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Homo- and heteronuclear hydrido lutetiecene complexes with bulky 1,3-di(tert-butyl)cyclopentadienyl ($C_5H_3{}^tBu_2$) ligands. The molecular structure of $[({}^tBu_2C_5H_3)LuH]_4[AlH_4 \cdot Et_2O]_2[AlH_4]_2$

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Abstract

Reactions occurring in the system $(Cp_2''LuCl)_2$–$MAlH_4$–L–solvent have been studied. It has been shown that the aluminohydride complexes $(Cp_2''LnAlH_4 \cdot L)_2$ formed are unstable and decompose, depending on reaction conditions, along three pathways: (a) desolvation, (b) dissociation of solvated aluminium hydride and (c) destruction of the cene moiety to produce the polynuclear monocyclopentadienyl hydridoaluminohydridic complex $[({}^tBu_2C_5H_3)LuH]_4[AlH_4 \cdot Et_2O]_2[AlH_4]_2$ (XII). Similar reaction of the departure of one of the cyclopentadienyl ligands is observed in $(Cp_2''LuCl)_2$ when it dissolved in aromatic solvents. Crystals of XII are triclinic: $a = 11.616(2)$, $b = 14.822(2)$, $c = 24.236(5)$ Å, $\alpha = 87.51(1)$, $\beta = 100.59(1)$, $\gamma = 75.83(1)°$, space group $P\bar{1}$, $Z = 2$. XII is characterized by the previously unknown tetrahedral metal core made of Lu atoms bound by bridging hydrogens and tri- (AlH_4) and tetra-dentate ($AlH_4 \cdot Et_2O$) groups.

Introduction

Biscyclopentadienyl hydride rare earth metal (REM) complexes are efficient catalysts of hydrogenation and polymerization [1]. Unfortunately, the synthesis of these compounds by hydrogenolysis [2] or pyrolysis [3] of the corresponding alkyls is rather complicated. The simplest exchange reaction of biscyclopentadienyl rare earth metal halides with binary alkali metal hydrides is heterogeneous in nature and thus is difficult to perform. At the same time homogeneous reactions with alkali metal aluminohydrides lead, as a rule, to coordinately saturated and, hence, catalytically inactive heteronuclear dimers $(Cp_2LnAlH_4 \cdot L)_2$ ($Cp = \eta^5$-C_5H_5, η^5-$C_5H_4{}^tBu$;

Ln = Y, Lu, Sm; L = NEt_3, Et_2O, THF) [4–6]. On heating or under high pressure, these compounds lose solvent molecules to afford $(Cp_2LnAlH_4)_n$, which reacts readily with alkenes in a stoichiometric rather than in a catalytic fashion [6]. In a large excess of triethylamine the complex $(Cp_2LnAlH_4 \cdot NEt_3)_2$ affords a mixture of two hydridic forms, $(Cp_2LuH \cdot NEt_3)_2$ and $(Cp_2LuH)_3$, which also do not display catalytic activity [7]. Several single crystals of the coordinately unsaturated 14e complex $Cp_2Lu(\mu_2\text{-}H)AlH_3 \cdot NEt_3$ were obtained from the corresponding dimer on X-ray irradiation (Mo-K_α) [8]. Other physical treatments either do not change its structure or result in complete destruction of the complex [5].

To this end, the literature data are indicative of a high stability of dimeric heterometallic aluminium or REM complexes with a common C_5H_5-ligand, one one hand, and their poor catalytic activity in hydrogenation and isomerization of alkenes, on the other. Introduction of two bulky tert-butyl groups into the cyclopentadienyl ring brings about additional pathways of decomposition of aluminohydride complexes involving elimination of aluminum hydrides [9] or of one Cp″-ligand [10].

In the present work we discuss the influence of various factors on the composition and the relative amount of the products formed in the system $Cp''_2Lu]_2\text{–}MAlH_4\text{–}L\text{–}solvent$ ($Cp'' = 1{,}3\text{-}C_5H_3{}^tBu_2$), as well as the results of an X-ray structural study and the reconstruction of the system of hydridic bonds in a novel crystallographic modification of the eight-nuclear monocyclopentadienyl aluminohydride complex $[Cp''_2Lu(H)AlH_4]_4 \cdot 2Et_2O$, which differs from that reported earlier [10] by the absence of the crystallization ether molecule.

Results and discussion

A heterogeneous reaction of $(Cp''_2LuCl)_2$ (I) with $LiAlH_4$ in an ether–pentane (1 : 10) mixture leads to the unstable etherate $Cp''_2LuAlH_4 \cdot Et_2O$ (II) (up to 70%) as a major product which decomposes in solution into the homonuclear hydride $[Cp''_2Lu(\mu\text{-}H)]_2$ (III) and aluminium hydride etherate (eq. 1). Decomposition of II is reversible and the precipitate of aluminium hydride etherate dissolves on heating.

$$(Cp''_2LuCl)_2^{\text{solid}} + 2LiAlH_4^{\text{susp}} \xrightarrow[-2LiCl]{Et_2O/C_5H_{12}} [Cp''_2LuAlH_4 \cdot Et_2O]_2^{\text{solut}}$$

$$[Cp''_2LuH]_2^{\text{solut}} + 2/n[AlH_3 \cdot xEt_2O]_n^{\text{solid}} \qquad (1)$$

According to the X-ray data [9], III is a dimer with the $\mathrm{Lu}\overset{\mathrm{H}}{\underset{\mathrm{H}}{<\;>}}\mathrm{Lu}$ metallacycle and the latter gives rise to a group of bands at 1280, 1090 and 820 cm^{-1} in the IR spectrum shifting to 930, 185 and 590 cm^{-1} on deuteration ($\nu(M\text{–}H)/\nu(M\text{–}D) = 1.38$) (Fig. 1a). Its structure (Fig. 2) is typical for REM biscyclopentadienyl chlorides rather than for REM biscyclopentadienyl hydrides [11]. It also differs from both $[Cp^*_2LnH \cdot THF]_2$ [12] and the asymmetrical dimer $[(C_5Me_5)_2Sm(\mu\text{-}H)Sm(H)(C_5Me_5)_2]$ [13]. The chemical properties of the complex are also different when compared with the related hydride species. In fact, in contrast to complexes with C_5Me_5-ligand [13], III does not afford solvated dimers, such as $[Cp_2LnH]_2$ [12], under the action of such bases as THF. It should be mentioned that III is very resistant to oxidation: its crystals do not change after 3–5 min exposure to air.

Reaction 1 also affords the ate-complex $Cp''_2LuCl_2Li \cdot 2Et_2O$ (IV) as a by-prod-

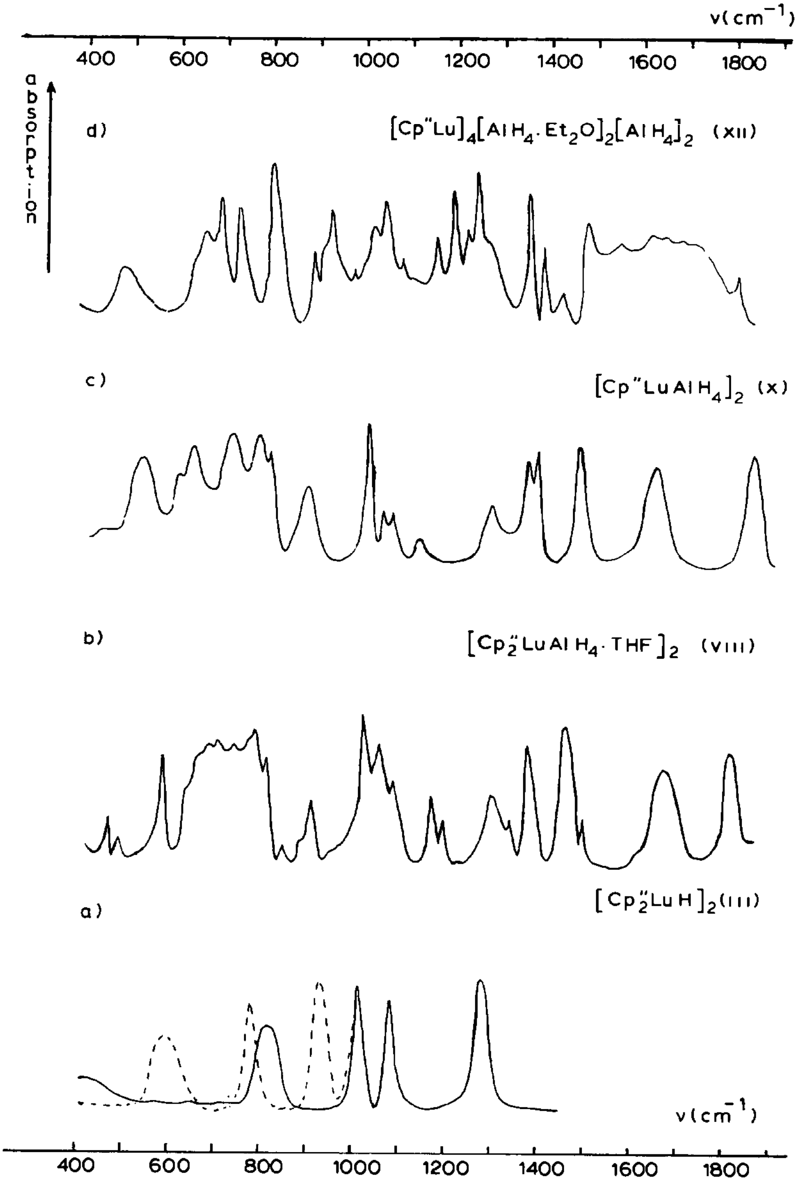


Fig. 1. IR spectra of lutetiecene hydride complexes.

uct which is resistant to the action of $LiAlH_4$. Addition of stoichiometric amounts of TMEDA or THF to the system increases the stability of the ate-complexes and their yields reach 50%. Along with III, $Cp_2''LuCl_2Li \cdot$ TMEDA (V) and $Cp_2''LuCl_2Li$ $\cdot$ THF (VI) crystallize from the reaction mixture. Structures of these compounds are described in refs. 11 and 15, respectively, and are identical to ate-complexes of the type $(C_5Me_5)_2Ln(\mu\text{-}Cl)_2Li \cdot L_2$ [11]. Under heterogeneous conditions the reaction 1

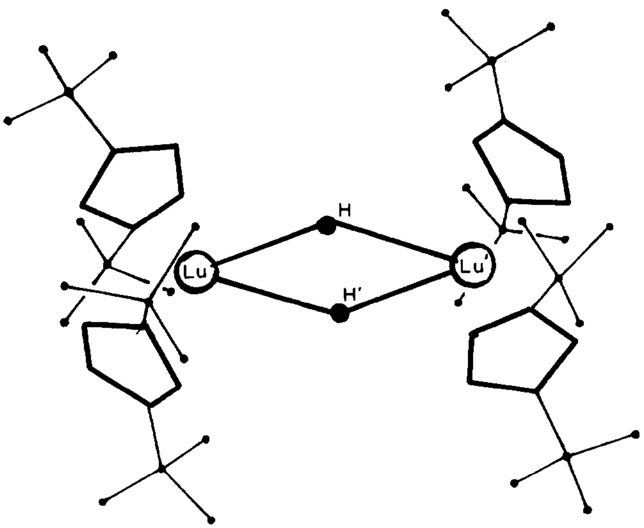


Fig. 2. The molecular structure of $[(^{t}Bu_2C_5H_3)_2Lu(\mu_2\text{-}H)]_2$ (III).

at low concentrations of $LiAlH_4$ leads to homometallic hydride III rather than to bimetallic hydride complexes.

An increasing the percentage of Et_2O in the ether–pentane mixture up to 50%, the concentration of $LiAlH_4$ in solution increases and the reaction becomes homogeneous in nature. This drastically changes its course: the formation of ate-complexes and hydrides (eq. 1) is retarded while a novel reaction leading to decomposition of the biscyclopentadienyl fragment in II is observed to begin. In pure ether, these reactions are accomplished in several hours and the compound which precipitates is formulated as $\{[(^{t}Bu_2C_5H_3)LuH]_4[AlH_4 \cdot Et_2O]_2[AlH_4]_2\} \cdot Et_2O$ (VII) on the basis of a preliminary X-ray investigation without location of the hydrogens [10].

The homogeneous reaction between I and $MAlH_4$ in THF affords $Cp_2''LuAlH_4 \cdot$ THF (VIII) in 95% yield. The IR spectrum of this amorphous uncrystallizable material (Fig. 1b) is close to the spectra of the tetranuclear complexes $[Cp_2M(\mu\text{-}H)]_2[AlH_3 \cdot THF]_2$ (IX) (M = Y [16], Lu [5]), i.e. in VIII the metals are bonded through μ_2- and μ_3-bridging hydrogens, as in the majority of compounds of this type [17]. The bands arising from metal–hydride bonds in VIII are shifted by 20–50 cm^{-1} to higher wavelengths (Fig. 1b) as compared with IX and this is expected in the light of a noticeable decrease of the strength of those bonds on going from C_5H_5 to Cp″ complexes. The latter is explained by a decrease in acidity of Ln on coordination of a more basic ligand. A consequence of the weakening of the metal–hydrogen bonds is a ready decomposition of VIII by pentane affording first a THF-free, fine-crystalline precipitate of $[Cp_2''LuAlH_4]_n$ (X) (its IR spectrum (Fig. 1c) is close to that of VIII but the Al–H bonds are shifted to lower wavelengths by 40–50 cm^{-1}) which in the presence of the mother liquor gives a solution of III and a precipitate consisting mainly of $AlH_3 \cdot THF$.

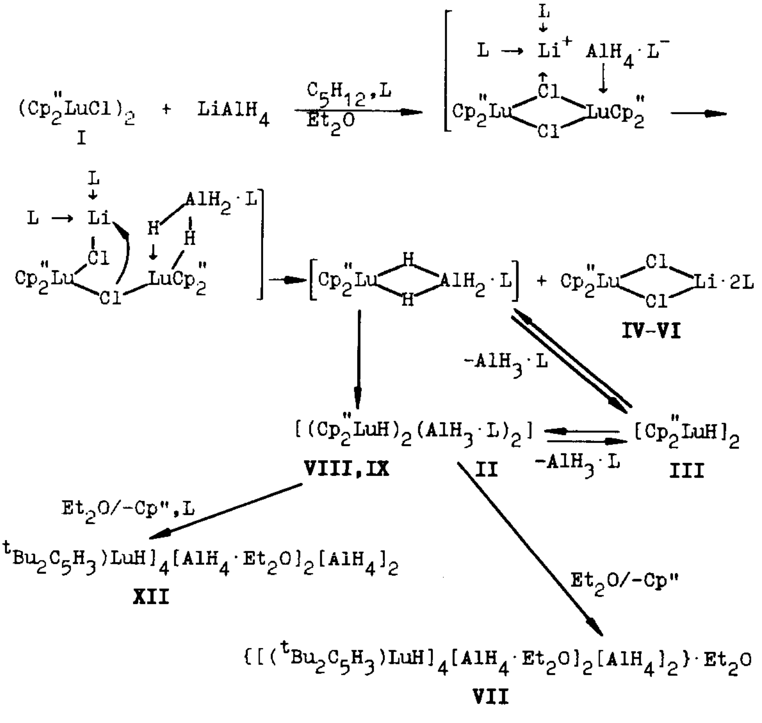
Complex VIII decomposes in the solid state and in a THF solution as well. In the latter case, the decomposition is irreversible, accompanied by the cleavage of the biscyclopentadienyl fragment and strongly accelerated by the presence of diethyl ether. Free $C_5H_4{}^tBu_2$ is detected in the reaction mixture by ^1H NMR after 2 d, while the IR spectrum of the precipitate (Fig. 1d) differs significantly from that of the starting material. On the treatment of VIII with ether, another remarkable process is observed, namely a replacement of a stronger base (THF) by a weaker one (Et_2O), possibly through the desolvation of the complex. A similar process is observed on treatment of the complex $[Cp_2''LuAlH_4 \cdot NEt_3]_2$ (XI) with ether. The crystal formed in both cases have composition $[(^tBu_2C_5H_3)LuH]_4[AlH_4 \cdot Et_2O]_2[AlH_4]_2$ (XII), being a novel crystallographic modification of polynuclear complex VII. All these observations suggest that the reactions taking place in the system $(Cp_2''LuCl)_2$–$LiAlH_4$–Et_2O–L–pentane may be rationalized in terms of Scheme 1.

The stoichiometry of complexes VII and XII suggests that these would have been prepared according to reaction 2, and, in fact, complex VII was obtained in this way, but in a low yield. A variety of other products, probably including the ate-complex $Cp''LuCl_3Li \cdot 2Et_2O$, were also obtained by reaction 2.

$$Cp''LuCl_2 + 2LiAlH_4 \xrightarrow[-2LiCl]{Et_2O} [Cp''Lu(AlH_4)_2] \longrightarrow$$

$$Cp''LuH(AlH_4) + AlH_3 \cdot L \quad (2)$$

The IR spectrum of XII (Fig. 1d) contains various bands arising from metal–hydride bonds including those at 1850 cm^{-1} are indicative of the presence of both



Scheme 1

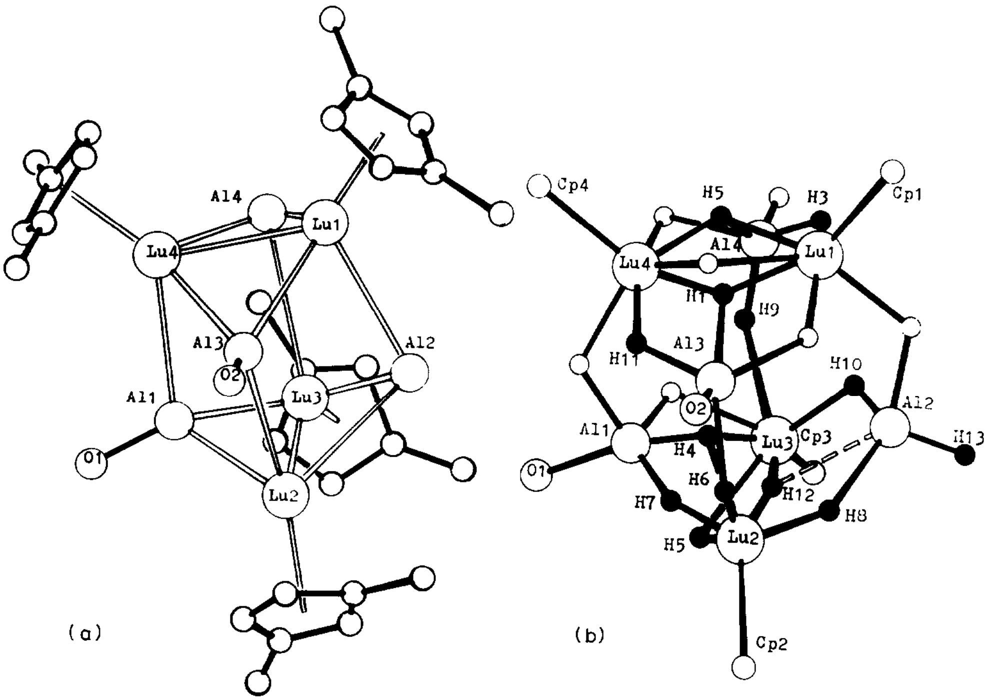


Fig. 3. (a) The metal core of $\{[({}^{t}Bu_2C_5H_3)LuH]_4[AlH_4\cdot Et_2O]_2[AlH_4]_2\}$ (XII). (b) The reconstruction of hydride bonding system (shaded circles indicate hydrogen atoms located by the difference synthesis).

bridging and terminal hydrogens. Complex XII is unstable and decomposes slowly on storing. Unfortunately it is also sensitive to X-ray irradiation. Therefore we were unable to localize all hydrogens in the X-ray structural determination and, hence, additional evidence was used for establishing the binding mode.

According to the X-ray data, the metal core of XII (Fig. 3a) is made of four η^5-Cp″-bound Lu atoms located in the apices of a tetrahedron elongated along its noncrystallographic second-order axis. Aluminium atoms are located above each $[Lu]_4$ triangle face of the tetrahedron closer to the shorter edges. The metal core is thus cubic, as observed, for example, in $(CpNiBH)_4$ [18] and $(CpCoBH)_4$ [19]. There are two short contacts Lu1 · · · Lu4 and Lu2 · · · Lu3, of 3.35(1) Å which are the lowest among the known Ln · · · Ln distances in hydride REM complexes. Other Lu · · · Lu distances lie in the range 5.23–5.49 Å. As in $(Cp_2YAlH_4)_2\cdot Et_2O$ (XIII) [4], the Al atoms are nonequivalent. Two of them coordinated by Et_2O (Al1 and Al3), are equally spaced from the closest Lu atoms by 2.93(1) Å, whereas the nonsolvated ones (Al2 and Al4) are separated by 3.24(1) Å. All four Al atoms are almost equally spaced (3.55–3.63 Å) from the third, the most remote of the $[Lu_3]$ triangle. It should be mentioned that the metal core in XII is much more symmetrical than in VII (the scatter of the values of the short metal–metal contacts is within experimental error (~ 0.015 Å, Table 1) vs. 0.05–0.1 Å in VII [10]).

The system of hydridic bonds in XII shown in Fig. 3b was based on the stoichiometry, the data on interatomic contacts and published data on yttrium

[4,16,17], lutetium [5,7,8], samarium [6] and ytterbium [7] complexes. Let us consider the main arguments in favour of this model.

Very short (Lu1 ··· Lu4 and Lu2 ··· Lu3) distances (Table 1) are nevertheless higher than the sum of the metal covalent radii (3.12 Å). Because of this and since Lu^{III} cannot be reduced to Lu^{II} by $LuAlH_4$, a direct intermetallic Lu–Lu bond should be eliminated in XII, but a short non-bonding contact Lu ··· Lu is obviously due to the presence of two or, more likely, three Lu–H–Lu bonds. The stoichiometry suggests that every Lu atom, in addition to AlH_4-moieties (or $AlH_4 \cdot Et_2O$), is bonded with additional hydrogen which undoubtedly forms a bridging bond with adjacent Lu, i.e. the metals within Lu1–Lu4 and Lu2–Lu3 pairs are mutually bonded by a double hydrogen bridge. Actually, the difference synthesis indicates that the Lu2–Lu3 pair has the bridging hydrogens H5 and H12. For the other pair, only H2 has been located (Fig. 3b).

The orientation of the coordinated ethers at Al1 and Al3 (the bond Al–O is practically perpendicular to the corresponding Lu_3 face) is indicative of the absence of terminal hydrogens, while the Al–O distance in XII (Table 1), close to that in complex XIII (1.94 Å [4]), $[(Cp_2YCl)_2AlH_3 \cdot OEt_2]_x$ (1.89 Å [20]) and $(Cp_2YAlH_4 \cdot THF)_2$ (1.97 Å [16]), leads to the conclusion that atoms Al1 and Al3 have a coordination number equal to 5. At the same time Al2 and Al4 must have a purely hydridic environment with a terminal Al–H bond. The latter is consistent with the IR data and the difference synthesis (Al2–H13 bond in Fig. 3b). The distances between all the aluminium atoms and the third remote apex are significantly larger than those between Al and the two closest Lu atoms (Table 1) and correspond to the distance M ··· Al in aluminohydride complexes with one three-centred M–H–Al bond (3.51–3.58 Å) [17,20] indicating the presence of four mono-bridges $Al{-}H{-}Lu_{distal}$ in XII (two of the four, H6 and H9 have been located). In addition, the close proximity of Al atoms to the short edges Lu1 ··· Lu4 and Lu2 ··· Lu3 and their equal separation from the Lu atoms supports the idea that Al and the closest Lu atoms should be bonded through two symmetrical Lu–H–Al bridges (five of the eight hydrogens—H3, H7, H8, H10 and H11—were located). The solvated Al atoms, as in complex XIII [4], are located much closer to the $[Lu_2]$ edge (~ 0.3 Å), than in the unsolvated ones. One may conclude, thus, that there is an additional bonding between these two Lu atoms and Al through a (μ_3-H) bridge. The latter is also supported by a deflection of the Lu–Cp″ bonds from a mirror symmetry plane of the tetrahedron $[Lu_4]$ opposite to these hydrogens. As a result, the angle Cp″–Lu–(μ_3-H) is close to 180°. The μ_3-hydrogen is located in the axial position of the trigonal bipyramid at Al (the second axial ligand is Et_2O). Its presence, along with two other bridging hydrogens between Lu atoms, accounts fairly well for the anomalously short contact between these atoms.

Three hydrogens of the unsolvated $[AlH_4]$ group are bonded with the three lutetiums of the corresponding edge of the tetrahedron, while the fourth is terminal. The analysis of the interatomic distances involving Al2 and Al4 atoms reveals rather short nonbonding Al2 ··· H12 and Al4 ··· H2 contacts in complex XII. Taking into account the shortening of the distance Al_{unsolv} ··· Lu by ~ 2.3 Å as compared with complex XIII having a tetrahedral environment at aluminium [4], these contacts might be treated as a secondary Al ··· H bond which increases the coordination number of Al2 and Al4 atoms to 5.

The construction of hydridic bonds thus made (Fig. 3b) seems to be realistic. Of

Table 1

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

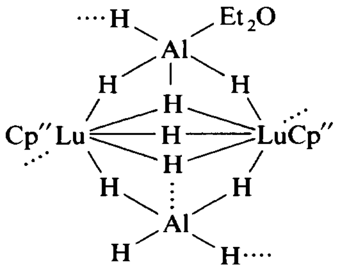
Atom	x	y	z	B_{eq}
Lu(1)	5615(1)	1724(1)	3671(1)	47(1)
Lu(2)	3135(1)	2025(1)	1621(1)	46(1)
Lu(3)	5570(1)	2819(1)	1553(1)	47(1)
Lu(4)	3830(1)	3902(1)	3322(1)	50(1)
Al(1)	3312(8)	3918(5)	1817(3)	50(3)
Al(2)	5796(9)	895(6)	2314(3)	64(4)
Al(3)	3077(8)	2192(5)	3077(3)	48(3)
Al(4)	6470(8)	3294(6)	2996(3)	56(4)
C(1)	5782(27)	576(23)	4516(12)	54(14)
C(2)	5989(31)	1384(18)	4726(11)	61(14)
C(3)	7125(29)	1460(19)	4637(10)	56(13)
C(4)	7556(25)	693(19)	4343(10)	52(12)
C(5)	6708(27)	131(18)	4286(11)	51(12)
C(6)	2561(26)	980(19)	847(10)	59(13)
C(7)	2288(28)	606(19)	1344(12)	58(13)
C(8)	1287(27)	1343(22)	1477(11)	71(14)
C(9)	1061(29)	2070(17)	1060(12)	65(14)
C(10)	1747(26)	1886(19)	673(10)	55(13)
C(11)	6982(29)	3647(18)	1130(11)	66(14)
C(12)	5920(27)	3728(20)	726(12)	70(14)
C(13)	5886(26)	2855(23)	521(12)	72(14)
C(14)	6921(27)	2195(18)	808(11)	54(13)
C(15)	7565(23)	2693(18)	1186(11)	64(12)
C(16)	2623(30)	5537(20)	3418(12)	68(14)
C(17)	3783(36)	5581(20)	3594(12)	43(16)
C(18)	4252(27)	4975(21)	4091(13)	67(14)
C(19)	3381(33)	4604(18)	4227(12)	69(15)
C(20)	2275(29)	4977(19)	3850(13)	60(15)
C(21)	7870(29)	2171(20)	4866(11)	74(14)
C(22)	7018(36)	3130(22)	4944(16)	138(20)
C(23)	8601(33)	1682(22)	5464(13)	107(18)
C(24)	8764(41)	2298(31)	4490(16)	139(26)
C(25)	6925(34)	−820(21)	4081(13)	81(16)
C(26)	5811(37)	−990(21)	3734(17)	127(21)
C(27)	7900(39)	−1009(23)	3699(14)	117(20)
C(28)	7390(42)	−1561(21)	4580(14)	119(23)
C(29)	2803(38)	−429(22)	1602(13)	86(17)
C(30)	2900(45)	−436(24)	2247(13)	150(25)
C(31)	1830(43)	−936(24)	1350(16)	141(23)
C(32)	3930(44)	−906(23)	1493(18)	119(23)
C(33)	1656(27)	2416(19)	118(11)	66(13)
C(34)	2803(33)	2344(27)	−51(13)	104(19)
C(35)	786(32)	2071(23)	−314(11)	95(16)
C(36)	1111(34)	3463(20)	152(13)	102(17)
C(37)	398(40)	5693(27)	4183(20)	136(20)
C(38)	7473(29)	4477(19)	1377(14)	76(15)
C(39)	8551(38)	4086(24)	1877(14)	113(19)
C(40)	6494(40)	5177(22)	1549(20)	145(25)
C(41)	8026(33)	4869(22)	908(13)	97(17)
C(32)	7350(30)	1208(22)	694(14)	80(15)
C(43)	6296(34)	801(25)	443(18)	119(22)

Table 1 (continued)

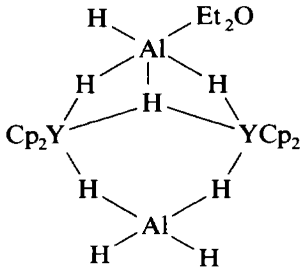
Atom	x	y	z	B_{eq}
C(44)	8125(39)	567(22)	1190(18)	122(21)
C(45)	8189(36)	1193(22)	267(15)	108(18)
C(46)	4398(31)	6246(19)	3336(13)	84(15)
C(47)	5778(35)	6012(24)	3539(19)	131(21)
C(48)	3898(37)	7241(22)	3494(17)	112(20)
C(49)	4172(35)	6309(22)	2713(17)	111(20)
C(50)	1005(33)	4898(20)	3841(16)	94(17)
C(51)	1116(42)	3965(28)	4162(17)	127(24)
C(52)	237(30)	4995(23)	3278(18)	100(18)
C(1)	2289(18)	5059(11)	1352(7)	69(8)
C(53)	2649(34)	5418(25)	849(23)	147(26)
C(54)	1019(25)	5376(23)	1339(16)	99(16)
C(55)	777(45)	6046(32)	1734(20)	171(29)
C(56)	2850(44)	6455(30)	773(23)	178(30)
O(2)	1801(24)	1801(11)	3346(6)	66(8)
C(57)	595(24)	2197(19)	3074(12)	74(13)
C(58)	−163(30)	1549(22)	2918(13)	97(15)
C(59)	1978(33)	1389(21)	3929(12)	88(16)
H(1)	424	259	332	
H(2)	505	298	370	
H(3)	625	218	339	
H(4)	418	234	218	
H(5)	383	250	131	
H(6)	297	201	111	
H(7)	251	292	181	
H(8)	416	143	182	
H(9)	638	327	236	
H(10)	682	175	217	
H(11)	235	334	307	
H(12)	487	228	175	
H(13)	659	7	219	

the 20 hydrogens, 13 were located in the difference synthesis, (shaded, numbered circles in Fig. 3b) and are positioned practically as the model predicts. The proximate Lu atoms are linked by one μ_2- and two μ_3-bridges (one inside and one outside the metallotetrahedron). They are also bound with remote and adjacent aluminium with one μ_2- and μ_2/μ_3-bridging hydrogens, respectively. All lutetiums have identical ligand environments with the coordination number of 9 and are bonded, in addition to the Cp″-ring, with 6 bridging hydrogens. The coordination polyhedron of Lu is a pentagonal bipyramid, the Cp″-ring and μ_3-hydrogen being axial ligands, resembling that in the monocyclopentadienyl rhenium complex Cp^*ReH_6 [21]. Complex XII thus appear to be the first representative of hydridic heterometallic compounds whose aluminohydride groups behave as complex μ_3-ligands with respect to a bulky metal core.

Although the mechanism of formation of XII is obscure, the experimental data obtained indicate the formation of some intermediates. If XII is considered as a composite of two fragments XIIa, one may see that the latter are related to yttrium aluminohydride XIII with the usual C_5H_5-rings [4]. The formation of the lutetium analogue of XIII from the heterometallic dimer $[Cp''_2LuAlH_4 \cdot L]_2$ requires a complete desolvation followed by resolvation of the latter, since only these steps may account for the formation of complex XII from the amine and THF complexes on addition of ether. The replacement of a weaker base by a stronger one is often observed in alane chemistry. In the present case, however, a unique reverse reaction is observed.



(XIIa)



(XIII)

The next step, which can also be parallel, is probably associated with the loss of the Cp″-ligand. If in the case of $Cp''LuCl_2$ (eq. 2) a way to the $\mathrm{Lu}\langle{}^{\mathrm{H}}_{\mathrm{H}}\rangle\mathrm{Lu}$ fragment is rather obvious, the nature of this process involving the cleavage of the cene (Cp_2M) fragment in the case of Cp''_2LuCl is unclear. However, since the yield of XII on decomposition of the aluminohydrides is not quantitative and $(Cp''_2LuH)_2$ and $AlH_3 \cdot Et_2O$ are formed in parallel reactions, it may be assumed that the ligand loss is associated with the exchange reaction (eq. 3).

$$Cp''_2LuX + AlH_3 \cdot Et_2O \longrightarrow Cp''LuH(X) + AlH_2Cp'' \cdot Et_2O \qquad (3)$$

The cleavage of the cene structure in the wedge-like C_5Me_5-complexes was described only in the oxidation of $Cp^*_2Yb(II)$ by silver fluoride [22] resulting in the mixed-valent compound $Cp^*_6Yb_4(\mu\text{-}F)_4$. This cleavage is probably more typical of ${}^tBu_2C_5H_3$-complexes. The C_5Me_5- and ${}^tBu_2C_5H_3$-ligands have close electronic and spatial characteristics, but the spatial anisotropy of the latter is higher. As a consequence, joint coordination of the two Cp″-rings and frontal ligands is complicated.

It should be mentioned here that attempts to dissolve starting monochloride I in aromatic solvents (benzene, toluene) also resulted in cleavage of the cene structure accompanied by the appearance of green (after stirring of the suspension at room temperature for 2–3 weeks) or red (after refluxing for 1–2 days) coloration. The ^1H NMR spectra of these solutions are much more complex than that of $Cp''_2LuCl \cdot THF$ and are difficult to assign. However, the signals from free $C_5H_4({}^tC_4H_9)_2$ are clearly observed. In fact, it was isolated in pure form. The cleavage of the cene structures under the action of weak π-bases such as benzene or toluene was not previously observed in transition metal complexes. These processes result in formation of charge-transfer complexes with maxima at 400 and 615 nm in toluene and at 616 nm in benzene. Their nature is now under study.

Despite the chemistry of I in aromatic solvents being poorly understood, such behaviour shows that aromatic solvents should not be used as a medium for transformations of the complexes.

The final reaction step, i.e. the coupling of XII, is thermodynamically favourable since it leads to the coordinately saturated species and the polycyclic structure.

In conclusion, the dimeric complexes $(Cp''_2LuH)_2(AlH_3 \cdot L)_2$ formed on interaction of Cp''_2LuCl and $LiAlH_4$ in the presence of Lewis bases L are unstable, contrary to similar compounds with Cp-ligands [4,5,16,17], and undergo partial decomposition via three pathways: dissociation of solvating ligand L to afford $(Cp''_2LuAlH_4)_2$ (probably the step necessary for further transformation), dissociation of the cyclopentadienyl ligand to form the coordinately saturated tetramer XII, or dissociation of the alane leading to unsaturated dimeric hydride III. Coordinately saturated eight-nuclear complex XII, and lutetium biscyclopentadienyl aluminohydrides [5], do not catalyse hydrogenation, isomerization and polymerization of alkenes. At the same time the dimeric homonuclear hydride III is a catalyst of the hydrogenation of hexene-1 by molecular hydrogen at a rate of 40 mol/g-atom Lu min. This value seems to be significant taking into account the substantial steric hindrance at the metal centre. In particular, the efficient catalyst of hydrogenation of alkenes, $(Cp_2Ti)_2AlH_4Cl$, probably forming the Cp_2TiH intermediate [23] has partial activity of 125 mol/mol cat min which decreases to 60 mol/mol cat min on going to $(^tBuC_5H_4)_2Ti]_2AlH_4Cl$, i.e. by a factor of 2 [24], and it should decrease even more on introducing the second ^tBu group into the cyclopentadienyl ring.

Experimental

1. $Cp''_2LuCl_2Li \cdot 2Et_2O$ (IV). To a suspension of I (1.68 g, 3.0 mmol) in 100 ml pentane, an equimolar amount of $LiAlH_4$ in 10 ml ether was added with mixing. The reaction mixture was stirred for 2 h and the residue filtered. The filtrate was evaporated by 50%. The colourless fine crystalline precipitate was separated and vacuum dried to yield 1.12 g $Cp''_2LuCl_2Li \cdot Et_2O$. Anal. Found: Lu, 23.4; Li, < 1.0; Cl, 9.5. $C_{34}H_{62}O_2LuCl_2Li$ calcd.: Lu, 23.15; Li, 0.92; Cl 9.38%.

2. $Cp''_2LuCl_2Li \cdot TMEDA$ (V). To a suspension of I (1.56 g, 2.8 mmol) in 150 ml of an ether–pentane mixture (1 : 1), an equimolar amount of $LiAlH_4$ in 8 ml ether was added. The mixture was stirred for 2 h, the precipitate removed, and 0.2 ml TMEDA in 10 ml ether was added to the filtrate. Colourless stick-like crystals were filtered and dried in vacuum to yield 0.67 g $Cp''_2LuCl_2Li \cdot TMEDA$. Anal. Found: Lu, 24.2; Li, ~ 1.0; Cl, 9.7. $C_{32}H_{58}N_2LuCl_2Li$ calcd.: Lu, 24.18; Li, 0.96; Cl, 9.78%.

3. $Cp''_2LuCl_2Li \cdot 2THF$ (VI). To a suspension of I (1.32 g, 2.3 mmol) in 100 ml of an ether–pentane mixture (1 : 1), 4 ml THF and on mixing $LiAlH_4$ (2.3 mmol) were added. The suspension was mixed for 2 h and then filtered. The filtrate was concentrated to 50 ml and cooled to $-10\,^\circ C$. The colourless cubic crystals formed were decanted and vacuum dried to yield 0.52 g $Cp''_2LuCl_2Li \cdot 2THF$. Anal. Found: Lu, 23.3; Li, < 1.0; Cl, 9.5. $C_{34}H_{58}O_2LuCl_2Li$ calcd.: Lu, 23.28; Li, 0.92; Cl, 9.43%.

4. $Cp''_2LuAlH_4 \cdot THF$ (VIII). To a solution of Cp''_2LuCl (1.63, 2.9 mmol) in 100 ml THF, a solution of $NaAlH_4$ (29 mmol) in THF was added dropwise. The solution was evaporated by 50% and the NaCl precipitated was removed. Evaporation of the solvent gave a yellow oily material. Found: Lu, 28.1; Al, 4.5. $C_{30}H_{54}O$-LuAl calcd.: Lu, 27.65; Al, 4.26%.

5. Cp''_2LuAlH_4 (X). Pentane (100 ml) was added to VIII. A white crystalline precipitate was formed after 10 min mixing, filtered and vacuum dried to afford

Cp''_2LuAlH_4 (with respect to Cp''_2LuCl: 79%). Found: Lu, 31.2; Al, 4.7. $C_{26}H_{46}LuAl$ calcd.: Lu, 31.21; Al, 4.81%.

6. *Cp''_2LuH (III).* (a) A suspension of X in pentane was stirred for 2 h and the precipitate filtered. The filtrate was concentrated to half the starting volume and cooled to −10 °C. A small amount of sticky crystals was formed. Further evaporation of solvent gave the microcrystalline material. Anal. Found: Lu, 33.0. $C_{26}H_{43}Lu$, calcd.: Lu, 32.98%.

(b) The mother liquor of synthesis 1 was concentrated to 10 ml. After separation of precipitated $AlH_3 \cdot Et_2O$, the solution was cooled to −20 °C, 0.35 g of crystalline III was formed.

7. *$Cp''_2LuAlH_4 \cdot NEt_3$ (XI).* Cp''_2LuCl (1.10 g, 2 mmol) was suspended in a mixture of ether and 5 ml NEt_3. A solution of $LiAlH_4$ (2 mmol) in 4 ml was added dropwise. The solution became homogeneous and the precipitation of LiCl began after several minutes. The precipitate was filtered after 1 h, and the solution concentrated to 20 ml. The crystals formed (square plates) were decanted, washed with cold pentane and vacuum dried. The substance is unstable in the solid state at room temperature. 0.55 g of $Cp''_2LuAlH_4 \cdot NEt_3$ was isolated. Anal. Found: Lu, 26.8; Al, 4.2. $C_{32}H_{57}NLuAl$ calcd.: Lu, 26.44; Al, 4.08%.

8. *$[(Cp''_2LuH)_4(AlH_4)_2(AlH_4 \cdot Et_2O)_2] \cdot Et_2O$ (VII).* Complex I (1.38 g, 2.4 mmol) was suspended in 100 mL ether and $LiAlH_4$ (2.4 mmol) in 10 ml ether was added dropwise on mixing. LiCl began to precipitate after several minutes and was then separated. The solution was evaporated to 30 ml, allowed to stand overnight and then cooled to −10 °C. The sticky crystals that precipitated were washed with cold

Table 2

Main interatomic distances *d* (Å) in $[(^tBu_2C_5H_3)LuH]_4[AlH_4 \cdot Et_2O]_2[AlH_4]_2$

$Lu-C_{av}$	2.58(4)	Lu3–H9	2.21
Lu1–CpI	2.295	Lu3–H10	2.2
Lu1 ··· Lu4	3.358(1)	Lu3–H12	1.4
Lu1 ··· Al3	2.932(8)	Lu4–CpIV	2.287
Lu1 ··· Al4	3.236(10)	Lu4 ··· Al3	2.927(9)
Lu1–H1	1.8	Lu4 ··· Al4	3.230(9)
Lu1–H2	1.8	Lu4–H1	1.9
Lu1–H3	1.4	Lu4–H2	1.8
Lu2–CpII	2.261	Lu4–H11	2.1
Lu2 ··· Lu3	3.345(2)	Al1–O1	1.98(2)
Lu2 ··· Al1	2.915(8)	Al1–H4	1.7
Lu2 ··· Al2	3.239(8)	Al1–H7	1.9
Lu2–H4	2.3	Al2–H8	2.0
Lu2–H5	1.5	Al2–H10	2.0
Lu2–H6	1.4	Al2–H13	1.4
Lu2–H7	1.5	Al2 ··· H12	2.3
Lu2–H8	1.3	Al3–O2	1.92(2)
Lu2–H12	2.1	Al3–H1	1.6
Lu3–CpIII	2.298	Al3–H6	2.3
Lu3 ··· Al1	2.926(8)	Al3–H11	1.7
Lu3 ··· Al2	3.255(9)	Al4–H3	1.9
Lu3–H4	2.4	Al4–H9	1.5
Lu3–H5	2.0	Al4 ··· H2	2.4

ether and vacuum dried to yield 0.85 g $[(Cp''_2LuH)_4(AlH_4)_2(AlH_4\cdot Et_2O)_2]\cdot Et_2O$. Anal. Found: Lu, 39.8; Al, 6.3. $C_{64}H_{134}O_3Lu_4Al_4$ calcd.: Lu, 39.78; Al, 6.13%.

9. $[(Cp''_2LuH)_4(AlH_4)_2(AlH_4\cdot Et_2O)]$ (XII). (a) The mother liquor of synthesis 7 was allowed to stand overnight. The prismatic crystals that formed were decanted, washed with cold ether and vacuum dried to afford 0.37 g $[(Cp''_2LuH)_4(AlH_4)_2(AlH_4\cdot Et_2O)]$. Anal. Found: Lu, 41.4; Al, 6.5. $C_{60}H_{124}O_2Lu_4Al_4$ calcd.: Lu, 41.53; Al, 6.40%.

(b) Complex VIII was dissolved in 50 ml ether and filtered. The filtrate was evaporated to half the starting volume and allowed to stand for 40 h. Prisms of $[(Cp''_2LuH)_4(AlH_4)_2(AlH_4\cdot Et_2O)]$ (XII) were obtained as in 9(a).

Table 3

Main bond angles ω (°) in XII

Lu4Lu1Al3	55.0(2)	H5Lu3H1	40
Lu4Lu1Al4	58.6(10	H9Lu3H10	62
Al3Lu1Al4	97.8(2)	H10Lu3H12	73
Cp1Lu1H1	145	Lu1Lu4Al3	55.1(1)
Cp1Lu1H2	117	Lu1Lu4Al4	58.8(2)
Cp1Lu1H3	119	Al3Lu4Al4	98.0(2)
H1Lu1H2	46	Cp4Lu4H1	145
H1Lu1H3	87	Cp4Lu4H2	100
H2Lu1H3	71	Cp4Lu4H11	134
Lu3Lu2Al1	55.2(2)	H1Lu4H2	46
Lu3Lu2Al2	59.2(2)	H1Lu4H11	66
Al1Lu2Al2	98.5(2)	H2Lu4H11	108
Cp2Lu2H4	169	Lu2Al1Lu3	69.9(2)
Cp2Lu2H5	114	Lu2Al1O1	124.7(6)
Cp2Lu2H6	111	Lu3Al1O1	123.0(7)
Cp2Lu2H7	111	O1Al1H4	177
Cp2Lu2H8	113	O1Al1H7	112
Cp2Lu2H12	146	H4Al1H7	67
H4Lu2H5	68	Lu2Al2Lu3	62.0(1)
H4Lu2H6	66	H8Al2H10	106
H4Lu2H7	58	H8Al2H12	45
H4Lu2H8	78	H8Al2H13	120
H4Lu2H12	42	H10Al2H12	62
H5Lu2H7	92	H10Al2H13	96
H5Lu2H12	43	H12Al2H13	128
H6Lu2H7	62	Lu1Al3Lu4	69.9(2)
H8Lu2H12	87	Lu1Al3O2	124.8(2)
Lu2Lu3Al1	54.9(2)	Lu4Al3O2	126.1(6)
Lu2Lu3Al2	58.8(2)	O2Al3H1	138
Al1Lu3Al2	97.9(2)	O2Al3H6	112
Cp3Lu3H4	168	O2Al3H11	92
Cp3Lu3H5	118	H1Al3H6	110
Cp3Lu3H9	112	H1Al3H11	81
Cp3Lu3H10	106	H6Al3H11	101
Cp3Lu3H12	145	Lu1Al4Lu4	62.6(2)
H4Lu3H5	59	H2Al4H3	44
H4Lu3H9	70	H2Al4H9	133
H4Lu3H10	86	H3Al4H9	116

The catalytic activity of the complexes in isomerization of hexene-1 was studied as described elsewhere [23].

An X-ray diffraction study was carried out on a automatic Syntex $P\bar{1}$ diffractometer. A single crystal was sealed in a glass capillary. Crystals of XII are triclinic: $a = 11.616(2)$, $b = 14.822(2)$, $c = 24.236(5)$ Å, $\alpha = 87.51.1)^\circ$, $\beta = 100.59(1)^\circ$, $\gamma = 78.83(1)^\circ$, $V = 3959.6(2)$ Å^3, space group $P\bar{1}$, $Z = 2$, $\rho_{\text{calcd}} = 1.41$ g/cm^3. 5808 unique reflections with $I > 3\sigma(I)$ were used. The structure was solved by the Patterson method and refined by the least-squares routine in an anisotropic (hydrogens in isotropic) approximation to $R = 0.069$ ($R_w = 0.075$). Hydridic hydrogens were located in the difference synthesis. Atomic coordinates are given in Table 1, and the main interatomic distances and bond angles in Tables 2 and 3, respectively.

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