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The crystal and molecular structure of the 20-electron alumohydride complex of bis(t-butylcyclopentadienyl)samarium $\{[(\eta^5\text{-}C_5H_4Bu^t)_2Sm(\mu_3\text{-}H)][(\mu_2\text{-}H)_2AlH\cdot OC_4H_8]\}_2$

Yu.K. Gun'ko, B.M. Bulychev *, A.I. Sizov,
Department of Chemistry, Moscow State University, 119899, Moscow (U.S.S.R.)

V.K. Bel'sky
L. Ya. Karpov Physico-Chemical Research Institute, 107120, Moscow (U.S.S.R.)

and G.L. Soloveichik
Institute of Chemical Physics, Academy of Sciences of the U.S.S.R., 142429, Chernogolovka (U.S.S.R.)

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Abstract

The reaction of one equivalent of the samarium(II) $Na[(C_5H_4Bu^t)_3Sm]\cdot THF$ complex with 2 equivalents of AlH_3 in THF oxidises the samarium and gives the Sm^{III} complex $\{[(\eta^5\text{-}C_5H_4Bu^t)_2Sm(\mu_3\text{-}H)][(\mu_2\text{-}H)_2AlH\cdot OC_4H_8]\}_2$ (I). Crystals of I are triclinic, a 10.030(1), b 13.328(2), c 10.349(1) Å, α 109.36(1), β 115.27(1), γ 89.45(1)°, space group $P\bar{1}$, $Z = 2$, ρ(calcd) 1.42 g/cm^3. Samarium is coordinated by four hydrides and has a formal 20e configuration. The coordination polyhedron of Al is a trigonal bipyramid.

Introduction

Most of the biscyclopentadienyl transition metal (TM) complexes follow the 'effective atomic number' rule. In addition, some TM complexes mainly of the III and IV groups of the Periodic Table have 14(15)- or 16(17)-electron configurations. The composition of all these species was rationalized in terms of the MO approach developed for complexes Cp_2ML_n [1]. However, several examples of complexes with a 20-electron configuration of the TM atom in $(\eta^5\text{-}C_5H_5)_3Zr(\eta^1\text{-}C_5H_5)$ [2], $[(\eta^5\text{-}C_5H_4Me)_2(\eta^1:\eta^5\text{-}C_5H_4Me)Nd]_4$ [3], and $(\eta^5\text{-}C_5H_4Me)_2Hf(\eta^2\text{-}BH_4)_2$ [4]) have been reported, whose structures do not follow the MO scheme proposed in ref. 1. The evaluation of conditions under which such compounds are formed is of practical and theoretical interest. Here we describe the X-ray diffraction study of the first

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alumohydride samarium complex $\{[(\eta^5\text{-}C_5H_4Bu^t)_2Sm(\mu_3\text{-}H)][(\mu_2\text{-}H)_2AlH \cdot OC_4H_8]\}_2$ (I) in which samarium has a formal 20e configuration.

Experimental

All synthetic manipulations and sampling were carried out either in vacuo or under dry argon as described previously [5].

The complex, $Na[(C_5H_4Bu^t)_3Sm] \cdot THF$, was obtained from the reaction of $NaC_5H_4Bu^t$ with SmI_2 in THF solution [6].

Preparation of I. To a solution of $Na(C_5H_4Bu^t)_3 \cdot THF$ (0.39 mmol) in a mixture of 25 ml Et_2O and 10 ml THF was added dropwise a solution of 1 mmol aluminium hydride in 50 ml of ether. On addition, dihydrogen was evolved followed by a colour change from violet to dark-green and the precipitation of Al metal (sometimes to the extent of a mirror). The mixture was stirred for 2 h, and then the precipitate was filtered off. The volume of the bright-yellow filtrate was reduced four-fold by evaporation and 20 ml hexane was then added. The parallelepiped-like yellow-green crystals that formed after 24 h were separated off, washed with cold pentane and dried in vacuo.

Further evaporation of the mother-liquor provides a white powder together with clear colourless crystals which decompose rapidly in vacuo or if kept under argon. The mixture was found to contain 0.5% Al, 0.5% Sm and small amount of Na.

Table 1

The major interatomic distances *d* (Å) and the bond angles ω (°) in $\{(\eta^5\text{-}C_5H_4Bu^t)_2Sm(\mu_3\text{-}H)(\mu_2\text{-}H)_2AlH\ OC_4H_8\}_2$ (I)

Bond	*d*	Bond	*d*
Sm–CpI	2.477	Sm · · · Al	3.245(1)
Sm–CpII	2.484	Al–H1	1.53
Sm–H2	2.37(–)	Al–H2 *	1.80
Sm–H2 *	2.35(–)	Al–H3	1.58
Sm–H3 *	2.21(–)	Al–H4	1.55
Sm–H4 *	2.28(–)	Al–O	2.003(3)
Sm · · · Sm	4.229(–)	Al · · · Al *	4.968
Sm · · · Al	3.278(1)		

Angle	ω	Angle	ω
CpISmCpII	125.8	H2*AlH$_3$	82.9
CpICpII	55.0	H3AlO	88.6
H2SmH2 *	52.7	H1AlO	93.1
H2SmH3 *	58.2	H4AlO	90.6
H2*SmH4	57.3	H1AlH3	124.4
H3*SmH4	139.6	H3AlH4	118.8
AlSmAl *	99.2	H1AlH4	116.7
SmH2Sm *	127.3	H2AlO	164.2
SmH2Al *	101.2	H1AlH2 *	102.7
Sm* H2Al *	103.5	H4AlH2 *	82.7
SmH3*Al *	116.9	CpI/C1-C6	10.2
SmH4Al	116.4	CpII/C10-C15	12.2

Structural determination of I. An X-ray diffraction study of I mounted in a glass capillary was carried out with an automatic diffractometer Syntex $P\bar{1}$ (Mo-K_α, $\theta/2\theta$ scanning). Crystals of I are triclinic, a 10.030(1), b 13.328(2), c 10.349(1) Å, α 109.36(1), β 115.27(1), γ 89.45(1)°, V 1166.2(3) Å^3, space group $P\bar{1}$, $Z = 2$, ρ(calcd) 1.42 g/cm^3. The 3345 reflections with $I \geqslant 3\sigma(I)$ were used without correction for absorption (μ(Mo-K_α) 26.0 cm^{-1}). The structure was solved by the Patterson routine and refined anisotropically (isotropically for hydrogen atoms) by least squares to $R = 0.020$ ($R_w = 0.023$). The main interatomic distances and bond angles of I are listed in Table 1.

Results and discussion

Reaction of Na [$(C_5H_4Bu^t)_3Sm$] · THF and AlH_3 · THF in an ether–THF mixture affords a compound formulated as $(C_5H_4Bu^t)_2SmAlH_4$ · THF. The evolution of H_2 and deposition of Al metal confirm its redox character.

The reactions probably proceed as follows: The coordination of aluminium hydride with samarocene(II) (eq. 1) and subsequent oxidative addition (eq. 2) to the samarocene with decomposition of $[AlH_2]^-$ gives samarocene hydride, which in turn reacts with an excess of aluminium hydride to give Cp'_2SmAlH_4 · THF (Eq.3).

$$\mathrm{Na[Cp'_3Sm] + AlH_3 \cdot THF \xrightarrow{THF} Cp'_2SmAlH_3THF + NaCp'} \qquad (1)$$

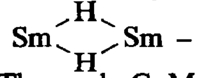
$$\mathrm{Cp'_2SmAlH_3 \cdot THF \xrightarrow{THF} Cp'_2SmHAlH_2 \cdot THF \longrightarrow Cp'_2SmH + Al + H_2} \qquad (2)$$

$$\mathrm{Cp'_2SmH + AlH_3 \cdot THF \longrightarrow Cp'_2SmAlH_4 \cdot THF} \qquad (3)$$

Evidently, similar processes can occur on interaction of metallocenes(II) with aluminium alkyls. The reaction between $(C_5Me_5)_2Yb$ and Al_2R_6 ceases after the coordination step [7]. The more powerful reducing agent, $(C_5Me_5)_2Sm$, reacts with Al_2Et_6 to afford the samarium(III) complex $(C_5Me_5)_2SmAlEt_4$ [8] (eq. 4). The

$$\mathrm{Cp^{\star}_2Sm + Al_2Et_6 \longrightarrow Cp^{\star}_2SmAlEt_4 + Al + C_2H_4 + C_2H_6} \qquad (4)$$

unique feature of reactions 1–4 is that strong reducing agents behave as oxidants towards Sm^{II}.

The complex $(C_5H_4Bu^t)_2SmAlH_4$ · THF (I) formed by reaction 3 has a composition similar to the known yttrium complexes $[Cp_2Y(\mu_3\text{-}H)]_2[(\mu_2\text{-}H)AlH_2L]_2$, where L = Et_2O, THF, and NEt_3 [5,9], but the closest analogue of I is the structurally characterized dimeric complex $[Cp_2Y(\mu_3\text{-}H)]_2[(\mu_2\text{-}H)AlH_2 \cdot THF]_2$ (II) [9]. The X-ray data show that the crystals of I are also made up of isolated dimeric molecules, but in contrast to complex II, molecules of I have a centre of symmetry (Fig. 1). The central fragment of I is a planar metallacycle –  $\mathrm{Sm}\begin{smallmatrix}\diagup\mathrm{H}\diagdown\\ \diagdown\mathrm{H}\diagup\end{smallmatrix}\mathrm{Sm}$ – each samarium atom is bonded with two η^5-cyclopentadienyl rings. The angle CpMCp is somewhat smaller than those in the yttrium complexes (Table 2), while the Sm–C distances are much greater, 2.48 and 2.36 Å although the covalent radius of Sm is only 0.04 Å greater than that of Y [10]. As in II, the cyclopentadienyl rings in I are in a *syn*-periplanar conformation while the attached t-butyl groups have an opposite orientation. The deviation of the t-butyl groups from the Cp planes is slight and comparable with that in $(C_5H_4Bu^t)_2TiCl_2$ [11], but less than in $(C_5H_4Bu^t)_2TaH_3$ · $2CuI_2$ in which the t-butyl groups have an identical orientation [12]. This is

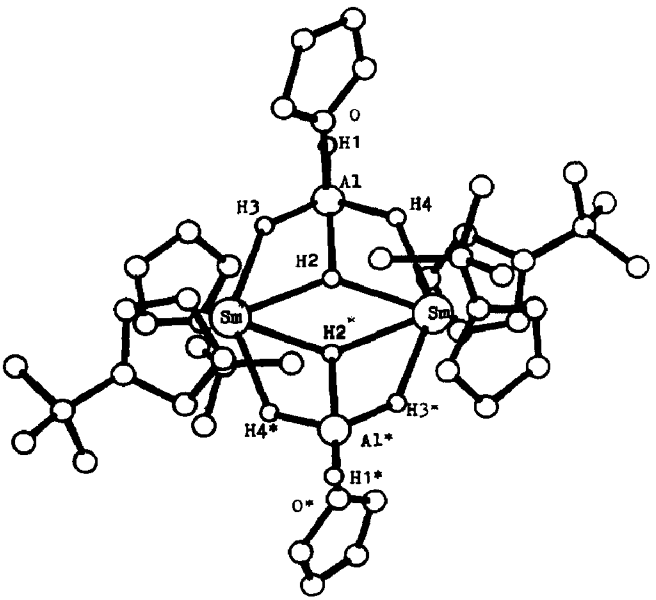


Fig. 1. The structure of $\{[(\eta^5\text{-}C_5H_4Bu^t)_2Sm(\mu_3\text{-}H)][(\mu_2\text{-}H)_2AlH \cdot OC_4H_8]\}_2$ (I).

indicative of the fact that the steric strain at samarium in I is not large. In addition to the two $C_5H_4Bu^t$ moieties, each samarium atom is bonded to the other samarium atom and to the aluminium atoms by the μ_3 and μ_2 bridging hydrogens. Thus, the aluminium hydride fragment is tridentate and binds to the two rare-earth metal atoms. The same binding mode has previously been observed in $Cp_2Y(\mu_2\text{-}Cl)(\mu_3\text{-}H)YCp_2(\mu_2\text{-}H)_2AlH \cdot THF$ (III) [13] and postulated for $Cp_2YAlH_4 \cdot 0.5Et_2O$: $(Cp_2Y)_2[(\mu_3\text{-}H)(\mu_2\text{-}H)_2AlH \cdot OEt_2][\eta^2\text{-}(\mu_2\text{-}H)_2AlH_2]$ (IV) [5] whose hydrogens could not be located. Again as in II, both aluminium atoms have a distorted trigonal bipyramidal configuration; the μ_3-H and the THF oxygen are in axial positions. The Sm ··· Al distance is close (in terms of the covalent radii) to the Y ··· Al distance in the $\mathrm{Y}{<}^{\mathrm{H}}_{\mathrm{H}}{>}\mathrm{Al}$ bridges in II–IV (Table 2). The bond lengths M–H and Al–H are also similar.

The Al atoms in I, as in III and IV, being equally separated from samarium atoms, differentiate complex I from II whose alumohydride group is bidentate [9]. However, despite the similarities and the differences the yttrium in the complexes, II–IV [1], always coordinates to three frontal ligands and has an 18e configuration, so that the metal atoms, the bridging hydrogens [5,9] and the chlorine [13] are located in one plane—the plane of wedge-sandwich Cp_2Y. The samarium in I coordinates four frontal ligands and formally has a 20e configuration (it should be pointed out that similar bonding was proposed by us earlier on the basis of an IR study of $Cp_2YAlH_4 \cdot OEt_2$ but was rejected as being highly improbable [5]). Coordination of four hydrogens with the transition metal provides an unprecendented feature in the chemistry of metallocene aluminium hydrides, namely, the deviation of the aluminium atoms above and below a plane of the rhomb $\mathrm{Sm}{<}^{\mathrm{H}}_{\mathrm{H}}{>}\mathrm{Sm}$ by 1.58 Å. Because of this, the eight-membered metallacycle $\overline{\mathrm{SmHAlHSmHAlH}}$ adopts a

Table 2

Selected bonds and angles in the complexes I–IV

Bond or angle	$(C_5H_4Bu^t)_2$-$SmAlH_4 \cdot THF$ (I)	$(Cp_2YAlH_4 \cdot THF)_2$ (II) [8]	$(Cp_2YAlH_4)_2 \cdot OEt_2$ (III) [5]	$(Cp_2Y)_2AlH_4Cl \cdot NEt_3$ (IV) [13]
M–Cp	2.48		2.36	2.36
M ··· M	4.23	3.75	4.38	3.95
M ··· Al	3.25	3.24	3.20	3.24
	3.28	4.00	3.57	–
Al–O	2.00	1.97	1.94	–
Cp–M–Cp	125.8	127.5	127.4	128.9
(μ_3-H)M(μ_3-H)	52.7	63	–	–
(μ_2-H)M(μ_3-H)	58.2	62	–	62
Al–M–Al	99.2	118	94.3	–
H–Al–O	164	164	–	155 [a]
α [b]	0	30	1.6	22

[a] HAl(μ_3-H). [b] The angle between the CpI–M–CpII plane and the M–M axis.

chair conformation with the edge-bridging hydrogens forming a single 'arm-rest' (Fig. 2). It seems that such a unique arrangement of the aluminium hydride moieties is responsible for the different orientations of the ring Bu^t groups, the decrease in the angle CpSmCp and the significant increase in the Sm ··· Sm distance to 4.23 Å. At the same time the angles (μ_2-H)Sm(μ_3-H) in I are practically the same as in $(Cp_2MAlH_4 \cdot L)_2$, while the (μ_3-H)Sm(μ_3-H) angles are much smaller (Table 2). Similar environment about the transition metal (four bridging frontal hydrogens) has been reported for hafnocene $(C_5H_4Me)_2Hf(\eta^2\text{-}H_2BH_2)_2$ (V) [4], although there are several examples which do not follow the classical MO scheme for Cp_2ML_n [1]. The following 20e compounds have been described: $(C_5H_4Me)_3Nd$ [3], Cp_3ZrX, where X = η^1-C_5H_5 [2], H [14]. The 22e species include Cp_3Ln where Ln = Pr [15] or La [16]. Thus the coordinative abilities of early transition metals, probably provided by involvement of *f*-orbitals in the formation of the MO are greater than is generally accepted. Although the rationalization of binding in complexes I and V in terms of the classical approach [1] by taking into account an overlap between the one frontal orbital of the wedge-sandwich Cp_2M and two *s*-orbitals of hydrogen, cannot be ignored. Undoubtedly, this key question on the theory of the structure of cene complexes needs special quantum-chemical investigation.

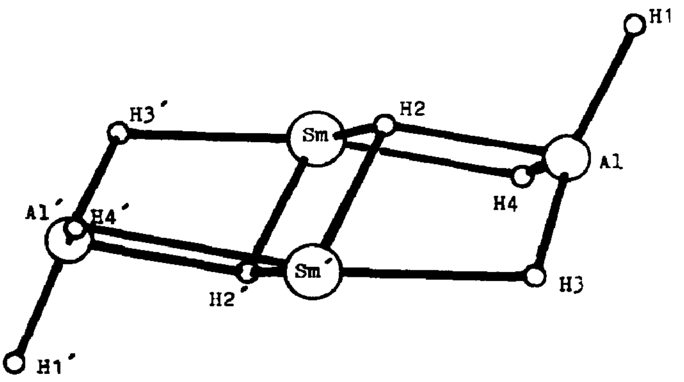


Fig. 2. Conformation of the metallacycle $\overline{\text{SmHAlHSmHAlH}}$ in I.

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