

EIGHTEEN- AND FOURTEEN-ELECTRON ALUMOHYDRIDE COMPLEXES OF DICYCLOPENTADIENYLLUTETIUM. THE CRYSTAL AND MOLECULAR STRUCTURE OF MONOMER $(\eta^5\text{-C}_5\text{H}_5)_2\text{Lu}(\mu_2\text{-H})\text{AlH}_3 \cdot \text{NEt}_3$ WITH A MONODENTATE ALUMOHYDRIDE GROUP

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Summary

Dicyclopentadienyllutetium monochloride interacts with LiAlH_4 in benzene (or toluene) and ether in the presence of a Lewis base to form coordination and electron saturated (18-electron configuration of the Lu atom) dimeric complexes $(\text{Cp}_2\text{LuAlH}_4 \cdot \text{L})_2$, where $\text{L} = \text{Et}_2\text{O}$ (I), NEt_3 (IIa), $\text{C}_4\text{H}_8\text{O}$ (III). Complexes IIa and III crystallize in monoclinic lattices with parameters: $a = 11.35$, $b = 13.34$, $c = 14.20$ Å, $\gamma = 102^\circ$, space group $P2_1/b$ for IIa; $a = 8.73$, $b = 11.06$, $c = 16.42$ Å, $\gamma = 95.6^\circ$, space group $P2_1/b$ for III. When a single crystal of IIa is exposed to hard X-rays (Mo-K_α , $\lambda = 0.7106$ nm) dissociation of the dimer takes place and a single crystal of monomeric $\text{Cp}_2\text{Lu}(\mu_2\text{-H})\text{AlH}_3 \cdot \text{NEt}_3$ (IIb) with a monodentate AlH_4 group and 14-electron configuration of the Lu atom is formed. IIb crystallizes in monoclinic lattice with parameters: $a = 13.278(4)$, $b = 9.697(3)$, $c = 14.099(4)$ Å, $\gamma = 94.22^\circ$, space group $P2_1/a$, $Z = 4$, $d_{\text{calc}} = 1.60$ g/cm³ ($R = 0.046$, $R_w = 0.047$).

Introduction

Recently extensive investigations of organometallic rare-earth element (REE) compounds resulted in a series of homometallic electron-deficient complexes with unique properties [1,2]. Some of these compounds were found to be high-efficiency catalysts for olefin polymerization [3,4], hydrogenation of multiple bonds [5] and capable of participating in stoichiometric reactions with alkanes [6]. At the same

time the heterometallic complexes of REE and non-transition elements have only rarely been synthesized. However experience with Ziegler-type systems suggests that these complexes can be even more active catalysts. For example, sixteen-electron dicyclopentadienylttrium (or ytterbium) and aluminium alkyl complexes $\text{Cp}_2\text{-MMe}_2\text{AlMe}_2$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) appeared to be more active and stable catalysts in ethylene polymerization than the corresponding homometallic complexes $(\text{Cp}_2\text{MMe})_2$ [3]. A series of 18-electron dicyclopentadienylttrium and aluminium hydride complexes was synthesized [7–10]. These, however, lacked catalytic activity [11]. The coordination number of the central atom in these wedge-like sandwich complexes can be reduced (i) by introducing bulky substituents into Cp ligand (for example, C_5Me_5) [2] or (ii) by reducing the size of the metal atom, as was demonstrated for complex-forming boron hydrides, $\text{Cp}_2\text{LnH}_2\text{BH}_2 \cdot n\text{THF}$ [12].

The present paper reports on the results of an investigation aimed at producing electron-deficient alumohydride complexes of lutetium, covalent radius of which is smaller than that of Y.

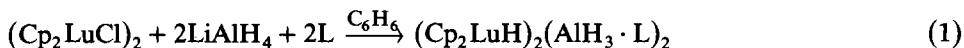
Experimental

All samples were synthesized and prepared for the physico-chemical examination under anaerobic conditions.

Cp_2LuCl was prepared as described in [13] and was purified by vacuum-sublimation. Pure lithium aluminium hydride (99%) was used. Solvents (benzene, toluene, Et_2O , NEt_3 , THF) were distilled over LiAlH_4 immediately before use. Lu and Al were determined as described in [14]. Weighed samples were decomposed by boiling in concentrated H_2SO_4 and addition of H_2O_2 .

IR spectra (suspension in Nujol) were recorded in the $400\text{--}3500\text{ cm}^{-1}$ region with a UR-20 spectrophotometer.

The synthesis of alumohydride complexes of dicyclopentadienyllutetium was carried out by the interaction of Cp_2LuCl with LiAlH_4 in the presence of a Lewis base (eq. 1)



The procedures were as follows.

(Cp₂LuH)₂(AlH₃ · Et₂O)₂ (I). To a stirred solution of 0.72 g 2 mmol of Cp_2LuCl in benzene (100 ml) was added dropwise, an equimolar quantity of LiAlH_4 in ether (3.5 ml). The precipitate of LiCl was filtered off and the volume of the filtrate reduced to 20 ml. A white residuc was isolated from mother liquor and dried in vacuo. Yield: 60%. Found: Lu, 39.9; Al, 7.0. Calculated for $(\text{Cp}_2\text{LuH})_2(\text{AlH}_2 \cdot \text{Et}_2\text{O})_2$ (I): Lu, 42.6; Al, 6.6%.

(Cp₂LuH)₂(AlH₃ · NEt₃)₃ (IIa). To a solution of Cp_2LuCl (1.75 g, 5.4 mmol) in triethylamine (3.5 ml, 5-fold excess) benzene (250 ml) was added. The mixture was then stirred for 20 min, and LiAlH_4 (5.4 mmol) in ether (9 ml) was added, the precipitated LiCl was filtered off and the solution evaporated to 1/6 of its original volume. Colourless crystals (1.8 g) which precipitated were isolated by decantation, washed in benzene (10 ml) and dried in vacuo. The volume of the mother liquor was reduced to 40 ml, and more crystals (0.25 g) precipitated. These were treated similarly. Produced: 2.05 g (87%) of a substance extremely sensitive to oxidation.

Found: Lu, 40.4; Al, 5.9. Calculated for $(Cp_2LuH)_2(AlH_3 \cdot NEt_3)_2$: Lu, 40.0; Al, 6.2%.

$(Cp_2LuH)_2(AlH_3 \cdot C_4H_8O)_2$ (III). To a stirred solution of Cp_2LuCl (1.51 g, 4.4 mmol) in benzene (150 ml) was added tetrahydrofuran (1 ml, 3-fold excess), and subsequently an equimolar quantity of $LiAlH_4$ in ether (8 ml) solution was then filtered and evaporated to 1/3 of its original volume. The small quantity of cubic crystals that separated were isolated, and dried in vacuo. Found: Lu, 43.0; Al, 5.9%. Calculated for $(Cp_2LuH)_2(AlH_3 \cdot C_4H_8O)_2$: Lu, 42.9; Al, 6.6%. Storage of the substance even in the dark is impossible because it decomposed in vacuo to produce the metal.

X-ray diffraction analysis was carried out on single crystals of IIa, IIb, III using an automatic Syntex $P\bar{1}$ diffractometer (Mo- K_α radiation, graphite monochromator, $\theta/2\theta$ scan). The main crystallographic parameters were determined for IIa and III only: IIa: $a = 11.35$, $b = 13.34$, $c = 14.20$ Å, $\gamma = 102^\circ$, space group $P2_1/b$; III: $a = 8.73$, $b = 11.06$, $c = 16.42$ Å, $\gamma = 95.6^\circ$, space group $P2_1/b$. They were almost identical with the well known yttrium aluminium hydride complexes [9,10] and the experiment was terminated.

Complex IIb crystallizes in monoclinic lattice with the parameters $a = 13.278(4)$, $b = 9.697(3)$, $c = 14.099(4)$ Å, $\gamma = 94.22^\circ$, space group $P2_1/a$, $Z = 4$, $d_{calc} = 1.60$ g/cm³. 1679 reflections with $I > 3\sigma(I)$ were collected. The absorption correction was $\mu_{Mo} = 57.6$ cm⁻¹, and crystal size $0.3 \times 0.3 \times 0.1$ mm. The structure was

TABLE 1

ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC THERMAL FACTORS OF ATOMS B_{iso}^{eq} (Å²) FOR IIb

Atom	x	y	z	B_{eq}
Lu	0.4123(1)	0.5366(1)	0.0998(1)	0.037(1)
Al	0.3177(4)	0.2706(5)	-0.0124(4)	0.045(2)
N	0.1863(9)	0.1436(13)	0.0261(9)	0.039(5)
C(1)	0.2484(12)	0.6542(17)	0.0885(14)	0.059(6)
C(2)	0.3047(16)	0.7279(22)	0.1524(15)	0.067(8)
C(3)	0.3932(15)	0.7956(18)	0.1075(17)	0.082(8)
C(4)	0.3813(15)	0.7602(20)	0.0114(15)	0.063(8)
C(5)	0.2940(13)	0.6708(18)	0.0005(15)	0.054(7)
C(6)	0.5538(14)	0.4505(28)	0.2098(15)	0.085(10)
C(7)	0.4808(30)	0.3432(25)	0.2083(19)	0.111(13)
C(8)	0.4015(16)	0.3879(27)	0.2540(14)	0.074(9)
C(9)	0.4203(26)	0.5112(35)	0.2834(14)	0.113(14)
C(10)	0.5176(21)	0.5642(24)	0.2550(15)	0.079(9)
C(11)	0.1883(14)	0.1319(20)	0.1327(13)	0.057(7)
C(12)	0.1002(17)	0.0416(22)	0.1755(15)	0.092(9)
C(13)	0.1977(14)	0.0022(17)	-0.0139(14)	0.066(7)
C(14)	0.2089(19)	-0.0063(21)	-0.1187(14)	0.081(9)
C(15)	0.0922(13)	0.1971(19)	-0.0087(13)	0.059(7)
C(16)	0.0663(15)	0.3345(19)	0.0278(15)	0.068(8)
H(1)	0.391(6)	0.158(9)	0.008(7)	
H(2)	0.319(11)	0.404(16)	0.077(10)	
H(3)	0.255(15)	0.303(21)	-0.106(14)	
H(4)	0.364(15)	0.332(21)	-0.096(13)	

TABLE 2

MAIN BOND LENGTHS (Å) AND BOND ANGLES (°) in IIb

Lu...Al	3.234(5)	Al-H3	1.60(20)
Lu...Lu'	3.638(1)	Al-H4	1.45(18)
Lu-H2	1.81(14)	Al-N	2.131(13)
Al-H1	1.54(10)	Lu-Cp(1) ^a	2.30
Al-H2	1.81(14)	Lu-Cp(2) ^a	2.31
Lu-H2-Al	127(8)	H(1)-Al-H(3)	131(8)
Cp-Lu-Cp	129	H(1)-Al-H(4)	100(9)
H2-Al-H1	114(6)	H(1)-Al-N	94(3)
H2-Al-H3	115(9)	H(3)-Al-H(4)	57
H2-Al-H4	107(9)	H(3)-Al-N	85(7)
H2-Al-N	102(5)	H(4)-Al-N	139(8)

^a Cp(1) root-mean-square plane of Cp ring C(1)-C(5). Cp(2) root-mean-square plane of Cp ring C(6)-C(10).

resolved by a combination of a direct and Patterson methods and refined by the least-squares method in an anisotropic/isotropic (H atoms) approximation to $R = 0.046$ ($R_w = 0.047$). Table 1 gives atomic coordinates and Table 2 the main interatomic distances and valence angles.

Results and discussion

Dicyclopentadienyllutetium monochloride interacts with lithium aluminium hydride in the presence of solvating solvents to form complexes $(Cp_2LuAlH_4 \cdot L)_2$, where $L = Et_2O$ (I), NEt_3 (II), C_4H_8O (III). The IR spectra of these compounds are very similar and differ very little from the IR spectra of analogous yttrium compounds $(Cp_2YH)_2(AlH_3 \cdot L)_2$ [9]. The IR absorption bands of complexes I-III were assigned by analogy to complexes in ref. 9 and comparison with the IR spectrum of deuterated complex IIa (see Table 3). The vibration frequency involving hydrogen atoms increased in the series $II < III < I$ (Table 3) which is in agreement with the decreasing donor properties of the ligand and donor number (DN) are 30.7, 20.0 and 19.2 respectively [15]. It is noteworthy that the metal-hydrogen frequencies in the complex IIa almost coincide with those of its yttrium analogue [9], although one might expect that their decrease is due to the increased mass of one of the metals. The same was observed for complexes I and III (Table 3).

The IR spectra of complexes I-III all coincide, and complexes IIa and III are isostructural to their yttrium analogues $(Cp_2YH)_2(AlH_3 \cdot L)_2$ [9,10]. This leads us to suggest that the compounds based on lutetocene and aluminium hydrides in the crystal state are coordination and electron (18-electron configuration) saturated dimers $(Cp_2LuH)_2(AlH_3 \cdot L)_2$ with structures identical with yttrium complexes (Fig. 1).

The data obtained may seem to indicate that the substitution of a central metal atom in complexes $(Cp_2MH)_2(AlH_3 \cdot L)_2$ with a smaller M atom causes no qualitative changes in the structure and properties of the bimetallic hydride complexes. However X-ray diffraction study of crystals of IIa unexpectedly revealed that when irradiated by sufficiently hard X-rays ($\lambda = 0.71069$ nm, Mo- K_α) the new crystal phase was formed with good reproducibility which retained the single-crystal

TABLE 3

THE VIBRATIONAL FREQUENCIES IN THE IR ABSORPTION SPECTRA (cm^{-1}) OF THE ALUMINIUM HYDRIDE COMPLEXES OF DICYCLOPENTADIENYLLUTETIUM ^a

$(\text{Cp}_2\text{LuH})_2$ $(\text{AlH}_3 \cdot \text{Et}_2\text{O})_2$ (I)	$(\text{Cp}_2\text{LuH})_2$ $(\text{AlH}_3 \cdot \text{NEt}_3)_2$ (IIa)	$(\text{Cp}_2\text{LuH})_2$ $(\text{AlH}_3 \cdot \text{C}_4\text{H}_8\text{O})_2$ (III)	Assignment
555	570		$\nu(\text{Al}-\text{O}, \text{Al}-\text{N})$
625			
655	645(465)	642	$\delta(\text{Lu}_2\text{HAl})$
740	715(525)	703	
760	730	773	
783	785	787	Cp
890	810(565)	870	$\nu(\text{Lu}_2\text{HAl})$
	910	925	L
1020	1020	1020	Cp
1060	1040(760)	1050	$\nu(\text{Lu}_2\text{HAl})$
1080			L
1160	1170(855)	1190	$\nu(\text{LuHAl})$
1320	1305(930)	1255	$\nu(\text{Lu}-\text{H}^b)$
1670	1660(1200)	1675	$\nu(\text{Al}-\text{H}^b)$
1885	1810(1305, 1320)	1830	$\nu(\text{Al}-\text{H}^c)$

^a Frequencies for the deuterated complex are given in parenthesis.

properties of the sample. After 10 h of irradiation the reflections of complex IIa changed by 85%, and after 24 h of exposure the transformation was complete.

The new crystal phase (IIb) formed on irradiation by X-ray quanta is an isomer

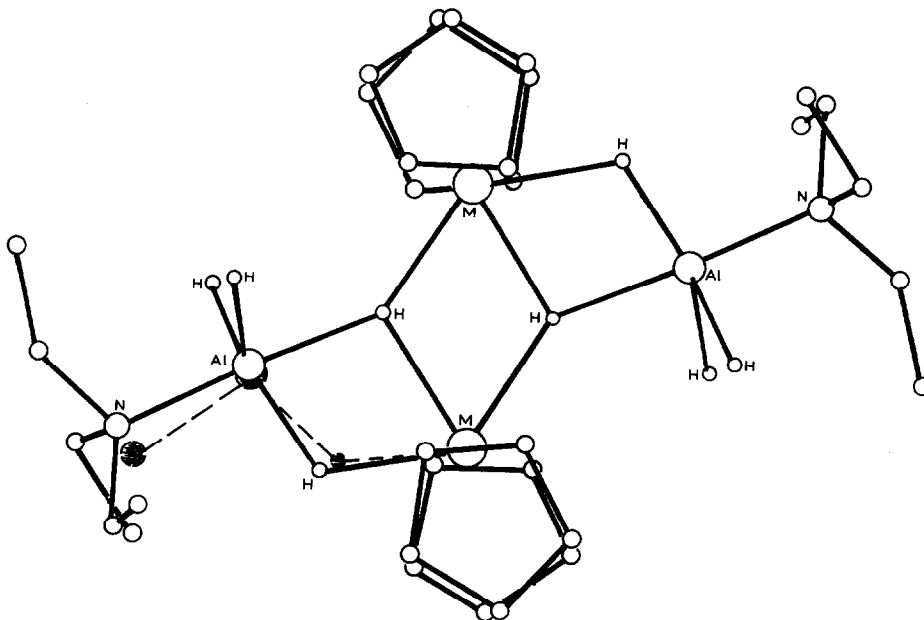


Fig. 1. Molecular structure of the complex $(\text{Cp}_2\text{LuH})_2(\text{AlH}_3 \cdot \text{NEt}_3)_2$ (IIa). The 'new' positions taken up by H^b, Al, and N atoms in complex IIb are indicated by shaded circles and dashed bonds.

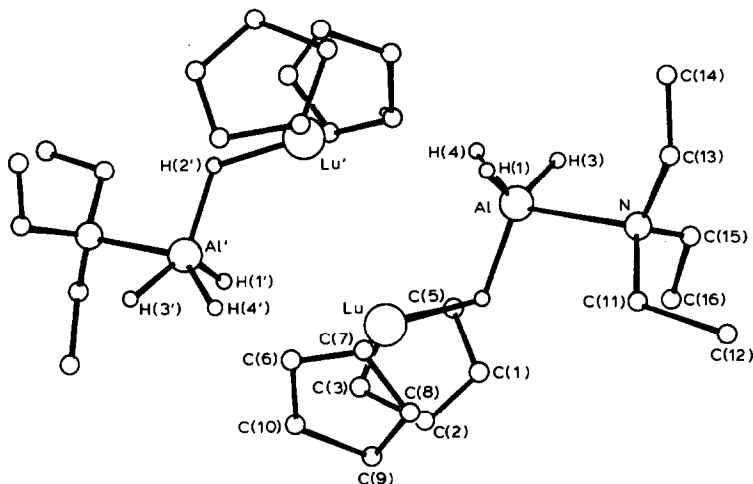


Fig. 2. Molecular structure of the complex $(\eta^5\text{-Cp})_2\text{Lu}(\mu_2\text{-H})\text{AlH}_3 \cdot \text{NEt}_3$ (IIb).

of IIa composed of monomer molecules of solvated lutetocene alumohydride $\text{Cp}_2\text{Lu}(\mu_2\text{-H})\text{AlH}_3 \cdot \text{NEt}_3$ (Fig. 2). All hydride atoms were located by difference Fourier synthesis and although their coordinates are not extremely accurate (especially H(3)) (Table 1), evidently Lu–Al atomic bonding can only be realized by an ordinary Lu–H–Al hydrogen bridge. The remaining hydrogen atoms are terminal. The Lu···Lu contact is definitely non-valent owing to a sufficiently large separation (3.638(1) Å), and to considerations of maintaining the valency of both metal atoms.

The coordination number of the Al atom remains at 5. However the coordination polyhedron changes from a trigonal bipyramid (IIa) to a distorted square pyramid with a bridge hydrogen atom as axial ligand. The distances Al–H^a and Al–N in molecule IIb do not differ significantly from those in complexes $(\text{Cp}_2\text{YH})_2(\text{AlH}_3 \cdot \text{THF})_2$ ($r_{\text{Al-H}} = 1.5\text{--}1.6$ Å) [10] and $(\text{Cp}_2\text{YH})_2(\text{AlH}_3 \cdot \text{NEt}_3)_2$ ($r_{\text{Al-N}} = 2.177(6)$ Å) [9]. At the same time the difference in the Al–H^b and Lu–H^b distances in IIb compared to those in $(\text{Cp}_2\text{YH})_2(\text{AlH}_3 \cdot \text{THF})_2$ * noticeably exceed the measurement error assuming a difference between the covalent radii of Y and Lu atoms of 0.06 Å. The Lu–H^b distance (1.81(15) Å) in complex IIb is considerably shorter than Y–H^b in the ordinary Y–H–Al bridge of the tetrahydrofuranate complex (2.17(6) Å) while the Al–H^b bond is longer in the Lu–H–Al bridge (1.81(14) Å) compared with that in the Y–H–Al bridge (1.57(6) Å).

Thus, the solid phase transformation results in the formation of an aluminium-hydride complex with a monodentate AlH_4 group. In the chemistry of aluminium hydride compounds with this structure were previously unknown, although mono-, bi-, tridentate BH_4 groups were studied in the complexes of its nearest analogue borane [16,17].

* Unfortunately, it is impossible to compare directly the structural data of IIb with $(\text{Cp}_2\text{YH})_2(\text{AlH}_3 \cdot \text{NEt}_3)_2$ because the coordinates of the hydride atoms in the latter are not known.

It follows from Fig. 3 that the arrangement of heavy atoms in molecule IIb is almost identical with their arrangement in the complex $(Cp_2YH)_2(AlH_3 \cdot NEt_3)_2$ and the space group preserves the symmetry. There are several reasons why the single-crystal structure undergoes the transformation IIa \rightarrow IIb unchanged. During transformation all four Lu–H bridge bonds in metallocycle $Lu(H)_2Lu$ of dimer IIa are broken. Naturally this cannot be compensated by strengthening of the Lu–H–Al bridge. Thus it can be assumed that the energy required for breaking the bonds in this case is compensated by increasing the energy of the crystal lattice: the unit cell volume of complex IIb is 15% less than that of IIa. However in agreement with the empiric Ostwald step rule and the 18-electron rule the dimer of smaller density always crystallizes first from a solution containing solvating solvent.

The monomer $Cp_2Lu(\mu_2-H)AlH_3 \cdot NEt_3$ is a coordination unsaturated 14-electron complex and possesses rather unique chemical and catalytic properties. To verify this assumption a method of preparing a sample of the monomer is being worked on. Unfortunately, the mechanism of the transformation IIa \rightarrow IIb is still obscure. Whatever it is, it does not depend purely on thermal treatment. The thermograms of $(Cp_2LuH)_2(AlH_3 \cdot NEt_3)_2$ taken in vacuo and under argon record only endo-effects and a loss in weight (9.6% at 105° and 17.7% at 130°) associated with decomposition of the compound.

X-ray induced solid phase transformations have not been observed previously, either for complexes I and III, or for analogous complexes of yttrium including the NEt_3 solvate [9]. Apparently, the combination of only two factors is decisive in stimulating the phase transformation of IIa \rightarrow IIb: (i) the decreased size of the metal atom enhances steric hindrances and (ii) the influence of a strong Lewis base that loosens the bridge hydrogen bond system.

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