Polymerization

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

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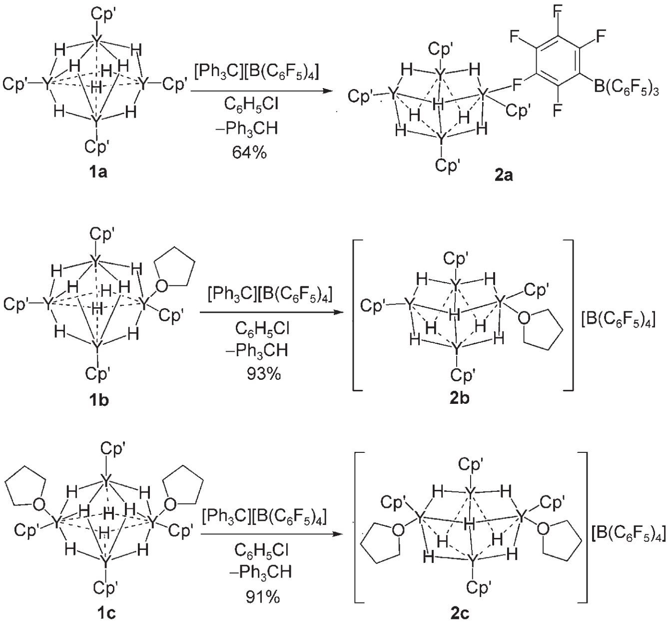
Metal hydrides are fundamental components in a wide range of stoichiometric and catalytic reactions. Their importance in modern inorganic and organic chemistry cannot be overemphasized. Rare-earth (Group 3 and lanthanide) hydrides are among the most active metal–hydride complexes. Together with their 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,[1] cationic complexes of this type have not been reported previously.

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-earth–hydride 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 1,4- and 1,2-poly(CHD)[6–10] or insoluble polymers,[10,11] and none was reported to produce pure soluble crystalline *cis*-1,4-linked 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 **2a** and 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′: $C_5Me_4SiMe_3$.

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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) 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 Y_4 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 $[(C_5Me_4SiMe_3)_4Y_4H_7]^+$ ion and the $[B(C_6F_5)_4]^-$ ion through a Y−F bond (Y1−F4: 2.405(4) Å) was also found in **2a**.[12]

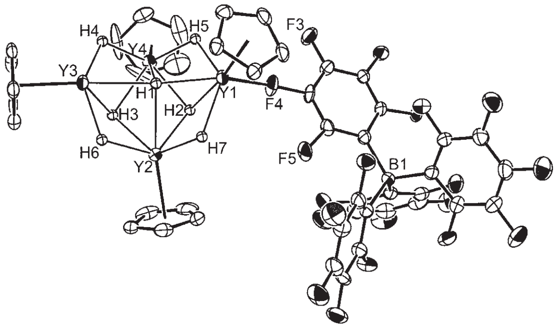


Figure 1. ORTEP drawing of **2a** with 30% thermal ellipsoids. The Me_3Si and Me groups in $C_5Me_4SiMe_3$ are omitted for clarity.

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

	1a[2f]	**1b**[2a,b]	**1c**[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−(μ_4-H)$_{avg}$	2.17(2)	2.20(4)	–	2.36(6)	2.45(3)	2.29(3)
Y−(μ_3-H)$_{avg}$	2.39(2)	2.27(3)	2.24(3)	2.28(6)	2.23(3)	2.26(3)
Y−(μ_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)	–	–

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 $C_5Me_4SiMe_3$ 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 ^{19}F 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 ^{19}F NMR spectra.

A similar reaction of the mono-thf complex, **1b**,[2a,b] with $[Ph_3C][B(C_6F_5)_4]$ in chlorobenzene afforded analogously complex **2b** (Scheme 1). In contrast to the observation made for **2a**, the four $C_5Me_4SiMe_3$ groups in **2b** gave four sets of signals and the seven hydride ligands showed a broad singlet (1 μ_4-H) at 1.45 ppm, a pair of quartets (2 μ_3-H) at 3.24 ($J_{Y,H} = 21.0$ Hz) and 3.53 ppm ($J_{Y,H} = 25.2$ Hz), and a pair of triplets (4 μ_2-H) at 4.98 ($J_{Y,H} = 37.5$ Hz) and 5.40 ppm ($J_{Y,H} = 36.9$ Hz) in the corresponding ^1H NMR spectrum in C_6D_5Cl 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 ^{19}F 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 $[Ph_3C][B(C_6F_5)_4]$ or by reaction of **1b** with $[Ph_3C][B(C_6F_5)_4]$ in THF (Scheme 1).

An X-ray analysis established that **2c** has a butterfly-like $\{Y_4\}$ 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 $\{Y_4H_8\}$ 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−(μ_3-H) and Y−(μ_2-H) bond lengths in **2c** are comparable with those in **1c** (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.

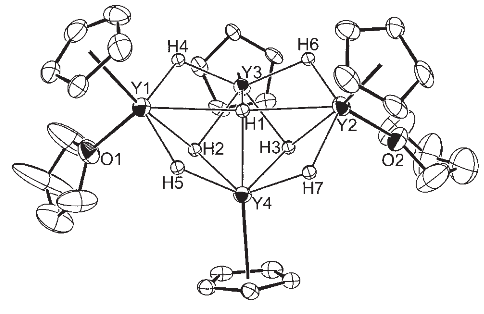


Figure 2. ORTEP drawing of **2c** with 30% thermal ellipsoids. The Me_3Si and Me groups in $C_5Me_4SiMe_3$, hydrogen atoms in THF, and the $[B(C_6F_5)_4]^-$ ion are omitted for clarity.

The $\{Y_4H_7(thf)_2\}$ 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 C_6D_5Cl. The four $C_5Me_4SiMe_3$ groups showed two sets of ^1H NMR signals, while the four C_6F_5 groups in the borate unit gave one set of ^{19}F 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 thf-free 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 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 (Table 2, entry 1).[18] The activators **B** and **C** alone showed no activity for CHD polymerization under the same conditions.

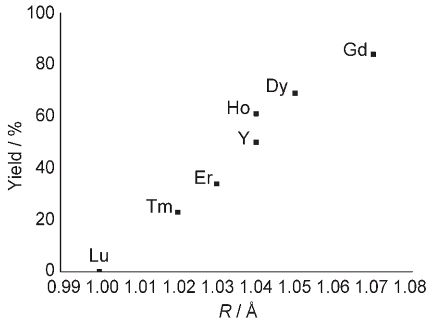
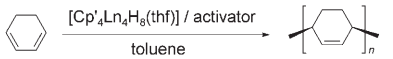


Figure 3. Plot of activity in the CHD polymerization versus the ionic radius, *R*, of the cationic rare-earth polyhydrido complexes.

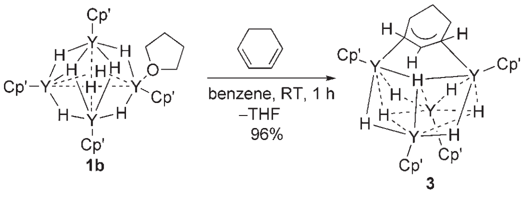
Table 2: Regio- and stereoselective polymerization of CHD by cationic rare-earth polyhydrido complexes.[a]



Entry	Ln	R[b] [Å]	A[c]	T [°C]	Polymer yield [g]	Polymer yield [%]	1,4-Poly(CHD) isomers[d] *trans*	*cis*	*tac*	M_n[e] [×10³]	M_w/M_n[e]	T_m[f] [°C]
1[g]	–	–	**A**	25	0.80	100	43[h]	57	–	1.9	2.17	–
2	Y	1.04	–	25	–	–	–	–	–	–	–	–
3	Y	1.04	**A**	25	0.40	50	1	99	73	6.1	2.23	253
4	Y	1.04	**B**	25	0.34	42	3	97	75	6.3	2.18	254
5	Y	1.04	**C**	25	0.07	9	5	95	–	4.2	2.00	236
6[i]	Gd	1.07	**A**	0	0.12	15	<1	>99	85	3.6	1.78	249
7	Gd	1.07	**A**	25	0.67	84	6	94	72	3.5	1.84	247
8	Gd	1.07	**A**	50	0.51	64	25	75	–	2.0	1.93	248
9	Dy	1.05	**A**	25	0.55	69	1	99	74	4.5	2.10	251
10	Ho	1.04	**A**	25	0.49	61	1	99	76	7.8	1.85	247
11	Er	1.03	**A**	25	0.27	34	1	99	72	6.8	1.89	250
12	Tm	1.02	**A**	25	0.18	23	1	99	70	2.9	1.72	226
13	Lu	1.00	**A**	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 ^{1}H and ^{13}C NMR spectroscopy. Tacticity (*tac*, either isotactic or syndiotactic) was determined by integrating the ratio of the ^{13}C 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.

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 $\{Y_4H_7\}$ core in **3** also has one μ_4-H, two μ_3-H, and four μ_2-H ligands. The ^{1}H NMR signals for the μ_4-H and the two μ_3-H ligands of **3** in C_6D_6 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, $J_{Y,H} = 35.7$ Hz) and 5.40 ppm (t, $J_{Y,H} = 35.7$ Hz),



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

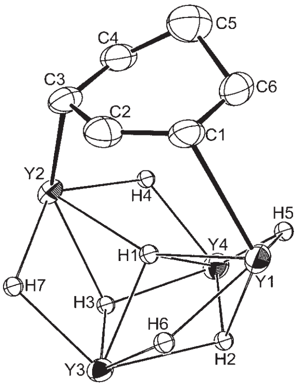


Figure 4. ORTEP drawing of **3** with thermal ellipsoids set at 30% probability. The $C_5Me_4SiMe_3$ ligands and hydrogen atoms in the CHD unit are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y1–C1 2.550(3), Y2–C3 2.568(3), C1–C2 1.357(5), C1–C6 1.476(6), C2–C3 1.401(5), C3–C4 1.524(6), 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.

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[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 $[Ph_3C][B(C_6F_5)_4]$.