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Synthesis and characterization of $(C_5H_9C_9H_6)_2Yb(THF)_2$(II) (**1**) and $[(C_5H_9C_5H_4)_2Yb(THF)]_2O_2$ (**2**), and ring-opening polymerization of lactones with **1**

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Abstract

Reaction of YbI_2 with two equivalents of cyclopentylindenyl lithium ($C_5H_9C_9H_6Li$) affords ytterbium(II) substituted indenyl complex $(C_5H_9C_9H_6)_2Yb(THF)_2$ (**1**) which shows high activity to ring-opening polymerization (ROP) of lactones. The reaction between YbI_2 and cyclopentylcyclopentadienyl sodium ($C_5H_9C_5H_4Na$) gives complex $[(C_5H_9C_5H_4)_2Yb(THF)]_2O_2$ (**2**) in the presence of a trace amount of O_2, the molecular structure of which comprises two $(C_5H_9C_5H_4)_2Yb(THF)$ bridged by an asymmetric O_2 unit. The O_2 unit and ytterbium atoms define a plane that contains a C_i symmetry center.

Keywords: Cyclopentylcyclopentadienyl; Cyclopentylindenyl; Ytterbium; Lanthanocene; Ring-opening polymerization; Lactones

1. Introduction

In recent years, indene-derived ligands have been found to exhibit wide application in organometallic chemistry, as planar shape of the indenyl group is expected to satisfy the requirement of steric saturation of the central metal and leave the easily accessible central metals. Though a few lanthanide(II) indenyl complexes, $(C_9H_7)_2Sm(THF)_x$ [1], $(C_9H_7)_2Yb(THF)_2$ [2], $(C_9H_7)_2Yb(DME)$ and $(CH_2)_2$[1-(4,7-$(CH_3)_2$-C_9H_4)]$Yb(THF)_2$ [3] have recently been synthesized and characterized by X-ray diffraction, known lanthanide(II) complexes with substituted indenyl ligands are still quite scarce. We report here the synthesis and crystalline structure of the non-bridged substituted bis(indenyl) complex (**1**) and also the examples for the polymerization of lactones with divalent ytterbocene. In addition, we report a X-ray crystalline structure of f-orbital elementary O_2 complex (**2**), a previously unknown type of ytterbium dioxygen coordination geometry.

2. Experimental

Since the complexes described below are extremely air- and moisture-sensitive, all experiments were conducted under pure argon by Schlenk techniques. Solvents, indene and cyclopentyl bromide were dried over 4A molecular sieves for several weeks and refluxed over sodium benzophenone ketyl for 1 day and distilled before use. Cyclopentylcyclopentadiene was prepared according to literature [4]. Analysis of Yb was accomplished using direct complexometric titration with disodium EDTA. Carbon and hydrogen were determined on a HEBI Instrument Factory (China) TQ-2 elementary analyzer. IR spectra were recorded on a Bio-Rad FTS135 spectrometer as KBr pellets. ^{1}H-NMR (^{13}C-NMR) spectra were obtained on a Varian Unity-400 (Unity-100) spectrometer in THF-d_8 (for complex **1**) and C_6D_6 (for complex **2**) solutions, respectively.

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Molecular weights of polylactones are measured on Waters 410 GPC.

2.1. Synthesis of $C_5H_9C_9H_7$

Freshly distilled indene (20 ml, 170 mmol) was reacted with slightly overweighed Na sands 4.5 g (195 mmol) in 60 ml THF at 50 °C for 24 h. The mixture was filtered to remove excess Na and then cyclopentyl bromide (18 ml, 170 mmol) was added dropwise at 0 °C. The resulting solution was stirred for 3 h and then washed with an aq. solution of NH_4Cl, and the resulting organic layer was collected. This procedure was repeated until the organic phase reached neutrality. Then, the organic compound solution was dried over $MgSO_4$ for 10 h, distilled, and the yellow distillate was collected at 95–100 °C/266 Pa. Yield: 39% (based on indene), $n_D^{20} = 1.566$. IR (cm^{-1}): 3065, 3017, 2952, 2867, 2776, 1684, 1606, 1574, 1458, 1396, 1301, 1266, 1169, 1120, 1021, 969, 940, 914, 767, 719. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 1.547 (s, s, CH_2, C_5H_9), 1.680 (br s, CH_2, C_5H_9), 1.694 (b, s, CH_2, C_5H_9), 1.772 (br, m, 2.065, CH_2, C_5H_9), 3.053 (t, w, CH, C_5H_9), 3.316 (s, s, CH_2, aromatic), 6.193 (s, m, CH, aromatic) 7.189–7.425 (multi, m, CH, aromatic). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 25.251, 31.669 (CH_2, C_5H_9); 37.495, 38.572 (CH, C_5H_9); 119.611, 123.678, 124.330, 125.347, 125.832 (CH, aromatic), 144.768, 145.496, 148.607 (C, aromatic).

2.2. Synthesis of $[(C_5H_9C_9H_6)_2Yb(THF)_2]$ (1)

A solution of $C_5H_9C_9H_6Li$ in THF (31.6 ml, 17.9 mmol) (at 0 °C, $C_5H_9C_9H_7$ was reacted with one equivalent C_6H_{14} solution of *n*-butyllithium for 12 h) was added to 130 ml THF solution of YbI_2 (8.9 mmol) at room temperature (r.t.). The mixture changed gradually from greenish brown to red and was stirred for 10 h. After centrifugation to remove the precipitates, the red THF solution was cooled at 0 °C to give red single crystals of complex **1** in yield 90.3% (based on YbI_2). Found: C, 62.22; H, 7.11; Yb, 25.18%. Anal. Calc. for $C_{36}H_{46}O_2Yb$: C, 63.23; H, 6.78; Yb, 25.30%. IR (cm^{-1}): 3030, 3050, 3067, 2954, 2869, 1662, 1606, 1574, 1458, 1396, 1172, 1068, 1046, 970, 915, 892, 769, 720. ^{1}H-NMR (400 MHz, THF-d_8) δ (ppm): 2.177 (br, m, CH_2, C_5H_9), 3.175 (br, m, CH, C_5H_9), 3.383 (br, m, CH, aromatic), 6.289 (br, m, CH_2, aromatic), 7.236–7.682 (multi, s, CH, aromatic). ^{13}C-NMR (100 MHz, THF-d_8) δ (ppm): 26.862, 68.338(CH_2, THF); 26.475, 32.985 (CH_2, C_5H_9), 38.578 (CH, C_5H_9); 40.032 (CH_2 aromatic); 120.747, 124.790, 125.602, 126.330, 127.021 (CH, aromatic); 146.124, 146.738, 149.940 (C, aromatic).

2.3. Synthesis of $[(C_5H_9C_5H_4)_2Yb(THF)]_2O_2$ (2)

A THF solution of $C_5H_9C_5H_4Na$ (21.2 ml, 12 mmol) was added dropwise to YbI_2 (6 mmol) in 125 ml THF solution at r.t. The mixture changed from greenish-brown to purplish-red and was standed for 10 h, and then was stripped off the THF solvent. The residue was extracted sequentially with 50 ml $C_6H_5CH_3$ (purplish-red) and 30 ml ethylene glycol dimethyl ether (DME) (bluish-green). The DME extract changed to yellowish-green when it was concentrated and later was cooled at 0 °C for 4 days to give yellow single crystals of complex **2** (14.9% based on YbI_2). Found: C, 55.34; H, 6.9; Yb, 32.24. Anal. Calc. for $C_{48}H_{68}O_4Yb_2$: C, 54.63; H, 6.45; Yb, 32.79%. ^{1}H-NMR (400 MHz, C_6D_6) δ (ppm): 1.694 (br, m, CH_2, C_5H_9), 2.15 (br, m, CH_2, C_5H_9), 3.213 (s, m, CH, C_5H_9), 3.423 (m, CH, aromatic), 6.037 (m, CH_2, aromatic), 6.430 (br, m, CH, aromatic). ^{13}C-NMR (100 MHz, C_6D_6) δ (ppm): 25.730, 25.912, (CH_2, THF), 68.212 (CH_2O, THF); 26.200 (s, w, CH_2, C_5H_9), 33.118 (s, w, CH_2, C_5H_9), 41.509 (s, w, CH, C_5H_9), 42.601 (s, w, CH_2 C_5H_4), 138.232 (s, w, CH, C_5H_4).

2.4. X-ray data collection and structure determination

A single crystal of complex **1** (**2**) was selected and sealed in a glass capillary tube under Ar. The intensity data were collected on a Siemens P4 four-circle diffractometer at r.t. using graphite monochromated Mo–K_a radiation ($\lambda = 0.71073$ Å) in the ω scan mode. A total of 7179 (5151) reflections were collected within the range of $3.2 \leq 2\theta \leq 50.02°$ ($3.44 \leq 2\theta \leq 49.98$) of which 5490 (3976) reflections with $I > 2.0\sigma(I)$ were considered independent. All the intensities were corrected for Lorentz, polarization and absorption effects. Calculations were carried out on an Eclipse S/140 microcomputer with the SHELXTL program. The position of the heavy atom was found from Patterson methods. The coordinates of non-hydrogen atoms were revealed by successive Fourier and difference Fourier syntheses while those of hydrogen atoms were determined according to theoretical modes. Further refinement by full-matrix least-squares method led to the final convergence at $R_1 = 0.0379$ (0.0632) and $wR_2 = 0.0725$ (0.1312). The crystal data were listed in Table 1.

2.5. Polymerization of lactones with 1

The typical polymerization of ε-caprolactone (CL) was carried out in an ampoule previously flamed, evacuated and purged with high purity Ar. Toluene (5 ml) was first added to the ampoule followed by addition of 0.10 ml toluene solution of complex **1** (0.073 M). After the ampoule was set in designated temperature, 0.5 ml CL was syringed into it. The color changed from red to yellow during the reaction and the system became

viscous in a few seconds. The polymerization was terminated by addition of 1 ml HCl–$CHCl_3$ (10%) solution and then the mixture was poured into MeOH to afford solid polycaprolactone dried later in vacuo.

Polymerization of δ-valerolactone was carried out in the same manner as described above.

Table 1
Crystallographic data and structure refinement for complexes **1** and **2**

Empirical formula	$C_{36}H_{46}O_2Yb$	$C_{48}H_{68}O_4Yb_2$
Formula weight (g mol^{-1})	683.77	1055.10
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	*pbca*
a (Å)	12.729(3)	9.950(4)
b (Å)	11.951(2)	19.169(5)
c (Å)	20.496(4)	23.707(5)
α (°)		
β (°)	92.04(3)	
γ (°)		
V (Å^3), *Z*	3116.0(11)	4522(2), 4
D_{calc} (g cm^{-3})	1.458	1.550
Absorption coefficient (mm^{-1})	3.031	4.151
F(000)	1393	2112
Crystal size (mm)	$0.52\times0.38\times0.36$	$0.52\times0.45\times0.28$
θ range for data collection (°)	1.60–25.01	1.72–24.99
Reflections collected	7179	5151
Independent reflections	5490 ($R_{int}=0.0311$)	3976 ($R_{int}=0.0316$)
Data/restraints/parameters	5490/0/352	3964/2/239
Final *R* indices [$I>2\sigma(I)$]	$R=0.0379$, $wR=0.0725$	$R=0.0632$, $R=0.1312$

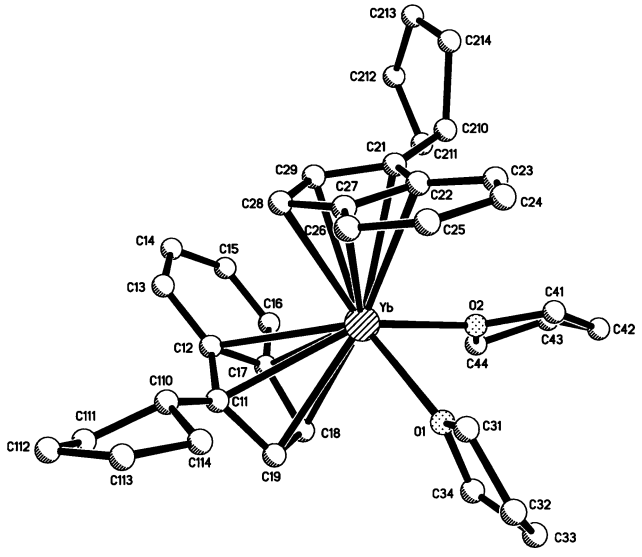

Fig. 1. Molecular structure of complex $(C_5H_9C_9H_6)_2Yb(THF)_2$(II) (**1**).

3. Results and discussion

3.1. Synthesis and molecular structure of complex *1*

Divalent ytterbium complexes are prepared usually by reduction of $[Cp_2LnCl]_2$ with Na, Na–Hg [5,6], or $Cp_2LnCl(THF)$ with 2,4-dimethylpentadienyl potassium (2,4-$C_7H_{11}K$) and KC_8H_{11} [7,8]. In this paper, divalent complex **1** is synthesized by reaction of $YbI_2(THF)_x$ with $C_5H_9C_9H_6Li$. Compared to the reduction procedure, it is a more convenient method and the yield is high up to 90.3%.

$$YbI_2 + 2C_5H_9C_9H_6Li + 2THF \rightarrow (C_5H_9C_9H_6)_2Yb(THF)_2 + 2LiI$$

Complex **1** was analyzed by XPS to confirm the valence of Yb. The electronic binding energy 186.3 eV of Yb_{4d} in **1**, in excess of 185.2 eV for Yb_{4d} in the reference trivalent Yb_2O_3 signifies that it is Yb^{2+} that is in complex **1**. In addition, the electronic binding energy 532.2 eV of O_{1s} in **1** is also different from 531.8 eV of O_{1s} in Yb_2O_3, suggesting the coordination of ytterbium atom to oxygen of THF. As ytterbium is paramagnetic, ^{1}H-NMR spectrum of complex **1** is complicated. The chemical shifts of the coordinated THF and CH_2 from ligand and those of THF-d_8 are overlapped; meanwhile, the peaks at 7.1–7.6 are broadened. Relatively, ^{13}C-NMR spectrum changes so much, although all of the chemical shifts move about 1.0–1.5 ppm downfield compared to those of the ligand itself.

The crystalline structure of complex **1** (Fig. 1) reveals that ytterbium atom is coordinated to two indenyl rings and bonded to the two oxygen atoms of the THF molecules. The centroids of the five-membered rings and the oxygen atoms form distorted tetrahedron geometry. The rotation angle, RA, is defined as the angle between the plane including the ytterbium and C(19) and the midpoint of C(12),C(17) and the plane including the ytterbium and C(29) and the midpoint of C(22),C(27) [9]. A rotation angle of 0° would indicate a completely eclipsed geometry whereas an angle of 180° corresponds to the fully staggered arrangement of the two rings. Thus a RA of 160.4° for **1** indicates the two indenyl rings are staggered. This is different from the reported complex $(C_9H_7)_2Yb{\cdot}DME$ [3], in which the two indenyl rings are eclipsed. This is attributed to larger steric crowding of the substituted indene ligand compared to that of indene. The large cyclopentylindenyl ligand endows good solubility of **1** in THF, DME, ether and toluene, in addition, makes **1** more stable even after it was exposed to the air for several minutes. The bond lengths Yb–O(1) and Yb–O(2) (2.431, 2.423 Å) (Table 2) are comparable to those in complexes $[(Me_3Si)C_5H_4]_2Yb(THF)_2$ (2.42 Å) [6], $(C_5Me_5)_2Yb(THF){\cdot}0.5CH_3C_6H_5$ (2.412 Å) [10],

Table 2
Selected bond lengths (Å) and angles (°) for complex **1**

Bond lengths (Å)			
Yb–C(11)	2.788(6)	Yb–C(21)	2.780(6)
Yb–C(12)	2.860(6)	Yb–C(22)	2.859(5)
Yb–C(17)	2.776(7)	Yb–C(27)	2.805(6)
Yb–C(18)	2.694(7)	Yb–C(28)	2.675(6)
Yb–C(19)	2.733(7)	Yb–C(29)	2.657(6)
Yb–C(ring1)ave	2.776(7)	Yb–C(ring2)ave	2.76(6)
Yb–O(1)	2.423(4)	Yb–O(2)	2.431(4)
C(11)–C(12)	1.440(9)	C(21)–C(22)	1.438(8)
C(12)–C(17)	1.445(9)	C(22)–C(27)	1.436(8)
C(17)–C(18)	1.407(9)	C(27)–C(28)	1.408(9)
C(18)–C(19)	1.402(10)	C(28)–C(29)	1.404(9)
C(11)–C(19)	1.422(9)	C(21)–C(29)	1.397(9)
Yb–Cent(1)	2.492	Yb–Cent(2)	2.480
Bond angles (°)			
Cent(1)–Yb–Cent(2)	125.1	O(1)–Yb–O(2)	79.6
Cent(1)–Yb–O(1)	104.5	Cent(2)–Yb–O(1)	117.5
Cent(1)–Yb–O(2)	114.5	Cent(2)–Yb–O(2)	106.8

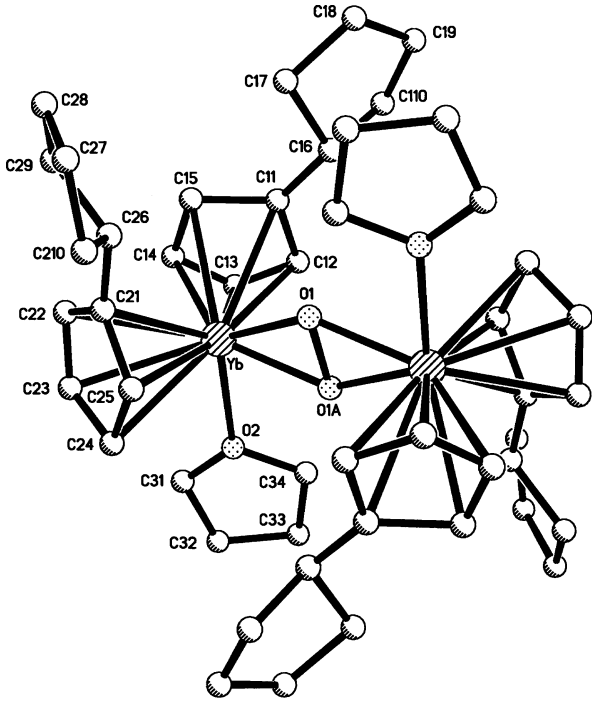

Fig. 2. Molecular structure of $[(C_5H_9C_5H_4)_2Yb(THF)]_2O_2$ (**2**).

($^tBuC_5H_4$)Yb(THF)$_2$ (2.43 Å) [5], $(C_9H_7)_2Yb{\cdot}DME$ (2.41 Å) and $(CH_2)_2(C_9H_6)_2Yb(THF)_2$ (2.346 Å) [3]. The Cent–Yb distances, 2.492 and 2.480 Å, are intermediate between 2.40 and 2.52 Å in complex $(C_9H_7)_2Yb{\cdot}THF_2$ [2]. They are longer than those in complexes like $(C_9H_7)_2Yb{\cdot}DME$, (2.432 Å), ethylene bridged bis-indenyl ytterbium complex $(CH_2)_2$-$(C_9H_6)_2Yb(THF)_2$ (2.44, 2.46 Å) [3] and also longer than those in many ytterbium bis(cyclopentadienyl) complexes with substituted rings: $(C_5H_4(CH_2)_3$-$C_5H_4)Yb(THF)_2$ [11], $(C_5H_5)_2Yb(THF)_2$ [8], $(C_5H_5)_2$-Yb(DME) [12], ($^tBuC_5H_4$)Yb(THF)$_2$ [5], (η^5-$(SiMe_3)_2C_5H_3$)]$_2$Yb(THF) [13], $(C_5Me_4Et)_2Yb(THF)$ [14], $(C_5H_4PPh_2)_2Yb(DME)$ [15], (1,2-$^tBuC_5H_3)_2Yb$ (DME) and (1,2-$^tBuC_5H_3)_2Yb(Et_2O)_2$ [16]. Angle Cent(1)–Yb–Cent(2), 125.1°, is larger than 118.3° in complex $(CH_2)_2(C_9H_6)_2Yb(THF)_2$ [3] and smaller than those in complexes like $(C_9H_7)_2Yb{\cdot}DME$ (129.4°) and $(C_9H_7)_2Yb{\cdot}THF_2$ (128.6°) and 133–144° for bis(cyclopentadienyl) complexes. The angle O(1)–Yb–O(2) is 79.6° which is only larger than those in DME solvated $(C_5H_5)_2Yb(DME)$ (67.2°) [12] and $(C_9H_7)_2Yb{\cdot}DME$ (68.5°) [9] but smaller than those in most other complexes (82.5–87.6°).

3.2. Synthesis and molecular structure of complex *2*

We prepared bis(cyclopentylcyclopentadienyl)ytterbium(II) complex $(C_5H_9C_5H_4)_2Yb(Et_2O)_2$ (**3**) by reaction of YbI_2 with $C_5H_9C_5H_4Na$ (1:2 molar ratio) in THF at room temperature for 10 h according to procedure as described for the synthesis of **1**, except that after removal of THF from the mixture, ether was used to extract the residue. The solution was kept at −30 °C for 10 h and purplish–red crystals were isolated at high yield (89.6% based on YbI_2). The crystals were characterized by IR, the main absorptions are (cm^{-1}): 3069, 2953, 2867, 1664, 1598, 1523, 1451, 1371, 1197, 1053, 1033, 948, 890, 810, 764, 676. The ^{1}H-NMR spectrum of complex **3** is very complicate, the peaks are broad at 1.4–2.2, 3.4–3.6 and 6.0–6.4 ppm. We also find chemical shifts at 1.24 (tr, s), 2.822 (s, m), 2.896 (s, m), 3.371 (s, w), 3.388 (d, m), 3.487 (s, w) and 6.59 ppm (multi, w). ^{13}C-NMR data are (ppm): 26.200, 36.183, 42.131, 71.352, 106.021. The structure of complex **3** is also characterized by X-ray diffraction; the unit cell dimensions were obtained but attempt to figure out the structure failed.

If the residue of the attempted complex **3** resulting from the primary THF solution was extracted with toluene rather than ether, the purple toluene extract changed to green on removal of toluene due to the incidentally introduced dioxygen. The residue was treated with DME, and the resulting yellow–green solution was cooled at 0 °C to give yellow crystals of $[(C_5H_9C_5H_4)_2Yb(THF)]_2O_2$ (**2**) (20.1% based on **3**). Obviously, complex **2** is the oxidation product of complex **3**.

The X-ray crystallographic structure and the selected bonds and angles of complex **2** are presented in Fig. 2, Table 3, respectively. The molecule of complex **2** consists of two $(C_5H_9C_5H_4)_2Yb(THF)$ units bridged by an O_2 ligand. The O_2 unit and the two Yb atoms define a plane that contains a C_i symmetry center. To our knowledge this is the first dioxygen complex of an f-element metal. Structurally, the close example is an

inorganic peroxo-derivative of [bis(trimethylsilyl)-amido]lanthanoid $[La_2\{N(SiMe_3)_2\}_4(O_2)(PPh_3O)_2]$ [17], if the nitrogen atoms are considered as the centroids of cyclopentylcyclopentadienyl rings in **2** and the phosphine oxygen atoms as the oxygen atoms of tetrahedrofuran molecules. Chemically, a samarium superoxo complex should be the most similar to **2**, except $\{HB(3,5\text{-}Me_2pz)_3\}_2Sm(\eta^2\text{-}O_2)$ [18] displaying end-on coordination of O_2. The average distances of Yb–C(ring), 2.69 and 2.66 Å, are comparable to that in the 7-coordinated ytterbium complex $(C_5Me_5)_2Yb(THF)\cdot 0.5CH_3C_6H_5$, 2.66 Å [10] and smaller than those in many 8-coordinated bis(cyclopentadienyl)ytterbium(II) complexes, 2.72–2.91 Å. The Cent–Yb distances, 2.480 and 2.372 Å, are comparable to those in complexes like $('BuC_5H_4)_2Yb(THF)_2$, 2.383 Å, [5] and $[(C_5H_5)_2Yb]_\infty$, 2.366 Å [19]. The bridging O_2 unit is not symmetrical and the bond lengths Yb–O(1) and Yb–O(1A) are 2.195 and 2.227 Å, respectively which are shorter than 2.415 Å for Yb–O(2) in the same molecule and also shorter than most of Yb–O band lengths in ytterbocene(II) complexes. However, these bond distances are comparable to those of La–O (2.42, 2.33 Å) and Sm–O (2.329, 2.321 Å) in $[La_2\{N(SiMe_3)_2\}_4(O_2)(PPh_3O)_2]$ [17] and $\{HB(3,5\text{-}Me_2pz)_3\}_2Sm(\eta^2\text{-}O_2)$ [18] respectively, if the differences of the ionic radii of the central metals are considered. Omitting solvated THF molecules, the X-ray crystal structure of **2** is quite similar to those of systems $[\{(SiMe_3)_2C_5H_3)\}_2Sm(\mu\text{-}OH)\}_2]$ and $[\{(SiMe_3C_5H_4)_2Yb(\mu\text{-}OH)\}_2]$ [20] which also have planar bridging units Sm–O–Sm′–O′ and Yb–O–Yb′–O′. However, in the later two cases, the bridging oxygen atoms are from hydroxyl groups, but in complex **2**, the bridging unit is an O_2. Thus, bond lengths and angles of these complexes are significantly different. For example, the angle Cent(1)–Yb–Cent(2) in **2**, 125.1°, is different from that of Cent(1)–Sm–Cent(2), 129.5°, and Cent(1)–Yb–Cent(2), 131.3°, in the later two complexes, which are consistent with those in methyl- or chlorine-bridged complexes$[\{YbCp_2(\mu\text{-}Me)\}_2]$ (128.2°) [21] and $[\{YbCp''_2(\mu\text{-}Cl)\}_2]$ (130°) [22]. The angle O–Yb (1A)–O(1A) in **2**, 41.1°, is comparable to 41.5° of the angle O(2)–La–O(2′) in $[La_2\{N(SiMe_3)_2\}_4(O_2)\ (PPh_3O)_2]$ [17] and larger than 33.0° of the angle O1–Sm–O2 in $\{HB(3,5\text{-}Me_2pz)_3\}_2Sm(\eta^2\text{-}O_2)$ [18], but much smaller than 77.9 and 76.6° in the above mentioned hydroxyl groups bridged ytterbium and samarium complexes [20]. Meanwhile, the O–O(1A) bond distance, 1.55(2) Å, is shorter than that of O(2)–O(2′) (1.65 Å, La) [17] and longer than that of O1–O2 (1.319 Å, Sm) [18] and the standard O–O bond length (1.48 Å), implying that the bond O–O(1A) is activated; And, there is no bond connection between the two O atoms in complex $\{(Me_3SiC_5H_4)_2Yb(\mu\text{-}OH)\}_2$.

Table 3
Selected bond lengths (Å) and angles (°) for complex **2**

Bond lengths (Å)			
Yb–C(11)	2.72(2)	Yb–C(21)	2.70(2)
Yb–C(12)	2.683(14)	Yb–C(22)	2.675(14)
Yb–C(13)	2.712(12)	Yb–C(23)	2.640(12)
Yb–C(14)	2.64(2)	Yb–C(24)	2.654(14)
Yb–C(15)	2.69(2)	Yb–C(25)	2.62(2)
Yb–C(ring1)ave	2.69(2)	Yb–C(ring2)ave	2.66(2)
O(1)–O(1A)	1.55(2)	Yb(1A)–O(1)	2.195(10)
Yb(1A)–O(1A)	2.227(10)		
Bond angles (°)			
O(1A)–Yb–O(1)	41.1	Cent(1)–Yb–O(1)	106.2
Cent(1)–Yb–O(1A)	114.0	Cent(2)–Yb–O(1)	104.7
Cent(2)–Yb–O(1A)	119.2	Cent(1)–Yb–O(2)	108.3
Cent(2)–Yb–O(2)	102.4	O(1A)–Yb–O(2)	78.5
Cent(1)–Yb–Cent(2)	125.1	Yb–O(1)–Yb(1A)	138.9(4)

3.3. Polymerization of lactones using complex *1*

Polylactones are receiving increasing attention for applications in biomedical fields, such as biodegradable sutures, artificial skins and implantable carriers for drug delivery systems, due to their biocompatibility and biodegradablility. Polylactones [23] were synthesized through ROP by tin(II) octanoate [24]. However, for biomedical applications, the clinical problem is the toxicity of tin(II) salts. In recent years, rare earth(III) compounds such as yttrium isopropoxide, lanthanide alkoxides and lanthanide hydride (or alkyl) have been reported to initiate ROP of lactones [25–28]. In contrast, divalent lanthanocene catalysts for ROP of lactones have so far been limited to samarium derivatives [29]. Complex **1** in this work is the first divalent ytterbocene used to ROP of lactones. It is highly active, both the conversion and molecular weight increase with an increase of reaction time, and ca. 100% conversion could be attained in less than an hour at room temperature (Table 4). Molecular weight did not decrease when the reaction time was prolonged up to 24 h, and molecular weight distribution, within the range of 1.6–2.6, kept monomodal, suggesting that back-biting or transesterification reaction was restricted in this system. This is different from what was observed in polymerization promoted by $(C_9H_7)_2Sm(THF)_x$ [29]. The latter yielded polymers showing, to some extent, bimodal molecular weight distributions and decrease in molecular weight due to the degradation of initially formed polymers by the samarium species. This may due to the shorter ionic radius of ytterbium of **1** and the larger steric crowding of the ligand, which cause lowering of catalytic activity in both propagation and degradation. Other conditions constant, the molecular weight increases linearly with the increase of the monomer–initiator ratio, but they do not parallel with theory values,

Table 4
Polymerization of ε-caprolactone using complex **1**

Number	M/C	T (min)	X (%)	M_n [a] $\times 10^{-3}$	M_w [a] $\times 10^{-3}$	M_w/M_n
1	400	5	29.58	9.5	15.2	1.61
2	400	10	39.53	11.2	16.8	1.50
3	400	15	40.66	10.7	21.0	1.96
4	400	30	75.38	17.3	31.7	1.83
5	400	40	86.13	23.8	44.5	1.87
6	400	50	95.44	26.4	46.2	1.75
7	400	60	100	26.3	53.9	2.05
8	400	1440	97.03	26.2	49.3	1.88

All reactions were carried out at room temperature in toluene; C, 6.94×10^{-3} mol l^{-1}; M, 2.0 mol l^{-1}.
[a] Determined by gel permeation chromatography (GPC) against polystyrene standard.

Table 5
Effect of monomer–catalyst molar ratio on molecular weight of poly(ε-caprolactone) and poly(δ-valerolactone)

Number	Monomer	M/C	X %	$M_n \times 10^{-3}$ [a]	$M_w \times 10^{-3}$ [a]	M_w/M_n
1	CL	200	94.5	15.5	29.5	1.90
2	CL	300	91.6	23.4	40.0	1.71
3	CL	500	53.6	40.6	87.3	2.15
4	VL [b]	300	72.0	14.7	23.5	1.60
5	VL [b]	500	100	39.9	104.8	2.62
6	VL [b]	800	92.3	49.4	121.5	2.46
7	VL [b]	1000	98.1	66.5	154	2.32

All reactions were carried out at room temperature in toluene; C, 1.0×10^{-3}M; reaction time, 1 h.
[a] Determined by gel permeation chromatography (GPC) against polystyrene standard.
[b] Reaction time, 2 h.

and the deviation is obvious especially when the ratio is high (Table 5). All these denote that the ROP of lactones using **1** is controllable and in living fashion; however, the propagation step is much faster than the initiation step [30] and chain-transfer reaction happens when the reaction system becomes extremely viscous. The mechanism of the polymerization is under investigation.

4. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 167804 and 167805 for compounds **1** and **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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