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Kinetically stable adduct of samarocene with aluminium deuteride $(\eta\text{-}C_5H_3{}^tBu_2)_2Sm(\mu_2\text{-}D)_2AlD \cdot Me_2NC_2H_4NMe_2$

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Abstract

The interaction of $(C_5H_3{}^tBu_2)_2Sm \cdot THF$ with AlD_3 in ether in the presence of TMEDA yields compounds of composition $(C_5H_3{}^tBu_2)_2SmAlD_3 \cdot TMEDA$ (**I**). Metal atoms are bonded by the double bridge SmD_2Al. The coordination polyhedron of Al in **I** is a trigonal bipyramid. Stability of this substance to redox reaction occurring in the $Cp''_2Sm \cdot THF\text{–}AlD_3$ system can be explained by the isotopic kinetic effect.

Introduction

Recently we have found that the reaction of samarium(+2) complexes with aluminium hydride solvates is a redox process running with H_2 evolution and yielding aluminohydride or hydride complexes of samarium(+3) and aluminium metal [1–3]. A similar reaction of permethylsamarocene with triethylaluminium was observed by Evans *et al.* [4]. Taking into account a high acidity of the samarium(+2) atom in biscyclopentadienyl complexes [5–7], it might be supposed that the reaction of Sm^{2+} oxidation during the interaction of samarocene with $AlH_3 \cdot L$ should go *via* an intermediate bimetallic complex formation rather than

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an outersphere oxidation. Unfortunately, under normal conditions this reaction proceeds too fast and it is impossible to isolate an intermediate. However, by changing $AlH_3 \cdot L$ for its deuterated analogue and using tetramethylethylenediamine (TMEDA) as the ancillary ligand, we have succeeded in producing a samarium(+2) adduct $(\eta\text{-}C_5H_3{}^tBu_2)_2Sm(\mu_2\text{-}D)_2\ AlD \cdot Me_2NC_2H_4NMe_2$ (**I**) and established its structure by X-ray analysis. The results of this study are presented.

Experimental

Synthetic operations and the preparation of samples for X-ray studies were carried out using the standard Schlenk technique under dry argon or *in vacuo*. Solvents were dried by boiling over $LiAlH_4$ and distilled in an argon atmosphere. $(C_5H_3{}^tBu_2)_2Sm \cdot THF$ was prepared as described previously [8].

Synthesis of $(C_5H_3{}^tBu_2)_2Sm \cdot AlD_3 \cdot Me_2NC_2H_4NMe_2$ *(I)*

A solution of 82.5 mg (2.5 mmol) AlD_3 in 40 mL of diethyl ether freshly prepared by exchange reaction of $LiAlD_4$ and $AlCl_3$ was added to a solution containing 630 mg (1.25 mmol) of $(C_5H_3{}^tBu_2)_2Sm$ in 150 mL of Et_2O with stirring. Then 730 mg (6.25 mmol) of TMEDA in 10 mL of Et_2O was introduced via a syringe. The solution colour changed from black to dark green and evolution of some hydrogen and Al metal was observed. After 2 h stirring, the precipitate was filtered off. The filtrate was evaporated *in vacuo* to *ca.* 10 mL and cooled in liquid nitrogen vapour. After 12 h, the dark green crystals formed were separated from the mother liquid by decantation and dried *in vacuo*: 230 mg (28%) of **I** was obtained.

X-Ray data collection and refinement

An X-ray diffraction study of a single crystal of **I** packed in glass capillary was performed on an automatic Nicolet P3 diffractometer (Mo-K_α irradiation, θ–2θ scanning up to $2\theta = 45°$).

Crystals of **I** were monoclinic: $a = 13.267(3)$, $b = 11.247(2)$, $c = 24.767(6)$ Å, $\gamma = 105.02(1)°$, $V = 3569.3(2.5)$ Å^3, space group $P2_1/a$, $Z = 4$, $\rho_{calc.} = 1.19$ g/cm^3; 1434 reflections with $I > 3\sigma(I)$ were used for the calculation. No correction for absorption was applied ($\mu_{Mo} = 16.9$ cm^{-1}).

The structure was solved by the Patterson method using the SHELXTL program package and verified by the least-squares method, with anisotropic (isotropic for D and H atoms) approximation in the weight scheme $w = 1/\sigma^2(F) + 0.010077F^2$ up to $R = 0.051$ ($R_w = 0.054$). Atomic coordinates are listed in Table 1 and the main interatomic distances and bond angles are given in Table 2.

Results and discussion

As shown earlier [1–3], the reaction of samarocene with two bulky substituents in the cyclopentadienyl ring yields hydride complexes samarium(+3). By changing the aluminium hydride solvate with its deuterated analogue, the redox reaction becomes much slower and besides partial oxidation of samarium(+2) (hydrogen evolution and sedimentation of Al metal), a bimetallic complex containing samarium(+2) and aluminium can be isolated from reaction mixture. From the X-ray

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}
Sm	2256(1)	2242(1)	1056(1)	42(1)
Al	3345(6)	4582(6)	1556(3)	58(3)
N1	3352(13)	6357(14)	1253(7)	56(8)
N2	2890(18)	5306(17)	2275(8)	95(11)
C1	1617(20)	2436(20)	−15(10)	53(11)
C2	1089(21)	3154(21)	280(11)	64(12)
C3	342(18)	2463(23)	618(11)	64(12)
C4	430(18)	1221(17)	550(11)	64(11)
C5	1156(17)	1231(23)	164(10)	57(12)
C6	2273(23)	2762(25)	−498(12)	71(14)
C7	3024(27)	3950(28)	−455(13)	126(17)
C8	1591(26)	2799(33)	−990(13)	140(20)
C9	2859(22)	1826(29)	−666(11)	105(15)
C10	−511(21)	2903(27)	876(12)	90(15)
C11	−863(25)	2235(33)	1399(14)	135(20)
C12	−228(21)	4269(25)	967(14)	116(16)
C13	−1445(22)	2658(29)	462(15)	137(19)
C14	3828(15)	991(17)	1134(8)	35(8)
C15	3393(16)	942(16)	1639(9)	45(9)
C16	2361(20)	173(17)	1638(7)	58(11)
C17	2162(16)	−205(15)	1099(10)	51(9)
C18	3070(17)	269(18)	770(8)	40(9)
C19	4997(15)	1569(18)	1025(11)	53(9)
C20	5561(16)	563(21)	1017(11)	83(11)
C21	5533(18)	2551(23)	1409(12)	86(12)
C22	5119(19)	2137(27)	455(12)	107(15)
C23	1540(23)	−138(24)	2061(10)	71(13)
C24	2073(26)	−193(39)	2557(16)	156(24)
C25	1025(27)	916(29)	2139(17)	192(24)
C26	780(27)	−1300(32)	2014(16)	170(22)
C27	3164(38)	7069(24)	1717(14)	166(24)
C28	2956(27)	6575(28)	2173(13)	118(18)
C29	3503(51)	5164(44)	2728(15)	275(38)
C30	1947(46)	4699(32)	2472(16)	232(31)
C31	4277(29)	6939(27)	986(20)	217(27)
C32	2612(31)	6443(27)	859(15)	179(23)
D1	260	304	157	90
D2	326	383	80	90
D3	445	496	165	90

analysis data, the complex is a monomer with common van der Waals contact between molecules (Fig. 1). A samarium atom is connected to two η^5-cyclopentadienyl rings and two deuterium atoms which are bridged between Sm and Al atoms. Sm–Cp and Sm–$C_{av.}$ distances in **I** have intermediate values between those for samarium(+2) complexes (for example, 2.55 and 2.81 Å in $(C_5H_3{}^tBu_2)_2Sm\cdot C_4H_8O$ (**II**) [8]) and samarium(III) complexes (2.46 and 2.74 Å in $[(C_5H_3{}^tBu_2)_2Sm(\mu\text{-}H)]_2$ (**III**) and $[(C_5H_3{}^tBu_2)_2Sm(\mu\text{-}BH_4)]_2$ (**IV**) [2], 2.46 and 2.72 Å in $[(C_5H_4{}^tBu)_2Sm(\mu\text{-}H)]_2[(\mu\text{-}H)_2AlH\cdot NEt_3]_2$ [9]). The valence angle CpSmCp in **I** (119.8°) is rather small. Similar values had been observed in bis(di-tert-butylcyclo-

Table 2

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

Bond	*d*	Angle	*ω*
Sm–Cp**I**	2.509	Cp**I**/Cp**II**	64.6
Sm–Cp**II**	2.498	Cp1–Sm–Cp2	119.8
Sm–C1	2.81(3)	D1–Sm–D2	74
Sm–C2	2.82(3)	D1–Al–D2	70
Sm–C3	2.83(3)	D1–Al–D3	124
Sm–C4	2.71(3)	D2–Al–D3	102
Sm–C5	2.73(3)	N1–Al–D1	142.4
Sm–C14	2.81(4)	N1–Al–D2	93.1
Sm–C15	2.76(3)	N1–Al–D3	91.6
Sm–C16	2.77(3)	N1–Al–N2	82.4(8)
Sm–C17	2.72(3)	N2–Al–D1	102.3
Sm–C18	2.80(3)	N2–Al–D2	160.8
Sm–$C_{av.}$	2.78(4)	N2–Al–D3	96.2
Sm–D1	1.6(1)	Al–N1–C27	106.1(2)
Sm–D2	2.0(1)	Al–N2–C28	106.6(2)
Sm · · · Al	2.292(6)	C1–C6/Cp**I**	12.5
Al–D1	1.8(1)	C3–C10/Cp**I**	13.0
Al–D2	2.0(1)	C14–C19/Cp**II**	8.1
Al–D3	1.4(1)	C16–C23/Cp**II**	7.1
Al–N1	2.13(2)	Cp1–Sm–Cp2/Sm–D_2–Al	67.3
Al–N2	2.11(2)	Sm–D_2–Al/AlN_2	41.1

pentadienyl)samarium complexes in a similar hydride environment of metal atoms, for example, in the metallocene moiety of molecule $(C_5H_3{}^tBu_2)_5Sm_4H_3(AlH_4)_4 \cdot 2Me_2NC_2H_4NMe_2$ (**V**) (115.5°) [3] or in borohydride complex **IV** (115.2°) [2]. The value of CpSmCp angle in other steric saturated bis(di-tert-butylcyclopenta-

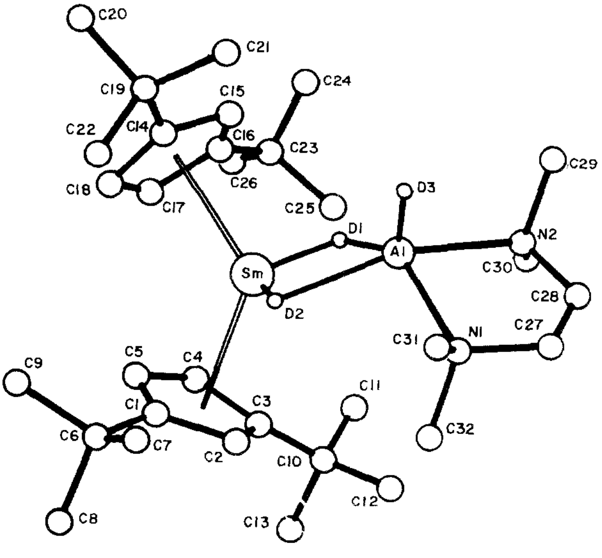


Fig. 1. Structure of $(C_5H_3{}^tBu_2)_2Sm(\mu\text{-}D)_2AlD \cdot Me_2NC_2H_4NMe_2$.

dienyl)samarium complexes is much more independent of the oxidation state of samarium: 125.5° in $[(C_5H_4{}^tBu)_2Sm]_2(\mu_2\text{-}H)\cdot\mu\text{-}[(\mu_3\text{-}H)_2Al(\mu_2\text{-}H)_2\cdot Me_2NC_2H_4NMe_2]$ (**VI**) [9], 121.5° in **III** [2] and 132.5° in **II** [8].

The aluminium atom is bound with one more terminal deuterium atom and two nitrogen atoms of the chelate TMEDA molecule, beside two bridged D atoms. No more atoms including deuterium hydride atoms are detected in the nearest coordination sphere of both metals, *i.e.* according to X-ray data, the oxidation state of samarium in **I** is +2. Nevertheless, taking into account the difficulties of localization of hydrogen atoms close to heavy metal atoms, let us consider the evidence for the existence of the fourth hydrogen atom in molecule **I** and, consequently, the samarium oxidation state of +3.

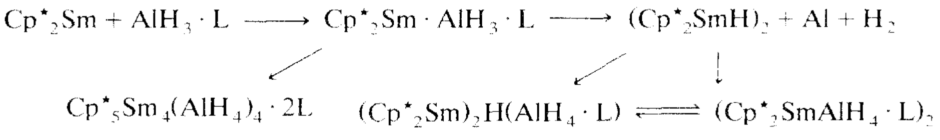
The characteristic signs of a redox process during the synthesis of complex **I** testify to the hypothesis of a change in the samarium oxidation state in forming the compound. The fourth hydride atom can be localized, in principle, both as a terminal atom bound to aluminium or samarium atoms and as a bridged atom forming a triple hydrogen bridge between these atoms. Indeed, the $Sm\cdots Al$ distance in **I** (2.92 Å) is markedly shorter than this distance in known aluminohydride complexes of samarium(+3) with double hydrogen bridges between metal atoms $[(C_5H_4{}^tBu)_2SmH]_2[H_2AlH\cdot L]_2$ (3.25–3.26 Å) (L = THF [1], NEt_3 [9]) and with a triple hydrogen bridge (3.04 Å in complex **VI** [9]). Nevertheless, the assumption of triple hydrogen bridge formation ought to be rejected because SmD_2Al metallocycle in **I** is practically flat (the dihedral angle between the SmD_2 and AlD_2 planes is 7.6°) and the Sm–D and Al–D distances for the third bridge atom must be too big under conditions of normal $D\cdots D$ nonbonding contacts. Thus, the dihedral angle in nonflat SmH_2Al metallocycle in the triple hydrogen bridge of molecule **VI** is 56.9° [9].

Three deuterium atoms and two nitrogen atoms near the aluminium atom in **I** form the trigonal bipyramid which is a typical coordination polyhedron for this class of compounds. On the other hand, an octahedron environment of an aluminium atom with valence angles between *trans*-ligands closed to 180° (for example, 168–172° in complexes **V** and **VI** with hexacoordinated aluminium atoms [3,9]) would be expected for the $[AlH_4\cdot Me_2NC_2H_4NMe_2]$ group with two terminal hydrogen atoms. It is evident that the version with two terminal hydride atoms bound to the Al atom ought also to be excluded.

The last possibility is the formation of a terminal Sm–H bond. An argument in favour of this assumption is the localization of deuterium bridge atoms beyond the bent sandwich Cp_2Sm bisector plane (the dihedral angle between Cp_2Sm and SmD_2Al planes is 67.3° instead of 90°). However, a similar phenomenon has been observed for all hydride complexes of samarocene [1–3,9] at first, and an aluminium atom in **I** deviates slightly from the idealized C_2 symmetry axis of the bent sandwich (the related angle is 10.6°) which indicates the absence of an additional coordination of samarium atom at second. Therefore the fact of the SmD_2Al metallocycle turning relative to the bisector plane of the bent sandwich is caused, obviously, by the requirements of the decrease in steric hindrances at the chelate TMEDA molecule localization at aluminium atom. Indeed, the AlNCCN metallocycle has an "envelope" conformation and the turning of AlN_2 plane is opposite to the AlD_2 plane that decreases the nonbonding contacts between the methyl groups of TMEDA and tert-butyl groups of cyclopentadienyl ligands. Nevertheless, the steric hindrances in the ring close to the TMEDA moiety are much more noticeable than in the other ring (mean angles of ring–^{t}Bu group bond deviation from the ring plane are 12.6° and 7.6°, respectively).

Thus, the analysis of structure peculiarities of molecule **I** unambiguously indicates the existence of only three hydride atoms in the coordination sphere of both metals, *i.e.* samarium in **I** has the oxidation state +2. The dark green colour of crystals of **I** is also characteristic of samarium(+2) complexes [5,8] while the alumohydride complexes of samarium(+3) are usually light green or yellow green in colour. Similar adducts are known for more oxidatively stable permethylytterbiocene with non-transition metal alkyls MeBeCp [6] and $AlEt_3 \cdot THF$ [7]. The $Sm \leftarrow H{-}Al$ bonds in **I** may be considered as analogues of agostic $Yb \cdots H{-}C$ bonds; however, a greater negative charge at the hydrogen atoms in aluminium hydride causes greater strength of these bonds and shorter (taking into account the differences in covalent radii) $Ln \cdots E$ contact.

The isolation of adduct **I** and the known literature data [1–3] permit us to describe the full chain of the chemical reactions taking place after mixing aluminium hydride solvate $AlH_3 \cdot L$ and $(C_5H_3{}^{t}Bu_2)_2Sm$ to produce the monometallic hydride **III** [2] in pure diethyl ether or octanuclear bimetallic complex **VI** [9] in an ether/pentane mixture.



$$\begin{tikzcd}
Cp^{\star}_2Sm + AlH_3 \cdot L \arrow[r] & Cp^{\star}_2Sm \cdot AlH_3 \cdot L \arrow[r] \arrow[dl] & (Cp^{\star}_2SmH)_2 + Al + H_2 \arrow[dl] \arrow[d] \\
Cp^{\star}_5Sm_4(AlH_4)_4 \cdot 2L & (Cp^{\star}_2Sm)_2H(AlH_4 \cdot L) \arrow[r, phantom, "\rightleftharpoons"] & (Cp^{\star}_2SmAlH_4 \cdot L)_2
\end{tikzcd}$$

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