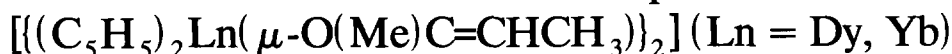


Dehydrogenation of organolanthanide alkoxides and X-ray crystal structures of the reaction product



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Abstract

Reaction of Cp_3Ln ($\text{Cp}=\text{C}_5\text{H}_5$; $\text{Ln} = \text{Dy}, \text{Yb}$) with 2-butanol in THF (THF = tetrahydrofuran) at room temperature yielded the complexes $[\text{Cp}_2\text{Ln}(\mu\text{-OCH}(\text{Me})\text{CH}_2\text{CH}_3)]_2$ [$\text{Ln} = \text{Dy}$ (1), Yb (2)], which have been characterized by elemental analysis, IR and MS spectra. The complexes 1 and 2 have been dehydrogenated to give the new enolate complexes $[\text{Cp}_2\text{Ln}(\mu\text{-O}(\text{Me})\text{C}=\text{CHCH}_3)]_2$ [$\text{Ln} = \text{Dy}$ (3), Yb (4)] upon refluxing in THF solution. The new complexes 3 and 4 have been structurally characterized by single-crystal diffraction studies. Complexes 3 and 4 crystallize from THF solution as isomorphous crystals of space group $Pnmm$ with the following unit cell parameters: 3[4]; $a = 9.910(5)[9.853(3)]$, $b = 10.940(2)[10.917(3)]$, $c = 12.258(2)[12.151(3)]$ Å, $V = 1329(1)[1307(1)]$ Å³, $Z = 2$, $D_c = 1.82[1.90]$ g cm⁻³, $R = 0.025[0.042]$, $R_w = 0.036[0.049]$. The molecules are oxygen-bridged dimers. The bridging unit Ln_2O_2 is completely planar. The metal atom is coordinated by two η^5 -Cp groups and two oxygen atoms of enolate ligands to form a pseudotetrahedral geometry. The average Ln–C bond lengths for 3 and 4 are 2.668(6) and 2.629(9) Å, respectively. The Ln–C distances of 3 and 4 are 2.256(4) and 2.210(2) Å, respectively. Complex 4 has been hydrolyzed to give the organic compound $\text{CH}_3\text{COCH}_2\text{CH}_3$, which has been confirmed by NMR spectra.

Keywords: Dysprosium; Ytterbium; Alkoxide; Cyclopentadienyl; Crystal structure

1. Introduction

Organolanthanide chemistry is currently one of the most rapidly developing areas of organometallic chemistry. Many studies have been published on the syntheses, structures and reactivities of organolanthanide complexes, which have demonstrated that these complexes usually possess unique structures and rapid reaction chemistry [1]. Also, organolanthanide alkoxides have recently attracted much attention [2–17]. Despite many synthetic and structural studies, relatively little is known of the reactivity of these complexes. Recently, we have found that upon refluxing in THF solution the complex $[\text{Cp}_2\text{Yb}(\mu\text{-OCH}_2\text{CH}=\text{CH}_2)]_2$ could be dehydrogenated into an enolate product $[\text{Cp}_2\text{Yb}(\mu\text{-OCH}=\text{C}=\text{CH}_2)]_2$ [18]. This unique reaction obviously still

remains to be explored. To investigate this reaction further, we report here the dehydrogenation of organolanthanide 2-butanoxides and the X-ray crystal structures of reaction products $[\text{Cp}_2\text{Ln}(\mu\text{-OC}(\text{Me})=\text{CHCH}_3)]_2$ ($\text{Ln} = \text{Dy}, \text{Yb}$).

2. Experimental section

2.1. Materials and instrumentation

All the manipulations were carried out on a Schlenk vacuum line or in a glovebox filled with a moisture- and oxygen-free argon atmosphere. THF solvent was refluxed and distilled over sodium benzophenone immediately before use. n-Hexane was distilled over finely divided LiAlH_4 prior to use. The 2-butanol was analytical pure grade and was redistilled before use. Anhydrous LnCl_3 [19] and Cp_3Ln [20,21] ($\text{Ln} = \text{Dy}, \text{Yb}$)

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were prepared according to literature methods. Metal analyses for Dy and Yb were accomplished using the literature procedure [22]. Elemental analyses for C and H were carried out on a Perkin-Elmer 240C analyzer. Infrared spectra were obtained on a Nicolet 170SX FI-IR spectrometer with samples prepared as Nujol mulls and in KBr pellets. Mass spectra were recorded on a VG ZAB-HS mass spectrometer operating in EI mode. The samples were rapidly introduced by direct inlet techniques with a source temperature 200°C and sample evaporation temperature in the range 50–300°C. The values of m/z are referred to the isotopes ^{12}C , ^1H , ^{16}O , ^{164}Dy and ^{174}Yb . The ^1H NMR spectrum was recorded on a Bruker 500 MHz DS-1000 instrument and chemical shifts are reported in δ units (ppm) with Me_4Si as internal reference.

2.2. Preparation of $[\text{Cp}_2\text{Dy}(\mu\text{-OCH}(\text{Me})\text{CH}_2\text{CH}_3)]_2$ (1) and $[\text{Cp}_2\text{Yb}(\mu\text{-OCH}(\text{Me})\text{CH}_2\text{CH}_3)]_2$ (2)

Cp_3Dy (0.28 g, 0.78 mmol) was dissolved in 20 ml THF in a Schlenk flask equipped with a stirbar. To this

solution, the equimolar 2-butanol was added via syringe at room temperature. The reaction solution was allowed to stir overnight, and was then concentrated by vacuum to ca. 3 ml. To this, 20 ml n-hexane was added and a pale-yellow solid precipitated out, which was separated by centrifugation, washed with n-hexane and dried in vacuo to afford a pale-yellow powder product (1) in 57.6% yield.

Following similar procedure, the yellow powder product of complex 2 could be readily obtained in 72.8% yield.

For 1: Anal. Found: C, 45.42; H, 5.01; Dy, 44.68. $\text{C}_{28}\text{H}_{38}\text{O}_2\text{Dy}_2$ calc.: C, 45.97; H, 5.24; Dy, 44.42%. IR (cm^{-1}): 3072w, 2928s, 2855s, 1642s, 1464m, 1442s, 1012s, 782s, 462s. MS: m/e [fragment, relative intensity %] = 731 [M - 3 = A, 0.1], 666 [A - Cp, 100.0], 658 [A - L, 2.6], 609 [A - Cp - R, 1.6], 593 [A - Cp - L, 8.7], 544 [A - 2Cp - R, 2.9], 536 [A - Cp - L - R, 5.7], 487 [A - 2Cp - 2R, 1.4], 470 [A - 2Cp - L - R, 10.0], 422 [A - 3Cp - 2R, 2.0], 404 [A - 3Cp - L - R, 2.9], 359 [M', 5.2], 338 [M/2 - Et, 2.7], 302 [M/2 - Cp, 4.4], 294 [M' - Cp, M/2 - L; 57.6], 273 [M/2 - Cp - Et,

Table 1
Crystal, data collection and refinement parameters

Complex	3	4
formula	$\text{C}_{28}\text{H}_{34}\text{O}_2\text{Dy}_2$	$\text{C}_{28}\text{H}_{34}\text{O}_2\text{Yb}_2$
Molecular weight	727.58	748.66
Crystal size (mm)	0.40 × 0.35 × 0.25	0.48 × 0.25 × 0.19
Crystal colour and shape	Pale-yellow hexagonal prism	Yellow-orange block
Crystal system	Orthorhombic	Orthorhombic
Space group	$Pnmm$ (No. 58)	$Pnmm$ (No. 58)
Cell constants		
a (Å)	9.910(5)	9.853(3)
b (Å)	10.940(2)	10.917(3)
c (Å)	12.258(2)	12.151(3)
V (Å ³)	1329(1)	1307(1)
Z	2	2
D_c (g cm^{-3})	1.82	1.90
Radiation (Å)	Mo $K\alpha$ ($\lambda = 0.71069$)	Mo $K\alpha$ ($\lambda = 0.71069$)
$F(000)$	700	716
μ (cm^{-1})	56.52	71.12
Range of hkl	$\pm 11, -13 - 0, 0 - 14$	$-13 - 0, 0 - 12, \pm 15$
Scan type	$\omega - 2\theta$	$\omega - 2\theta$
2θ max (°)	50	52
Scan width (°)	$0.50 + 0.35 \tan \theta$	$0.50 + 0.35 \tan \theta$
Scan speed (° min^{-1})	< 5.49	< 5.49
No. of reflections measured	2589	2870
No. of unique reflections	2169	1507
No. of reflections observed with $I \geq 3\sigma$	1105	1162
T max, min	0.865, 1.326	0.396, 1.419
No. of variables	83	83
R	0.025	0.042
R_w	0.036	0.049
GOF	1.23	1.33
Weight scheme	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$
Maximum shift/error	< 0.01	< 0.01
$\Delta\rho$ max, min (e Å^{-3})	0.68, -0.699	2.087, -1.664

2.4], 229 [M' - 2Cp, M/2 - Cp - L; 13.1], 164 [Dy, 3.0], 73 [L, 1.2], 66 [HCp, 31.0], 65 [Cp, 19.1]. {M = [Cp₂Dy(OCH(Me)CH₂CH₃)₂]; M/2 = Cp₂DyOCH(Me)CH₂CH₃; M' = Cp₃Dy; L = OCH(Me)CH₂CH₃; R = CH(Me)CH₂CH₃}.

For 2: Anal. Found: C, 44.13; H, 4.85; Yb, 46.06. C₂₈H₃₈O₂Yb₂ calc.: C, 44.68; H, 5.09; Yb, 45.98%. IR (cm⁻¹): 3078w, 2925s, 2853s, 1640m, 1461s, 1261m, 1011s, 778s, 464s. MS: *m/e* [fragment, relative intensity %] = 687 [M - Cp - 2 = A, 64.4], 622 [A - Cp, 3.1], 614 [A - L, 4.0], 565 [A - Cp - R, 3.2], 549 [A - Cp - L, 5.7], 508 [A - Cp - 2R, 1.1], 492 [A - Cp - L - R, 5.0], 433 [A - 2Cp - 2R, 1.2], 427 [A - 2Cp - L - R, 4.8], 378 [Yb₂O₂, 0.7], 362 [Yb₂O, 1.3], 348 [M/2 - Et, 1.5], 312 [M/2 - Cp, 1.3], 304 [M/2 - L, 12.0], 283 [M/2 - Cp - Et, 0.5], 239 [M/2 - Cp - L, 21.4], 218 [M/2 - 2Cp - Et, 0.7], 174 [Yb, 5.4], 73 [L, 1.2], 66 [HCp, 54.3], 65 [Cp, 37.2], 45 [C₂H₅O, 100.0]. {M = [Cp₂Yb(OCH(Me)CH₂CH₃)₂]; M/2 = Cp₂YbOCH(Me)CH₂CH₃; L = OCH(Me)CH₂CH₃; R = CH(Me)CH₂CH₃}.

2.3. Dehydrogenation of complexes 1 and 2

An appropriate amount of 1 or 2 was redissolved in 20 ml THF solvent. The resulting solution was refluxed for ca. 1 h. Then, it was cooled to room temperature and concentrated by vacuum to give a turbid mixture. The resulting mixture was heated again to give a transparent solution. The hot solution was then slowly cooled to room temperature to give a pale-yellow crystal product of 3 in yield 32.5% or a yellow-orange product of 4 in yield 43.6%. For 3: Anal. Found: C, 45.93; H, 4.45; Dy, 44.84. C₂₈H₃₄O₂Dy₂ calc.: C, 46.22; H, 4.71; Dy, 44.67%. For 4: Anal. Found: C, 44.56; H, 4.48; Yb, 46.55. C₂₈H₃₄O₂Yb₂ calc.: C, 44.92; H, 4.58; Yb, 46.23%.

2.4. Hydrolysis of complex 4

Crystals of complex 4 were put in a glass tube and the stoichiometric amount of water was added. Then, 0.5 ml D₂O was added to the above mixture. The clear hydrolysis solution was added into a NMR tube by syringe. ¹HNMR data (δ) for hydrolysate CH₃COCH₂CH₃ (D₂O, 296 K): 1.04 (CH₃-), 2.12 (CH₃CO), 2.54(-CH₂CO).

2.5. X-ray crystal structure determinations of complexes 3 and 4

Crystals of 3 and 4 suitable for X-ray analysis were sealed under argon in Lindemann capillaries. Accurate cell dimensions and the crystal orientation matrices were determined by a least-squares treatment of the setting angles of 25 reflections with 12.99° < θ < 14.95°

(for 3) and 13.06° < θ < 14.63° (for 4). Data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation. Intensities of three standard reflections measured every hour showed no decay. Data were corrected for Lorentz, polarization and absorption effects. Relevant crystal and data collection parameters for the present study are given in Table 1.

Systematic absences of two crystals are consistent with the space groups *Pnn2* (No. 34), *Pnmm* (No. 58) or *Pmmm* (No. 47). The Laue symmetry check showed that the crystals belonged to space group *Pmmm*. Lanthanide atoms were located by the direct methods. After some false starts in the space group *Pnn2* or *Pmmm*, the structures were solved by routine direct methods in the space group *Pnmm*. All the remaining nonhydrogen atoms were found via the difference Fourier syntheses. Refinement proceeded by full-matrix least-squares calculations, initially with isotropic then with anisotropic thermal parameters. The hydrogen atoms were added at the calculated positions using a C-H bond length of 0.95 Å and ideal bond angles, and were included in the structure factor calculation. Scattering factors were taken from ref. [23]. All calculations were performed on a Micro VAX 3100 computer using the MSC/Rigaku TEXSAN programme. Atomic coordinates of complexes 3 and 4 are given in Table 2 and 3. In the final difference-Fourier map of 4, the residue (ρ max = 2.087 e Å⁻³) is close to the metal and has no significant features.

3. Results and discussion

3.1. Syntheses and spectroscopic characterization of 1 and 2

Syntheses of organolanthanide alkoxides have interested chemists for many years. Traditionally, these complexes were prepared by the exchange reaction of a metal halide with an alkali-metal derivative of an alco-

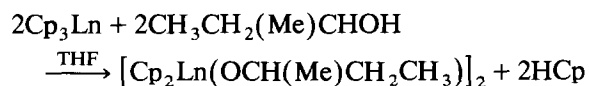
Table 2
Final positional parameters for 3

Atom	x	y	z	B _{eq}
Dy	0.86425(3)	0.10685(3)	0	2.12(2)
O	1.0936(5)	0.0938(3)	0	2.4(2)
C1	1.1791(9)	0.1971(7)	0	8.0(6)
C2	1.3214(8)	0.1705(8)	0	4.3(4)
C3	1.1280(8)	0.309(1)	0	8.1(8)
C4	1.201(1)	0.4252(7)	0	5.3(5)
C11	0.8863(6)	0.1470(7)	0.2142(5)	4.3(3)
C12	0.7802(7)	0.0654(5)	0.2008(4)	4.8(3)
C13	0.6756(6)	0.1304(7)	0.1520(5)	5.2(3)
C14	0.7186(7)	0.2485(6)	0.1354(5)	5.3(3)
C15	0.8472(6)	0.2566(6)	0.1733(5)	5.0(3)

Table 3
Final positional parameters for 4

Atom	x	y	z	B _{eq}
Yb	0.63412(3)	0.10441(3)	0	2.29(2)
O	0.4096(7)	0.0935(4)	0	2.1(2)
C1	0.323(1)	0.197(1)	0	7.7(9)
C2	0.177(1)	0.171(1)	0	4.6(5)
C3	0.374(1)	0.311(1)	0	9(1)
C4	0.301(2)	0.426(1)	0	5.1(6)
C11	0.654(1)	0.2538(8)	0.1718(9)	5.5(5)
C12	0.6120(8)	0.145(1)	0.2113(7)	4.5(4)
C13	0.718(1)	0.0608(7)	0.1992(7)	4.7(4)
C14	0.8218(9)	0.131(1)	0.151(1)	6.1(5)
C15	0.780(1)	0.2462(8)	0.1323(8)	5.3(5)

hol [7,15,24]. Many studies have demonstrated that this synthetic method is not without difficulties due to contamination by halide or oxide as well as the formation of anionic complexes [15,25]. Recently, several research groups [4,13,14,16,17] have proved that cyclopentadienyllanthanide alkoxides can readily be prepared by the proton-exchange reaction between a lanthanide metallocene and an alcohol. In this paper, using this simple synthetic method, we have synthesized complexes 1 and 2 by reaction of Cp₃Ln (Ln = Dy, Yb) with equimolar 2-butanol in THF at room temperature.

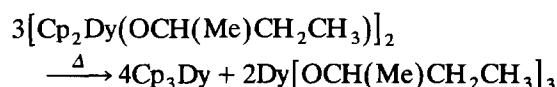


The [Cp₂Ln(μ-OR)]₂-type complexes are usually obtained from the non-coordinating solvents such as heptane, hexane, benzene and toluene. Nevertheless, it was found that these complexes could also be obtained from the coordinative solvent THF by selecting an appropriate steric bulky OR group. Steric factors are important in organolanthanide chemistry and can affect the structures as well as the stabilities of Cp₂LnOR complexes. With a larger OR group such as the α-naphtholate ligand OC₁₀H₇, only the solvated monomeric complex Cp₂Yb(OC₁₀H₇)(THF) can be obtained from THF solution [14]. Under the same conditions, however, for the larger lanthanide earlier in the series La–Nd, neither [Cp₂Ln(μ-OR)]₂-type nor the stable Cp₂Ln(OR)(THF)-type [R = CH₂CH₂CH₃, –CH₂–CH=CH₂, –(CH₂)₃CH₃, –CH(CH₃)CH₂CH₃, –(CH₂)₄CH₃ etc.] complexes could be obtained from the THF solution due to the steric and coordinated unsaturation around the metal. Hence, to obtain the stable earlier organolanthanide alkoxides, the steric bulk of the Cp or OR ligand must be increased.

Complexes 1 and 2 have been characterized by elemental analysis, IR and MS spectra. The analytical data for 1 and 2 conformed to their formulae. Their IR spectra exhibit the characteristic absorptions for the η⁵-Cp ligand at ca. 3080, 1440, 1010 and 780 cm⁻¹ [26].

The absorptions for 2-butanoxide ligands appear markedly at about 2925, 2850, 1462, 1380, 1260 and 740 cm⁻¹. The molecular ions relating to 1 are clearly shown in the mass spectra and are characterized by the loss of the Cp group from the molecule with the [M – Cp]⁺ ion as a strong peak in the spectra. The mass spectra of 2 displayed a series of peaks, which could be assigned to fragments containing two Yb atoms, and which clearly represents fragments derived from the dimer [Cp₂Yb(OCH(Me)CH₂CH₃)₂], although peaks due to the molecular ions were not observed. The two complexes have similar mass spectra cleavage patterns. The presence of the peaks corresponding to [CpLn₂O₂]⁺, [CpLn₂O]⁺, [Ln₂O₂]⁺ and [Ln₂O]⁺ in the spectra evidently indicate the oxygen bridging structures of 1 and 2. Significantly, the peaks attributable to fragments containing one metal atom were observed in both spectra of 1 and 2, indicating the probable existence of dissociated monomeric species Cp₂LnOCH(Me)CH₂CH₃ in the vapour state.

It is interesting to note that in the mass spectra of 1 not only the molecular ions and resulting fragments were observed, but the peaks corresponding to the [Cp₃Dy]⁺ and related fragments appeared also at the same time. Nevertheless, this phenomenon did not occur in the mass spectra of 2. Based on our previous studies [27–37], we predict that complex 1 may be unstable to heat and decomposition reaction may take place at the evaporation temperature of the sample following the equation:

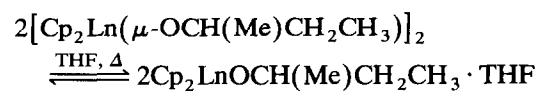


The high thermal stability of the Yb complex *vs.* the Dy complex is obviously due to the greater degree of steric saturation around the small metal [1c].

3.2. Dehydrogenation of complexes 1 and 2

Complexes 1 and 2 were redissolved in THF and refluxed for ca. 1 h to give the new dehydrogenated products [Cp₂Ln(OC(Me)=CHCH₃)₂] [Ln = Dy (3), Yb (4)], which have been studied by X-ray crystallography. Complex 4 was hydrolyzed by water. The ¹HNMR data indicate that the hydrolysate CH₃CH=C(Me)OH of 3 and 4 is readily converted into butanone. This result is consistent with our previous studies [18].

As indicated in the Experimental section, the solubility of 1 or 2 in THF solvent is sensitive to temperature and increases with the elevation of temperature. Obviously, a temperature-dependent equilibrium exists between dimeric and solvated monomeric complexes in THF solution, as shown below:



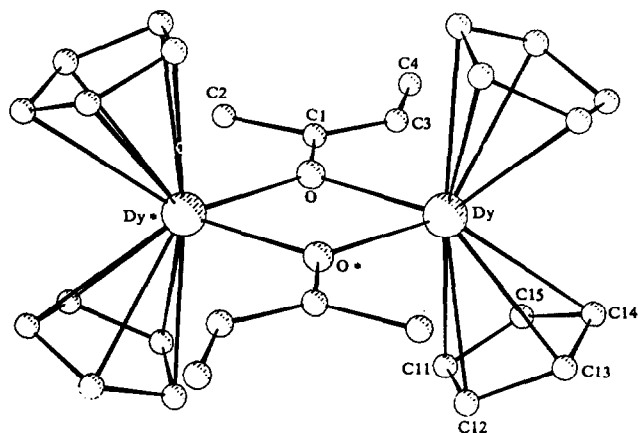


Fig. 1. The molecular structure of **3** with the hydrogen atoms omitted for clarity.

Evans has pointed out that organolanthanide complexes are more reactive with terminal ligands than with bridging ligands [1c]. The dehydrogenation of **1** and **2** was carried out in refluxing THF solution. Therefore, although the mechanism of this reaction is presently not clear, we can postulate that the reaction probably takes place through the THF-solvated monomeric molecule $\text{Cp}_2\text{LnOCH}(\text{Me})\text{CH}_2\text{CH}_3 \cdot \text{THF}$ in which the R group can easily rotate to form the reaction intermediate.

3.3. Description and discussion of X-ray crystal structures of **3** and **4**

The molecular structures of **3** and **4** (Figs. 1 and 2) show that the complexes are oxygen-bridging dimers. The bridging unit Ln_2O_2 is completely planar. The structures are typical bent metallocenes and are similar

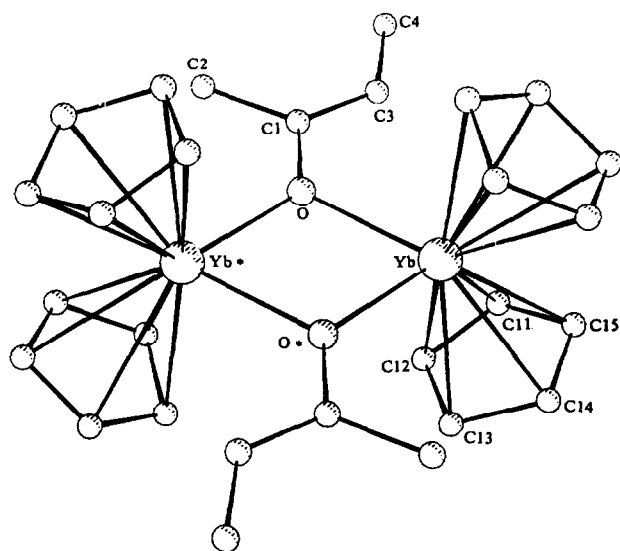


Fig. 2. The molecular structure of **4** with the hydrogen atoms omitted for clarity.

Table 4
Important bond distances (Å) and angles (°) for **3**

Dy–Dy *	3.564(2)	C1–C3	1.32(1)
Dy–O *	2.234(4)	C1–C2	1.44(1)
Dy–O	2.278(5)	C3–C4	1.46(1)
Dy–C11	2.671(6)	C11–C12	1.39(1)
Dy–C12	2.638(5)	C12–C13	1.39(1)
Dy–C13	2.653(6)	C13–C14	1.38(1)
Dy–C14	2.691(5)	C14–C15	1.359(8)
Dy–C15	2.687(6)	C15–C11	1.36(1)
Dy–Cav	2.668(6)	O–C1	1.413(9)
Dy–Cp ^a	2.397		
Dy–O–Dy *	104.4(2)	O–C1–C2	115.2(7)
O–Dy–O *	75.6(2)	O–C1–C3	120.7(8)
C1–O–Dy	123.2(5)	C1–C3–C4	127.9(8)
C1–O–Dy *	132.4(5)	C2–C1–C3	124.2(8)
Cp–Dy–Cp	128.5		

^a Cp represents the cyclopentadienyl ring centroid.

Symmetry operations: *: 2–x, –y, +z.

to other known binuclear biscyclopentadienyl lanthanide alkoxides [4,8,13–17], enolates [7,18] and hydroxides [38,39]. The lanthanide metal is coordinated by two Cp ring centroids and two oxygen atoms of 2-butenolate ligands to form a distorted tetrahedral geometry, giving the central metal a formal coordination number of 8 if the Cp group is regarded as occupying three coordinated sites.

Selected bond distances and angles for **3** and **4** are listed in Tables 4 and 5. The bond distances and angles for the Cp_2Ln units of **3** and **4** are unexceptional. The Ln–C(Cp) distances range from 2.638(5) to 2.691(5) Å, and average 2.668(6) Å for **3** and range from 2.601(8) to 2.657(9) Å, with average 2.629(9) Å for **4**. These averages are compatible with those found in corresponding related $[\text{Cp}_2\text{LnX}]_2$ structures: $[\text{Cp}_2\text{DyCl}]_2$, 2.63 Å [40]; $[\text{Cp}_2\text{Dy}(\text{ONCMe}_2)]_2$, 2.68(2) Å [41]; $[\text{Cp}_2\text{YbCl}]_2$, 2.58(1) Å [42]; $[\text{Cp}_2\text{Yb}(\text{OCH}_2\text{CH}=\text{CHCH}_2)]_2$, 2.643 Å [16]; $[\text{Cp}_2\text{Yb}(\text{OCH}=\text{C}=\text{CH}_2)]_2$, 2.601(5) Å [18].

Table 5
Important bond distances (Å) and angles (°) for **4**

Yb–Yb *	3.490(2)	C1–C3	1.34(2)
Yb–O *	2.203(5)	C1–C2	1.47(2)
Yb–O	2.216(7)	C3–C4	1.45(2)
Yb–C11	2.657(9)	C11–C15	1.33(1)
Yb–C12	2.614(9)	C11–C12	1.35(1)
Yb–C13	2.601(8)	C12–C13	1.40(1)
Yb–C14	2.617(9)	C13–C14	1.41(2)
Yb–C15	2.655(8)	C14–C15	1.35(2)
Yb–Cav	2.629(9)	O–C1	1.41(1)
Yb–Cp ^a	2.355		
Yb–O–Yb *	104.3(2)	O–C1–C2	116(1)
O–Yb–O *	75.7(2)	O–C1–C3	121(1)
C1–O–Yb	124.1(6)	C1–C3–C4	128(1)
C1–O–Yb *	131.6(7)	C2–C1–C3	123(1)
Cp–Yb–Yb	128.9		

^a Cp represents the cyclopentadienyl ring centroid.

Symmetry operations: *: 1–x, –y, +z.

Table 6
Comparative crystallographic data for some $[\text{Cp}_2\text{Ln}(\mu\text{-OR})_2]$ -type complexes

Complex ^a	Ln–C _{av} (Å)	Ln–O (Å)	Ln–Ln (Å)	Ln–O–Ln (°)	O–Ln–O (°)	Cp–Ln–Cp(°)	ref.
$[\text{Cp}'_2\text{Y}(\mu\text{-OMe})_2]$	2.67(1)	2.217(3) 2.233(3)	3.562(1)	106.4(1)	73.6(1)	131.3	15
$[\text{Cp}''_2\text{Y}(\mu\text{-OCH=CH}_2)_2]$	2.651(5)	2.275(3) 2.290(3)	3.667(1)	106.9(1)	73.1(7)	128.1	7
$[\text{Cp}^*_2\text{Ce}(\mu\text{-OCHMe}_2)_2]$	2.83(4)	2.373(3) 2.369(3)	3.844(2)	108.3(1)	71.7(1)	128.5	4
$[\text{Cp}_2\text{Yb}(\mu\text{-OCH=C=CH}_2)_2]$	2.601(16)	2.195(5) 2.204(5)	3.581(1)	106.2(2)	73.8(2)	126.2	18
$[\text{Cp}_2\text{Yb}(\mu\text{-OCH}_2\text{CH=CHCH}_3)_2]$	2.643	2.220(11) 2.197(11)	3.5324(15)	106.3(4)	73.7(4)	127.11(4)	16
$[\text{Cp}_2\text{Lu}(\mu\text{-O}(\text{CH}_2)_4\text{PPh}_2)_2]$		2.184(1)	3.4757(6)	105.2(1)	74.8(1)	127.2(1)	8
$[\text{Cp}_2\text{Dy}(\mu\text{-O}(\text{Me})\text{C=CHCH}_3)_2]$	2.668(6)	2.278(5) 2.234(4)	3.564(2)	104.4(2)	75.6(2)	128.5	b
$[\text{Cp}_2\text{Yb}(\mu\text{-O}(\text{Me})\text{C=CHCH}_3)_2]$	2.629(9)	2.203(5) 2.216(7)	3.490(2)	104.3(2)	75.7(2)	128.9	b

^a Cp' = Me₃SiC₅H₄; Cp'' = MeC₅H₄; Cp* = Me₃CC₅H₄.

^b This work.

A comparison of bonding parameters between **3** and **4** and the closely related bimetallic organolanthanide alkoxides is given in Table 6. This shows that all the complexes in Table 6 have similar Ln–C, Ln–O and Ln–Ln distances, when the difference in the size of the metal was considered. In addition, in these structures the Cp–Ln–Cp, O–Ln–O and Ln–O–Ln angles are also similar. This result revealed that the rigid bridging unit Ln₂O₂ in the structures of $[\text{Cp}_2\text{Ln}(\mu\text{-OR})_2]$ -type complexes are stable regardless of the difference in the size of the metal and OR group.

As indicated in the above discussion, the title complexes can dissolve in THF to form the solvated monomer $\text{Cp}_2\text{LnO}(\text{Me})\text{C=CHCH}_3 \cdot \text{THF}$. This feature demonstrates that the Ln–O bond in the bridging complexes **3** or **4** can easily break by the attack of THF molecule. In fact, the bridging Ln–O bond is only slightly shorter than the Ln–O(THF) bond. For example, the Yb–O distances in $[\text{Cp}_2\text{Yb}(\mu\text{-OCH=C=CH}_2)_2]$, 2.204(5) and 2.195(5) Å [18]; $[\text{Cp}_2\text{Yb}(\mu\text{-OCH}_2\text{CH=CHCH}_3)_2]$, 2.220(11) and 2.157(11) Å [16]; and $[\text{Cp}_2\text{Yb}(\mu\text{-O}(\text{Me})\text{C=CHCH}_3)_2]$, 2.216(7) and 2.203(5) Å are about 0.10 Å shorter than the Yb–O(THF) bond [2.30(1) Å] in the $\text{Cp}_2\text{Yb}(\text{OC}_{10}\text{H}_7)(\text{THF})$ complex [14].

The C1–C3 bond lengths in **3** and **4** are 1.32(1) and 1.34(2) Å, respectively, which are quite reasonable for a sp² carbon–carbon double bond and compare well with the distances found in other related complexes containing unsaturated OR groups [7,16,43–45]. The C1–C2 and C3–C4 bond lengths in **3** [1.44(1) and 1.46(1) Å] and **4** [1.47(2) and 1.45(2) Å] are consistent with the description for a sp³ carbon–carbon single bond [46]. In view of the bond angles, one can see that in two structures all the angles around C1 and C3 atoms are normal for a sp² hybrid carbon atom. Moreover, the O, C1, C2, C3 and C4 atoms are all in a single

plane. Thus, the above results evidently show that the bond distances and angles for the O(Me)C=CHCH₃ ligand are all reasonable.

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