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Syntheses and molecular structures of mono(guanidinate) lanthanide borohydrides and their catalytic activity for MMA-polymerization

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Abstract

The mono(guanidinate) lanthanide borohydride complexes of $[(Me_3Si)_2NC(NCy)_2]Ln(BH_4)_2(THF)_2$ (Ln = Yb (1), Er (2)) have been synthesized by the reactions of corresponding Ln(BH₄)₃(THF)₃ with sodium guanidinate of $[(Me_3Si)_2NC(NCy)_2]Na$ in a 1:1 molar ratio in THF. They were characterized by elemental analysis, infrared spectrum and X-ray diffraction analysis. 1 and 2 have similar structures. The lanthanide ion was bonded by an η^2 -guanidinate ligand, two η^3 -BH₄ ligands and two THF molecules as a distorted octahedron. The two BH₄ ligands in a complex are equivalent and *cis* to each other. The structure of solvated sodium guanidinate of $\{[(Me_3Si)_2NC(N-Cy)_2]Na(THF)\}_2$ (3) was also presented. In a dimeric molecule of 3, each Na atom is bound to three nitrogen atoms from two guanidinate groups and one oxygen atom from the THF molecule. 1 and 2 displayed moderate high catalytic activity for the polymerization of methyl methacrylate. The Er complex is more active than the Yb complex. © 2006 Elsevier B.V. All rights reserved.

Keywords: Lanthanide; Borohydride; Guanidinate; Polymerization

1. Introduction

Covalent borohydride complexes of d-transition metals, with the exception of those of group IV, are generally thermally unstable and readily decompose into the corresponding hydrides with elimination of diborane [1]. In contrast, f-element borohydrides can be easily isolated, thus allowing structural and chemical studies of the BH₄ ligand [1,2]. Organolanthanide complexes containing Ln–C, Ln–H and Ln–N bonds have been found to exhibit good catalytic activity in various chemical transformations. Especially, they are very effective single-component catalysts for the polymerization of polar or non-polar monomers [3]. However, although the parent complexes Ln(BH₄)₃(THF)_n were prepared in 1960 [4] and structurally characterized for Y(BH₄)₃(THF)₃ about 20 years later [5], lanthanide borohydrides have seldom been introduced as polymerization

* Corresponding author. *E-mail address:* yuanbox@szcatv.com.cn (F. Yuan). catalysts until recently. Guillaume and coworkers reported the ring-opening polymerization of ε -caprolactone by Nd(BH₄)₃(THF)₃ [6], and studied the polymerization mechanism with Cp₂^{*}Sm(BH₄)(THF) [7]. Mountford and coworkers found that methyl methacrylate (MMA) can be polymerized by lanthanide borohydride complexes with polydentate diamide–diamide ligands [8]. Very recently, the *trans*-specific diene polymerization by Nd(BH₄)₃(THF)₃ in the presence of MgBu₂ was also achieved [9]. These results revealed that lanthanide borohydride complexes were new types of polymerization catalysts, and their catalytic ability has not fully been evaluated.

The potentially superior control over metal-centered reactivity has promoted the search for non-cyclopentadienyl ligand environments for the lanthanide metals. This is especially relevant for the design of new polymerization catalysts. Cyclopentadienyl-alternative ligands such as amidinates [10], β -diketiminates [11] and guanidinates [12] have been developed to understand their lanthanide chemistry. Of those, guanidinate ligand is one of the most attractive. For example, bis(guanidinate) lanthanide methyl

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complexes were found to be effective catalysts not only for the polymerization of ε -caprolactone and MMA [13], but also for the polymerization of styrene [14], which is normally quite difficult to achieve with lanthanocene catalysts. Bis(guanidinate) lanthanide diisopropylamide complexes exhibited comparable activity with the corresponding lanthanocene complexes for MMA-polymerization [15]. These fascinating results should be relevant with the open coordination environment and the strong electronic donor ability of the guanidinate ligand.

Under these background, we started to prepare lanthanide borohydride complexes with guanidinate ligand and investigated their catalytic activity for the polymerization of MMA. We found that the guanidinate lanthanide borohydride complexes could be readily prepared from sodium guanidinate and homoleptic $Ln(BH_4)_3(THF)_3$ in THF. These complexes displayed moderate high catalytic activity for the polymerization of MMA. To the best of our knowledge, it is the first example with respect to the structure and catalytic activity of guanidinate lanthanide borohydride complexes.

2. Results and discussion

2.1. Syntheses and structures of mono(guanidinate) lanthanide borohydrides

The reaction of $Ln(BH_4)_3(THF)_x$ with alkali anionic reagents is a convenient synthetic route to some lanthanide borohydride complexes such as [(COT)Nd(BH₄)(THF)]₂ [16], $(THF)(BH_4)_2Nd(\mu-\eta^7:\eta^7-C_7H_7)Nd(BH_4)(THF)_2$ [17] $[K(18-crown-6)\{(C_{13}H_8)CPh_2(C_5H_4)Nd(BH_4)_2\}]_2$. and $C_4H_8O_2$ [18]. We wish to synthesize guanidinate lanthanide borohydrides similarly by the reactions of $Ln(BH_4)_3(THF)_x$ with [(Me₃Si)₂NC(NCy)₂]Na. As an equivalent of [(Me₃-Si)₂NC(NCy)₂]Na was added into the suspension of Yb(BH₄)₃(THF)₃ in THF, the color of the mixture changed from nearly colorless to orange, indicating the reaction proceeding. After workup, red crystals of [(Me₃Si)₂NC(N- Cy_2 [Yb(BH₄)₂(THF)₂ (1) were successfully obtained from the THF-Et₂O solution. The reaction was also applicable for Er element. Similar reaction of Er(BH₄)₃(THF)₃ and [(Me₃Si)₂NC(NCy)₂]Na in a 1:1 molar ratio in THF afforded the analogous $[(Me_3Si)_2NC(NCy)_2]Er(BH_4)_2(THF)_2$ (2).

 $Ln(BH_4)_3(THF)_3+[(Me_3Si)_2NC(NCy)_2]Na$ $\xrightarrow{THF} [(Me_3Si)_2NC(NCy)_2]Ln(BH_4)_2(THF)_2+NaBH_4$ (Ln=Yb(1), Er(2))

The molecular structures of 1 and 2 are shown in Figs. 1 and 2, respectively. The selected bond parameters are listed in Table 1. 1 is isostructural with 2. The lanthanide ion is bonded by an anionic guanidinate ligand, two BH_4^- ligands



Fig. 1. The molecular structure of 1.



Fig. 2. The molecular structure of 2.

and two THF molecules. The N(1)-N(1A)-B(1)-B(1A)four atoms are coplanar with the Ln atom. The overall geometry around the Ln atom can be described as a distorted octahedron, with N(1)-N(1A)-B(1)-B(1A) atoms defining the equatorial plane and O(1) and O(1A) atoms being in axial positions. The two THF rings were bended away from the bulky guanidinate ligand. The four-member-ring formed by the guanidinate ligand and the lanthanide atom is a complete plane. The two C-N distances within a chelating guanidinate ligand are equivalent. They are shorter than the C–N single bond length (1.47 Å), but significantly longer than the C=N double bond length (1.29 Å), and consistent with a π -electron-delocalized guanidinate ligand. The Yb-N bond lengths (2.3044(18) Å) in complex 1 are consistent with those in [(SiMe₃)₂NC(N- $Cy_{2}Yb[N(SiMe_{3})_{2}]$ (2.301(15) to 2.329(13) Å) [12a] and

Table 1 Selected bond lengths (\AA) and angles (\circ) for 1 and 2

Bond length (Å)	1	2	Bond length (Å)	1	2
Ln(1)-N(1)	2.3044(18)	2.328(2)	Ln(1)-O(1)	2.3745(17)	2.3864(19)
Ln(1)-B(1)	2.534(3)	2.559(4)	N(1)-C(1)	1.337(2)	1.336(3)
N(1)-C(2)	1.465(3)	1.461(3)	N(2)–C(1)	1.434(4)	1.443(5)
Angle (°)			Angle (°)		
N(1)-Ln(1)-N(1A)	57.82(9)	57.41(10)	B(1)-Ln(1)-B(1A)	102.78(14)	102.97(17)
O(1)-Ln(1)-N(1)	87.71(6)	87.61(7)	O(1)-Ln(1)-N(1A)	86.85(6)	86.53(7)
O(1)-Ln(1)-B(1)	89.76(9)	89.67(10)	O(1)-Ln(1)-B(1A)	94.12(9)	94.49(11)
O(1)-Ln(1)-O(1A)	173.78(8)	173.31(9)	N(1)-C(1)-N(1A)	112.9(3)	113.7(3)
N(1)-C(1)-N(2)	123.56(13)	123.17(16)	N(1A)-C(1)-N(2)	123.56(13)	123.17(16)

 $\begin{array}{ll} [(SiMe_3)_2NC(N^iPr)_2]_2Yb(\mu\text{-}Cl)_2Li(THF)_2] & (2.295(3) & to \\ 2.332(3) \text{ \AA}) & [13]. \\ \text{The Ln-N bond lengths in 1 and 2 are } \\ \text{very consistent, considering there is } 0.02 \text{ \AA} & ionic radius difference between } Er^{3+} & \text{and } Yb^{3+}. \end{array}$

The important structural feature of complexes 1 and 2 is the mode of attachment of the tetrahedral BH₄ ligands. In each complex, the two BH₄ ligands involved are equivalent and *cis* to each other. The Yb–BH₄ distances in 1 (2.534(3) Å) are comparable with the Er–BH₄ distances in 2 (2.559(4) Å), if allowing 0.02 Å for the difference of ionic radii of Er³⁺ and Yb³⁺. These Ln–BH₄ distances are significantly shorter than the corresponding Ln– η^2 -BH₄ distances in Y(BH₄)₃(THF)₃ (2.68(2) Å) [5] and (CH₃O-CH₂CH₂C₉H₆)₂Y(BH₄) (2.693(8) Å) [19]. The short distances are characteristics of tridentate BH₄ ligands. Hence, all the boron atoms in the two complexes are linked to the metal center via three bridging hydrogen atoms.

2.2. Structure of the solvated sodium guanidinate complex

Anionic guanidinate ligand, $(Me_3Si)_2NC(NCy)_2^-$, has long been introduced into the lanthanide complexes [12a]. The structures of solvent-base-free alkali-metal guanidinates have also been reported [20]. We found that reaction



Fig. 3. The molecular structure of 3.

of sodium bis(trimethylsilyl)amide and N,N'-dicyclohexylcarbodiimide in THF afforded the THF-solvated sodium guanidinate of $\{[(Me_3Si)_2NC(NCy)_2]Na(THF)\}_2$ (3). The molecular structure of 3 is shown in Fig. 3. The selected bond lengths and angles are listed in Table 2. In contrast to the trimeric { $[(Me_3Si)_2NC(NCy)_2]Na$ }, complex 3 is dimeric in the solid state. Each Na atom is bound to three nitrogen atoms from two guanidinate groups and one oxygen atom from the THF molecule as formally fourcoordinate. The two planes of N(1)-Na(1)-N(2) and N(1A)-Na(1A)-N(2A) are approximately parallel. The N(1)-Na(1)-N(1A)-Na(1A) four atoms construct a plane. This quadrilateral is nearly vertical to the planes of N(1)-Na(1)-N(2) and N(1A)-Na(1A)-N(2A). The overall geometry of 3 is like two steps of a flight. Different from those in $\{[(Me_3Si)_2NC(NCy)_2]Na\}_3$ (2.335(7) to 2.726(7) Å), the Na-N bond lengths in 3 change little (2.400(3) to 2.463(3) Å). The C(1) atom deviates a little from the N(1)-Na(1)-N(2) plane, resulting in the inclination of the $Me_3Si(1)$ group toward the Na(1) atom. But the orientation of (Me₃Si)₂N group relative to the corresponding N-Na-N plane is still vertical. The two C-N bond distances (1.329(3) and 1.315(3) Å, respectively) in a guanidinate ligand are a little shorter than those in 1 and 2 (1.337(2) and 1.336(3) Å, respectively).

$$(Me_{3}Si)_{2}NNa+CyN=C=NCy$$

$$\xrightarrow{\text{THF}} 0.5 \{[(Me_{3}Si)_{2}NC(NCy)_{2}]Na(THF)\}_{2}$$
(3)

Table 2				
Selected	bond	lengths (Å) and	angles (°) fo	or 3
		0		

2.310(2)	Na(1) - N(1)	2.463(3)
2.400(3)	Na(1)-N(1A)	2.423(3)
1.329(3)	N(1)–C(2)	1.458(3)
1.315(3)	N(2)–C(8)	1.453(3)
1.469(3)		
124.45(10)	O(1)-Na(1)-N(2)	111.87(10)
124.16(10)	N(1)-Na(1)-N(2)	55.20(8)
110.75(7)	N(2)-Na(1)-N(1A)	105.35(9)
89.39(16)	Na(1A)-N(1)-Na(1)	69.25(7)
92.50(16)	N(1)-C(1)-N(2)	116.9(2)
121.3(2)	N(2)-C(1)-N(3)	121.8(2)
	$\begin{array}{c} 2.310(2)\\ 2.400(3)\\ 1.329(3)\\ 1.315(3)\\ 1.469(3)\\ \end{array}$	$\begin{array}{cccc} 2.310(2) & Na(1)-N(1) \\ 2.400(3) & Na(1)-N(1A) \\ 1.329(3) & N(1)-C(2) \\ 1.315(3) & N(2)-C(8) \\ 1.469(3) \end{array}$

Table 3	
MMA-polymerization with complexes 1 and 2^{a}	

Entry	Catalyst	[MMA]/[Cat]	Temperature (°C)	Time (h)	Yield (%)	$M_{\rm n} \times 10^{-4}$	$M_{\rm w}/M_{\rm n}$
1	2	200	0	1.0	47.8	2.59	2.66
2	2	200	0	1.5	60.5	2.58	2.54
3	2	300	0	1.5	47.4	2.89	2.75
4	2	300	15	1.5	41.6	2.37	2.89
5	2	300	30	1.5	33.4	2.16	2.42
6	2	300	45	2.5	20.4	1.71	1.50
7	2	400	0	1.5	34.4	3.33	2.65
8	2	600	0	2.5	27.5	3.77	2.15
9	1	300	0	1.5	40.9	1.51	2.21
10	1	300	15	1.5	36.9	1.36	1.88

^a Polymerization condition: in toluene; [MMA] 4.644 mol \cdot L⁻¹.

2.3. Polymerization of MMA with 1 and 2

The polymerization results are listed in Table 3. Both 1 and 2 afford PMMA under mild conditions. The Er complex is more active than the Yb complex. Under similar polymerization conditions, the catalytic activities of complex 2 are comparable with those of $[(Me_3Si)_2NC(N^iPr)_2]_2YN(^iPr)_2$ [15] and $[(N_2NN^{TMS})Sm(BH_4)]_2 [N_2NN^{TMS} = (2-C_5H_4N)$ - $CH_2N(CH_2CH_2NSiMe_3)_2$ [8]. For example, using $[(Me_3Si)_2NC(N^iPr)_2]_2YN(^iPr)_2$ as the catalyst at [MMA]/ [Ln] = 200 at 0 °C for 2 h, 58.3% of yield of PMMA was obtained, while complex 2 can produce the PMMA in a 60.5% yield in 1.5 h (Table 3 entry 2). As [MMA]/[Ln] was kept at 400, $[(N_2NN^{TMS})Sm(BH_4)]_2$ gives a 50% yield of PMMA at 0 °C for 3 h, while complex 2 achieves a 34.4%yield in 1.5 h (Table 3 entry 7). It is noteworthy that homoleptic guanidinate complexes are completely inert to the polymerization. This demonstrates the presence of BH₄ group in the catalyst is crucial for the polymerization. Moreover, the BH_4 groups in 1 and 2 are located at terminal positions, while they link two samarium atoms as two bridges in $[(N_2NN^{TMS})Sm(BH_4)]_2.$

The effect of temperature on polymerization is great. As the temperature increases, the polymerization activity decreases and the molecular weight of PMMA decreases too. The lower catalytic activity and molecular weight at higher reaction temperatures is due to more facile catalyst deactivation processes at higher temperatures (e.g. backbiting), which is normally found in MMA-polymerization cases by organolanthanide complexes [3].

3. Experimental

All manipulations were carried out under an atmosphere of argon using Schlenk techniques. Solvents were distilled from sodium/benzophenone ketyl prior to use. Sodium bis(trimethylsilyl)amide and N,N'-dicyclohexylcarbodiimide were purchased from Acros and used as received without further purification. Ln(BH₄)₃(THF)₃ (Ln = Yb, Er) were prepared according to the literature procedures [4,5]. Carbon, hydrogen and nitrogen analyses were carried out by direct combustion on an EA1110-CHNSO elemental analyzer. Lanthanide metal analyses were carried out by complexometric titration. The IR spectra were recorded on a Magna 550 spectrometer. MMA was dried over CaH₂ and distilled. ¹H NMR spectra were obtained using a Unity Inova-400 spectrometer. The molecular weights and molecular weight distributions of polymers were determined by a Waters 1515 gel permeation chromatography (GPC).

3.1. Synthesis of $\{[(Me_3Si)_2NC(NCy)_2]Na(THF)\}_2 \cdot THF (\mathbf{3} \cdot THF)$

A flask was charged with N,N'-dicyclohexylcarbodiimide (18.06 g, 0.0875 mol), and THF (about 100 mL) was condensed in. It was stirred to become a clear solution. To the solution was added the THF solution (about 80 mL) of sodium bis(trimethylsilyl)amide (0.0875 mol). The mixture was stirred at room temperature for 2 h, and the product of $\mathbf{3} \cdot$ THF was precipitated due to the solubility limit. It was collected by filtration and dried under vacuum (36.54 g, 0.0367 mol, 83.9%). The single crystals of $\mathbf{3} \cdot$ THF were produced from the THF solution at room temperature. ¹H NMR (C₆D₆, δ): 3.61 (s, 8H, THF), 3.43 (d, 4H, unique Cy H), 1.80–1.00 (m, 40H + 8H, C₆H₁₀ and THF), 0.50–0.14 (m, 36H, SiMe₃) ppm.

3.2. Synthesis of [(Me₃Si)₂NC(NCy)₂]Yb(BH₄)₂(THF)₂ (1)

A flask was charged with Yb(BH₄)₃(THF)₃ (0.833 g, 1.92 mmol) and **3** · THF (0.956 g, 0.96 mmol), and THF (about 25 mL) was condensed in. The reaction mixture was stirred at 50 °C and turned orange quickly. After being stirred for 12 h, the mixture was centrifugalized. The clear THF solution was evaporated off under vacuum, and the residue was extracted with diethyl ether. The red extract solution was concentrated and kept at -20 °C. Red crystals of **1** (0.75 g, 1.05 mmol, 54.7%) were produced. Anal. Calc. for C₂₇H₆₄B₂N₃O₂Si₂Yb: C, 45.44; H, 9.04; N, 5.89; Yb, 24.25. Found: C, 45.36; H, 8.98; N, 5.76; Yb, 24.18%. IR (KBr pellet, cm⁻¹): 2387 (w), 2293 (s), 2227 (m), 1633 (w), 1450 (s), 1350 (s), 1252 (s), 1184 (s), 1137 (s), 1071 (m), 1004 (s), 965 (s), 937 (s), 863 (s), 838 (s), 756 (m), 665 (m), 642 (m).

Table 4 Details of the crystallographic data collection and refinement for 1-3

	1	2	$3 \cdot \text{THF}$
Empirical formula	$C_{27}H_{64}B_2N_3O_2Si_2Yb$	$C_{27}H_{64}B_2N_3O_2Si_2Er$	C50H104N6Na2O3Si4
Molecular weight	713.65	707.87	995.73
Temperature (K)	193(2)	193(2)	193(2)
Wavelength (Å)	0.71070	0.71070	0.71070
Size (mm)	$0.49 \times 0.40 \times 0.30$	$0.30 \times 0.20 \times 0.18$	$0.51 \times 0.48 \times 0.39$
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	p2/n	p2/n	c2/c
<i>a</i> (Å)	9.2922(8)	9.2956(12)	24.665(4)
$b(\mathbf{A})$	11.2692(12)	11.2863(12)	15.670(2)
c (Å)	17.594(2)	17.618(2)	17.111(3)
α (°)	90	90	90
β (°)	103.461(3)	103.535(4)	113.395(4)
γ (°)	90	90	90
$V(\text{\AA}^3)$	1791.7(3)	1797.0(4)	6070.0(15)
Ζ	2	2	4
$D_{\text{calcd.}}$ (g/cm ³)	1.323	1.308	1.090
Absorption coefficient (mm^{-1})	2.702	2.474	0.153
<i>F</i> (000)	742	738	2192
θ Range for collection (°)	3.32-25.35	3.32-25.35	3.32-25.35
Reflections collected	17,265	16,904	29,567
Independent reflections	3290	3295	5554
Variables	189	189	288
Goodness-of-fit on F^2	1.075	1.108	1.116
$R, Rw [I > 2\sigma(I)]$	0.0194, 0.0484	0.0239, 0.0509	0.0666, 0.1790
R, Rw (all data)	0.0198, 0.0487	0.0256, 0.0517	0.0737, 0.1848

3.3. Synthesis of [(Me₃Si)₂NC(NCy)₂]Er(BH₄)₂(THF)₂ (2)

The procedure followed was similar to that for **1**. Complex **2** was obtained as pink crystals in a 58.6% yield. Anal. Calc. for $C_{27}H_{64}B_2N_3O_2Si_2Er$: C, 45.81; H, 9.11; N, 5.94; Er, 23.63. Found: C, 45.74; H, 8.86; N, 5.85; Er, 23.48%. IR (KBr pellet, cm⁻¹): 2293 (s), 2227 (m), 1636 (w), 1444 (s), 1344 (s), 1298 (m), 1250 (s), 1174 (s), 1137 (s), 1061 (m), 1004 (s), 965 (s), 941 (s), 863 (s), 804 (s), 756 (m), 642 (m).

3.4. Typical procedure for the polymerization reaction

A flask equipped with a magnetic stirring bar, to which were added the catalyst and toluene solvent, was then placed in a thermostatic bath. After some time, the monomer was added into the flask using a syringe. The contents of the flask were stirred for a determined time. The reaction was quenched by addition of ethanol containing hydrochloric acid. The polymer was washed with ethanol containing acid, dried under vacuum at 45 °C and weighed.

3.5. X-ray structure determination of 1-3

Suitable single crystals of complexes 1–3 were each sealed in a thin walled glass capillary, and intensity data were collected on a Rigaku Mercury CCD equipped with graphite-monochromated Mo K α ($\lambda = 0.71070$ Å) radiation. Details of the intensity data collection and crystal data are given in Table 4. The crystal structures of these complexes were solved by direct methods and expanded

by Fourier techniques. Atomic coordinates and thermal parameters were refined by full-matrix least-squares analysis on F^2 . All non-hydrogen atoms were refined anisotropically. The hydroborate hydrogen atoms were refined isotropically and the other hydrogen atoms were introduced in calculated positions. CCDC-273907 (for 1), -274215 (for 2) and -274214 (for 3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk or from the Cambridge CB2 1EZ, UK [Fax: (internat.) +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk].

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