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Crystal and molecular structures of the octanuclear aluminohydride samarium complex $(\eta^5\text{-}C_5H_3{}^tBu_2)Sm[(\mu_2\text{-}H)_2(\mu_3\text{-}H)_2Al(Me_2NC_2H_4NMe_2)]_2$ $[(\eta^5\text{-}C_5H_3{}^tBu_2)SmH]_2[(\mu_2\text{-}H)_3Al(\mu_2\text{-}H)Al(\mu_2\text{-}H)_3]$ $[(\mu_3\text{-}H)_2Sm(\eta^5\text{-}C_5H_3{}^tBu_2)_2]$

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Abstract

The reaction of $(C_5H_4{}^tBu_2)_2Sm$ with AlH_3 in ether or $(C_5H_4{}^tBu_2)_2Sm\cdot THF$ with AlH_3 in THF in the presence of excess of TMEDA and pentane involves the oxidation of Sm(2+) to Sm(3+), partial loss of Cp″-ligands and formation of the octanuclear complex $Cp''_5Sm_4(AlH_4)_3\cdot 2Me_2NC_2H_4NMe_2$, the cyclic metal core of which resembles a sitting frog. Atoms Sm1, Sm3 and Sm4 are coordinated with one Cp″-ligand each, while Sm2 is bonded with two Cp″-ligands. All metals of the complex are bonded by μ_2- and μ_3-bridging hydrogens.

Introduction

It has previously noted that dinuclear titanocene [1] and lutetiecene [2] aluminohydrides are unstable and have a tendency to form polynuclear, hydrogen-bridged clusters. In the titanium case, for example, there is a partial dissociation of aluminium hydride and crystallization of the hexanuclear complex $[Cp_2TiH_2Al(H)\text{-}(C_5H_4)TiCp]_2$ ($Cp = \eta^5\text{-}C_5H_5$, $Cp'' = \eta^5\text{-}C_5H_3{}^tBu_2$, $Cp^* = \eta^5\text{-}C_5Me_5$) with a metal core of sea-gull type [1]. This compound is probably more stable in the system $(Cp_2TiCl)_2\text{–}LiAlH_4\text{–}Et_2O$ and may be formed in different crystalline forms in the presence of traces of oxygen and water [3], or of compounds with acidic hydrogen [4], as well on decomposition of the trinuclear complex $(Cp_2Ti)_2AlH_4X$ (X = Alk, Ph) [4,5]. The octanuclear complex $\{[Cp^{*}(C_5Me_4CH_2)TiH_2Al]_2O\}_2$ crystallizes from the system $Cp_2^{*}TiCl–LiAlH_4–Et_2O$ in the presence of traces of water [6].

The other pathway involving a dissociation of the bulky di-tert-butylcyclopentadienyl ligand leads to the octanuclear lutetium complex $[Cp''Lu(H)AlH_4 \cdot 0.5Et_2O]_4$ with a cubic metal core which was also obtained in two crystalline modifications [7].

A study of such polynuclear compounds is important for understanding the "aging" and deactivation of the Ziegler–Natta catalytic systems which include aluminium alkyls or hydrides.

In this work we report the results of an X-ray diffraction study and the construction of the system of hydridic bonds in the samarium complex of the general formula $Cp_5''Sm_4H_3(ALH_4)_4 \cdot 2Me_2NC_2H_4NMe_2$ (I) formed form $Cp_2''Sm \cdot THF$ and $AlH_3 \cdot L$.

Results and discussion

Contrary to what might be expected, the reaction of $Cp_2''Sm \cdot THF$ or $Cp_2''Sm$ with aluminium hydride in ether does not lead to a stable adduct analogous to $Cp_2^{*}Yb(\mu\text{-}Et)AlEt_2 \cdot THF$ [8] or $Cp_2^{*}Yb(\mu\text{-}Me)BeCp^{*}$ [9], but results in evolution of H_2 and precipitation of Al metal. After separation of the precipitate, concentrating and successive treatment of the solution with $Me_2NC_2H_4NMe_2$ (TMEDA) and pentane, yellow-green crystals of I as apex-linked rhombs or plates begin to appear. The analytical data suggest a Sm : Al ratio of about 1 : 1 and a general formula of $Cp_5''Sm_4(AlH_4)_4H_x \cdot 2Me_2NC_2H_4NMe_2$. The evolution of H_2 and precipitation of aluminium suggests that the formation of I, as well as the reaction of the anionic complex $Na[Sm(C_5H_4{}^tBu)_3]$. THF with aluminium hydride tetrahydrofuranate leading to $[(C_5H_4{}^tBu)_2Sm(\mu_3\text{-}H)]_2[(\mu_2\text{-}H)_2AlH \cdot THF]_2$ (II) [10], involves the oxidation of samarium(2 +) into samarium(3 +). In the complex, however, the ratio Cp″ : Sm is much less than 2 indicating a partial cleavage of the metallocene structure, probably as a result of the transfer of Cp″ at aluminium. It should be pointed out that the formation of I depends neither on the presence of THF in the reaction medium nor on the step at which TMEDA is added, but on the alkane treatment. It indicates that together with the oxidation of samarium(2 +) the synthesis of I involves re-solvation (of ether or THF by TMEDA) and desolvation (on dilution with inert solvent). Such steps were invoked to account for the formation of the octanuclear lutetium and aluminium complex $Cp_4''Lu_4H_4(AlH_4)_4 \cdot 2Et_2O$ (III) [7].

Only the bands from the bridging Sm–H–Al and Al–H–Al bonds are observed in the IR spectrum: $\nu(Al–H^b) = 1600–1560\ cm^{-1}$, respectively. There is no direct evidence for the presence of terminal Sm–H bonds in the IR spectrum. The corresponding part of the spectrum is too complicated and difficult to analyze, since the literature concerning $\nu(Sm–H^t)$ is too scarce.

The diffraction X-ray data reveal that the crystals of I comprise isolated octanuclear molecules containing four samarium and four aluminium atoms (Fig. 1). Samarium atoms are located in one plane (deviations 0.01–0.02 Å) in the apices of the tetragon with mutually equal edges and one acute angle. At the apex of the acute angle, there Sm2 is coordinated with two $\eta^5\text{-}C_5H_3{}^tBu_2$-ligands. Three other samariums are coordinated with only one cyclopentadienyl ligand. Similar mixed binding of Cp^{*}-ligands with ytterbium was observed previously in $[Cp_5^{*}Yb_5OCl_8(Et_2O)_2]$ [11] (it should however be mentioned that in addition to one wedge-like

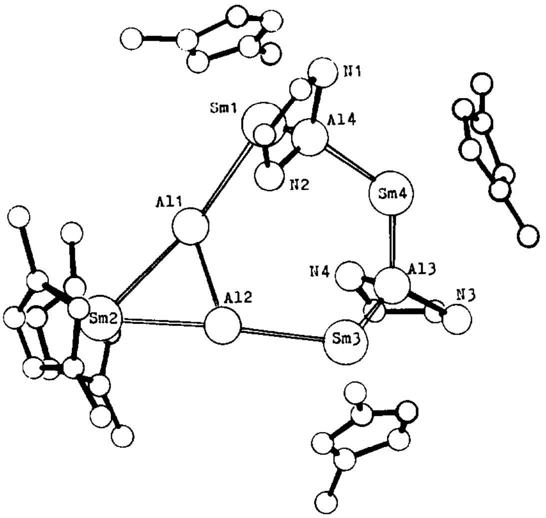


Fig. 1. The metal core of $(\eta^5\text{-}C_5H_3{}^tBu_2)Sm[(\mu_2\text{-}H)_2(\mu_3\text{-}H)_2Al(Me_2NC_2H_4NMe_2)]_2[(\eta^5\text{-}C_5H_3{}^tBu_2)\text{-}SmH]_2[(\mu_2\text{-}H)_3Al(\mu_2\text{-}H)Al(\mu_2\text{-}H)_3][(\mu_3\text{-}H)_2Sm(\eta^5\text{-}C_5H_3{}^tBu_2)_2]$.

sandwich Cp_2^*Yb and three Cp^*Yb fragments there is one Yb centre with a purely inorganic environment). As in III [7] and $Cp_2Y[(\mu_2\text{-}H)_2(\mu_3\text{-}H)AlH \cdot Et_2O][(\mu_2\text{-}H)_2\text{-}AlH_2]YCp_2$ (IV) [12], aluminium centres in I are nonequivalent: two of the four aluminiums (Al1 and Al2), probably having a purely hydrogen environment, are practically in the samarium plane deviating (in opposite directions) by ca. 0.1 Å, while the remaining ones are coordinated by TMEDA and substantially out of this plane (by ca. 2.4 Å). To this end, the metal core of I has a symmetry close to C_2, the pseudo two-fold axis passing through Sm2 and Sm4.

Unfortunately, the difference syntheses did not provide the coordinates of all the hydrogens, the precision being low because of the necessity of taking many atoms into account. Therefore, on the basis of the stoichiometry of the complex and the literature data concerning the composition of aluminohydride REM complexes with yttrium, we have constructed a system of the hydride bonding in molecule I. The following bond lengths have been used: Sm–H 2.2–2.3 Å and Al–H 1.7–1.8 Å [13].

Obviously, the number of hydrogens in I is determined by the oxidation state of samarium. It is seen from Table 1 that all Sm–Cp″ distances are very similar to each other and to the Sm–Cp′ distance in complex II incorporating samarium(3 +) (2.48 Å). In samarium(2 +) complexes, the distance Sm–Cp is much larger, 2.56–2.66 Å in $Na[Sm(C_5H_4{}^tBu)_3] \cdot THF$ and 2.55 Å in $Cp_2''Sm \cdot THF$ [14]. Taking also into account the fact that the formation of I proceeds with oxidation of samarium(2 +) it may be concluded that all REM in the complex have the same oxidation state of 3 + . Hence, the composition of the complex should be formulated as $Cp_5''Sm_4H_3\text{-}(AlH_4)_4 \cdot 2Me_2NC_2H_4NMe_2$.

The symmetry of I suggests that the ways of the binding of pairs of atoms Sm1 and Sm4, Sm3 and Sm4, on one hand, and Sm1 and Sm2, Sm2 and Sm3, on the other, may be identical. Solvated by TMEDA, the aluminohydride groups are located, as in related complexes [10,12,15], symmetrically with respect to the bridged pairs of atoms Sm4 ··· Sm1(Sm3). However, the coordination sphere of Al in I

Table 1

Main interatomic distances *d* (Å) in molecule I

Sm1–CpI	2.46	Sm3–H6	2.2(1)
Sm2–CpII	2.48	Sm3–H9	2.2(1)
Sm2–CpIII	2.49	Sm4 ··· Al3	3.13(1)
Sm3–CpIV	2.45	Sm4 ··· Al4	3.13(1)
Sm4–CpV	2.52	Sm4–H8	2.3(1)
$Sm-C_{av}$	2.80(6)	Sm4–H9	2.3(1)
Sm1 ··· Al1	3.12(1)	Al1 ··· Al2	2.56(1)
Sm1 ··· Al4	3.00(1)	Al1–H4	1.7(1)
Sm1 ··· Sm4	3.75(1)	Al1–H5	1.6(1)
Sm1–H3	2.0(1)	Al1–H10	2.3(1)
Sm1–H5	1.9(1)	Al2–H2	1.8(1)
Sm1–H10	1.6(1)	Al2–H6	1.9(1)
Sm2 ··· Al1	3.09(1)	Al2–H7	1.7(1)
Sm2 ··· Al2	3.09(1)	Al3–N3	2.14(4)
Sm2–H4	1.7(1)	Al3–N4	2.15(3)
Sm2–H7	2.3(1)	Al3–H1	2.1(1)
Sm3 ··· Al2	3.07(1)	Al3–H9	1.6(1)
Sm3 ··· Al3	2.96(1)	Al4–N1	2.12(3)
Sm3 ··· Sm4	3.75(1)	Al4–N2	2.06(3)
Sm3–H1	1.9(1)	Al4–H3	1.8(1)
Sm3–H2	2.1(1)	Al4–H8	1.4(1)

contains two, rather than one, donor atoms of the Lewis base. It should be mentioned that in all the known aluminohydride complexes solvated with TMEDA, the latter usually behaves as a bidentate binucleating ligand. For the complexes $[AlH_3 \cdot Me_2NC_2H_4NMe_2]_n$ ($d_{Al-N} = 2.20$ Å) [16] the nitrogens are in the axial positions of a trigonal bipyramid around Al (*trans*), whereas in $[Cp_2TiH_2AlH_2]_2 \cdot Me_2NC_2H_4NMe_2$ ($d_{Al-N} = 2.11$ Å) the nitrogens are in a *cis* position. Such a coordination of TMEDA precludes terminal hydrogens at Al. Evidently, two nitrogens may be positioned *cis*, since bridging $Al-H^b$ bonds are much longer than the terminal ones. Therefore, two coordination polyhedra are possible around Al3 and Al4: either a trigonal bipyramid, typical of transition metal aluminohydrides [13] with the equatorial and the axial ligands being two nitrogens, one μ_3-hydrogen and μ_2-hydrogens, respectively, or a distorted octahedron with two nitrogens and two μ_3-hydrogens in *cis* position and two μ_2-hydrogens in *trans* position. Since the oxidation state of all samariums in I is three, the latter model seems to be more likely. In its favour are the values of the bond angles N–Al–(μ_3-H) (Table 2) close to 90 and 180°, rather than to 120°, as well as the short non-bonding distances Sm ··· Sm and Sm ··· Al in these fragments. In particular, in I the distances Sm ··· Al are shorter than those in the complexes with the trigonal bipyramid ligation of Al by 0.15–0.32 Å in II with two μ_2- and one μ_3-bridging hydrogens [10], by 0.07–0.24 Å in IV [12], by 0.11–0.28 Å in $(Cp_2Y)_2(\mu_2\text{-Cl})(\mu_2\text{-H})_2(\mu_3\text{-H})AlH \cdot NEt_3$ (V) [18] (although the covalent radius of Sm is 0.04 Å larger than that of Y). Therefore, assuming the octahedral coordination at Al3 and Al4, one may assume with confidence that the $AlH_4 \cdot$TMEDA groups in I are tetradentate, $8e^-$ ligands with two μ_2- and two μ_3-hydrogens (both types, H1, H8 and H3, H9, respectively, were located in the difference synthesis). A similar coordination mode was previ-

Table 2

Main bond angles ω (°) in molecule I

Cp1Sm1Al1	116.5	Cp5Sm4Al3	113.6
Cp1Sm1Al4	126.8	Cp5Sm4Al4	112.6
Cp1Sm1H3	97.0	Cp5Sm4H8	94.6
Cp1Sm1H5	122.1	Cp5Sm4H9	142.1
Cp1Sm1H10	83.3	Sm1Sm4Sm3	97.8(1)
AlSm1Al4	101.7(3)	Al4Sm4Sm3	138.1(3)
AlSm1Sm4	99.6(3)	H8Sm4H9	107.6
H3Sm1H5	76.5	Sm1Al1Sm2	171.8(4)
H3Sm1H10	140.6	H4Al1H5	140.7
H5Sm1H10	70.9	H4Al1H10	140.5
CpIISm2CpIII	115.6	H5Al1H10	70.5
Al1Sm2Al2	48.9(3)	Sm2Al2Sm3	174.4(4)
H4Sm2H7	103.4	H2Al2H6	79.9
Cp4Sm3Al2	115.5	H2Al2H7	96.0
Cp4Sm3Al3	128.0	H6Al2H7	114.3
Cp4Sm3H1	97.1	N3Al3N4	87.0(13)
Cp4Sm3H2	94.3	N3Al3H1	97.6
Cp4Sm3H6	103.2	N3Al3H9	169.6
Cp4Sm3H9	158.0	N4Al3H1	98.6
H1Sm3H2	65.1	N4Al3H9	103.3
H1Sm3H6	132.6	H1Al3H9	70.1
H1Sm3H	69.9	Sm3Al3Sm4	76.8(3)
H2Sm3H6	67.6	N1Al4N2	85.5(11)
H2Sm3H9	87.7	N1Al4H3	96.5
H6Sm3H9	107.6	N1Al4H8	97.7
Al2Sm3Al3	139.3(3)	N2Al4H3	96.5
Al2Sm3Sm4	101.5(3)	N2Al4H8	168.9
Sm1Al4Sm4	75.5(2)	H3Al4H8	93.1

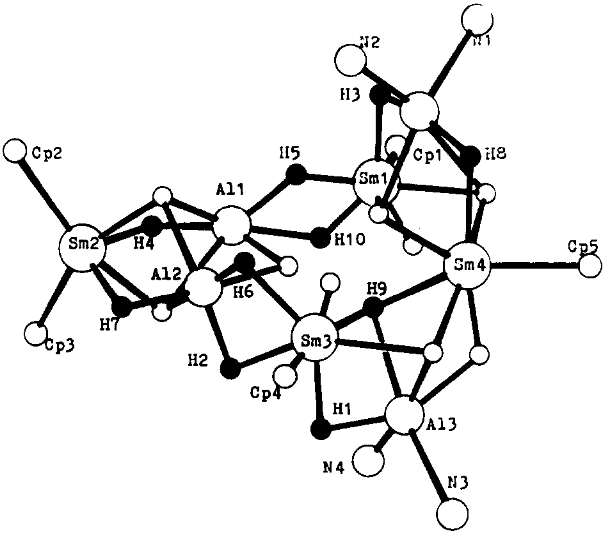


Fig. 2. The reconstruction of the hydride bonding system (shaded circles showing the hydrogen atoms located by difference synthesis).

Table 3

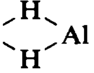
Atomic coordinates ($\times 10^4$, hydrogen atoms $\times 10^3$) and equivalent isotropic displacement coefficients

Atom	x	y	z	B_{eq}
Sm1	4406(1)	1420(1)	3363(1)	53(1)
Sm2	3088(1)	4057(1)	3709(1)	55(1)
Sm3	3283(1)	1688(1)	1551(1)	54(1)
Sm4	4177(1)	407(1)	2116(1)	74(1)
Al1	3737(3)	2740(6)	3582(5)	56(4)
Al2	3189(3)	2801(6)	2673(5)	58(4)
Al3	3790(4)	−95(6)	3432(5)	74(5)
Al4	4257(4)	1933(6)	1254(5)	78(5)
C1	5271(8)	2003(17)	4062(17)	65(12)
C2	4960(12)	2329(20)	4513(16)	59(16)
C3	4725(8)	1706(16)	4870(11)	62(12)
C4	4861(11)	946(19)	4661(16)	73(16)
C5	5197(9)	1142(15)	4181(14)	81(13)
C6	5639(8)	2465(17)	3680(13)	78(13)
C7	5465(11)	3307(17)	3482(15)	99(16)
C8	6069(10)	2665(22)	4101(16)	118(18)
C9	5750(10)	1947(19)	3098(13)	108(15)
C10	4431(11)	1848(22)	5428(15)	68(16)
C11	4730(10)	1801(18)	6027(12)	94(15)
C12	4261(10)	2696(17)	5384(13)	84(14)
C13	4049(10)	1151(17)	5475(14)	96(15)
C14	2148(10)	3350(19)	3892(13)	91(15)
C15	2403(12)	3024(22)	4281(18)	87(17)
C16	2609(10)	3513(18)	4756(15)	88(15)
C17	2520(10)	4298(22)	4649(11)	92(15)
C18	2288(10)	4324(16)	4138(14)	86(15)
C19	1768(11)	3201(19)	3427(16)	119(17)
C20	1322(10)	3116(30)	3747(21)	171(25)
C21	1896(11)	2374(27)	3166(20)	194(24)
C22	1772(13)	3738(26)	2843(19)	176(23)
C23	2831(16)	3215(25)	5366(21)	90(22)
C24	3188(16)	3798(27)	5594(16)	116(23)
C25	2434(11)	3125(22)	5874(16)	137(19)
C26	2970(11)	2389(19)	5278(15)	109(17)
C27	3817(11)	5274(15)	3886(14)	64(14)
C28	3743(10)	5245(14)	3239(15)	72(14)
C29	3309(10)	5499(17)	3070(13)	88(15)
C30	3127(12)	5681(20)	3672(25)	90(7)
C31	3433(18)	5537(22)	4135(17)	65(18)
C32	4259(8)	5251(18)	4216(18)	93(16)
C33	4201(12)	4919(22)	4883(16)	129(19)
C34	4491(9)	6190(19)	4202(17)	117(17)
C35	4552(9)	4691(21)	2873(20)	149(20)
C36	3133(15)	5713(24)	2445(18)	83(19)
C37	3391(14)	5194(22)	1939(13)	143(21)
C38	3283(13)	6656(14)	2352(13)	155(18)
C39	2624(11)	5505(20)	2396(13)	133(17)
C40	2448(12)	995(13)	1141(16)	59(17)
C41	2413(13)	1862(28)	1178(18)	77(19)
C42	2674(15)	2284(24)	742(22)	90(21)
C43	2916(11)	1716(26)	404(15)	67(16)

Table 3 (continued)

Atom	*x*	*y*	*z*	B_{eq}
C44	2754(12)	947(21)	671(17)	71(16)
C45	2156(11)	310(22)	1473(15)	66(15)
C46	2362(12)	−454(17)	1473(18)	141(19)
C47	2060(11)	619(19)	2153(15)	97(16)
C48	1677(12)	326(21)	1149(17)	123(18)
C49	2656(15)	3153(23)	514(20)	82(20)
C50	2360(12)	3206(20)	−28(15)	136(18)
C51	3114(15)	3573(29)	415(22)	155(28)
C52	2522(13)	3667(16)	1060(15)	115(18)
C53	4229(13)	−888(22)	1291(19)	76(17)
C54	4626(11)	−410(19)	1199(16)	121(17)
C55	4906(13)	−448(23)	1764(22)	73(19)
C56	4618(18)	−940(26)	2129(20)	108(22)
C57	4202(16)	−1217(25)	1901(24)	130(24)
C58	3894(13)	−1198(23)	807(17)	99(18)
C59	3943(11)	−2070(16)	575(16)	127(17)
C60	3403(16)	−1055(25)	1041(20)	158(24)
C61	3946(15)	−574(27)	209(223)	146(25)
C62	5403(12)	−234(24)	1887(18)	86(18)
C63	5688(15)	−864(26)	1587(20)	125(23)
C64	5476(14)	−212(23)	2608(21)	142(22)
C65	5561(14)	632(27)	1652(19)	136(22)
N1	3807(8)	−1202(16)	3914(12)	100(14)
N2	3120(8)	−180(15)	3690(12)	79(12)
C66	3925(13)	−1832(22)	3521(17)	129(19)
C67	4134(10)	−1071(18)	4463(14)	110(16)
C68	3386(18)	−1368(31)	4120(24)	198(28)
C69	3055(16)	−811(28)	4112(22)	168(26)
C70	2856(14)	−451(25)	3129(20)	141(23)
C71	2979(11)	533(22)	3876(24)	189(25)
N3	4539(13)	2074(23)	339(16)	109(17)
N4	4662(9)	3035(15)	1494(12)	92(13)
C72	4790(12)	1392(23)	140(16)	114(18)
C73	4168(11)	2228(23)	−139(12)	127(18)
C74	4848(18)	2767(33)	410(23)	184(29)
C75	4804(13)	3412(22)	937(18)	152(21)
C76	4383(12)	3575(21)	1897(17)	147(19)
C77	5022(11)	2872(19)	1890(16)	116(17)
H1	365	243	110	70
H2	330	289	186	70
H3	401	50	411	70
H4	353	352	391	70
H5	385	183	375	70
H6	286	181	238	70
H7	289	357	271	70
H8	422	−4	313	70
H9	399	170	187	70
H10	448	241	362	70

ously found by us for the BH_4-group in $\{Cp''_2Ce(\mu\text{-}[(\mu_2\text{-}H)_2B(\mu_3\text{-}H)_2])\}_2\{Cp''_2Ce(\mu\text{-}[(\mu_2\text{-}H)_2B(\mu_3\text{-}H)_2])\}_2$ [19] and assumed for the fragment $[AlH_4 \cdot OEt_2]$ in complex III [2,7].

As mentioned above, Al1 and Al2 are surrounded by hydrogens only. The same was previously assumed to occur in complexes III [7] and IV [12] for non-solvated aluminium atoms. If the coordination of Al is 4, the distance Y · · · Al in IV is equal to 3.55 Å, but if it is 5, the distance Ln · · · Al in III lies in the range 3.23–3.25 Å [7]. In complex I, the distance Al1(Al2) · · · Sm is much shorter (Table 1) and may be indicative of an increasing coordination number of these Al atoms to 6. Binding with Sm1 and Sm3 probably occurs through double hydrogen bridges  $\mathrm{Sm}\!<\!\overset{\mathrm{H}}{\underset{\mathrm{H}}{\,}}\!>\!\mathrm{Al}$ including H2, H5, H6 and H10 revealed from the difference synthesis.

One can note a very short non bonding contact, Al1 · · · Al2 (Table 1) which is noticeably lower than that in the sterically hindered complex $\{[(Me_3Si)_2CH]_2Al\}_2$ having a direct intermetallic bond Al–Al (2.66 Å) [20]. The occurrence of these in I, however, is much less probable, since this would indicate the reduction of Al to a lower oxidation state. The hexagonal modification of polymeric aluminium hydride $(AlH_3)_n$ ($d_{Al \cdots Al} = 3.26$ Å) involves bonding between Al atoms through hydrogens located in the apices of the octahedrons (AlH_6) (single Al–H–Al bridge) [21]. Assuming that undistorted octahedra are linked through common edges (double hydrogen bridging), the interatomic distance Al · · · Al is estimated to be about 2.65 Å (it is possible that such bonding is realized in one of the numerous crystallographic modifications of Al hydride [22]). For example, in $[Cp^*_2TiH_2AlH(\mu_2\text{-}H)]_2$ with a double hydrogen bridge trigonal bipyramid Al atoms the distance Al · · · Al decreases to 2.80 Å [23]. Even the more pronounced shortening may be expected on binding Al atoms by a triple hydrogen bridge. In fact an estimate of the Al · · · Al distance on the assumption that the bond angle is close to 65° (typical of the complex with $Al\text{–}H^b$ bridges) gives the value of ca. 2.6 Å close to that in the complex (Table 1). Since the structural model of I adopts this coordination at Al1 and Al2, we shall take it into account further.

The geometry of the one wedge-like sandwich $(\eta^5\text{-}C_5H_3{}^tBu_2)_2Sm$ in I differs from that in biscyclopentadienylaluminohydride complexes of yttrium and REM by the lower bond angles Cp–M–Cp (Table 2) (for example, 10° lower than in II [10]). This, as well as the eclipsed conformation of the cyclopentadienyl rings, is obviously due to the absence of bulky frontal ligands at Sm and non-hydrogen ligands in the second coordination sphere. Together with the short non bonding Sm2 · · · Al distance (Table 1) and the large bond angle H4–Sm–H7 (Table 2), this leads to the conclusion that besides the $Sm\text{–}(\mu_2\text{-}H)\text{–}Al$ bridges confirmed by the difference synthesis, there is additional binding in I, through the μ_3-hydrogens. Calculations show that these atoms cannot be located in the bisector plane of the wedge-like sandwich because of the short non bonding contacts, and the atoms probably leave the plane. Assuming that the triple bridge AlH_3Al is made of two μ_3-hydrogens from the bisector plane and one μ_2-hydrogen locating in this plane, one arrives at the octahedral polyhedron at Al1 and Al2 elongated along the order axis. Thus, the Al · · · Al2 fragment can be regarded as a complex ligand $[Al_2H_9]^{3-}$ which binds three samarium(3 +) ions.

Naturally, the short Sm2–Cp″ distance is insufficient evidence for ruling out the presence of samarium(2 +) in complex I, especially if the synthetic pathway to this compound and inability to prepare it from $Cp_2''SmCl$ are taken into account. In this case the bonding between Sm2 and Al1, Al2 should involve two μ_2- and μ_3-hydrogen locating in the bisector plane of the wedge-like sandwich, while the coordination number of Al atoms in $[Al_2H_8]^{2-}$ should be equal to 5. However, taking into consideration the short non bonding contacts Sm2 ··· Al and Al1 ··· Al2: for the former model coordination number of Al equal to 6 and samarium(3 +) seems to be more probable.

According to the stoichiometry of complex I, there are two more hydrides. Since Al atoms in $[AlH_4 \cdot Me_2NC_2H_4NMe_2]$ and $[Al_2H_9]$ are coordinatively saturated, these two are linked with Sm1 and Sm3, respectively, and positioned in the "empty" space between them ($d_{Sm1 \cdots Sm3} = 5.75$ Å). If this is so, each samarium in the monocyclopentadienyl fragments of I is bonded with 6 hydrogens and has an $18e^-$ configuration (coordination number of Sm = 9).

The proposed model is shown in Fig. 2. It accounts for all the features observed, including the IR spectral data. Localized in the difference synthesis, hydrogens H1–H10 are located in positions close to those calculated on the basis of the model. Therefore, the formation of octanuclear complex I in the system $Cp_2''Sm$–THF–AlH_3–L demonstrates again the tendency of aluminohydride metallocene complexes to form polynuclear, polycyclic structures characterized by increased stability.

Experimental

Synthesis of $Cp_5''Sm_4(AlH_4)_4H_3 \cdot 2Me_2NC_2H_4NMe_2$. To a solution of unsolvated $(C_5H_3{}^tBu_2)_2Sm$ (0.25 g, ca. 0.5 mmol) in 90 ml anhydrous diethyl ether a solution of AlH_3 (0.33 g, 1.1 mmol) in 25 ml ether was slowly added dropwise. The addition was accompanied by evolution of gas, formation of a dark-grey, almost black, precipitate and a change in colour from dark green to dark brown and finally to green–yellow. After addition of $AlH_3 \cdot$ TMEDA (0.6 ml, 4 mmol) was introduced into the reaction mixture. The mixture was stirred for 24 h, the precipitate filtered off, and the filtrate was concentrated fivefold. Yellow–green crystals of I appeared on the flash walls after 48 h and were separated, washed with cold pentane and vacuum dried to yield 0.27 g (35%) of the material. Anal. Found: Sm, 39.1; Al, 7.1. I. $C_{77}H_{156}N_4Al_4Sm_4$ calcd.: Sm, 38.83; A., 6.99%.

An X-ray diffraction study of I. A single crystal of I packed in a glass capillary was mounted on a Syntex $P\bar{1}$ diffractometer (Mo-K_α radiation, Nb-filter, $\theta/2\theta$-scanning, $2\theta_{max} = 45°$). Crystals of I are monoclinic: $a = 29.801(6)$, $b = 16.649(3)$, $c = 21.469(4)$ Å, $\gamma = 96.12(2)°$, $V = 10592(6)$ Å^3, space group $P2_1/a$, $Z = 4$, $\rho = 1.17$ g/cm^3. Calculations were based the 3807 independent reflections with $I > 3\sigma(I)$. The structure was solved by the Patterson method using SHELXTL program. Coordinates of cyclopentadienyl, ethylene, TMEDA and methyl hydrogens were not used in the refinement. Ten metal-bonded hydrogens were revealed in the difference synthesis. The structure was refined by the least-squares technique in anisotropic (hydrogens in isotropic) approximation with the weight scheme $w = 1/\sigma^2(F) + 0.00122F^2$ to the final value of $R = 0.054$ ($R_w = 0.057$). Atomic coordinates, main interatomic distances and bond angles are listed in Tables 1–3.

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