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Lanthanide Borohydride Complexes of Bulky Guanidinate Ligands $[(Me_3Si)_2NC(N\text{-}Cy)_2]_2Ln(\mu\text{-}BH_4)_2Li(THF)_2$ (Ln = Nd, Sm, Yb): Synthesis, Structure and Catalytic Activity in Lactide Polymerization

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A series of new lanthanide borohydride complexes supported by bulky guanidinate ligands $[(Me_3Si)_2NC(N\text{-}Cy)_2]_2Ln(\mu\text{-}BH_4)_2Li(THF)_2$ [Ln = Nd (**1**), Sm (**2**), Yb (**3**)] was synthesized by the reaction of related tris(borohydride)s $Ln(BH_4)_3(THF)_2$ with a twofold molar excess of $[(Me_3Si)_2NC(N\text{-}Cy)_2]Li$ in toluene at 65 °C. The complexes were isolated after recrystallization from hexane in 66, 64, and 68 % yield, respectively. X-ray diffraction studies revealed that compounds **1**–**3** are heterodimetallic complexes that have two borohydride ligands μ-bridging the lanthanide and lithium atoms. Those compounds, especially neodymium complex **1**, act as mono-initiators for the ring-opening polymerization of racemic lactide, providing atactic polymers with a good degree of control, that is, controlled molecular weights and relatively narrow polydispersities ($1.09 < M_w/M_n < 1.77$), provided moderate substrate-to-initiator ratios are used.

Introduction

Metallocene-type lanthanide borohydride complexes have been known for three decades;[1] nevertheless, this class of compounds still attracts considerable attention because of their structural diversity and high catalytic activity.[2] Monoanionic borohydride groups can perform both μ-bridging and terminal coordination modes that result in formation of dimeric[3,4] or monomeric organolanthanide complexes.[5–7] Depending on the central atom size and its coordination environment, borohydride anions can act in monomeric complexes as bi-[1,3,5,7,8] and tridentate[1,4,9,10] ligands. For dimeric complexes μ^3:μ^2-bridging coordination has been described.[4,11] A renewed interest in lanthanide borohydride complexes arose from communications on their catalytic activity in lactone,[12] lactide,[13] and methyl methacrylate[14] polymerizations. Also, some lanthanide sandwich and half-sandwich borohydrides have been used as precatalysts in two-component systems for ethylene,[9] styrene,[10a,10b] and isoprene[9,10a] polymerizations.

The stability, structures and reactivity of organic derivatives of lanthanides are known to be mainly determined by the electropositivity, Lewis acidity, and large ionic radii of these elements. These factors render organolanthanides highly sensitive to steric saturation of the metal coordination sphere and, therefore, design of the environment about the metal center is crucial. On the other hand, investigation of the influence of the ancillary ligation on the reactivity of Ln–C and Ln–H bonds may be rewarding, as it may serve as a useful tool for modification of catalytic activity of lanthanide hydrocarbyl and hydrido complexes. To date, lanthanide borohydride complexes are mainly presented by sandwich- and half-sandwich-type derivatives,[2] while compounds supported by non-cyclopentadienyl ligands still remain virtually unexplored. The yttrium borohydride complex $[Ph(NSiMe_3)_2]_2Y(BH_4)(THF)$ supported by amidinate ligands was reported by Teuben and co-workers.[15] Recently, synthesis of lanthanide borohydrides containing aryl oxide,[16] polydentate diamino-bis(phenoxide),[13] and diamide–diamine[14] ligands was described. In our continuing research we have shown that bulky guanidinate ligands provide a useful coordination environment, which allows the synthesis of isolable lanthanide hydrocarbyl[17,18] and hydrido[19,20] species. That is why we employed the guanidinate ligands for preparing lanthanide mono-[21a] and bis(borohydride)[21b] complexes. Later, Yuan and co-workers synthesized the mono(guanidinate) lanthanide borohydride complexes $[(Me_3Si)_2NC(N\text{-}Cy)_2]Ln(BH_4)_2(THF)_2$ (Ln = Er, Yb).[22] Herein we report on the synthesis, structure, and

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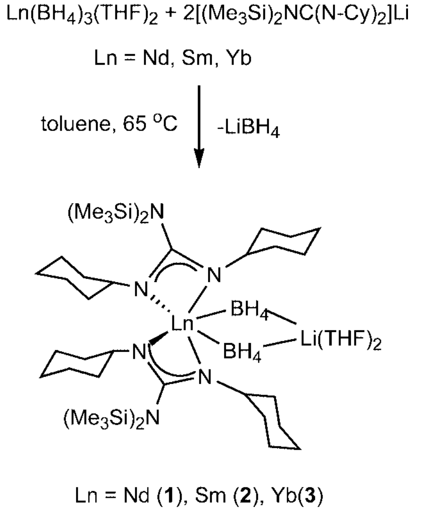
catalytic activity in lactide polymerization of heterodimetallic bis(guanidinate) borohydride complexes $\{(Me_3Si)_2NC(N\text{-}Cy)_2\}_2Ln(BH_4)_2Li(THF)_2$ (Ln = Nd, Sm, Yb).

Results and Discussion

Synthesis and Characterization of Lanthanide Bis(guanidinate) Borohydrides

Initially the metathesis reactions of lanthanide bis(guanidinate)chloride complexes $[\{(Me_3Si)_2NC(N\text{-}Cy)_2\}_2LnCl]_2$ (Ln = Nd, Sm) with $NaBH_4$ were investigated as a synthetic route to the related borohydrides. However, this method was found to be inefficient as the prolonged heating (48 h) of equimolar amounts of the starting reagents in THF at 65° did not allow preparation of the borohydride complexes in good yields. Increasing the amount of $NaBH_4$ (to a 1.5-fold molar excess) did not result in a higher product yield and considerable amounts (about 15–20%) of the starting chloride complexes $[\{(Me_3Si)_2NC(N\text{-}Cy)_2\}_2LnCl]_2$ were recovered in the reaction mixture. This hampered isolation and purification of the borohydride complexes. Moreover, the reaction of $[\{(Me_3Si)_2NC(N\text{-}i\text{Pr})_2\}_2SmCl]_2$ with $NaBH_4$ was found to occur with redistribution of guanidinate ligands and formation of the bis(borohydride) derivative $\{(Me_3Si)_2NC(N\text{-}i\text{Pr})_2\}Sm(BH_4)_2(DME)$.[21a] During the past decade, several reports[10–14,16] on the successful conversions of lanthanide tris(borohydrides) $Ln(BH_4)_3(THF)_n$[23–25] into new derivatives by reactions with anionic reagents have appeared. This prompted us to use $Ln(BH_4)_3(THF)_n$ complexes as starting reagents for preparation of related bis(guanidinate) borohydrides.

The reactions of $Ln(BH_4)_3(THF)_2$ (Ln = Nd, Sm, Yb) with a twofold molar excess of the lithium guanidinate $[(Me_3Si)_2NC(N\text{-}Cy)_2]Li$, obtained in situ from the amide $(Me_3Si)_2NLi(Et_2O)$ and 1,3-dicyclohexylcarbodiimide, were carried out in toluene at 65 °C (Scheme 1).



Scheme 1.

Filtration of the reaction mixture, evaporation of toluene, subsequent recrystallization of the solid residue from hexane, and drying in vacuo at room temperature afforded complexes $[(Me_3Si)_2NC(N\text{-}Cy)_2]_2Ln(\mu\text{-}BH_4)_2Li(THF)_2$ [Ln = Nd (**1**), Sm (**2**), Yb (**3**)] in 66, 64, and 68% yield, respectively. Complex **1** was isolated as blue, **2** yellow and **3** orange crystalline solids. Complexes **1**–**3** are highly air- and moisture-sensitive. Nevertheless, in an inert atmosphere, they can be stored for weeks without decomposition at room temperature. They are readily soluble in hydrocarbon solvents, which hampers their isolation by recrystallization and decreases the yields. The IR spectra of complexes **1**–**3** show, in the region 2000–2500 cm^{-1}, four strong absorptions diagnostic of μ^3- and μ^2-bridging borohydride ligands.[4,5] The ^1H and ^{13}C NMR spectra of the slightly paramagnetic complex **2** in $[D_6]$benzene at 20 °C show the expected sets of resonances for the guanidinate ligand and the coordinated THF. The borohydride group appears in the ^1H NMR spectrum as a broad singlet at $\delta = -1.34$ ppm. The ^7Li and ^{11}B NMR spectra contain sole singlets at $\delta = 0.03$ and 49.04 ppm, respectively.

Crystals suitable for single-crystal X-ray diffraction studies of **1**–**3** were obtained from hexane solutions by slow evaporation of the solvent at room temperature and were isolated as the hexane solvates $[(Me_3Si)_2NC(N\text{-}Cy)_2]_2Ln(\mu\text{-}BH_4)_2Li(THF)_2\cdot(C_6H_{14})_{0.5}$. The X-ray crystal structure investigations revealed that complexes **1**–**3** have similar structures. The molecular structure of **3** is depicted in Figure 1; the crystal and structural refinement data, and selected bond lengths and angles for **1**–**3** are listed in Tables 1 and 2, respectively. The molecular structure (Figure 1) shows that compounds **1**–**3** are heterodimetallic complexes containing one residual $LiBH_4$ per $[(Me_3Si)_2NC(N\text{-}Cy)_2]_2Ln(BH_4)$ unit in which the lanthanide and the lithium atoms are connected by two μ-bridging BH_4 groups. The coordination sphere of the lanthanide atoms in complexes **1**–**3** is set up by four nitrogen atoms of two guanidinate ligands and by two borohydride anions. The lithium atom is further coordinated by two THF molecules.

Despite the fact that both borohydride groups in complexes **1**–**3** are μ-bridging, their coordination modes are different: one group is tridentate with respect to the lanthanide atom and bidentate with respect to the lithium, while the second one is $\mu\text{-}\eta^2{:}\eta^2$-bridging in complexes **1** and **2**, but $\mu\text{-}\eta^2{:}\eta^1$-bridging in complex **3** (Figure 2).

The Ln–H and Li–H distances fall in the ranges 2.42(2)–2.56(2) and 1.89(2)–2.29(2) Å in complex **1**, 2.36(2)–2.53(2) and 1.88(2)–2.30(2) Å in **2**, and 2.29(2)–2.47(2) and 1.92(2)–2.13(2) Å in **3**, respectively. It should be noted that the interatomic Li(1)···H(2A) distance in **3** [2.91(2) Å] is noticeably longer than the other Li–H distances in **1**–**3** [1.89(2)–2.29(2) Å]. Obviously, the difference of the coordination modes of borohydride groups in complex **3** is caused by steric factors, which is consistent with the smallest ionic radius of ytterbium in the series of the prepared lanthanide compounds.[26] The difference in the coordination mode of the borohydride moieties to the lanthanide atom does not strongly affect the Ln–B distances: in all three complexes

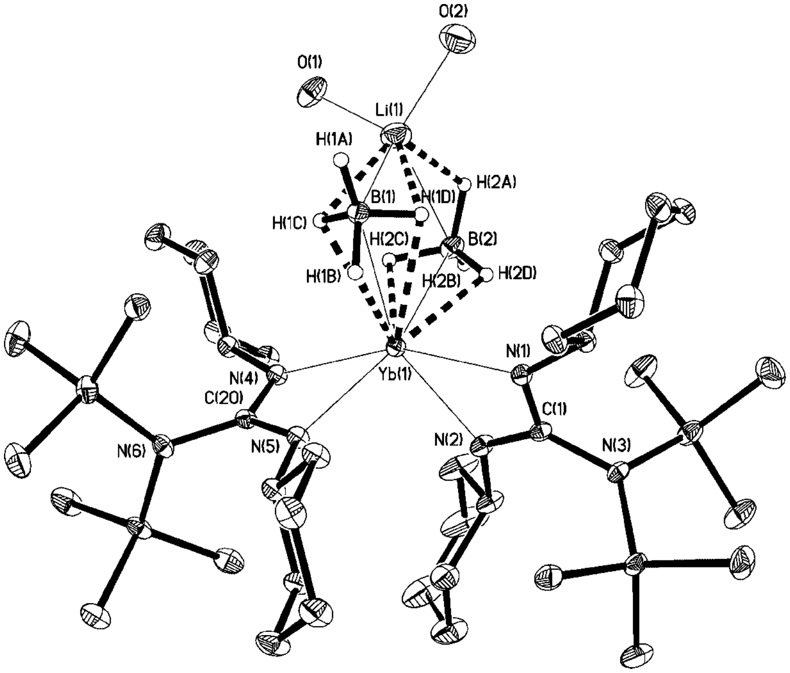


Figure 1. ORTEP diagram (30% probability thermal ellipsoids) of $[(Me_3Si)_2NC(N\text{-}Cy)_2]_2Yb(\mu\text{-}BH_4)_2Li(THF)_2$ (**3**). Hydrogen atoms of the guanidinate ligands and THF methylene groups are omitted.

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

	1	**2**	**3**
Empirical formula	$C_{49}H_{111}B_2LiN_6NdO_2Si_4$	$C_{49}H_{111}B_2LiN_6O_2Si_4Sm$	$C_{49}H_{111}B_2LiN_6O_2Si_4Yb$
Formula mass	1101.6	1107.7	1130.4
T [K]	100(2)	100(2)	100(2)
λ [Å]	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	13.7938(6)	13.7979(8)	13.8325(5)
b [Å]	15.0978(7)	15.0630(9)	14.9469(6)
c [Å]	17.2382(7)	17.215(1)	17.1896(7)
α [°]	86.854(1)	86.906(1)	81.886(1)
β [°]	77.232(1)	77.355(1)	78.015(1)
γ [°]	63.041(1)	62.918(1)	62.505(1)
V [Å^3]	3116.48(8)	3104.1(3)	3079.7(2)
Z	2	2	2
D_{calcd} [g/cm]	1.179	1.185	1.219
Absorption coefficient [mm^{-1}]	0.952	1.061	1.635
F(000)	1184	1188	1204
Crystal size [mm]	0.37 × 0.24 × 0.22	0.31 × 0.17 × 0.15	0.36 × 0.30 × 0.27
θ range for data collection [°]	1.70–29.30	1.70–29.00	1.70–29.18
Index ranges	$-18 \le h \le 18$ $-20 \le k \le 20$ $-23 \le l \le 23$	$-18 \le h \le 18$ $-20 \le k \le 20$ $-23 \le l \le 22$	$-18 \le h \le 18$ $-20 \le k \le 20$ $-23 \le l \le 23$
Reflections collected	33266	32642	32805
Independent reflections	16392 (R_{int} = 0.0168)	16107 (R_{int} = 0.0227)	16163 (R_{int} = 0.0189)
Completeness to θ	96.6	99.9	97.4
Data/restraints/parameters	16392/61/1024	25718/108/1378	16107/55/1034
Goodness-of-fit on F^2	1.068	1.259	1.044
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0263, wR_2 = 0.0640	R_1 = 0.0664, wR_2 = 0.1350	R_1 = 0.0287, wR_2 = 0.0648
R indices (all data)	R_1 = 0.0309, wR_2 = 0.0660	R_1 = 0.0377, wR_2 = 0.0685	R_1 = 0.0307, wR_2 = 0.0698
Largest diff. peak and hole [e/Å^3]	1.421/–0.379	1.308/–0.378	1.861/–0.752

one distance is substantially longer than the second one (Table 2). The average Ln–N bond lengths in complexes **1**–**3** [**1**, 2.4483(8); **2**, 2.4248(10); **3**, 2.3315(11) Å] are comparable to those previously reported for related bis(guanidinate) derivatives[21,27–29] and their values decrease in the series Nd > Sm > Yb, reflecting the lanthanide contraction.[26] The Ln–B and Ln–Li distances in complexes **1**–**3** also correspond to this tendency and diminish from Nd to

Table 2. Selected bond lengths [Å] and angles [°] for complexes **1**–**3**.

	1	**2**	**3**
Bond lengths [Å]			
Ln–N(1)	2.4812(8)	2.4612(10)	2.3528(11)
Ln–N(2)	2.4158(10)	2.3852(12)	2.3044(11)
Ln–N(4)	2.4284(8)	2.4025(10)	2.3454(12)
Ln–N(5)	2.4680(8)	2.4505(9)	2.3235(13)
Li–B(1)	2.454(3)	2.450(3)	2.428(4)
Li–B(2)	2.504(3)	2.498(3)	2.507(3)
Ln–Li	3.663(3)	3.643(3)	3.595(3)
Ln–H	2.42(2)–2.56(2)	2.36(2)–2.53(2)	2.29(2)–2.47(2)
Li–H	1.89(2)–2.29(2)	1.88(2)–2.30(2)	1.92(2)–2.13(2)
N(1)–C(1)	1.3344(13)	1.3311(16)	1.3334(16)
N(2)–C(1)	1.3296(12)	1.3324(14)	1.3298(18)
N(4)–C(20)	1.3275(13)	1.3311(15)	1.3341(19)
N(5)–C(20)	1.3320(14)	1.3310(17)	1.3274(16)
Distances Ln–B [Å]			
Ln–B(1)	2.7390(13)	2.7019(15)	2.6193(16)
Ln–B(2)	2.9251(14)	2.8937(17)	2.7935(19)
Bond angles [°]			
N(1)–Ln–N(2)	54.53(3)	55.02(3)	57.33(4)
N(4)–Ln–N(5)	54.51(3)	55.04(4)	57.27(4)
B(1)–Ln–B(2)	84.49(4)	84.83(5)	86.07(5)
B(1)–Li–B(2)	100.44(10)	99.52(12)	96.98(12)

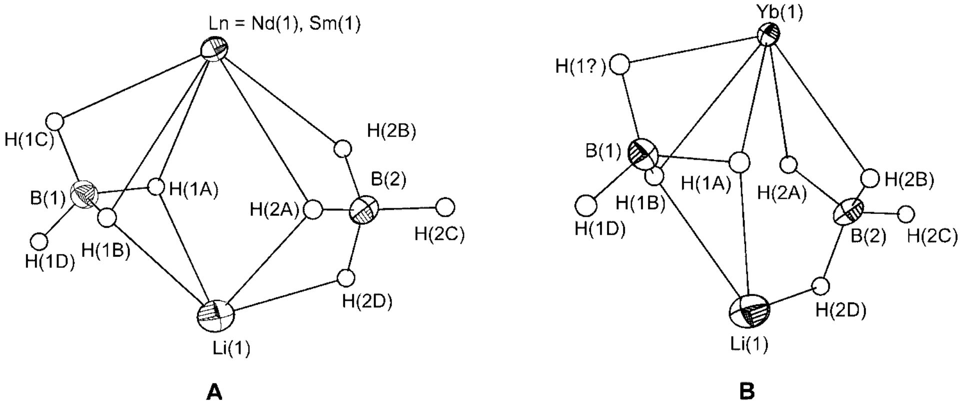


Figure 2. The coordination modes of borohydride groups in complexes $[(Me_3Si)_2NC(N\text{-}Cy)_2]_2Ln(\mu\text{-}BH_4)_2Li(THF)_2$ (A, **1**, **2**; B, **3**).

Yb. The Ln–B distances for bridging borohydride groups in complexes **1**–**3** are expectedly longer than those in complexes with terminal BH_4 groups[6,8,10,21] and comparable to the values reported for related dimeric compounds.[11,14] The N–C distances in the guanidinate ligands of **1**–**3** differ only slightly between each other (Table 2), which reflects the electron delocalization within the anionic NCN units. Shortening of the Ln–N, Ln–B, and Ln···Li distances in complexes **1**–**3** should lead to an increase of nonvalent interactions in the coordination sphere of the Ln atoms. Calculations[30] of the steric saturation degree about the Ln atoms have shown that the total metal atom shielding increases in the series of complexes **1** [86.6(2)%], **2** [87.8(2)%], and **3** [91.3(2)%] and reflects the steric crowding in the coordination sphere of the metal centers. The value of the dihedral angle between the N(1)C(1)N(2) and N(4)C(20)N(5) planes in **3** [78.1(1)°] is noticeably smaller than the analogous parameters in complexes **1** [79.7(1)°] and **2** [79.7(1)°], thus providing evidence for the strongest nonvalent interactions in the coordination sphere of the Yb atom.

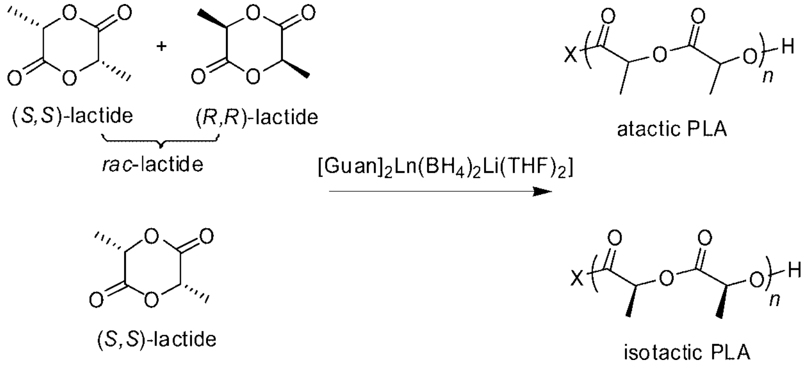
Ring-Opening Polymerization of *rac*-Lactide and (*S*,*S*)-Lactide

There is considerable interest in the controlled ring-opening polymerization (ROP) of lactides (LAs) by well-defined metal initiators because of the biodegradable and biocompatible nature of polylactides (PLAs) and their potential commercial applications.[31–34] Bonnet, Mountford et al. have studied the ROP of racemic (*S*,*S*/*R*,*R*)- and (*S*,*S*)-lactide with monoborohydride rare earth complexes (Y, Sm, Nd) supported by diamino-bis(phenolate) ligands.[13] These systems feature moderate activity and enable the formation of heterotactic-enriched (up to 87% P_r) or isotactic PLAs, with relatively narrow molecular-weight distributions (M_w/M_n = 1.3–1.7), though the molecular weights were lower than expected, because of chain transfer reactions. Arnold and co-workers have investigated the ROP of lactide with monoguanidinate–lanthanum complexes having two reactive phenolate ligands.[35] The PLAs obtained had relatively broad molecular-weight distributions (M_w/M_n = 1.5–2.0) and no control over the stereochemistry of the polymer was observed. Interestingly, the molecular weights increased linearly with a monomer-to-metal ratio up to 500, but dramatically decreased for higher [LA]/[La] ratios, an observation indicative of a high degree of chain transfer, ascribed to the presence of two phenoxide groups per metal center.

Complexes **1**–**3** have been evaluated in the ROP of *rac*- and (*S*,*S*)-lactide (Scheme 2). A blank experiment using $LiBH_4$ showed this compound is not active for the ROP of *rac*-lactide under the conditions used. This observation is in line with previous observations in the ROP of cyclic esters (ε-caprolactone) and carbonates (TMC) (S. Guillaume, personal communication), and discards the possibility that ROP is initiated by $LiBH_4$ arising from dissociation of complexes **1**–**3**.

Representative results are summarized in Table 3. Complexes **1**–**3** are moderately active under mild conditions, allowing conversion of 100–400 equiv. of lactide in 10–1000 min at room temperature in either toluene or THF solutions at [LA] = 0.5 mol/L. Kinetic monitoring revealed, however, that activities of the complexes are dramatically affected by the nature of the metal center and polymerization solvent. With the three complexes investigated, the reactions proceeded much faster in an apolar, noncoordinating solvent such as toluene than in THF. It is assumed that the latter solvent, because of its high affinity for oxophilic metals such as lanthanides, competes with the lactide monomer in the coordination onto the metal center, thus accounting for the longer completion times. A similar detrimental effect of THF on the rate of ROP reactions promoted by group 3 metal complexes is often observed.[36] Nevertheless, it is noteworthy that Bonnet, Mountford et al. have observed an opposite trend for the ROP of lactides with diamino-bis(phenolate)-lanthanide borohydride complexes; that is, polymerization rates are higher in THF than in toluene.[13] For both series of reactions carried out in toluene and in THF with complexes **1**–**3**, the observed decreasing order of activity was Nd >> Yb > Sm. There is, therefore, no direct correlation of the polymerization activity with ionic radii of the lanthanide centers, and this observation rather points out that more subtle parameters should be taken into account.

All the PLAs produced from *rac*-lactide with the initiators **1**–**3** show atactic microstructures, as determined by NMR analysis.[37–39] Contrary to our previous observations with [amino-ether-bis(phenolate)]-lanthanide amido systems,[13,37] decreasing the temperature down to –20 °C and changing the solvent (toluene vs. THF) resulted in no en-



Scheme 2.

Table 3. Polymerization of *rac*- and (*S*,*S*)-lactide with complexes **1**–**3**.[a]

Entry	M	Complex	[M]/[Ln]	Solvent	Time[b] [min]	Conv.[c] [mol-%]	$M_{n,th}$[d] [g/mol]	$M_{n,exp}$[e] [g/mol]	M_w/M_n[e]
1	*rac*-LA	**1**	100	toluene	17	>98	14100	16500	1.98
2	*rac*-LA	**1**	200	toluene	10	62	17900	20800	1.68
3	*rac*-LA	**1**	200	toluene	30	>98	25900	26300	1.51
4	*rac*-LA	**1**	400	toluene	60	>98	51800	52000	1.09
5	*rac*-LA	**1**	100	THF	60	97	8400	6500	2.16
6	(*S*,*S*)-LA	**1**	200	THF	20	30	8600	6000	1.44
7	(*S*,*S*)-LA	**1**	200	THF	60	98	28200	17300	1.63
8	*rac*-LA	**2**	100	toluene	300	95	13700	9100	1.50
9	*rac*-LA	**2**	200	toluene	480	96	27600	23500	1.16
10	*rac*-LA	**2**	400	toluene	1000	95	54700	20100	2.73
11	(*S*,*S*)-LA	**2**	200	THF	60	12	3400	2200	1.56
12	*rac*-LA	**2**	200	THF	1000	98	28200	9400	2.99
13	*rac*-LA	**3**	100	toluene	150	95	13700	11100	1.24
14	*rac*-LA	**3**	200	toluene	270	95	27400	15500	1.77
15	*rac*-LA	**3**	400	toluene	1000	94	54100	25000	2.17

[a] General conditions: [LA] = 0.5 mol/L, T = 20 °C. [b] Reaction time was not necessarily optimized. [c] Conversion of monomer M as determined by ^1H NMR spectroscopy. [d] M_n value calculated assuming one polymer chain per metal center, from the relation: 144 × conv × [M]/[Ln]. [e] Experimental (corrected; see Exp. Sect.) M_n and M_w/M_n values determined by GPC in THF vs. polystyrene standards.

hancement of stereoselectivity. Polymerization of (*S*,*S*)-lactide by **2** (entry 11) or **1** resulted in pure isotactic PLA; the decoupled ^{1}H NMR spectrum of the polymer showed one sharp resonance for the methine region. This observation supports the lack of base-promoted epimerization of lactide or PLA and argues against an anionic polymerization mechanism being operative.[40,41]

Experiments aimed at investigating the degree of control of polymerizations were carried out. All the PLAs obtained with borohydride complexes **1**–**3** showed monomodal GPC traces with polydispersity values in the range M_w/M_n = 1.09–2.99. In general, quite narrow molecular-weight distributions ($1.09 < M_w/M_n < 1.50$) were observed for polymerizations carried out in toluene and for monomer-to-metal ratios ≤200, indicative of a single-site character under these conditions. For the three initiators, the number-average molecular mass (M_n) values increase monotonously, though not linearly, with the monomer-to-metal ratio. An important issue with complexes **1**–**3** is to assess if they act as mono- or di-initiators; that is, if only one or both borohydride groups initiate a polymer chain. The corrected experimental number-average molecular mass (M_n) values of PLAs produced with **1** are in most cases close to the theoretical ones, calculated on the assumption that a single HBH_3 group initiates the polymerization, that is a single PLA chain is produced per metal center (entries 1–4). For PLAs produced by **2** and **3**, the experimental M_n values approximately matched the calculated ones on the latter principle, but only if the monomer-to-metal ratio was low. For [LA]/[Sm] = 400 and [LA]/[Yb] > 200, the molecular weight distributions were large, which hampers meaningful comparisons of M_n values. Thus, system **1** features overall a better control of polymerizations than complexes **2** and **3** do. This observation corroborates the aforementioned difference in activity between **1**, and **2** and **3**, and suggests that the former and latter complexes may have different initiation processes.

The ^{1}H NMR spectra in $CDCl_3$ of relatively low-molecular-weight samples of PLA (e.g., entry 6) all show the quartet characteristic of the C*H*(Me)OH terminal group at δ = 4.33 ppm. The latter group is formed after hydrolysis of the metal–alkoxide bond, an observation that is indicative of a classical coordination/insertion mechanism with an initial ring-opening through acyl–oxygen bond cleavage.[42–45] It has been recently reported by Guillaume and co-workers that, in the ROP of ε-caprolactone with lanthanide borohydride complexes, the [HBH_3] functionality acts as both an initiating group and a reducing agent, yielding α,ω-telechelic poly(ε-caprolactone) diols by reduction of the aldehyde formed after the insertion of the first monomer into the metal–hydride bond.[12,46,47] A similar result was asserted about the ROP of *rac*- and (*S*,*S*)-lactide with diamino-bis(phenolate)-lanthanide borohydride initiators, yielding α,ω-telechelic PLA diols, however without supporting this statement with experimental data.[13] In our case, the presence of a second alcohol function at the other extremity of the polymer chain could not be established unambiguously; additional resonances were observed, which include a doublet of doublet at δ = 5.50 ppm and two doublets/quartets at δ = 4.15 and 4.45 ppm, which could correspond to CH_2OH end-groups; but their lower than expected intensity and diversity suggest incomplete and/or multiple processes (see Supporting Information; see footnote on the first page of this article).

Conclusions

Bulky guanidinate ligands provide a suitable coordination environment that allows synthesis of isolable monomeric borohydride derivatives $[(Me_3Si)_2NC(N\text{-}Cy)_2]_2Ln(\mu\text{-}BH_4)_2Li(THF)_2$ (Ln = Nd, Sm, Yb) in reasonable yields. The complexes, especially neodymium complex **1**, act as monoinitiators for the ring-opening polymerization of racemic lactide, providing atactic polymers with a certain degree of control, that is, controlled molecular weights and relatively narrow polydispersities, provided moderate substrate-to-initiator ratios are used.

Experimental Section

General Conditions: All experiments were performed in evacuated tubes, using standard Schlenk techniques, with rigorous exclusion of traces of moisture and air. After drying over KOH, THF was purified by distillation from sodium/benzophenone ketyl, and hexane and toluene were dried by distillation from sodium/triglyme and benzophenone ketyl prior to use. [D$_6$]benzene was dried with sodium and condensed in vacuo into the NMR tubes prior to use. *N*,*N*′-Dicyclohexylcarbodiimide was purchased from Acros. Anhydrous $LnCl_3$,[48] and $(Me_3Si)_2NLi(Et_2O)$[49] were prepared according to literature procedures. All other commercially available chemicals were used after the appropriate purification.

Instruments and Measurements: NMR spectra were recorded with a Bruker DPX 200 spectrometer (^{1}H, 200 MHz; ^{13}C, 50 MHz; ^{11}B, 64.2 MHz; ^{7}Li, 77.7 MHz). Chemical shifts for ^{1}H and ^{13}C spectra were referenced internally using the residual solvent resonances and are reported relative to TMS. IR spectra were recorded as Nujol mulls with a Specord M80 instrument. Lanthanide metal analysis was carried out by complexometric titration and the C,H elemental analysis by the microanalytical laboratory of IOMC. Size exclusion chromatography (SEC) of PLAs was performed in THF at 20 °C using a Waters SIS HPLC pump, a Waters 410 refractometer, a DAD-UV detector, and Waters styragel columns (HR2, HR3, HR4, HR5E) or PL-GEL Mixte B and 100A columns. The number average molecular masses (M_n) and polydispersity index (M_w/M_n) of the resultant polymers were calculated with reference to a polystyrene calibration. M_n values were corrected with a Mark-Houwink factor of 0.58 to account for the difference in hydrodynamic volumes between polystyrene and polylactide (PLA).[50,51] The microstructure of PLAs was measured by homodecoupling ^{1}H NMR spectroscopy at 20 °C in $CDCl_3$ on a Bruker AC-500 spectrometer.[37]

Synthesis of $[(Me_3Si)_2NC(N\text{-}Cy)_2]_2Nd(\mu\text{-}BH_4)_2Li(THF)_2$ (1): CyN=C=NCy (0.52 g, 2.52 mmol) was added to a solution of $(Me_3Si)_2NLi(Et_2O)$ (0.61 g, 2.52 mmol) in toluene (30 mL) at 20 °C and after 45 min stirring $Nd(BH_4)_3(THF)_2$ (0.43 g, 1.26 mmol) was added. The reaction mixture was stirred and heated at 65 °C for a further 12 h. The reaction mixture was filtered off and from the clear solution the solvent was evaporated in vacuo. The remaining solid was extracted with hexane (2 × 20 mL). After filtration of the hexane extracts, the resulting solution was slowly concentrated under vacuum at room temperature. The blue crystalline solid formed overnight was washed with cold hexane and dried in vacuo at room temperature for 40 min, yielding **1** (0.88 g, 66%) as a blue crystalline solid. $C_{46}H_{104}B_2LiN_6NdO_2Si_4$ (1057.7): calcd. C 52.23, H 9.83, Nd 13.63; found C 52.00, H 9.41, Nd 13.23. IR (Nujol, KBr): $\tilde{\nu}$ = 2265 (m), 2408 (s), 2308 (s), 2242 (s), 2220 (s), 1638 (s), 1538 (s), 1347 (s), 1300 (s), 1249 (s), 1175 (s), 1132 (s), 1079 (s), 948 (s), 834 (s), 756 (m) cm^{-1}.

Synthesis of $[(Me_3Si)_2NC(N\text{-}Cy)_2]_2Sm(\mu\text{-}BH_4)_2Li(THF)_2$ (2): Complex **2** was synthesized following the standard procedure described for **1** starting from $(Me_3Si)_2NLi(Et_2O)$ (0.58 g, 2.42 mmol), CyN=C=NCy (0.50 g, 2.42 mmol), and $Sm(BH_4)_3(THF)_2$ (0.40 g, 1.21 mmol) in toluene (30 mL). Complex **2** was isolated as a yellow crystalline solid (0.83 g, 64%). $C_{46}H_{104}B_2LiN_6O_2Si_4Sm$ (1063.9): calcd. C 51.93, H 9.77, Sm 14.13; found C 51.55, H 9.34, Sm 14.26. ^1H NMR (200 MHz, $[D_6]$benzene): δ = –1.34 (br. s, 8 H, BH_4), 0.28, 0.35 [both s, together 36 H, $Si(CH_3)_3$], 1.32–1.94 (br. m, 48 H, CH_2 Cy, β-CH_2, THF), 2.83 (br. m, 4 H, CH Cy), 3.56 (br. s, 8 H, α-CH_2, THF) ppm. ^7Li NMR (77.7 MHz, $[D_6]$benzene): δ = 0.03 ppm. ^{11}B NMR (64.2 MHz, $[D_6]$benzene): δ = 49.04 ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $[D_6]$benzene): δ = 4.2 $[(NSiCH_3)_2]$, 25.4 (β-CH_2, THF), 22.0, 25.7, 26.3, 31.9, 36.7 (CH_2, Cy), 53.3 (CH, Cy), 68.3 (α-CH_2, THF), 208.6 (CN_3) ppm. IR (Nujol, KBr): $\tilde{\nu}$ = 2658 (m), 2419 (s), 2396 (s), 2244 (s), 2204 (s), 1638 (s), 1600 (m), 1405 (s), 1355 (s), 1300 (s), 1187 (m), 1175 (m), 1136 (m), 1071 (m), 1057 (s), 1004 (s), 943 (s), 841 (s), 676 (m) cm^{-1}.

Synthesis of $[(Me_3Si)_2NC(N\text{-}Cy)_2]_2Yb(\mu\text{-}BH_4)_2Li(THF)_2$ (3): Complex **3** was synthesized following the standard procedure described for **1** starting from $(Me_3Si)_2NLi(Et_2O)$ (0.89 g, 3.73 mmol), CyN=C=NCy (0.77 g, 3.73 mmol), and $Yb(BH_4)_3(THF)_2$ (0.67 g, 1.86 mmol) in toluene (30 mL). Complex **3** was isolated as an orange crystalline solid (1.37 g, 68%). $C_{46}H_{104}B_2LiN_6O_2Si_4Yb$ (1086.5): calcd. C 50.85, H 9.57, Yb 15.92; found C 50.39, H 9.21, Yb 16.06. IR (Nujol, KBr): $\tilde{\nu}$ = 2661 (m), 2431 (s), 2296 (s), 2246 (s), 2200 (s), 1634 (s), 1600 (m), 1405 (s), 1358 (s), 1304 (s), 1249 (s), 1190 (s), 1136 (m), 1073 (m), 1050 (s), 1002 (s), 944 (s), 842 (s), 678 (m) cm^{-1}.

General Procedure for Lactide Polymerization: In the glovebox, a Schlenk flask was charged with a solution of the metal initiator (typically 0.019 mmol, about 10 mg) in toluene (0.2 mL) or THF (0.2 mL). A solution of the monomer [*rac*-LA, (*S*,*S*)-LA; previously recrystallized twice from dry toluene and then sublimed under vacuum at 50 °C] was added rapidly to this solution in the appropriate ratio in toluene or THF (3.0 mL). The mixture was immediately stirred with a magnetic stir bar at room temperature. Aliquots were periodically removed with a pipette for monitoring the monomer conversion by ^1H NMR spectroscopy. After completion or the desired time, the reaction was quenched with acidic methanol (0.5 mL of a 1.2 M HCl solution), and the polymer was precipitated with excess methanol (100 mL). The polymer was then dried under vacuum to constant weight.

X-ray Crystallographic Study: The crystal data and details of data collection are given in Table 1. X-ray data were collected on a SMART APEX diffractometer (graphite-monochromated Mo-K_α radiation, λ = 0.71073 Å, ϕ-ω-scan technique) at –100 °C. The intensity data were integrated in the SAINT program.[52] SADABS[53] was used to perform area-detector scaling and absorption corrections. The structures were solved by direct methods and were refined on F^2 using all reflections with SHELXTL.[54] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms in **1** and **2** were found from the Fourier syntheses of electron density except the H atoms of THF ligands and solvate hexane molecules. The H atoms of BH_4 groups in **3** were found from the Fourier syntheses of electron density whereas the remaining hydrogen atoms were placed in calculated positions. The H atoms in **1**–**3**, found from the differential syntheses of electron density, were refined isotropically, whereas all other hydrogen atoms were refined in the "riding model".

CCDC-634981 (for **1**), -634982 (for **2**), and -634983 (for **3**) 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.

Supporting Information (see also the footnote on the first page of this article): Details of the ^1H NMR spectrum and GPC trace of a PLA sample.

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[1] T. J. Marks, G. W. Grynkewich, *Inorg. Chem.* **1976**, *15*, 1302–1307.

[2] M. Ephritikhine, *Chem. Rev.* **1997**, *97*, 2193–2242.

[3] Y. K. Gun'ko, B. M. Bulychev, G. L. Soloveichik, V. K. Belsky, *J. Organomet. Chem.* **1992**, *424*, 289–300.

[4] E. B. Lobkovsky, Y. K. Gun'ko, B. M. Bulychev, V. K. Belsky, G. L. Soloveichik, M. Yu. Antipin, *J. Organomet. Chem.* **1991**, *406*, 343–352.

[5] M. F. Lappert, A. Singh, J. L. Atwood, W. E. Hunter, *J. Chem. Soc., Chem. Commun.* **1983**, 206–207.

[6] A. V. Khvostov, V. V. Nesterov, B. M. Bulychev, A. I. Sizov, M. Yu. Antipin, *J. Organomet. Chem.* **1999**, *583*, 222–225.

[7] D. Deng, X. Zheng, C. Qian, J. Sun, L. Chang, *J. Organomet. Chem.* **1994**, *466*, 95–100.

[8] H. Schumann, M. R. Keitsch, J. Demtschuk, S. Mühle, *Z. Anorg. Allg. Chem.* **1998**, *624*, 1811–1818.

[9] M. Visseaux, T. Chenal, P. Roussel, A. Mortreux, *J. Organomet. Chem.* **2006**, *691*, 86–92.

[10] a) D. Barbier-Baudry, O. Blacque, A. Hafid, A. Nyassi, H. Sitzmann, M. Visseaux, *Eur. J. Inorg. Chem.* **2000**, 2333–2336; b) P. Zink, M. Visseaux, A. Mortreux, *Z. Anorg. Allg. Chem.* **2006**, *632*, 1943–1944.

[11] S. M. Cendrowski-Guillaume, M. Nierlich, M. Lance, M. Ephritikhine, *Organometallics* **1998**, *17*, 786–788.

[12] I. Palard, A. Soum, S. M. Guillaume, *Chem. Eur. J.* **2004**, *10*, 4054–4062.

[13] F. Bonnet, A. R. Cowley, P. Mountford, *Inorg. Chem.* **2005**, *44*, 9046–9055.

[14] F. Bonnet, A. C. Hilier, A. Collins, S. R. Dubberley, P. Mountford, *Dalton Trans.* **2005**, 421–423.

[15] R. Duchateau, C. T. van Wee, A. Meetsma, P. Th. Van Duijnen, J. H. Teuben, *Organometallics* **1996**, *15*, 2279–2290.

[16] F. Yuan, J. Yang, L. Xiong, *J. Organomet. Chem.* **2006**, *691*, 2534–2539.

[17] A. A. Trifonov, D. M. Lyubov, G. K. Fukin, E. V. Baranov, Yu. A. Kurskii, *Organometallics* **2006**, *25*, 3935–3942.

[18] A. A. Trifonov, D. M. Lyubov, E. A. Fedorova, G. K. Fukin, H. Schumann, S. Mühle, M. Hummert, M. N. Bochkarev, *Eur. J. Inorg. Chem.* **2006**, 747–756.

[19] A. A. Trifonov, E. A. Fedorova, G. K. Fukin, M. N. Bochkarev, *Eur. J. Inorg. Chem.* **2004**, 4396–4401.

[20] A. A. Trifonov, G. G. Skvortsov, D. M. Lyubov, N. A. Skorodumova, G. K. Fukin, E. V. Baranov, V. N. Glushakova, *Chem. Eur. J.* **2006**, *12*, 5320–5327.

[21] a) A. A. Trifonov, G. G. Skvortsov, D. M. Lyubov, G. K. Fukin, E. A. Fedorova, M. N. Bochkarev, *Russ. Chem. Bull.* **2005**, *54*, 2511–2518; b) G. G. Skvortsov, M. V. Yakovenko, G. K. Fukin, E. V. Baranov, Yu. A. Kurskii, A. A. Trifonov, *Russ. Chem. Bull.* accepted for publication.

[22] F. Yuan, Y. Zhu, L. Xiong, *J. Organomet. Chem.* **2006**, *691*, 3377–3382.

[23] U. Mirsaidov, A. Kurbonbekov, T. Rotenberg, K. Dzhuraev, *Neorg. Mater.* **1978**, *14*, 1340–1343.

[24] U. Mirsaidov, A. Rakhimova, T. Dymova, *Neorg. Mater.* **1979**, *15*, 1248–1251.

[25] U. Mirsaidov, I. Shaimuradov, M. Khikmatov, *Zh. Neorg. Khim.* **1986**, *31*, 753–755.

[26] R. D. Schannon, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1976**, *32*, 751–767.

[27] Y. Yao, Y. Luo, J. Chen, Z. Zhang, Y. Zhang, Q. Shen, *J. Organomet. Chem.* **2003**, *679*, 229–237.

[28] Y. Luo, Y. Yao, Q. Shen, K. Yu, L. Weng, *Eur. J. Inorg. Chem.* **2003**, 318–323.

[29] M. Deng, Y. Yao, Y. Zhang, Q. Shen, *Chem. Commun.* **2004**, 2742–2743.

[30] I. A. Guzei, M. Wendt, *Dalton Trans.* **2006**, 3991–3999.

[31] C. K. Ha, J. A. Gardella Jr, *Chem. Rev.* **2005**, *105*, 4205–4232.

[32] O. D. Cabaret, B.-M. Vaca, D. Bourissou, *Chem. Rev.* **2004**, *104*, 6147–6176.

[33] R. E. Drumright, P. R. Gruber, D. E. Henton, *Adv. Mater.* **2000**, *12*, 1841–1846.

[34] M. H. Chisholm, Z. Zhou, *J. Mater. Chem.* **2004**, *14*, 3081–3092.

[35] G. R. Giesbrecht, G. D. Whitener, J. Arnold, *J. Chem. Soc., Dalton Trans.* **2001**, 923–927.

[36] See for example: A. Amgoune, C. M. Thomas, S. Ilinca, T. Roisnel, J.-F. Carpentier, *Angew. Chem. Int. Ed.* **2006**, *45*, 2782–2784 and references cited therein.

[37] A. Amgoune, C. M. Thomas, T. Roisnel, J.-F. Carpentier, *Chem. Eur. J.* **2006**, *12*, 169–179.

[38] K. A. M. Thakur, R. T. Kean, E. S. Hall, J. J. Kolstad, T. A. Lindgren, M. A. Doscotch, J. I. Siepmann, E. J. Munson, *Macromolecules* **1997**, *30*, 2422–2428.

[39] J. E. Kasperczyk, *Macromolecules* **1995**, *28*, 3937–3939.

[40] B. M. Chamberlain, Y. Sun, J. R. Hagadorn, E. W. Hemmesch, V. G. Young Jr, M. Pink, M. A. Hillmyer, W. B. Tolman, *Macromolecules* **1999**, *32*, 2400–2402.

[41] M. H. Chisholm, N. W. Eilerts, *Chem. Commun.* **1996**, 853–854.

[42] H. R. Kricheldorf, M. Berl, N. Scharnagi, *Macromolecules* **1988**, *21*, 286–293.

[43] P. Dubois, C. Jacobs, R. Jérôme, P. Teyssié, *Macromolecules* **1991**, *24*, 2266–2270.

[44] M. Lahcini, P. M. Castro, M. Kalmi, M. Leskelä, T. Repo, *Organometallics* **2004**, *23*, 4547–4549.

[45] M. Kalmi, M. Lahcini, P. M. Castro, O. Lehtonen, A. Belfkira, M. Leskelä, T. Repo, *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 1901–1911.

[46] S. M. Guillaume, M. Schappacher, A. Soum, *Macromolecules* **2003**, *36*, 54–60.

[47] I. Palard, A. Soum, S. M. Guillaume, *Macromolecules* **2005**, *38*, 6888–6894.

[48] M. D. Taylor, C. P. Carter, *J. Inorg. Nucl. Chem.* **1962**, *24*, 387–393.

[49] L. E. Manzer, *Inorg. Chem.* **1978**, *17*, 1552–1558.

[50] I. Barakat, P. Dubois, R. Jerome, P. Teyssie, *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 505–514.

[51] H. Ma, J. Okuda, *Macromolecules* **2005**, *38*, 2665–2673.

[52] Bruker, SAINTPlus Data Reduction and Correction Program v.6.02a, *Bruker AXS*, Madison, WI, USA, **2000**.

[53] G. M. Sheldrick, SADABS v.2.01, *Bruker/Siemens Area Detector Absorption Correction Program*, Bruker AXS, Madison, WI, USA, **1998**.

[54] G. M. Sheldrick, SHELXTL v.6.12, Structure Determination Software Suite, Bruker AXS, Madison, WI, USA, **2000**

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