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Unsolvated lanthanidocene hydrides and borohydrides. X-Ray crystal structure of $[(\eta^5\text{-}C_5H_3{}^tBu_2)_2Ln(\mu\text{-}H)]_2$ (Ln = Ce, Sm) and $[(\eta^5\text{-}C_5H_3{}^tBu_2)_2Sm(\mu\text{-}BH_4)]_2$

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Abstract

The treatment of lanthanidocene alumohydrides $(Cp''_2LnAlH_4 \cdot L)_2$ having bulky cyclopentadienyl ligands $C_5H_3{}^tBu_2$ with an excess of triethylaminalane yields related unsolvated hydrides $[(C_5H_3{}^tBu_2)_2Ln(\mu\text{-}H)]_2$ (Ln = Ce (I), Sm (II)). Complex II was also obtained by the redox reaction of $Cp''_2Sm \cdot THF$ with $AlH_3 \cdot NEt_3$. Crystals of I are triclinic, $P\bar{1}$, $a = 10.741(2)$ Å, $b = 11.302(2)$ Å, $c = 12.425(2)$ Å, $\alpha = 65.20(1)°$, $\beta = 73.93(1)°$, $\gamma = 89.69(1)°$, $Z = 2$, $R = 0.031$, $R_w = 0.034$. Crystals of II are triclinic, $P\bar{1}$, $a = 10.723(2)$ Å, $b = 11.305(3)$ Å, $c = 12.289(3)$ Å, $\alpha = 115.73(2)°$, $\beta = 105.15(2)°$, $\gamma = 90.43(2)°$, $Z = 2$, $R = 0.054$, $R_w = 0.057$. Unlike the lanthanidocene alumohydrides the related borohydrides are resistant to Lewis bases and crystallize from donor solvents as unsolvated dimers $(Cp^*_2LnBH_4)_2$. For complex $[(C_5H_3{}^tBu_2)_2Sm(\mu\text{-}BH_4)]_2$ (VI) X-ray structural information is convenient with the presence of bridge $[(\mu_3\text{-}H)_2B(\mu_2\text{-}H)_2]$ groups. Crystals of VI are rhombic, *Pnaa*, $a = 24.448(4)$ Å, $b = 13.023(2)$ Å, $c = 17.218(3)$ Å, $Z = 8$, $R = 0.088$, $R_w = 0.084$.

Introduction

Unsolvated hydrides of lanthanidocenes attract the attention of researchers owing to their intriguing catalytic properties in some processes, e.g. C–H bond activation in alkanes [1,2] and hydrogenation of alkynes [3]. The structure and degree of association of these compounds depend very much on the nature of the ligand and on metal atom size and may vary from polymers of compounds with an ordinary C_5H_5 ligand [4] to trimers of $[(\eta^5\text{-}C_5H_3Me_2)_2Y(\mu\text{-}H)]_3$ [5] and dimers of $[(\eta^5\text{-}C_5Me_5)_2Lu(\mu\text{-}H)]_2$ [1] and $[(\eta^5\text{-}C_5H_3{}^tBu_2)_2Lu(\mu\text{-}H)]_2$ [6]. Methods of preparation of homonuclear metallocene hydrides are based on hydrogenolysis [2–4] and pyrolysis [7] of related alkyl metallocene derivatives, or on desolvation of Cp_2LnH L complexes [5]. Recently we have found that the reaction of $[(\eta^5\text{-}C_5H_3{}^tBu_2)_2Lu(\mu\text{-}Cl)]_2$ with lithium aluminium hydride in diethyl ether yields directly to the unsolvated hydride $[(\eta^5\text{-}C_5H_3{}^tBu_2)_2Lu(\mu\text{-}H)]_2$ [6]. In this paper the advantages of synthesis of lanthanidocene hydrides by the reaction of related chlorides with alumino- and borohydrides of alkali metals are evaluated and the X-ray crystal structures of the unsolvated hydrides, $[(\eta^5\text{-}C_5H_3{}^tBu_2)_2Ln(\mu\text{-}H)]_2$ (Ln = Ce, Sm), and samarium borohydride, $[(\eta^5\text{-}C_5H_3{}^tBu_2)_2Sm(\mu\text{-}BH_4)]_2$, are presented.

Results and discussion

The reaction of Cp''_2LnCl ($Cp'' = \eta^5\text{-}C_5H_3{}^tBu_2$, Ln = Ce, Sm) with $LiAlH_4$ in diethyl ether does not yield homonuclear metallocene hydrides, unlike the analogous reaction involving Cp''_2LuCl [6]. However the interaction of these chlorides with $NaAlH_4$ in a THF–triethylamine mixture results in crystallization of hydrides of the elemental formula Cp''_2LnH, Ln = Ce (I), Sm (II), from solution (eq. 1). In the case of Ln = Sm the reaction may be carried out in pure THF, followed by dilution of the resulting $(Cp''_2LnAlH_4\cdot THF)_2$ solution with pentane.

$$2Cp''_2LnCl + 2NaAlH_4 \xrightarrow[THF]{NEt_3} \{(Cp''_2LnAlH_4\cdot NEt_3)_2\} \longrightarrow$$

$$\times 2AlH_3\cdot NEt_3 + (Cp''_2LnH)_2 \quad (1)$$

Complex II was also obtained during the treatment of samariocene solvate $Cp''_2Sm\cdot THF$ with triethylaminalane (eq. 2).

$$Cp''_2Sm\cdot THF + AlH_3\cdot NEt_3 \xrightarrow{Et_2O} \tfrac{1}{2}(Cp''_2SmH)_2 + Al + NEt_3 + H_2 \quad (2)$$

The path of redox reaction 2 confirms the scheme [8,9] of Sm^{3+} aluminohydride complex formation from samarium(II) complexes. The addition of a strong bidentate Lewis base, tetramethylethylenediamine (TMEDA), into the $Cp''_2Sm\cdot THF$ solution modifies the reaction pathway and yields stable alumohydride structures, e.g. $Cp''_5Sm_4Al_4H_{19}\cdot 2TMEDA$ [9] and $(Cp'_2Sm)_2(H)(AlH_4\cdot TMEDA)$ ($Cp' = C_5H_4{}^tBu$) [10]. It should also be noted that the reactions 1 and 2 proceed only for disubstituted $C_5H_3{}^tBu_2$-ligands. In the case of $Cp' = C_5H_4{}^tBu$ the result of the reaction is a yellow oily product which is a mixture of at least two substances according to IR data, and in the case of $Cp' = C_5H_5$ and a large excess of triethylamine the end product is the solvate $[Cp_2Sm(\mu\text{-}H)\cdot NEt_3]_2$. The IR spectrum of this complex shows ν(Sm–H) stretchings at 1250 and 1320 cm^{-1} (compare 1330 cm^{-1} in $[(C_5H_4Me)_2Er(\mu\text{-}H)\cdot THF]_2$ [11] and 1360 cm^{-1} in $[Cp_2Lu(\mu\text{-}H)\cdot THF]_2$ [12]).

The ν(Ln–H) stretchings for unsolvated biscyclopentadienyl hydrides I and II are observed in a region of longer wavelength—1130 and 1150 cm^{-1} respectively (compare 1280 and 1090 cm^{-1} in complex $[Cp''_2Lu(\mu\text{-}H)]_2$ (III) [6]). The presence of bridging hydrogens in hydrides I and II has been confirmed by X-ray single crystal analysis.

Both hydrides and complex III [6] are isostructural compounds. The molecules of all three complexes are centrisymmetrical dimers $[(\eta^5\text{-}C_5H_3{}^tBu_2)_2Ln(\mu\text{-}H)]_2$

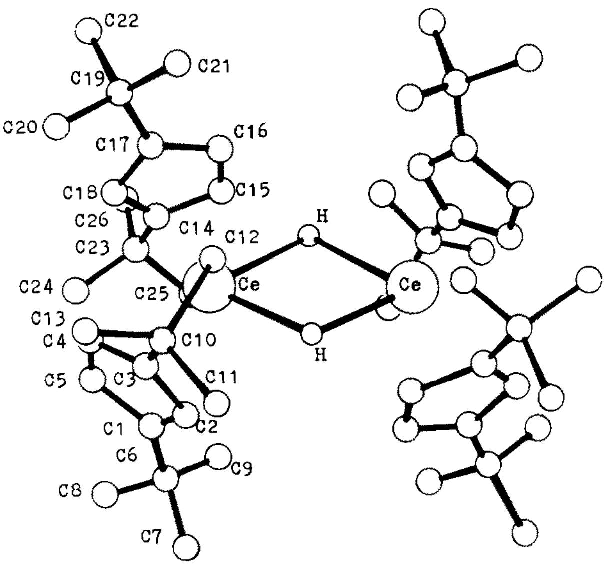

Fig. 1. Molecular structure of complex $[(C_5H_3{}^tBu_2)_2Ce(\mu\text{-}H)]_2$ (I) (the hydrogen atoms of the cyclopentadienyl groups are omitted for clarity). The structure of complex $[(C_5H_3{}^tBu_2)_2Sm(\mu\text{-}H)]_2$ is analogous.

(Fig. 1). Their metal atoms having a 16 electron configuration are bounded with two η^5-cyclopentadienyl rings and two bridging hydrogen atoms. An analogous chloride complex of lutetium $[(\eta^5\text{-}C_5H_3{}^tBu_2)_2Lu(\mu\text{-}Cl)]_2$ has a similar structure [13], while the dimeric molecule of complex $[(\eta^5\text{-}C_5H_3{}^tBu_2)_2Ce(\mu\text{-}Cl)]_2$ has symmetry C_2 [14]. The characteristic staggered conformation of cyclopentadienyl rings in I and II (Fig. 2a) reveals the departure of tert-butyl groups from the ring plane which is noticeably larger for one ligand (CpII) than for the other (CpI) (Table 1). Steric hindrances in these complexes decrease with the increase in metal atom size: the mean angle of the departure of the ring tert-butyl group bond from the ring plane decreases from 12.2° (III) [6] to 9.4° (II) and 8.1° (I). The changes in such characteristics of molecules I–III as $Ln\text{–}C_{av.}$ and $Ln \cdots Ln$ distances, which

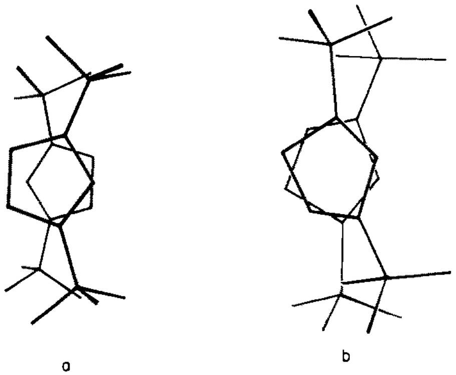

Fig. 2. The conformation of cyclopentadienyl rings in complexes I and II (a) and VI (b) (a view of the MX_2M plane).

Table 1

Main interatomic distances d (Å) and bond angles ω (deg) in molecules $[(\eta^5\text{-}C_5H_3{}^tBu_2)_2Ce(\mu\text{-}H)]_2$ (I) and $[(\eta^5\text{-}C_5H_3{}^tBu_2)_2Sm(\mu\text{-}H)]_2$ (II)

Bond	d		Angle	ω	
	I	II		I	II
M-CpI	2.55	2.47	CpIMCp2	133.5	121.5
M-CpII	2.52	2.45	HMH′	81.7	69.9
M-$C_{av.}$	2.81(4)	2.74(5)	MHM′	98.3	110.1
M-H	2.5(1)	1.80(15)	CpIMCp2/M_2H_2	89.8	74.2
M-H′	2.6(1)	2.75(15)	C3-C6/CpI	7.3	6.8
M···M′	3.901(1)	3.771(2)	C5-C10/CpI	5.8	7.2
			C15-C19/CpII	10.8	10.7
			C18-C23/CpII	8.3	12.6
			CpI/CpII	47.6	58.5

show linear dependence on the ionic radius of a rare earth metal (Fig. 3), also obey the general rule.

However, some geometric parameters for the samariocene hydride, i.e. the angle characteristics of the LnH_2Ln bridge, depart from the general rule. This situation is caused by the characteristic structural properties of II. Thus, unlike complexes I and III the bridging hydride atoms in II protrude out of the bisector plane of the bent sandwich Cp''_2Ln (the angle between the CpISmCp2 and SmH_2Sm planes is 74.2 °), and the SmH_2Sm bridge is noticeably asymmetric. One of the Sm–H distances in II is 0.2–0.4 Å shorter than in known rare earth metal hydrides (Table 2), the other being substantially longer and in satisfactory agreement with a secondary bond $Sm\cdots H$ (Table 1). Nevertheless, the value of the ν(Sm–H) stretch in the IR spectrum of complex II (1150 cm^{-1}), falling between the values for complexes I and III [12], and the isotopic shift ν(Sm–H)/ν(Sm–D) = 1.34 confirm the bridge nature of the Sm–H bond. In addition to the deflection of the bridge hydrogen atoms out of the bisector plane, an extraordinarily low value of Cp″SmCp″ angle should be noted (Table 1). The reasons for these anomalies in complex II are obscure. In principle those may be due to a distinct type of hybrid MO orbital orientation for the Cp''_2Sm moiety (out of the bent sandwich bisector plane). This proposal is in agreement with X-ray structure

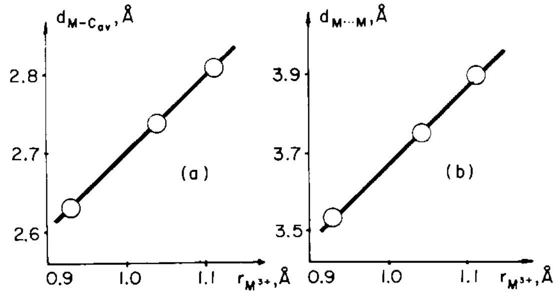

Fig. 3. Plot of M–$C_{av.}$ (a) and M···M (b) distances in $[(C_5H_3{}^tBu_2)_2Ln(\mu\text{-}H)]_2$ versus the ionic radius of the metal.

Table 2

Parameters of MH_2M metallocycle in dimeric biscyclopentadienyl metal hydrides

No.	Complex	$M\cdots M$	$M-C_{av.}$	$M-H^b$	H^bM-H^b	Refs.
1	$[(C_5H_4Me)_2Zr(H)(\mu\text{-}H)]_2$	3.46	2.52	1.94, 2.05	60.0	18
2	$[(C_5H_3{}^tBu_2)_2Lu(\mu\text{-}H)]_2$	3.53	2.63	2.27, 2.32	79.2	6
3	$Cp_2W(H)(\mu\text{-}H)W(H)Cp_2$	3.63	2.42	–	–	19
4	$[(C_5H_4Me)_2Y(\mu\text{-}H)\cdot THF]_2$	3.66	2.69	2.17, 2.19		11
5	$[(C_5H_3Me_2)_2Y(\mu\text{-}H)\cdot THF]_2$	3.68	2.69	2.02, 2.27	62.3	5
6	$[(C_5H_3{}^tBu_2)_2Sm(\mu\text{-}H)]_2$	3.77	2.74	1.80, 2.75	69.9	This work
7	$[(C_5Me_5)_2SmH]_2$	3.90	2.76	–	–	3
8	$[(C_5H_3{}^tBu_2)_2Ce(\mu\text{-}H)]_2$	3.90	2.81	2.52, 2.64	81.7	This work
9	$[(C_5Me_5)_2ThH(\mu\text{-}H)]_2$	4.01	2.83	2.29	58.0	20
10	$[(C_5H_3Me_2)_2Y(\mu\text{-}H)]_3$	4.10	2.62	–	–	5

analysis data for the row of samariocene hydride complexes [8–10,14] in which some or all of the bridge hydrogen atoms connected with the samarium atom protrude out of the bisector plane.

The reaction of biscyclopentadienyl samarium chlorides with lithium borohydride in ether yields related borohydride complexes Cp'_2SmBH_4 as has been observed with cerium analogues [14]. All the attempts at obtaining monometallic hydrides by the well known treatment of the borohydrides with triethylamine (for example, for $Cp_2Zr(BH_4)_2$ this procedure yields triethylaminoborane and mono- or dihydride [15]) were unsuccessful. Samariocene borohydrides Cp'_2SmBH_4 ($Cp' = C_5H_5$ (IV), $C_5H_4{}^tBu$ (V), $C_5H_3{}^tBu_2$ (VI)) are easily soluble in non-solvating solvents (benzene, pentane) while the solubility of IV is noticeably lower. In IR spectra of these compounds there is a broad intense band in the field of the B–H bond stretch at 2260 (IV), 2270 (V) and 2280 (VI) cm^{-1} with weak shoulders at 2435, 2430 and 2420 cm^{-1} respectively. The analogous bands at 2250 and 2400 cm^{-1} in IR spectrum of the dimer $[(C_5H_3{}^tBu_2)_2Ce(\mu\text{-}BH_4)]_2$ (VII) were assigned to the vibrations of the bridge borohydride group $[(\mu_3\text{-}H)_2B(\mu_2\text{-}H)_2]$ [14]. The broad absorption band at 2280 cm^{-1} in IR spectra of the unsolvated complexes $(C_5H_5)_2LnBH_4$ (Ln = Er, Yb) (2260 cm^{-1} for $(C_5H_5)_2SmBH_4$) was assigned to the vibrations of the bridge group $[(\mu_2\text{-}H)_2B(\mu_2\text{-}H)_2]$ in the polymeric molecule [16]. The comparison of shape of the absorption band ν(B–H) and the regularity of their frequency change with the nature of the metal and the level of substitution in cyclopentadienyl rings allow us to conclude that all the unsolvated rare earth metal biscyclopentadienyl borohydrides have the same structure and are dimers with the bridge $[(\mu_3\text{-}H)_2B(\mu_2\text{-}H)_2]$ groups. Both the fact of their easy sublimation (Ln = Er) and their solubility in hydrocarbons indicate the molecular nature of $(C_5H_5)_2LnBH_4$. This deduction was confirmed by the results of the X-ray structure analysis of complex VI.

Tetragonal crystals of complex VI are isostructural to complex VII [14] and are composed of discrete dimeric molecules having the C_2 symmetry (Fig. 5). The bent sandwiches Cp''_2Sm have a staggered conformation illustrated in Fig. 2b and are likely to be connected by two bridge borohydride groups. Although the hydride hydrogen atoms in molecule VI have not been localized, the relative disposition of nonhydrogen atoms is very similar to that observed in cerium complex VII with the localized hydrogen atoms [14]. Thus, the $Sm\cdots B$ distance in VI (0.07 Å), Table 3,

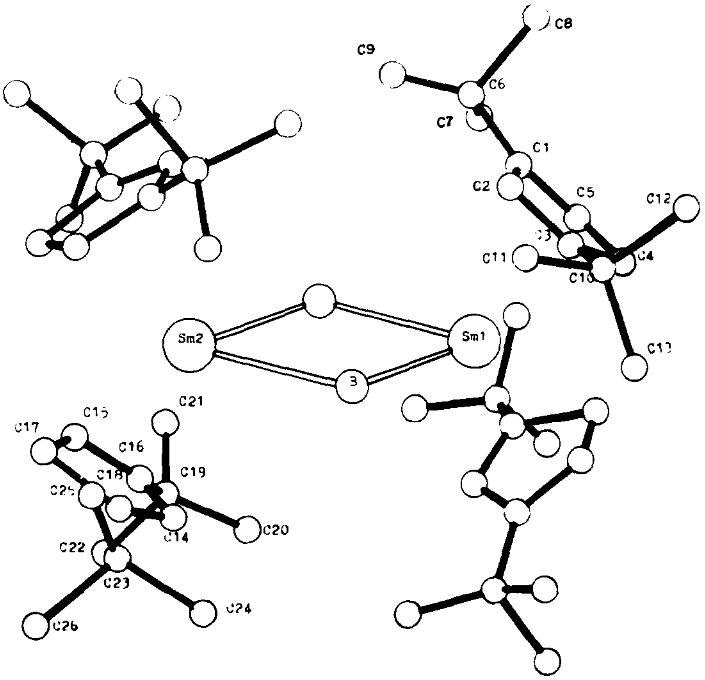

Fig. 4. Molecular structure of complex $[(C_5H_3{}^tBu_2)_2Sm(\mu\text{-}BH_4)]_2$ (VI). The hydrogen atoms of the cyclopentadienyl groups are omitted for clarity.

is shorter than in VII (2.93 Å) [14]. This difference is consistent with the difference in the ionic radii of Sm (1.04 Å) and Ce (1.11 Å). The boron atoms are more protruded from the bisector plane of the bent sandwich Cp''_2Ln in complex VI. The same difference (0.07 Å) is also observed for Ln–C distances in complexes VI and VII. This suggests that the system of hydride bonds in complexes VI and VII is the same, i.e. the metal atoms are connected by two $[(\mu_3\text{-}H)_2B(\mu_2\text{-}H)_2]$ groups. It is of

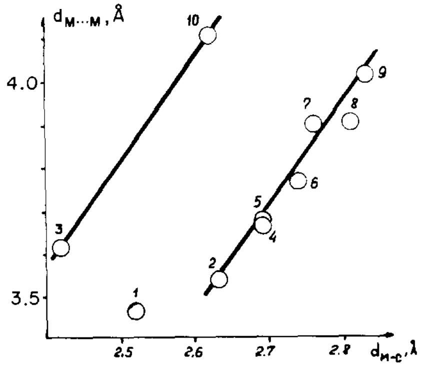

Fig. 5. Plot of M···M distance in biscyclopentadienyl metal hydrides versus $M–C_{av.}$ distance. The point numbers correspond with the numbers in Table 2.

Table 3

Main interatomic distances *d* (Å) and bond angles *ω* (deg) in molecule $[(\eta^5\text{-}C_5H_3{}^tBu_2)_2Sm(\mu\text{-}BH_4)]_2$ (VI)

Bond	*d*	Angle	*ω*
Sm1–CpI	2.46	CpISm1CpI′	115.3
Sm2–CpII	2.46	CpIISm2CpII′	115.2
Sm1–$C_{av.}$	2.74(9)	BSm1B′	75.0
Sm2–$C_{av.}$	2.74(7)	BSm2B′	73.5
Sm1 ··· Sm2	4.556(3)	Sm1BSm2	105.7
Sm1 ··· B	2.833(6)	C1–C6/CpI	9.8
Sm2 ··· B	2.882(6)	C3–C10/CpI	11.3
		C16–C19/CpII	12.8
		C18–C23/CpII	8.9
		Cp1Sm1Cp1′/Sm_2B_2	93.9
		Cp2Sm2Cp2′/Sm_2B_2	83.2

interest that the Cp″SmCp″ angle and the steric hindrances, which are characterized by a mean angle of deviation of the ring tert-butyl group bond from the ring plane, are noticeably smaller in complex VI (115.2 ° and 10.7 ° respectively) than in VII (119.4 ° and 12.2 °) [14], but the Ln ··· Ln distance does not decrease with the transition from the cerium to the samarium complex. Taking into account the relative size of Ce and Sm atoms the relationship would be expected to be inverse. Perhaps this behaviour is concerned with the different arrangement of hydride atoms near the Cp''_2Ln bent sandwich in VI and VII attributed as a characteristic property of the Cp''_2Sm fragment hybrid MO described above.

The analysis of the structure of $[(C_5H_3{}^tBu_2)_2Ln(\mu\text{-}X)]_2$ ($X = Cl$, H, BH_4) complexes shows that all complexes are crystallized only in two structural types, $[(C_5H_3{}^tBu_2)_2Lu(\mu\text{-}Cl)]_2$ [13] and $[(C_5H_3{}^tBu_2)_2Ce(\mu\text{-}Cl)]_2$ [14]. These structures are formed by centrisymmetrical dimeric molecules and dimers with C_2 symmetry respectively whose cyclopentadienyl rings are of different conformation (Fig. 2). Both the geometric parameters of the molecules and their crystallographic characteristics change proportionally with the metal ionic radii. Thus, the volume of the unit cell, except for that in complex VI, decreases linearly with the decrease of the metal ionic radius; its relative decrease does not depend on the structure type. As shown in Fig. 5 and Table 2, the relationship between the Ln ··· Ln distance and the Ln–$C_{av.}$ distance (the latter might be considered as the sum of carbon and rare earth metal covalent radii [17]) is practically linear for dimeric complexes with MH_2M bridges. It should be noted that points representing complexes with a single hydrogen bridge, $[(C_5H_3Me_2)_2Y(\mu\text{-}H)]_3$ [5] and $Cp_2W(H)(\mu\text{-}H)W(H)Cp_2$ with relatively perpendicular bent sandwiches (3.63 Å [18]), fall distinctly above this line. As follows from the relationship (Fig. 5), the dimeric hydride $[(C_5Me_5)_2SmH]_2$ is probably not an analogue of $Cp_2W(H)(\mu\text{-}H)W(H)Cp_2$ as previously proposed [3], but may be classified as a structure of the $[(C_5H_3{}^tBu_2)_2Ce(\mu\text{-}Cl)]_2$ type proposed subsequently [14]. Therefore $[(C_5Me_5)_2SmH]_2$ has a symmetric structure with double hydrogen bridge as hydrides I–III. This conclusion also confirms the fact that the M ··· M distance in complex $(C_5Me_5)_2Y(\mu\text{-}Cl)Y(Cl)(C_5Me_5)_2$ (5.35 Å) [21] is longer than those in complexes with an $LnCl_2Ln$ double bridge (3.89–4.54 Å).

Experimental

All the procedures of the synthesis and manipulations with the extremely air- and moisture-sensitive substances described were carried out using standard Schlenk and vacuum-line techniques.

Preparation of $[(\eta^5\text{-}C_5H_3{}^tBu_2)_2Ce(\mu\text{-}H)]_2$ *(I)*

A solution of 0.07 g (1.3 mmol) $NaAlH_4$ and 1.37 g (13 mmol) NEt_3 in 20 ml of THF was added dropwise to a stirred solution of 0.69 g (1.3 mmol) $(C_5H_3{}^tBu_2)_2CeCl$ in 120 ml of diethyl ether. On addition, the colour changed from yellow to red-orange followed within 20 min by precipitation of a bright-yellow solid. The mixture was stirred for 2 h and the precipitate filtered off. The filtrate was evaporated *in vacuo* to ~ 10 ml and 50 ml hexane was then added. After 24 h a small amount of precipitated solid was filtered off and the filtrate volume was reduced two-fold by evaporation. The cubic crimson crystals (0.21 g, 33%) that formed after 12 h were separated off, washed with cold hexane and dried *in vacuo*. Anal. Found: Ce, 28.1. $C_{26}H_{43}Ce$ calc.: Ce, 28.28%.

Preparation of $[(\eta^5\text{-}C_5H_3{}^tBu_2)_2Sm(\mu\text{-}H)]_2$ *(II)*

(a) A solution of 0.081 g (1.5 mmol) $NaAlH_4$ in 20 ml of THF was added to a stirred solution of 0.81 g (1.5 mmol) $(C_5H_3{}^tBu_2)_2SmCl$ in 100 ml of THF. The

Table 4

Summary of crystal data for complexes $[(\eta^5\text{-}C_5H_3{}^tBu_2)_2Ce(\mu\text{-}H)]_2$ (I), $[(\eta^5\text{-}C_5H_3{}^tBu_2)_2Sm(\mu\text{-}H)]_2$ (II) and $[(\eta^5\text{-}C_5H_3{}^tBu_2)_2Sm(\mu\text{-}BH_4)]_2$ (VI)

	I	II	VI
Molecular formula	$C_{26}H_{43}Ce$	$C_{26}H_{43}Sm$	$C_{26}H_{46}BSm$
Formula weight	495.75	505.99	519.83
Crystal	triclinic	triclinic	rhombic
a (Å)	10.741(2)	10.723(2)	24.448(4)
b (Å)	11.302(2)	11.305(3)	13.023(2)
c (Å)	12.425(2)	12.289(3)	17.218(3)
α (deg)	65.20(1)	115.73(2)	90
β (deg)	73.93(1)	105.15(2)	90
γ (deg)	89.69(1)	90.43(2)	90
V (Å^3)	1305.1(0.5)	1283.0(1)	5482.0(2.7)
μ_{Mo} (cm^{-1})	19.5	13.3	25.4
Space group	$P\bar{1}$	$P\bar{1}$	*Pnaa*
Z	2	2	8
$\rho_{calcd.}$ (g/cm^3)	1.26	1.31	1.26
Diffractometer	Nicolet P3	Syntex $P\bar{1}$	Nicolet P3
Scan technique	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
Irradiation	Mo-K_α	Mo-K_α	Mo-K_α
No. of unique reflections with $I > 3\sigma(I)$	2838	1584	1301
Programs	SHELXTL	SHELXTL	SHELXTL
Solution	Patterson	Patterson	Patterson
R	0.031	0.054	0.088
R_w	0.034	0.057	0.084

solution became turbid followed by a colour change from yellow-orange to yellow-green. The mixture was stirred for 1 h, and then a small amount of precipitated solid was filtered off. The filtrate was evaporated *in vacuo* to 10 ml and 60 ml of pentane was then added. After 12 h the solution was filtered once more, and the filtrate was evaporated to less than a half the initial volume. After 12 h this operation was repeated. The yellow cubic crystals (0.21 g, 28%) that formed after 24 h were separated off, washed with cold pentane and dried *in vacuo*. Anal. Found: Sm, 29.5. $C_{26}H_{43}Sm$ calc.: Sm, 29.70%.

(b) A solution of 0.07 g (1.3 mmol) $NaAlH_4$ and 1.37 g (13 mmol) NEt_3 in 25 ml of THF was added dropwise to a stirred solution of 0.71 g (1.3 mmol) $(C_5H_3{}^tBu_2)_2SmCl$ in 160 ml of diethyl ether. On addition, the colour changed from yellow-orange to yellow-green. Within 1 h a bright yellow solid was precipitated. The mixture was stirred for a further 2 h, then the precipitate was filtered off. The filtrate was evaporated *in vacuo* to 10 ml and 20 ml of pentane was then added. After 24 h cubic yellow crystals formed (0.23 g, 36%) and were separated off, washed with cold pentane and dried *in vacuo*. The IR spectrum of the substance obtained is in agreement with that recorded for crystals produced by method (a). Anal. Found: Sm, 29.5.

Table 5

Atomic coordinates ($\times 10^4$; hydrogen atoms, $\times 10^3$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) in complex $[(\eta^5\text{-}C_5H_3{}^tBu_2)_2Ce(\mu\text{-}H)]_2$ (I)

Atom	x	y	z	B_{eq}
Ce	5021(1)	5086(1)	3394(1)	48(1)
C1	4568(5)	7628(5)	1815(5)	59(2)
C2	5754(5)	7849(5)	2032(5)	55(2)
C3	6762(5)	7330(5)	1440(5)	57(2)
C4	6186(6)	6696(5)	889(5)	64(3)
C5	4843(5)	6897(5)	1112(5)	60(3)
C6	3323(5)	8196(5)	2105(5)	62(3)
C7	3623(9)	9576(12)	1898(19)	247(16)
C8	2569(11)	8302(15)	1253(13)	177(11)
C9	2516(12)	7402(18)	3368(11)	260(10)
C10	8211(5)	7482(5)	1294(5)	64(3)
C11	8546(6)	8662(27)	1534(7)	86(3)
C12	8566(7)	6281(8)	2282(10)	119(5)
C13	8993(7)	7740(11)	8(8)	124(6)
C14	3342(5)	3006(5)	3659(5)	64(3)
C15	3670(6)	2583(6)	4764(5)	69(3)
C16	5011(6)	2393(5)	4493(6)	67(3)
C17	5509(5)	2709(5)	3238(5)	61(3)
C18	4471(6)	3113(5)	2720(5)	65(3)
C19	6808(5)	2407(6)	2602(6)	71(3)
C20	7368(8)	3418(10)	1249(8)	125(5)
C21	7813(8)	2379(10)	3244(9)	119(6)
C22	6619(9)	1105(10)	2591(13)	159(8)
C23	1950(5)	3079(6)	3562(6)	77(3)
C24	1911(7)	3977(10)	2290(8)	115(5)
C25	1055(9)	3461(13)	4514(9)	147(7)
C26	1373(11)	1699(11)	3889(18)	213(11)
H1	658(5)	476(5)	465(5)	70(20)

(c) A solution of 0.175 g (1.33 mmol) $AlH_3 \cdot NEt_3$ in 20 ml of ether was added to a stirred solution of 0.77 g (1.33 mmol) $(C_5H_3{}^tBu_2)_2Sm \cdot THF$ in 100 ml of ether. On addition of triethylaminalane, the evolution of hydrogen, the precipitation of black Al metal, and a colour change from deep green to yellow were observed. The mixture was stirred for 3 h, the precipitate was then filtered off and the filtrate was evaporated to ~ 10 ml *in vacuo*. Within 24 h crystals like cubes or square prisms were separated off, washed with cold pentane and dried *in vacuo*. 0.36 g (53%) of yellow crystals were obtained with the same IR spectrum as the preparations obtained by procedures a and b. Anal. Found: Sm, 29.5%.

Preparation of $[Cp_2Sm(\mu\text{-}H) \cdot NEt_3]_2$

A solution of 0.048 g (1.25 mmol) $LiAlH_4$ and 2.9 g (28.7 mmol) NEt_3 in 50 ml of Et_2O was added to a stirred suspension of 0.385 g (1.22 mmol) Cp_2SmCl in 150 ml of diethyl ether. The mixture was stirred for 5 h, the precipitate was then filtered off, and the filtrate was evaporated *in vacuo* to a third of the initial volume. After 24 h small petal-like green crystals (0.21 g, 45%) were isolated. In the IR spectrum the absorption band of ν(Sm–H)b is present at 1170 cm^{-1}. Anal. Found: Sm, 39.2. $C_{16}H_{29}BNSm$ calc.: Sm, 39.27%.

Table 6

Atomic coordinates ($\times 10^4$; hydrogen atoms, $\times 10^3$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) in complex $[(\eta^5\text{-}C_5H_3{}^tBu_2)_2Sm(\mu\text{-}H)]_2$ (II)

Atom	*x*	*y*	*z*	B_{eq}
Sm	5036(1)	5064(1)	6567(1)	42(1)
C(1)	4810(21)	6798(14)	8824(15)	47(10)
C(2)	6170(23)	6678(14)	9034(14)	58(10)
C(3)	6745(17)	7273(13)	8491(13)	56(8)
C(4)	5766(23)	7805(14)	7929(14)	51(10)
C(5)	4595(21)	7549(14)	8180(14)	48(10)
C(6)	8183(28)	7461(15)	8653(16)	51(11)
C(7)	8531(16)	8681(17)	8433(16)	83(10)
C(8)	8609(21)	6235(18)	7678(25)	114(16)
C(9)	8992(20)	7792(22)	9945(19)	99(13)
C(10)	3324(19)	8140(16)	7888(15)	49(10)
C(11)	3605(26)	9421(31)	7965(41)	188(33)
C(12)	2433(25)	7282(32)	6620(24)	160(20)
C(13)	2636(28)	8260(31)	8809(31)	151(24)
C(14)	4513(23)	3161(15)	7277(17)	53(11)
C(15)	5554(21)	2749(15)	6751(17)	48(11)
C(16)	5040(17)	2414(13)	5465(14)	53(9)
C(17)	3715(24)	2617(16)	5220(15)	60(11)
C(18)	3346(16)	3041(14)	6349(16)	50(10)
C(19)	6930(17)	2446(15)	7361(16)	58(10)
C(20)	7442(22)	3432(21)	8716(20)	90(14)
C(21)	7837(23)	2371(21)	6697(22)	109(14)
C(22)	6560(23)	1093(19)	7306(27)	135(18)
C(23)	2000(16)	3050(16)	6465(17)	61(10)
C(24)	1952(22)	3992(22)	7792(20)	93(14)
C(25)	1511(24)	1660(25)	6175(31)	147(22)
C(26)	1056(24)	3329(30)	5462(22)	113(19)
H1	501(5)	623(5)	593(5)	70(20)

Preparation of $[(\eta^5\text{-}C_5H_5)_2Sm(\mu\text{-}BH_4)]_2$ *(IV)*

The solution of 0.023 g (1 mmol) $LiBH_4$ in 30 ml of Et_2O was added to a stirred suspension of 0.32 g (1 mmol) Cp_2SmCl in 200 ml of diethyl ether. The solution changed in colour from yellow to yellow-green. The mixture was stirred for 2 h, then the LiCl precipitate was filtered off. The filtrate was evaporated to ~ 10 ml *in vacuo* and 50 ml of pentane was then added. 24 h later the needle-like yellow crystals formed (0.20 g, 66%) were separated off, washed with cold pentane and dried *in vacuo*. Anal. Found: Sm, 50.8. $C_{10}H_{14}BSm$ calc.: Sm, 50.85%.

The yellow-green crystals of complex $[(\eta^5\text{-}C_5H_4{}^tBu)_2Sm(\mu\text{-}BH_4)]_2$ (V) were obtained by an analogous procedure (yield 60%). Anal. Found: Sm, 36.7. $C_{18}H_{30}BSm$ calc.: Sm, 36.85%.

Preparation of $[(\eta^5\text{-}C_5H_3{}^tBu_2)_2Sm(\mu\text{-}BH_4)]_2$ *(VI)*

A solution of 0.024 g (1.1 mmol) $LiBH_4$ in 50 ml of Et_2O was added to a stirred suspension of 0.59 g (1.1 mmol) $(C_5H_3{}^tBu_2)_2SmCl$ in 50 ml of ether. The mixture was stirred for 3 h, and the solvent was then removed by vacuum evaporation. The dry residue was extracted twice with pentane (50 ml). The extract was concentrated

Table 7

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) in complex $[(\eta^5\text{-}C_5H_3{}^tBu_2)_2Sm(\mu\text{-}BH_4)]_2$ (VI)

Atom	x	y	z	B_{eq}
Sm1	1124(1)	2500	2500	32(1)
Sm2	2988(1)	2500	2500	32(1)
B	2043(22)	3459(26)	3191(24)	13(13)
C1	833(18)	642(33)	3244(27)	28(17)
C2	1009(19)	1323(40)	3821(26)	40(19)
C3	677(20)	2032(33)	3916(31)	39(19)
C4	195(20)	2005(32)	3357(30)	44(18)
C5	414(33)	1142(36)	2953(27)	80(35)
C6	1067(33)	−449(38)	3077(33)	75(34)
C7	876(20)	−748(38)	2259(23)	48(24)
C8	672(26)	−1117(37)	3632(35)	80(26)
C9	1613(26)	−582(41)	3292(35)	83(27)
C10	647(24)	2895(39)	4631(28)	57(23)
C11	1182(35)	3014(49)	5034(31)	125(39)
C12	218(22)	2506(65)	5177(27)	98(25)
C13	477(23)	3933(41)	4362(33)	79(23)
C14	3078(18)	4281(35)	1625(28)	34(20)
C15	3694(31)	3079(33)	1446(32)	80(28)
C16	3255(23)	3504(37)	1110(29)	46(19)
C17	3906(19)	3614(36)	2124(27)	37(18)
C18	3456(20)	4388(32)	2211(25)	39(19)
C19	3055(27)	3299(42)	306(27)	60(28)
C20	2488(29)	3766(43)	175(30)	84(29)
C21	3006(38)	2189(37)	64(31)	124(45)
C22	3444(27)	3863(47)	−270(30)	90(30)
C23	3515(20)	5268(32)	2811(27)	43(19)
C24	3020(32)	5967(36)	2862(33)	107(35)
C25	3662(27)	4921(39)	3611(35)	86(27)
C26	4006(20)	5949(34)	2572(50)	83(23)

to ~ 10 ml and was cooled with vapour from liquid nitrogen. The precipitated stick-like yellow-orange crystals (0.22 g, 39%) were separated by decantation and dried *in vacuo*. Anal. Found: Sm, 28.8. $C_{26}H_{46}BSm$ calc.: Sm, 28.90%.

X-Ray structure determination of I, II, and VI

Single crystals of complexes I, II, and VI were mounted in glass capillaries. The X-ray diffraction study was carried out with Nicolet P3 and Syntex P1 diffractometers. Detailed data on collection, structure determination and refinement are given in Table 4. The atomic coordinates and equivalent isotropic displacement coefficients for complexes I, II, and VI are listed in Tables 5–7, and the main interatomic distances and bond angles are listed in Tables 1 and 3.

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