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Crystal and molecular structures of bis(1,3-di-tert-butylcyclopentadienyl)cerium chloride and borohydride. First example of the bridging tetradentate BH_4-group with two μ_3-hydrogens: $\mu:\eta^4$-[$(\mu_3\text{-H})_2B(\mu_2\text{-H})_2$]

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Abstract

Interaction between $CeCl_3$ and two equivalents of $(C_5H_3Bu^t_2)Na$ leads to the complex $[(\eta^5\text{-}C_5H_3Bu^t_2)_2Ce(\mu_2\text{-Cl})]_2$ (I). Crystals of I are rhombic, $a = 13.032(3)$, $b = 24.629(5)$, $c = 17.044(3)$ Å, space group *Pbnb*, $Z = 4$, $d = 1.630$ g cm^{-3}. Complex I reacts with one equivalent of $LiBH_4$ to afford $\{(\eta^5\text{-}C_5H_3Bu^t_2)_2Ce[\mu:\eta^4\text{-}(\eta_3\text{-H})_2B(\mu_2\text{-H})_2]\}_2$ (II) which is isostructural to I. Two BH_4 groups in complex II are tetradentate and contain two μ_3- and two μ_2-bridging hydrogens. Cerium has a 20e environment.

Introduction

The rapid development that has been seen in recent years of the chemistry of biscyclopentadienyl complexes of lanthanides of the cerium subgroup and of actinides began with the introduction into synthetic practice of bulky cyclopentadienyl ligands, such as C_5Me_5, $C_5H_3(SiMe_3)_2$, and $C_5H_3Bu^t_2$, which effectively shield large metal atoms. However, structural data on these complexes are still scarce in particular, for cerium, which possesses one of the largest radii, only three biscyclopentadienyl structures relating to binary salts with alkali metal chlorides have been reported [1–3]. In this paper we report an X-ray structural study of two

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dimeric neutral complexes of cerium, i.e. $[(\eta^5\text{-}C_5H_3Bu^t_2)_2Ce(\mu_2\text{-}Cl)]_2$ (I) and $[(\eta^5\text{-}C_5H_3Bu^t_2)_2Ce\{\mu:\eta^4\text{-}(\mu_3\text{-}H)_2B(\mu_2\text{-}H)_2\}]_2$ (II).

Experimental

All operations associated with the synthesis and the physicochemical study were carried out either *in vacuo* or under inert atmosphere using the standard Schlenk technique. Solvents were dried by refluxing and distillation over $LiAlH_4$. IR spectra (in Nujol) were recorded on a Specord-75 spectrophotometer. Anhydrous cerium chloride was obtained by heating the hydrated salt with NH_4Cl [4]. Di-tert-butylcyclopentadiene [5] was metalated with sodium amide in liquid ammonia.

Synthesis of $[(C_5H_3Bu^t_2)_2CeCl]_2$ *(I).* To anhydrous $CeCl_3$ (2.5 g, 10 mmol) in 100 ml THF a solution of $C_5H_3Bu^t_2Na$ (4 g, 20 mmol) in 70 ml THF was added dropwise, with stirring at 0 °C. After 1 h the mixture was heated and kept at room temperature for 24 h. The solvent was then evaporated, the residue worked up with 150 ml pentane, the precipitate filtered, and one third of the solvent was removed. The cubic crystals that formed after 10 h were separated, washed with cold pentane, and dried *in vacuo*. Yield of monocrystals ca. 60%. Found: Ce, 26.1; Cl, 6.6. $C_{26}H_{41}CeCl$ calcd.: Ce, 26.44; Cl, 6.70%.

Synthesis of $[(C_5H_3Bu^t_2)_2CeBH_4]_2$ *(II).* To a solution of $[(C_5H_3Bu^t_2)_2CeCl]_2$ (0.85 g, 1.6 mmol) in 80 ml of dry ether $LiBH_4$ (0.04 g, 1.6 mmol) in 35 ml ether was added dropwise, with stirring at room temperature. The solution changed in color from bright yellow to yellow-green. The suspension was then mixed at this temperature for 3 h, precipitated LiCl removed, the solvent evaporated, and the residue treated with 100 ml pentane. The undissolved precipitate, of a pale-yellow colour, was filtered off, and the bright-orange filtrate concentrated threefold, producing yellow-orange cubic crystals in two hours. The crystals were separated, washed with cold pentane and air dried. Yield ca. 40% Found: C, 61.18; H, 9.15; Ce, 27.3. $C_{26}H_{45}CeB$ calcd.: C 61.30; H 9.03; Ce 27.51%.

Crystal structure determination. An X-ray structural analysis of monocrystals I and II was carried in glass capillaries on automatic diffractometers Nicolet *P*3 (complex I) and Hilger–Watts (complex II). The corresponding data are summarized in Table 1.

The structure of I was solve by the heavy atom method. Cerium coordinates were determined from the Patterson synthesis. Other atoms were localized by consecutive approximations. Borohydride hydrogens and some of the hydrogens of organic ligands were localized objectively by Fourier synthesis. Coordinates of the remaining hydrogens were calculated geometrically. It should be pointed out that maxima of electron density corresponding to hydridic hydrogens are noticably higher, one-and-a-half to two times those of the other hydrogen atoms. The structure was refined by the full matrix least squares routine in anisotropic (isotropic for H atoms) approximation up to $R = 0.041$. All calculations were made on a Eklips 5/200 computer with INEXTL.

During the solution of structure II, we obtained first a dimeric model with two bridging BH_4 ligands and two orthogonal bent sandwiches $Cp_2Ce(1)$ and $Cp_2Ce(2)$. It is evident that such geometry, should lead to very short contacts between bridging and cyclopentadienyl ligands, but this contradicts the known structural data on composition of similar compounds and the theoretical view on the orientation of

Table 1

Crystal data of complexes I and II

	I	II
formula	$[(C_5H_3Bu^t{}_2)_2CeCl]_2$	$[(C_5H_3Bu^t{}_2)_2CeBH_4]_2$
crystal system	rhombic	rhombic
space group	*Pbnb*	*Pccn*
Z	4	4
a, Å	13.032(3)	13.072(1)
b, Å	24.629(5)	17.189(1)
c, Å	17.044(3)	24.610(2)
V, Å^3	5470(1)	5529.6(3)
(Mo-K_α), cm^{-1}	17.2	16.8
$d_{calcd.}$, g cm^{-3}	1.63	1.226
radiation	Mo-K_α, Nb-filter	Mo-K_α
scan type	$\theta/2\theta$	$\theta/2\theta$
$2\theta_{max}$, deg	50	60
no. of unique intensities	3323	2560
no. of reflections $F>4\sigma(F)$	1416	1926
weighting scheme	$1/\sigma^2(F)+0.00035F^2$	$1/\omega=(F^2)+0.005F^2$
$R(F)$	0.046	0.041
$R_w(F)$	0.043	0.047

Table 2

Atomic coordinates ($\times 10^4$) and temperature factors (Å$^2\times 10^3$) for $[(\eta^5\text{-}C_5H_3Bu^t{}_2)_2Ce(\mu\text{-}Cl)]_2$ (I)

Atom	x	y	z	U
Ce(1)	2500	2966(1)	2500	40(1)
Ce(2)	2500	1110(1)	2500	41(1)
Cl	1510(3)	2038(2)	1822(2)	50(1)
C(1)	1492(15)	3233(7)	3894(10)	48(7)
C(2)	678(12)	3078(5)	3408(9)	40(6)
C(3)	579(11)	3461(6)	2801(8)	39(6)
C(4)	1366(13)	3864(6)	2911(9)	39(6)
C(5)	1906(11)	3714(7)	3598(8)	44(6)
C(6)	1674(13)	3011(8)	4729(11)	59(8)
C(7)	1167(20)	3367(10)	5341(12)	128(13)
C(8)	2831(12)	2971(10)	4901(10)	71(8)
C(9)	1300(16)	2417(8)	4791(11)	88(9)
C(10)	−275(12)	3501(7)	2205(10)	55(7)
C(11)	−989(15)	3983(9)	2449(18)	130(11)
C(12)	107(15)	3615(11)	1400(12)	115(12)
C(13)	−916(14)	3002(9)	2179(11)	100(9)
C(14)	2848(11)	633(6)	1019(10)	41(6)
C(15)	2976(11)	235(6)	1589(9)	49(6)
C(16)	3894(12)	345(5)	2010(10)	51(6)
C(17)	4302(14)	813(6)	1715(11)	46(7)
C(18)	3654(13)	992(6)	1085(10)	49(6)
C(19)	5414(13)	993(7)	1843(10)	56(7)
C(20)	5720(13)	915(9)	2696(11)	96(10)
C(21)	6116(16)	684(9)	1332(14)	108(11)
C(22)	5514(14)	1603(8)	1683(13)	87(9)
C(23)	2030(15)	618(8)	374(10)	74(8)
C(24)	1923(19)	1170(11)	−45(14)	108(13)
C(25)	2305(22)	196(10)	−242(12)	132(13)
C(26)	988(17)	481(11)	666(14)	119(12)

Table 3

Main interatomic distances (Å) and bond angles (deg.) in complex I

Ce1–CpI [a]	2.52	CpICe1CpI′ [a]	115.3
Ce2–CpII [a]	2.52	CpIICe2CpII′ [a]	114.0
Ce1–Cl	2.868(4)	ClCe1Cl′	74.3(2)
Ce2–Cl	2.868(4)	ClCe2Cl′	74.3(2)
Ce1–C1	2.79(2)	Ce1ClCe2	105.7(1)
Ce1–C2	2.85(2)	Cp1Ce1Cp1′/Ce2Cl2 [b]	98.4
Ce1–C3	2.83(2)	Cp2Ce2Cp2′/Ce2Cl2 [b]	86.0
Ce1–C4	2.75(1)	CpI/C1–C6 [a]	14.6
Ce1–C5	2.79(1)	CpI/C3–C10 [a]	8.1
Ce1–C_{mean}	2.79(5)	CpII/C14–C23 [a]	7.3
Ce2–C14	2.82(2)	CpII/C17–C19 [a]	15.6
Ce2–C15	2.73(1)		
Ce2–C16	2.75(1)		
Ce2–C17	2.80(2)		
Ce2–C18	2.86(2)		
Ce2–C_{mean}	2.79(5)		
$(C–C)^{ring}_{mean}$	1.41(2)		
$(C–C)^{Bu^t}_{mean}$	1.52(3)		
Ce1 ··· Ce2	4.573		
Cl ··· Cl′	3.464		

[a] CpI and CpII are the ring planes. [b] Cp1 and Cp2 are the geometrical centers of the ring planes.

MO in the Cp_2M fragment. Interestingly, such an absurd model could be easily refined with the least squares routine by decreasing the R-factor up to 10%.

Repeated study of the Fourier synthesis formulated on the basis of two cerium atoms provided another structure model in which the centres of all four Cp″ groups are in one plane. Such an orientation of the fragments $Cp_2''M$, which provides easy location of ligands in the common bisector plane of both bent sandwiches is usual for dimers of the type $(Cp_2MX)_2$.

The problems associated with choosing a structure model were met in the case of complex I. This structure was solved by the Patterson method. Hydrogens were calculated geometrically and were included in the refinement in anisotropic (isotropic for H atoms) approximation. The final value of the R-factor was 0.046. The calculations were made on a Nova-3 computer by SHELXTL. Atomic coordinates of I and II are given in Tables 2 and 4, representative bond distances and bond angles in Tables 3 and 5.

Results and discussion

The immediate environment of the metal in I (two η^5-Cp″ rings and two chlorides) and the general composition of the molecule (a chloride bridging dimer) are typical features of biscyclopentadienyl chlorides of rare earth metals (Fig. 1), but some details differ considerably. In particular, all models of $[Cp''_2M(\mu_2\text{-}Cl)]_2$ (M = rare earth metal) known from the literature have a center of symmetry. In contrast, I has only the C_2 axis passing through two cerium atoms. This arises from the different conformation of cyclopentadienyl rings and the orientation of the attached substituents. Complexes already described, such as $[Cp''_2M(\mu_2\text{-}Cl)]_2$ with disubstituted cyclopentadienyl ligands Cp″ = $C_5H_3(SiMe_3)_2$, M = Sc, Yb, Pr [6], U

Table 4

Atomic coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for $\{(\eta^5\text{-}C_5H_3Bu^t_2)_2Ce[\mu:\eta^4\text{-}(\mu_3\text{-}H)_2B(\mu_2\text{-}H)_2]\}_2$ (II)

Atom	x	y	z	U
Ce(1)	2500	2500	2990(4)	29(2)
Ce(2)	2500	2500	1140(3)	30(2)
B	1457(11)	1776(8)	2066(6)	32(4)
C(1)	1926(10)	3595(7)	3757(5)	35(4)
C(2)	1387(9)	2895(8)	3898(5)	37(4)
C(3)	591(9)	2773(7)	3500(5)	33(4)
C(4)	654(9)	3403(7)	3114(5)	30(4)
C(5)	1469(10)	3900(8)	3275(5)	34(4)
C(6)	3895(9)	2062(7)	345(5)	35(4)
C(7)	2981(10)	1627(8)	246(5)	39(4)
C(8)	2868(9)	1035(8)	660(5)	40(4)
C(9)	3694(10)	1115(8)	1021(5)	34(4)
C(10)	4330(10)	1732(8)	829(5)	35(4)
C(11)	−297(10)	2175(8)	3570(6)	45(4)
C(12)	−968(10)	2455(16)	4038(5)	64(5)
C(13)	−991(11)	2157(9)	3040(7)	65(6)
C(14)	155(12)	1365(8)	3678(8)	62(6)
C(15)	1625(10)	4721(7)	3043(6)	41(4)
C(16)	1111(14)	5315(9)	3426(6)	65(6)
C(17)	1156(14)	4805(9)	2460(7)	63(6)
C(18)	2794(9)	4922(7)	3009(7)	53(5)
C(19)	2082(11)	343(8)	641(6)	53(5)
C(20)	2488(22)	−224(8)	214(6)	77(5)
C(21)	1015(11)	662(9)	458(7)	57(5)
C(22)	2002(12)	−98(9)	1203(7)	60(5)
C(23)	5454(10)	1883(8)	1031(6)	42(4)
C(24)	5578(11)	1696(10)	1640(6)	53(5)
C(25)	6137(11)	1300(9)	693(7)	58(5)
C(26)	5772(10)	2724(7)	906(7)	51(5)
H(1)	123	175	243	40
H(2)	125	150	162	40
H(3)	132	247	209	40
H(4)	250	162	212	40

[7]; $Cp'' = C_5H_3Bu^t_2$, M = Lu [8], possess the antiperiplanar ring conformation which accounts for the maximal distances between corresponding substituents of different bent sandwiches Cp''_2M (Fig. 2, type **A**), while complex I also with antiperiplanar conformation gives an example of an alternative orientation of substituents (type **B**). Such conformation has been reported for $[(C_5H_3Bu^t_2)_2U(\mu_2\text{-}Cl)]_2$ (III) [9] where uranium has the same ionic radius as cerium (1.11 Å [10]), and for the dimetallic complexes $\alpha\text{-}[(C_5H_3Bu^t_2)_2Ce(\mu_2\text{-}Cl)_2 \cdot Li \cdot Me_2NC_2H_4NMe_2]$ (IV) [2] and $\{[C_5H_3(SiMe_3)_2]_2Nd(\mu_2\text{-}Cl)_2 \cdot Li \cdot (THF)_2\}$ [11]. In conformation **B**, compared with the other, one pair of substituents of the fragment Cp''_2M is much closer to the bridging chlorides. In structure I this is manifested in the considerable variation (6–7°) in the angles between the cyclopentadienyl plane and the ring-quaternary carbon bond (Table 3). The lower values are comparable with the analogous parameter of complex IV (5.6–8.9°) [2], while the highest is close to that

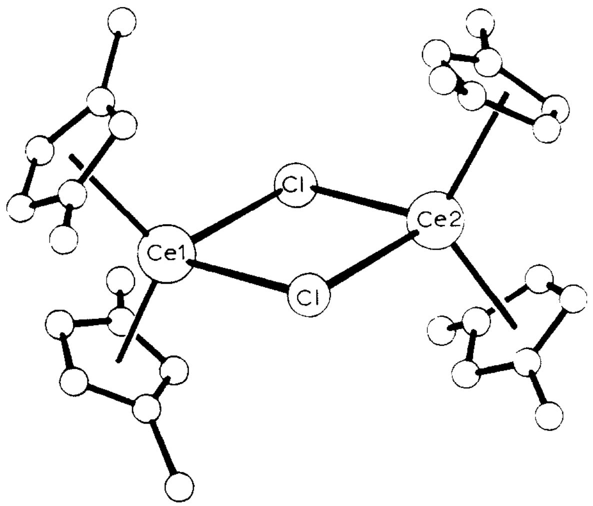

Fig. 1. The molecular structure of $[(\eta^5\text{-}C_5H_3Bu^t_2)_2Ce(\mu_2\text{-}Cl)]_2$ (I).

in the sterically constrained complex II: $[(C_5H_3Bu^t_2)_2Lu(\mu_2\text{-}Cl)]_2$ (15.2°) [8]. This mutual repulsion of the ring substituents and the bridging ligands may account for the observed departure of the chloro ligands from the bisector planes of the bent sandwiches Cp''_2Ce (Table 3).

The Ce–C distance in I varies within the range 2.75–2.86 Å, but the cyclopentadienyl rings are planar, within 0.01 Å. The mean distance Ce–C in I (2.79 Å) is comparable with that in complexes α-IV (2.80 Å) [2], β-IV (2.81 Å) [3] and the uranium complex III (2.79 Å) [9]. Interatomic distances M–Cl are also practically the same in I, III (2.86 Å) [9] and $\{[C_5H_3(SiMe_3)_2]_2U(\mu_2\text{-}Cl)\}_2$ (2.82 Å) [7]. This is indicative of the similar nature of bonding in the uranium and cerium cyclopentadienyl complexes.

The large size of cerium results in anomalously small angles Cp″MCp″ in I (Table 3). These angles are usually in the range 127–131° for $[Cp''M(\mu_2\text{-}Cl)_2]_2$, and only more found in III (120.5°) [9] and β-IV (117.4°) [3] are close to the values realized in I.

The borohydride complex II is isostructural to chloro complex I (Table 1). This is not surprising considering the similarity of the close Van der Waals radii of the

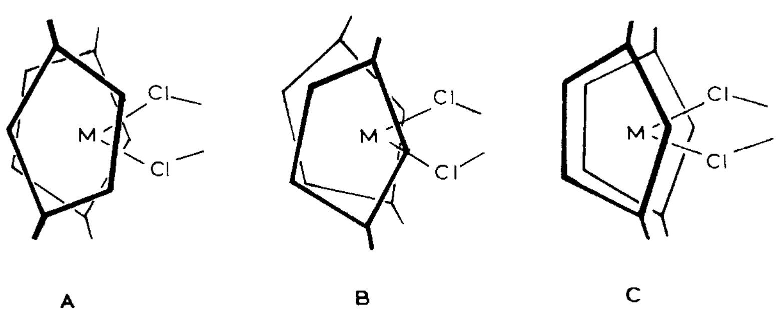

Fig. 2. The conformational types of the cyclopentadienyl rings in complexes $[Cp''_2M(\mu_2\text{-}Cl)]_2$.

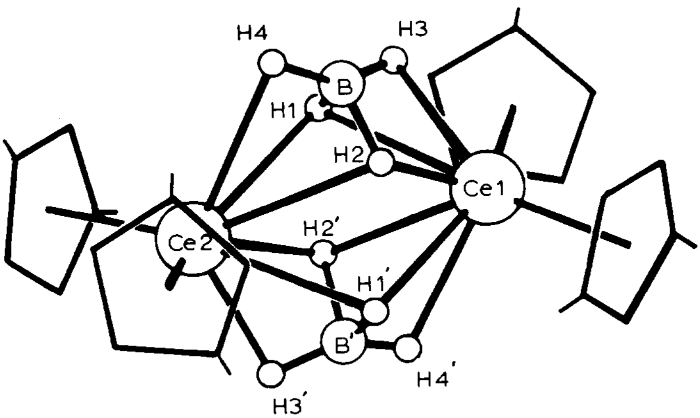

Fig. 3. The molecular structure of $\{(\eta^5\text{-}C_5H_3Bu^t{}_2)_2Ce[\mu:\eta^4\text{-}(\mu_3\text{-}H)_2B(\mu_2\text{-}H)_2]\}_2$ (II).

borohydride group and of the chlorine atom as well as the structural similarity of many borohydride and chloro transition metal complexes [12].

Like molecule I, complex II has crystallographic symmetry 2 and Ce atoms are located on the second order axis (Fig. 3). The geometry of the $(C_5H_3Bu^t{}_2)_2Ce$ groups in complexes I and II is the same within the limits of experimental error (Tables 3 and 5), although one can note longer bonds in II. Two groups Cp''_2Ce are linked by bridging borohydride groups.

The most remarkable result of the present work is the evaluation of the novel structural mode of the binding of the borohydride moiety with transition metals. Up to now, three structural modes of locating the borohydride group between two metal centres have been reported (Fig. 4): the bidentate monobridged $(\mu_2\text{-}H)_2BH_2$ (**D**) bonding in complexes $[(C_5Me_5)IrH]_2(\mu_2\text{-}H)(\mu\text{-}BH_4)$ [13], $Mn_2(\mu_2\text{-}H)(\mu\text{-}BH_4)(CO)_6$ dppm [14], tridentate $(\mu_3\text{-}H)(\mu_2\text{-}H)_2BH$ (**E**) in complexes $Co_2(\mu\text{-}BH_4)_2Ph_2PC_5H_{10}$-

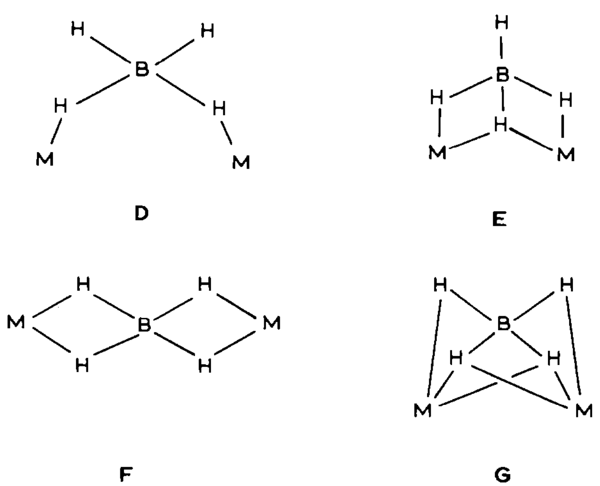

Fig. 4. The various types of bridging in the borohydride groups.

$PPh_2 \cdot 0.5C_6H_6$ [15], $[Th(\mu\text{-}BH_3CH_3)(BH_3CH_3)_3]_2 \cdot OR_2$ (V) [16], and tetradentate bonding $(\mu_2\text{-}H)_2B(\mu_2\text{-}H)_2$ (**F**) in complexes $[\{(PPh_3)_2Cu\}_2(\mu\text{-}BH_4)][ClO_4]$ [17], $[CH_3C(CH_2PPh_2)_3Ru]_2(\mu\text{-}BH_4)$ [18].

The borohydride group in II is also tetradentate, but, in contrast to type **F**, cerium is bonded to boron through triple hydrogen bridges as depicted in Fig. 4 (**G**). Such an alteration of the coordination mode allows the borohydride complex to have two bridging BH_4 ligands. Since every group contains only bridging hydrogens (two atoms with μ_3 and two atoms with μ_2 coordination), the IR spectrum of II has only one group of bands at 2100, 2180 and 2290 cm^{-1} which should be ascribed [19] to the stretching frequencies of the B–H bonds. These values are close to those of $\nu(B\text{-}H^b)$ of complex V (2100, 2200 cm^{-1}) [16] with the borohydride group of type **E**.

There is no significant difference in the bond distances $B\text{-}\mu_2\text{-}H$ and $B\text{-}\mu_3\text{-}H$, while the mean value of the bond distance B–H (1.19 Å) is the same as that in the complex $[C_5H_3(SiMe_3)_2]_2Sc(\mu_2\text{-}H)_2BH_2$ (VI) with a terminal bidentate borohydride function [20].

The tetrahedron BH_4 in II is strongly distorted. It is manifested in a large value of the bond angle $(\mu_2\text{-}H)B(\mu_2\text{-}H)$, 139.4°, compared with 128° for the angle H^tBH^t in complex VI [20]. The distance Ce $\cdots$ B in II is considerably larger than the distances U $\cdots$ B in complexes with the tridentate terminal borohydride ligand (2.46–2.64 Å [21]), and is also larger than those in complexes with the bidentate bridging borohydride ligand (2.83–2.85 Å [22]). At the same time the bond distance Th $\cdots$ B in complex V (2.91–2.97 Å) [16], in which the most structurally similar bonding of the BH_4 group is realized (type **B**), is comparable with that in complex II (Table 5). The distances $M\text{-}\mu_3\text{-}H$ in complexes II and V (2.73 Å [16]) are practically the same, while the distances $M\text{-}\mu_2\text{-}H$ are approximately 0.3 Å longer than in V. This is also manifested in the decrease of the bond angles $Ce(\mu_2\text{-}H)B$ in II as compared with V (Table 5).

The slight distortion of the tetrahedral BH_4 group, the orientation of hydridic hydrogens with respect to both metal atoms, the IR data as well as the structural data for complex V [16], all suggest that complex II should be a covalent compound. The very large distance Ce $\cdots$ B points to the fact that a contribution of an ionic nature to the Ce–H–B bond is considerable.

The immediate environment of every cerium in II contains six hydridic hydrogens which are usually considered as two electron ligands. However, such an approach to calculation of the total number of electrons of a complex in some cases may provide absurd results, for example, when a complex possesses μ_3-hydrogens. Thus complex II would then have a 24e configuration, while the borohydride group should be regarded a 12e ligand. Since neither BH_4, nor AlH_4 groups can donate more than 8 electrons, we believe that the total number of electrons must be calculated taking into account this consideration, i.e. one must consider a whole group as a complex ligand rather than as separate hydrogen atoms. In this case, the alumohydride group in the complex $[(C_5H_4Bu^t)_2Sm(\mu_3\text{-}H)(\mu_2\text{-}H)_2AlH \cdot C_4H_8O]_2$ [23] will be a 6e donor and samarium (since the molecule is a dimer) will not have a 20e ligand environment, but a common 18e configuration. The borohydride group in complex II is a 8e donor and samarium atoms (since the molecule is dimeric) have a formal 20e configuration. The latter is very rare among lanthanides and is observed, for example, in triscyclopentadienyl complexes. Of the bridging hydrogens

Table 5

Main interatomic distances (Å) and bond angles (deg.) in complex II

Ce1–CpI	2.53	CpICe1CpI′	119.6
Ce1–CpI	2.54	Cp2Ce2Cp2′	119.2
Ce2–CpII	2.53	BCe1B′	78.1(4)
Ce2–CpI	2.53	BCe2B′	78.0(4)
Ce···B	2.93(2)	CpICe1CpI′/Ce2B2	89.6
Ce1–H1	2.52	Cp2Ce2Cp2′/Ce2B2	93.3
Ce1–H3	2.70	CpI/C3–C11	11.7
Ce1–H4	2.61	CpI/C5–C15	12.8
Ce2–H2	2.65	CpII/C8–C19	10.8
Ce2–H3	2.80	CpII/C10–C23	13.4
Ce2–H4	2.85	Ce1BCe2	101.9(5)
Ce1–C_{mean}	2.81(5)	Ce1H1B	106.7
Ce2–C_{mean}	2.81(5)	Ce1H3B	88.5
B–H1	0.94	Ce1H4B	88.1
B–H2	1.22	Ce2H2B	90.7
B–H3	1.21	Ce2H3B	84.0
B–H4	1.40	Ce2H4B	79.5
Ce1···Ce2	4.553	$H1BH_2$	139.4(1.5)
B···B′	3.69	$H1BH_3$	87.7(1.1)
H3···H4	2.20	H1BH4	101.4(1.2)
$(C{-}C)^{ring}_{mean}$	1.43(1)	H2BH3	113.1(1.2)
$(C{-}C)^{Bu^t}_{mean}$	1.55(2)	$H2BH_4$	103.8(1.1)
$(C_{ring}{-}C_{Bu^t})_{mean}$	1.56(1)	H3BH4	108.8(1.1)

of II, μ_2-atoms are only slightly removed from the bisector plane (by 0.16 Å), while this effect is much more pronounced for the μ_3-atoms. Interestingly, a similar arrangement of the frontal ligands is realized in the 20e complex $\{[C_5H_3(SiMe_3)_2]_2$-$U(\mu$-$F)\mu$-$[(\mu_2$-$F)_2BF_2]\}_2$ [24] in which two of the four fluoro ligands lie in the bisector plane of the bent sandwich, but the remaining two are located in the orthogonal plane Cp″UCp″. Therefore, the MO model of the fragment Cp_2M that has been proposed [25] is not the only model possible and needs further investigation when *f*-elements are considered. It is possible that the coordination of larger number of ligands than that predicted by the model can be explained by the metal AO having a diffusive nature or even by involvement of inner *f*-orbitals in metal–ligand bonding.

In conclusion, it should be emphasized that solving structures I and II involved dealing with a rather unexpected fact: two basically different structural models of these compounds each provided satisfactory agreement between the experimental and calculated amplitudes. The same was probably observed on solving the structure $[(C_5Me_5)_2Sm(\mu_2$-$H)]_2$ [26]. As in I and II, the metal atoms lie on the second order axis and two fragments $Cp^{\star}{}_2Sm$ are twisted with respect to each other by 87%. To account for this effect, it was suggested [26] that the fragments are mono-bridged through hydrogen atom through in this study hydridic atoms were not objectively located. However, such an interpretation is probably erroneous and, in the light of the present work, the X-ray data published in ref. 26 should be revised. One might assume that ambiguities in the treatment of X-ray structural data may arise as a consequence of the presence in the molecule of a small number of heavy atoms in particular positions and a large number of light atoms in a unit cell of large radius.

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