Dehydrogenation of Organolanthanide Alkoxides and X-Ray Crystal Structure of Reaction Product $[(C_5H_5)_2Yb(\mu\text{-}OCH{=}C{=}CH_2)]_2$

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$[Cp_3Yb]$ reacts with HOR ($Cp = C_5H_5$; $R = CH_2CH{=}CH_2, CH_2CH_2Me$) in thf (thf = tetrahydrofuran) at room temperature to give complexes $[\{Cp_2Yb(\mu\text{-}OR)\}_2]$, which are dehydrogenated to yield the new complex $[\{Cp_2Yb(\mu\text{-}OCH{=}C{=}CH_2)\}_2]$ in refluxing thf solution; the X-ray crystal structure shows that the new complex is dimeric with oxygen atoms as bridging groups.

Since lanthanide elements possess the nature of both main group and d-block elements, organolanthanide complexes have shown some unique properties, such as sensitivity to air and moisture, the nature of ionic and covalent bonding, large coordination number and high catalytic activity.[1] Recently, Jin *et al.* reported that the reaction of $[(C_8H_8)SmCl]\cdot thf$ (thf = tetrahydrofuran) with 2,4-dimethylcyclopentadienylpotassium gave a ring-opened cyclopentadienyl complex.[2] Evans reported that biscyclopentadienyllanthanide alkyls can leave thf to form organolanthanide enolate complexes $[\{Cp_2Ln(\mu\text{-}OCH{=}CH_2)\}]$.[3] In 1990 Schumann found that the complex $[Cp_2YbPPh_2]$ also can cleave to give a biscyclopentadienyl ytterbium alkoxide $[\{Cp_2Yb(\mu\text{-}OCH_2CH_2CH_2CH_2PPh_2)\}_2]$.[4] These results have encouraged us to investigate the reactivity of lanthanide metallocenes. In this communication, we report the first dehydrogenation reaction of organolanthanide alkoxides and the crystal structure of $[\{Cp_2Yb(\mu\text{-}OCH{=}C{=}CH_2)\}_2]$.

The complex $[\{Cp_2Yb(\mu\text{-}OCH{=}C{=}CH_2)\}_2]$ was synthesized as follows:† to a mixture of solid $[Cp_3Yb]$ (1.46 mmol) and thf (20 ml), $CH_2{=}CHCH_2OH$ (1.46 mmol) was added dropwise. The mixture was stirred overnight at room temperature, and a yellow precipitate was formed, which was separated by centrifugation and dried *in vacuo* to give $[\{Cp_2Yb(\mu\text{-}OCH_2CH{=}CH_2)\}_2]$ **1** as a yellow powder in 65% yield. This product was redissolved in thf (20 ml). The resulting mixture was refluxed for 1 h and the colour of the solution turned from yellow to orange. The mixture was then filtered immediately, and the hot filtrate slowly cooled to *ca.* −25 °C for 48 h to produce the orange crystalline product $[\{Cp_2Yb(\mu\text{-}OCH{=}C{=}CH_2)\}_2]$ **3** (yield 72%) (Scheme 1).

$2[Cp_3Yb] + 2\ CH_2{=}CHCH_2OH$
thf ↓ room temp.
$[\{Cp_2Yb(\mu\text{-}OCH_2CH{=}CH_2\}_2]$
1
thf ↓ reflux
$[\{Cp_2Yb\ (\mu\text{-}OCH{=}C{=}CH_2\}]$
3
thf ↑ reflux
$[\{Cp_2Yb\ (\mu\text{-}OCH_2CH_2Me\}_2]$
2
thf ↑ room temp.
$2\ [Cp_3Yb] + 2\ MeCH_2CH_2OH$

Scheme 1

By similar procedure, the reaction of $[Cp_3Yb]$ with $MeCH_2CH_2OH$ in thf at room temperature gave the complex $[\{Cp_2Yb(\mu\text{-}OC_3H_7)\}_2]$ **2**, which also gave the complex $[\{Cp_2Yb(\mu\text{-}OC_3H_3)\}_2]$ **3** (yield 54%) in refluxing thf solution.

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† All the manipulations were performed under a moisture- and oxygen-free argon atmosphere or in a glovebox.

The complexes **1**, **2** and **3** have been characterized by elemental analysis, and their IR and mass spectra.‡ Complex **3** obtained both from **1** and from **2** was also studied by X-ray crystallography.§ Hydrolysis of complex **3** by H_2O gives acrolein and free cyclopentadiene. The ^1H NMR spectra of the hydrolysis product clearly show peaks due to acrolein,‡ showing that the free enolate ligand is not stable and is easily converted to acrolein.

Elemental analyses fo the complexes **1** and **3** confirmed their formulae. Their IR spectra exhibit the characteristic absorptions for the η^5-Cp ligand and ν(C–H) vibrations for the methylene and methyl groups. However, absorptions for the –$CH=CH_2$ and –$CH=C=CH_2$ groups could not be distinguished, because they were masked by the absorptions of the Cp ligands. The mass spectra all show clearly their molecular ions.

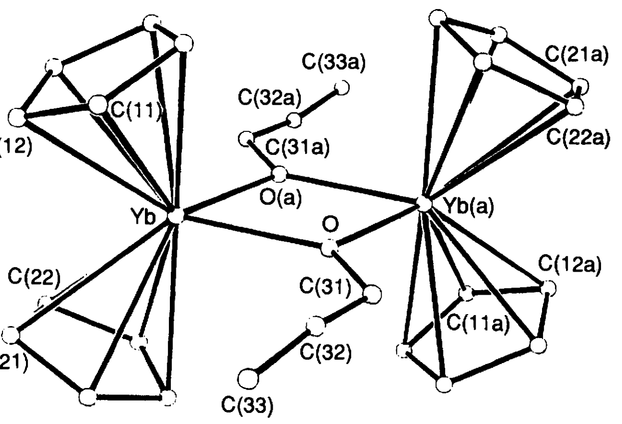

Fig. 1 Molecular structure and atom numbering scheme for **3** obtained from **1** [data for **3** obtained from **2** in square brackets]. Selected bond distances (Å) and angles (°): Yb–O 2.195(5) [2.190(5)], Yb–O(a) 2.204(5) [2.207(6)], C(31)–C(32) 1.207(25) [1.198(27)], C(32)–C(33) 1.191(25) [1.203(27)], O–(31) 1.391(17) [1.406(19)], Yb–C(C_5H_5)$_{av.}$ 2.601(16) [2.589(17)], Yb–Cp(1) 2.329 [2.329], Yb–Cp(2) 2.343 [2.325], O–Yb–O(a) 73.8(2) [73.6(2)], Yb–O–Yb(a) 106.2(2) [106.4(2)], C(31)–O–Yb(a) 122.5(6) [122.3(6)], C(31)–O–Yb 131.3(6) [131.2(6)], O–C(31)–C(32) 126.8(13) [128.2(13)], C(31)–C(32)–C(33) 178.6(24) [173.6(25)], Cp(11-Yb–Cp(2) 126.2 [126.3] (Cp = centroid of cyclopentadienyl ring).

The molecular structure of **3** (Fig. 1) shows that the complex is an oxygen-bridged dimer. The structure is typical of a bent metallocene and is similar to that of other known biscyclopentadienyl lanthanide alkoxides.[3–6] The ytterbium atom is coordinated by two cyclopentadienyl ligands and two oxygen atoms to form a distorted tetrahedral geometry, if the η^5-bonded cyclopentadienyl is regarded as occupying a single polyhedral vertex. The Yb–C(Cp) bond lengths in the two structures are 2.601(16) Å (from **1**) and 2.589(17) Å (from **2**) respectively, and are similar to those found in related known ytterbium complexes: [$Cp_2Yb(OC_9H_7)$]·thf, 2.587(17) Å;[7] [Cp_2YbMe]·thf. 2.60(2) Å;[8] [$Cp_2YbMeCOCHCOMe$), 2.611 Å.[9] The average Yb–O distance [2.199(6) Å] in the two structures is comparable with the distances of the bridging Ln–O bonds found in other known dicyclopentadiely lanthanide alkoxide dimers,[3–6] when the difference in metallic ion radii is taken into account.

The C–C bond distances for the $OCH=C=CH_2$ ligand in the two structures [1.198(27) and 1.203(27) Å; 1.207(25) and 1.191(25) Å] are significantly shorter than the C–C bond length [1.287(8) Å] for the $OCH=CH_2$ ligand in the complex [{$MeC_5H_4)_2Y(\mu$-$OCH=CH_2)$}$_2$].[3] The C–C–C angles for the $OCH=C=CH_2$ ligand in the two structures [178.6(24) and 173.6(25)°] are close to 180°. The O–C bond distance [1.391(17), 1.406(19) Å] for the $OCH=C=CH_2$ ligand is slightly longer than that [1.1324(6) Å] for the $OCH=CH_2$ ligand,[3] but the O–C–C angle [126.8(13), 128.2(13)° is similar to that [128.0(6)°] reported for $OCH=CH_2$.[3] These results show that the bond distances and angles for the $OCH=C=CH_2$ ligand are reasonable.

The Cp–Yb–Cp angle [126.2, 126.3°] is *ca.* 5° smaller than that (131.1°) in the complex [$Cp_2Yb(OC_9H_7)$]·thf.[7] This deviation is normal for bridging compared with terminal complexes,[10] and is mainly due to the presence of steric repulsion between the two bent Cp_2Yb units.

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‡ Elemental analyses and spectroscopic data: for **1**, found: C, 42.8; H, 3.9; Yb, 47.8. $C_{26}H_{30}O_2Yb_2$ requires C, 43.3; H, 4.2; Yb, 48.0%; IR (Nujol and Fluorolube mulls): ν(Yb–C) 258s cm^{-1}, ν(Yb–O) 468m cm^{-1}; MS (EI, ^{12}C, ^1H, ^{16}O and ^{174}Yb) *m/z* 722 (M, 1.5%). For **2**, the characterization results have been reported in Z. Wu, Z. Xu, X. You, X. Zhou and Z. Jin, *Polyhedron*, 1992, **11**, 2673. For **3**, found: C, 43.2; H, 3.5; Yb, 48.6. $C_{26}H_{26}O_2Yb_2$ requires C, 43.6; H, 3.7; Yb, 48.3%; IR: ν(Yb–C) 252s cm^{-1}, ν(Yb–O) 465m cm^{-1}; MS: *m/z* 718 (M, 0.6%); ^1H NMR data for hydrolysis product $CH_2=CHCHO$: δ 9.58 (–CHO), 6.32–6.42 ($CH_2=$) and 6.50 (=CH–).

§ *Crystal data* for **3** $C_{26}H_{26}O_2Yb_2$, M = 716.6, monoclinic, space group $P2_1/n$, for complex obtained from **1** [data for complex obtained from **2** in square brackets]: a = 8.792(1) [8.797(4)], b = 8.665(2), [8.662(2)], c = 15.982(4) [15.995(5)] Å, β = 95.77(1) [95.77(3)]°, V = 1211.3(5) [1212.6(5)] Å^3, Z = 2, $F(000)$ = 684, μ = 80.9 [80.8] cm^{-1}, D_c = 1.97 [1.97] g cm^{-3}. Data were collected on a Nicolet R3m/E four-circle X-ray diffractometer at room temperature, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Scan type ω–2θ, $2\theta_{max}$ = 58° [50°] 2321 [1539] unique reflections with $I > 3\sigma(I)$ were used in the refinement, R = 0.041 [0.031]. The intensities were corrected for Lorentz–polarization effects and empirically for absorption. The structures were solved by direct methods and Fourier syntheses. All nonhydrogen atoms were refined anisotropically by full-matrix least-squares. All hydrogen atoms were placed in calculated positions 0.96 Å from the carbon atoms to which they are bonded. All calculations were performed on an Eclipse S/140 computer using SHELXTL programs. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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