Polymerization

DOI: 10.1002/anie.200603450

Cationic Rare-Earth Polyhydrido Complexes: Synthesis, Structure, and Catalytic Activity for the *cis*-1,4-Selective Polymerization of 1,3-Cyclohexadiene**

Xiaofang Li, Jens Baldamus, Masayoshi Nishiura, Olivier Tardif, and Zhaomin Hou*

Metal hydrides are fundamental components in a wide range of stoichiometric and catalytic reactions. Their importance in modern inorganic and organic chemistry cannot be overemphasized. Rare-earth (Group 3 and lanthanide) hydrides are among the most active metal-hydride complexes. Together with their alkyl analogues, metal-hydride complexes of the rare-earth metals have occupied an especially important position in the development of the organometallic chemistry of the rare-earth elements. Generally, cationic complexes differ in their structure and reactivity from their neutral analogues. However, although a large number of metal-hydride complexes of the rare-earth metals have been synthesized and structurally characterized,^[11] cationic complexes of this type have not been reported previously.

[*] Dr. X. Li, J. Baldamus, Dr. M. Nishiura, Dr. O. Tardif, Prof. Dr. Z. Hou Organometallic Chemistry Laboratory RIKEN (The Institute of Physical and Chemical Research) Hirosawa 2-1, Wako, Saitama 351-0198 (Japan) and PRESTO Japan Science and Technology Agency (JST) (Japan) Fax: (+81) 48-462-4665 E-mail: houz@riken.jp
[**] This work was partly supported by Grant-in-Aid for Scientific

- [**] This work was partly supported by Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.
- Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

We recently reported the synthesis and hydrogenation reactions of a new class of polynuclear rare-earth polyhydrido complexes exemplified by $[Y_4(C_5Me_4SiMe_3)_4H_8(thf)_n]$ (1a: n = 0, 1b: n = 1, 1c: n = 2).^[2,3] In view of the unique reactivity of these hydride clusters^[2b-e,g] and the excellent olefin-polymerization activity of the related cationic rare-earth-alkyl complexes,^[4,5] we became interested in the cationic hydrido species generated from these rare-earth-hydride clusters.

Herein, we report the synthesis, structural characterization, and olefin-polymerization catalysis of the cationic hydride complexes obtained from 1a-c (Scheme 1) and related rare-earth-hydride clusters. These cationic polyhydrido complexes not only are the first cationic rare-earthhydride complexes but also show excellent regio- and stereoselectivity for the polymerization of 1,3-cyclohexadiene (CHD), which afforded, for the first time, soluble crystalline cis-1,4-linked poly(CHD) (1,4 selectivity: 100%; cis selectivity: 99%). For comparison, the reaction of the neutral hydride cluster, 1b, with CHD is also described. This reaction leads to the formation of a structurally well-defined CHD insertion product instead of the polymerization of CHD. Various metal catalysts and initiators were reported previously for the polymerization of CHD, but most yielded a mixture of 1,4and 1,2-poly(CHD)^[6-10] or insoluble polymers,^[10,11] and none was reported to produce pure soluble crystalline cis-1,4linked poly(CHD).

Reaction of the thf-free octahydrido yttrium cluster $1a^{[2b,f]}$ with one equivalent of $[Ph_3C][B(C_6F_5)_4]$ in chlorobenzene or toluene at 25 °C gave the cationic heptahydrido complex 2aand Ph_3CH (Scheme 1). In contrast to the neutral complex 1a, which shows a good solubility in most organic solvents, the cationic complex 2a was only slightly soluble in benzene and toluene, and almost insoluble in hexane. Recrystallization of 2a from chlorobenzene/hexane afforded colorless single







Scheme 1. Synthesis of cationic yttrium-hydride clusters. Cp': $C_5Me_4SiMe_3$.

8184

C 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

crystals suitable for an X-ray diffraction study. X-ray analysis revealed that **2a** has a distorted tetrahedral Y_4 frame, which is bound by seven hydride ligands, one in μ_4 , two in μ_3 , and four in μ_2 bonding modes (Figure 1 and Table 1). The Y–(μ_4 -H)



Figure 1. ORTEP drawing of 2a with 30% thermal ellipsoids. The Me₃Si and Me groups in C₅Me₄SiMe₃ are omitted for clarity.

Table 1: Summary of selected bond lengths (Å) of neutral and cationic yttrium-hydride clusters.^[13] Cp': $C_5Me_4SiMe_3$.

	l a ^[2 f]	1 b ^[2a,b]	1 c ^[2a, 3b]	2a	2c	3
Cp'-Y _{avg}	2.599(3)	2.624(4)	2.669(3)	2.583(10)	2.614(5)	2.626(4)
$Y - (\mu_4 - H)_{avg}$	2.17(2)	2.20(4)	_	2.36(6)	2.45(3)	2.29(3)
$Y-(\mu_3-H)_{avg}$	2.39(2)	2.27(3)	2.24(3)	2.28(6)	2.23(3)	2.26(3)
$Y-(\mu_2-H)_{avg}$	2.17(3)	2.16(3)	2.12(3)	2.08(6)	2.07(2)	2.10(3)
Y-O _{avg}	_	2.403(3)	2.407(2)	_	2.304(3)	_
Y1-F4	-	-		2.405(4)		-

bonds in **2a** with lengths from 2.23(6) Å (Y1–H1) to 2.43(6) Å (Y3–H1) and an average value of 2.36(6) Å are significantly longer than those in **1a** (average 2.17(2) Å),^[2f] as a result of more distortion of the Y₄ frame in **2a** than in **1a** from a normal tetrahedron. The lengths of the Y–(μ_3 -H) and Y–(μ_2 -H) bonds in **2a** are, however, similar to those in **1a** (Table 1). A direct bonding interaction between the [(C₅Me₄SiMe₃)₄Y₄H₇]⁺ ion and the [B(C₆F₅)₄]⁻ ion through a Y–F bond (Y1–F4: 2.405(4) Å) was also found in **2a**.^[12]

The ¹H NMR spectrum of **2a** in C_6D_5Cl at room temperature showed a broad singlet at 4.62 ppm for the seven hydride ligands and one set of signals for the four $C_3Me_4SiMe_3$ ligands (see the Supporting Information). Similarly, the four C_6F_5 groups in the borate ion $[B(C_6F_5)_4]^-$ also showed one set of ¹⁹F NMR signals. These results suggest that **2a** is highly fluxional in solution, probably because of the rapid dissociation and coordination of $[B(C_6F_5)_4]^-$ ions or solvent molecules. This fluxionality was not fixed even at -40 °C in C_6D_5Cl , which was shown by the ¹H and ¹⁹F NMR spectra.

A similar reaction of the mono-thf complex, $\mathbf{1b}_{,}^{[2a,b]}$ with [Ph₃C][B(C₆F₅)₄] in chlorobenzene afforded analogously complex **2b** (Scheme 1). In contrast to the observation made for **2a**, the four C₅Me₄SiMe₃ groups in **2b** gave four sets of signals and the seven hydride ligands showed a broad singlet (1 µ₄-H) at 1.45 ppm, a pair of quartets (2 µ₃-H) at 3.24 ($J_{Y,H} = 21.0 \text{ Hz}$) and 3.53 ppm ($J_{Y,H} = 25.2 \text{ Hz}$), and a pair of triplets (4 µ₂-H) at 4.98 ($J_{Y,H} = 37.5 \text{ Hz}$) and 5.40 ppm ($J_{Y,H} = 36.9 \text{ Hz}$) in the corresponding ¹H NMR spectrum in C₆D₅Cl at

room temperature, which suggests that the unsymmetrical $\{Y_4H_7(thf)\}\$ core in **2b** is rigid. The four C_6F_5 groups in the borate unit, however, showed one set of ¹⁹F NMR signals, which indicates that the $[B(C_6F_5)_4]^-$ ion of **2b** does not have a strong (or direct bonding) interaction with the cation. Attempts to obtain a single crystal of the mono-thf complex **2b** were not successful: Recrystallization of **2b** from THF yielded colorless single crystals of the bis-thf adduct **2c**. Alternatively, **2c** could be made by reaction of the bis-thf neutral complex **1c**^[2a,3b] with [Ph₃C][B(C₆F₅)₄] or by reaction of **1b** with [Ph₃C][B(C₆F₅)₄] in THF (Scheme 1).

An X-ray analysis established that **2c** has a butterfly-like {Y₄} core bound by one μ_{4^-} , two μ_{3^-} , and four μ_2 -hydride ligands (Figure 2), which contrasts with the structure of the neutral precursor **1c**. This complex adopts a tetrahedral {Y₄H₈} core structure with four μ_{3^-} and four μ_2 -hydride ligands.^[14] The interatomic distance between Y1 and Y2 in **2c** (5.2879(6) Å) is much longer than the other Y…Y interatomic distances (3.4947(6)–3.5539(5) Å), and also much longer than

the Y…Y separations found in 1c (3.3287(5)-3.9220(4) Å).^[14] In accordance with the butterfly arrangement of the four Y atoms in 2c, the Y1–H1 and Y2–H1 bonds are much longer than the Y3–H1 and Y4–H1 bonds (2.68(3) and 2.61(3) versus 2.31(3) Å and 2.21(3) Å), while the Y–(µ₃-H) and Y–(µ₂-H) bond lengths in 2c are comparable with those in 1c



Figure 2. ORTEP drawing of **2 c** with 30% thermal ellipsoids. The Me₃Si and Me groups in C₅Me₄SiMe₃, hydrogen atoms in THF, and the $[B(C_6F_5)_4]^-$ ion are omitted for clarity.

(Table 1). Because of the greater electron deficiency of the cationic metal centers in 2c, the Y–Cp' bonds in 2c are significantly shorter than those in 1c, as are the Y–O(thf) separations (Table 1). No direct bonding interaction between the $[(C_5Me_4SiMe_3)_4Y_4H_7(thf)_2]^+$ ion and the $[B(C_6F_5)_4]^-$ ion was observed.

The {Y₄H₇(thf)₂} core in **2c** showed a similarly high rigidity in solution as that in **2b**. Signals corresponding to μ_4 -H, μ_3 -H, and μ_2 -H ligands could be distinguished at 2.83 ppm (br s), 3.14 ppm (br m), and 5.41 ppm (dd, $J_{Y,H}$ = 39.6, 36.8 Hz), respectively, in the room-temperature NMR spectrum of **2b** in C₆D₅Cl. The four C₅Me₄SiMe₃ groups showed two sets of ¹H NMR signals, while the four C₆F₅ groups in the

Communications

borate unit gave one set of ¹⁹F NMR signals. These results are consistent with the crystal structure of **2c**.

To the best of our knowledge, complexes 2a-c are the first examples of cationic rare-earth-hydride complexes. The thffree cationic complex 2a and its mono-thf adduct 2b showed very high activity for the polymerization of ethylene (ca. 10^3 kg of polyethylene per mol of Y, h, and atm) and syndiospecific polymerization of styrene (ca. 10 kg of polystyrene per mol of Y and h, rrrr > 99%).^[15] More remarkably, these cationic complexes showed excellent regio- and stereoselectivity for the polymerization of CHD, which afforded almost pure cis-1,4-poly(CHD) (1,4 selectivity: 100%; cis selectivity: 99%; see the Supporting Information for details). The bis-thf adduct 2c did not show polymerization activity under the same conditions. Use of an isolated cationic hydrido complex such as 2a or 2b is not required for the polymerization of CHD. The cationic species generated in situ by the reaction of **1a** or **1b** with one equivalent of $[Ph_3C][B(C_6F_5)_4]$ also showed similar or higher activity (Table 2, entry 3). As an

Table 2: Regio- and stereoselective polymerization of CHD by cationic rare-earth polyhydrido complexes.^[a]

			A ^[c]		}	$\frac{[Cp'_4Ln_4H_8(thf)] / activator}{toluene} \qquad \qquad$						
Entry	Ln	R ^[b] [Å]		т [°С]	Polymer yield		1,4-Poly(CHD) isomers ^[d]			<i>M</i> _n ^[e] [×10 ³]	$M_{\rm w}/M_{\rm n}^{\rm [e]}$	T _m ^[f] [°C]
					[g]	[%]	trans	cis	tac			
] ^[g]	-	-	Α	25	0.80	100	43 ^[h]	57	-	1.9	2.17	_
2	Y	1.04	-	25	-	-	-	-	-	-	_	-
3	Y	1.04	Α	25	0.40	50	1	99	73	6.1	2.23	253
4	Y	1.04	В	25	0.34	42	3	97	75	6.3	2.18	254
5	Y	1.04	С	25	0.07	9	5	95	-	4.2	2.00	236
6 ^[i]	Gd	1.07	Α	0	0.12	15	<1	>99	85	3.6	1.78	249
7	Gd	1.07	Α	25	0.67	84	6	94	72	3.5	1.84	247
8	Gd	1.07	Α	50	0.51	64	25	75	-	2.0	1.93	248
9	Dy	1.05	Α	25	0.55	69	1	99	74	4.5	2.10	251
10	Ho	1.04	Α	25	0.49	61	1	99	76	7.8	1.85	247
11	Er	1.03	Α	25	0.27	34	1	99	72	6.8	1.89	250
12	Tm	1.02	Α	25	0.18	23	1	99	70	2.9	1.72	226
13	Lu	1.00	Α	25	trace	-	-	-	-	-	-	-

[a] Conditions: $[(C_5Me_4SiMe_3)_4Ln_4H_8(thf)]$: 40 µmol, activator: 40 µmol, CHD: 10 mmol, V=2 mL (toluene), t=15 h, unless otherwise noted. [b] Ionic radius of Ln^{3+} for CN=6; see reference [16]. [c] Activator: $A = [Ph_3C][B(C_6F_5)_4]$, $B = [PhMe_2NH][B(C_6F_5)_4]$, $C = B(C_6F_5)_3$. [d] Determined by ¹H and ¹³C NMR spectroscopy. Tacticity (*tac*, either isotactic or syndiotactic) was determined by integrating the ratio of the ¹³C NMR signals at 39.42 and 39.64 ppm for the *cis*-1,4-polymer, but was not unequivocally identified. [e] Determined by gel permeation chromatography (GPC) in *o*-dichlorobenzene at 140 °C with polystyrene standard. M_n : number-average molecular weight of the polymer, M_w : weight-average molecular weight. [f] Melting temperature of the polymer; measured by differential scanning calorimetry (DSC). [g] t=1 min. [h] 1,4-Structure: 75%. [i] t=35 h.

activator, $[PhMe_2NH][B(C_6F_5)_4]$ (**B**) was also effective, whereas $B(C_6F_5)_3$ (**C**) showed much lower activity under the same conditions (Table 2, entries 4 and 5). In addition to Y, analogous rare-earth metal clusters, such as those of Gd, Dy, Ho, Er, Tm, and Lu,^[17] were also effective catalysts for the *cis*-1,4-selective polymerization of CHD under similar conditions (Table 2). Moreover, a significant influence of the ionic radius of the rare-earth metal centers on the catalytic activity was observed, that is, an increase of the ionic radius led to an almost linear increase in the catalytic activity among the metals examined (Figure 3). In contrast, the polymerization initiated by the trityl cation, $[Ph_3C][B(C_6F_5)_4]$ (**A**), alone showed very poor regio- and stereoselectivity and yielded poly(CHD) with mixed 1,2- and 1,4-*cis/trans* microstructures



Figure 3. Plot of activity in the CHD polymerization versus the ionic radius, *R*, of the cationic rare-earth polyhydrido complexes.

(Table 2, entry 1).^[18] The activators **B** and **C** alone showed no activity for CHD polymerization under the same conditions.

For comparison, the reaction of the neutral polyhydrido complex 1b with CHD was also examined. It gave selectively the single CHD insertion product, 3, in a quantitative yield (Scheme 2). The overall structure of the Y_4 frame in **3** is similar to that of 1b. The resultant cyclohexenyl ligand adopts an allylic form, which bridges two Y atoms through the two terminal carbon atoms of the allyl moiety, each bonding to one metal center in an η^1 fashion (Figure 4). As with those of 2a and 2c, the {Y₄H₇} core in 3 also has one μ_4 -H, two μ_3 -H, and four μ_2 -H ligands. The ¹H NMR signals for the μ_4 -H and the two μ_3 -H ligands of **3** in C₆D₆ at room temperature appear at 2.50 ppm (br s) and 3.91 ppm (br m), respectively, while those for the four μ_2 -H ligands give two triplets at 5.15 (t, $J_{Y,H} = 35.7 \text{ Hz}$) and 5.40 ppm (t, $J_{Y,H} = 35.7$ Hz),



Scheme 2. Reaction of 1b with 1,3-cyclohexadiene.



Figure 4. ORTEP drawing of 3 with thermal ellipsoids set at 30% probability. The C₅Me₄SiMe₃ ligands and hydrogen atoms in the CHD unit are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y1–C1 2.550(3), Y2–C3 2.568(3), C1–C2 1.357(5), C1–C6 1.476(6), C2–C3 1.401(5), C3–C4 1.524(6), C4–C5 1.484(5), C5–C6 1.552(5); C2-C1-C6 115.4(3), C1-C2-C3 128.4(4), C2-C3-C4 115.8(3), C2-C1-Y1 114.6(2), C2-C3-Y2 114.7(2).

respectively. These results are consistent with the crystal structure of **3** and show that the $\{Y_4H_7(C_6H_9)\}$ core of **3** is rigid.^[19] No reaction was observed between **3** and CHD at room temperature in $[D_8]$ toluene. However, on treatment with one equivalent of $[Ph_3C][B(C_6F_5)_4]$, **3** became active for the *cis*-1,4-polymerization of CHD.^[20]

In summary, by treating neutral rare-earth-hydride clusters such as 1a-c with one equivalent of a borate compound such as $[Ph_3C][B(C_6F_5)_4]$, we have isolated and structurally characterized the corresponding cationic polyhydrido complexes such as 2a,c. In contrast to the neutral hydride cluster 1b, which yielded a single Y-H addition product, 3, on treatment with CHD, the cationic hydride clusters (either isolated or generated in situ) act as excellent catalysts for the regio- and stereoselective *cis*-1,4-polymerization of CHD. Studies on the reactions of cationic rare-earth-hydride clusters with other unsaturated substrates, the activation of small molecules, and the polymerization/copolymerization of CHD by related cationic rare-earth-alkyl complexes are in progress.

Received: August 23, 2006 Revised: September 25, 2006 Published online: November 14, 2006

Keywords: cations · cluster compounds · hydride ligands · polymerization · rare earths

Selected reviews: a) Z. Hou, Bull. Chem. Soc. Jpn. 2003, 76, 2253-2266; b) J. Okuda, Dalton Trans. 2003, 2367-2378; c) S. Arndt, J. Okuda, Chem. Rev. 2002, 102, 1953-1976; d) G. A. Molander, J. A. C. Romero, Chem. Rev. 2002, 102, 2161-2185; e) R. Anwander in Applied Homogeneous Catalysis with Organometallic Compounds, Vol. 2 (Eds.: B. Cornils, W. A. Herrmann), VCH, Weinheim, 1996, pp. 866-892; f) Z. Hou, Y. Wakatsuki in Science of Synthesis, Vol. 2 (Eds.: T. Imamoto, R. Noyori), Thieme, Stuttgart, 2002, pp. 849-942; g) A. J. Hoskin,

D. W. Stephan, Coord. Chem. Rev. 2002, 233–234, 107–129;
h) M. Ephritikhine, Chem. Rev. 1997, 97, 2193–2242;
i) H. Schumann, J. A. Meese-Marktscheffel, L. Esser, Chem. Rev. 1995, 95, 865–986;
j) F. T. Edelmann in Comprehensive Organometallic Chemistry II, Vol. 4 (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson, M. F. Lappert), Pergamon, Oxford, 1995, pp. 11–192;
k) C. J. Schaverien, Adv. Organomet. Chem. 1994, 36, 283–362.

- [2] a) O. Tardif, M. Nishiura, Z. Hou, Organometallics 2003, 22, 1171-1173; b) D. Cui, O. Tardif, Z. Hou, J. Am. Chem. Soc. 2004, 126, 1312-1313; c) O. Tardif, D. Hashizume, Z. Hou, J. Am. Chem. Soc. 2004, 126, 8080-8081; d) D. Cui, M. Nishiura, Z. Hou, Angew. Chem. 2005, 117, 981-984; Angew. Chem. Int. Ed. 2005, 44, 959-962; e) D. Cui, M. Nishiura, Z. Hou, Macromolecules 2005, 38, 4089-4095; f) Y. Luo, J. Baldamus, O. Tardif, Z. Hou, Organometallics 2005, 24, 4362-4366; g) T. Shima, Z. Hou, J. Am. Chem. Soc. 2006, 128, 8124-8125.
- [3] For the formation and structure of 1c, see also: a) K. C. Hultzsch, T. P. Spaniol, J. Okuda, *Angew. Chem.* 1999, 111, 163–165; *Angew. Chem. Int. Ed.* 1999, 38, 227–230; b) K. C. Hultzsch, P. Voth, T. P. Spaniol, J. Okuda, *Z. Anorg. Allg. Chem.* 2003, 629, 1272–1276.
- [4] Selected reviews on cationic rare-earth-alkyl complexes:
 a) P. M. Zeimentz, S. Arndt, B. R. Elvidge, J. Okuda, *Chem. Rev.* 2006, 106, 2404-2433;
 b) Z. Hou, Y. Luo, X. Li, J. Organomet. Chem. 2006, 691, 3114-3121;
 c) S. Arndt, J. Okuda, Adv. Synth. Catal. 2005, 347, 339-354;
 d) J. Gromada, J. F. Carpentier, A. Mortreux, Coord. Chem. Rev. 2004, 248, 397-410;
 e) W. E. Piers, D. J. H. Emslie, Coord. Chem. Rev. 2002, 233-234, 131-135;
 f) Z. Hou, Y. Wakatsuki, Coord. Chem. Rev. 2002, 231, 1-22.
- [5] a) Y. Luo, J. Baldamus, Z. Hou, J. Am. Chem. Soc. 2004, 126, 13910-13911; b) X. Li, Z. Hou, Macromolecules 2005, 38, 6767-6769; c) X. Li, J. Baldamus, Z. Hou, Angew. Chem. 2005, 117, 984-987; Angew. Chem. Int. Ed. 2005, 44, 962-964; d) L. Zhang, Y. Luo, Z. Hou, J. Am. Chem. Soc. 2005, 127, 14562-14563.
- [6] For examples of CHD polymerization by radical initiators, see:
 a) G. Lefebvre, F. Dawans, J. Polym. Sci. Part A 1964, 2, 3277–3295;
 b) H. Stücklen, H. Thayer, P. Willis, J. Am. Chem. Soc. 1940, 62, 1717–1719.
- [7] For examples of CHD polymerization by anionic initiators, see:
 a) H. Lussi, J. Braman, *Helv. Chim. Acta* 1967, 50, 1233-1243;
 b) L. A. Mango, R. W. Lenz, *Polym. Prepr. Am. Chem. Soc. Polym. Chem. Div.* 1971, 12, 402-409;
 c) Z. Sharaby, J. Jagur-Grodzinski, M. Martan, D. Vofsi, *J. Polym. Sci. Polym. Chem. Ed.* 1982, 20, 901-915;
 d) B. François, X. F. Zhong, *Makromol. Chem.* 1990, 191, 2743-2753;
 e) P. E. Cassidy, C. S. Marvel, S. Ray, *J. Polym. Sci. Part A* 1965, 3, 1553-1565;
 f) I. Natori, S. Inoue, *Macromolecules* 1998, 31, 4687-4694;
 g) K. L. Hong, J. W. Mays, *Macromolecules* 2001, 34, 782-786;
 h) D. T. Wiliamson, J. F. Elman, P. H. Masison, A. J. Pasquale, T. E. Long, *Macromolecules* 2001, 34, 2108-2114;
 i) R. P. Quirk, F. You, C. Wesdemiotis, M. A. Arnould, *Macromolecules* 2004, 37, 1234-1242.
- [8] For examples of CHD polymerization by cationic initiators, see:
 a) D. A. Frey, M. Hasegawa, C. S. Marvel, *J. Polym. Sci. Part A* 1963, *1*, 2057–2065; b) G. Lefebvre, F. Dawans, *J. Polym. Sci. Part A* 1964, *2*, 3277–3295.
- [9] For examples of CHD polymerization by Ziegler-Natta catalysts, see: a) C. S. Marvel, G. E. Hartzell, *J. Am. Chem. Soc.* 1959, 81, 448-452; b) A. H. K. Yousufzi, V. End, T. Otsu, *J. Polym. Sci. Polym. Chem. Ed.* 1975, 13, 1601-1605.
- [10] For examples of CHD polymerization by homogeneous titanium catalysts, see: D. E. Heiser, J. Okuda, S. Gambarotta, R. Mülhaupt, *Macromol. Chem. Phys.* 2005, 206, 195–202.

Communications

- [11] For examples of CHD polymerization by nickel catalysts, see:
 a) D. L. Gin, V. P. Conticello, R. H. Grubbs, J. Am. Chem. Soc. 1994, 116, 10507-10519; b) M. Nakano, Q. Yao, A. Usuki, S. Tanimura, T. Matsuoka, Chem. Commun. 2000, 2207-2208;
 c) R. Po, R. Santi, A. M. Romano, J. Polym. Sci. Part A 2000, 38, 3004-3009; d) P. Longo, C. Freda, O. R. Ballesteros, F. Grisi, Macromol. Chem. Phys. 2001, 202, 409-412.
- [12] Interactions between rare-earth metals and fluorine were observed previously in analogous base-free tetrakis(pentaflur-ophenyl)borate complexes; see: a) M. W. Bouwkamp, P. H. M. Budzelaar, J. Gercama, I. D. H. Morales, J. de Wolf, A. Meetsma, S. I. Troyanov, J. H. Teuben, B. Hessen, J. Am. Chem. Soc. 2005, 127, 14310-14319; b) S. Kaita, Z. Hou, M. Nishiura, Y. Doi, J. Kurazumi, A. C. Horiuchi, Y. Wakatsuki, Macromol. Rapid Commun. 2003, 24, 179-184; c) P. G. Hayes, W. E. Piers, R. McDonald, J. Am. Chem. Soc. 2002, 124, 2132-2133; d) X. Song, M. Thornton-Pett, M. Bochmann, Organometallics 1998, 17, 1004-1006.
- [13] CCDC-617797 (1c), CCDC-617794 (2a), CCDC-617795 (2c), and CCDC-617796 (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.
- [14] See the Supporting Information for details. See also references [2a] and [3b].
- [15] The reaction of the neutral hydride cluster **1b** with styrene was reported previously and gave a simple Y–H insertion product: reference [2b].
- [16] R. D. Shannon, Acta Crystallogr. Sect. A 1976, 32, 751-767.
- [17] The Lu complex was reported previously; see reference [2a]. Other rare-earth-hydride clusters were prepared analogously to 1b. The Dy and Gd complexes were also structurally characterized by X-ray analyses, which showed a tetranuclear structure similar to that of 1b. More details will be reported elsewhere.
- [18] Z. Sharaby, M. Martan, J. Jagur-Grodzinski, *Macromolecules* 1982, 15, 1167–1173.
- [19] The $\{Y_4H_7(C_6H_9)\}$ core in **3** can be viewed as having a quasi "mirror" symmetry, with Y1, Y3, H1, C2, and C5 being placed in the mirror plane.
- [20] In the absence of CHD, 2a was obtained when 3 was treated with one equivalent of $[Ph_3C][B(C_6F_5)_4]$.