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Synthesis of bis(t-butylcyclopentadienyl)ytterbium(II). Derivatives and molecular structure of bis(t-butylcyclopentadienyl)bis(tetrahydrofuran)ytterbium(II)

Qi Shen *, Dongshui Zheng, Lin Lin and Yonghua Lin

Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied chemistry, Academia Sinica, 109 Stalin Street, Changchun 130022 (P.R. China)

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Abstract

Bis(η^5-t-butylcyclopentadienyl)ytterbium(II) $(t\text{-}C_4H_9C_5H_4)_2Yb(THF)_2$ has been synthesized by metallic sodium reduction of the corresponding chloride $(t\text{-}C_4H_9C_5H_4)_2YbCl(THF)$ in THF. The reaction of $(t\text{-}C_4H_9C_5H_4)_2Yb(THF)_2$ with $OPPh_3$ in toluene gives $(t\text{-}C_4H_9C_5H_4)_2Yb(OPPh_3)(THF)$. $(t\text{-}C_4H_9C_5H_4)_2Yb(THF)_2$ crystallizes from THF in the monoclinic space group $P2_1/n$, with unit cell constants a 13.434(2), b 9.885(2), c 20.100(4) Å, β 105.34(1)°, V 2573.99 Å^3 and D_{calcd} 1.44 g cm^{-3} for $Z = 4$. Least-squares refinement of 4186 unique observed reflections led to a final R of 0.060. The two ring centroids of the t-butylcyclopentadienyl rings and the two oxygen atoms of the THF form a distorted tetrahedron around the central ion of ytterbium(II). The molecule has an approximate C_2 symmetry with the average bond distances: Yb–C(ring) 2.722(16) Å, Yb–O(THF) 2.431(8) Å, and Yb–C_p (centroid) distance 2.442(0) Å.

Introduction

Reduction of a trivalent organoytterbium compound is one of the usual methods for the synthesis of divalent organoytterbium complexes. Metallic sodium or ytterbium reduction of $(C_5H_5)_2YbCl$ or $(C_5H_5)_3Yb$ gives the corresponding insoluble $(C_5H_5)_2Yb$ [1,2]. Reduction of $(((CH_3)_3SiC_5H_4)_2YbCl)_2$ by Na–Hg in tetrahydrofuran (THF) yields the purple, diamagnetic, toluene-soluble complex $((CH_3)_3SiC_5H_4)_2Yb(THF)_2$ which shows a roughly tetrahedral disposition around Yb [3].

Here we report the reduction by metallic sodium of $(t\text{-}C_4H_9C_5H_4)_2YbCl(THF)$, the reaction of the reduction product, $(t\text{-}C_4H_9C_5H_4)_2Yb(THF)_2$, with $OPPh_3$ in toluene and the molecular structure of $(t\text{-}C_4H_9C_5H_4)_2Yb(THF)_2$.

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Experimental

Since the complexes described below are extremely air- and moisture-sensitive, all experiments were conducted under pure argon by Schlenk techniques.

THF and hexane were refluxed over and distilled from sodium benzophenone ketyl under argon. Anhydrous ytterbium trichloride was prepared by a previously published procedure [4]. $Na(t\text{-}C_4H_9C_5H_4)$ was prepared by the reaction of NaH with $t\text{-}C_4H_9C_5H_5$ which was synthesized as described previously [5]. $OPPh_3$ (Merck Schuchart) was used as received. THF-d_8 was distilled from sodium. Analyses of rare earth metals were carried out by direct complexometric titration. Carbon and hydrogen analyses were determined by use of the combustion method. Melting points were determined in sealed argon filled capillaries and are uncorrected.

^1H NMR spectra were obtained on a Varian EM-390 90 MHz spectrometer in THF-d_8 solution and referenced to Me_4Si. Infrared spectrum was obtained on a Digilab FTS-20E spectrometer as KBr pellet.

$(t\text{-}C_4H_9C_5H_4)_2Yb(THF)_2$

To a suspension of $YbCl_3$ (1.22 g, 4.37 mmol) in THF (20 ml) was added a THF solution of $Na(t\text{-}C_4H_9C_5H_4)$ (1.31 g, 8.74 mmol). The suspension was stirred at 60 °C for 2 days, then 0.1 g (4.35 mmol) metallic Na was added and the mixture was stirred at 65 °C for another 2 days. The suspension gradually turned from dark red to dark purple. After centrifugation to remove NaCl, the solution was concentrated and cooled to −30 °C to yield the purple crystals of $(t\text{-}C_4H_9C_5H_4)_2Yb(THF)_2$ (0.765 g, 31.3%). Anal. Found: C, 54.7; H, 7.47; Yb, 31.0. $C_{26}H_{42}O_2Yb$ calcd.: C, 55.76; H, 7.57; Yb, 30.9%. ^1H NMR: 1.25(s,18H), 5.4(t,4H), 5.6(t,4H). IR (KBr, cm^{-1}) 2960s, 2860m, 1600s, 1460m, 1365s, 1280w, 1250m, 1195m, 1156m, 1040s, 1023s, 860m, 816s, 750s, 670s.

$(t\text{-}C_4H_9C_5H_4)_2Yb(OPPh_3)(THF)$

$(t\text{-}C_4H_9C_5H_4)_2Yb(THF)_2$ (0.143 g, 0.272 mmol) was added to a 10 ml toluene solution of $OPPh_3$ (0.082 g, 0.30 mmol). The mixture was stirred at 50 °C for 2 days and crystallized at room temperature; 0.141 g of black crystals of $(t\text{-}C_4H_9C_5H_4)_2Yb(OPPh_3)(THF)$ were collected (56.3%), mp: 242–244 °C. Anal. Found: Yb, 22.1. $YbC_{40}H_{49}PO_2$ calcd.: Yb, 22.9%. IR (KBr, cm^{-1}) 3430m, 3055m, 2958s, 2860w, 1592w, 1484w, 1438s, 1198s, 1120s, 1070m, 1030m, 996w, 752m, 721s, 695s.

Crystal structure of $(t\text{-}C_4H_9C_5H_4)_2Yb(THF)_2$

A single crystal of 0.36 × 0.40 × 0.46 mm was sealed in a thin glass capillary under argon and placed in a stream of cold nitrogen in a Nicolet R3M/E diffractometer equipped with a low-temperature device. Table 1 lists the details of the data collection and refinement. The cell dimensions were obtained by least-squares refinement of the setting angles for 25 reflections having $3 < \theta < 11.5°$. Intensities of all reflections with $3 \leqslant 2\theta \leqslant 56°$ were collected by use of ω scan techniques and graphite-monochromated Mo-K_α radiation. Three intense reflections, measured every 69 reflections during data collection, showed the variations in intensity of a standard reflection ($30\bar{7}$) to be about ±2% (mean). The intensities were corrected for Lorentz and polarization, but not for absorption, effects. The

Table 1

Crystal data

Compound	$(t\text{-}C_4H_9C_5H_5)_2Yb(THF)_2$
Mol wt	559.5
Crystal size, mm	0.36 × 0.40 × 0.46
Cell constants	
a, Å	13.434(2)
b, Å	9.885(2)
c, Å	20.100(4)
β, deg	105.34(1)
V, Å^3	2573.99
scan range 2θ, deg	3–56
number of reflections	6386
number of reflections for $I > 3\sigma(I)$	4186
Space group	$P2_1/n$
Z	4
D, g/cm^3	1.44
R	0.0600
R_w	0.0702
$F(000)$	1151

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (e.s.d.'s in last significant digit)

	x	y	z	U
Yb	4804(1)	5240(1)	7332(1)	31(1)
Ca(1)	4998(10)	6477(11)	8599(6)	33(5)
Ca(2)	4207(12)	5486(13)	8527(7)	51(6)
Ca(3)	3360(11)	5810(15)	8021(6)	46(6)
Ca(4)	3614(11)	7064(14)	7727(7)	42(6)
Ca(5)	4632(11)	7453(13)	8083(7)	44(6)
Ca(6)	5998(11)	6545(12)	9164(6)	41(5)
Ca(7)	6443(15)	5131(15)	9370(10)	79(8)
Ca(8)	6841(13)	7358(20)	8935(9)	78(8)
Ca(9)	5808(16)	7204(21)	9819(8)	90(9)
Cb(1)	5595(11)	6756(12)	6403(7)	42(6)
Cb(2)	5472(14)	5387(14)	6133(7)	62(7)
Cb(3)	6223(14)	4575(16)	6643(9)	65(8)
Cb(4)	6706(11)	5377(16)	7189(8)	53(6)
Cb(5)	6329(12)	6733(14)	7052(7)	49(6)
Cb(6)	5070(13)	7960(14)	6004(7)	45(6)
Cb(7)	5281(17)	9212(18)	6451(11)	108(10)
Cb(8)	3932(19)	7799(23)	5835(12)	124(13)
Cb(9)	5415(25)	8105(24)	5360(13)	147(16)
O(1)	5139(7)	2936(8)	7768(4)	41(4)
C(11)	4472(12)	2041(15)	8023(8)	60(7)
C(12)	5169(15)	1404(14)	8660(7)	62(8)
C(13)	6212(15)	1280(16)	8491(8)	68(8)
C(14)	6149(10)	2245(12)	7901(7)	41(5)
O(2)	3329(7)	4195(10)	6533(4)	49(4)
C(21)	2299(12)	4743(15)	6260(7)	53(6)
C(22)	1879(15)	4154(20)	5572(9)	93(9)
C(23)	2499(15)	2986(21)	5555(10)	107(10)
C(24)	3418(14)	2954(14)	6155(8)	71(7)

range for h was 0 to 18, for k 0 to 14 and for l −27 to 27. Systematic absences indicated the space group to be $P2_1/n$.

The position of the ytterbium atom was located with Patterson and Fourier techniques and refined by least squares. All the non-hydrogen atoms were refined with anisotropic temperature factors by full-matrix least-squares methods, final $R = 0.0600$, $R_w = 0.0702$, max. $\Delta/\delta = 0.005$. Table 2 lists the final atomic positional and thermal parameters.

Calculations were carried out with the SHELXTL system of computer programs. Atomic scattering factors for Yb, O and C were taken from Cromer and Waber [6] and anomalous dispersion terms were from Cromer and Liberman [7].

Results and discussion

Synthesis

The reduction of $(t\text{-}C_4H_9C_5H_4)_2YbCl(THF)$, which had previously been formed in situ from the reaction of ytterbium trichloride with two equiv. of $Na(t\text{-}C_4H_9C_5H_4)$ in THF, with metallic sodium in THF gives the purple divalent compound $(t\text{-}C_4H_9C_5H_4)_2Yb(THF)_2$ (eq. 1 and 2):

$$YbCl_3 + 2Na(t\text{-}C_4H_9C_5H_4) \xrightarrow{THF} (t\text{-}C_4H_9C_5H_4)_2YbCl(THF) + 2NaCl \tag{1}$$

$$(t\text{-}C_4H_9C_5H_4)_2YbCl(THF) + Na \xrightarrow{THF} (t\text{-}C_4H_9C_5H_4)_2Yb(THF)_2 + NaCl \tag{2}$$

The compound is thermally stable; however, when the compound is heated to 200 °C under vacuum, the solvated THF is removed to give the green solvate-free ytterbium compound $(t\text{-}C_4H_9C_5H_4)_2Yb(II)$ (Found: Yb, 41.5. $C_{18}H_{26}Yb$ calcd.: Yb, 41.7%) (eq. 3)

$$(t\text{-}C_4H_9C_5H_4)_2Yb(THF)_2 \xrightarrow{\text{heated to } 200\,^\circ C} (t\text{-}C_4H_9C_5H_4)_2Yb \tag{3}$$

$(t\text{-}C_4H_9C_5H_4)_2Yb(THF)_2$ reacts with triphenylphosphine oxide in toluene to give the black precipitate of $(t\text{-}C_4H_9C_5H_4)_2Yb(THF)(OPPh_3)$ in good yield (eq. 4):

$$(t\text{-}C_4H_9C_5H_4)_2Yb(THF)_2 + OPPh_3 \xrightarrow{\text{toluene}} (t\text{-}C_4H_9C_5H_4)_2Yb(THF)(OPPh_3) + THF \tag{4}$$

The compound $(t\text{-}C_4H_9C_5H_4)_2Yb(THF)(OPPh_3)$ was identified from its infrared spectrum and elemental analysis. The infrared spectrum is similar to that of $(C_5Me_5)_2Sm(THF)(OPPh_3)$ especially in the range of 1600–400 cm^{-1} [8].

Molecular structure of $(t\text{-}C_4H_9C_5H_4)_2Yb(THF)_2$

Figure 1 depicts the structure of the compound. The geometry around the ytterbium ion can be described as an approximate tetrahedron with the centroids of the t-butylcyclopentadienyl rings and the oxygens of two THF forming the apices of the tetrahedron. The molecule shows approximate C_2 symmetry about the O_2–Yb–O_1 axis. The two t-butylcyclopentadienyl ligands are staggered (Fig. 2). The t-butyl groups are located at opposite sides of the molecule and are directed away from each other. Selected bond lengths and angles are listed in Tables 3 and 4. The cent–Yb–cent angle 134.0(0)°, the average cent–Yb–O angle 106.9(3)° and O_2–Yb–O_1 angle 83.1(4)° are comparable with the relevant angles reported for

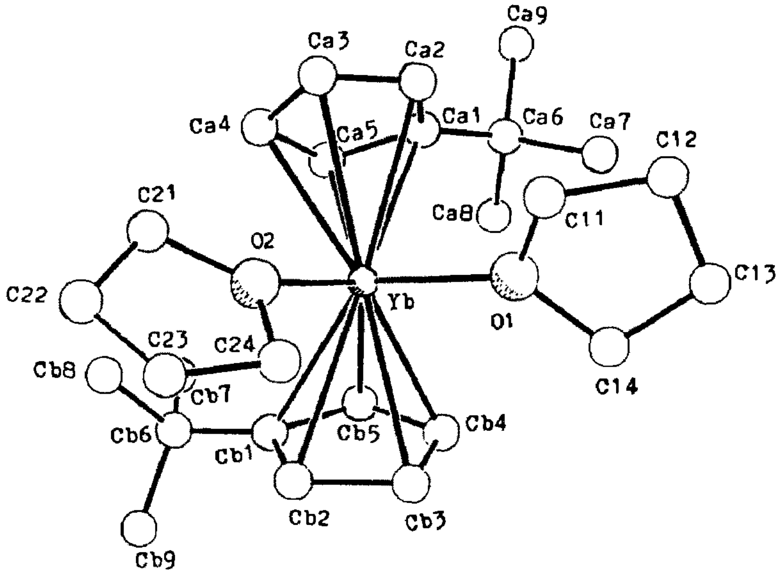

Fig. 1. Molecular structure of $(t\text{-}C_4H_9C_5H_4)_2Yb(THF)_2$.

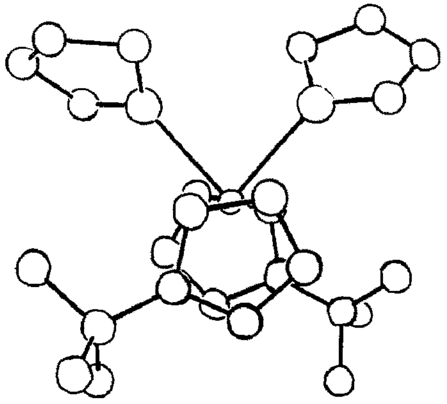

Fig. 2. View of the molecule depicting the staggered $t\text{-}C_4H_9C_5H_4$ rings.

Table 3

Bond lengths (Å) (e.s.d.'s in last significant digit)

Yb–Ca(1)	2.772(12)	Yb–Ca(2)	2.733(15)
Yb–Ca(2)	2.720(16)	Yb–Ca(4)	2.661(15)
Yb–Ca(5)	2.697(13)	Yb–Cb(1)	2.807(15)
Yb–Cb(2)	2.782(17)	Yb–Cb(3)	2.711(20)
Yb–Cb(4)	2.645(16)	Yb–Cb(5)	2.697(16)
Yb–O(1)	2.435(8)	Yb–O(2)	2.426(9)
Ca(1)–Ca(2)	1.422(19)	Ca(2)–Ca(3)	1.348(18)
Ca(3)–Ca(4)	1.450(20)	Ca(4)–Ca(5)	1.417(19)
Ca(1)–Ca(5)	1.406(17)	Ca(1)–Ca(6)	1.513(16)
Ca(6)–Ca(7)	1.530(20)	Ca(6)–Ca(8)	1.551(24)
Ca(6)–Ca(9)	1.548(23)	Cb(1)–Cb(2)	1.448(19)
Cb(2)–Cb(3)	1.471(21)	Cb(3)–Cb(4)	1.369(21)
Cb(4)–Cb(5)	1.430(20)	Cb(1)–Cb(5)	1.412(17)
Cb(1)–Cb(6)	1.500(18)	Cb(6)–Cb(7)	1.509(23)
Cb(6)–Cb(8)	1.483(30)	Cb(6)–Cb(9)	1.489(35)
Yb–cent(1)	2.438(0)	Yb–cent(2)	2.445(0)
Yb–C(ring)$_{av}$	2.723(15)		

Table 4

Bond angles (°) (e.s.d.'s in last significant digit)

Ca(2)–Ca(1)–Ca(5)	106.8(10)	Ca(1)–Ca(2)–Ca(3)	111.9(12)
Ca(2)–Ca(3)–Ca(4)	105.4(12)	Ca(3)–Ca(4)–Ca(5)	109.0(11)
Ca(1)–Ca(5)–Ca(4)	106.8(12)	Cb(2)–Cb(1)–Cb(5)	108.2(11)
Cb(1)–Cb(2)–Cb(3)	104.9(12)	Cb(2)–Cb(3)–Cb(4)	109.7(13)
Cb(3)–Cb(4)–Cb(5)	108.5(12)	Cb(1)–Cb(5)–Cb(4)	108.6(11)
cent(1)–Yb–Cent(2)	134.0(0)	cent(1)–Yb–O(1)	105.8(3)
cent(1)–Yb–O(2)	107.1(3)	cent(2)–Yb–O(1)	107.6(3)
cent(2)–Yb–O(2)	107.5(3)	O(1)–Yb–O(2)	83.3(4)

$((CH_3)_3SiC_5H_4)_2Yb(THF)_2$ [3], $(C_5Me_5)_2Yb(Py)_2$ [9], and $(C_5Me_5)_2Yb(NH_3)(THF)$ [10].

The ring carbon atoms all lie within 0.0253 Å of the calculated mean plane. The carbon atoms of the t-butyl group are displaced outwards by a mean of 0.0315 Å from the plane of the ring. Yb–C(ring) distances range from 2.645(16) to 2.807(15) Å. The average Yb–C distance is 2.723(15) Å which is comparable with that found in $(C_5H_5)_2Yb(DME)$ [11]. $(C_5Me_5)_2Yb(Py)_2$ [9] and $((CH_3)_3SiC_5H_4)_2Yb(THF)_2$ [3].

The average Yb–O distance, 2.43(8)Å compares well with the average Yb–O distance 2.41(2) Å in $((CH_3)_3SiC_5H_4)_2Yb(THF)_2$.

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Supplementary Material Available: Tables of bond lengths and angles, temperature factors and least-squares planes (7 pages) a listing of calculated and observed structure factors (17 pages) are available from the authors.

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