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Coordinationally oversaturated metallocene derivatives. The crystal and molecular structure of $[(\eta^5\text{-}C_5H_5)_2Sm(\mu_3\text{-}H)]_2[(\mu_2\text{-}H)_2AlH\cdot N(C_2H_5)_3]_2$ and $[(\eta^5\text{-}C_5H_4{}^tBu)_2Sm]_2(\mu_2\text{-}H)\mu\text{-}[(\mu_3\text{-}H)_2Al(\mu_2\text{-}H)_2\cdot Me_2NC_2H_4NMe_2]$ complexes

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Abstract

The interaction of Cp'_2SmCl ($Cp' = C_5H_5$, $C_5H_4{}^tBu$) with $LiAlH_4$ at the reagent ratio 1:1 yields compounds of composition $[(\eta^5\text{-}C_5H_5)_2Sm(\mu_3\text{-}H)]_2[(\mu_2\text{-}H)_2AlH\cdot N(C_2H_5)_3]_2$ (I) and $[(\eta^5\text{-}C_5H_4{}^tBu)_2Sm]_2(\mu_2\text{-}H)\mu\text{-}[(\mu_3\text{-}H)_2Al(\mu_2\text{-}H)_2\cdot Me_2NC_2H_4NMe_2]$ (II) depending on the nature of the solvating Lewis base. Crystals of I are triclinic, $a = 11.012(3)$, $b = 11.911(3)$, $c = 14.314(4)$ Å, $\alpha = 88.76(2)$, $\beta = 78.65(2)$, $\gamma = 96.17(2)°$, space group $P\bar{1}$, $Z = 4$, $\rho_{calc} = 1.47$ g/cm^3. Crystals of II are monoclinic, $a = 16.652(5)$, $b = 18.720(5)$, $c = 16.499(5)$ Å, $\gamma = 91.77(2)°$, space group $B2b$, $Z = 8$, $\rho_{calc} = 1.18$ g/cm^3. In both complexes samarium atom is coordinated by four hydrides and has a formal 20e configuration. Probable reasons for this coordinational oversaturation are discussed. The novel type of bridging alumohydride group coordination with two μ_3- and two μ_2-hydrogen atoms is described for II.

Introduction

The majority of metallocenes and their derivatives are known to obey the 18-electron rule and their structure is described by the molecular orbital scheme proposed in ref. 1. According to ref. 1 the valent MO of Cp_2M fragment ($1a_1$, b_2 and $2a_1$) located in the bent sandwich bisecting plane can coordinate no more than three ligands. The alumino- and borohydride metallocene complexes of the early *d*-elements are also governed by the same rule, if each hydride hydrogen atom coordinated to the metal atom is considered as a two-electron donor. However, the *f*-elements and the late *d*-elements with the filled *f*-sublevel exhibit a greater number of H-atoms bound with a metal atom. For example, in $[(C_5H_4{}^tBu)_2Sm(\mu_3\text{-}$

$H)]_2[(\mu_2\text{-}H)_2AlH \cdot THF]_2$ [2] and $[(C_5H_5)_2Lu(\mu_2\text{-}H)]_2[(\mu_2\text{-}H)_2AlH \cdot N(C_2H_5)_3] \cdot C_6H_6$ [3], the metal atom coordinates four hydrogen atoms, thus formally acquiring a 20-electron configuration. An analogous supercoordination was also registered for the borohydride complexes of hafnium $(C_5H_4Me)_2Hf[(\mu_2\text{-}H)_2BH_2]_2$ [4] and cerium $(C_5H_3{}^tBu)_2Ce\{\mu\text{-}[(\mu_3\text{-}H)_2B(\mu_2\text{-}H)_2]_2\}_2$ [5]. Since the coordination oversaturation problem is very important to the elucidation and prediction of the reactivity and catalytic activity of the transition metal complexes, the systematic study of the effect of the nature of a transition metal atom and stabilizing ligands on the structure of the metal complex, remains currently interesting. In the present paper the results of the X-ray structure studies of the two new samariecene complexes, $[(\eta^5\text{-}C_5H_5)_2Sm(\mu_3\text{-}H)]_2[(\mu_2\text{-}H)_2AlH \cdot N(C_2H_5)_3]_2$ (I) and $[(\eta^5\text{-}C_5H_4{}^tBu)_2Sm]_2(\mu_2\text{-}H)\mu\text{-}[(\mu_3\text{-}H)_2Al(\mu_2\text{-}H)_2 \cdot Me_2NC_2H_4NMe_2]$ (II), formally with 20-electron configuration are discussed.

Results and discussion

The interaction of Cp'_2SmCl ($Cp' = C_5H_5$, $C_5H_4{}^tBu$) with lithium aluminium hydride at the reagent ratio 1 : 1 yields compounds of different composition depending on the nature of the solvating Lewis base (L) in the reaction mixture. At $L = NEt_3$ the initial ratio Sm/Al is preserved in the final product and the compound composition can be described by the empirical formula $Cp'_2SmAlH_4 \cdot NEt_3$. The X-ray analysis performed for the complex with $Cp' = C_5H_5$ showed that this compound like many other alumohydride metallocene complexes with the general formula $Cp'_2LnAlH_4 \cdot L$ (where $L = NEt_3$ (Ln = Y [6], Yb, Lu [3]) or THF (Ln = Y [7], Sm [2])) was the dimer $(Cp'_2SmAlH_4 \cdot NEt_3)_2$ (I). The reaction of its synthesis may be presented by eq. 1:

$$Cp'_2SmCl + LiAlH_4 \xrightarrow{NEt_3} 1/2(Cp'_2SmAlH_4 \cdot NEt_3)_2 + LiCl \qquad (1)$$

However, the change in NEt_3 in reaction 1 for the bidentate Lewis base $Me_2NC_2H_4NMe_2$ (TMEDA) leads to crystallization of two compounds from solution after the separation of lithium chloride precipitate that is the solvate of aluminium hydride $AlH_3 \cdot TMEDA$ and samarium aluminohydride complex $(Cp'_2Sm)_2H(AlH_4 \cdot TMEDA)$ (II). Taking into account the composition of complex II conformed by X-ray analysis for $Cp' = C_5H_4{}^tBu$, it may suggested that the first stage of its synthesis is the formation of the "common" aluminohydride complex with Sm/Al = 1 : 1 (reaction 1) which decomposes in the presence of a strong Lewis base according to eq. 2:

$$(Cp'_2SmAlH_4 \cdot TMEDA)_2 \rightarrow AlH_3 \cdot TMEDA + (Cp'_2Sm)_2H(AlH_4 \cdot TMEDA) \qquad (2)$$

The reaction of an aluminium hydride solvate elimination of the heterometallic transition metal hydride complexes yielding the related complexes with M/Al = 2 : 1 was previously observed for tungsten complexes stabilized by trimethylphosphine [8] and permethyltitanocene [9]. For titanocene alumohydride with unsubstituted C_5H_5-ligands this reaction is accompanied by hydrogen elimination and the formation of complex $[Cp_2TiH_2Al(H)(C_5H_4)TiCp]_2$ [10]. For biscyclopentadienyl aluminohydride complexes of lutetium and samarium with bulky $C_5H_3{}^tBu_2$-ligands

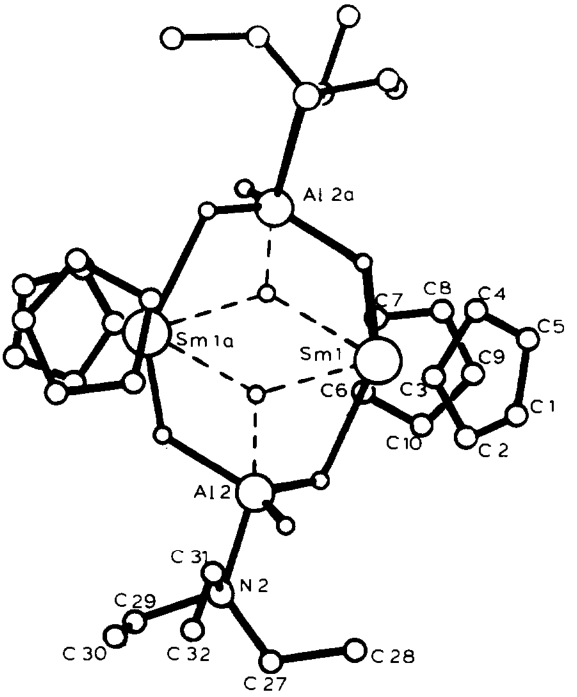

Fig. 1. The structure of $[(\eta^5\text{-}C_5H_5)_2Sm(\mu_3\text{-}H)]_2[(\mu_2\text{-}H)_2AlH \cdot N(C_2H_5)_3]_2$ (I).

the reaction of decomposition of $(Cp'_2LnAlH_4 \cdot TMEDA)_2$ is not accomplished by the stage of complex type II formation but yields homometallic hydrides $[Cp''_2Ln(\mu\text{-}H)]_2$ [11,12] (eq. 3).

$$(Cp'_2LnAlH_4 \cdot TMEDA)_2 \rightarrow 2\,AlH_3 \cdot TMEDA + [Cp''_2Ln(\mu\text{-}H)]_2 \tag{3}$$

Obviously, the metathesis reaction of transition metal halogenides with $LiAlH_4$ which constitutes a well-known method of preparation of related hydride complexes [13], proceeds generally via an intermediate stage of formation of "common" aluminohydride L_nMAlH_4 with M–H–Al bridge bonds and, in the case of its dimerization, aluminohydride complex with $M/Al = 2:1$. The rate and depth of aluminohydride intermediate decomposition with elimination of the $AlH_3 \cdot L$ increases at lower metal acidity, greater steric hindrances and basicity of L.

The structure of a dimeric centrisymmetric molecule I (Fig. 1) is in general analogous to that of the known rare earth metal complexes with general formula $[Cp_2LnAlH_4 \cdot L]_2$, which are adducts of dimeric metallocene hydride and aluminium hydride solvate [2,3,6,7]. Depending on the nature of the metal, ligands and even the presence of a solvent in the crystal matrix, the type of $AlH_3 \cdot L$ bonding with organometallic moiety changes from the bidentate type for $[Cp_2Ln(\mu_3\text{-}H)]_2[(\mu_2\text{-}H)AlH_2 \cdot L]_2$ ($Ln = Y$, $L = NEt_3$ (III) [6], THF (IV) [7], $Ln = Yb$, $L = NEt_3$ (V) [3]) to tridentate type for $[(C_5H_5)_2Y]_2(\mu_2\text{-}Cl)[(\mu_3\text{-}H)]_2(\mu_2\text{-}H)_2AlH \cdot N(C_2H_5)_3]$ (VI) [12] and $[(C_5H_4{}^tBu)_2Sm(\mu_3\text{-}H)]_2[(\mu_2\text{-}H)_2AlH \cdot THF]_2$ (VII) [2]. In complex $[(C_5H_5)_2Lu(\mu_2\text{-}H)]_2[(\mu_2\text{-}H)_2AlH \cdot N(C_2H_5)_3]_2 \cdot C_6H_6$ (VIII) under conservation of two Ln–(μ_2-H)–Al bridges, the bond between the Al atom and hydrogen atoms of

Table 1

Atomic coordinates ($\times 10^4$, hydrogen atoms, $\times 10^3$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for complex I

Atom	x	y	z	B_{eq}
Sm1	3439(1)	5828(1)	5175(1)	38(1)
Sm2	−1431(1)	9325(1)	11052(1)	35(1)
Al1	5769(5)	6142(4)	6304(3)	37(2)
Al2	8990(4)	8090(4)	−116(3)	47(2)
C1	1495(22)	6205(18)	6585(18)	78(10)
C2	2280(25)	5777(28)	7033(12)	111(12)
C3	2382(21)	4715(27)	6822(18)	107(10)
C4	1511(29)	4439(19)	6247(17)	104(11)
C5	988(18)	5380(23)	6139(13)	79(9)
C6	4316(19)	7547(22)	3872(20)	87(10)
C7	3692(29)	6767(18)	3396(13)	80(10)
C8	2461(25)	6724(19)	3772(19)	83(11)
C9	2295(24)	7479(27)	4428(21)	108(13)
C10	3413(44)	7996(17)	4558(18)	133(17)
C11	−2397(22)	9836(33)	12861(17)	108(13)
C12	−1537(48)	10586(21)	12568(16)	138(18)
C13	−422(27)	10387(33)	12445(16)	146(13)
C14	−561(30)	9240(35)	12700(17)	121(14)
C15	−1815(32)	8900(16)	12862(11)	97(12)
C16	−2091(20)	7401(16)	11147(16)	86(9)
C17	−2453(17)	7493(17)	10225(18)	71(9)
C18	−2764(22)	9410(21)	9808(14)	84(10)
C19	−3610(19)	8914(17)	10434(15)	70(9)
C20	−3782(15)	8297(16)	11248(12)	82(8)
N1	6961(11)	7598(10)	6492(9)	52(5)
C21	6467(23)	8228(18)	7325(15)	111(11)
C22	5270(23)	8736(17)	7260(17)	115(12)
C23	8172(17)	7218(14)	6722(14)	77(8)
C24	8089(20)	6428(18)	7475(15)	99(10)
C25	7326(16)	8224(13)	5560(12)	69(8)
C26	8229(19)	9324(15)	5496(13)	81(8)
N2	2116(10)	7121(10)	438(8)	44(4)
C27	2969(21)	6751(23)	−321(13)	126(12)
C28	3907(23)	6008(24)	−192(13)	145(14)
C29	1583(30)	6490(34)	1271(22)	291(22)
C30	337(19)	5529(12)	1089(13)	73(8)
C31	3051(24)	7886(22)	883(15)	158(13)
C32	2802(17)	8692(14)	1493(12)	73(8)
H1	502	703	574	90
H2	513	575	737	90
H3	687	532	553	90
H5	45	734	−81	90

Lu–H–Lu bridges is noticeably weakened and it can be considered as a secondary one [3]. Unfortunately, the differential Furies synthesis did not allow us to localize the position of all hydrogen atoms in I. Three H atoms out of four are localized for one independent molecule and only one atom for the other (Table 1). That is why the conclusion on the type of binding in I can be drawn proceeding from only the

Table 2

The main interatomic distances *d* (Å) and valent angles *ω* (degrees) for complex I

Bond	*d*		Bond	*d*	
	1	2		1	2
Sm–Cp	2.469	2.462	Sm–H3	1.76	–
	2.458	2.468	Al–N	2.11(1)	2.11(1)
Sm–$C_{av.}$	2.72(3)	2.72(3)	Al–H	1.69	–
Sm ··· Al	3.283(5)	3.282(5)	Al–H2	1.59	1.47
Sm ··· Al′	3.268(5)	3.277(4)	Al–H3	1.86	–
Sm ··· Sm′	4.096(4)	4.068(4)	N–$C_{av.}$	1.44(8)	1.50(4)
Al ··· Al′	5.113	5.144	C–$C_{av.}^{Et}$	1.50(8)	1.49(8)
Sm–H_1	2.41	–	C–$C_{av.}^{Cp}$	1.35(4)	1.34(5)
Angle	*ω*		Angle	*ω*	
	1	2		1	2
CpSmCp	123.6	124.4	Na1H1	85.9	–
AlSmAl′	102.6(1)	103.3(1)	NA1H2	102.3	102.4
H1SmH3′	145.9	–	Na1H3	101.2	–
SmAlSm′	77.4(1)	76.7(1)	H1A1H2	116.8	–
SmAlN	130.8(4)	129.2(3)	H1AlH3	116.1	–
Sm′AlN	124.6(4)	128.5(3)	H2AlH3	123.0	–

analysis of mutual position of non-hydrogen atoms and three hydride atoms determined in one of the independent molecules.

The bent sandwich $(C_5H_5)_2Sm$ in I has a staggered conformation and its geometric parameters (Table 2) are close, for example, to those observed for $(C_5H_4{}^tBu)_2Sm$ in complex VII ($r_{Sm-Cp} = 2.48$ Å, the angle CpSmCp is equal to 125.8° [2]). The Sm ··· Sm distance in I is markedly longer than that expected from the data on complexes of yttrium and ytterbium taking into account the difference in covalent radii therein (Table 3). However, the Sm ··· Al distances in all studied aluminohydride metallocene complexes of rare earth metals, including I, are changed

Table 3

Main interatomic distances (in Å) for dimeric biscyclopentadienyl aluminohydride complexes of lantanides and Y

Complex [a]	M ··· M	M ··· Al	M–μ_2H	Al–μ_2H	Al–L	Reference
$(Cp_2YAlH_4 \cdot NEt_3)_2$	3.70	3.30	–	–	2.13	6
$(Cp_2SmAlH_4 \cdot NEt_3)_2$	4.10	3.27	1.7, 2.4	1.7–1.9	2.11	This work
	4.07	3.28	–	–	2.11	
$(Cp_2YbAlH_4 \cdot NEt_3)_2 \cdot C_6H_6$	3.62	3.26	2.2	1.6	2.11	3
$(Cp_2LuAlH_4 \cdot NEt_3)_2 \cdot C_6H_6$	3.61	3.26	2.6	1.7–1.9	2.13	3
$(Cp_2Y)_2Cl(AlH_4 \cdot NEt_3)$	3.95	3.24			2.09	12
$(Cp_2YAlH_4 \cdot THF)_2$	3.75	3.24			1.97	7
$[Cp'_2SmAlH_4 \cdot THF]_2$	4.23	3.25			2.00	2
$Cp''_5Sm_4H_3(AlH_4)_4 \cdot 2$ TMEDA	3.75	2.96	1.9	2.1	2.12–	13
		3.13	2.3	1.8	2.15	
$(Cp'_2Sm)_2H(AlH_4 \cdot TMEDA)$	3.71	3.04	2.1	1.7	2.09	This work

[a] $Cp' = C_5H_4{}^tBu$, $Cp'' = C_5H_3{}^tBu_2$.

within a more narrow interval (Table 3). The aluminium atoms in I are situated in the bisecting plane of the bent sandwich $(C_5H_5)_2Sm$ as those in III–V and VIII [3,6,7], and are bound with Sm and Sma atoms via at least two hydrogen bridges (H1 and H3 atoms are taken from the differential synthesis), i.e. as well as in complexes VI–VIII. This conclusion is in a good agreement with the fact that nitrogen atoms of the triethylamine molecule escape from the bisecting Sm_2Al_2 plane, whereas these atoms in III–V complexes are situated in the Ln_2Al_2 plane [3,6,7]. Considering these facts it may be supposed that the type of binding in I is analogous to that found for VIII [3] and is described by the formula $[(C_5H_5)_2Sm(\mu_2\text{-}H)]_2[(\mu_2\text{-}H)_2AlH \cdot N(C_2H_5)_3]_2$. Comparing with [3], in this case the bridge hydrogen atoms in the SmH_2Sm metallacycle should protruded out of the bisecting plane of the bent sandwich $(C_5H_5)_2Sm$ and, consequently, are bound to the aluminium atoms by the relatively weak secondary bonds (Fig. 1, dashed lines). It should be noted, however, that if Lu–H bonds in VIII in both Lu–$(\mu_2$-H)–Al bridges are considerably weakened (r_{Lu-H} = 2.4 and 2.6 Å) (it is probably the main reason for ready elimination of an $AlH_3 \cdot NEt_3$ molecule [3]), then these bonds in I are much shorter (1.8 and 2.4 Å respectively) and the compound is more stable even at a large excess of amine.

The introduction of a strong bidentate Lewis base, tetramethylethylendiamine, into the reacting system considerably changes both the character of the interaction between the components and the type of binding of the aluminohydride moiety with the rare earth metal atom in the final product. In fact a new type of AlH_4-group binding is realized in II as previously proposed for an eight nuclear complex of $Cp''_5Sm_4H_3(AlH_4)_4 \cdot 2TMEDA$ (IX) ($Cp'' = \eta^5\text{-}C_5H_3{}^tBu_2$) [14].

The molecule of complex II contains two bent sandwiches $(C_5H_4{}^tBu)_2Sm$ connected by one hydrogen bridge and bridging solvating aluminohydride group. The symmetry of this molecule is C_2 (Fig. 2). The geometric parameters of the bent sandwiches do not differ much from those determined for I (Tables 2,4) and VII [2]. The substituent orientation in cyclopentadienyl rings for II (Fig. 2) caused by the presence of the only aluminohydride group provides smaller steric hindrances than those in II. Thus, the values of angles formed by the ring–^{t}Bu-group bond and the plane of the cyclopentadienyl ring are equal to 7.8, 8.5° and 10.2, 12.2° in complex VII [2]. The Sm–H3 bond length in the Sm–$(\mu_2$-H)–Sm single bridge is practically in agreement with those found for the complex $[(C_5H_4Me)_2Y(\mu\text{-}H) \cdot THF]_2$ (2.2 Å) [15] but is markedly smaller than those in the Sm–$(\mu_3$-H)–Sm bridge in complex VII (2.35 Å) [2] in which the hydrogen μ_3-atom is additionally bonded with the aluminium atom.

The aluminium atom bonding with each samarium atom occurs via triple asymmetric hydride bridge formed by one μ_2- and two μ_3-atoms of hydrogen. This type of coordination is characteristic of a boron atom in transition metal borohydride complexes [16] but similar complexes for aluminium are rather rare. Thus, the M–$(\mu_2$-H$)_3$–Al bridge has been described only for two compounds $(MePh_2P)_3HRe(\mu_2\text{-}H)_3AlMe_2$ [17] and $[Me_3P)_3H_2W(\mu_2\text{-}H)_3AlCl_2 \cdot NMe_3$ [18] and the presence of the M–$(\mu_2$-H$)(\mu_3$-H$)_2$–Al bridge is supposed in IX [13]. The Sm–H bond lengths for the hydrogen μ_2-atom somewhat shorter than those for μ_3-atoms (Table 4) thought within the typical limits for the rare earth metal aluminohydride complexes. The experimental data showed that the Sm–$(\mu_2$-H)–Sm and Sm–$(\mu_2$-H)–Al bridges were situated in the common bisecting plane of $(C_5H_4{}^tBu)_2Sm$ bent

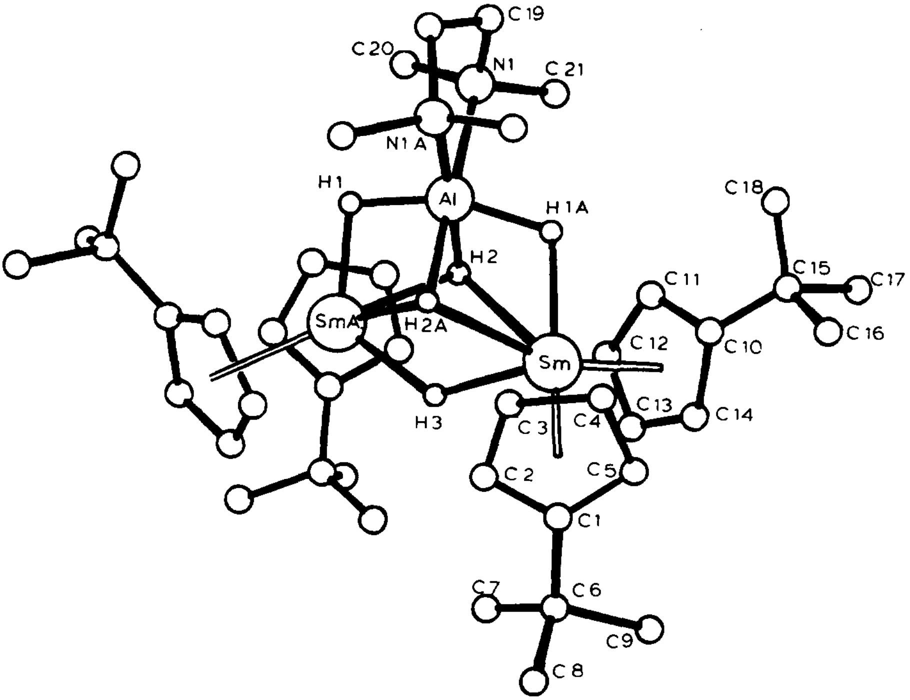

Fig. 2. The structure of $[(\eta^5\text{-}C_5H_4{}^tBu)_2Sm]_2(\mu_2\text{-}H)\mu\text{-}[(\mu_3\text{-}H)_2Al(\mu_2\text{-}H)_2 \cdot Me_2NC_2H_4NMe_2]$ (II).

Table 4

The main interatomic distances *d* (Å) and valent angles *ω* (degrees) for complex II

Bond	*d*	Bond	*d*
Sm–Cp	2.499	Sm–H2′	2.18
Sm–$C_{av.}$	2.77(4)	Sm–H3	2.16
Sm ··· Al	3.044(3)	Al–H1	1.70
Sm ··· Sm′	3.712(1)	Al–H2	1.70
Sm–H1′	2.14	Al–N	2.091(8)
Sm–H2	2.32	Al–N′	2.091(8)
Angle	*ω*	Angle	*ω*
CpISmCpII	125.5	H2A1N	107.6
Cp1SmCp2	123.5	H2A1N′	168.0
AlSmSm′	52.4	SmAlSm′	75.1(1)
H1′SmH2	61.0	AlH1Sm′	104.4
H1′SmH2′	60.4	AlH2Sm	97.1
H2SmH2′	44.7	AlH2Sm′	102.6
NA1N′	84.4(5)	SmH2Sm′	111.1
H1A1H2	79.8	SmH3Sm′	118.0
H1A1N	92.8	Cp1SmCp2/H2′SmH1′	109.1
H1AlN′	101.4	Cp1SmCp2/H_2SmH1′	98.4
H1A1H1′	160.9	Cp1SmCp2/H2′SmH2	6.3
H1A1H2′	83.7	C1–C6/CpI	7.8
H2A1H2′	60.5	C10–C15/CpII	8.5

sandwiches (the deviation did not exceed 0.07 Å). The aluminium atom lies practically in the same plane (two-sided angle between CpSmCp and Sm_2AlH3 planes are equal to 93.6°) but the hydrogen μ_3-atoms protrude from both sides of the plane.

Besides four hydrogen atoms, there are two nitrogen atoms of the TMEDA molecule in the first coordination sphere of the aluminium atom. Thus, in this complex, tetramethylethylendiamine acts as a chelate bidentate ligand as it does in complex IX. The coordinational polyhedron of the Al atom in II is a distorted octahedron (the valence angles with *trans* ligands deviate from 180° to 10–12°) (Table 4). The values of H–Al–H angles for *cis* ligands are noticeably smaller and the N–Al–H angles are larger than 90°, respectively (Table 4). It is noteworthy that this type of TMEDA coordination has not yet been detected in aluminium hydride chemistry. In known monometallic ($AlH_3 \cdot$ TMEDA [19]) or heterometallic ($[Cp_2Ti(\mu_2\text{-}H)_2AlH_2]_2 \cdot$ TMEDA [20]) species, the molecule of TMEDA is a bridging non-chelating ligand. Heterometallic hydride complexes with the octahedron surrounding the aluminium atom are also a rare case; $(Me_3P)_3H_2W(\mu_2\text{-}H)_3AlCl_2 \cdot NMe_3$ is the only complex known in which an Al atom has the coordination number 6 [17]. Obviously, for the realization of maximum coordination number it is necessary to increase the Al atom acidity and also the presence of bridge hydrogen atoms within the structure which allows arrangement of the additional ligands owing to the increase in M–H distances. In the tungsten complex these conditions are reliazed by coordination of two accepter chlorine atoms to Al and by coordination of aluminohydride group to two accepter centers (two samarium atoms) in II. The value of the Al–N bond length in II is also in agreement with the enhanced acidity of the aluminium atom. This value is comparable with that of chlorine containing complex $(Cp_2Y)_2Cl(AlH_4 \cdot NEt_3)$ (2.09 å) [12] but smaller than in complexes without accepter chlorine atoms (Table 3).

Thus, considering the structure of molecule II in general it is seen that samarium atoms coordinate besides two cyclopentadienyl ligands, four hydride ligands thereby acquiring formally a 20-electron configuration like in complexes I, VII, VIII. The bridging aluminohydride group $[(\mu_3\text{-}H)_2Al(\mu_2\text{-}H)_2 \cdot Me_2NC_2H_4NMe_2]$ in complex II acts as an eight-electron donor ligand. The analogous type of binding with the borohydride group involved was also detected for complex $(C_5H_3{}^tBu_2)_2Ce\{\mu_3\text{-}H)_2B(\mu_2\text{-}H)_2]_2\}_2$ [5]. This fact confirms the marked similarity in the behavior of boro- and aluminohydride groups as donor ligands, whereas the main differences in the structure of the complexes formed can be attributed to the greater coordination possibility of aluminium atom whose hybridization can vary from *sp*^{3} to *sp*^{3}*d*^{2} via *sp*^{3}*d*.

As seen from Table 4 the Sm ··· Al distance in II is markedly shorter compared to that in complexes with double hydrogen bridges between aluminium and rare earth metal atoms (3.24–3.30 Å) (Table 3) and is comparable with the average value (3.08 Å) for the aluminohydride group solvated by TMEDA in IX [13]. Considering good coincidence of these distances, Sm–Al–Sm angles (75.1° and 75.5°, 76.8° respectively) and the same orientation of the diamine molecule with respect to the SmAlSm triangle in II and IX, it may be concluded that the type of the aluminohydride group binding with the rare earth metal atom in both complexes is identical. As a consequence, the reconstruction of the hydride bond system in IX performed in [13] is reliable.

The isolation of the two novel biscyclopentadienyl complexes added to those already known which the metal atom coordinates four and more rather than three ligands, allows us to conclude that this phenomenon is not an exception. The data of refs. 2, 3, 5 and the present paper indicate the greater coordinational convenience for the Cp_2M moiety as was expected from the MO scheme [1]. This fact is to be taken into account while evaluating the reactivity and catalytic activity of rare earth metal and late transition metal metallocene complexes in reactions involving small molecules. The supercoordination in the Cp_2M moiety may be caused for two reasons: (a) an appreciable increase in the vertical component of three hybrid MO ($1a_1$, b_2 and $2a_1$) with respect to the bent sandwich bisecting plane and, probably, their partial outlet from the plane particular of samarium (it secures suitable overlapping with valence orbitals of ligands which are not situated in the given plane) or (b) an increase in the frontier orbital number due to participation in hybridization *f*-orbitals of a metal.

It should be noted that in all electron and coordinational oversaturated hydride derivatives of metallocenes described all or part of the hydride ligands escape from the bent sandwich bisecting plane. Thus, in complexes II and VIII [3] two internal hydrogen atoms are located out of the plane, however, the same position is occupied by two external ones in VII and by all four hydrogen atoms in I and $(C_5H_4Me)_2Hf[(\mu_2\text{-}H)_2BH_2]_2$ [4]. In complex $(C_5H_3{}^tBu_2)_2Ce\{\mu\text{-}[(\mu_3\text{-}H)_2B(\mu_2\text{-}H)_2]_2\}_2$ [5] four internal ones out of an overall number 6 are also situated out of the

Table 5

Summary of crystal data for complexes I and II

	I	II
Formula	$C_{32}H_{58}N_2Al_2Sm_2$	$C_{42}H_{73}N_2AlSm_2$
Mol. weight	825.51	933.76
a (Å)	11.012(3)	16.652(5)
b (Å)	11.911(3)	18.720(5)
c (Å)	14.314(4)	16.499(5)
α (deg)	88.76(2)	90
β (deg)	78.65(2)	90
γ (deg)	96.17(2)	91.77(2)
V (Å^3)	1828.3(1.4)	5140.7(4.3)
μ_{Mo} (cm^{-1})	33.1	23.1
Space group	Triclinic, $P\bar{1}$	Monoclinic, $B2/b$
Z	4	8
$\rho_{calc.}$ (g/cm^3)	1.47	1.18
Diffractometer	Syntex $P\bar{1}$	Nicolet P3
Monochromator	None	None
Scan technique	$\theta/2\theta$	$\theta/2\theta$
Irradiation	Mo-K_α	Mo-K_α
No. of reflections with $I > 3\sigma(I)$	2758	1965
Programs	SHELXTL	SHELXTL
Solution	Direct method	Direct method
Weight	$1/\sigma^2(F)+0.00422F^2$	$1/\sigma^2(F)+0.00229F^2$
GOF	1.04	0.98
R	0.051	0.036
R_w	0.058	0.040

plane. This diversity of the coordination types caused rather by steric hindrances favor the first proposal. Supercoordination was observed for both the elements at the start (Ce) and the end (Lu) of the lantanide row although the *f*-level energy showed considerable changes [21].

Experimental

All synthetic and sampling procedures were carried out under vacuum or dry argon as described in ref. 6.

Samaricene chlorides $[(C_5H_4{}^tBu)_2Sm(\mu\text{-}Cl)]_2$ and $[(C_5H_5)_2Sm(\mu\text{-}Cl)]_2$ were prepared by the exchange reaction of $SmCl_3$ with sodium salts of corresponding cyclopentadienes and were purified by sublimation in vacuum.

$[(C_5H_5)_2Sm(\mu_3\text{-}H)]_2[(\mu_2\text{-}H)_2AlH \cdot N(C_2H_5)_3]_2$ *(I)*

A solution of 0.04 g (1.03 mmol) of $LiAlH_4$ in 20 ml of diethyl ether was added to a suspension of 0.326 g (1.03 mmol) of $(C_5H_5)_2SmCl$ in 200 ml of diethyl ether under stirring. Then a solution of 0.726 g (7.2 mmol) of triethylamine was added and the reaction mixture was stirred for 5 h. The color of the solution changed from yellow to yellow-green and a white precipitate of LiCl sedimented. The sediment

Table 6

Atomic coordinates ($\times 10^4$, hydrogen atoms, $\times 10^3$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for complex II

Atom	*x*	*y*	*z*	B_{eq}
Sm	945(1)	3053(1)	924(1)	58(1)
Al	0000	2500	−538(2)	57(1)
C1	811(6)	4193(5)	2024(6)	68(4)
C2	82(7)	4160(5)	1607(8)	88(5)
C3	229(10)	4331(6)	810(8)	101(6)
C4	1020(13)	4497(6)	709(7)	123(7)
C5	1400(7)	4413(5)	1470(7)	92(5)
C6	848(6)	4137(5)	2962(6)	76(4)
C7	380(8)	3506(7)	3265(7)	114(6)
C8	514(12)	4807(9)	3318(9)	178(9)
C9	1731(8)	4068(8)	3232(7)	126(6)
C10	2599(6)	2799(8)	712(6)	93(5)
C11	2193(6)	2136(7)	558(8)	97(5)
C12	1840(8)	1903(9)	1303(13)	129(7)
C13	2013(9)	2410(11)	1900(8)	120(7)
C14	2476(7)	2916(9)	1563(7)	113(6)
C15	3171(7)	3167(8)	139(7)	107(6)
C16	3304(19)	3905(14)	317(15)	352(19)
C17	3994(10)	2885(24)	251(13)	374(28)
C18	2992(10)	3060(10)	−697(8)	153(8)
N	341(6)	1823(4)	−1477(5)	81(3)
C19	333(9)	2271(7)	−2219(6)	130(7)
C20	−217(9)	1181(7)	−1543(8)	122(6)
C21	1185(8)	1576(6)	−1361(8)	118(6)
H1	−87	203	−37	120
H2	23	210	35	80
H3	000	250	160	120

was filtered off and the filtrate was evaporated to half volume. In 24 h a small amount of additional LiCl precipitate was filtered off and the evaporation was repeated. In 48 h yellow-green trapeze-like plates (0.18 g, yield 42%) were separated from the mother liquid by decantation, washed by cold pentane and dried under vacuum. Found: Sm, 36.2; Al, 6.4. $C_{32}H_{58}N_2Al_2Sm_2$ calc.: Sm, 36.43; Al, 6.54%.

$[(C_5H_4{}^tBu)_2Sm]_2(\mu_2\text{-}H)\mu\text{-}[(\mu_3\text{-}H)_2Al(\mu_2\text{-}H)_2 \cdot Me_2NC_2H_4NMe_2]$ (II) A solution of 0.037 g (0.97 mmol) of $LiAlH_4$ and 0.78 g (6.7 mmol) of TMEDA in 15 ml of diethyl ether was added dropwise to a suspension of 0.415 g (0.97 mmol) of $(C_5H_4{}^tBu)_2SmCl$ in 110 ml of ether. The color of the solution changed from yellow to light green and a white precipitate formed. The reaction mixture was stirred for 2 h. Then the precipitate of LiCl was filtered off and the filtrate was evaporated under vacuum to ~ 15 ml. Colorless triangle plate crystals separated in 48 h. According to elemental analysis (found: Al, 15.4; $C_6H_{22}N_2Al_2$ calc.: Al, 15.36%) and the IR data, this substance is the TMEDA solvate of aluminium hydride. After separation of $(AlH_3)_2 \cdot$ TMEDA, the mother solution was evaporated to ~ 10 ml and allowed to stand overnight. Then the solid was separated, washed with cold pentane and dried under vacuum; 0.22 g (yield 48%) of green cubic crystals were obtained. Found: Sm, 32.0; Al, 3.0. $C_{42}H_{73}N_2AlSm_2$ calc.: Sm, 32.20; Al, 2.89%.

X-Ray crystal analysis of I and II Single crystals of complexes I and II were sealed in a glass capillary. Their crystal parameters and X-ray analysis data are given in Table 5. A characteristic feature of the crystal structure of complex I is the presence of two crystallographically independent molecules in the unit cell. The hydride hydrogen atoms for both structures were localized by differential synthesis. The structures were solved by the direct method and verified by the least-squares method in the anisotropic (isotropic for hydrogen atoms) approximation up to *R* values listed in Table 5. The atomic coordinates are listed in Tables 1 and 6; the main interatomic distances and bond angles are given in Tables 2 and 4.

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