

Organometallic Early Lanthanide Clusters: Syntheses and X-ray Structures of New Monocyclopentadienyl Complexes

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The reaction of $\text{Ln}(\text{BH}_4)_3(\text{THF})_3$ or $\text{LnCl}_3(\text{THF})_3$ with 1 equiv of KCp^{**} ligand ($\text{Cp}^{**} = \text{C}_5\text{Me}_4n\text{-Pr}$) afforded the new monocyclopentadienyl complexes $\text{Cp}^{**}\text{LnX}_2(\text{THF})_n$ ($\text{X} = \text{BH}_4$, $\text{Ln} = \text{Sm}$, $n = 1$, **1a**, $\text{Ln} = \text{Nd}$, $n = 2$, **1b**; $\text{X} = \text{Cl}$, $\text{Ln} = \text{Sm}$, $n = 1$, **3a**) and $[\text{Cp}^{**}\text{LnX}_2]_n$ ($\text{X} = \text{BH}_4$, $n' = 6$, $\text{Ln} = \text{Sm}$, **2a**, $\text{Ln} = \text{Nd}$, **2b**; $\text{X} = \text{Cl}$, $\text{Ln} = \text{Nd}$, **4b**). All these compounds were characterized by elemental analysis and ^1H NMR. Crystals of mixed borohydrido/chloro-bridged $[\text{Cp}^{**}_6\text{Ln}_6(\text{BH}_4)_{(12-x)}\text{Cl}_x(\text{THF})_n]$ ($x = 10$, $n' = 4$, $\text{Ln} = \text{Sm}$, **2a'**, $\text{Ln} = \text{Nd}$, **2b'**; $x = 5$, $n = 2$, $\text{Ln} = \text{Sm}$, **2a''**) were also isolated. Compounds **2a**, **2b**, **2a'**, **2b'**, and **2a''** were structurally characterized; they all exhibit a hexameric structure in the solid state containing the $[\text{Cp}^{**}_3\text{Ln}_3\text{X}_5(\text{THF})]$ building block. The easy clustering of THF adducts first isolated is illustrative of the well-known bridging ability of the BH_4 group. Hexameric **2a** was found to be unstable in the presence of THF vapors; this may be correlated to the opening of unsymmetrical borohydride bridges observed in the molecular structure.

1. Introduction

One of the major interests of the molecular chemistry of rare earths, which has known a growing development since the past decade, deals with its potential in homogeneous catalysis, and particularly polymerization. In this specific field, beside the traditional metallocenes^{1–3} or the linked Cp–heteroatom “CGC” catalysts,^{4,5} an alternative consists of the elaboration of heteroleptic compounds. This new generation of catalysts bears one Cp-type and one heteroatom-based ligand.^{6,7}

In the course of our studies concerning such heteroleptic complexes, we were interested in the mastering of the synthesis of monocyclopentadienyl derivatives. We focused our attention on the early lanthanides neodymium and samarium, the best candidates for catalysis applications.^{8–10} In order to avoid the formation of bis-substituted complexes or the rearrangement into homoleptic triscyclopentadienyl derivatives, commonly observed in the early series,⁴ we used the tetramethylpropylcyclopentadienyl $\text{C}_5\text{Me}_4n\text{-Pr}$ (here abbreviated as Cp^{**}), an analogue of the ubiquitous permethylcyclopentadienyl ($\text{C}_5\text{Me}_5 = \text{Cp}^*$). That commercially available ligand allows a better interpretation of the NMR spectra: though it must be remembered that it is generally not possible to make the signals' assignments as a function of the chemical shift for paramagnetic complexes,¹¹ the number and the integral values of the signals allow, however, the correlation of a set of signals to a ligand (pattern 3, 2, 2, 6, 6 for Cp^{**} hydrogen signals). Also, the number of the

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§ LSEO, Structure and Modelling Group.

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Cp* ligands may be unambiguously established for borohydride complexes by comparison of the integral values with that of the BH₄ signal. The presence of the propyl chain might induce as well a better solubility in nonpolar solvents as some steric control around the metal. The electronic donor ability of Cp* is expected to be similar to that of Cp*.

We performed our syntheses with LnCl₃(THF)₃ and Ln(BH₄)₃(THF)₃ as starting materials; the latter allow, if necessary, synthetic work in nonpolar solvents, and the recording of NMR control spectra in deuterated benzene.¹² The presence of the BH₄ group may also lead to neutral or less associated molecular structures.¹³ On the other hand, the chloride group may be more convenient for the alkylation of precatalysts at the time of generation of catalytic active species.

We present in this work the syntheses and characterizations of a series of new cyclopentadienyl complexes of samarium and neodymium of general formula Cp*LnX₂(THF)_n (X = BH₄, Ln = Sm, n = 1, **1a**, Ln = Nd, n = 2, **1b**; X = Cl, Ln = Sm, n = 1, **3a**) and [Cp*LnX₂]_{n'} (X = BH₄, n' = 6, Ln = Sm, **2a**, Ln = Nd, **2b**; X = Cl, Ln = Nd, **4b**). The X-ray structures of **2a** and **2b**, as well as those of the unexpected mixed chloro/borohydrido hexameric complexes [Cp*₆Ln₆(BH₄)_(12-x)Cl_x(THF)_{n'}] (x = 10, n' = 4, Ln = Sm, **2a'**, Ln = Nd, **2b'**; x = 5, n = 2, Ln = Sm, **2a''**) are described and discussed.

2. Experimental Section

2.1. Instruments and Methods. All operations were performed under argon using standard vacuum line techniques or in an argon-filled Jacomex glovebox (O₂ < 2 ppm). ¹H NMR spectra were recorded on a Bruker Avance 300 spectrometer at 298 K. Chemical shifts are expressed in parts per millions downfield from external TMS. IR spectra were recorded in Nujol mulls on a Bruker IFS/66V spectrometer. Elemental analyses were performed with a Fisons EA 1108 CHON apparatus.

2.2. Reagents and Standards. Solvents were stored over sodium/benzophenone ketyl and transferred by distillation to reaction vessels. LnCl₃(THF)₃ was prepared by THF extraction of the commercial LnCl₃ (Strem), and Ln(BH₄)₃(THF)₃ was obtained following a published method.¹⁴ Cp*H was purchased from Aldrich. The absence of the chloride in trisborohydrides was established by the AgNO₃ test.

2.3. Syntheses. Cp*K (Cp* = C₅Me₄n-Pr). A THF solution (20 mL) of 5 g (0.03 mol) of HCp* was slowly added at -78 °C to a suspension of KH (1.22 g; 0.03 mol) in 50 mL of THF. The mixture was allowed to reach room temperature. The color of the suspension turned to pale yellow. After 48 h of stirring, the solution was filtered and the solvent removed. The solid was washed with pentane and dried under vacuum to yield 4.82 g (78%) of a white solid.

Cp*Sm(BH₄)₂(THF) (1a) and [Cp*Sm(BH₄)₂]₆ (2a). The following is a description of a preliminary NMR-scale synthesis: Sm(BH₄)₃(THF)₃ (3.1 mg, 7.5 μmol) and 1 equiv of Cp*K (1.5 mg) were weighed in an NMR tube, and 0.4 mL of C₆D₆ was added.

¹H NMR recorded immediately showed a set of signals compatible with the formula Cp*Sm(BH₄)₂(THF)₃.

The following is a description of a bulk-scale synthesis: In the glovebox, a flame dried vessel was charged with 800 mg (1.95 mmol) of highly purified Sm(BH₄)₃(THF)₃ (the purity was reached by three cycles of toluene extraction and evaporation, and checked by a negative AgNO₃ test) and 395 mg (1.95 mmol) of Cp*K. The vessel was then connected to a vacuum line and toluene (30 mL) condensed at -78 °C. The mixture was allowed to warm to room temperature and stirred for 7 h; the color turned orange-red. The salts were eliminated by filtration, and the solvent was removed in a vacuum, leaving a deep-red solid. This crude material was dissolved in pentane (15 mL), and filtered again in order to remove some remaining salts. After evaporation of the solvent, 725 mg (89% yield) of **1a** as a red solid was obtained. ¹H NMR (C₆D₆): δ 2.18 (2H, C₅Me₄n-Pr), 1.28 (5H, C₅Me₄n-Pr), 0.92 (4H, THF) and 0.21 (4H, THF), 0.56 and 0.45 (12H, C₅Me₄n-Pr), -17 (8H, BH₄). IR (Nujol): ν (cm⁻¹) = 2434, 2282, 2216, 2161, 2151. Anal. Calcd for C₁₆H₃₅B₂O₅Sm: C, 46.25; H, 8.49. Found: C, 45.96; H, 8.41. When stored for some days under an argon atmosphere, the red solid turned out into a soft opaque coral substance. Its redissolution in pentane (5 mL) and overnight standing at room temperature yielded a crop (30% yield for **1a**) of well-formed red crystals. X-ray crystal structure analysis revealed the hexameric structure **2a**. Once more, when these crystals were stored in the flask with the traces of mother liquor, they turned out into a coral powder. The ¹H NMR spectrum of this powder was found to be identical to that recorded for **1a**.

Cp*Nd(BH₄)₂(THF)₂ (1b) and [Cp*Nd(BH₄)₂]₆ (2b). As described for Sm, a preliminary NMR-scale synthesis (Nd(BH₄)₃(THF)₃, 3 mg, 7.5 μmol; Cp*K, 1.5 mg, 7.5 μmol) showed the immediate formation of a compound compatible with the formula Cp*Nd(BH₄)₂(THF)₃.

A description of the bulk-scale synthesis follows: 400 mg (0.98 mmol) of highly purified Nd(BH₄)₃(THF)₃ (checked with AgNO₃ as for Sm series) and 200 mg (0.98 mmol) of Cp*K were stirred overnight in THF (20 mL) at room temperature. The mixture was filtered, and the salts were rinsed with THF (2 × 5 mL) in order to extract more of the product. The combined solutions were evaporated to dryness yielding 333 mg (71%) of a light blue powder of crude Cp*Nd(BH₄)₂(THF)₂ (**1b**). Anal. Calcd for C₂₀H₄₃B₂O₂Nd: C, 49.90; H, 9.00. Found: C, 48.66; H, 9.95. ¹H NMR (C₆D₆): δ 95.70 (8H, BH₄), 8.53 (6H, C₅Me₄n-Pr), 8.05 (6H, C₅Me₄n-Pr), 3.41 (3H, C₅Me₄n-Pr), 1.87 (2H, C₅Me₄n-Pr), -1.23 (8H, THF), -4.00 (8H, THF), one CH₂ group may be hidden in the baseline. IR (Nujol): ν (cm⁻¹) = 2418, 2274, 2217, 2160, 2140. This blue powder (100 mg) was dissolved in boiling pentane. A slight quantity of salts was eliminated, and after 24 h standing at room temperature, blue crystals of **2b** could be collected. Numerous signals were observed in its ¹H NMR spectrum.

Cp*SmCl₂(THF) (3a). SmCl₃(THF)₃ (930 mg, 1.97 mmol) and Cp*K (400 mg, 1.97 mmol) were stirred overnight in THF (30 mL) at room temperature. After filtration (elimination of the salts) the resulting bright orange-red solution was evaporated to dryness, leading to an expanded sticky paste insoluble in a pentane/THF (20/2 mL) mixture. The solvents were then evaporated again, and 20 mL of new pentane/THF (50/50) was added. A new off-white precipitate was formed, the mixture filtered and the resulting solution evaporated, leading to red oil, which solidified after addition of 20 mL of pentane. The pentane was decanted, and the brick-red solid dried under vacuum for 4 h (740 mg, 82% yield). Anal. Calcd for C₁₆H₂₇Cl₂O₅Sm: C, 42.08; H, 5.96. Found: C, 41.35; H, 5.56. ¹H NMR (THF-d₈, 298 K): numerous overlapped

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signals in the range 0.4–3.5 ppm. A recrystallization was undertaken with 100 mg of the red solid in 25 mL of a THF/pentane (50/50) mixture. After a week at room temperature, orange-red crystals were obtained. Once taken out of the mother liquor in the glovebox, they immediately turned opaque.

[Cp*NdCl₂]_n (4b). NdCl₃(THF)₃ (923 mg, 1.97 mmol) and Cp*K (400 mg, 1.97 mmol) were stirred in THF (30 mL) overnight. The mixture was filtered to eliminate the salts, and the resulting light blue solution was evaporated. The residual solid was dissolved in 30 mL of a THF/pentane (50/50) mixture, followed with a filtration. The solution was concentrated to a volume of 1 mL. Pentane (10 mL) was added and then slowly evaporated leading to 530 mg of a pale blue solid whose elemental analysis was consistent with the formula Cp*NdCl₂ (4b) (71% yield). Anal. Calcd for C₁₂H₁₉Cl₂Nd: C, 38.09; H, 5.06. Found: C, 38.97; H, 5.21. The ¹H NMR spectrum showed numerous paramagnetic signals (THF-d₅): δ 11.73, 11.45, 9.20, 6.7 (br), 4.14, -2.3 (br), 9.43, 9.01, 8.07, 4.45, 3.90, 2.36, -5.5.

Chloro/Borohydrido-Bridged Hexamers: Crystals of (μ₂-BH₄)₂[Cp*₃Ln₃Cl₅(THF)₂], (Ln = Sm, 2a'; Ln = Nd, 2b') and [Cp*Sm(BH₄)₂]₆{(μ₂-BH₄)₂[Cp*₃Sm₃Cl₅(THF)₂] (2a''). The procedures given below have only an informative meaning and are not considered as usual operation modes because the rate of contamination of starting borohydrides with residual chlorides was not defined. In a typical procedure (given for 2b'), a mixture containing 200 mg (0.49 mmol) of Nd(BH₄)₃(THF)₃ (¹H NMR data correct,¹⁵ but AgNO₃ test slightly positive) and 100 mg (0.49 mmol) of Cp*K in THF (10 mL) were stirred overnight at room temperature. The mixture was filtered to eliminate the salts, and evaporation of the light blue solution gave a crude solid, from which the expected neutral complex was extracted with pentane (10 mL). After a new filtration followed by concentration to 1/3, some pale-blue, transparent crystals were obtained (yield less than 10%). One of them was selected for X-ray analysis, which revealed a hexameric molecular structure (μ₂-BH₄)₂[Cp*₃Nd₃Cl₅(THF)₂] (2b'), containing 2 borohydrido and 10 chloro bridges.

A similar procedure, conducted with samarium derivatives, led to the formation of red well-formed crystals among a coral-pink powder, in low yield. X-ray studies carried out on one selected red crystal revealed the hexamer 2a', homologous to 2b'.

Crystals of 2a'' were isolated from another experience carried out in similar conditions but with a different sample of starting Sm(BH₄)₃(THF)₃, which is certainly less contaminated by chlorides than that leading to the formation of 2a'.

2.4. X-ray Structure Analyses. Selected crystals were mounted on a goniometric head in a glovebox purged with argon and immediately transferred (less than 3 min) on the goniometer unit of a Nonius KappaCCD diffractometer already prepared for low temperature (110 K) experiment under cold nitrogen stream. The unit cell determinations and data collections were carried out with Mo Kα radiation. The measured intensities were reduced with Denzo and Scalepack programs.¹⁶ The heavy atoms have been located either from direct methods or from Patterson syntheses with SHELXS97.¹⁷ Other non-hydrogen atoms were found from subsequent difference Fourier maps. The models were further refined with full-matrix least-squares (SHELXL97)¹⁷ based on *F*². All non-hydrogen atoms in all structures were refined with anisotropic thermal parameters. In the structure of 2a'', a disorder of pending

n-propyl substituents was observed for some Cp ligands without alteration of metal coordination. The hydrogen atoms of BH₄ ligands could not be located from difference Fourier maps and were neglected in final refinements. All other hydrogen atoms in the structures were included in calculated positions and isotropically refined in a riding model. Crystallographic and refinement data are gathered in Table 1.

3. Results and Discussion

3.1. Structural studies. 3.1.1. Hexamers [Cp*Ln-(BH₄)₂]₆ (2a, Ln = Sm; 2b, Ln = Nd). The borohydride complexes 2a and 2b are isostructural. The X-ray analyses of these complexes revealed a nearly regular octahedral frame of metals, a rare class of molecular clusters in organolanthanide series. All 12 edges of the metallic octahedron are spanned with μ₂-BH₄ bridges. In both 2a and 2b hexamers, each metal atom has a four-legged piano stool (tetragonal pyramid) local geometry with formally seven coordinated metal.

Both 2a and 2b complexes crystallize in a monoclinic *C2/c* space group with eight hexamers in the unit cell. However, these eight hexamers do not lie in general positions allowed in the *C2/c* group. The multiplicity of the set of general equivalent positions in *C2/c* group is equal to 8, and if it would be the case for our structures, there should be only one independent hexamer in the unit cell. In fact, four hexamers (viz. bearing in 2a the Sm1, Sm2, and Sm3 atoms, named C₂-cluster) have crystallographic C₂ symmetry with B(11) and B(3) atoms placed on 2-fold axis (Figure 1a), whereas the second set of four clusters (Sm4, Sm5, and Sm6, named C₇-cluster) lies over the inversion centers (Figure 1b).

In the C₂-clusters, the mean value of Ln–Ln distances is equal to 5.205 Å (5.138(1)–5.233(1) Å range) for 2a and to 5.239 Å (5.176(1)–5.269(1) Å) for 2b. The Ln–B–Ln bridges are symmetric with the mean Ln–B distance of 2.816 Å (range 2.783(5)–2.888(14) Å) for 2a and of 2.840 Å (range 2.804(4)–2.870(11) Å) for 2b. The mean values of Ln–B–Ln angles are equal to 135.4° (2a) and 135.0° (2b). In the second set of four centrosymmetric C₇-clusters, the Ln–Ln distances are slightly longer (5.217 Å for 2a, 5.255 Å for 2b). More interestingly, and contrary to the C₂-clusters, an asymmetry of bridging Ln–B distances is observed in C₇-clusters: there are two sets of six short (mean 2.662 Å (2a) and 2.694 Å (2b)) and of six long (mean 2.976 Å (2a) and 2.995 Å (2b)) ones. Note that the mean values of these distances (2.819 Å (2a) and 2.844 Å (2b)) fit well the corresponding values found for C₂-clusters. As a consequence of the asymmetry in Ln–B distances, there are also two sets of small (132.2° (2a) and 131.6° (2b)) and large (138.8° (2a) and 138.4° (2b)) Ln–B–Ln angles, the means of them fitting well those of C₂-clusters.

The nature of the borohydride bridges is not directly given by X-ray data because the hydrogen atoms could not be located. It is, however, well-known that the terminal BH₄ group acts either as a tridentate (η³-H₃BH) or as a bidentate (η²-H₂BH₂) ligand^{12,13,18,19} and the mode of ligation may be

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Table 1. Crystallographic Data for Complexes Studied by X-ray Diffraction

	2a	2b	2a'	2b'	2a''
color	red	blue	orange	blue	red
shape	prism	irregular	prism	prism	prism
size (mm ³)	0.15 × 0.10 × 0.03	0.25 × 0.15 × 0.05	0.20 × 0.15 × 0.10	0.6 × 0.4 × 0.2	0.25 × 0.20 × 0.15
chemical formula	C ₇₂ H ₁₆₂ B ₁₂ Sm ₆	C ₇₂ H ₁₆₂ B ₁₂ Nd ₆	C ₈₀ H ₁₃₈ O ₂ B ₂ Cl ₁₀ Sm ₆	C ₈₀ H ₁₃₀ O ₂ B ₂ Cl ₁₀ Nd ₆	C _{77.25} H ₁₅₃ B ₇ Cl ₅ O ₁ Sm ₆
fw	2059.84	2023.18	1205.06	1186.73	2253.02
cryst syst	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	C2/c	C2/c (No. 15)	P $\bar{1}$ (No. 2)	P $\bar{1}$ (No. 2)	P2 ₁ /a (No. 14)
T (K)	120	120	110	110	110
a (Å)	40.5603(5)	40.7065(3)	12.2203(4)	13.4131(5)	24.4601(3)
b (Å)	16.5683(2)	16.6327(1)	12.3948(5)	13.8180(7)	16.3719(3)
c (Å)	28.4245(4)	28.4858(3)	16.9574(7)	14.5334(8)	25.9070(4)
α (deg)	90.0000(0)	90.0000(0)	97.849(2)	70.127(3)	90.0000(0)
β (deg)	105.6023(6)	105.5873(3)	109.217(2)	67.838(2)	111.8850(10)
γ (deg)	90.0000(0)	90.0000(0)	101.279(2)	85.979(3)	90.0000(0)
V (Å ³)	18397.8(4)	18577.2(3)	2321.87(15)	2340.9(2)	9627.0(3)
Z	8	8	2	2	4
D _{calcd} (g·cm ⁻³)	1.487	1.447	1.724	1.684	1.554
μ(Mo Kα) (Mm ⁻¹)	3.801	3.325	4.060	3.591	3.775
λ(Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
F(000)	8208	8112	1186	1174	4466
θ range (deg)	1.018; 30.508	1.018; 30.508	1.018; 30.508	1.018; 30.508	1.018; 30.508
h range	[−57; 57]	[−57; 57]	[−17; 10]	[−18; 16]	[−31; 31]
k range	[−23; 22]	[−22; 23]	[−13; 16]	[−19; 15]	[−20; 21]
l range	[−40; 39]	[−40; 40]	[−21; 23]	[−19; 16]	[−34; 32]
collected reflns	49010	49725	14357	14393	31312
unique	25882	26221	11556	11028	21011
obsd [I > 2σ(I)]	12072	13740	7469	7909	16877
(R _{int})	0.1374	0.0960	0.0413	0.0428	0.0318
params	812	812	451	460	1018
restraints	0	0	0	0	0
GOF on F ²	0.948	0.959	1.019	1.024	1.020
R(F), R _w (F ²) ^a [I > 2σ(I)]	0.0593, 0.0966	0.0516, 0.0935	0.0669, 0.1413	0.0574, 0.1285	0.0439, 0.1035
R(F), R _w (F ²) ^a (all data)	0.1925, 0.1265	0.1545, 0.1184	0.1205, 0.1643	0.0928, 0.1480	0.0612, 0.1145
w ^b /a, b	0.0477, 0.0000	0.0504, 0.0000	0.0626, 17.9614	0.0663, 14.4391	0.0477, 59.3988
ρ _{min} , ρ _{max} (e·Å ⁻³)	−1.441, 1.281	−1.463, 1.438	−1.891, 1.867	−1.919, 1.724	−2.111, 1.583

$$^a R(F) = \sum |F_o| - |F_c| / \sum |F_o|; R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}. ^b w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP] \text{ with } P = (F_o^2 + 2F_c^2)/3.$$

deduced from IR data or from Ln–B distances; the shortest distance corresponds to a trihapto η^3 ligation. In dinuclear dibridged [(cot)Nd(BH₄)(THF)]₂²⁰ (cot = cyclooctatetraenyl) and [(Cp^{*t*}-Bu)₂Ln(BH₄)]₂^{21,22} (Ln = Ce, Sm), all four hydrogen atoms of μ_2 -BH₄ bridging ligands are involved in the bonding with the metals in an $\eta^{3:3}$ mode with two hydrogens acting as μ_3 -BLn₂ and the other two as μ_2 -BLn. The longer Ln–Ln distances (5.205 and 5.239 Å, respectively) and larger Ln–B–Ln (135.4° and 135.0°) angles observed for C₂-hexamers with respect to those reported for dibridged dinuclear structures (e.g., 4.360 Å and 97.1° for Nd dimer and 4.557 Å and 105.7° for Sm dimer) argue for a break of μ_3 -H–BLn₂ interactions observed in the dimer, and transform the two B–Ln μ_3 -bridging hydrogens into the terminal BH₂ ones. The μ_2 -H–BLn interaction found for dimers is certainly retained in the C₂-hexamers, as required at least for the boron atoms located on 2-fold axis of C2/c group (and by analogy of metric parameters for other B atoms). Thus, the coordination mode of BH₄ bridges in C₂-hexamers is μ_2 - $\eta^{1:1}$.

On the other hand, there is an asymmetry of some 0.3 Å in Ln–B distances in C_i-hexamers of **2a** and **2b**. The short distances of 2.66 and 2.69 Å, respectively, correspond well to those observed for terminal trihapto Ln– η^3 -H₃BH bonding, while the long Ln–B ones of 2.976 Å (2.995 Å for **2b**) may be considered as related to a monodentate Ln– η^1 -HBH₃ type of bonding.²³ Consequently, the best description of BH₄ ligation mode in C_i-hexamers should be, likely, a μ_2 - $\eta^{3:1}$ one. We are so in the presence of a fluxional crystallo-chemical Cp*^{*+*}Ln(μ_2 - $\eta^{1:1}/\mu_2$ - $\eta^{3:1}$ -BH₄)Ln Cp*^{*+*} system.

3.1.2. Mixed Chloro/Borohydrido Complexes: (μ_2 -BH₄)₂[Cp*^{*+*}₃Ln₃Cl₅(THF)]₂, (Ln = Sm, **2a'; Ln = Nd, **2b'**) and [Cp*^{*+*}₆Sm₆(BH₄)₁₂][Cp*^{*+*}₆Sm₆(BH₄)₂Cl₁₀(THF)₂]·0.25pentane (**2a''**).** During the first attempts of syntheses of **2a** and **2b**, the samples of Ln(BH₄)₃(THF)₃ starting materials were contaminated with residual chlorides. Such contamination is quite common, as reported by Mirsaidov et al.¹⁴ They led in some cases to small quantities of X-ray quality crystals of mixed chloro/borohydrido complexes **2a'**, **2b'**, and **2a''**. Although quite unpredicted, the formation of these well-defined product is worth noting because it shows a subtle competition for crystallization between the compounds with borohydride and chloride ligands. X-ray structure determinations revealed the hexameric molecules in which the chlorine atoms substitute most of the BH₄ groups.

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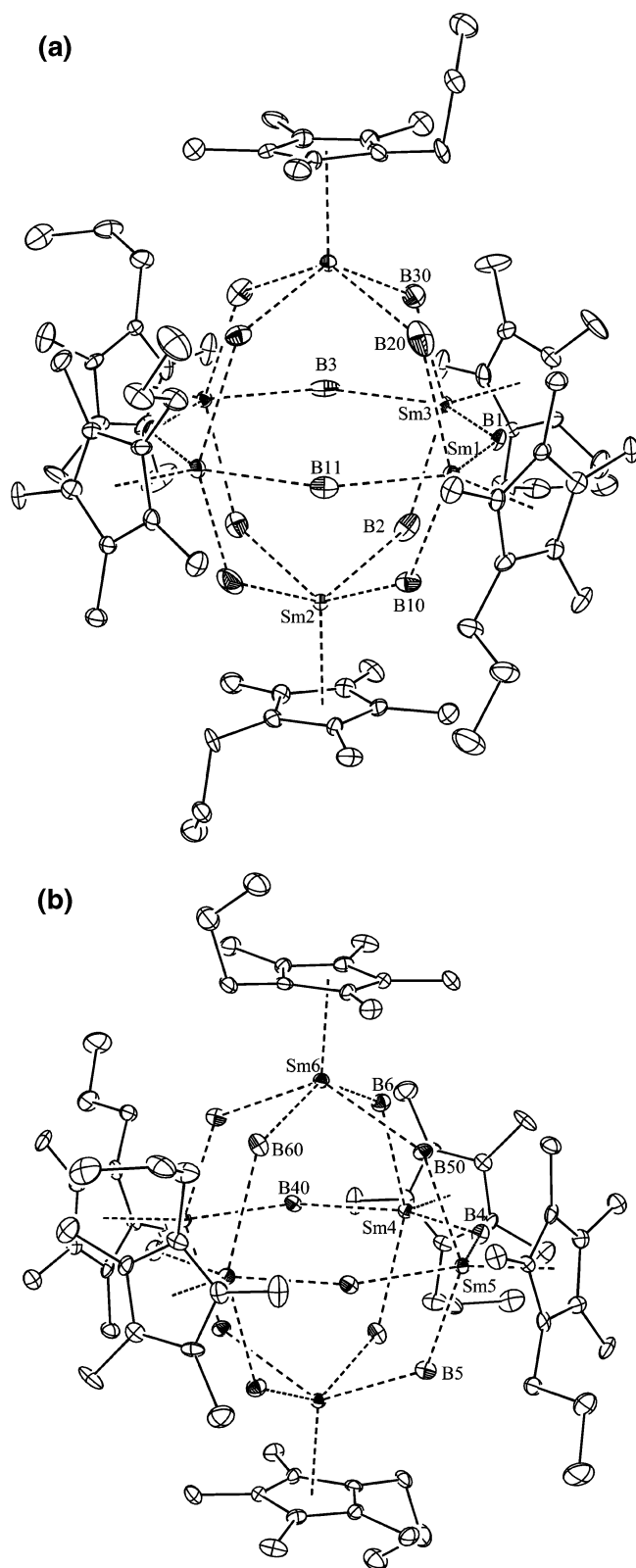


Figure 1. ORTEP drawings (30% probability level) of C_2 -cluster (a) and C_7 -cluster (b) in the structure of samarium complex **2a**. Metric parameters for isostructural neodymium compound are given in square brackets [**2b**]. Selected mean bond lengths (Å) and angles (deg) follow. C_2 -cluster: Ln–Ln = 5.205 [5.239], Ln–CNT = 2.39 [2.41], Ln–B = 2.82 [2.84], Ln–B–Ln 135.4 [135.0]. C_7 -cluster: Ln–Ln = 5.217 [5.255], Ln–CNT = 2.39 [2.42], three short Ln–B = 2.66 [2.69], three long Ln–B = 2.98 [2.99], three small Ln–B–Ln = 132.2 [131.6], three large Ln–B–Ln = 138.8 [138.4].

Complexes **2a'** and **2b'** are built of discrete hexamers $Cp^*{}'_6Ln_6(BH_4)_2Cl_{10}(THF)_2$ (Ln = Sm: **2a'**, Ln = Nd: **2b'**), while **2a''** contains a picturesque association of both the pure (Sm/ BH_4) [$Cp^*{}'_6Sm(BH_4)_2$] C_7 -molecule, already found in **2a**, together with the mixed $Cp^*{}'_6Sm_6(BH_4)_2Cl_{10}(THF)_2$ one observed in the structure of **2a'**. The presence of THF molecule in mixed Cl/ BH_4 hexamers is necessary to ensure the stereoelectronic saturation of the cluster. Such a contribution of solvent molecule in a MCl_n moiety, which is not necessary for the homologous $M(BH_4)_n$ series, is a general feature in the f-metals chemistry.^{18,24}

Both **2a'** and **2b'** compounds crystallize in centrosymmetric triclinic space group $P\bar{1}$ with one $Cp^*{}'_3Ln_3Cl_5(THF)$ formally cationic fragment and one BH_4 anion in the asymmetric unit. However, **2a'** and **2b'** are not isostructural. In fact, they differ as well in relative conformations of THF and the *n*-propyl substituent on the Cp ring bound to the Ln atom bearing the THF ligand as in conformations of THF itself. The torsion angles O(THF)–Ln–CNT (centroid of C_5 atoms of Cp ring)–C(*ipso* carbon atom bearing *n*-propyl) are equal to 2.6° (“*cis*” conformation **2a'** samarium) and 143.6° (pseudo “*trans*” conformation **2b'** neodymium) (Figure 2). A value of 56.1° was calculated for mixed Cl/ BH_4 hexamer in the structure of **2a''** (samarium). All structures reported in this paper are the molecular ones with weak intermolecular van der Waals interactions, which seem, however, to be strong enough for determination of conformations (see, e.g., the values of torsion angles) in the mixed Cl/ BH_4 clusters.

There are two μ_3 and three μ_2 bridging chlorine atoms in each Ln_3Cl_5 unit resulting in a hexagonal bipyramidal polyhedron with $Ln_3(\mu_2-Cl)_3$ base and two μ_3-Cl atoms in apical positions (Figure 2). The metal atoms in hexameric molecules are arranged in a chairlike geometry with $Cp^*{}'_Ln$ –(THF) ends (Figure 3). The borohydride bridges in **2a'** and in **2b'** are essentially symmetrical. The bridging mode of BH_4 ligand in **2a'**, **2b'**, and **2a''** is best described as $\mu_2-\eta^{1:1}$.

Compounds **2a'** and **2b'** afford a $(CpLn)_3Cl_5$ building block which is not common, though already characterized by X-ray diffraction for the late lanthanides, $\{[CpYb(THF)]_3Cl_5\}^+$ and $\{[(Cp^*Yb)_3Cl_5]Cl_3K(DME)_2\}^-$,^{25,26} as well as for the early lanthanides, $[(2,4-C_7H_{11})_6Nd_6Cl_{12}(THF)_2]$.²⁷ The molecular shapes in the latter, bearing the “open” pentadienyl ligands and Nd_6Cl_{12} heavy atom core,²⁷ and the molecular shapes found in **2a'** and **2b'** with the $Cp^*{}'_$ cyclopentadienyl and $Ln_6(BH_4)_2Cl_{10}$ core are similar. All of them consist of two Ln_3Cl_5 fragments symmetrically bridged either with the μ_2 -chloride (former pentadienyl complex) or with the μ_2 -borohydride (latter complexes **2a'** and **2b'** with cyclopentadienyl ligands). One observes that in the structures of **2a'**,

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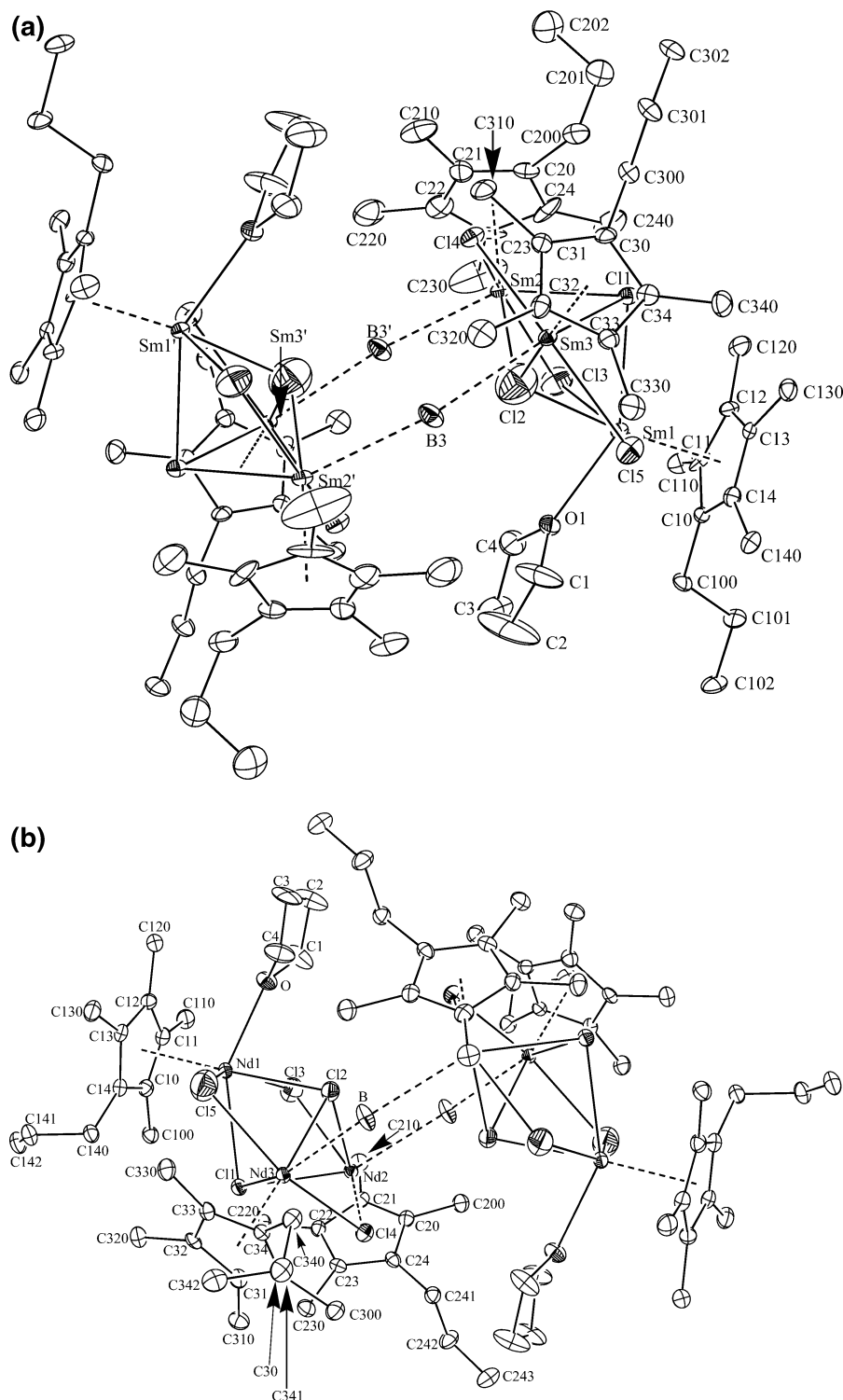


Figure 2. ORTEP drawings (30% probability level) of samarium **2a'** (a) and neodymium **2b'** (b) showing different Cp*/THF and THF conformations. Metric parameters for neodymium complex are given in square brackets [**2b'**]. Selected mean bond lengths (Å) and angles (deg): Ln–CNT = 2.40 [2.43], Ln1–Ln2–Ln3 = 3.876 [4.125], Ln2–Ln3' = 5.585 [5.469], Ln– μ_3 -Cl1 = 2.93 [2.96], Ln– μ_3 -Cl2 = 2.46 [2.88], Ln– μ_2 -Cl = 2.77 [2.81], Ln–B = 2.83 [2.85], Ln2–B–Ln3' = 161.4 [147.2]. Mean equivalent data for mixed Cl/BH₄ molecule in **2a''**: Sm–CNT = 2.40, Sm1–Sm2–Sm3 = 4.102, Sm2–Sm3' = 5.425, Sm– μ_3 -Cl1 = 2.94, Sm– μ_3 -Cl2 = 2.90, Sm– μ_2 -Cl = 2.78, Sm–B = 2.81, Sm2–B–Sm3' = 150.1.

2b', and **2a''** there are two different sets of apical Ln– μ_3 -Cl bonds in the hexagonal bipyramid of the Ln₃Cl₅ moiety. The shorter one concerns the chloride atom located on the side of the THF ligand in a chair conformation of the hexametallc unit (Figure 3), evidence for steric hindrances between the THF and one of the μ_3 -Cl ligands.

3.2. Syntheses and Clustering. Monocyclopentadienyl derivatives of lanthanides have been mostly described as solvated, monomeric, or dimeric species.^{4,5,28} Some of them exist, however, as structurally well-defined clusters.^{25,29} The

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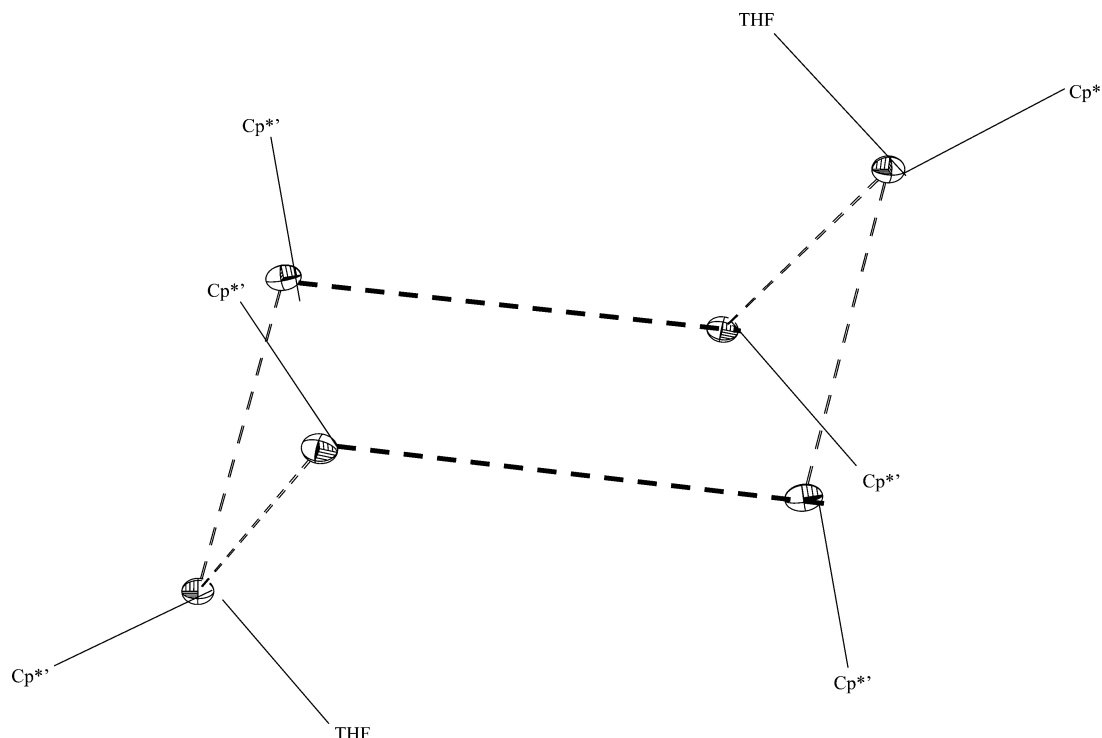
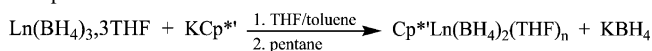


Figure 3. Chairlike structure of metallic atoms in complexes **2a'** and **2b'**.

pseudo-octahedral hexametallic ("Cp"Ln)₆ systems have been also reported for complex Sm/Se(Se₂),³⁰ Yb/I,³¹ and Sm/O(OH)³² clusters. The formation of a hexameric structure generally appears to be the final step of a chemical transformation: desolvation,²⁵ comproportionation,²⁷ oxidation,^{30,33} or hydrolysis.³² Considering merely the larger early lanthanides, the monocyclopentadienylbishalogenide (or pseudohalogenide) complexes affording a monomeric structure are the neutral Cp*CeI₂(THF)₃,³⁴ Cp*NdI₂(py)₃,³⁵ and [(Cp⁴ⁱ)Ln(BH₄)₂(THF)] (Ln = Nd, Sm, Cp⁴ⁱ = C₅Hi-Pr₄)¹² or ionic KtmpSmCl₂ (tmp = C₄Me₄P)³⁶ complexes.

3.2.1. Synthesis of Borohydride Complexes. The procedure was similar to that used to prepare the neutral monomeric Cp⁴ⁱLn(BH₄)₂(THF) (Ln = Sm and Nd)¹² from Ln(BH₄)₃(THF)₃ but with the corresponding potassium salt of the less bulky Cp* ligand. A THF adduct, Cp*Sm(BH₄)₂(THF) (**1a**), was obtained in high yield (89% of red solid). A blue powder was isolated (78% yield) in the same way, from Nd(BH₄)₃(THF)₃ but in THF instead of toluene (Scheme 1, eq 1). ¹H NMR spectrum and elemental analysis both agree with the formula Cp*Nd(BH₄)₂(THF)₂ (**1b**).

Scheme 1. Syntheses of Monocyclopentadienylbisborohydrido Complexes



1a : Sm, n = 1

1b : Nd, n = 2

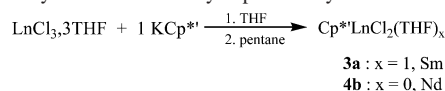
All attempted crystallizations of **1a** or **1b** in the presence of THF to get crystals of Cp*Ln(BH₄)₂(THF)_n adducts were unsuccessful. Their infrared data do not correspond to single trihapto BH₄ group but are in accordance with the presence of both bidentate (bridging) and tridentate (terminal) BH₄ units.^{37,38} Therefore, the complexity of IR spectra argue for the formation of oligomers, likely dimers or trimers considering their solubility in pentane.

3.2.2. Clustering. After several days of storage under an argon atmosphere, the red microcrystalline sample of monocyclopentadienyl samarium derivative **1a** was transformed into an opaque material. Some red crystals of X-ray quality could be obtained after recrystallization of this opaque material in pentane. Crystal structure determination revealed desolvated discrete hexameric molecules [Cp*Sm(BH₄)₂]₆ (**2a**) (see section 3.1.1). In the same manner, storage at room temperature for several days of a solution of crude **1b** in pentane afforded X-ray quality crystals of the cluster [Cp*Nd(BH₄)₂]₆ (**2b**).

In an astonishing way, isolated crystals of **2a** were found unstable: within the time necessary to make the collection of X-ray data on one selected crystal, the other ones, standing in the flask above a small quantity of residual mother liquor, were transformed into a coral powder. The ¹H NMR spectrum of this sample was the same as that of **1a**,

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Scheme 2. Syntheses of Monocyclopentadienylbischloro Complexes

suggesting the trapping of THF vapors present in the flask by the crystals of **2a**. Such instability of the crystals of **2a** in the presence of Lewis base may be correlated to a structural feature: borohydride bridges in the C_i -cluster of **2a** are unsymmetrical ($\mu_2\text{-}\eta^{3:1}$ mode of bonding). An asymmetric Sm($\mu\text{-Cl}$)Sm bridging mode (2.678(1) and 2.891(1) Å) was already found but in a mixed valence [(C₅Me₄-i-Pr)₂-Sm]₂($\mu\text{-Cl}$) complex.³⁹ We have a precursor able to undergo an opening of the bridge in the presence of THF vapors. Easy formation of **2a** is also illustrative of the well-known bridging ability of the BH₄ group, and similar behavior was reported for the monomeric THF adduct (cot)Nd(BH₄)(THF)₂¹⁹ which loses one THF molecule, giving rise to the dibridged dimer [(cot)Nd(BH₄)(THF)]₂.²⁰ Crystals of **2b** were not unstable; this was tentatively attributed to the larger size of the neodymium atom, and the borohydride bridges are less strained, and therefore less reactive than in **2a**.

3.2.3. Chloride and Chloro/Borohydride Complexes.

Because of the lower solubility of chloride derivatives with respect to the borohydride ones, the syntheses of the former were conducted in THF. After a similar workup as for borohydrides, the reactions of SmCl₃(THF)₃ and NdCl₃(THF)₃ with KCp* afforded compounds corresponding to the formula Cp*SmCl₂(THF) (**3a**) and [Cp*NdCl₂]_n (**4b**), according to elemental analyses (Scheme 2). They correspond more exactly to the following molecular formula: Cp*SmCl₂(THF)_{0.8} and Cp*NdCl₂(THF)_{0.1} (calcd C, 41.28; H, 5.79 and C, 38.62; H, 5.18, respectively). The tendency of the larger neodymium atom to form associated species, together with an easier desolvation, is classical behavior in early lanthanides chemistry.³⁴

Despite numerous attempts, we were not able to get the crystals of **3a** and **4b**. Their ¹H NMR spectrum could not be interpreted but was nevertheless informative: a high number of resonances recorded is typical of the presence of nonmonomeric species,⁴⁰ probably similar to the polymeric chains observed in [Cp*CeI₂(THF)]_n.³⁴ The elemental analyses were in quite accordance with the formation of mono-Cp* compounds; the well-known rearrangement into biscyclopentadienyl complexes did not occur. Therefore, we used these chloro complexes as starting materials and succeeded in some clean syntheses; the original heteroleptic {Cp*NdCl[(*p*-tolNCMe)₂CH]}₂ complex was isolated.⁴¹

One can ask for the reason for failure of formation of the pure crystallized chloro complexes whereas the borohydrides were easily isolated. It must be remembered that the latter ones are desolvated hexamers. The substitution of a borohydride for a chloride goes together with the formation of

THF adducts, and for steric reasons the presence of too many coordinated THF molecules may not favor the formation of hexamers. The clustering of chloro compounds with complete loss of ancillary molecules has been previously observed but for complexes bearing unsubstituted Cp, e.g. CpLnCl₂(THF)_x (Ln = Yb, Sm), and it required high temperatures.²⁵ It is not the case for our Cp* complexes.

Hexameric clusters with high chlorine atoms content could be otherwise obtained: mixed Cl/BH₄ **2a'**, **2b'**, and **2a''**. They had been isolated in an attempted synthesis of borohydrides (see Experimental Section). It was found subsequently that the starting material Ln(BH₄)₃(THF)₃ could contain residual NaCl (lanthanides trisborohydrides are often contaminated by chloride residues using Mirsaidov's procedure¹⁴). Chlorolanthanide complexes exhibit, however, a poor solubility and always precipitate/crystallize more easily than the analogous borohydrides. It is postulated that, in solution, in the easy formed clusters **2a** and **2b**, the external BH₄ groups can be substituted by chlorines, leading to less soluble chloro-clusters which consequently crystallized.

Finally, it appears that the trinuclear [Cp*₃Ln₃Cl₅(THF)] unit found in the structures of **2a'**, **2b'**, and **2a''** is a basic building block for extended molecular structures for "Cp"/Ln/Cl systems. From our observations, the mixed chloro/borohydrido complexes **2a'** and **2b'** could be considered as the most chloride-containing crystallizable compounds in this mono-Cp* series.

Conclusion

Several monocyclopentadienyl complexes of samarium and neodymium with bulky tetramethylpropylcyclopentadienyl (Cp*) ligand have been synthesized. X-ray structure analyses carried out on pure monocyclopentadienyl borohydrides **2a** and **2b** revealed the hexametallic clusters containing the discrete molecules with symmetric ($\mu_2\text{-}\eta^{1:1}$) and unsymmetrical ($\mu_2\text{-}\eta^{3:1}$) BH₄ bridges. Molecules of **2a** with unsymmetrical bridges may undergo an easy opening of the bridge upon the action of Lewis bases. Clustering of solvated **1a** and **1b** may result from the concomitant presence, in the coordination sphere of the Ln metal, of borohydride groups offering a good bridging ability, together with severely reduced amount of THF.

We opted for presentation in this paper of some unpredictably obtained mixed chloro/borohydrido compounds (**2a'**, **2b'**, and **2a''**) for two reasons: (i) their crystallizations and the nature of the products depend on subtle modifications of crystallization medium (competition Cl/BH₄), and (ii) they exhibit the hexametallic molecules such as in the pure **2a** and **2b**. X-ray studies carried out on these mixed compounds revealed the trinuclear [Cp*₃Ln₃Cl₅(THF)] fragment, which may be considered as a main building block in "Cp"/Ln/Cl chemistry.

The monocyclopentadienyl derivatives **1a** and **1b** are the convenient precursors for synthesis of heteroleptic early lanthanide compounds. The presence of borohydrides renders the syntheses softer than with the chlorides, leading to the soluble compounds containing the NMR BH₄ probe. The

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chloro complexes **3a** and **4b** are not structurally characterized, but as they stand, they were found to be useful precursors for further syntheses.

All these compounds are potential precursors for polymerization catalysis. Generation of active species is generally achieved by alkylation, and the displacement of a halogeno

ligand may occur more readily than that of a pseudohalogenide BH_4 group. Therefore, chloride complexes remain also versatile precursors, as long as strong internal chloro-bridges are not formed.

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