Synthesis and X-ray Crystal Structures of $(C_5HiPr_4)Ln(BH_4)_2(THF)$ (Ln = Nd and Sm), Versatile Precursors for Polymerization Catalysts

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The new half metallocenes $[(C_5HiPr_4)Ln(BH_4)_2(THF)]$ [Ln = Sm (**1**) and Nd (**2**)], and $[(C_5HiPr_4)U(BH_4)_3]$ (**3**) have been synthesized. The crystal structures of **1** and **2** and of the metallocenes $[(C_5HiPr_4)_2Ln(BH_4)]$ [Ln = Sm (**4**) and Nd (**5**)] have been determined. The substitution of the BH_4 groups of **1** and **2** by a nitrogen-based ligand is possible. In the presence of butyllithium, these complexes show an activity in isoprene and styrene polymerization.

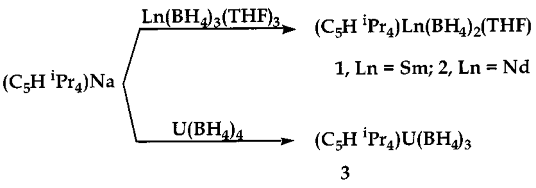
Introduction

A large number of metallocene catalysts for olefin polymerization have been reported during the last decade. Nowadays, much interest has been placed in the synthesis of half metallocenes, such as, for example, amidocyclopentadienyl compounds for the stereospecific polymerization of α-olefins or styrene.[1] Lanthanide organometallic complexes are analogous to cationic zirconium derivatives and the synthesis of monocyclopentadienyl complexes of the early lanthanides could offer the opportunity to access a great variety of new catalysts. The organometallic chemistry of these elements is actually largely based on biscyclopentadienyl (or related) complexes.[2] We considered that the use of the sterically demanding ligand C_5HiPr_4 [3] could allow an easy synthesis of monocyclopentadienyl derivatives. In order to avoid the incorporation of alkali metal salts leading to the formation of undesirable anionic complexes,[4] borohydrides were used, the pseudohalide BH_4 anion being more electron donating than the chloride ion. In this preliminary communication we present the synthesis and some aspects of the reactivity of $[(C_5HiPr_4)Ln(BH_4)_2(THF)]$ [Ln = Sm (**1**) and Nd (**2**)] and $[(C_5HiPr_4)U(BH_4)_3]$ (**3**). The latter uranium complex, which is tetracoordinate, could be considered as a model of both zirconium and anionic lanthanide $[(C_5HiPr_4)Ln(BH_4)_3]^-$ moieties. Until now, no example of a lanthanide monocyclopentadienylbisborohydride has been reported.

Results and Discussion

Synthesis

Reaction of the tetraisopropylcyclopentadienyl sodium salt C_5HiPr_4Na with $[Sm(BH_4)_3(THF)_3]$, $[Nd(BH_4)_3(THF)_3]$ or unsolvated $[U(BH_4)_4]$ in toluene (or THF) at room temperature, affords the analytically pure monocyclopentadienyl complexes $[(C_5HiPr_4)Sm(BH_4)_2(THF)]$ (**1**), $[(C_5HiPr_4)Nd(BH_4)_2(THF)]$ (**2**) and $[(C_5HiPr_4)U(BH_4)_3]$ (**3**), isolated in ca. 50−60% yield (Scheme 1). These complexes are stable and melt without decomposition around 170 °C. The monomeric structure of **1** and **2** was established by an X-ray structural analysis. The easy sublimation of **3** also indicates a monomeric structure, as is usually observed for analogous uranium compounds.[5]



Scheme 1. Synthesis of complexes **1**−**3**

Monopermethylated cyclopentadienyl lanthanide complexes are less numerous than the disubstituted ones, and most of the complexes obtained from the halide compounds are hexacoordinated complexes of general formula $[Cp^*LnX_2(THF)_3]$ or $[Cp^*LnX_3M(THF)_2]$ ($Cp^* = C_5Me_5$, X = Cl or I, M = Li or Na).[6] The simultaneous use of the very bulky tetraisopropylcyclopentadienyl ligand and of the borohydrides as starting materials allows the formation of monomeric, four-coordinate complexes.

Characterisation

The IR spectra of complexes **1**, **2**, and **3** show the characteristic pattern of a tridentate BH_4 group.[7]

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Table 1. ^{1}H NMR spectra of compounds **1−6** (C_6D_6, 300 K)

Product[metal]	HCp	H*i*Pr	Me*i*Pr	BH_4
1[a] [Sm]	8	4.2; 3.0	2.2; 1.1 −0.5; −0.7	−10.5
4 [Sm]	17.1	6.8; −0.1	1.8; −0.5 −0.9; −5.1	−7.5
2[a] [Nd]	−15.2	8.4; 1.1	9.8; −3.5 −7.6; −11.0	114.0
5 [Nd]	−9.8	29.0; 0.8	6.8; 5.1 −3.7; −33.7	74.4
3 [U]	24.9	−0.3; −1.1	20.8; 2.00 −12.3; −27.1	53.6
6 [U]	−41.0	43.1; −6.0	23.3; 11.4 2.1; −31.9	−57.8

[a] THF: δ = −0.01 and −0.51* (**1**), −3.5* and −9.16 (**2**). * Confused with a methyl signal, separated at higher temperature.

The NMR spectra of these paramagnetic complexes were recorded in C_6D_6, at variable temperature, to differentiate overlapping signals. The large signal of the BH_4 group, the coordinated THF and the seven signals of the substituted cyclopentadienyl ligand are observed (Table 1). In the spectrum of **2,** the borohydride signal is observed at very low field, as expected in consequence of the strong contact contribution in a neodymium complex. As generally observed for analogous neodymium and samarium complexes, the signals of the H atoms with the highest contact influence (CpH and BH_4) are observed at opposite ends of the spectrum: [Sm]CpH: δ = 10.7; [Nd]CpH: δ = −15.2 (see Table 1). The line widths are similar to those usually observed for paramagnetic uranium, samarium and neodymium complexes,[8] except for two very large signals, which are shifted to much higher field, for the methyl groups of **1** and **2**. At higher temperature (70 °C), these signals are significantly sharpened and exhibit a normal line width. The broadening of these signals cannot be explained only on the basis of the paramagnetic nature of the complexes, but is more likely to be related to a dynamic process: at ambient temperature the rotation of the four methyl groups located close to the metal would be restricted.

For **3,** no significant broadening of the methyl signals was observed; the rotation appears to be free, probably because of the decreased steric hindrance when a THF molecule is replaced by a BH_4 group.

The X-ray crystallographic analyses of **1** and **2** (Figure 1, Ln = Nd) reveal the same monomeric pseudo-tetrahedral structure, with one THF molecule coordinated.[9]

Reactivity

On an NMR scale, we looked at the substitution of the borohydride groups by other ligands. We tried to obtain first the hindered biscyclopentadienyl complexes. In the presence of an excess of C_5HiPr_4Na, with gentle heating (50 °C), the monocyclopentadienyl complexes **1**,**2** and **3** can be slowly (48 h) converted into the corresponding biscyclopentadienyl complexes **4**, **5** and **6**, respectively. Bulk syntheses of **4** and **5** afforded crude material which could not be obtained analytically pure, even after crystallisation. Nevertheless, crops of X-ray quality crystals of **4** and **5** were obtained, and the two compounds were found to be isostructural (Figure 2, Ln = Sm). These monomeric borohydrides are the first examples of tetracoordinated complexes of the early lanthanides; all the other early lanthanide borohydrides described are pentacoordinate,[10] dimeric,[11] or dinuclear complexes.[12]

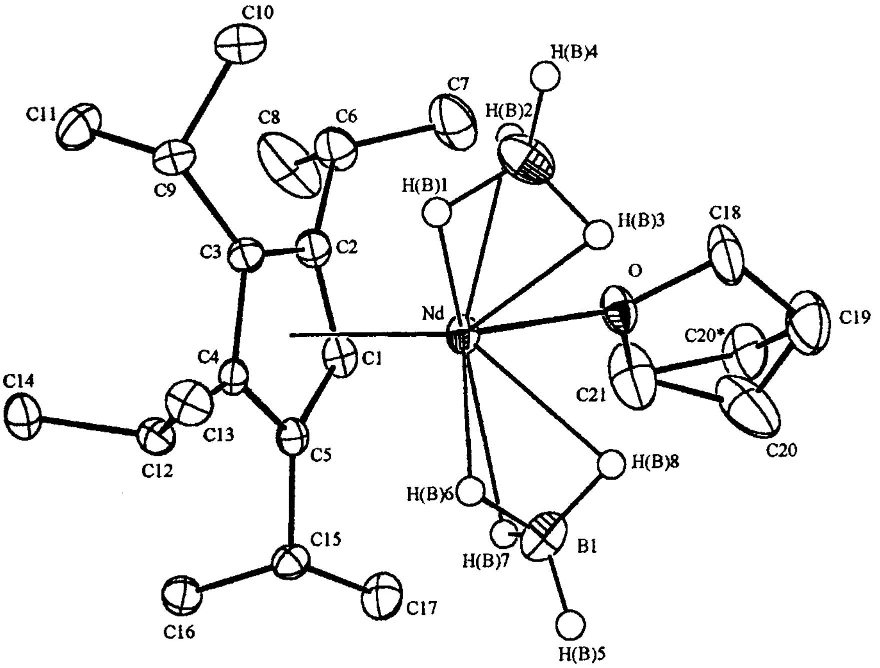


Figure 1. Molecular structure of **2**; selected interatomic distances (Å): Nd−Cp1 2.446, Nd−B1 2.605(3), Nd−B2 2.595(3), Nd−H(B)1 2.32(3), Nd−H(B)2 2.33(3), Nd−H(B)3 2.41(4), Nd−H(B)6 2.28(6), Nd−H(B)7 2.33(4), Nd−H(B)8 2.38(5); Cp1 is the geometric center of the C1−C5 ring

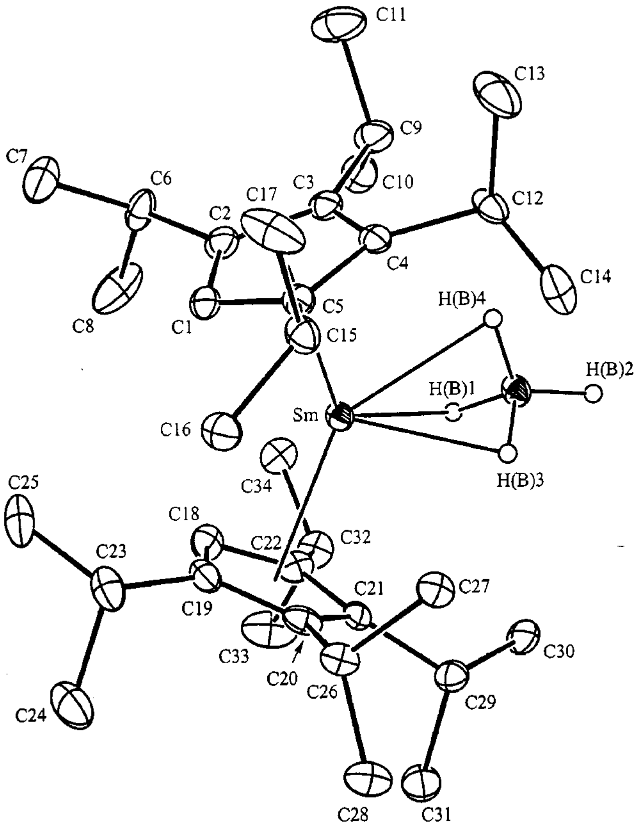
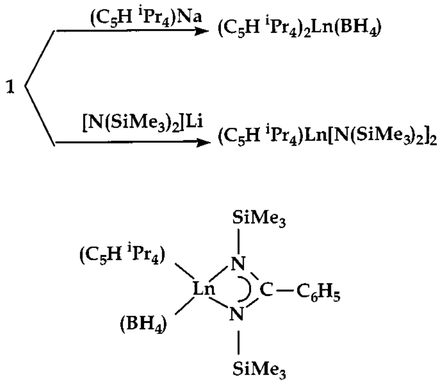


Figure 2. Molecular structure of **4**; selected interatomic distances (Å) and angles (°): Sm−Cp1 2.475, Sm−Cp2 2.436, Sm−B 2.579(3), Sm−H(B)1 2.30(4), Sm−H(B)3 2.28(4), Sm−H(B)4 2.45(4), Cp1−Sm−Cp2 138.7; Cp1 and Cp2 are the geometric centers of the C1−C5 and C18−C22 rings

Ligand exchanges are commonly observed for uranium and lanthanide complexes, but here the bulkiness of the tetraisopropylcyclopentadienyl ligand markedly slows down the exchange process: the complete equilibrium shift of a mixture of [(C_5HiPr_4)$_2$Sm(BH_4)] **(4)** and [Sm(BH_4)$_3$(THF)$_3$] to form **1** requires one week, whereas the metathesis of C_5H_4tBu derivatives requires only one day.[13]

By mixing a stoichiometric amount of **1** and LiN($SiMe_3$)$_2$, a new set of signals reveals the presence of the diamido complex [(C_5HiPr_4)Sm{N($SiMe_3$)$_2$}$_2$] mixed with ca 50% of unreacted **1**. By using the more bulky chelating benzamidinate ligand $C_6H_5C(NSiMe_3)_2$, it was possible to substitute one BH_4 ligand of **1** or **3** (Scheme 2).



Scheme 2. Reactivity of compound **1**

Polymerization Experiments

The above-described experiments clearly showed that a new series of organolanthanide complexes could be synthesized from tetraisopropylcyclopentadienyllanthanide borohydrides. We are currently investigating the access to catalytic systems: After addition of one equivalent of BuLi, a benzene solution of **1** or **2** was found to be active towards the polymerization of isoprene, affording 95% of 1,4-*trans*-poly(isoprene) (5 h, 50 °C, M_n = 90 000, I_p = 1.5). These results are in good agreement with the formation of an active organolanthanide species; anionic polymerization with BuLi gives a high percentage of 1,4-*cis*-poly(isoprene).

Under the same conditions, styrene is polymerized to give syndiotactic rich (ca 75% by ^{13}C NMR) polystyrene (16 h, 50 °C, yield 90%, M_n = 300 000, I_p = 1.6).

Conclusion

We have reported the first structures of half-metallocene bisborohydrides of lanthanides. The simultaneous use of the very bulky tetraisopropylcyclopentadienyl and borohydride ligands allows the easy production of monocyclopentadienyl complexes of neodymium and samarium, with an unusually low coordination number. The stable hemimetallocene complexes **1** and **2** are convenient precursors of new catalysts for styrene and isoprene polymerization. From these complexes, one expect the development of a rich new organolanthanide chemistry.

Experimental Section

General Procedures: All reactions were performed under an argon atmosphere in a Jacomex glove box or on a vacuum line. The solvents were dried, deoxygenated and distilled from benzophenone ketyl just before use. NMR spectra were recorded on AC 80, AC 200 or DRX 500 Bruker spectrometers at 300 K. IR spectra were recorded in nujol mulls with a Bruker IFS/66V spectrometer. The syntheses of C_5HiPr_4Na,[3] U(BH_4)$_4$,[14] Ln(BH_4)$_3$(THF)$_n$ (Ln = Nd,[15] Sm[16]), and the benzamidinate ligand[17] were made as previously described. Polymerization experiments were performed by classical procedures,[18] and GPC analyses were carried out on a Gynkotek P580 apparatus. Elemental analyses were performed with a Fisons EA 1108 CHON apparatus. X ray Data collection: Nonius Kappa CCD diffractometer, Mo-K_α radiation (λ = 0.71073 Å), graphite monochromator.

[(C_5HiPr_4)Sm(BH_4)$_2$(THF)] (1): [Sm(BH_4)$_3$(THF)$_3$] (600 mg, 1.45 mmol) and C_5HiPr_4Na (370 mg, 1.45 mmol) were placed in a flask connected to a vacuum line, and toluene (25 mL) was added by condensation. After stirring for one hour at ambient temperature, the resulting orange solution was separated by filtration and the solvent was removed in vacuo. The crude solid was extracted with pentane and, after a slow crystallization, crystals suitable for X-ray analysis were obtained. After concentration of the mother liquor, a second crop of analytically pure crystals of **1** was obtained (yield 60%). M.p. 165 °C. − IR: $\tilde{\nu}$ = 2461 cm^{-1}, 2200, 2130 (BH_4). − $C_{21}H_{45}B_2OSm$ (486): calcd. C 51.94, H 9.34; found C 52.24, H 9.21.

[(C_5H*i*Pr_4)Nd(BH_4)$_2$(THF)] (2): As described for **1**, but with THF as solvent, the dichroic blue-pink **2** was obtained in 55% yield from $Nd(BH_4)_3(THF)_3$ (104 mg, 0.26 mmol) and C_5H*i*Pr_4Na (65.7 mg, 0.26 mmol). M.p. 170 °C. − IR: $\tilde{\nu}$ = 2457 cm^{-1}, 2193, 2127 (BH_4). − $C_{21}H_{45}B_2ONd$ (479): calcd. C 52.60, H 9.46; found C 53.36, H 10.09.

[(C_5H*i*Pr_4)U(BH_4)$_4$] (3): From $U(BH_4)_4$ (260 mg, 0.872 mmol) and C_5H*i*Pr_4Na (223 mg, 0.872 mmol), the synthesis of **3** was performed as for **1**, except that the pure compound was obtained as pale orange crystals by sublimation (100 °C, 2 Torr) of the crude material. By crystallization from cold pentane, very thin needles, unsuitable for X-ray structural determination, were obtained. M.p. 160 °C. − IR: $\tilde{\nu}$ = 2516 cm^{-1}, 2178, 2100 (BH_4). − $C_{17}H_{41}B_3U$ (516): calcd. C 39.57, H 8.01; found C 39.77, H 8.36.

[(C_5H*i*Pr_4)$_2$Sm(BH_4)] (4), [(C_5H*i*Pr_4)$_2$Nd(BH_4)] (5), and [(C_5H*i*Pr_4)$_2$U(BH_4)$_2$] (6): Preliminary experiments on an NMR scale allowed the determination of the reaction time and the nature of the obtained products before the attempts at bulk synthesis. Typical experiment for **4**: Compound **1** (8 mg, 0.016 mmol) and C_5H*i*Pr_4Na (4.2 mg, 0.016 mmol) were weighed in an NMR tube, 0.5 mL of C_6D_6 was added and the mixture was stirred by sonication until the two solids dissolved. After 48 h at 50° C, an orange red solution and a colorless precipitate were obtained. The volatiles were then removed in vacuo and a new aliquot of C_6D_6 was added. The spectrum of **4** (mixed with diamagnetic impurities) was observed.

Bulk synthesis allowed the production of crude **4**, **5** and **6** as pasty colored solids mixed with pale, oily, impurities. Slow crystallization from cold pentane afforded some crystals of **4** (red) and **5** (green) suitable for X ray analyses. These crystals were collected for analysis and analytically pure samples of **4** and **5** were obtained after repeating the crystallization. $C_{34}H_{62}BSm$ (631): calcd. C 64.61, H 9.88; found C 64.85, H 10.23. − $C_{34}H_{62}BNd$ (625): calcd. C 65.24, H 10.99; found C 65.49, H 10.44.

X-ray Analysis: Needles of **1** (orange), **2** (blue), **4** (red), and **5** (green) obtained from the bulk synthesis were cut and mounted on a goniometer head.[9] Compounds **1** and **2**, and compounds **4** and **5,** were found to be isostructural.

Crystallographic data (excluding structure factors) for compounds **2** and **4** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-143895 (**2**) and CCDC-143896 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk].

Reactivity: [(C_5H*i*Pr_4)Sm(BH_4)$_2$(THF)] (11 mg, 0.023 mmol) and $Na(NSiMe_3)_2$ (4.2 mg, 0.023 mmol) were weighed in an NMR tube, 0.5 mL of C_6D_6 was added and the mixture was stirred by sonication until the two solids dissolved. After 3 h, a yellow-orange solution and a colorless precipitate were obtained. The volatiles were then removed in vacuo and a new aliquot of C_6D_6 was added. A mixture of **1,** $Sm[(N(SiMe_3)_2]_3$ (ca 5%) and [(C_5H*i*Pr_4)$_2$Sm{$N(SiMe_3)_2$}$_2$] was observed. Silylamido compound: ^1H NMR (C_6D_6): δ = 13.97 (HCp), 3.35 and 2.00 (H*i*Pr), 2.51, 1.86, 0.87, −0.19(Me), −4.05 ($SiMe_3$). The mixture was heated for four days at 50 °C, beside the previously observed signals, only a small set of new signals, ca 10% intensity, was observed. Similar experiments were conducted with $Li[C_6H_5C(NSiMe_3)_2]$, and a new benzamidinate complex was formed: ^1H NMR (C_6D_6): δ = 12.50 (HCp), 10.89, 8.18, 7.99 (C_6H_5), 4.94, 3.85, 3.30, and 2.95 (H*i*Pr), 2.23, 2.06, 1.05, 1.00, 0.87, 0.10 (6 H) and −0.68 (Me), 0.28, 0.14 and −1.26 (MeSi), −2.62 ($SiMe_3$), −10.88 (BH_4).

Polymerizations: Polymerizations were performed as previously described:[18] In a glove box, the lanthanide precursor (5 mg) was introduced into the polymerization flask, a stoichiometric amount of BuLi (1 M hexane solution) was added with a syringe and the monomer (1 mL) was immediately added. The reaction mixture was kept in a thermostatic bath at 50 °C for a given time. After the polymerization was finished, the flask was opened and the solution was poured into 200 mL of ethanol. The crude polymer was washed twice with ethanol and dried under vacuum. The polymers were analyzed by ^1H and ^{13}C NMR spectroscopy, the molecular weights were determined by GPC with a polystyrene standard.

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[9] Crystal data: Complex **2**: $C_{21}H_{45}B_2NdO$, *FW* = 479.43, blue crystal, 0.5 × 0.3 × 0.2 mm, monoclinic, space group $P2_1/c$ (No. 14), a = 11.9660(4) Å, b = 8.7190(3) Å, c = 23.7070(7) Å, β = 94.710(1), V = 2465.0(1) Å^3, Z = 4, $\rho_{calcd.}$ = 1.292 g·cm^{-3}, $F(000)$ = 996, μ = 2.112 mm^{-1}, T = 110(2) K, 21799 reflections collected, 5402 independent and 5014 observed reflections [$I \geq 2\sigma(I)$], 268 refined parameters, R = 0.028, wR^2 = 0.071, max. residual electron density 0.89 (−1.13) e·Å^{-3}; complex **4**: $C_{34}H_{62}BSm$, *FW* = 632.0, red crystal, 0.25 × 0.15 × 0.10 mm, monoclinic, space group $P2_1/n$ (No. 14), a = 9.8440(2) Å, b = 15.2450(3) Å, c = 23.1310(3) Å, β = 101.9730(9), V = 3395.8(1) Å^3, Z = 4, $\rho_{calcd.}$ = 1.236 g·cm^{-3}, $F(000)$ = 1332, μ = 1.748 mm^{-1}, T = 110(2) K, 179884 reflections collected, 7732 independent and 6709 observed reflections [$I \geq 2\sigma(I)$], 357 refined parameters, R = 0.032, wR^2 = 0.077, max. residual electron density 1.26 (−1.37) e·Å^{-3}.

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