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Postmetallocene Lanthanide–Hydrido Chemistry: A New Family of Complexes $[\{Ln\{(Me_3Si)_2NC(N\mathit{i}Pr)_2\}_2(\mu\text{-}H)\}_2]$ (Ln = Y, Nd, Sm, Gd, Yb) Supported by Guanidinate Ligands—Synthesis, Structure, and Catalytic Activity in Olefin Polymerization

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Abstract: The new family of Lewis base free hydrido complexes of rare-earth metals supported by guanidinate ligands $[\{Ln\{(Me_3Si)_2NC(N\mathit{i}Pr)_2\}_2(\mu\text{-}H)\}_2]$ (Ln = Y, Nd, Sm, Gd, Yb) was synthesized and structurally characterized. Single-crystal X-ray and solution NMR studies revealed that these complexes are dimeric in both solid state and in [D$_6$]benzene. The dimeric hydrido complexes can adopt eclipsed (Nd, Sm, Gd) or staggered (Y, Yb, Lu) conformations depending on the metal-atom size. Catalytic activity of these $[\{Ln\{(Me_3Si)_2NC(N\mathit{i}Pr)_2\}_2(\mu\text{-}H)\}_2]$ complexes in the polymerization of ethylene, propylene, and styrene has been investigated. Complexes of Sm and Y have high catalytic activity in ethylene polymerization (1268 and 442 $g\,mmol^{-1}\,atm^{-1}\,h^{-1}$, respectively).

Keywords: guanidinate ligands · homogeneous catalysis · hydrides · lanthanides · polymerization

Introduction

Sandwich and half-sandwich type alkyl and hydrido complexes of lanthanides are highly reactive and have demonstrated very rich and unique chemistry.[1–5] They have been shown to mediate a wide range of transformations of unsaturated substrates.[6–15] Enhanced reactivity of lanthanide alkyl and hydrido complexes also leads to hydrocarbon activation[16–18] and alkane functionalization.[19] Reactivity of lanthanide compounds is known to be driven by electrophilicity and coordination unsaturation of the metal center and can be controlled through tuning of the electronic and steric properties of the ancillary ligation. In contrast to the well-developed chemistry of cyclopentadienyl-derived hydrido complexes of lanthanides, their analogues in alternative coordination environments still remain extremely poorly investigated.[20–27] Recently, research activity has been directed to design new ligand sets to extend the means of modification and control of reactivity of complexes. In an attempt to increase the electrophilicity of the metal center many research groups have focused their work on "harder" polydentate N and/or O coordinating ligands. These ligands should provide enough steric bulk to prevent further coordination of Lewis bases, dimerization, or ligand redistribution reactions, but do not dampen reactivity of complexes.[20–23] Ligand frameworks containing electronegative nitrogen atoms turned out to be the most promising ligands, since they show a high affinity to the hard Lewis acidic atoms of the rare-earth metals combined with structural diversity.[28,29] We focused on the tetrasubstituted guanidinate ligand system,[30] because its electronic and steric properties can be rationally modified by variation of the substituents at the nitrogen atoms. Several examples of alkyl complexes of rare-earth metals supported by guanidinate ligands were published recently.[31–34] We employed the advantages of the $[(Me_3Si)_2NC(N\mathit{i}Pr)_2]^-$ coordination environment for the stabilization of lanthanide hydride, and synthesized the first complex of this type, $[\{Lu\{(Me_3Si)_2NC(N\mathit{i}Pr)_2\}_2(\mu\text{-}H)\}_2]$.[35] We report here

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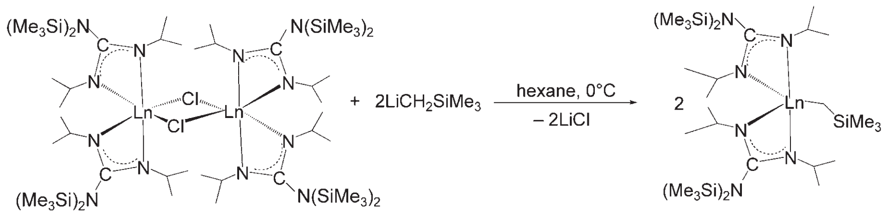
on synthesis, structure and reactivity of a new family of lanthanide–hydrido complexes [{Ln{(Me$_3$Si)$_2$NC(N*i*Pr)$_2$}$_2$(μ-H)}$_2$] (Ln = Y, Nd, Sm, Gd, Yb).

Results and Discussion

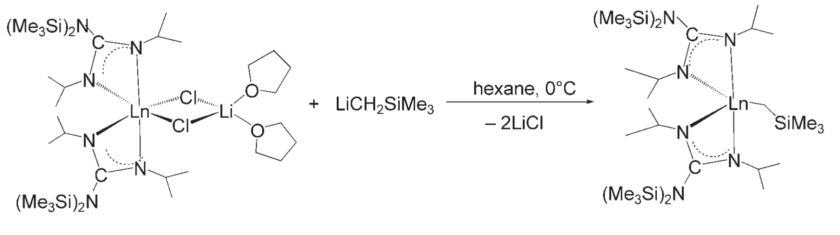
The most common synthetic route to lanthanide–hydrido complexes is σ-bond metathesis reaction of parent alkyls under treatment with dihydrogen[36,37] or phenylsilane.[38] We recently reported that the alkylation reaction of bis(guanidinate)lutetium chloride [Lu{(Me$_3$Si)$_2$NC(N*i*Pr)$_2$}$_2$(μ-Cl)$_2$Li(thf)$_2$] with an equimolar amount of Me$_3$SiCH$_2$Li in hexane at 0 °C leads to the isolation of the alkyl–lutetium complex [Lu{(Me$_3$Si)$_2$NC(N*i*Pr)$_2$}$_2$(CH$_2$SiMe$_3$)].[35] To prepare bis(guanidinate) alkyl complexes of other lanthanide metals we have employed the same synthetic approach. Dimeric bis(guanidinate) chlorides [{Ln{(Me$_3$Si)$_2$NC(N*i*Pr)$_2$}$_2$-(μ-Cl)}$_2$] (Ln = Nd (**1**),[39] Sm (**2**)[40]) and bis(guanidinate) chlorido ate complexes [Ln{(Me$_3$Si)$_2$NC(N*i*Pr)$_2$}$_2$(μ-Cl)$_2$Li-(thf)$_2$] (Ln = Y (**3**),[40] Gd (**4**),[40] Yb (**5**)[33]) were treated with Me$_3$SiCH$_2$Li in hexane at 0 °C [Eqs. (1) and (2)].



(1)

Ln = Nd (**1**), Sm (**2**)

Ln = Nd (**6**), Sm (**7**)



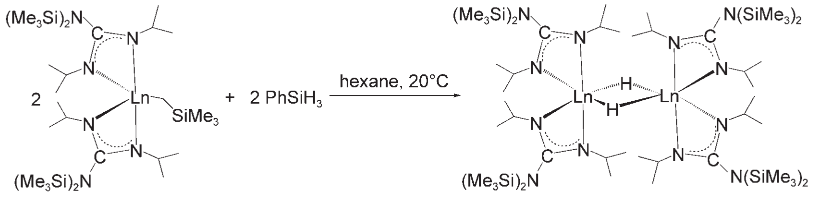
(2)

Ln = Y (**3**), Gd (**4**), Yb (**5**)

Ln = Y (**8**), Gd (**9**), Yb (**10**)

Separation of the precipitate of LiCl and evaporation of hexane in vacuo afforded the alkylation products **6–10**, which were isolated as viscous oils. Unfortunately all attempts to obtain crystalline samples of complexes **6–10** failed. According to ^{1}H and ^{13}C{^{1}H} NMR spectra the diamagnetic yttrium compound **8** is pure, but we did not succeed in obtaining satisfactory microanalysis data, because of the difficulty of preparation of samples of highly sensitive waxy compounds. Complex **8** does not contain coordinated THF molecules. In the ^{1}H and ^{13}C{^{1}H} NMR spectra of **8**, a single set of signals corresponding to the guanidinate fragments indicate the equivalence of both ligands. The presence of the CH$_2$SiMe$_3$ group in **8** is proved by a high-field-shifted doublet at $\delta = -0.29$ ppm (J(Y,H) = 3 Hz) in the ^{1}H NMR spectrum, corresponding to the two protons of the methylene group attached to the yttrium atom, and by a singlet at $\delta = 0.38$ ppm corresponding to the protons of the Me$_3$Si group. The carbon atoms of these groups appear as a doublet at $\delta = 34.9$ ppm (J(C,Y) = 42 Hz) and a singlet at $\delta = 4.9$ ppm in the ^{13}C{^{1}H} NMR spectrum of **8**. Complex **8** is thermally unstable and completely decomposes in [D$_6$]benzene within two days at 20 °C. Decomposition of **8** leads to disappearance of the signal at $\delta = -0.29$ ppm in the ^{1}H NMR spectrum and quantitative formation of Me$_4$Si. Because of the difficulties of isolation and instability of alkyl species **6–10**, they were generated "in situ" and used for synthesis of related hydrido derivatives as solutions in hexane after separation of LiCl.

We have investigated σ-bond metathesis reactions of alkyl complexes **6–10** with phenylsilane as a synthetic route to rare-earth bis(guanidinate) hydrides. Reactions of **6–10** with equimolar amounts of PhSiH$_3$ were carried out in hexane at room temperature and resulted in immediate crystallization of hydrido complexes [{Ln{(Me$_3$Si)$_2$NC(N*i*Pr)$_2$}$_2$(μ-H)}$_2$] (Ln = Y (**11**), Nd (**12**), Sm (**13**), Gd (**14**), Yb (**15**)) from the reaction mixture [Eq. (3)]. Complexes **11** and **15** crystallize from hexane as solvates with one or half a solvent molecule per unit cell, respectively, while crystals of **12**, **13**, **14** do not contain the solvent molecules. Exposure of complexes **11** and **15** at room temperature to dynamic vacuum (0.5–1 h) lead to removal of hexane and the isolation of nonsolvated compounds.



(3)

Ln = Y (**11**), Nd (**12**), Sm (**13**), Gd (**14**), Yb (**15**)

The hydrides were isolated in reasonable to high reproducible yields (82 (**11**), 79 (**12**), 72 (**13**), 81 (**14**), and 58

(**15**) %). Hydrido complexes are extremely air- and moisture-sensitive crystalline solids. They are sparingly soluble in aromatic hydrocarbons and poorly soluble in hexane. Complexes **11** and **14** are colorless, **12** is cherry-red, **13** is yellow, and **15** is orange. Complexes **11**–**15** can be kept in solid state in dry argon or in sealed evacuated tubes at 0 °C for several weeks without decomposition. The ^{1}H NMR samples of **11** in [D$_6$]benzene do not show any traces of decomposition or solvent metalation over a period of four days at 20 °C. The ^{1}H and $^{13}C\{^1H\}$ NMR spectra of diamagnetic complex **11** (20 °C, C_6D_6) are consistent with a dimeric molecule with an internal mirror plane. The hydrido ligands appear in the ^{1}H NMR spectrum of **11** as a sharp well-resolved triplet at $\delta = 7.94$ ppm ($^1J(Y,H) = 26.2$ Hz), thus indicating coupling of each hydrido ligand with two equivalent ^{89}Y nuclei (Figure 1).

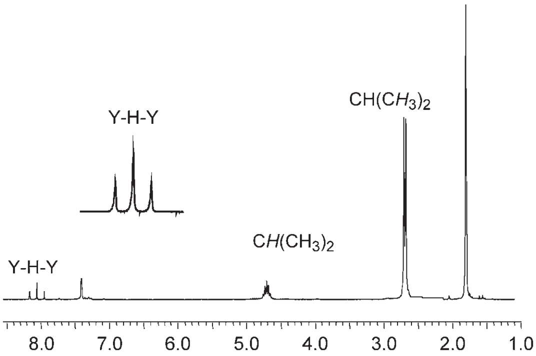


Figure 1. ^{1}H NMR spectrum of complex $[\{Y\{(Me_3Si)_2NC(N\mathit{i}Pr)_2\}_2(\mu\text{-}H)\}_2]$ (**11**), [D$_6$]benzene, 20 °C.

The signal of hydrido ligands of **11** is substantially shifted to the low field compared to the positions of respective signals of the other reported sandwich and half-sandwich yttrium hydrides ($[\{Y(\mathit{t}BuC_5H_4)_2(\mu\text{-}H)\}_2]$ $\delta = 3.09$ ppm, $^1J(Y,H) = 32.8$ Hz;[38] $[\{Y(Cp)_2(thf)(\mu\text{-}H)\}_2]$ $^1J(Y,H) = 2.02$, 27.0 Hz;[41] $[\{Y(2,4,7\text{-}Me_3C_9H_4)_2(\mu\text{-}H)\}_2]$ $^1J(Y,H) = 2.69$, 32.7 Hz;[14] $[\{Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)Y(thf)(\mu\text{-}H)\}_2]$ $^1J(Y,H) = 5.50$, 28.8 Hz;[42] $[\{Y(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NCMe_3)(thf)(\mu\text{-}H)\}_2]$ $^1J(Y,H) = 5.50$, 26.8 Hz[43]) and is close to the chemical shift of the related amidinate supported complex ($[\{Y\{PhC(NSiMe_3)_2\}_2Y(\mu\text{-}H)\}_2]$ $^1J(Y,H) = 8.28$, 27.6 Hz).[15] This observation is consistent with enhanced electron-withdrawing properties of guanidinate ligands relative to those of cyclopentadienyl ligands. Unlike the lutetium analogue $[\{Lu\{(Me_3Si)_2NC(N\mathit{i}Pr)_2\}_2(\mu\text{-}H)\}_2]$ the guanidinate ligands of **11** give a single set of signals in the ^{1}H and $^{13}C\{^1H\}$ NMR spectra, indicating equivalence of both $\{(Me_3Si)_2NC(N\mathit{i}Pr)_2\}$ fragments.

Clear colorless single-crystal samples of **11** suitable for X-ray crystal structure determination were obtained by slow cooling of a solution of **11** in hexane from 40 to 20 °C. The molecular structure of **1** is depicted in Figure 2; the crystal data and structural refinement data are listed in Tables 1 and 2. The results of the X-ray single-crystal structure analysis show that **11** adopts a dimeric structure (Figure 2). The coordination sphere of the metal centre is determined by the four nitrogen atoms of the two guanidinate ligands and by two bridging hydrido ligands. The formal coordination number of the metal atom is six.

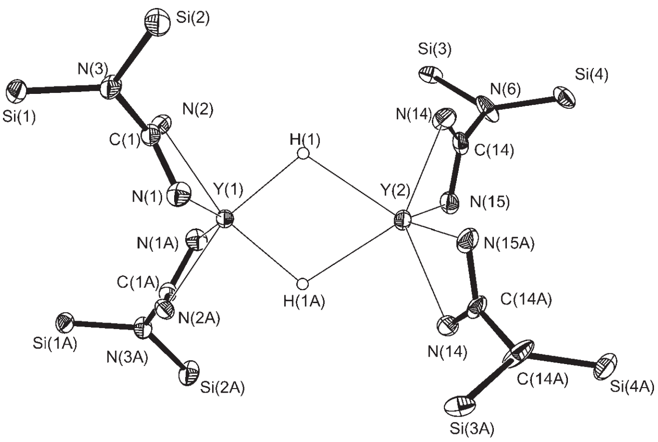


Figure 2. Molecular structure of complex **11** with 30 % ellipsoid probability; the isopropyl and methyl groups of $SiMe_3$ fragments are omitted.

In the planar tetranuclear Y_2H_2-core the Y–H bond lengths are noticeably different: 2.15(3) and 2.50(4) Å. One is comparable to those in reported metallocene- and bis(amidinate)hydrido complexes $[\{Y(MeC_5H_4)_2(thf)(\mu\text{-}H)\}_2]$ (2.17(8), 2.19(8) Å), $[\{Y(1,3\text{-}Me_2C_5H_3)_2(thf)(\mu\text{-}H)\}_2]$ (2.03(7), 2.27(6) Å),[44] ($[\{Y\{PhC(NSiMe_3)_2\}_2(\mu\text{-}H)\}_2]$ (2.11(3), 2.16(3)[15] while the second one is substantially longer. The Y-Y distance in **11** (3.6825(5) Å) are very close to that found in the complexes $[Y(MeC_5H_4)_2(thf)(\mu\text{-}H)]_2$ (3.66(1) Å), $[Y(1,3\text{-}Me_2C_5H_3)_2(thf)(\mu\text{-}H)]_2$ (3.68(1) Å),[44] $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NCMe_3)(thf)(\mu\text{-}H)]_2$ (3.7085(8) Å).[43] The Y-H-Y angles in the Y_2H_2-core are comparable to those in other dimeric μ^2-hydrido bridged yttrium complexes in bis(cyclopentadienyl)[41,44], amidocyclopentadienyl[42,43] and bis(amidinate)[15] ancillary ligation. Unlike the lutetium analogue $[\{Lu\{(Me_3Si)_2NC(N\mathit{i}Pr)_2\}_2(\mu\text{-}H)\}_2]$[35] (**16**) in which the $\{Lu\{(Me_3Si)_2NC(N\mathit{i}Pr)_2\}_2\}$ fragments are nonequivalent due to substantial difference of the M–N bond lengths in **11** the related distances are very similar (2.349(2) and 2.365(2) Å). The N–C distances in the guanidinate ligands of **11** differ only slightly between each other (1.353(3), 1.334(3), 1.346(4), and 1.344(4) Å) which reflects electron delocalization within the anionic NCN units. The results of the X-ray diffraction study reveal equivalence of the guanidinate ligands in **11** thus proving the solution ^{1}H and ^{13}C NMR data. The "bite" angles between two carbon atoms that can be regarded as centroids of guanidinate ligands in $\{Y\{(Me_3Si)_2NC(N\mathit{i}Pr)_2\}_2\}$ moieties are C(1)-Y(1)-C(1A) 122.2(1)° and C(14)-Y(2)-C(14A) 121.9(1)°. Remarkably, the disposition of the two $\{Y\{(Me_3Si)_2NC(N\mathit{i}Pr)_2\}_2\}$ groups is such that the planes defined by C(1)Y(1)C(1A) and C(14)Y(2)C(14A) are nearly orthogonal (86.0(1)°); this geometry leads to a decrease in the steric hindrance in the coordination sphere of the Y atoms.

Table 1. Bond lengths and angles for complexes **11**–**15**.

	Bond lengths [Å]				Bond angles [°]		
	M–H	M–N	N–C	M–M	M-H-M	C-M-C	dihedral angle[a]
11	2.15(3)	2.349(2)	1.353(3)	3.6825(5)	104.6(1)	122.2(1)	86.0(1)
	2.50(4)	2.349(2)	1.334(3)			121.9(1)	
		2.365(2)	1.346(4)				
		2.365(2)	1.344(4)				
12	2.54(4)	2.431(2)	1.336(4)	3.8892(2)	100.0(8)	120.99(8)	7.6(2)
	2.54(4)	2.440(2)	1.340(4)		99.9(8)	124.59(8)	
	2.53(4)	2.471(2)	1.332(4)				
	2.53(4)	2.487(3)	1.325(4)				
		2.443(2)	1.340(4)				
		2.460(3)	1.312(4)				
		2.462(3)	1.334(4)				
		2.479(2)	1.320(4)				
13	2.33(2)	2.402(2)	1.337(2)	3.8102(2)	107.1(5)	120.88(5)	7.7(2)
	2.40(2)	2.403(2)	1.325(3)		108.1(5)	123.90(5)	
	2.40(2)	2.452(2)	1.323(2)				
	2.31(2)	2.466(2)	1.328(2)				
		2.418(2)	1.320(2)				
		2.428(2)	1.333(2)				
		2.445(2)	1.325(2)				
		2.447(2)	1.344(3)				
14	2.53(2)	2.377(2)	1.342(3)	3.8069(2)	97.3(6)	120.39(6)	7.5(2)
	2.60(2)	2.382(2)	1.333(3)		94.7(3)	123.31(6)	
	2.57(2)	2.432(2)	1.324(3)				
	2.54(2)	2.444(2)	1.330(3)				
		2.385(2)	1.329(3)				
		2.417(2)	1.349(3)				
		2.425(2)	1.322(3)				
		2.425(2)	1.332(3)				
15	2.15(3)	2.305(3)	1.352(7)	3.5971(4)	113.9(1)	121.9(1)	87.6(1)
	2.14(3)	2.331(3)	1.335(7)			121.2(2)	
		2.303(3)	1.315(5)				
		2.328(3)	1.380(5)				

[a] Dihedral angle between the planes defined by the centroids of guanidinate ligands and the metal atoms (C-M(1)-C and C-M(2)-C) of two $M\{(Me_3Si)_2NC(N\textit{i}Pr)_2\}_2$ moieties.

Single-crystal samples of complexes **12**–**15** were obtained by slow cooling of solutions of the complexes in hexane from 40 to 20 °C. The crystal data and structural refinement data for complexes **12**–**15** are listed in Tables 1 and 2.

X-ray diffraction studies have revealed that complexes **12**–**15** are dimeric with similar coordination environment of the central metal atoms. The structures of hydrido complexes **11**–**15** can be divided in two groups accordingly to their principal distinction, that is, reciprocal orientation of the $M\{(Me_3Si)_2NC(N\textit{i}Pr)_2\}_2$ moieties in dimer. The value of the dihedral angles between two planes defined by the central carbon atoms of two guanidinate ligands and the metal atom (for example C(1)-Y(1)-C(1A), C(14)-Y(2)-C(14A) for **11** and C(1)-Nd(1)-C(14), C(27)-Nd(2)-C(40) for **12**) were used for quantitative estimation of mutual disposition of two $M\{(Me_3Si)_2NC(N\textit{i}Pr)_2\}_2$ fragments. For yttrium, ytterbium, and lutetium, which all have smaller ion sizes, these planes are nearly orthogonal (point group C_2) with the value of dihedral angle being 86.0(1), 87.6(1) and 86.9(1)°, respectively, resulting staggered conformation of the dimers. This structural type is presented by complex **11** in Figure 2. In the complexes of the larger lanthanide atoms neodymium, samarium and gadolinium, these planes are nearly coplanar (7.6(2), 7.7(2), 7.5(2)°) and the dimers are close to adopt eclipsed conformation (point ghroup D_{2h}). The structure of this type is represented by complex **12** in Figure 3. The staggered conformation of dimeric complexes of yttrium, ytterbium, and lutetium leads to a decrease in the steric hindrance in the coordination sphere of the metal atoms. The geometric parameters within the guanidinate ligands of complexes **1**–**15** are similar.

Initial reactivity studies were carried out for diamagnetic yttrium compound **11**, which was chosen as a model complex for a new hydride series. Despite of the fact that the terminal hydride functionality in $[Y(Cp^*)_2H]$ was shown to be much more reactive than those in bridging hydrides $[\{Y(Cp^*)_2H\}_2]$,[46] the number of known monomeric hydrides still remains very limited.[18,24,47–49] In an effort to generate highly active monomeric hydrido species we treated complex **11** in $[D_6]$benzene with 0.2 equivalents of $[D_8]$THF at 20 °C and monitored the reaction by ^{1}H NMR spectroscopy. Addition of $[D_8]$THF resulted in a complication of the spectrum and appearance of a new doublet at $\delta = 7.54$ ppm with $^1J(Y,H) = 60.2$ Hz together with usual triplet at $\delta = 7.94$ ppm ($^1J(Y,H) = 26.2$ Hz). Dissolving **11** in an excess of $[D_8]$THF at 20 °C leads to complete disappearance of the triplet at $\delta = 7.94$ ppm, while the doublet at $\delta = 7.54$ ppm remains. Previously, Teuben et al. and Tilley et al. described monomeric hydrido complexes containing coordinated molecule of THF $[Y(Cp^*)_2H(thf)]$[18] and $[Y(C_9Me_7)_2H(thf)]$.[47] In the ^{1}H NMR spectra of these compounds the terminal hydride ligands were identified by doublets with large coupling constants ($[Y(Cp^*)_2H(thf)]$: $\delta = 6.17$ ppm, $^1J(Y,H) = 81.74$ Hz; $[Y(C_9Me_7)_2H(thf)]$: $\delta = 6.04$ ppm, $^1J(Y,H) = 82.0$ Hz). Probably the doublet at $\delta = 7.54$ ppm in the ^{1}H NMR spectrum of **11** can be attributed to terminal hydrido ligand of monomeric THF adduct $[Y\{(Me_3Si)_2NC(N\textit{i}Pr)_2\}_2(H)(thf)_n]$. Our efforts to isolate the THF adduct failed because of its low stability in solution. To provoke dissociation of a dimeric **11** a twentyfold molar excess of PMe_3 was added to a solution of the complex in hexane. This treatment did not result in coordination of a Lewis base to the metal atom. Evaporation of volatiles and recrystallization of the solid residue from hexane lead to the recovery of complex **11**. Complex **11** turned out to be rather inert with respect to addition to mul-

Table 2. Crystallographic data and structure refinement details for **11**–**15**.

	11	**12**	**13**	**14**	**15**
formula	$C_{58}H_{144}N_{12}Si_8Y_2$	$C_{52}H_{130}N_{12}Nd_2Si_8$	$C_{52}H_{130}N_{12}Si_8Sm_2$	$C_{52}H_{130}Gd_2N_{12}Si_8$	$C_{55}H_{137}N_{12}Si_8Yb_2$
M_r	1409.10	1436.88	1448.09	1462.90	1527.49
T [K]	100(2) K	100(2) K	100(2) K	100(2) K	100(2) K
crystal system	trigonal	orthorhombic	orthorhombic	orthorhombic	trigonal
space group	$P3_221$	$Pna2_1$	$Pna2_1$	$Pna2_1$	$P3_221$
a [Å]	14.8543(6)	19.7837(9)	19.7465(8)	19.7254(8)	14.8471(4)
b [Å]	14.8543(6)	20.5623(10)	20.5430(8)	20.5171(8)	14.8471(4)
c [Å]	32.8284(19)	19.2253(9)	19.1232(8)	19.1192(8)	32.0685(17)
α [°]	90	90	90	90	90
β [°]	90	90	90	90	90
γ [°]	120	90	90	90	120
V [Å^3]	6273.1(5)	7820.8(6)	7757.4(5)	7737.7(5)	6122.0(4)
Z	3	4	4	4	3
ρ_{calcd} [Mg m^{-3}]	1.082	1.220	1.240	1.256	1.243
μ [mm^{-1}]	1.532	1.473	1.660	1.861	2.432
$F(000)$	2202	3032	3044	3064	2379
crystal size [mm^3]	$0.35\times0.30\times0.25$	$0.20\times0.17\times0.11$	$0.20\times0.18\times0.15$	$0.40\times0.32\times0.25$	$0.30\times0.20\times0.15$
θ range [°]	1.58–24.99	1.45–21.00	1.78–25.00	1.43–25.00	1.58–23.98
index ranges	$-17\leq h\leq 17$	$-19\leq h\leq 19$	$-23\leq h\leq 23$	$-23\leq h\leq 23$	$-16\leq h\leq 16$
	$-17\leq k\leq 17$	$-20\leq k\leq 20$	$-24\leq k\leq 24$	$-24\leq k\leq 24$	$-16\leq k\leq 16$
	$-39\leq 1\leq 38$	$-19\leq l\leq 19$	$-22\leq l\leq 22$	$-22\leq l\leq 22$	$-36\leq l\leq 36$
reflns collected	49308	40783	59367	59566	44153
independent reflns	7377	8373	13628	13617	6362
	[R(int) = 0.0523]	[R(int) = 0.0368]	[R(int) = 0.0237]	[R(int) = 0.0329]	[R(int) = 0.0403]
completeness to θ [%]	99.9	99.8	100.0	100.0	99.4
max/min transmission	0.821/0.616	0.8548/0.7572	0.7888/0.7325	0.6534/0.5232	0.7118/0.5291
data/restraints/parameters	7377/64/420	8373/9/701	13628/11/711	13617/9/709	6362/294/516
goodness-of-fit on F	1.051	1.025	1.043	1.040	1.170
final R indices [$I>2\sigma(I)$]	$R1=0.0555$,	$R1=0.0228$,	$R1=0.0184$,	$R1=0.0230$,	$R1=0.0562$,
	$wR2=0.1510$	$wR2=0.0527$	$wR2=0.0472$	$wR2=0.0608$	$wR2=0.1477$
R indices (all data)	$R1=0.0726$,	$R1=0.0251$,	$R1=0.0192$,	$R1=0.0240$,	$R1=0.0563$,
	$wR2=0.1562$	$wR2=0.0535$	$wR2=0.0476$	$wR2=0.0613$	$wR2=0.1478$
absolute structure parameter	0.000(3)	0.024(7)	0.411(3)	0.007(5)	0.06(3)
largest diff. peak/hole [e Å^{-3}]	1.214/−0.535	0.524/−0.196	0.812/−0.244	2.329/−0.449	1.362/−2.815

tiple carbon–carbon bonds of substituted olefins; it does not react with styrene, stilbene, tolane or bis(trimethylsilyl)acetylene ([D$_6$]benzene, 20 °C, 96 h). Evidently the bis(guanidinate) ligand system creates steric saturation of the coordination sphere of the metal atom providing its kinetic stability, but also dampening reactivity.

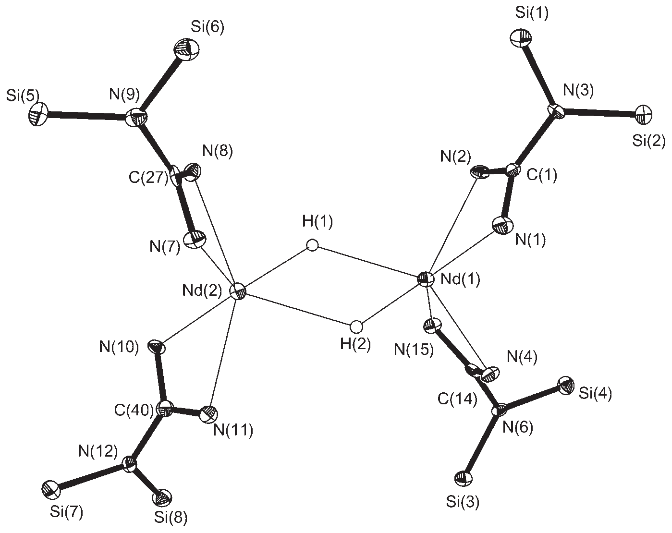


Figure 3. Molecular structure of complex **12** with 30 % ellipsoid probability; the isopropyl and methyl groups of $SiMe_3$ fragments are omitted.

The catalytic tests of complexes **11**–**15** with ethylene were carried out under rigorously anaerobic conditions in sealed glass manometric system (toluene 5 mL, catalyst concentration 1.6–5.9 × 10^{-6} mol L^{-1}, 20 °C, ethylene pressure 0.5 atm); this set up allowed us to monitor the polymerization process by absorption of the monomer. Catalysts efficiencies were estimated by both monomer absorption and by quenching the polymerization reaction after measured time intervals and weighing the quantity of polyethylene produced. The results on ethylene polymerization are shown in Figure 4. The ethylene polymerization activity of the samarium–hydrido complex **13**, 1268 g mmol^{-1} atm^{-1} h^{-1} was the highest among tested compounds. By the end of one day the complex was still active without loss of the reaction rate. In the case of the yttrium derivative **11** the polymerization process was less rapid (442 g mmol^{-1} atm^{-1} h^{-1}) and the catalyst did not demonstrate loss of the reaction rate during three days. Unexpectedly[36] the neodimium complex **12** had very low activity as a catalyst for the polymerization of ethylene and after

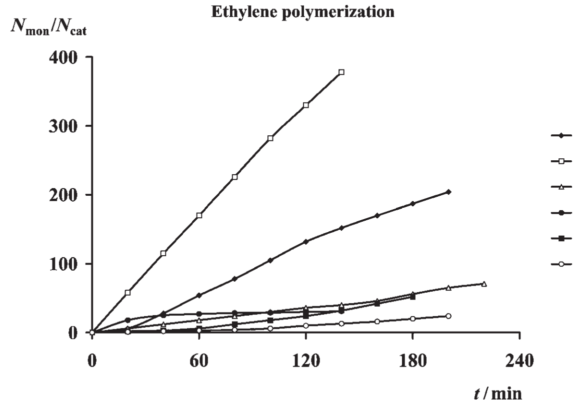


Figure 4. Polymerization of ethylene catalyzed by $[\{Ln\{(Me_3Si)_2NC(N\textit{i}Pr)_2\}_2(\mu\text{-}H)\}_2]$ complexes (Ln = Y (**11**), Nd (**12**), Sm (**13**), Gd (**14**), Yb (**15**), Lu (**16**); toluene 5 mL, catalyst concentration $1.6–5.9\cdot10^{-6}$ mol L^{-1}, 20 °C, ethylene pressure 0.5 atm).

1 h the reaction stopped. Complexes of gadolinium, ytterbium, and lutetium have shown modest catalytic activity (281, 77, and 76 g mmol^{-1} atm^{-1} h^{-1}, respectively). Most of the lanthanide complexes that readily polymerize ethylene are inactive in propylene polymerization.[36] Complexes **11**–**15** have been tested in catalysis of propylene polymerization (Figure 5).

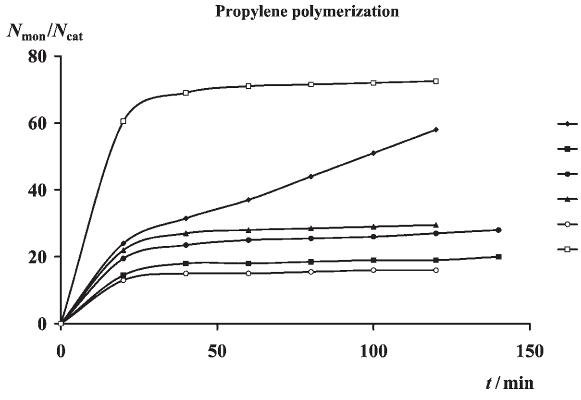


Figure 5. Polymerization of propylene catalyzed by $[\{Ln\{(Me_3Si)_2NC(N\textit{i}Pr)_2\}_2(\mu\text{-}H)\}_2]$ complexes (Ln = Y (**11**), Nd (**12**), Sm (**13**), Gd (**14**), Yb (**15**), Lu (**16**); toluene 5 mL, catalyst concentration $1.9–6.1\times10^{-6}$ mol L^{-1}, 0 °C, propylene pressure 0.5 atm).

The yttrium derivative **11** had low activity in propylene polymerization. Over a period of two hours the monomer absorption reached 58 mol per mole of catalyst, whereupon the catalytic activity was lost. Complexes **12**–**15** were even less active and became inactive after 15–20 min. In styrene polymerization, only derivatives of smallest lanthanide metals showed catalytic activity. Complex **16** initiates polymerization of styrene (20 °C, neat styrene, 5 % of **16**), and 90 % conversion was reached in six days; the polystyrene obtained had a high molecular weight ($M_n = 811\,000$ g mol^{-1}, $M_w = 1250\,000$ g mol^{-1}), a narrow molecular-weight distribution ($M_w/M_n = 1.54$), and melting temperature 255–260 °C. In the case of **15** (20 °C, neat styrene, 1 mol % of **15**, total conversion in three days) the obtained polymer had a higher molecular-weight distribution $M_w/M_n = 2.6$ ($M_n = 90\,000$ g mol^{-1}, $M_w = 237\,700$ g mol^{-1}; melting temperature 289–293 °C). The ^{13}C NMR spectra of both polystyrenes indicate their high syndiotactisity.

A stoichiometric reaction of **11** with ethylene in [D$_6$]benzene at room temperature under ^1H NMR spectroscopic control did not afford an insertion product $[Y\{(Me_3Si)_2NC(N\textit{i}Pr)_2\}_2(CH_2CH_3)]$, but resulted in rapid polyethylene formation.

Conclusions

Bis(guanidinate) ligand set was demonstrated to be a suitable coordination environment for the stabilization of the hydrido complexes of rare-earth metals with different ion size. Due to bulky substituents on the nitrogen atoms this ancillary ligation provides high solubility of the lanthanide derivatives and allows us to obtain Lewis base free hydrides with extremely low coordination number at the metal atom. The new family of hydrido complexes of rare-earth metals was synthesized and structurally characterized. Bis(guanidinate)-hydrido complexes of samarium and yttrium have shown high catalytic activity in ethylene polymerization. Studies on reactivity and catalytic activity of bis(guanidinate)hydrido derivatives of the lanthanides are currently in progress.

Experimental Section

General remarks: All experiments were performed in evacuated tubes, using standard Schlenk techniques with rigorous exclusion of traces of moisture and air. THF, benzene, toluene, and hexane were purified by distillation from sodium/benzophenone ketyl and were condensed in vacuum prior to use. *N,N'*-Diisopropylcarbodiimide was purchased from Acros, dried with molecular sieves and purified by distillation. Anhydrous $LnCl_3$[50] and $[LiN(SiMe_3)_2(Et_2O)]$[51] were prepared according to literature procedures. All other commercially available chemicals were used after the appropriate purification. IR spectra were recorded as Nujol mulls on a Specord M80 spectrophotometer. NMR spectra were recorded on a Bruker DPX 200 spectrometer (^1H, 200 MHz; ^{13}C, 50 MHz) in C_6D_6 at 20 °C, unless otherwise stated. Deuterated benzene was dried with sodium benzophenone ketyl and vacuum-transferred. Chemical shifts for ^1H and ^{13}C spectra were referenced internally according to the residual solvent resonances and reported relative to tetramethylsilane. Lanthanide metal analyses were carried out by complexometric titration. Molecular weight and molecular weight distributions were determined against polystyrene standards by gel permeation chromatography (GPC) with a Knauer apparatus with Phenogel columns (10 um, Linear 2) using chloroform as the eluent.

Synthesis of $[Y\{(Me_3Si)_2NC(N\textit{i}Pr)_2\}_2CH_2SiMe_3]$ (8): A solution of Me_3SiCH_2Li (0.087 g, 0.93 mmol) in hexane (10 mL) was added to a solution of **3** (0.82 g, 0.93 mmol) in hexane (20 mL) at 0 °C, and the reaction mixture was stirred for 1 h. The pale yellow solution was filtered and hexane was evaporated in vacuo. Complex **8** was isolated as pale yellow viscous oil (0.60 g, 86 %). ^1H NMR (200 MHz, [D$_6$]benzene): $\delta = -0.29$ (d, $^2J(Y,H) = 3$ Hz, 2H; CH_2SiMe_3), 0.25 (s, 36H; $NSi(CH_3)_3$), 0.38 (s, 9H; $Si(CH_3)_3$), 1.30 (d, $^3J(H,H) = 6.2$ Hz, 24H; $CH(CH_3)_2$), 3.78 ppm (br m, 4H; $CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (50 MHz, [D$_6$]benzene): $\delta = 2.5$ ($(NSiCH_3)_2$), 4.9 (CH_2SiCH_3), 27.1 ($CH(CH_3)_2$), 34.5 (d, $J(C,Y) = 42$ Hz, YCH_2), 46.2 ($CH(CH_3)_2$), 169.2 ppm (CN_3); IR (nujol, KBr): $\tilde{\nu}=1635$ (s), 1315 (w), 1245 (s), 1200 (s), 1215 (m), 960 (s), 935 (m), 825 cm^{-1} (s).

Synthesis of [{Y{(Me$_3$Si)$_2$NC(N*i*Pr)$_2$}$_2$(μ-H)}$_2$] (11): Phenylsilane (0.069 mL, 0.55 mmol) was added to a solution of **8** obtained in situ from 0.491 g (0.55 mmol) of **3** and 0.052 g (0.55 mmol) of Me_3SiCH_2Li in hexane (20 mL) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C and then concentrated in vacuo to approximately a quarter 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 colorless solid was washed with cold hexane and dried in vacuo at room temperature for 45 min to give **11** as a colorless microcrystalline solid (0.301 g, 82 %). ^{1}H NMR (200 MHz, [D$_6$]benzene): $\delta=0.36$ (s, 72 H; NSi(CH_3)$_3$), 1.44 (d, ^3J(H,H) = 6.4 Hz, 48 H; CH(CH_3)$_2$), 3.89 (sept, ^3J(H,H) = 6.4 Hz, 8 H; CH(CH_3)$_2$), 7.95 ppm (t, ^1J(Y,H) = 26.0 Hz, 2 H; YH); ^{13}C{^{1}H} NMR (50 MHz, [D$_6$]benzene): $\delta=2.9$ (N(SiCH_3)$_2$), 28.3 (CH(CH_3)$_2$), 46.4 (CH(CH$_3$)$_2$), 168.8 ppm (CN_3); IR (Nujol, KBr): $\tilde{\nu}=1630$ (s), 1605 (m), 1320 (s), 1250 (s), 1205 (s), 1050 (s), 950 (s), 820 cm^{-1} (s); elemental analysis calcd (%) for $C_{52}H_{130}N_{12}Si_8Y_2$ (1325.1): C 47.13, H 9.81, Y 13.41; found: C 46.79, H 9.66, Y 13.70.

Synthesis of [{Nd{(Me$_3$Si)$_2$NC(N*i*Pr)$_2$}$_2$(μ-H)}$_2$] (12): A solution of Me_3SiCH_2Li (0.070 g, 0.74 mmol) in hexane (10 mL) was slowly added to a solution of **1** (0.550 g, 0.36 mmol) in hexane (40 mL) at 0 °C. The reaction mixture was stirred for 1 h and filtered. Phenylsilane (0.092 mL, 0.74 mmol) was added to a reaction mixture at 0 °C. The solution was stirred for 30 min at 0 °C and then concentrated in vacuo to approximately one quarter 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 colorless solid was washed with cold hexane and dried in vacuo at room temperature for 45 min to give **12** as a cherry-red crystalline solid (0.408 g, 79 %). IR (Nujol, KBr): $\tilde{\nu}=1639$ (s), 1406 (s), 1313 (s), 1252 (s), 1194 (s), 1167 (m), 1103 (s), 1047 (s), 955 (s), 833 cm^{-1} (s); elemental analysis calcd (%) for $C_{52}H_{130}N_{12}Nd_2Si_8$ (1436.8): C 43.46, H 9.04, Nd 20.07; found: C 43.09, H 9.32, Nd 20.33.

Synthesis of [{Sm{(Me$_3$Si)$_2$NC(N*i*Pr)$_2$}$_2$(μ-H)}$_2$] (13): The proceedure described for complex **12** was used, but with Me_3SiCH_2Li (0.090 g, 0.96 mmol) in hexane (10 mL), **2** (0.730 g, 0.48 mmol) in hexane (40 mL), and phenylsilane (0.126 mL, 1.00 mmol). Complex **13** was isolated as a yellow crystalline solid (0.500 g, 72 %). IR (Nujol, KBr): $\tilde{\nu}=1639$ (s), 1409 (s), 1315 (s), 1254 (s), 1196(s), 1168 (m), 1120 (m), 1050 (s), 955 (s), 840(s), 760 cm^{-1} (m); elemental analysis calcd (%) for $C_{52}H_{130}N_{12}Si_8Sm_2$ (1448.1): C 43.13, H 8.97, Sm 20.76; found: C 42.88, H 8.73, Sm 21.00.

Synthesis of [{Gd{(Me$_3$Si)$_2$NC(N*i*Pr)$_2$}$_2$(μ-H)}$_2$] (14): The proceedure described for complex **12** was used, but with Me_3SiCH_2Li (0.110 g, 1.17 mmol) in hexane (10 mL), **4** (1.020 g, 1.07 mmol) in hexane (40 mL), and phenylsilane (0.137 mL, 1.11 mmol). Complex **14** was isolated as a colorless crystalline solid (0.630 g, 81 %); IR (Nujol, KBr): $\tilde{\nu}=1639$ (s), 1407 (s), 1318 (s), 1253 (s), 1198(s), 1169 (m), 1123 (m), 1049 (s), 955 (s), 841 (s), 757 cm^{-1} (m); elemental analysis calcd (%) for $C_{52}H_{130}Gd_2N_{12}Si_8$ (1462.9): C 42.69, H 8.88, Gd 21.49; found: C 42.27, H 8.50, Gd 21.68.

Synthesis of [{Yb{(Me$_3$Si)$_2$NC(N*i*Pr)$_2$}$_2$(μ-H)}$_2$] (15): The proceedure described for complex **12** was used, but with Me_3SiCH_2Li (0.070 g, 0.74 mmol) in hexane (10 mL), **5** (0.680 g, 0.70 mmol) in hexane (20 mL), and phenylsilane (0.092 mL, 0.74 mmol). Complex **15** was isolated as an orange crystalline solid (0.300 g, 58 %); IR (Nujol, KBr): $\tilde{\nu}=1638$ (s), 1407 (s), 1331 (s), 1253 (s), 1229 (s), 1182(s), 1123 (m), 1050 (s), 955 (s), 919 (s), 880 (s), 833 (s), 760 cm^{-1} (m); elemental analysis calcd (%) for $C_{52}H_{130}N_{12}Si_8Yb_2$ (1493.3): C 41.82, H 8.70, Yb 23.17; found: C 41.40, H 8.59, Yb 22.92.

Catalytic tests procedures. Catalytic tests with ethylene and propylene were carried out under rigorously anaerobic conditions in sealed glass manometric system (ethylene: toluene 5 mL, catalyst concentration 1.6–5.9 × 10^{-6} mol L^{-1}, 20 °C, ethylene pressure 0.5 atm; propylene: toluene 5 mL, catalyst concentration 1.9–6.1 × 10^{-6} mol L^{-1}, 0 °C, propylene pressure 0.5 atm). The reactions were monitored by monomer absorption. Catalysts efficiencies were estimated by both monomer absorption and by quenching the polymerization reaction after measured time intervals and weighing the quantitaty of polymer produced. The polymers were washed with dilute HCl and methanol, and dried in vacuo to constant weight.

Crystal structure determinations: Intensity data were collected on a Smart Apex diffractometer (graphite monochromator, Mo$_{K\alpha}$ radiation ($\lambda=0.71073$ Å), ϕ–ω scan mode ($\omega=0.3°$, 10 s for each frame) Absorption corrections were made by SADABS program.[52] The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods by using SHELXTL.[53] All non-hydrogen atoms were refined anisotropically. The H atoms in all complexes were placed in calculated positions and refined in the riding model ($U_{iso}(H)=1.5\,U_{eq}(C)$ Å^2 for alkyl hydrogen atoms). The μ$_2$-H atoms in all complexes were found from Fourier synthesis and refined with fixed U_{iso} parameters isotropically. All complexes contain disordered in two positions SiMe$_3$, Me and *i*Pr groups.

Complexes **11** and **15** crystallize as the hexane solvate, whereas complexes **12**–**14** do not contain the solvent molecules.

Table 2 summarizes the crystal data and some details of the data collection and refinement for **11**–**15**. Selected bond distances and angles for molecules **11**–**15** are given in Table 1.

CCDC- 256428–256431 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.

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