Studies on Organolanthanide Complexes.
XI.** Preparation of Dimeric Dicyclopentadienyllutetium Hydride by Reduction of Dicyclopentadienyl Lutetium Chloride with Sodium Hydride; its X-ray Crystal Structure and Reactivity

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Abstract

Dimeric di-η^5-cyclopentadienyllutetium hydride was prepared by the reaction of dicyclopentadienyllutetium chloride with sodium hydride in THF at ambient temperature. The solution was concentrated and cooled to –30 °C to afford the crystalline complex $[(\eta^5\text{-}C_5H_5)_2LuH\cdot OC_4H_8]_2$. The crystals of $[(\eta^5\text{-}C_5H_5)_2LuH\cdot OC_4H_8]_2$ belong to the triclinic space group $P\bar{1}$ with $a = 8.022(2)$, $b = 10.868(3)$, $c = 8.008(3)$ Å, $\alpha = 109.48(2)$, $\beta = 103.06(2)$, $\gamma = 90.84(2)°$, $V = 618.0(3)$ Å^3, $Z = 1$, $D_c = 2.033$ g cm^{-3}, $\mu(\text{Mo K}\alpha) = 83.66$ cm^{-1}. The least-squares refinement based on 1964 observed reflections led to a final R value of 0.062. The two independent Lu–H (bridge) distances are 1.99(2) and 2.10(2) Å, respectively. The reactions of $[(\eta^5\text{-}C_5H_5)_2LuH\cdot OC_4H_8]_2$ with 1-hexene, 1-hexyne, phenylacetylene and diphenylethyne were studied.

Introduction

Synthesis of organolanthanide hydride complexes is usually achieved by hydrogenolysis of lanthanide complexes containing a Ln–C σ-bond. The following hydrides $[(C_5H_5)_2NdH\cdot THF]_2$ [1], $[(C_5H_5)_2LuH\cdot THF]_2$ [2, 3], $[(C_5H_4R)_2LnH\cdot THF]_2$ (R = H, CH_3; Ln = Y, Er, Lu) [4], $[(C_5Me_5)_2LuH]_2$ [5], $[(C_5Me_5)_2SmH]_2$ [6], $[(C_5Me_5)_2LnH]_2$ (Ln = La, Nd, Lu) [7, 8], $[Me_2Si(C_5Me_4)_2LnH]_2$ (Ln = Nd, Sm, Lu) [9], $[(C_5H_5)_2YbH\cdot THF]_2$, $\{[(C_5H_5)_2YbH]_3H\}\{Li(THF)_4\}$ [10], $\{[(C_5H_5)_2ErH]_3Cl\}\{Li(THF)_4\}$ [11] and $\{[(C_5H_5)_2YH]_3H\}\{Li(THF)_4\}$ [12] have been synthesized. Recently, Schumann *et al.* [3] reported that dicyclopentadienyllutetium chloride reacts with sodium hydride in THF to form $[Na(THF)_6][(C_5H_5)_3LuHLu(C_5H_5)_3]$ rather than the neutral dimeric hydride $[Cp_2LuH\cdot THF]_2$ (Cp = cyclopentadienyl). They claimed that the $[Cp_2LuH\cdot THF]_2$ which was obtained by the hydrogenolysis of $Cp_2Lu–R$ did not react with olefins [2]. Evans *et al.* [4] suggested also that the presence of an alkali-metal salt can drastically change the course of the reaction, so it is not unexpected that the product formed with NaH is different from the neutral dimeric hydride. Here we wish to report the direct preparation of the neutral dimeric hydride $[Cp_2LuH\cdot THF]_2$, by reaction of dicyclopentadienyllutetium chloride with NaH. The X-ray crystal structure and reactivity of $[Cp_2LuH\cdot THF]_2$ with unsaturated hydrocarbons are also described.

Experimental

All operations for the preparation of organolanthanide complexes were performed under prepurified argon using Schlenk techniques in a glovebox. All solvents were refluxed and distilled over finely divided $LiAlH_4$ or blue sodium benzophenone under argon, immediately before use. The synthesis of $(C_5H_5)_2LuCl$ was carried out by the literature method [13]. Sodium hydride (E. Merck, with 20% paraffin oil) was washed by THF or pentane and dried in a vacuum. 1-Hexene (Fluka) was dried by treatment with Na/K alloy and distilled under argon. Phenylacetylene and 1-hexyne were dried over molecular sieves activated by heating overnight under vacuum. Diphenylethyne was used as received.

Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer as Nujol and Fluorolube mulls and were examined between disc-shaped CsI crystals. The mulls were prepared in an argon-filled glovebox. Gas chromatography–mass spectra were determined on a Finnigan 4021 GC–MS. ^{1}H NMR spectra were obtained on a Varian XL-200 (200 MHz) spectrometer referenced to external Me_4Si. THF-d_8 (E. Merck, spectroscopy grade) was dried over Na/K alloy and was degassed by freeze–thaw cycles on a vacuum line.

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Analyses of complexes of rare earth metals were accomplished using a direct complexometric titration procedure with disodium EDTA. Carbon and hydrogen analyses were performed by the combustion method in an aluminium tube.

Dimeric Di-η⁵-cyclopentadienyllutetium Hydride·THF

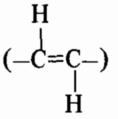
NaH (0.089 g, 3.73 mmol) was slurred in 18 ml of dry THF and solid Cp_2LuCl (0.99 g, 2.91 mmol) was added at 34 °C. The mixture was stirred for 48 h at 34 °C. The resulting pale solution was centrifuged and the grey solid was extracted with 2 × 5 ml THF. The solution was combined and concentrated to about 15 ml. The solution was cooled to −30 °C, and the colourless crystals were collected and dried (0.495 g, 45%). *Anal.* Calc. for $C_{14}H_{19}LuO$: C, 44.44; H, 5.06; Lu, 46.24. Found: C, 42.92; H, 4.80; Lu, 46.48%. IR (Nujol and Fluorolube, cm^{-1}): 3070m, 1443s, 1010s, 770s((C_5H_5); 1345m (Lu–H–Lu); 1046s, 887m (THF). ^1H NMR (200 MHz, THF-d_8, 20 °C, ppm): 6.02 (s, C_5H_5); 3.61, 1.77 (m, THF); 5.05 (s, Lu–H–Lu).

Reaction of [$Cp_2LuH \cdot OC_4H_8]_2$ with 1-Hexene

The reactor was a 3-ml Schlenk tube with a Teflon stopcock and a stirring bar was placed in it. This reactor was charged with 53.0 mg (0.14 mmol) of $[Cp_2LuH \cdot OC_4H_8]_2$ and cooled to −78 °C. 1-Hexene (6.0 μl, 0.11 mmol) and 0.64 ml THF were added by a syringe to the Schlenk tube and the stopcock was closed. The reaction mixture was allowed to warm to room temperature and the reaction was carried out at 45 °C with stirring. The amount of hexane was determined at intervals of 4, 8, 24 and 72 h by GC.

Reaction of [$Cp_2LuH \cdot OC_4H_8]_2$ with Phenylacetylene

Phenylacetylene (7.1 μl, 6.65 mg, 0.0651 mmol) was added to 31.9 mg (0.084 mmol) $[Cp_2LuH \cdot OC_4H_8]_2$ in 0.5 ml C_6D_6 at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 4 h. The resulting solution was centrifuged and clear solutions were placed in an NMR tube. ^1H NMR spectra were recorded (referenced to internal Me_4Si) at 20 °C. δ (ppm): 1.69, 3.64 (THF), 2.73 (PhC≡CH), 5.33, J_{HH} = 16 Hz



$$(-\overset{H}{C}=\underset{H}{C}-)$$

After hydrolysis of the clear solution, styrene [M^+ = 104] was observed by GC–MS.

The reaction of $[Cp_2LuH \cdot OC_4H_8]_2$ with 1-hexyne is similar to that described for phenylacetylene.

X-ray Data Collection

Single crystals of $[Cp_2LuH \cdot THF]_2$ (from THF at −30 °C) were sealed in capillaries under dried argon. The crystals are triclinic, with space group $P\bar{1}$ and a = 8.022(2), b = 10.868(3), c = 8.008(3) Å, α = 109.48(2), β = 103.06(2), γ = 90.84(2)°, V = 618.0(3) Å³, Z = 1, D_c = 2.033 g cm^{-3}, μ(Mo Kα) = 83.66 cm^{-1}. The intensity data were collected at −50 – −60 °C on a Nicolet XRD R3 diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.71069 Å) and θ–2θ scan mode. Independent reflections (2209) were measured in the range $3° < 2\theta < 58°$ and 1964 reflections with $|F_o| > 3\sigma(|F_o|)$ were considered to be observed. The intensity data were corrected for Lp and absorption effects.

Structure Solution and Refinement

The Lu atom position was located by the heavy-atom Patterson method and the others were subsequently determined.

The structure was refined by a block-diagonal matrix least-squares technique with anisotropic thermal parameters for non-hydrogen atoms and isotropic parameters for the bridged hydrogen atom. Including the hydrogen atoms theoretically calculated, the final R and R_w values ($= \Sigma w||F_o| - |F_c||/\Sigma w|F_o|$, where $w = 1/[\sigma^2(F_o) + aF_o + b(F_o)^2]$, a = −0.005, b = 0.0097) are 0.062 and 0.069 respectively for the observed reflections. All calculations were performed on a VAX-11/780 computer using HBLS and DAPH programs [14].

Results and Discussion

The reduction of dicyclopentadienyllutetium chloride with a slight excess of NaH was carried out in THF at 34 °C. The mixture was stirred for 48 h, then the solution was concentrated and cooled to −30 °C to afford colourless crystals of $[(\eta^5\text{-}C_5H_5)_2LuH \cdot THF]_2$ in 45% yield according to eqn. (1).

$$2Cp_2LuCl + 2NaH \xrightarrow[34\ °C,\ 48\ h]{THF} [Cp_2LuH \cdot THF]_2 + 2NaCl \quad (1)$$

The structure of the product was determined by elemental analysis, infrared spectra and ^1H NMR. The characteristic absorption peak of the Lu–H–Lu bond was located at 1345 cm^{-1}. Its ^1H NMR chemical shift value was at δ 5.05. All operations must be carried out under an atmosphere of prepurified argon, since $[Cp_2LuH \cdot THF]_2$ is extremely air-sensitive.

The molecular structure is shown in Fig. 1. The disorder THF ligand with the probability of 0.5 for C(13A), C(14A), C(13B) and C(14B) is also found in the structure. The two independent Lu–H(bridge)

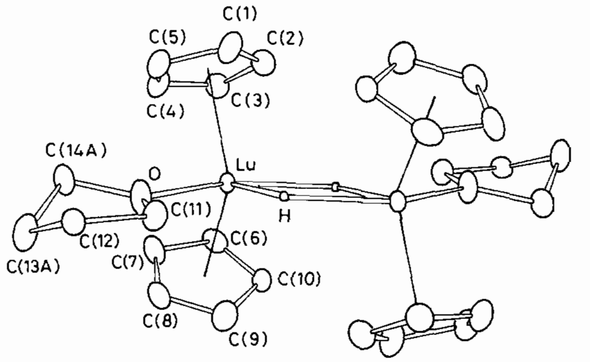


Fig. 1. ORTEP drawing of the molecular structure of $Cp_4Lu_2H_2{\cdot}2OC_4H_8$ with independent atom labelling.

distances are 1.99(2) and 2.10(2) Å, which are shorter than the 2.18(8) Å of the average Y–H(bridge) in $[(CH_3C_5H_4)_2YH{\cdot}THF]_2$ [4], the ionic radius of Y^{3+} being only 0.05 Å larger than Lu^{3+} [15]. In $[(C_5H_5)_2LuH{\cdot}OC_4H_8]_2$, the Lu–O bond length of 2.43(1) Å is longer than the 2.27(1) Å found in $Cp_2LuCl{\cdot}THF$ [13] and is slightly larger than the 2.39(2) Å found in $Cp_3Lu{\cdot}THF$ [16]; the Lu–C(5) bond lengths range from 2.57(2) to 2.64(2) Å and the average is 2.63(2) Å; the average of Lu–centroid is 2.35 Å. The bond angles are: Lu–H–Lu′, 118(10)°; H–Lu–H′, 62(8)°; cent1–Lu–cent2, 125.8°; cent1–Lu–H, 114.5°; cent2–Lu–H, 119.4°; cent2–Lu–O, 102.5°; cent1–Lu–O, 99.5° and H–Lu–O, 71(6)°.

The final atomic coordinates and thermal parameters are listed in Table I. The bond lengths and angles are given in Tables II and III.

No reaction was observed with $[Cp_2LuH{\cdot}THF]_2$ and 1-hexene in THF at 14 °C for 4 h. A temperature of up to 45 °C is required for $[Cp_2LuH{\cdot}THF]_2$ to react with 1-hexene to form the corresponding alkyl complex, after hydrolysis giving hexane. The yield of hexane was enhanced by increasing the reaction time. After 114 h, the yield of hexane rose to 95%. The relation between the yield of hexane and the reaction time is illustrated by data in Table IV.

TABLE I. Final Atomic Fractional Coordinates and Equivalent Isotropic Thermal Parameters

Atoms	x	y	z	B_{eq}
Lu(1)	0.0319(0)	0.1720(0)	0.0871(1)	2.10(1)
H	0.1110(25)	0.0020(19)	0.1000(26)	3.5(39)
C(1)	0.2392(19)	0.1665(15)	−0.1239(27)	4.5(6)
C(2)	0.0798(21)	0.1625(16)	−0.2229(22)	4.2(6)
C(3)	0.0125(22)	0.2871(15)	−0.1580(23)	4.1(5)
C(4)	0.1422(18)	0.3570(13)	−0.0212(24)	4.0(5)
C(5)	0.2832(16)	0.2897(15)	0.0154(23)	4.0(5)
C(6)	0.2505(15)	0.2949(16)	0.0975(20)	3.7(5)
C(7)	−0.1259(24)	0.3675(14)	0.2562(23)	4.8(6)
C(8)	0.0872(23)	0.2960(16)	0.3735(21)	4.1(5)
C(9)	0.1791(24)	0.1775(14)	0.2976(27)	4.9(6)
C(10)	0.2885(16)	0.1717(13)	0.1179(20)	3.3(4)
O(1)	0.2805(14)	0.2171(9)	0.3455(15)	4.5(4)
C(11)	0.3661(16)	0.1247(14)	0.4110(20)	3.5(5)
C(12)	0.5068(18)	0.2048(16)	0.5767(18)	3.5(4)
C(13A)	0.4336(42)	0.3432(28)	0.6194(54)	4.7(12)
C(13B)	0.5223(30)	0.3385(31)	0.5739(46)	5.1(10)
C(14A)	0.3651(39)	0.3500(31)	0.4355(42)	4.3(10)
C(14B)	0.3128(35)	0.3447(33)	0.5064(45)	4.8(10)

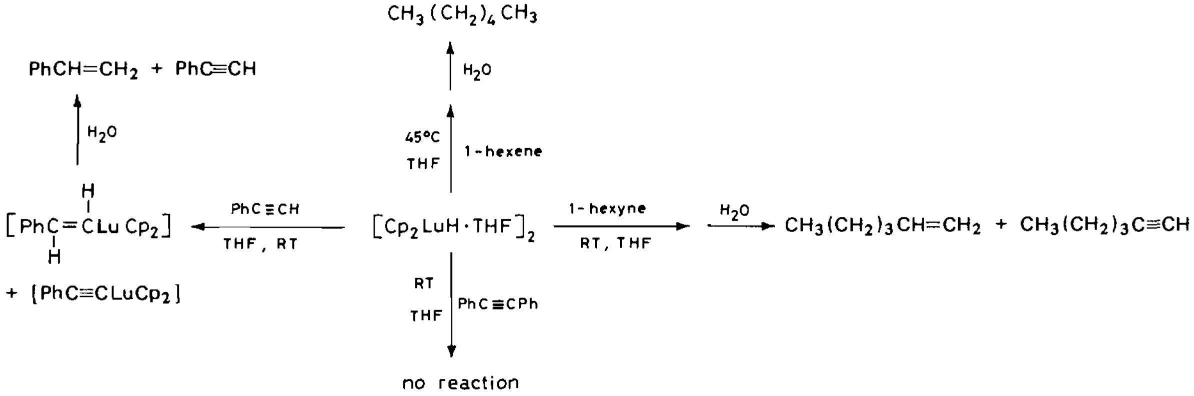
TABLE II Bond Lengths (Å)

Lu–C(1)	2.614(21)	Lu–C(2)	2.566(18)
Lu–C(3)	2.637(19)	Lu–C(4)	2.653(19)
Lu–C(5)	2.640(19)	Lu–C(6)	2.651(17)
Lu–C(7)	2.625(19)	Lu–C(8)	2.638(18)
Lu–C(9)	2.634(22)	Lu–C(10)	2.637(16)
Lu–O(1)	2.435(12)	C(1)–C(2)	1.335(28)
C(1)–C(5)	1.405(28)	C(2)–C(3)	1.440(26)
C(3)–C(4)	1.329(27)	C(4)–C(5)	1.385(27)
C(6)–C(7)	1.404(26)	C(6)–C(10)	1.438(23)
C(7)–C(8)	1.394(27)	C(8)–C(9)	1.349(29)
C(9)–C(10)	1.487(27)	O(1)–C(11)	1.402(20)
O(1)–C(14A)	1.457(36)	O(1)–C(14B)	1.516(38)
C(11)–C(12)	1.522(23)	C(12)–C(13A)	1.581(46)
C(12)–C(13B)	1.464(41)	C(13A)–C(14A)	1.478(55)
C(13B)–C(14B)	1.655(52)	Lu–Lu′	3.510(1)
Lu–H	1.99(21)	Lu–H′	2.10(21)
Lu–Cent1	2.345	Lu–Cent2	2.346
Lu–C( )	2.630		

Evans *et al.* [17] indicated that the reaction of organoyttrium hydride with terminal alkynes does not involve Y–H addition across the unsaturated carbon–carbon bond. Instead, metallation at the acidic terminal position occurs to generate hydrogen and an alkynide complex. However, in the reaction of $[Cp_2LuH{\cdot}THF]_2$ with phenylacetylene, 1,2-addition of Lu–H to the carbon–carbon unsaturated bond also occurs to form the corresponding alkenyl intermediate, $Cp_2LuCH{=}CHPh$, besides forming an alkynide complex. The *trans*-proton of the ethylene moiety is observed in the ^{1}H NMR spectrum at δ = 5.33, J_{HH} = 16 Hz. The hydrolytic product of $[Cp_2LuCH{=}CHPh]$ is styrene ($[M^+] = 104$) which was determined by GC–MS. Similar results were obtained when $[Cp_2LuH{\cdot}THF]_2$ reacted with 1-hexyne, the hydrolytic product being 1-hexene and 1-hexyne. Hydrolysis of $(PhC{\equiv}C)_2M$ (M = Yb, Eu) derivatives to yield the alkyne $PhC{\equiv}CH$, together with the alkene $PhCH{=}CH_2$ has been reported [18, 19]. However, the reaction pathway is different from our hydrolysis. Deacon *et al.* [18, 19] suggested that the alkene formation on hydrolysis of di(alkynyl)

TABLE III Bond Angles (°)

C(2)–C(1)–C(5)	109(2)	C(1)–C(2)–C(3)	110(2)
C(2)–C(3)–C(4)	102(2)	C(3)–C(4)–C(5)	115(2)
C(1)–C(5)–C(4)	103(2)	C(7)–C(6)–C(10)	106(2)
C(6)–C(7)–C(8)	110(2)	C(7)–C(8)–C(9)	110(2)
C(8)–C(9)–C(10)	107(2)	C(6)–C(10)–C(9)	106(1)
C(11)–O(1)–C(14A)	114(2)	C(11)–O(1)–C(14B)	106(2)
O(1)–C(11)–C(12)	105(1)	C(11)–C(12)–C(13A)	100(2)
C(11)–C(12)–C(13B)	108(2)	C(12)–C(13A)–C(14A)	103(3)
C(12)–C(13B)–C(14B)	95(2)	O(1)–C(14A)–C(13A)	98(3)
O(1)–C(14B)–C(13B)	96(2)	Lu–O(1)–C(11)	127(1)
Lu–O(1)–C(14A)	120(1)	Lu–O(1)–C(14B)	122(2)
H–Lu–O(1)	71(6)	H′–Lu–O(1)	133(6)
H–Lu–H′	62(8)	Lu–H–Lu′	118(10)
Cent1–Lu–H	114	Cent2–Lu–H	120
Cent1–Lu–H′	102	Cent2–Lu–H′	98
Cent1–Lu–O(1)	100	Cent2–Lu–O(1)	103
Cent1–Lu–Cent2	126		



Scheme 1.

lanthanoids arises from hydrogenation of the organometallic, and that hydrogen transfer occurs from the coordinated water to the triple bond.

In addition, no reaction product was observed after 4 h at room temperature using diphenylethyne as a substrate, based on ^{1}H NMR. This indicates that the Lu–H addition across the multiple bond of diphenylethyne does not take place under these reaction conditions. The reactions mentioned above may be depicted in Scheme 1.

TABLE IV. The Relation Between the Yield and the Reaction Time[a]

Time (h)	4	8	24	72	114[b]
Yield (%)					
Hexane	12	22	44	63	95
1-Hexene	88	78	56	37	5

[a] $[Cp_2LuH{\cdot}THF]_2$:hexene = 1.3:1. [b] $[Cp_2LuH{\cdot}THF]_2$:hexene = 4:1.

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