environment; Synthesis, Structure and Catalytic Activity in Olefin Polymerization

Alexander A. Trifonov,*[a] Elena A. Fedorova,[a] Georgy K. Fukin,[a] and Mikhail N. Bochkarev[a]

Keywords: Alkyl complexes / Homogeneous catalysis / Hydride ligands / Lanthanides / N ligands

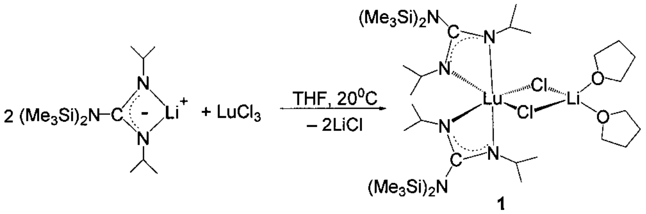
The reaction of anhydrous $LuCl_3$ with a twofold molar excess of lithium guanidinate $[Li\{(Me_3Si)_2NC(NiPr)_2\}]$, obtained in situ from the amide $[LiN(SiMe_3)_2(Et_2O)]$ and 1,3-diisopropylcarbodiimide in THF, yields the bis(guanidinate) "ate" complex $[Lu\{(Me_3Si)_2NC(NiPr)_2\}_2(\mu\text{-}Cl)_2Li(THF)_2]$ (**1**). The alkyllutetium derivative $[Lu\{(Me_3Si)_2NC(NiPr)_2\}_2(CH_2SiMe_3)]$ (**2**) was synthesized by a metathesis reaction of **1** with $LiCH_2SiMe_3$ in toluene. The treatment of **2** with an equimolar amount of $PhSiH_3$ in hexane at room temperature results in the first known dimeric lanthanide hydride in a bis(guanidinate) coordination environment, $[Lu\{(Me_3Si)_2NC(NiPr)_2\}_2(\mu\text{-}H)]_2$ (**3**). The crystal structures of complexes **1** and **3** have been determined by X-ray crystallography. The hydrido complex **3** was found to catalyze polymerization of ethylene, propylene and styrene.

Introduction

Mono- and bis(cyclopentadienyl) and -hydridolanthanide compounds have a very rich and unique chemistry[1−5] and have been found to be efficient catalysts or precatalysts in a wide range of transformations of unsaturated substrates.[6−10] Since the chemical properties of these compounds are known to be profoundly influenced by the nature of the ancillary ligands coordinated to the lanthanide atom,[11−13] related complexes in a stabilizing environment different from cyclopentadienyl one seem to be challenging targets for the exploration of stoichiometric and catalytic performance. In contrast to the well-developed chemistry of cyclopentadienyl-derived alkyl and hydrido complexes of lanthanides, their non-cyclopentadienyl analogues still remain extremely poorly investigated.[14−18] We decided to focus on the tetrasubstituted guanidinate ligand system[19] because its electronic and steric properties can be easily modified to provide stability and a high degree of unsaturation of the coordination sphere of the lanthanide atom due to the bulky substituents at the nitrogen atoms. Several examples of alkyl complexes of rare earth metals coordinated by guanidinate ligands have been reported recently.[20−22] We employed the advantages of the $\{(Me_3Si)_2NC(NiPr)_2\}^-$ ligand for the stabilization of lanthanide hydride, and report here the synthesis of the first complex of this type — $[Lu\{(Me_3Si)_2NC(NiPr)_2\}_2(\mu\text{-}H)]_2$ — and its structure and catalytic activity in olefin polymerization.

Results and Discussion

The monochloro bis(guanidinate) derivative of lutetium, $[Lu\{(Me_3Si)_2NC(NiPr)_2\}_2(\mu\text{-}Cl)_2Li(THF)_2]$ (**1**), was synthesized by a metathesis reaction of a twofold molar excess of the lithium guanidinate $[Li\{(Me_3Si)_2NC(NiPr)_2\}]$, obtained in situ from the amide $[Li\{N(SiMe_3)_2\}(Et_2O)]$ and 1,3-diisopropylcarbodiimide in THF, with anhydrous $LuCl_3$ at room temperature (Scheme 1).



Scheme 1

Complex **1** was isolated in an analytically pure form as a colorless air- and moisture-sensitive crystalline solid by recrystallization from hexane in 76% yield. It is worth noting that the reaction of YCl_3 with 2 equiv. of

---

[a] G. A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences,
Tropinina 49, 603950 Nizhny Novgorod, GSP-445, Russia
Fax: + 7-8312-661-497
E-mail: trif@imoc.sinn.ru

$[Li\{(Me_3Si)_2NC(NiPr)_2\}]$ in diethyl ether resulted, after the same treatment, in the isolation of the neutral solvent-free dinuclear guanidinate complex $[Y\{(Me_3Si)_2NC(NiPr)_2\}_2(\mu\text{-}Cl)]_2$;[21] formation of the analogous "ate" complexes $[Ln\{(Me_3Si)_2NC(NiPr)_2\}_2(\mu\text{-}Cl)_2Li(THF)_2]$ (Ln = Y,[21] Yb[22]) has been reported when the reactions are carried out in THF. Complex **1** is soluble in ethers and aromatic and aliphatic hydrocarbons. The ^1H and ^{13}C NMR spectra of **1** in C_6D_6 at 20 °C do not have any notable features and reflect the equivalence of the two guanidinate ligands, with the expected single set of resonances indicating an increased rate of fluctionality compared to the more rigid dinuclear framework of $[Y\{(Me_3Si)_2NC(NiPr)_2\}_2(\mu\text{-}Cl)]_2$.[21] Both sets of THF methylene protons appear in the ^1H NMR spectrum of **1** as broad singlets, indicating their lability.

Clear, colorless single-crystals of **1** suitable for an X-ray crystal-structure determination were obtained by slow concentration of its hexane solution. An ORTEP diagram of **1** is presented in Figure 1; crystal and structural refinement data are listed in the Exp. Sect. The X-ray diffraction study revealed that **1** is a monomeric heterodimetallic "ate" complex that is isomorphous to the previously described $[Yb\{(Me_3Si)_2NC(NiPr)_2\}_2(\mu\text{-}Cl)_2Li(THF)_2]$.[22]

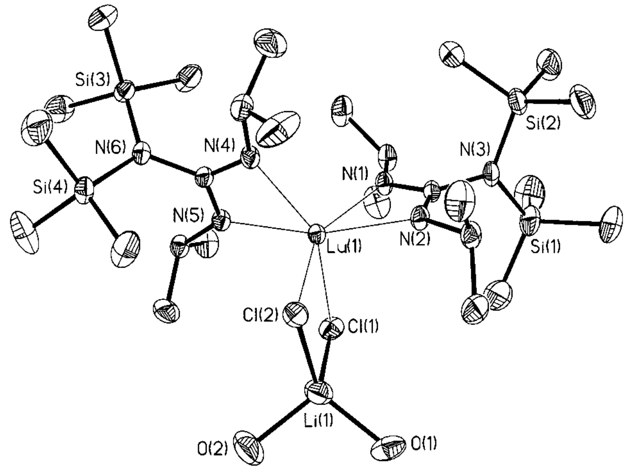


Figure 1. Molecular structure of **1**; the hydrogen atoms are omitted as well as the carbon atoms of the THF molecules; selected bond lengths [Å] and angles [°]: Lu(1)−N(1) 2.285(1), Lu(1)−N(4) 2.290(2), Lu(1)−N(5) 2.329(2), Lu(1)−N(2) 2.346(2), Lu(1)−Cl(1) 2.600(1), Lu(1)−Cl(2) 2.623(1), Lu(1)−C(14) 2.739(2), Lu(1)−C(1) 2.745(2); N(4)−Lu(1)−N(5) 57.87(6), N(1)−Lu(1)−N(2) 57.86(6), C(14)−Lu(1)−C(1) 132.30(6)

The coordination environment of the lutetium atom in **1** is defined by four nitrogen atoms of the bidentate guanidinate ligands, and two chlorine atoms, which form μ^2-bridges to the lithium atom. The lithium atom is also bonded to oxygen atoms of the two THF molecules. The formal coordination number of the lutetium atom is six, which is rather low for lanthanide derivatives.[1] The luthetium−nitrogen bonds in **1** have very similar lengths, which fall in the region 2.285(1)−2.346(1) Å. These bonds are much shorter than the coordination bonds in $[Lu(\eta^8\text{-}C_8H_8)\{o\text{-}C_6H_4CH_2N(CH_3)_2\}(THF)]$ [2.479(6) Å][23] and $[Lu\{o\text{-}C_6H_4CH_2N(CH_3)_2\}_3]$ [2.468(6), 2.4588(5) Å],[24] but similar to the length of the covalent bond in the anionic compound $[\{Li(THF)_4\}\{Lu(C_5H_5)_2(NPh_2)_2\}]$ [2.290(7), 2.293(7) Å].[25] The Lu−Cl distances in **1** [2.600(1) 2.622(1) Å] are very close to the values reported for the Cp analogue $[LuCp_2(\mu\text{-}Cl)_2Li(TMEDA)]$.[26] The Yb−N [2.295(3)−2.332(3) Å] and Yb−Cl [2.608(1), 2.631(1) Å] distances in an isomorphous Yb complex[22] are close to the analogous distances in **1**.

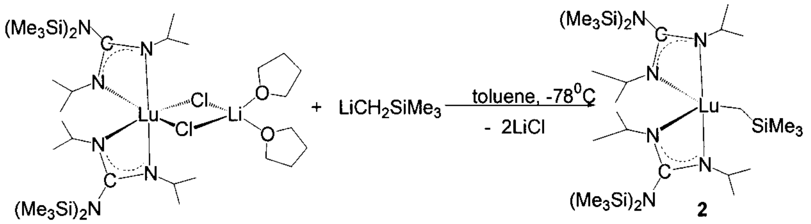
The alkylation of **1** with $LiCH_2SiMe_3$ in toluene yielded the solvent-free alkyl complex $[Lu\{(Me_3Si)_2NC(NiPr)_2\}_2(CH_2SiMe_3)]$ (**2**; Scheme 2), which was isolated as a colorless amorphous powder in 71% yield after extraction with hexane.

The air- and moisture-sensitive complex **2** is highly soluble in organic solvents. The presence of the CH_2SiMe_3 group in **2** is proved by a high-field-shifted singlet at $\delta = -0.49$ ppm in the ^1H NMR spectrum, corresponding to the two protons of the methylene group attached to the lutetium atom, and by a singlet at $\delta = 0.37$ ppm corresponding to the protons of the Me_3Si group. The carbon atoms of these groups produce resonances at $\delta = 40.0$ and 4.9 ppm, respectively, in the ^{13}C NMR spectrum of **2**.

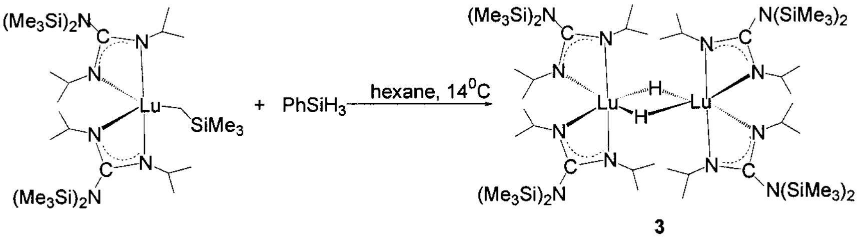
The alkyl complex **2** was treated with an equimolar amount of phenylsilane in hexane at room temperature to yield the dimeric hydride $[Lu\{(Me_3Si)_2NC(NiPr)_2\}_2(\mu\text{-}H)]_2$ (**3**; Scheme 3).

Complex **3** was isolated in 84% yield as a colorless microcrystalline solid after recrystallization from hexane and drying in vacuo. Complex **3** is an air- and moisture-sensitive compound that is sparingly soluble in hexane and aromatic hydrocarbons. Crystallization of **3** by slow cooling of a warm (40 °C) saturated hexane solution to 20 °C resulted in the formation of single crystals of $[Lu\{(Me_3Si)_2NC(NiPr)_2\}_2(\mu\text{-}H)]_2(C_6H_{14})$. An X-ray crystal structure analysis revealed that **3** adopts a dimeric structure. Each of the two metal centres are coordinated by the four nitrogen atoms of the two guanidinate ligands and by two bridging hydrido ligands (Figure 2).

The two lutetium atoms and the two hydrido ligands are coplanar. The Lu−H [2.12(4), 2.04(4) Å] and Lu−Lu [3.577(1) Å] distances in the Lu_2H_2 core are similar to those in other dimeric μ^2-hydrido-bridged lutetium complexes with bis(cyclopentadienyl) and amido(cyclopentadienyl) ancillary ligation.[27,28] The dihedral angles between the planar four-membered cycles Lu(1)N(1)C(1)N(2) and Lu(1)N(1A)C(1A)N(2A), and Lu(2)C(14)N(4)N(5) and Lu(2)C(14A)N(4A)N(5A), are 66.8(1) and 60.6(1)°, respectively. Remarkably, the disposition of the two $Lu\{(Me_3Si)_2NC(NiPr)_2\}_2$ groups is such that the C(1)Lu(1)C(1A) and C(14)Lu(2)C(14A) planes are nearly orthogonal [86.90(11)°], which allows a reduction of the steric hindrance in the coordination sphere of the Lu atoms. A particularity of the structure of **3** is the difference of the bonding parameters within the $Lu\{(Me_3Si)_2NC(NiPr)_2\}_2$ fragments of the dimer, which results in their inequivalence. In one moiety the Lu(1)−N(1) and Lu(1)−N(2) distances are nearly similar [2.304(3) and 2.315(3) Å], while in the other one they differ noticeably [Lu(2)−N(4): 2.266(3) Å; Lu(2)−N(5): 2.372(5) Å]. The shortest Lu−N bond in **3** is



Scheme 2



Scheme 3

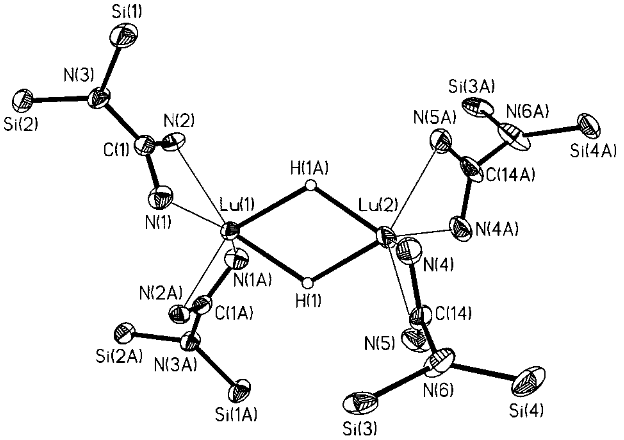


Figure 2. Molecular structure of **3**; the hydrogen atoms as well as methyl radicals of Me_3Si groups and isopropyl groups are omitted; selected bond lengths [Å] and angles [°]: Lu(1)−H(1) 2.12(4), Lu(2)−H(2) 2.03(4), Lu(1)−N(1) 2.304(3), Lu(1)−N(2) 2.315(3), Lu(1)−C(1) 2.747(3), Lu(1)−Lu(2) 3.5767(3), Lu(2)−N(4) 2.266(3), Lu(2)−N(5A) 2.372(3), Lu(2)−C(14) 2.733(3); N(1A)−Lu(1)−N(1) 144.71(16), N(1A)−Lu(1)−N(2A) 58.02(10), N(1)−Lu(1)−N(2A) 101.14(11), N(1)−Lu(1)−N(2) 58.02(10)

nevertheless significantly longer than the covalent Lu−N bond in the complex $[Lu\{Me_2Si(C_9H_5Me)_2\}\{N(SiMe_3)_2\}]$,[29] whereas the longest one is shorter than the coordination bonds in the above-mentioned complexes $[Lu(\eta^8\text{-}C_8H_8)(o\text{-}C_6H_4CH_2N(CH_3)_2(THF)]$[23] and $[Lu\{o\text{-}C_6H_4CH_2N(CH_3)_2\}_3]$.[24] The bonding situation within the NCN fragments does not indicate a significant difference of the π-system delocalization in the guanidinate ligands or the presence of different resonance forms. Such a structure obviously results from a steric repulsion of the bulky trimethylsilyl and isopropyl groups in the adjacent moieties and demonstrates the flexibility of coordination of guanidinate ligands. The strong geometry distortion in **3**, compared to the related dinuclear yttrium chloride bis(guanidinate) $[Y\{(Me_3Si)_2NC(NiPr)_2\}_2(\mu\text{-Cl})]_2$,[21] may suggest a greater steric encumbrance of the metal coordination sphere in the lutetium compound, resulting from the smaller ion sizes of Lu and H compared to those of Y and Cl.[30]

The hydrido ligands appear in the ^1H NMR spectrum of **3** as a singlet at $\delta = 12.96$ ppm, which is at substantially lower field than the respective signals of previously reported lutetium hydrides.[11,13,27,28,31−34] This observation is consistent with the enhanced electron-withdrawing properties of guanidinate ligands compared to those of cyclopentadienyl ligands. The ^1H and ^{13}C NMR spectra of **3** indicate that the guanidinate ligands remain inequivalent in solution (20 °C, C_6D_6). The methyl and methyne protons of the isopropyl groups appear in the ^1H NMR spectrum of **3** as complex multiplets, rather than the expected doublet and septuplet, respectively.

The catalytic reactions of **3** with ethylene (20 °C, 0.48 bar) and propylene (0 °C, 0.75 bar) in toluene were monitored by recording the absorption of the monomers. The polymerization of ethylene was rather slow; the catalyst retained similar activity during 3 d, and the reaction was stopped after this time (activity: 0.1 g polyethylene/mmol Lu·h·bar). The polyethylenes obtained with this catalyst are highly crystalline, with a melting temperature of 124 °C. Most of the lanthanide complexes which readily polymerize ethylene are inactive in propylene polymerization. On the contrary, **3** catalyzes propylene polymerization. The reaction proceeds much faster than in the case of ethylene, but the catalyst loses activity 1 h after the beginning of the process (activity: 3.9 g polypropylene/mmol Lu·h·bar). The solid polymer formed in this reaction is insoluble in organic solvents. Complex **3** also catalyzes polymerization of styrene (room temperature, neat styrene, 5% of **3**). A conversion of 90% was reached after 6 d, and the polystyrene obtained has a high molecular weight (M_n = 811000 g mol^{-1}; M_w = 1250000 g mol^{-1}), a narrow molecular weight distribution (M_w/M_n = 1.54), and a melting temperature of 255−260 °C.

Conclusion

The bis(guanidinate) ligand has been demonstrated to be a suitable alternative to the cyclopentadienyl ligand for the stabilization of hydridolanthanide complexes. Due to the bulky substituents on the nitrogen atoms this coordination environment provides a high solubility of the lanthanide derivatives and a low coordination number at the metal atom. The first hydridolanthanide complex with a bis(guanidinate) coordination environment was synthesized and structurally characterized. This complex demonstrates modest activity in olefin polymerization. Studies on the synthesis of hydrido bis(guanidinate) derivatives of other lanthanide metals and investigation of their properties in catalysis of olefin polymerization and hydrosilylation are currently in progress.

Experimental Section

General Remarks: All procedures were performed under vacuum using standard Schlenk-tube techniques. After drying with KOH, THF was distilled from sodium benzophenone ketyl prior to use. Hexane and toluene were purified by distillation from sodium/triglyme benzophenone ketyl. Deuterated benzene was dried with sodium and vacuum-transferred. Diisopropylcarbodiimide was purchased from Acros and purified by distillation. Anhydrous $LuCl_3$ [35] and $[Li\{N(SiMe_3)_2\}(Et_2O)]$[36] were prepared according to literature procedures. All other commercially available chemicals were used after the appropriate purification. NMR spectra were recorded with a Bruker DPX 200 spectrometer (^{1}H, 200 MHz; ^{13}C, 50 MHz) in C_6D_6 at 20 °C, unless otherwise stated. Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced internally to the residual solvent resonances and are reported relative to tetramethylsilane. IR spectra were recorded with a Specord M80 instrument as Nujol mulls. Molecular weights and molecular-weight distributions were determined against polystyrene standards by gel-permeation chromatography (GPC) with a Knauer apparatus with Phenogel columns (10 µm, Linear 2) using chloroform as the eluent. Lanthanide metal analysis was carried out by complexometric titration. Elemental analysis was performed by the Microanalytical Laboratory of this institute.

Synthesis of $[Lu\{(Me_3Si)_2NC(N\textit{i}Pr)_2\}_2(\mu\text{-}Cl)_2Li(THF)_2]$ (1): Diisopropylcarbodiimide (0.99 g, 7.90 mmol) was slowly added to a solution of $[Li\{N(SiMe_3)_2\}(Et_2O)]$ (1.91 g, 7.90 mmol) in THF (30 mL) at 20 °C and the reaction mixture was stirred for 45 min. $LuCl_3$ (1.11 g, 3.95 mmol) was added and the reaction mixture was stirred overnight. The solution was filtered, the solvent was evaporated in vacuo and the solid residue was extracted with toluene (2 × 20 mL). The toluene extracts were filtered and toluene was evaporated in vacuo. The off-white solid was dissolved in hot hexane (30 mL). The solution was slowly concentrated at room temperature to one quarter of its volume, cooled to −30 °C and left overnight. The crystalline precipitate was washed with cold hexane and dried in vacuo at room temperature for 20 min. Complex **1** was obtained as a colorless crystalline solid (2.91 g, 76%). $C_{34}H_{80}Cl_2LiLuN_6O_2Si_4$ (970.21): calcd. C 42.09, H 8.24, Lu 18.03; found C 41.80, H 8.69, Lu 17.88. ^{1}H NMR (200 MHz, [D$_6$]benzene): δ = 0.49 [s, 36 H, Si(C*H*$_3$)$_3$], 1.46 (br. s, 8 H, β-C*H*$_2$, THF), 1.61 [d, $^3J_{H,H}$ = 4.8 Hz, 24 H, (C*H*$_3$)$_2$CH], 3.76 (br. s, 8 H, α-C*H*$_2$, THF), 4.15 (sept, $^3J_{H,H}$ = 6.2 Hz, 4 H, C*H*Me$_2$) ppm. ^{13}C{^{1}H} NMR (50 MHz, [D$_6$]benzene): δ = 2.8 [(NSi*C*H$_3$)$_2$], 25.2 (β-*C*H$_2$, THF), 26.9 [(*C*H$_3$)$_2$CH], 46.1 (*C*HMe$_2$), 68.5 (α-*C*H$_2$, THF), 168.4 (*C*N$_3$) ppm. IR (nujol, KBr): $\tilde{\nu}$ = 1630 (s), 1310 (s), 1250 (s), 1200 (s), 1050 (m), 940 (s), 860 (m), 820(s) cm^{-1}.

Synthesis of $[Lu\{(Me_3Si)_2NC(N\textit{i}Pr)_2\}_2(CH_2SiMe_3)]$ (2): A solution of Me_3SiCH_2Li (0.14 g, 1.48 mmol) in toluene (5 mL) was slowly added at −78 °C to a solution of **1** (1.44 g, 1.48 mmol) in toluene (25 mL). The reaction mixture was allowed to warm to room temperature and stirred for 3 h. The pale-yellow solution was filtered and toluene was evaporated in vacuo. The residue was extracted with hexane (2 × 10 mL), the extracts were filtered, and hexane was removed in vacuo to give **2** as an off-white amorphous powder (0.83 g, 71%). $C_{30}H_{75}LuN_6Si_5$ (834.74): calcd. C 43.16, H 8.98, Lu 20.96; found C 42.70, H 9.33, Lu 20.74. ^{1}H NMR (200 MHz, [D$_6$]benzene): δ = −0.49 (s, 2 H, LuC*H*$_2$), 0.29 [s, 36 H, NSi(C*H*$_3$)$_3$], 0.37 [s, 9 H, CH$_2$Si(C*H*$_3$)$_3$], 1.29 [d, $^3J_{H,H}$ = 6.4 Hz, 24 H, (C*H*$_3$)$_2$CH], 3.92 (sept, $^3J_{H,H}$ = 6.4 Hz, 4 H, C*H*Me$_2$) ppm. ^{13}C{^{1}H} NMR (50 MHz, [D$_6$]benzene): δ = 2.2 (NSi*C*H$_3$)$_2$], 4.8 (CH$_2$Si*C*H$_3$), 27.1 [(*C*H$_3$)$_2$CH], 40.0 (Lu*C*H$_2$), 46.0 (*C*HMe$_2$), 168.9 (*C*N$_3$) 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 $[Lu\{(Me_3Si)_2NC(N\textit{i}Pr)_2\}_2(\mu\text{-}H)]_2$ (3): A solution of $PhSiH_3$ (0.12 g, 1.08 mmol) in hexane (2 mL) was added at room temperature to a solution of **2** (0.86 g, 1.08 mmol) in hexane (10 mL). The reaction mixture was stirred for 45 min and then concentrated in vacuo to approximately one third of its initial volume. When crystallization started, the solution was cooled to −30 °C and kept at that temperature overnight. The mother liqueur was decanted, the solid was washed with cold hexane and dried in vacuo at room temperature for 45 min to give **3** as a colorless microcrystalline solid (0.68 g, 84%). $C_{52}H_{130}Lu_2N_{12}Si_8$ (1497.2): calcd. C 41.71, H 8.68, Lu 23.37; found C 41.18, H 8.39, Lu 23.71. ^{1}H NMR (200 MHz, [D$_6$]benzene): δ = 0.45 [s, 72 H, NSi(C*H*$_3$)$_3$], 1.53 [m, 48 H, (C*H*$_3$)$_2$CH], 4.10 (m, 8 H, C*H*Me$_2$), 12.96 (s, 2 H, Lu*H*) ppm. ^{13}C{^{1}H} NMR (50 MHz, [D$_6$]benzene): δ = 3.1, 3.3 [N(Si*C*H$_3$)$_2$], 27.1, 28.2, 28.6 [(*C*H$_3$)$_2$CH], 46.5, 46.6 (*C*HMe$_2$), 168.7, 170.8 (*C*N$_3$) ppm. IR (Nujol, KBr): $\tilde{\nu}$ = 1630 (s), 1605 (m), 1320 (s), 1250 (s), 1205 (s), 1050 (s), 950 (s), 820(s) cm^{-1}.

Ethylene Polymerization: Ethylene polymerization tests were carried out in a constant-volume glass vessel connected to a Hg manometer (20 °C, $p_{monomer}$ = 0.48 bar). A solution of **3** (0.088 g, 0.0588 mmol) in toluene (5 mL) was loaded into the reaction vessel, which was then charged with ethylene, and the reaction mixture stirred. The reaction was monitored by the absorption of ethylene. After 72 h, the reaction vessel was disconnected and methanol was added (ca. 20 mL). The polymer was collected by filtration, washed with a 15% solution of HCl, then with methanol, and dried in vacuo to a constant weight; 0.192 g of polyethylene was isolated.

Propylene Polymerization: Propylene polymerization tests were carried out in a constant-volume glass vessel connected to a Hg manometer (0 °C, $p_{monomer}$ = 0.75 bar). A solution of **3** (0.053 g, 0.0353 mmol) in toluene (5 mL) was loaded into the reaction vessel, which was charged with propylene, and the reaction mixture stirred. The reaction was monitored by the absorption of the monomer. After 1 h, the reaction vessel was disconnected and methanol

Table 1. Crystallographic data and structure refinement details for **1** and **3**

	1	**3**
Empirical formula	$C_{34}H_{80}Cl_2LiLuN_6O_2Si_4$	C_{58} H_{144} Lu_2 N_{12} Si_8
Formula mass	970.21	1534.37
T [K]	100(2)	100(2)
λ [Å]	0.71073	0.71073
Crystal system	triclinic	trigonal
Space group	$P\bar{1}$	$P3_221$
Unit cell dimensions	a = 9.8860(8) Å	a = 14.7379(4) Å
	b = 14.7621(12) Å	b = 14.7379(4) Å
	c = 18.2178(15) Å	c = 32.7706(19) Å
	α = 75.231(2)°	α = 90°
	β = 86.632(2)°	β = 90°
	γ = 79.344(2)°	γ = 120°
Volume [Å$^{]}$)	2526.3(4)	6164.3(4)
Z	2	3
$D_{\text{calcd.}}$ [g/cm^3]	1.275	1.240
Absorption coefficient [mm^{-1}]	2.187	2.542
F(000)	1012	2394
Crystal size [mm]	0.08 × 0.08 × 0.02	0.45 × 0.40 × 0.32
θ range for data collection [°]	1.45−29.09	1.86−28.06
Index ranges	$-9 \le h \le 13$	$-19 \le h \le 19$
	$-19 \le k \le 18$	$-19 \le k \le 19$
	$-24 \le l \le 24$	$-43 \le l \le 43$
Reflections collected	18359	51913
Independent reflections	12927 (R_{int} = 0.0190)	9959 (R_{int} = 0.0377)
Completeness to θ	29.09°, 95.4%	28.06°, 99.5%
Data/restraints/parameters	12927/6/471	9959/59/422
Goodness-of-fit on F^2	1.030	1.101
Final R_{int} [$I > 2\sigma(I)$]	$R1$ = 0.0313, $wR2$ = 0.0766	$R1$ = 0.0338, $wR2$ = 0.0823
R_{int} (all data)	$R1$ = 0.0363, $wR2$ = 0.0790	$R1$ = 0.0361, $wR2$ = 0.0834
Largest diff. peak/hole [e·Å^3]	2.542/−1.603	1.454/−1.698

was added (ca. 20 mL). The polymer was collected by filtration, washed with a 15% solution of HCl, then with methanol, and dried in vacuo to a constant weight; 0.105 g of polypropylene was isolated.

Styrene Polymerization: Complex **3** (0.045 g, 0.0300 mmol) was added to styrene (1 mL) and the reaction mixture was stirred at room temperature. After 6 d, the volatiles were evaporated in vacuo. The polymer was washed with methanol (2 × 10 mL), HCl (10%, 10 mL), dissolved in toluene (20 mL), filtered, and precipitated into methanol (100 mL). The polymer was collected by filtration, washed with methanol, and dried in vacuo to a constant weight; 0.815 g of polystyrene was isolated.

X-ray Crystallographic Study: Single crystals of **1** and **3** for X-ray structure analysis were obtained from hexane solutions. The data were collected with a Bruker AXS SMART APEX diffractometer (graphite-monochromated Mo-K_α-radiation, φ/ω-scan technique, λ = 0.71073 Å). The intensity data were integrated with the SAINT program.[37] The structures were solved by direct methods and refined on F^2 using all reflections with SHELXL-97.[38] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms in **1** and **3** were placed in calculated positions and refined in the "riding-model". Only the hydride atom H(1) in **3** was found from Fourier synthesis and refined isotropically with fixed U_{iso} (0.08 Å^2). The crystal of **3** contained a solvate disordered molecule of hexene. SADABS[39] was used to perform area-detector scaling and absorption corrections. The details of crystallographic, collection and refinement data are shown in Table 1. CCDC-235927 (**1**) and -235926 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/const/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by the Russian Foundation of Basic Research (Grant no. 02-03-32112). We gratefully acknowledge Dr. Yu. A. Kurskii for recording the NMR spectra, and Dr. V.N. Glushakova and Mrs. N. A. Skorodumova for assistance with polymerization tests.

---

[1] M. N. Bochkarev, L. N. Zakharov, G. N. Kalinina, *Organo Derivatives of Rare Earth Elements*, Kluwer Academic Publishers, Dordrecht, **1995**.

[2] H. Schumann, J. A. Meese-Marktscheffel, L. Esser, *Chem. Rev.* **1995**, *95*, 865−893.

[3] S. Arndt, J. Okuda, *Chem. Rev.* **2002**, *102*, 1953−1976.

[4] M. Ephritikhine, *Chem. Rev.* **1997**, *97*, 2193−2242.

[5] J. Okuda, *Dalton Trans.* **2003**, 2367−2378.

[6] G. A. Molander, J. A. C. Romero, *Chem. Rev.* **2002**, *102*, 2161−2185.

[7] Z. Hou, Y. Wakatsuki, *Coord. Chem. Rev.* **2002**, *231*, 1−22.

[8] T. E. Mueller, M. Beller, *Chem. Rev.* **1998**, *98*, 675−703.

[9] H. Yasuda, *J. Organomet. Chem.* **2002**, *647*, 128−138.

[10] G. A. Molander, E. C. Dowdy, *Top. Organomet. Chem.* **1999**, *2*, 119−155.

[11] G. Jeske, H. Lauke, H. Mauermann, P. N. Swepston, H. Schumann, T. J. Marks, *J. Am. Chem. Soc.* **1985**, *107*, 8091−8103.

[12] G. Jeske, L. E. Schock, P. N. Swepston, H. Schumann, T. J. Marks, *J. Am. Chem. Soc.* **1985**, *107*, 8103−8110.

[13] D. Stern, M. Sabat, T. J. Marks, *J. Am. Chem. Soc.* **1990**, *112*, 9558−9575.
[14] F. T. Edelmann, D. M. M. Freckmann, H. Schumann, *Chem. Rev.* **2002**, *102*, 1851−1896.
[15] F. T. Edelmann, *Coord. Chem. Rev.* **1994**, *137*, 403−481.
[16] W. E. Piers, D. J. H. Emslie, *Coord. Chem. Rev.* **2002**, *233−234*, 131−155.
[17] P. Mountford, B. D. Ward, *Chem. Commun.* **2003**, 1797−1803.
[18] T. Dubé, S. Gambarotta, G. Yapp, *Organometallics* **2000**, *19*, 121−126.
[19] P. J. Bailey, S. Pace, *Coord. Chem. Rev.* **2001**, *214*, 91−141.
[20] Y. Zhou, G. P. A. Yapp, D. S. Richeson, *Organometallics* **1998**, *17*, 4387−4391.
[21] Z. Lu, G. P. A. Yapp, D. S. Richeson, *Organometallics* **2001**, *20*, 706−712.
[22] Y. Luo, Y. Yao, Q. Shen, K. Yu, L. Weng, *Eur. J. Inorg. Chem.* **2003**, 318−323.
[23] A. L. Wayda, R. D. Rogers, *Organometallics* **1985**, *4*, 1440−1444.
[24] A. L. Wayda, J. L. Atwood, W. E. Hunter, *Organometallics* **1984**, *3*, 939−941.
[25] H. Schumann, E. Palamidis, J. Loebel, *J. Organomet. Chem.* **1990**, *390*, 45−52.
[26] V. K. Belsky, S. Ya. Knyazhansky, B. M. Bulychev, G. L. Soloveitchik, *Metalloorg. Khim.* **1989**, *2*, 754−756.
[27] H. Schumann, W. Genthe, E. Hahn, M. B. Hossain, D. Van Der Helm, *J. Organomet. Chem.* **1986**, *299*, 67−84.
[28] S. Arndt, P. Voth, T. P. Spaniol, J. Okuda, *Organometallics* **2000**, *19*, 4690−4700.
[29] J. Eppinger, M. Spiegler, W. Hieringer, W. A. Herrmann, R. Anwander, *J. Am. Chem. Soc.* **2000**, *122*, 3080−3096.
[30] S. S Batsanov, *Russ. J. Inorg. Chem.* **1991**, *36*, 1694−1706.
[31] A. Z. Voskoboynikov, I. N. Parshina, A. K. Shestakova, K. P. Butin, I. P. Beletyskaya, L. G. Kuz'mina, J. A. K. Howard, *Organometallics* **1997**, *16*, 4041−4055.
[32] Y. K. Gun'ko, B. M. Bulychev, G. L. Soloveichik, V. K. Bel'skii, *J. Organomet. Chem.* **1992**, *24*, 289−300.
[33] P. W. Roesky, U. Denninger, C. L. Stern, T. J. Marks, *Organometallics* **1997**, *16*, 4886−4492.
[34] O. Tardif, M. Nishiura, Z. Hou, *Tetrahedron* **2003**, *59*, 10525−10539.
[35] M. D. Taylor, C. P. Carter, *J. Inorg. Nucl. Chem.* **1962**, *24*, 387−393.
[36] L. E. Manzer, *Inorg. Chem.* **1978**, *17*, 1552−1558.
[37] Bruker, *SAINTPlus Data Reduction and Correction Program*, v. 6.02a, Bruker AXS, Madison, Wisconsin, USA, **2000**.
[38] G. M. Sheldrick, *SHELXTL, Structure Determination Software Suite*, v. 6.12, Bruker AXS, Madison, Wisconsin, USA, **2000**.
[39] G. M. Sheldrick, *SADABS, Bruker/Siemens Area Detector Absorption Correction Program*, v.2.01, Bruker AXS, Madison, Wisconsin, USA, **1998**.

Received May 21, 2004
Early View Article