

Synthesis and molecular structure of $[(t\text{-C}_4\text{H}_9\text{C}_5\text{H}_4)_2\text{Yb}(\text{THF})_2][\text{BPh}_4] \cdot \text{THF}$ and its catalytic activity for the polymerization of styrene

Fugen Yuan^a, Qi Shen^{a,*}, Jie Sun^b

^a School of Chemistry and Chemical Engineering, Suzhou University, Suzhou, 215006, People's Republic of China

^b Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Academia Sinica, Shanghai, 200032, People's Republic of China

Abstract

The complex of $[(t\text{-C}_4\text{H}_9\text{C}_5\text{H}_4)_2\text{Yb}(\text{THF})_2][\text{BPh}_4] \cdot \text{THF}$ (**1**) has been synthesized by one-electron oxidation of $(t\text{-C}_4\text{H}_9\text{C}_5\text{H}_4)_2\text{Yb}(\text{THF})_2$ (**2**) with AgBPh_4 . **1** crystallized from THF–toluene in space group $P2_1/n$ (#13) with unit cell constants: $a = 12.362(9) \text{ \AA}$, $b = 14.855(5) \text{ \AA}$, $c = 14.093(6) \text{ \AA}$, $\beta = 109.20(4)^\circ$, $V = 2444(2) \text{ \AA}^3$ and $Z = 2$ for $D_{\text{calc}} = 1.292 \text{ g cm}^{-3}$. Least squares refinement of the model based on 2257 observed reflections led to final R of 0.046. This complex shows catalytic activity for the polymerization of styrene at high temperature.

Keywords: Cation; Ytterbium; Cyclopentadienyl; Crystal structure

1. Introduction

The steadily growing interest in the development of cationic compounds of the rare earth elements is due to the assumption that cationic species are of importance in olefin polymerization process by Ziegler–Natta- and Kaminsky-type catalysts [1]. However, bis(cyclopentadienyl)lanthanides with a rare earth metal in the cation can still be counted on one's fingers. Only the following complexes have been synthesized and structurally characterized: $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2][\text{BPh}_4]$ [2], $[(\text{C}_5\text{Me}_5)_2\text{Ce}(\text{THT})_2][\text{BPh}_4]$ [3], $\{[(1,3\text{-Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{La}(\text{DME})(\text{NCMe})\}[\text{BPh}_4] \cdot 0.5\text{DME}$ [4], $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{N}_2\text{H}_4)(\text{THF})][\text{BPh}_4]$ [5] and $[(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Yb}(\text{THF})][\text{Co}(\text{CO})_4]$ [6]. Moreover, the study on the chemistry of such cationic compounds has still been quite limited. $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2][\text{BPh}_4]$ was tested to react with CO, ethylene, azobenzene, phenylacetylene, epoxybutane and pyridine and had no reactivity at all [2]. Although $[(\text{C}_5\text{Me}_5)_2\text{Ce}(\text{THT})_2][\text{BPh}_4]$ was reported to be able to react with terminal alkynes, no details were published [3].

In view of above-mentioned background, we started studying the chemistry of cationic organolanthanide complexes. We synthesized and structurally characterized the complex of $[(t\text{-C}_4\text{H}_9\text{C}_5\text{H}_4)_2\text{Yb}(\text{THF})_2][\text{BPh}_4] \cdot \text{THF}$ (**1**) from the reaction of $(t\text{-C}_4\text{H}_9\text{C}_5\text{H}_4)_2\text{Yb}(\text{THF})_2$ (**2**) with AgBPh_4 and found that **1** can catalyze styrene polymerization under certain conditions.

2. Experimental

The complex described below is extremely air- and moisture-sensitive. Therefore, both the syntheses and subsequent manipulations were carried out under pure argon by Schlenk techniques. THF and toluene were predried with CaCl_2 and distilled from sodium benzophenone ketyl before use. **2** was synthesized according to the literature [7]. AgBPh_4 was prepared from NaBPh_4 and AgNO_3 [8]. Styrene was dried over CaH_2 for 1 day and the distillate was further dried over activated 5 Å molecular sieves for more than 1 week. Analysis of rare earth metals was made by direct complexometric titration. Infrared spectra were recorded on a Magna 550 spectrometer (KBr pellet).

* Corresponding author.

2.1. $[(t-C_4H_9C_5H_4)_2Yb(THF)_2][BPh_4] \cdot THF$

A slight excess of $AgBPh_4$ (1.414 g, 3.31 mmol) was added to a purple solution of **2** (1.50 g, 2.69 mmol) in 80 ml of THF. The reaction mixture turned black immediately and was stirred at 50 °C for 24 h. Then the mixture was kept at the same temperature until the whole blackish silver deposit was precipitated and a clear red solution was obtained. The hot solution was transferred out with a stainless iron capillary, concentrated and kept at r.t. for crystallization. Red wool-like or needle crystals of **1** (0.507 g, 21.5%) were obtained. Crystals suitable for X-ray analysis were grown from THF with proper volumes of toluene solution at r.t.; m.p. (dec.): 130–135 °C. Anal. Found: C, 68.08%; H, 7.35%; Yb, 18.22%. $C_{54}H_{70}BO_3Yb$ calcd.: C, 68.20%; H, 7.42%; Yb, 18.21%. IR (KBr, cm^{-1}): 3057(m), 2962(s), 2870(m), 1637(s), 1602(s), 1479(s), 1427(m), 1364(m), 1263(w), 1155(w), 1047(m), 791(m), 742(s), 710(s), 604(m).

2.2. Polymerization

The polymerization tube was dried by flaming in vacuum and flushed with argon. The procedure was repeated three times. **1** and toluene were mixed in the tube. Styrene was then added, and the reaction mixture was kept in a thermostated bath for a given time. The polymerization was terminated by adding excess ethanol containing 10 vol.% of HCl. The polymer precipitated was washed with ethanol and dried under vacuum. Intrinsic viscosity was determined in toluene at 30 °C and the molecular weight was calculated using the following relation: $[\eta] = 0.94 \times 10^{-4} M^{0.72}$ [9].

Table 1
Crystallographic data for **1**

Formula	$C_{54}H_{70}O_3BYb$
Mol. wt.	950.95
Crystal dimensions (mm^3)	$0.20 \times 0.30 \times 0.40$
Crystal system	monoclinic
Space group	$P2/n$ (#13)
Cell constants	
a (Å)	12.362(9)
b (Å)	14.855(5)
c (Å)	14.093(6)
β (deg)	109.20(4)
V (Å ³)	2444(2)
Z	2
D_{calc} ($g\ cm^{-3}$)	1.292
R	0.046
R_w	0.060
$F(000)$	986
μ (Mo K α) (cm^{-1})	19.53

Table 2
Atomic coordinates and equivalent isotropic thermal parameters

Atom	x	y	z	B_{eq} (Å ²)
Yb	0.7500	0.19852(4)	0.7500	4.12(2)
O(1)	0.8469(5)	0.3113(4)	0.7017(4)	4.3(1)
O(2)	0.2500	0.179(3)	0.2500	27(1)
C(1)	0.568(1)	0.1920(9)	0.5900(10)	8.4(4)
C(2)	0.665(1)	0.175(1)	0.5605(8)	7.7(4)
C(3)	0.715(1)	0.100(1)	0.597(1)	9.9(5)
C(4)	0.650(1)	0.0613(8)	0.6458(10)	8.5(4)
C(5)	0.556(1)	0.1147(8)	0.6472(7)	6.3(3)
C(6)	0.454(1)	0.092(1)	0.679(1)	9.7(4)
C(7)	0.449(2)	0.108(2)	0.773(2)	18.0(8)
C(8)	0.483(3)	-0.004(3)	0.718(3)	28(1)
C(9)	0.353(2)	0.058(1)	0.597(1)	13.4(5)
C(10)	0.9044(10)	0.3855(7)	0.7711(8)	6.7(3)
C(11)	0.939(1)	0.4499(8)	0.7067(9)	8.1(4)
C(12)	0.9655(9)	0.3927(8)	0.6292(8)	6.7(3)
C(13)	0.8740(8)	0.3220(6)	0.6068(7)	4.8(2)
C(14)	0.7953(7)	0.3894(6)	0.1747(6)	3.6(2)
C(15)	0.7417(7)	0.4690(7)	0.1353(7)	4.9(2)
C(16)	0.7736(9)	0.5203(7)	0.0643(8)	6.2(3)
C(17)	0.859(1)	0.4894(9)	0.0306(8)	6.4(3)
C(18)	0.9119(8)	0.4122(9)	0.0655(8)	6.0(3)
C(19)	0.8803(7)	0.3600(6)	0.1371(7)	4.5(2)
C(20)	0.6484(6)	0.2653(6)	0.1733(6)	3.4(2)
C(21)	0.6705(7)	0.1814(6)	0.1363(6)	4.0(2)
C(22)	0.5877(9)	0.1323(6)	0.0666(7)	5.0(3)
C(23)	0.4760(10)	0.1640(8)	0.0295(8)	6.1(3)
C(24)	0.4510(8)	0.2454(9)	0.0597(8)	6.6(3)
C(25)	0.5365(8)	0.2967(6)	0.1312(7)	5.1(3)
C(26)	0.178(3)	0.230(3)	0.161(3)	25(1)
C(27)	0.220(2)	0.319(2)	0.195(2)	17.1(8)
B	0.7500	0.3269(9)	0.2500	3.7(3)

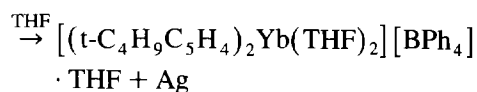
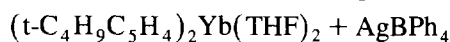
2.3. Crystal structure determination of **1**

A red plate crystal of approximate dimensions $0.20 \times 0.30 \times 0.40\ mm^3$ was sealed in a thin-walled glass capillary under argon. Measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo K α radiation. Cell constants and an orientation matrix for data collection were obtained from a least squares refinement using the setting angles of 21 carefully centered reflections in the range $18.28 \leq 2\theta \leq 21.37^\circ$. The data were collected at a temperature of $20 \pm 1^\circ\ C$ using the $\omega-2\theta$ scan technique to a maximum 2θ value of 45° . Of the 2766 reflections collected, 2590 were unique ($R_{int} = 0.076$). The structure was solved by direct methods and expanded using Fourier techniques. The final cycle of full-matrix least squares refinement was based on 2257 observed reflections ($I > 3.00\sigma(I)$) and 235 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.046$, $R_w = 0.060$. The crystallographic data and atomic coordinates and equivalent isotropic thermal parameters are listed in Tables 1 and 2 respectively.

3. Results and discussion

3.1. Synthesis and molecular structure of **1**

The oxidation of the most reactive $(C_5Me_5)_2Sm(THF)_2$ with $AgBPh_4$ gives the cationic compound $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$ in good yields [2]. The similar reaction should occur with Yb^{2+} as AgF is reduced by $(C_5Me_5)_2Yb$ [10], although Yb^{2+} is a weaker reducing agent in comparison with Sm^{2+} . We tested the reaction of **2** with $AgBPh_4$. While **2** was added to the suspension of $AgBPh_4$ in THF, the color of the mixture turned immediately from purple to dark indicating the formation of Ag precipitate. After work-up the expected red trivalent compound **1** was isolated.



1 was characterized by elemental analysis, IR spec-

troscopy and an X-ray crystal structure. **1** is soluble in THF but not in toluene. **1** is thermally stable and will decompose at above $130^\circ C$.

The molecular structure of **1** is shown in Fig. 1, and selected bond distances and angles are given in Table 3. The BPh_4^- anion has normal distances and angles and is well separated from the cation, which is similar to that of $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$ [2]. $[(t-C_4H_9C_5H_4)_2Yb(THF)_2]^+$ has an overall structure similar to that of **2**. The geometry around the ytterbium ion can be described as a distorted tetrahedron with the centroids of the t-butylcyclopentadienyl rings and the oxygen atoms of two THF forming the apices of the tetrahedron. The t-butyl groups are located at opposite sides of the cation and are directed away from each other. The differences between bond distances and bond angles in **1** and **2** are similar to those between $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$ and $(C_5Me_5)_2Sm(THF)_2$. For example, the 126.4° Cen(1)–Yb–Cen(1*) angle in **1** is smaller than the $134.0(0)^\circ$ angle in **2**. The $86.0(3)^\circ$

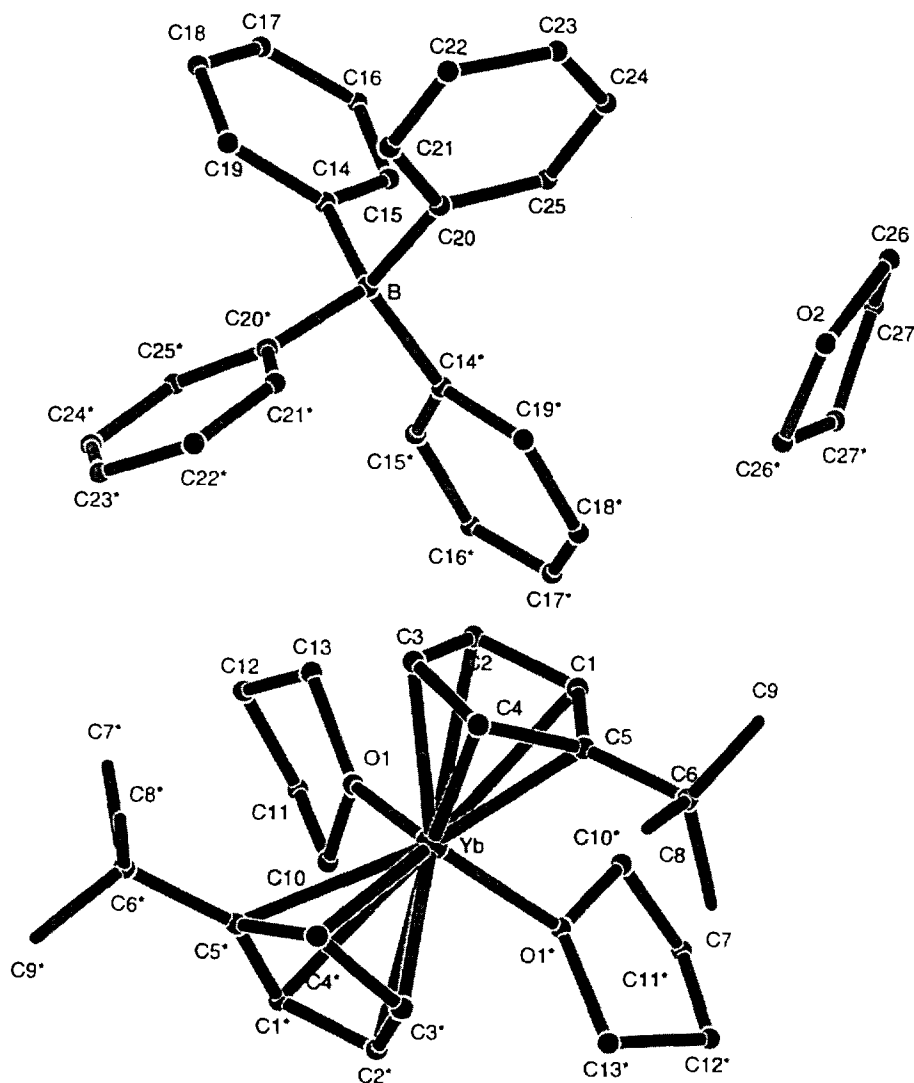


Fig. 1. Molecular structure of **1**.

O(1)–Yb–O(1*) angle in **1** is larger than the analogous 83.3(4)° angle in **2**. The 2.586(1) Å average Yb–C(ring 1)_{av} distance in **1** is comparable with the analogous 2.628(10) Å average in (t-C₄H₉C₅H₄)₂YbCl(THF) [11], but less than the analogous 2.723(15) Å average in **2**. The mean Yb–O(1) distance of 2.290(5) Å in **1** is also comparable with the analogous 2.333(6) Å in (t-C₄H₉C₅H₄)₂YbCl(THF) and shorter than the corresponding distance of 2.431(8) Å in **2**. These distance differences can be compared to the 0.155 Å difference between eight-coordinated Yb²⁺ and Yb³⁺ in the halide structure [12].

3.2. Catalytic activity for the polymerization of styrene

Eu(CH₃CN)₃(BF₄)₃ [13] was reported to be a catalyst for the polymerization of styrene. One of the authors found that Ln(CH₃CN)₃(AlCl₄)₃·CH₃CN shows a fairly high catalytic activity for styrene polymerization [14]. However, the chemistry of cationic bis(cyclopentadienyl) lanthanide compounds is still undeveloped, so we tested the catalytic activity of **1** for polymerization of styrene. Styrene can be self-polymerized at high temperature. In order to get rid of the thermal effect on the polymerization, we made the comparison between the catalytic polymerization and the non-catalytic (thermal) polymerization under the same experimental conditions. Polymerization results are listed in Table 4.

When the polymerization temperature is lower than 80 °C, the catalyst displays no or little catalytic activity. However, when the temperature rises to 100 °C, **1** shows its catalytic activity evidently. Even if polymerization keeps for 8 h, there are obvious differences in yield and molecular weight between the catalytic system and non-catalytic system. It is noticed that the average molecular weights in the catalytic system are much lower than those in the non-catalytic system. As polymerization goes on, the average molecular weight

Table 3
Selected bond lengths (Å) and bond angles (deg)

Yb–O(1)	2.290(5)	C(1)–C(2)	1.41(2)
Yb–C(1)	2.61(1)	C(2)–C(3)	1.30(2)
Yb–C(2)	2.55(1)	C(3)–C(4)	1.35(2)
Yb–C(3)	2.52(1)	C(4)–C(5)	1.41(2)
Yb–C(4)	2.58(1)	C(5)–C(1)	1.44(2)
Yb–C(5)	2.67(1)	C(5)–C(6)	1.50(2)
Yb–Cen(1)	2.30		
O(1)–Yb–O(1*)	86.0(3)	C(1)–C(2)–C(3)	112(1)
O(1)–Yb–Cen(1) ^a	108.6	C(2)–C(3)–C(4)	106(1)
O(1)–Yb–Cen(1*)	109.9	C(3)–C(4)–C(5)	113(1)
Cen(1)–Yb–Cen(1*)	126.4	C(4)–C(5)–C(1)	101(1)
		C(5)–C(1)–C(2)	106(1)

^a Cen(1) represents the centroid of C(1)–C(5) cyclopentadienyl ring (ring 1).

Table 4
Polymerization results

No.	[Cat.]/[M] ^a (mol. ratio)	[M] ^a (vol.%)	Temp. (°C)	Time (h)	Yield (%)	Mol. wt. (× 10 ⁴)
1	1.0%	50.0	60	24	14.75	3.43
2	0	50.0	60	24	12.87	1.48
3	1.0%	50.0	80	24	21.36	6.82
4	0	50.0	80	24	14.22	3.83
5	1.0%	50.0	100	24	72.62	8.02
6	0	50.0	100	24	39.50	19.60
7	1.0%	20.0	100	24	67.45	4.53
8	1.0%	70.0	100	24	79.51	10.38
9	1.0%	50.0	100	8	39.97	7.61
10	0	50.0	100	8	18.40	17.39
11	1.0%	50.0	100	16	66.08	7.89
12	0	50.0	100	16	36.44	18.74

^a M = monomer.

changes little. The polymer yield increases with the increasing of monomer concentration. All the polymers are soluble in methyl ethyl ketone at 80 °C. This demonstrates they are random [15].

Although the catalytic activity is not very high, the results demonstrate that cationic organolanthanide has potential in catalytic chemistry and the exploration of the desired complex and its reactions are planned. The research is currently proceeding.

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