

Studies on organolanthanide complexes

LXIII*. Synthesis, spectroscopic and X-ray crystallographic characterization of new early organolanthanide, organoyttrium hydride and organoholmium hydroxide complexes *

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Abstract

Organolanthanide chloride complexes $[(CH_3OCH_2CH_2C_5H_4)_2Ln(\mu-Cl)]_2$ ($Ln = La, Pr, Ho$ and Y) react with excess NaH in THF at $45^\circ C$ to give the dimeric hydride complexes $[(CH_3OCH_2CH_2C_5H_4)_2Ln(\mu-H)]_2$, which have been characterized by IR, 1H NMR, MS and XPS spectroscopy, elemental analyses and X-ray crystallography. $[(CH_3OCH_2CH_2C_5H_4)_2Y(\mu-H)]_2$ crystallizes from THF/n-hexane at $-30^\circ C$, in the triclinic space group $P1$ with $a = 8.795(2) \text{ \AA}$, $b = 11.040(1) \text{ \AA}$, $c = 16.602(2) \text{ \AA}$, $\alpha = 93.73(1)^\circ$, $\beta = 91.82(1)^\circ$, $\gamma = 94.21(1)^\circ$, $D_c = 1.393 \text{ g cm}^{-3}$ for $Z = 2$ dimers. However, crystals of $[(CH_3OCH_2CH_2C_5H_4)_2Ho(\mu-OH)]_2$ were obtained by recrystallization of holmium hydride in THF/n-hexane at $-30^\circ C$, in the orthorhombic space group $Pbca$ with $a = 11.217(2) \text{ \AA}$, $b = 15.865(7) \text{ \AA}$, $c = 17.608(4) \text{ \AA}$, $D_c = 1.816 \text{ g cm}^{-3}$ for $Z = 4$ dimers. In the complexes of yttrium and holmium, each Ln atom of the dimers is coordinated by two substituted cyclopentadienyl ligands, one oxygen atom and two hydrogen atoms (for the Y atom) or two hydroxyl groups (for the Ho atom) to form a distorted trigonal bipyramid if the $C(\eta^5)$ -bonded cyclopentadienyl is regarded as occupying a single polyhedral vertex.

Key words: Lanthanum; Praseodymium; Holmium; Yttrium; Cycloheptatrienyl; Hydride; X-ray diffraction

1. Introduction

Organometallic hydride complexes are fundamental components in a wide range of stoichiometric and catalytic organometallic reactions [1–3]. The d-transition metal organic hydrides have been extensively and deeply studied. However, for f-transition metals, the organolanthanide hydride complexes have been previ-

ously described only in the early 1980s. Recently many organometallic chemists have attempted synthesis of organolanthanide hydride complexes. Obviously, the synthesis and definitive characterization of hydride complexes of these metals are of fundamental importance to the advancement of this rapidly developing area of organolanthanide chemistry. Evans was the first to succeed in the synthesis of crystallographically characterized lanthanide and yttrium hydride complexes via a hydrogenolysis reaction [4]. An equally reasonable method of generating organolanthanide hydrides from tert-butyl-lanthanide complexes is the β -hydrogen

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* For Part LXII see ref. 2.

elimination reaction [5,6]. Many neutral organolanthanide hydrides have been synthesized via hydrogenolysis or β -H elimination reaction of pure neutral complexes containing the Ln-C δ bond, for example $[(C_5H_4R)_2LnH \cdot THF]_2$ (R = H, CH₃; Ln = Y, Er, Lu) [4], $[Cp_2NdH \cdot THF]_2$ [7], $[Cp_2LuH \cdot THF]_2$ [8,9], $[(C_5Me_5)_2LnH]_2$ (Ln = Lu [10], Sm [11], La, Nd [12,13]), $[Me_2Si(C_5Me_4)_2LnH]_2$ (Ln = Nd, Sm, Lu) [14], $[Cp_2YbH \cdot THF]_2$ [15], $[(1,3-Me_2C_5H_3)_2Y(\mu-H)]_3$ and $[(1,3-Me_2C_5H_3)_2Y(\mu-H)(THF)]_2$ [16]. The precursors of C σ -bonded organolanthanide complexes are lanthanocene chlorides. In order to simplify the process of synthesis of neutral hydrides, we have developed a third synthetic method, by direct reduction of lanthanocene chloride with sodium hydride in THF for the syntheses of neutral organolanthanide hydride complexes [17,18]. We have focussed on an extension of the reduction method with sodium hydride.

In the present report, we describe the synthesis and spectroscopic studies of two new early organolanthanide hydrides and an yttrium hydride with ether-substituted cyclopentadienyl ligand, $[(MeOCH_2CH_2C_5H_4)_2Ln(\mu-H)]_2$ (Ln = La, Pr, Y), and the X-ray crystallographic investigation of organoyttrium hydride, as well as the partial hydrolysis product of organoholmium hydride, the organoholmium hydroxide complexes.

2. Experimental details

All operations on these organolanthanide complexes were performed under prepurified argon using Schlenk techniques or in a glovebox. All solvents were refluxed and distilled over finely divided LiAlH₄ or blue sodium benzophenone under argon immediately before use. Anhydrous lanthanide chlorides were prepared from the hydrates by a published method [18]. Infrared spectra were recorded on Perkin-Elmer 983 or Digilab FTS-20/E Fourier Transform IR spectrometers with Nujol and Floirolube mulls and were examined between disk-shaped CsI crystals. The mulls were prepared in an argon-filled glovebox. Mass spectra were recorded on a Finnigan 4021 spectrometer. ¹H NMR spectra were obtained on a Varian XL-200 (200 MHz) spectrometer referenced to internal Me₄Si. THF-*d*₈ (E. Merck, for NMR spectroscopy) and C₆D₆ were dried over Na/K alloy and were degassed by freeze-thaw cycles on a vacuum line. X-ray photoelectron spectra were recorded on a NP-1 spectrometer equipped with a Mg K α X-ray source.

Analyses of rare earth metals were by direct complexometric titration with disodium EDTA [19]. Carbon and hydrogen analyses were performed by combustion in an aluminium tube.

Sodium 2-methoxyethylcyclopentadienide and bis(2-methoxyethylcyclopentadienyl)lanthanide chlorides were prepared according to the literature procedures [20–22]. Full details of these chloride complexes will be described elsewhere.

2.1. $[(MeOCH_2CH_2C_5H_4)_2La(\mu-H)]_2$ (1)

Sodium hydride (0.107 g, 4.46 mmol) was added to a magnetically stirred THF solution (16 ml) of bis(2-methoxyethylcyclopentadienyl)lanthanum chloride (0.94 g, 2.23 mmol) in a Schlenk flask at room temperature. The reaction mixture was stirred for 3 days at 45°C. The Schlenk flask was centrifuged, the precipitate was separated from the solution, and the THF solution reduced in volume to about 4 ml. Addition of 30 ml of n-hexane gave a white solid at -78°C. The solid product was washed with n-hexane (25 ml) and then dried *in vacuo* at 45°C to give a white solid (0.64 g, yield 74%). Calcd. for C₁₆H₂₃O₂La, C, 49.75; H, 6.00; La, 35.96. Found: C, 49.68; H, 6.07; La, 36.37%. IR(cm⁻¹): 210s, 240m, 260w, 320m, 375w, 410w, 520w, 595w, 660w, 725m, 762s, 810m, 970m, 1025m, 1045m, 1075s, 1105s, 1375m, 1430m, 1450m, 2830m, 2890s, 2930s, 2980m, 3075m, 3180w. ¹H NMR (benzene-*d*₆) 6.86 (s, 1H), 5.59 (s, 4H), 3.06 (t, 2H), 2.79 (s, 3H), 2.36 (t, 2H); mass spectrum: *m/e*[M]⁺ 386 (monomer).

2.2. $[(MeOCH_2CH_2C_5H_4)_2Pr(\mu-H)]_2$ (2)

The procedure followed was similar to that for 1. A yellow solid 2 was obtained; yield 81%. Calcd. for C₁₆H₂₃O₂Pr: C, 49.49; H, 5.97; Pr, 36.29. Found: C, 49.88, H, 5.97, Pr, 34.36%. IR(cm⁻¹): 210m, 240m, 275s, 320s, 380s, 410m, 520s, 580s, 670m, 720s, 747s, 810s, 962m, 1022m, 1040m, 1070s, 1090s, 1110s, 1380s, 1440m, 1455m, 2830m, 2890s, 2920s, 2960m, 3055m, 3180m; mass spectrum: *m/e*[M]⁺ 388 (monomer).

2.3. $[(MeOCH_2CH_2C_5H_4)_2Y(\mu-H)]_2$ (3)

The procedure followed was similar to that for 1. A white solid was obtained; yield 75%. Calcd. for C₁₆H₂₃O₂Y: C, 57.17; H, 6.89; Y, 26.44; Found: C, 57.13; H, 6.83; Y, 26.50%. IR(cm⁻¹): 215w, 240w, 1024m, 315m, 381s, 436s, 580m, 680m, 725m, 765s, 810s, 825m, 965m, 995m, 1055m, 1080s, 1100s, 1375s, 1450m, 1470m, 2840m, 2900s, 2930s, 2980m, 3080m, 3170m; ¹H NMR(THF-*d*₈) 5.51–5.97 (m, 4H), 3.33–3.51 (m, 2H), 3.17–3.25 (m, 2H), 2.39–2.59 (m, 2H), 1.85 (t, 1H, *J*(YH) = 28.3 Hz); mass spectrum: *m/e*[M]⁺ 336 (monomer).

2.4. $[(MeOCH_2CH_2C_5H_4)_2Ho(\mu-H)]_2$ (4)

The procedure followed was similar to that for 1. A pale brown solid of holmium hydride 4 was obtained; yield 80%. When complex 4 was recrystallized from

THF/hexane, complex 5, $[(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Ho}(\mu\text{-OH})]_2$, was isolated as light yellow crystals.

2.5. X-ray crystallographic study of $[(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Y}(\mu\text{-H})]_2$ (3)

Regular, colourless transparent crystals suitable for diffraction were obtained by recrystallizing the crude solid reaction product in THF with hexane, centrifuging, and cooling the centrifugate at -30°C . A crystal of approximate dimensions $0.4 \times 0.4 \times 0.2$ mm was sealed in a glass capillary filled with argon and examined with an Enraf-Nonius CAD4 diffractometer with monochromated Mo K α radiation ($\lambda = 0.7107$ Å). Accurate unit cell parameters were obtained by carefully centred 25 reflections ($12^\circ < \theta < 17^\circ$). Of 5634 unique reflections measured with $2^\circ < 2\theta < 50^\circ$, 3278 reflections with $F^2 > 3\sigma(F^2)$ were used in the refinement. The structure was solved by Patterson and Fourier methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares. Final *R* and *S* values were 0.045 and 2.05, respectively. Crystal data: *M* = 672.53, triclinic, space group *P*1, *a* = 8.795(2), *b* = 11.040(1), *c* = 16.602(2) Å, $\alpha = 93.73(1)$, $\beta = 91.82(1)$, $\gamma = 94.21(1)^\circ$, *V* = 1603.2 Å³, *Z* = 2, *D*_c = 1.393 g cm⁻³, *F*(000) = 696.

2.6. X-ray crystallographic study of $[(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Ho}(\mu\text{-OH})]_2$ (5)

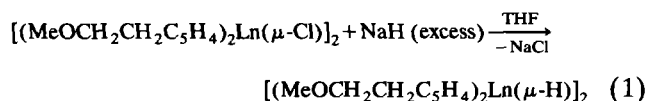
Light yellow crystals of $[(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Ho}(\mu\text{-OH})]_2$ suitable for diffraction studies were obtained by recrystallizing holmium hydride in THF with hexane, centrifuging and slowly cooling the centrifugate at -30°C . A crystal of approximate dimensions $0.15 \times 0.15 \times 0.2$ mm was sealed in a glass capillary filled with argon and examined on an Enraf-Nonius CAD4 diffractometer with monochromated Mo K α radiation ($\lambda = 0.7107$ Å). Accurate unit cell parameters were obtained from 25 carefully centred reflections ($13^\circ < \theta < 17^\circ$). Of 2744 unique reflections measured with $2^\circ < 2\theta < 50^\circ$, 1900 reflections with $F^2 > 3\sigma(F^2)$ were used in the refinement. The structure was solved by Patterson and Fourier methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares. Final *R* and *S* values were 0.025 and 3.35, respectively. Crystal data: *M* = 856.58, orthorhombic, space group *Pbca*, *a* = 11.217(2), *b* = 15.865(7), *c* = 17.608(4) Å, *V* = 3133.1 Å³, *Z* = 4, *D*_c = 1.816 g cm⁻³, *F*(000) = 1680.

3. Results and discussion

3.1. Syntheses of complexes 1–4

Bis(2-methoxyethylcyclopentadienyl) hydride complexes can be prepared by using the reduction of

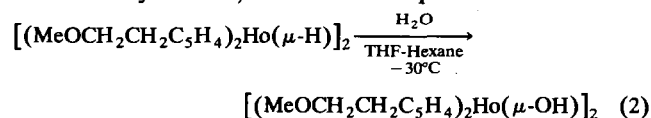
bis(2-methoxyethylcyclopentadienyl) lanthanum, praseodymium, holmium or yttrium chlorides [21,22] with excess sodium hydride in THF at 45°C in good yields as shown in eqn. (1).



1–4

Ln = La(1), Pr(2), 4(3), Ho(4); *n* = 2 for La, Pr, *n* = 1 for 4, Ho.

The bis(2-methoxyethylcyclopentadienyl) lanthanide hydrides are much more soluble in THF than their unsubstituted C₅H₅ analogues, but insoluble in hydrocarbons such as hexane at room temperature. The three new hydride complexes are unsolvated dimers containing intramolecular coordination bonds. The elemental analyses are consistent with their structure. No praseodymium hydride containing an organic ligand has been reported before. These hydride complexes are more sensitive than those of organolanthanide chlorides to air and moisture. The partially hydrolyzed product 5 of holmium hydride 4 was formed after recrystallization in THF with hexane at -30°C . Maybe it is because there is a very small amount of water in the solvent that there is partial hydrolysis of the holmium hydride complex [24–26] to form organo-holmium hydroxide, as shown in eqn. 2.



We have reported the EI mass spectra of dicyclopentadienyl lanthanide chlorides and 1,1'-(3-oxapentamethylene) dicyclopentadienyl lanthanide chlorides [27]. The present investigation of the EI mass spectra of the three new hydride complexes shows that a monomeric parent molecular ion and related fragments including $[\text{M} - \text{H}]^+$, $[\text{M} - \text{CH}_3\text{O}]^+$, $[\text{M} - \text{CH}_3\text{OCH}_2\text{CH}_2\text{C}_5\text{H}_4]^+$ were found. The ion peaks of *m/e* larger than $[\text{M}]^+$ were also found on the enlarged mass spectra. However, *m/e* equal to 72 or 71 did not appear. This indicated these new hydride complexes to be solvent-free dimeric complexes and the $\mu\text{-H}$ bonds of dimeric molecules are more easily dissociated. The Ln–H bond in the monomer is very easily cleaved giving very high relative intensity peaks of $[\text{M} - \text{H}]^+$.

The coordination of oxygen atom to rare earth metals in bis(2-methoxyethylcyclopentadienyl) lanthanide chlorides has previously been studied by XPS [23]. XPS of the complexes 1–3 were measured and the results are listed in Table 1. It shows that the binding energies of the rare earth metal atoms all decrease in the hydride complexes as compared with those in the tricyclopentadienyl lanthanides and the dicyclopentadienyl

TABLE 1. Binding energy data (eV) for complexes

Complex ^a	O _{1s}		Ln _{3d5/2}	
	BE	ΔE ^b	BE	ΔE
Cp'Na	531.0			
Cp ₃ La			836.7	
Cp' ₂ LaH (1)	531.8	+0.8	836.3	-0.4 ^c
Cp' ₂ LaCl	532.4	+1.4	836.6	-0.1 ^e
Cp ₃ Pr			932.4	
Cp' ₂ PrH (2)	531.2	+0.2	931.0	-1.4 ^c
Cp' ₂ PrCl	531.8	+0.8	932.3	-0.1 ^e
Cp ₂ YCl			159.4	
Cp' ₂ YH (3)	531.5	+0.5	158.7	-0.7 ^d
Cp' ₂ YCl	532.5	+1.5	158.9	-0.5 ^f

^a Cp' = CH₃OCH₂CH₂C₅H₄^b ΔE = B.E. (O_{1s} (1-3)) - B.E. (O_{1s}(Cp'Na))^c ΔE = B.E. (Ln_{3d5/2} (1-3)) - B.E. (Ln_{3d5/2}(Cp₃Ln))^d ΔE = B.E. (Ln_{3d5/2} (1-3)) - B.E. (Ln_{3d5/2}(Cp₂YCl))^e ΔE = B.E. (Ln_{3d5/2}(Cp'₂LnCl)) - B.E. (Ln_{3d5/2}(Cp₃Ln))^f ΔE = B.E. (Ln_{3d5/2}(Cp'₂YCl)) - B.E. (Ln_{3d5/2}(Cp₂YCl))

yttrium chloride, and that the binding energies of O_{1s} increase in these hydride complexes as compared with that in CH₃OCH₂CH₂C₅H₄Na. Thus the lone pair of electrons on the oxygen atom in these complexes is partially transferred from oxygen to the rare earth metal. The possible structures of the complexes can be shown as in Fig. 1.

Furthermore, ΔE(O_{1s}) values for the chloride complexes are about 2 to 4 times those of ΔE(O_{1s}) for the hydride complexes. The ΔE (Ln_{3d5/2}) values for Cp'₂LaCl-Cp₃La and Cp'₂PrCl-Cp₃Pr show almost no change. However, absolute values for ΔE(Ln_{3d5/2}) of Cp'₂LnCl are smaller than those of the corresponding hydrides. This is because the chlorine atom has a

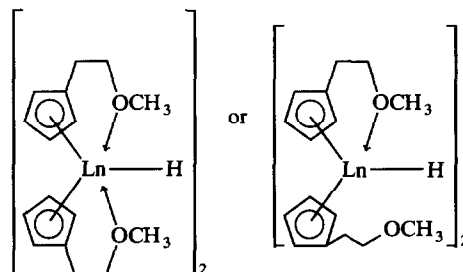


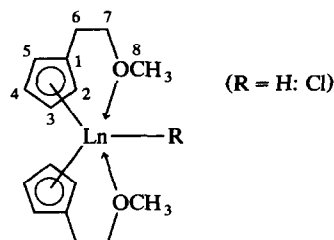
Fig. 1. Possible structures for the title complexes.

strong negativity and moves the charge of the metals and increases the binding energies of Ln_{3d5/2} for Cp'₂LaCl and Cp'₂PrCl. The ability of oxygen to coordinate to central metal in the chloride complexes is much stronger than that of the hydride complexes.

The IR spectra of complexes 1-3 and sodium 2-methoxyethylcyclopentadienide were measured from 4000 to 200 cm⁻¹. The spectral features of these hydride complexes are very similar. The complexes exhibit six characteristic absorption peaks in the low frequency region, and the absorption peak at about 240 cm⁻¹ was assigned to a characteristic absorption of π-bonded substituted cyclopentadienyl group to Ln metal [19,28]. The characteristic cyclopentadienyl absorptions appear at about 760, 1020, 1440, 3080 cm⁻¹ in the complexes, but at 785, 1020, 1440 and 3060 cm⁻¹ in the sodium salt. The complexes show two C-O-C asymmetric stretching vibrations at 1040 and 1055 cm⁻¹. Compare the C-O-C bands of the complexes with those of MeOCH₂CH₂C₅H₄Na which shift to lower frequencies. This implies that an intramolecular

TABLE 2. ¹H NMR proton shift (δ, TMS, ppm, 25°C)

Complex	(C ₅ H ₄) ₂	7-CH ₂	8-CH ₃	6-CH ₂	Ln-H	Ref.
CH ₃ OCH ₂ CH ₂ C ₅ H ₄ Na	5.31 5.18	3.28	3.05	2.50		
[(CH ₃ OCH ₂ CH ₂ C ₅ H ₄) ₂ LaH] ₂	5.59	3.06	2.79	2.36	6.86	
[(CH ₃ OCH ₂ CH ₂ C ₅ H ₄) ₂ LaCl] ₂	5.63	3.60	3.40	2.60		22
[(CH ₃ OCH ₂ CH ₂ C ₅ H ₄) ₂ YH] ₂	5.97	3.51	3.25	2.59	1.85	
	5.51	3.33	3.17	2.39	(J(YH) = 28.3 Hz)	
(CH ₃ OCH ₂ CH ₂ C ₅ H ₄) ₂ YCl	5.88 5.80	3.80	3.42	2.54		22



coordination bond is present [29]. For the title complexes, the absorption peak at about 1110 cm^{-1} may be the characteristic absorption of La–H and Pr–H bonds [11,13,30]. The characteristic absorption for the Y–H bond may be at about 1375 cm^{-1} [5,10].

The ^1H NMR spectra of complexes and the sodium salt were measured using perdeuterotetrahydrofuran as a solvent (Table 2), with the ^1H NMR data of the chloride complexes for comparison.

This table shows that when the complexes are formed, the Cp signals shift to lower field, which indicates that negative charge of the ring is transferred to Ln^{3+} . The interesting thing is that the proton signals on the chain of Cp' for La hydride all shift to higher field and that of Y hydride all shift to lower field. Obviously, proton signals for Y hydride are much more complex than those for La hydride. For the La hydride, the La–H chemical shift is 6.86 ppm. The chemical

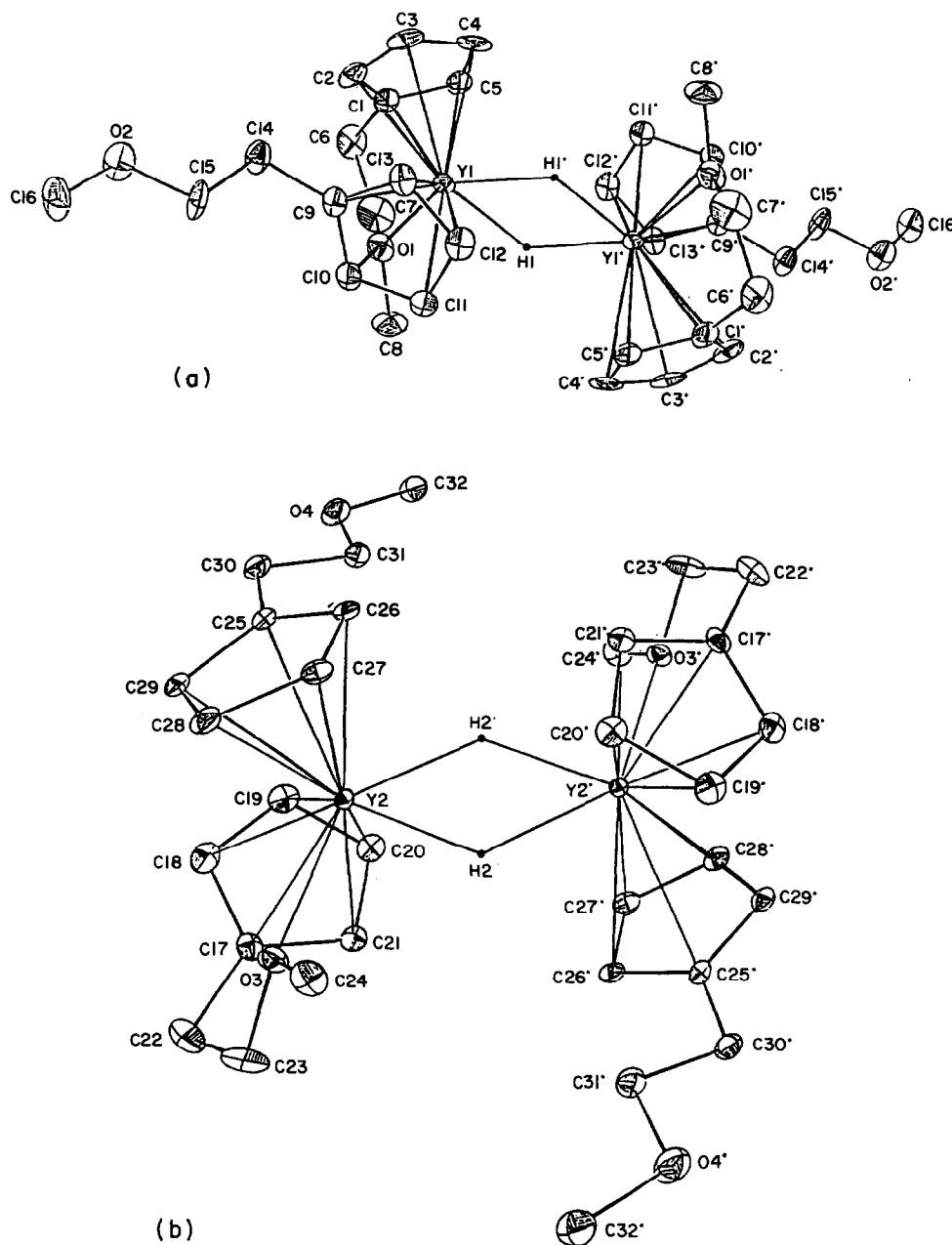


Fig. 2. Perspective ORTEP drawing of the crystal of $[(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Y}(\mu\text{-H})]_2$ (3) showing the two crystallographically nonequivalent molecules (a and b).

shift of cyclopentadienyl is 5.59 ppm and exhibits a single peak. Possibly a 'twinking' effect of the cyclopentadienyl protons led to their equality and single ^1H NMR peak [22]. For the yttrium ($I = 1/2$) hydride, the chemical shift of Y–H occurs at 1.86 ppm as a triplet ($J(\text{YH}) = 28.3$ Hz) due to coupling to two equivalent yttrium atoms [4]. The cyclopentadienyl protons are two groups of triplet at 5.51 and 5.97 ppm. Fortunately, the great solubility of these lanthanide hydrides in THF will facilitate further studies.

3.2. Structure

The structures of **3** and **5** are shown in Fig. 2 and Fig. 3, respectively. Their final atomic parameters (for non-hydrogen atoms), bond lengths and angles are listed in Table 3 to Table 6, respectively.

Complex **3** is a hydrogen-bridged dimer with a symmetric centre. In the unit cell there are two dimers which are not identical, as shown in Fig. 2. However, in both dimers, each Y atom is coordinated by two cyclopentadienyl ligands, one oxygen (from one ether group) and two hydrogen atoms to form a distorted trigonal bipyramid if the $\text{C}(\eta)^5$ -bonded cyclopentadienyl is regarded as occupying a single polyhedral vertex. The equatorial plane of every trigonal bipyramid is nearly formed by two centres of cyclopentadienyl ligands and one bridged hydrogen atom. In the structure, only one oxygen atom of the two substituted ethers is coordinated to a Y atom, and another oxygen atom is

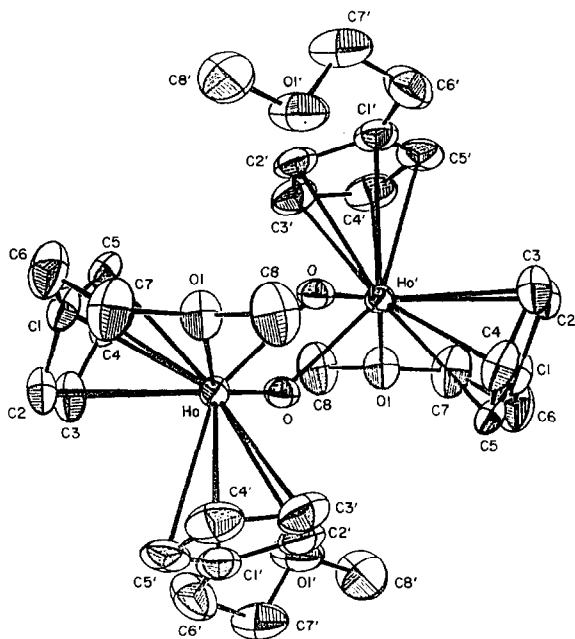


Fig. 3. ORTEP plot of the molecular structure of $[(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Ho}(\mu\text{-OH})_2]$ (**5**).

TABLE 3. Positional parameters and their estimated standard deviations for $[(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Y}(\mu\text{-H})_2]$ (**3**)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
Y(1)	0.05321(8)	0.38331(7)	0.06448(4)	2.84(1)
Y(2)	0.47337(8)	0.15931(7)	0.48922(4)	2.77(1)
O(1)	0.2025(7)	0.4966(6)	0.1768(3)	5.1(1)
O(2)	0.3907(8)	−0.0596(6)	0.1496(4)	6.4(2)
O(3)	0.6466(7)	0.2161(5)	0.3823(3)	4.8(1)
O(4)	0.0861(8)	0.2119(7)	0.7265(4)	6.8(2)
C(1)	−0.074(1)	0.3722(9)	0.2071(5)	4.5(2)
C(2)	−0.054(1)	0.2509(8)	0.1819(6)	5.2(2)
C(3)	−0.153(1)	0.217(1)	0.1138(6)	6.2(2)
C(4)	−0.240(1)	0.320(1)	0.0975(6)	6.1(3)
C(5)	−0.1878(9)	0.4173(9)	0.1558(5)	4.6(2)
C(6)	0.019(1)	0.444(1)	0.2750(6)	6.8(3)
C(7)	0.124(1)	0.540(1)	0.2454(6)	7.7(3)
C(8)	0.327(1)	0.585(1)	0.1600(7)	7.2(3)
C(9)	0.2327(9)	0.1951(8)	0.0522(5)	3.9(2)
C(10)	0.3322(9)	0.3020(8)	0.0538(5)	4.3(2)
C(11)	0.3049(9)	0.3626(8)	−0.0184(5)	4.3(2)
C(12)	0.187(1)	0.2922(8)	−0.0643(5)	4.4(2)
C(13)	0.142(1)	0.1886(8)	−0.0209(5)	4.3(3)
C(14)	0.236(1)	0.0968(8)	0.1111(5)	4.8(2)
C(15)	0.379(1)	0.0272(8)	0.0926(6)	6.0(2)
C(16)	0.517(1)	−0.130(1)	0.1319(7)	7.0(3)
C(17)	0.334(1)	0.2329(8)	0.3593(5)	4.7(2)
C(18)	0.275(1)	0.3005(9)	0.4252(6)	5.6(2)
C(19)	0.184(1)	0.2176(9)	0.4690(6)	5.4(2)
C(20)	0.187(1)	0.0982(9)	0.4306(6)	5.0(2)
C(21)	0.280(1)	0.1079(8)	0.3623(5)	4.4(2)
C(22)	0.444(1)	0.286(1)	0.3002(7)	7.1(3)
C(23)	0.588(1)	0.224(1)	0.3005(6)	8.1(4)
C(24)	0.804(1)	0.184(1)	0.3864(7)	6.1(3)
C(25)	0.460(1)	0.2880(7)	0.6329(5)	4.0(2)
C(26)	0.565(1)	0.1984(8)	0.6457(5)	4.0(2)
C(27)	0.696(1)	0.2254(9)	0.6002(5)	4.9(2)
C(28)	0.671(1)	0.3325(8)	0.5580(6)	4.9(2)
C(29)	0.525(1)	0.3704(8)	0.5786(5)	4.5(2)
C(30)	0.308(1)	0.3042(9)	0.6738(6)	5.1(2)
C(31)	0.222(1)	0.1805(9)	0.6892(6)	5.0(2)
C(32)	0.004(1)	0.107(1)	0.7540(7)	6.5(3)
H(1)	0.07(1)	0.560(8)	0.029(5)	4.0*
H(2)	0.41(1)	0.000(8)	0.539(5)	4.0*

free. The average lengths of the Y–C bonds of cyclopentadienyl ligands for the two dimers are 2.676, 2.674, 2.674 and 2.683 Å, respectively. The bond lengths of Y–C(centre) are 2.384, 2.383, 2.382 and 2.392 Å, respectively; which are within the range of those observed in other structures $[(\text{MeC}_5\text{H}_4)_2(\text{THF})\text{Y}(\mu\text{-H})_2]$ and $[1,3\text{-Me}_2\text{C}_5\text{H}_3)_2(\text{THF})\text{Y}(\mu\text{-H})_2]$ [16]. The bond lengths of Y–O (Cp') are 2.462 and 2.458 Å (Cp' = $\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4$). They are close to those of Y–O(THF) in $[(\text{MeC}_5\text{H}_4)_2(\text{THF})\text{Y}(\mu\text{-H})_2]$ [2.460(8) Å] [4] and $\text{Cp}_3\text{Y}(\text{THF})$ [2.451(4) Å] [24]. The complex **3** has Y–H bond lengths of 2.02–2.15 Å with Y–H–Y angles of 119–126°. The Y–H distances are shorter than the corresponding values of $[(\text{MeC}_5\text{H}_4)_2\text{Y}(\text{THF}) (\mu\text{-H})_2]$, but the Y–H–Y angles are larger.

Complex 5 is a hydroxyl-bridged dimer with a symmetric centre. There are two identical dimers in a unit cell, as shown in Fig. 3. The Ho atom is coordinated by two cyclopentadienyl ligands and three oxygen atoms,

one of which is from one ether of cyclopentadienyl ligands besides two bridging hydroxyl groups. The coordination polyhedron surrounding the Ho atom is a distorted trigonal-bipyramid with three oxygen atoms

TABLE 4. Selected bond distances (Å) and angles (deg) for [(MeOCH₂CH₂C₅H₄)₂Y(μ-H)]₂ (3)

Y(1)–Y(1*)	3.611(2)	O(1)–C(8)	1.456(8)
Y(2)–Y(2*)	3.622(2)	O(2)–C(15)	1.396(8)
Y(1)–O(1)	2.462(5)	O(2)–C(16)	1.431(8)
Y(1)–C(1)	2.658(6)	O(3)–C(23)	1.447(9)
Y(1)–C(2)	2.667(2)	O(3)–C(24)	1.460(8)
Y(1)–C(3)	2.671(2)	O(4)–C(31)	1.420(8)
Y(1)–C(4)	2.703(6)	O(4)–C(32)	1.427(8)
Y(1)–C(5)	2.680(6)	C(1)–C(2)	1.40(1)
Y(1)–C(9)	2.701(6)	C(1)–C(5)	1.428(9)
Y(1)–C(10)	2.682(6)	C(2)–C(3)	1.42(2)
Y(1)–C(11)	2.659(6)	C(3)–C(4)	1.44(2)
Y(1)–C(12)	2.651(6)	C(4)–C(5)	1.44(1)
Y(1)–C(13)	2.675(6)	C(9)–C(10)	1.415(9)
Y(1)–H(1)	2.07(6)	C(9)–C(13)	1.426(8)
Y(1)–H(1*)	2.02(6)	C(10)–C(11)	1.433(9)
Y(2)–O(3)	2.458(4)	C(11)–C(12)	1.42(1)
Y(2)–C(17)	2.649(6)	C(12)–C(13)	1.430(9)
Y(2)–C(18)	2.663(7)	C(14)–C(15)	1.551(9)
Y(2)–C(19)	2.687(6)	C(17)–C(18)	1.42(1)
Y(2)–C(20)	2.691(6)	C(17)–C(21)	1.430(9)
Y(2)–C(21)	2.670(6)	C(18)–C(19)	1.42(2)
Y(2)–C(25)	2.707(6)	C(19)–C(20)	1.43(1)
Y(2)–C(26)	2.693(5)	C(20)–C(21)	1.422(9)
Y(2)–C(27)	2.674(6)	C(25)–C(26)	1.424(8)
Y(2)–C(28)	2.663(7)	C(25)–C(29)	1.427(8)
Y(2)–C(29)	2.682(6)	C(26)–C(27)	1.426(9)
Y(2)–H(2)	2.04(6)	C(27)–C(28)	1.440(9)
Y(2)–H(2*)	2.15(6)	C(28)–C(29)	1.427(9)
O(1)–C(7)	1.427(8)		
O(1)–Y(1)–C(1)	65.7(2)	C(10)–C(11)–C(12)	107.4(6)
O(1)–Y(1)–H(1)	78(2)	C(11)–C(12)–C(13)	108.4(6)
O(1)–Y(1)–H(1*)	132(2)	C(9)–C(13)–C(12)	107.8(6)
H(1)–Y(1)–H(1*)	56(4)	C(9)–C(14)–C(15)	106.4(5)
O(3)–Y(2)–C(17)	66.0(2)	O(2)–C(15)–C(14)	107.6(5)
O(3)–Y(2)–H(2)	135(2)	C(18)–C(17)–C(21)	108.5(7)
O(3)–Y(2)–H(2*)	75(2)	C(18)–C(17)–C(22)	124.2(8)
H(2)–Y(2)–H(2*)	61(3)	C(21)–C(17)–C(22)	127.2(8)
C(7)–O(1)–C(8)	109.8(7)	C(17)–C(18)–C(19)	107.5(6)
C(15)–O(2)–C(16)	109.3(5)	C(18)–C(19)–C(20)	108.6(7)
C(23)–O(3)–C(24)	113.3(6)	C(19)–C(20)–C(21)	107.5(6)
C(31)–O(4)–C(32)	111.0(6)	C(17)–C(21)–C(20)	108.0(7)
C(2)–C(1)–C(5)	109.4(7)	C(17)–C(22)–C(23)	110.9(7)
C(2)–C(1)–C(6)	124.1(7)	O(3)–C(23)–C(22)	110.8(7)
C(5)–C(1)–C(6)	126.6(7)	C(26)–C(25)–C(29)	108.0(6)
C(1)–C(2)–C(3)	108.2(7)	C(26)–C(25)–C(30)	128.0(6)
C(2)–C(3)–C(4)	108.3(7)	C(29)–C(25)–C(30)	123.8(6)
C(3)–C(4)–C(5)	107.0(7)	C(25)–C(26)–C(27)	108.4(6)
C(1)–C(5)–C(4)	107.2(6)	C(26)–C(27)–C(28)	107.7(6)
C(1)–C(6)–C(7)	112.5(6)	C(27)–C(28)–C(29)	107.8(6)
O(1)–C(7)–C(6)	111.5(7)	C(25)–C(29)–C(28)	108.2(7)
C(10)–C(9)–C(13)	107.7(6)	C(25)–C(30)–C(31)	112.3(5)
C(10)–C(9)–C(14)	126.2(7)	O(4)–C(31)–C(30)	104.9(5)
C(13)–C(9)–C(14)	125.7(6)	Y(1)–H(1)–Y(1*)	125(4)
C(9)–C(10)–C(11)	108.7(6)	Y(2)–H(2)–Y(2*)	119(3)

TABLE 5. Positional parameters and their estimated standard deviations for [(MeOCH₂CH₂C₅H₄)₂Ho(μ-OH)]₂ (5)

	x	y	z	B _{eq} (Å ²)
Ho	0.88218(2)	0.07083(1)	0.03122(1)	1.932(4)
O	1.0539(3)	0.0616(2)	-0.0343(2)	2.53(7)
O(1)	0.7320(4)	-0.0107(3)	0.1102(2)	3.33(9)
O(1')	1.0599(5)	0.1742(3)	-0.1714(3)	5.0(1)
C(1')	0.8170(6)	0.1743(4)	-0.0861(4)	3.6(1)
C(1)	0.8539(6)	0.1186(4)	0.1778(3)	3.1(1)
C(2)	0.8449(6)	0.1929(4)	0.1355(3)	3.2(1)
C(2')	0.8139(6)	0.0913(4)	-0.1144(3)	3.9(1)
C(3)	0.9581(6)	0.2096(4)	0.1026(4)	3.7(1)
C(3')	0.7221(6)	0.0473(5)	0.0800(4)	4.3(2)
C(4')	0.6664(5)	0.1033(5)	-0.0282(4)	4.4(1)
C(4)	1.0361(6)	0.1449(4)	0.1262(4)	3.7(1)
C(5')	0.7246(5)	0.1809(4)	-0.0340(4)	4.0(1)
C(5)	0.9708(6)	0.0896(4)	0.1713(3)	3.3(1)
C(6)	0.7557(7)	0.0751(5)	0.2211(4)	4.6(1)
C(6')	0.8978(7)	0.2452(4)	-0.1111(4)	5.2(2)
C(7')	0.9662(7)	0.2318(5)	-0.1837(4)	5.1(2)
C(7)	0.6676(6)	0.0326(5)	0.1692(4)	4.6(2)
C(8)	0.6654(6)	-0.0799(5)	0.0799(5)	4.9(2)
C(8')	1.1202(9)	0.1551(5)	-0.2406(4)	6.1(2)

nearly lying in the equatorial plane. The average Ho–C bond lengths for two cyclopentadienyl ligands are 2.694 and 2.711 Å, respectively. The bond lengths of Ho–

TABLE 6. Selected bond distances (Å) and angles (deg) for [(MeOCH₂CH₂C₅H₄)₂Ho(μ-OH)]₂ (5)

Ho–O	2.250(3)	O(1')–C(8')	1.426(5)
Ho–O(1)	2.538(2)	C(1')–C(2')	1.409(6)
Ho–C(1')	2.738(4)	C(1')–C(5')	1.387(6)
Ho–C(1)	2.709(3)	C(1')–C(6')	1.510(6)
Ho–C(2)	2.702(4)	C(1)–C(2)	1.398(5)
Ho–C(2')	2.696(4)	C(1)–C(5)	1.395(6)
Ho–C(3)	2.674(4)	C(1)–C(6)	1.507(6)
Ho–C(3')	2.683(4)	C(2)–C(3)	1.421(6)
Ho–C(4')	2.686(4)	C(2')–C(3')	1.383(7)
Ho–C(4)	2.675(4)	C(3)–C(4)	1.411(7)
Ho–C(5')	2.738(3)	C(3')–C(4')	1.419(6)
Ho–C(5)	2.676(3)	C(4')–C(5')	1.398(6)
O(1)–C(7)	1.440(5)	C(4)–C(5)	1.391(6)
O(1)–C(8)	1.431(5)	C(6)–C(7)	1.505(6)
O(1')–C(7')	1.409(5)	C(6')–C(7')	1.506(6)
O–Ho–O(1)	144.7(1)	C(1)–C(6)–C(7)	112.2(3)
O–Ho–C(1')	83.2(1)	C(7)–O(1)–C(8)	111.8(4)
O–Ho–C(1)	127.4(2)	C(7')–O(1')–C(8')	111.2(4)
O(1)–Ho–C(1')	122.8(2)	C(2')–C(1')–C(5')	106.6(5)
O(1)–Ho–C(1)	62.9(1)	C(2')–C(1')–C(6')	127.4(4)
C(1')–Ho–C(1)	121.3(1)	C(5')–C(1')–C(6')	125.8(4)
C(1')–C(2')–C(3')	109.6(4)	C(2)–C(1)–C(5)	107.6(4)
C(2)–C(3)–C(4)	107.3(4)	C(2)–C(1)–C(6)	127.1(4)
C(2')–C(3')–C(4')	107.1(5)	C(5)–C(1)–C(6)	125.3(4)
C(3')–C(4')–C(5')	107.3(4)	C(1)–C(2)–C(3)	108.1(4)
C(3)–C(4)–C(5)	107.5(4)	C(1')–C(6')–C(7')	116.7(5)
C(1')–C(5')–C(4')	109.4(5)	O(1')–C(7')–C(6')	110.0(4)
C(1)–C(5)–C(4)	109.5(4)	O(1)–C(7)–C(6)	108.9(3)

C(centre) are 2.405 and 2.438 Å, respectively. The bond length of Ho–O(Cp') is 2.538 Å. It is longer than that of Y–O in complex 3. The distance Ho–O(OH) is 2.256 Å which is longer than those of Y–O(OH) in [O(CH₂CH₂C₅H₄)₂Y(μ-OH)]₂ (2.238 Å) [24], and in [O(CH₂CH₂C₅H₄)₂Y(μ-N₂C₃HMe₂)(μ-OH)]₂ [2.202(2) Å] [25], but shorter than the 2.345 Å found in [(C₅H₅)₂Y(μ-OH)]₂(C₆H₅C≡CC₆H₅) [31].

4. Conclusion

The crystallographic data confirm assignments made from the spectral and chemical evidence that the crystalline products of the reduction of [(CH₃OCH₂CH₂C₅H₄)₂Ln(μ-Cl)]₂ are the solvent-free dimeric lanthanide hydrides, [(CH₃OCH₂CH₂C₅H₄)₂Ln(μ-H)]₂ which contain an intramolecular coordination bond for each central metal atom. This study demonstrates that direct reduction of lanthanocene chloride with sodium hydride is of value in organolanthanide chemistry.

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