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A new half-sandwich Yb(II) complex with the tridentate cyclopentadienyl ligand $[C_5H_4CH_2CH(O)CH_2OBu^n]^{2-}$: synthesis, self-assembly of a tetranuclear cubane-like framework $\{[(\eta^5\text{-}C_5H_4)CH_2CH(\mu^3{:}\eta^1\text{-}O)CH_2OBu^n]Yb\}_4$ and oxidative alkylation by Me_2Hg to the Yb(III) derivative $[(\eta^5\text{-}C_5H_4)CH_2CH(\eta^1\text{-}O)CH_2OBu^n]YbMe(THF)$

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Abstract

The synthesis and crystal structure of the tetranuclear Yb(II) half-sandwich complex $\{[(\eta^5\text{-}C_5H_4)CH_2CH(\mu^3{:}\eta^1\text{-}O)CH_2OBu^n]Yb\}_4$ (**1**) are presented. Redox transmetalation reaction of **1** with Me_2Hg yields a methyl derivative of trivalent ytterbium, $[(\eta^5\text{-}C_5H_4)CH_2CH(\eta^1\text{-}O)CH_2OBu^n]YbMe(THF)$ (**2**). Complex **2** is shown to possess a low catalytic activity in propylene polymerization. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Tridentate cyclopentadienyl ligand; Half-sandwich complex; Lanthanides; Redox transmetalation

1. Introduction

Being more electron-deficient and sterically accessible than their sandwich analogues, half-sandwich complexes have been shown to be of considerable interest as prospective catalysts of various processes involving unsaturated substrates. Bidentate-linked cyclopentadienyl-amido ligands have been first introduced as a novel ancillary in rare-earth metals chemistry by Bercaw et al. [1a,1b] as an alternative to more sterically demanding *ansa*-bis(cyclopentadienyl) system and were actively investigated in the last decade [1]. Alkyl and hydrido complexes of Sc, Y and lanthanide metals based on the linked cyclopentadienyl-amido ligands have been shown to be active single-component catalysts for both olefin [1a,1b,1e] and polar monomer [1d,2] polymerization. Tridentate cyclopentadienyl ligands bearing the pendant Lewis base group provide additional possibilities to design the coordination sphere of the central metal and to gain stereocontrol. The complexes with related ligands have been described by Okuda et al. [2,3].

Cyclopentadienyl-alkoxy ligands have not been employed to a considerable extent in transition metal chemistry, and derived complexes are presented by the Ti and Zr compounds described by Marks [4] and Rieger [4].

Recently, we have reported the synthesis of both trivalent [5] and divalent [5] half-sandwich lanthanide complexes derived from cyclopentadienyl-alkoxy ligands.

The present research is aimed towards the synthesis of the divalent ytterbium complex with the tridentate cyclopentadienyl ligand, $[C_5H_4CH_2CH(O)CH_2OBu^n]^{2-}$, and the investigation of its structure and reactivity.

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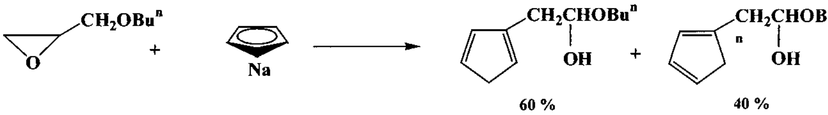


Scheme 1. Reagents and conditions, (i) DME, 80 °C, 5 h; (ii) hydrolysis.

2. Results and discussion

Racemic 3-cyclopentadienyl-1-butoxy-2-propanol (**3**) was obtained as a mixture of two regioisomers (ca. in 3:2 ratio by NMR) by nucleophilic ring opening of racemic *n*-butyl-glycidyl ether by CpNa following the procedure described for related compounds [6] (Scheme 1).

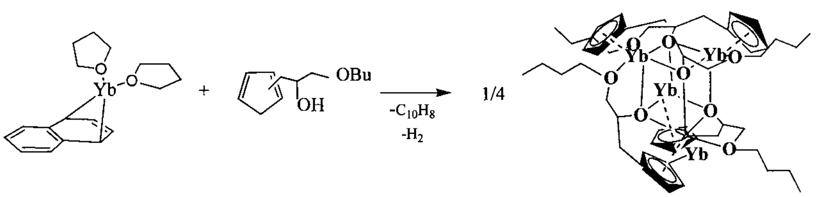
To synthesize **1** the reaction of protolytic substitution of the naphthalene ligand in the complex $C_{10}H_8Yb(THF)_2$ **4** by the ligand **3** was used. This synthetic method has been recently developed and has been shown to be a convenient synthetic route to both Yb(II) and Yb(III) derivatives [5b,5c,7]. It allows to avoid formation of *ate*-complexes and contamination of the targeted product by halides of alkaline metals, which are known to hamper synthesis of the most organolanthanides. Complex **4** was found to react readily with **3** in THF media at room temperature (Scheme 2).

Different procedures of the product isolation have led to different Yb(II) complexes. Thus slow condensation of hexane vapor into a slightly cooled (5 °C) THF solution of crude product resulted in formation of a red microcrystalline solid, which on the basis of NMR, IR-spectroscopy and microanalysis data has been formulated as $[(\eta^5\text{-}C_5H_4)CH_2CH(\eta^1\text{-}O)CH_2OBu^n]Yb(THF)$ (**5**) [5c]. Unfortunately, all attempts to prepare crystalline samples of **5** suitable for X-ray crystal structure determination failed.

Fast addition of hexane to a THF solution of the crude product at room temperature affords reddish–brown oil. When cooling for a long time in mother liquor ($>$ 1 month) at -5 °C this oil has transformed to ruby-red crystals of **1**, which have been characterized by the means of NMR, IR-spectroscopy, microanalysis and X-ray diffraction. Compound **1** is highly sensitive to oxygen and moisture, soluble in THF, DME and pyridine and insoluble in aromatic and aliphatic hydrocarbons. Complex **1** is diamagnetic corresponding to the Yb^{2+} oxidation state [8]. The crystals of **1** contain one molecule of THF per unit.

The X-ray diffraction study has revealed a tetranuclear cubane-like framework with alternating ytterbium and oxygen atoms. Each of the four $[C_5H_4CH_2CH(O)CH_2OBu^n]^{2-}$ ligands is coordinated in a η^5-fashion via the cyclopentadienyl ring to one Yb atom, while the oxygen atom of the alkoxy group μ^3-bridges three Yb atoms. The oxygen atom of the ether group is coordinated to one of the Yb atoms. The combination of such diverse metal–ligand interactions provides for the formation of the heteronuclear Yb_4O_4 core. The molecule of the cubane complex **1** crystallizes in a (rare) acentric space group. However, even though the structure is not centrosymmetric, it does contain a symmetry element (*c*) that imposes both enantiomers are included in the crystal. The picture shows just one of them, but the compound is a racemic mixture. The average value of Yb–C bond distances in **1** (2.69 Å) is slightly shorter compared with one reported for $Cp_2Yb(DME)$ [9]. The endohedral ytterbium–oxygen bond lengths lie in a range from 2.365(4) to 2.402(4) Å. The length of the exohedral ytterbium–oxygen bonds is very close to the Yb–O distance in $Cp_2Yb(DME)$ [9] and well coincides with the values observed for complexes of divalent ytterbium [10]. The hetero-cubane framework is significantly distorted: the O(2)(endohedral)–Yb–O(2)-(endohedral) angles range from 79.70(13) to 80.45(13)° whereas the Yb–O(2)–Yb angles show higher values from 98.58(13) to 99.73(14)°. The average ytterbium–ytterbium distance is 3.63(1) Å. The cyclopentadienyl–ytterbium centroid distance is 2.418 Å; with the angles O(1)–Yb-centroid 112.1° and O(2)(endohedral)–Yb-centroid 95.4°. The absolute configuration of the asymmetric carbon atom has not been determined (Fig. 1, Tables 1 and 2).

The ^{1}H-NMR spectrum of **1** has been recorded in d_5-*py* shows a triplet at 0.94 ppm from the methyl group and two multiplets (at 1.36 and at 1.70 ppm) from the β- and γ-methylene protons of the butoxy radical. The protons of the three methylene groups (the CH_2-group near the cyclopentadienyl ring and the



Scheme 2. Reagents and conditions, THF, room temperature, 6 h.

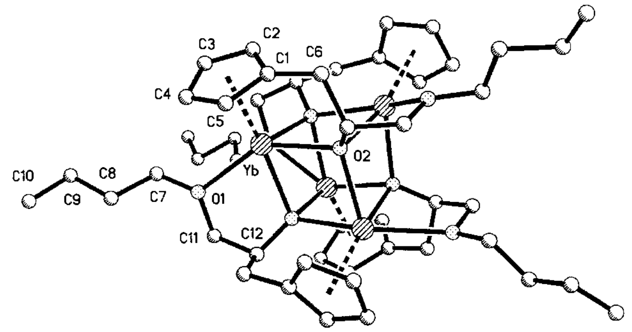


Fig. 1. ORTEP drawing and numbering scheme of the molecular structure of **1**; all hydrogen atoms have been omitted for clarity; selected bond lengths (Å) and angles (°; Cp_{Cent} is defined by the ring atoms C(1), C(2), C(3), C(4), C(5)): Yb–C(1) 2.668(6), Yb–C(2) 2.682(6), Yb–C(3) 2.717(8), Yb–C(4)2.720(7), Yb–C(5) 2.678(7) Yb–Cp_{Cent} 2.418, Yb–O(2) # 1 2.365(4), Yb–O(2) 2.386(4), Yb–O(2) # 2 2.402(4), Yb–O(1) 2.459(4), Yb–Yb # 3 3.6135(4), O(2) # 1–Yb–O(2) 80.45(13), O(2) # 1–Yb–O(2) # 2 80.52(13), O(2)–Yb–O(2) # 2 79.70(13), O(2) # 1–Yb–O(1) 107.85(15), O(2)–Yb–O(1) 144.44(14), O(2) # 2–Yb–O(1) 68.20(14), Yb # 2–O(2)–Yb 99.73(14), Yb # 2–O(2)–Yb # 1 98.58(13),Yb–O(2)–Yb # 1 98.67(13).

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

Empirical formula	$C_{48}H_{72}O_8Yb_4$
Formula weight	1469.22
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Tetragonal
Space group	$P(-4)2_1/c$
Unit cell dimensions	
a (Å)	14.2859(6)
b (Å)	14.2859(6)
c (Å)	14.0246(8)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	2862.2(2)
Z	2
D_{calc} (mg m^{-3})	1.705
Absorption coefficient (mm^{-1})	6.516
F(000)	1408
Crystal size (mm)	0.32 × 0.22 × 0.08
Goodness-of-fit on F^2	1.063
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0303$, $wR_2 = 0.0687$

methylene groups adjacent to the oxygen atom) appear as the following sets of signals, 2.57 and 2.93 (Cp-CH_2), 3.44 and 3.61 (CH–CH_2–O), 3.72 and 4.09 (α-CH_2, C_4H_9). The non-equivalence of the methylene protons is probably due to hindered rotation resulting from the formation of a metallocycle. Three singlets at 6.02, 6.15 and 6.37 of relative intensity 1:2:1 correspond to the four cyclopentadienyl protons. The broadening of all the signals in the ^{1}H-NMR spectrum gives the evidence of a dynamic process in the pyridin solution of **1** presumably due to the dissociation of the tetramer.

Complex **1** has been found to possess low catalytic activity in styrene polymerization and to be completely inactive in propylene polymerization. As mentioned above alkyl and hydrido complexes of lanthanides with linked amido-cyclopentadienyl ligands are capable to polymerize olefins with high activity. In order to synthesize an alkyl derivative of Yb(III) with the tridentate cyclopentadienyl-alkoxy ligand the oxidative methylation of **1** by Me_2Hg in THF was carried out (Scheme 3).

Complex **2** was isolated in 98% yield as light-brown microcrystalline solid, soluble in THF, DME and sparingly soluble in toluene. Magnetic moment of **3** at room temperature was found to be 4.3 BM corresponding to the Yb^{3+} oxidation state [8]. To prove a presence of methyl group in **2** the reaction of iodination was carried out. Among the volatile reaction products iodomethane (80%) was found by GLC.

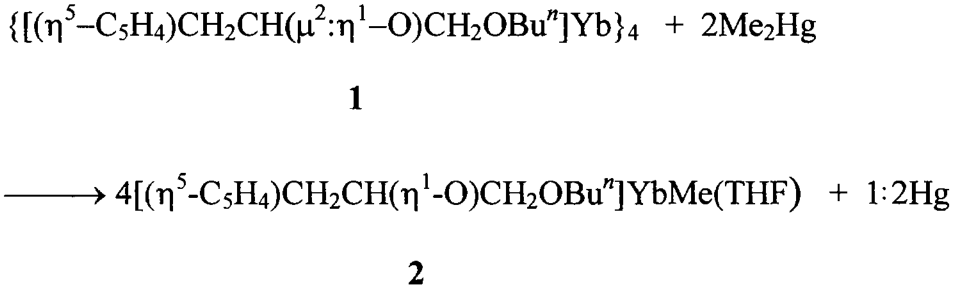
Complex **3** catalyzes propylene polymerization at 20 °C and 1 atm pressure in low activity.

Table 2
Selected geometric parameters (Å, °) for **1** [a]

Bond distances (Å)	
Yb–C(1)	2.668(6)
Yb–C(2)	2.682(6)
Yb–C(3)	2.717(8)
Yb–C(4)	2.720(7)
Yb–C(5)	2.678(7)
Yb–O(2) # 1	2.365(4)
Yb–O(2)	2.386(4)
Yb–O(2) # 2	2.402(4)
Yb–O(1)	2.459(4)
Yb–Yb # 3	3.6135(4)
Yb–Yb # 1	3.6322(4)
Yb–Yb # 2	3.6322(4)
O(2)–Yb # 2	2.365(4)
O(2)–Yb # 1	2.402(4)
Yb–Cp_{Cent} [b]	2.418
Bond angles (°)	
O(2) # 1–Yb–O(2)	80.45(13)
O(2) # 1–Yb–O(2) # 2	80.52(13)
O(2)–Yb–O(2) # 2	79.70(13)
O(2) # 1–Yb–O(1)	107.85(15)
O(2)–Yb–O(1)	144.44(14)
O(2) # 2–Yb–O(1)	68.20(14)
Yb # 2–O(2)–Yb	99.73(14)
Yb # 2–O(2)–Yb # 1	98.58(13)
Yb–O(2)–Yb # 1	98.67(13)
Cp_{Cent}–Yb–O(1)	112.14
Cp_{Cent}–Yb–O(2)	95.35

[a] Symmetry transformations used to generate equivalent atoms, # 1, $-y+1, x-1, -z$; # 2, $y+1, -x+1, -z$; # 3, $-x+2, -y, z$; # 4, $-x+2, -y+1, z$.

[b] Cp_{Cent}, centroid of C(1)–C(5).



$$\underset{\mathbf{1}}{\{[(\eta^5\text{-}C_5H_4)CH_2CH(\mu^2:\eta^1\text{-}O)CH_2OBu^n]Yb\}_4} + 2Me_2Hg \longrightarrow \underset{\mathbf{2}}{4[(\eta^5\text{-}C_5H_4)CH_2CH(\eta^1\text{-}O)CH_2OBu^n]YbMe(THF)} + 1{:}2Hg$$

Scheme 3. Reagents and conditions, $\{[(\eta^5\text{-}C_5H_4)CH_2CH(\mu^3:\eta^1\text{-}O)CH_2OBu^n]Yb\}_4:Me_2Hg = 2:1$, THF, 60 h, 60 °C.

3. Experimental

All manipulations were conducted under vacuum by using standard Schlenk techniques. Solvents were distilled from sodium/benzophenone ketyl and degassed prior to use. Complex $C_{10}H_8Yb(THF)_2$ was prepared according to the literature method [7a]. GC analyses were performed by using 'Tzvet-530' gas chromatograph. NMR spectra were recorded with 200 MHz spectrometer (Bruker DPX-200) using *d*$_5$-*py* at 298 K. IR spectra were recorded in the Nujol mulls with a Specord-M80 spectrometer.

*3.1. Synthesis of 3-cyclopentadienyl-1-butoxy-2-propanol (**3**)*

A solution of 5.8 g (45 mmol) of *n*-butyl glycidyl ether in 20 ml of DME was slowly added to a solution of 20.0 g (227 mmol) of CpNa in 125 ml of DME at 80 °C and was stirred for 5 h. The reaction mixture was hydrolyzed with 25 ml of 20% solution of NH_4Cl and 200 ml of water were added. The organic layer was separated and the water layer was extracted twice with 100 ml of ether. The ether solution was dried over $CaCl_2$ and volatiles were removed under vacuo. Distillation of the residue (130–132 °C/15 Torr) yielded 3.0 g (34%) of **3** as pale-yellow oil. Major isomer: ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 0.92$ (t, 3H, $J = 7.2$ Hz, CH_3); 1.36 (m, 2H, γ-CH_2, C_4H_9); 1.55 (m, 2H, β-CH_2, C_4H_9); 2.55 (m, 2H, $CH_2C_5H_5$); 2.69 (s, 1H, OH), 2.97 (m, 2H, CH_2, C_5H_5); 3.25–3.50 (m, 2H, CH_2O); 3.45 (t, 2H, $J = 6.8$ Hz, α-CH_2, C_4H_9); 4.00 (m, 1H, CHO); 6.12, 6.25, 6.43 (m, 3H, C_5H_5). ^{13}C-NMR ($CDCl_3$, 50 MHz): $\delta = 13.9$ (CH_3); 19.2 (γ-CH_2, C_4H_9); 31.6 (β-CH_2, C_4H_9); 33.9 ($CH_2C_5H_5$); 41.4 (CH_2, C_5H_5); 69.6 (CHOH); 71.1 (α-CH_2, C_4H_9); 74.4 (CH_2O); 128.6, 128.8, 134.1 (CH, C_5H_5); 142.9 (C, C_5H_5). Minor isomer: ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 0.92$ (t, 3H, $J = 7.2$ Hz, CH_3); 1.35 (m, 2H, γ-CH_2, CH_2, C_4H_9); 1.55 (m, 2H, β-CH_2, C_4H_9); 2.59 (m, 2H, $CH_2C_5H_5$); 2.69 (s, 1H, OH), 2.95 (m, 2H, CH_2, C_5H_5); 3.25–3.50 (m, 2H, CH_2O); 3.45 (t, 2H, $J = 6.8$ Hz, α-CH_2, C_4H_9); 3.94 (m, 1H, CHO); 6.29, 6.43, 6.47 (m, 3H, C_5H_5). ^{13}C-NMR ($CDCl_3$, 50 MHz): $\delta = 13.9$ (CH_3); 19.3 (γ-CH_2, C_4H_9); 31.6 (β-CH_2, C_4H_9); 34.7 ($CH_2C_5H_5$); 43.8 (CH_2, C_5H_5), 70.1 (CHOH); 71.2 (α-CH_2, C_4H_9); 74.5 (CH_2O); 131.4, 132.3, 134.7 (CH ?$_5$H$_5$); 145.1 (C, C_5H_5). Anal. Found: C, 73.86; H, 10.32. Calc. for $C_{12}H_{20}O_2$ (196.3): C, 73.62; H, 10.02%.

*3.2. Synthesis of $\{[(\eta^5\text{-}C_5H_4)CH_2CH(\mu^2:\eta^1\text{-}O)CH_2OBu^n]Yb\}_4$ (**1**)*

To a suspension of 4.7 g (10.6 mmol) of **4** in 60 ml of THF a solution of 2.0 g (10.3 mmol) of **3** in 25 ml of THF was added slowly under vigorous stirring. The reaction mixture turned red, the residue slowly dissolved and H_2 was eliminated. After 6 h the solution was filtered, THF was removed under vacuum and the resulting red residue was extracted with hexane to separate naphthalene (1.22 g, 90%). The red solid was redissolved in 25 ml of THF and 20 ml of hexane was slowly added at r.t. to afford reddish–brown oil. Long cooling (1 month, −5 °C) of the oil in mother liquor resulted in 0.77 g (19%) of **1** as dark red crystals. ^{1}H-NMR (*d*$_5$-*py*, 200 MHz): $\delta = 0.94$ (t, $^3J_{HH} = 7.4$ Hz, 3H, Me); 1.36 (m, 2H, γ-CH_2, C_4H_9); 1.56 (m, 1H, α-CH_2, THF) 1.70 (m, 2H, β-CH_2, C_4H_9), 2.57 (dd, $^2J_{HH} = 13.8$ Hz, $^3J_{HH} = 11.5$ Hz, 1H, CH*H*, Cp-CH_2), 2.93 (dd, $^2J_{HH} = 13.8$ Hz, $^3J_{HH} = 3.0$ Hz, 1H, C*H*H, Cp-CH_2), 3.44 and 3.61 (m, 1H, CH_2, CH–C*H*$_2$–O), 3.60 (m, 1H, β-CH_2, THF), 3.72 (m, 1H, α-CH*H*, C_4H_9), 4.09 (dt, $^2J_{HH} = 11.3$ Hz, $^3J_{HH} = 8.0$ Hz, 1H, α-C*H*H, C_4H_9), 4.67 (m, 1H, CHO), 6.02 and 6.37 (m, 1H, Cp), 6.15 (m, 2H, Cp). ^{13}?-NMR (*d*$_8$-py, 200 MHz): $\delta = 14.1$ (Me), 18.9 (β-CH_2, C_4H_9), 25.7 (α-CH_2, THF), 30.4 (γ-CH_2, C_4H_9), 36.6 (*C*H$_2$–Cp), 67.8 (β-CH_2, THF), 73.1 (α-CH_2, C_4H_9), 76.2 (CH–*C*H$_2$O), 78.4 (CHO), 103.4 (Cp), 105.1 (Cp), 109.7(Cp), 110.9 (Cp), 128.6 (Cp). IR (Nujol, KBr, cm^{-1}): 1325 m, 1260 m, 1180 w, 1170 w, 1120 m, 1075 m, 1040 w, 1025 w, 1010 w, 985 m, 950 m, 925 m, 890 w, 860 m, 840 m, 800 m, 730 s, 660 m, 640 m, 540 m, 475 w. Anal. Found: C, 41.0; H, 5.44; Yb, 45.1. Calc. for $C_{52}H_{80}O_9Yb_4$ (1469.22): C, 40.52; H, 5.23; Yb, 44.90%.

3.2.1. Synthesis of $[(\eta^5\text{-}C_5H_4)CH_2CH(\eta^1\text{-}O)CH_2OBu^n]YbMe(THF)$ (**2**)

To a solution of 1.8 g (1.17 mmol) of **1** in 45 ml of THF 0.54 g (2.33 mmol) of dimethylmercury was added. The reaction mixture was refluxed for 60 h at 60 °C and turned brownish–yellow. The resulting solution was decanted from the metallic mercury (0.46 g, 98%). Slow diffusion of hexane vapor into the solution yielded 2.08 g (98%) as a light-brown microcrystalline solid. IR (Nujol, KBr, cm^{-1}): 1325 m, 1260 w, 1180 m, 1170 m, 1120 s, 1075 m, 1040 w, 1025 m, 1010 w, 985 w, 950 m, 925 m, 850 m, 800 m, 730 s, 700 m, 660 m, 540 m. Anal. Found: C, 44.79; H, 6.20; Yb, 38.2. Calc. for $C_{17}H_{29}O_3Yb$ (454.42): C, 44.93; H, 6.43; Yb, 38.08%.

3.3. Reaction of iodination of **2**

To a solution of 2.3 g (5.06 mmol) of **2** in 15 ml of THF a solution of twofold molar excess of iodine (2.57 g) in 25 ml of THF was added. Reaction mixture was stirred for 5 h. The volatiles were removed and analyzed. GLC found 0.57 g of CH_3I (80%). Recrystallization of the residue from THF yielded 2.61 g (74%) of $YbI_3(THF)_2$.

3.4. Styrene polymerization

To a solution of **2** (0.2 mmol) in 10 ml of toluene a solution of 3.0 g (28.8 mmol) of styrene in 10 ml of toluene was added. The reaction mixture was stirred at room temperature (r.t.) for 24 h. The polymerization was then quenched by injecting methanol (0.5 ml) and the reaction mixture was filtrated. Resulting polymer was precipitated by 30 ml of methanol, washed and dried under vacuum. 0.27 g (9%) of polystyrene was obtained.

3.5. Propylene polymerization

Propylene polymerization was conducted in a 350 ml reaction vessel fitted with Teflon stir. To a solution of **2** (0.04 mmol) in 20 ml of toluene at −60 °C 0.65 g of propylene was condensed. The reaction mixture was warmed to a r.t. and stirred for 24 h. The polymerization was then quenched by injecting methanol (0.5 ml). The reaction mixture was filtrated and resulting polymer was precipitated by 30 ml of methanol, washed and dried under vacuum, which afforded 0.064 g (10%) of polypropylene insoluble in THF and $CDCl_3$.

3.6. X-ray crystal structure analysis of **1**

The measurement was performed at −100 °C using a Siemens SMART CCD system with $Mo{-}K_\alpha$ X-radiation ($\lambda = 0.71073$ Å) and graphite monochromator. A selected crystal of **1** was coated with mineral oil, mounted on a glass fiber and transferred to the cold nitrogen stream (Siemens LT-2 attachment). A full hemisphere of the reciprocal space was scanned by ω in three sets of frames of 0.3°. As an absorption correction the SADABS routine was applied.

1, $C_{48}H_{72}O_8Yb_4$, ruby-red crystal, $0.32 \times 0.22 \times 0.08$ mm, $M = 1469.22$, tetragonal, space group $P(-4)2_1/c$, $a = 14.2859(6)$, $b = 14.2859(6)$, $c = 14.0246(8)$ Å, $U = 2862.2(2)$ Å^3, $Z = 4$, $D = 1.705$ mg m^{-3}, $F(000) = 1408$, μ ($Mo{-}K_\alpha$) $= 6.52$ mm^{-1}, max/min transmission 1.00/0.62, red tablet $0.32 \times 0.22 \times 0.08$ mm. A total of 19 028 reflections were collected, over a range of $2.0 < \theta < 28.3°$, of which 3552 were independent ($R_{int} = 0.052$). The structure was solved by direct methods. Refinement was by full-matrix least-squares on F^2 and converged to $R_1 = 0.030$ (conventional) and $wR_2 = 0.072$ (all data), with goodness-of-fit = 1.06, 148 refined parameters, weighting scheme $[\sigma^2(F_o^2) + 0.0402P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. The absolute configuration was determined with $x = 0.03(2)$ [11–13].

4. Supplementary material

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for this material should quote the full literature citation and the reference no. 177453. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk).

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