二价镧系均配金属化合物“Open-Metallocenes”——双(2,4-二叔丁基戊二烯基)钐和镱配合物

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摘要：双(2,4-二叔丁基戊二烯基)镧系金属化合物(η^5-Pdl′)$_2$Yb(THF) (**1**)和(η^5-Pdl′)$_2$Sm(DME) (**2**)可以经 LnI_2 和 2,4-二叔丁基戊二烯基钾(K(Pdl′))由置换反应制得。K(Pdl′)和 $LnCl_3$ 发生氧化还原反应也能够得到化合物 **1** 和 **2**。对 2 个化合物进行了表征。X 射线单晶衍射结果显示,2 个化合物中 Pdl′基都是以 η^5 模式配位到金属上。2 个化合物都能够在室温下引发己内酯聚合并表现出高活性,得到分子量分布窄的聚己内酯。

关键词：钐；镱；戊二烯基；聚合；己内酯
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Homoleptic Divalent Lanthanide “Open-Metallocenes”—Bis(2,4-^{t}Bu$_2$-pentadienyl)Sm and Yb Complexes

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Abstract: The bis(2,4-^{t}Bu$_2$-pentadienyl)lanthanide complexes (η^5-Pdl′)$_2$Yb(THF) (**1**) and (η^5-Pdl′)$_2$Sm(DME) (**2**) were successfully prepared in high yield by direct salt metathesis between LnI_2 and 2,4-di-butyl-pentadienyl potassium(K(Pdl′)). Complexes **1** and **2** could also be obtained smoothly from the reaction of $LnCl_3$ and K(Pdl′) through oxidation-reduction reaction. These two compounds were characterized and the X-ray single crystal analysis revealed a predominantly η^5-pentadienyl-metal bonding. Both two compounds could initiate ring-opening polymerization of ε-caprolactone rapidly at room temperature and led to narrow polydispersities with high activity. CCDC: 1045037, **1**; 1045038, **2**.

Key words: Samarium; Ytterbium; pentadienyl; polymerization; ε-caprolactone

0 Introduction

In last decades, Pdl(pentadienyl) ligand arouse lots of interest and various kinds of Pdl have been synthesized and used in organometallics (“open-metallocenes”). Besides bonding to metal in a variety of η^1, η^3 and η^5 modes, it was found that the usual η^5-Pdl is a more sterically demanding[1], and even more strongly bonding to center metal than cyclopentadienyl[2]. Another significant feature of Pdl ligands is its great preference on bonding to metals in low oxidation especially divalence[3]. The steric and electronic properties of Pdl ligands can be easily adjusted by using different substituted derivatives such as 2,4-C_7H_{11}(2,4-

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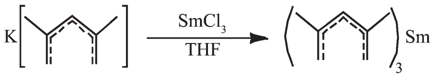
Me_2-Pdl), 1,5-($(Me_3Si)_2$-C_5H_5[1,4], edge-bridged pentadienyl[5], chiral pentadienyl[6], "open indenyl"[7], bridged bis(pentadienyl)[8], and even hetero-pentadienyl[9]. Although the high reactivity of the electronically pentadienyl ligands has led to a wide applications in organometallic synthesis and coupling reactions[10], it is surprising that the usual bis(η^5-Pdl) Sm(Ⅱ) compound, i.e. pure "open-samarocenes", is still elusive. The classical bis-coordination mode of the Pdl ligand seems fade it′s favor when interaction with Sm(Ⅱ). The reaction of $SmCl_3$ with K(2,4-C_7H_{11}) (Molar ratio: 1∶1 or 1∶2) in THF all gave the Sm (2,4-$C_7H_{11})_3$ compound instead of expected Sm(2,4-C_7H_{11})Cl_2 or Sm(2,4-$C_7H_{11})_2$Cl (Scheme 1)[11]. In contrast to Sm complex, the same reaction of $YbCl_3$ with K(2,4-C_7H_{11}) (Molar ratio: 1∶3) led to the divalent Yb(2,4-$C_7H_{11})_2$(DME) (DME=dimethoxyethane) compound due to the reduction pathway[11b]. This could be explained by the higher reduction potential of Sm^{3+}/Sm^{2+} (−1.55 V) than Yb^{3+}/Yb^{2+} (−1.15 V)[12].



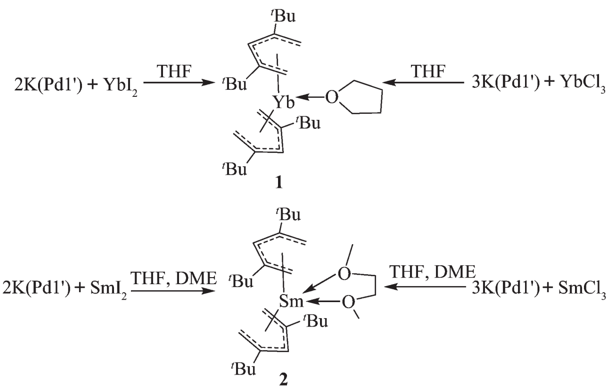
Scheme 1

There were limited examples on the pentadienyl rare earth complexes used for coordination polymerization. A systematical comparison of the stereoselectivity of these tris-, bis- and mono-(2,4-C_7H_{11}) ligated Nd complexes on butadiene polymerization has already been reported by Geitner[13]. Nevertheless, the "open-metallocenes" has not been applied in ester polymerization. In contrast to the well-known, aromatic-soluble metallocene $(C_5Me_5)_2Sm(THF)_2$, which has been widely used in the polymerizations of olefins[14] and esters[15], the classical pentadienyl 2,4-C_7H_{11} ligated lanthanide complexes showed poor solubility in common solvents, precluding the further utilization in stoichiometric or catalytic reactions[16]. Introduction of steric bulkier substituents such as ^{t}Bu or $SiMe_3$ groups on pentadienyl ligand could enhance the solubility and stabilization of the corresponding metal complexes[17]. Herein, we report the synthesis of the novel bis(2,4-^{t}Bu_2-C_5H_5)Sm(Ⅱ) and Yb(Ⅱ) complexes by the salt metathesis reactions between 2,4-di-butyl-pentadienyl potassium(K(Pdl′)) and lanthanide halides, and the application in ring-opening polymerization of ε-caprol-acton.

1 Experimental

1.1 General

The K(Pdl′), $YbCl_3$, $SmCl_3$, $YbI_2(THF)_2$ and $SmI_2(THF)_2$ were prepared according to the literature[17b,18]. All solvents were purified with an MBraun SPS system. Organometallic samples for NMR spectroscopic measurements were prepared in the glovebox by use of NMR tubes sealed by paraffin film. NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. All the subsequent operations were carried out in the gloves box or Schleck line under N_2 atmosphere.



Scheme 2 Syntheses of complexes **1** and **2**

1.2 Synthesis of (2,4-(^{t}Bu)$_2$-C_5H_5)$_2$Yb(THF) (1)

Path A: From $YbI_2(THF)_2$ and K(Pdl′)

K(Pdl′)(0.38 g, 1.76 mmol) was added to a slurry of $YbI_2(THF)_2$ (0.50 g, 0.88 mmol) in 20 mL THF. The solution turned dark green immediately, and the suspension was stirred for 1 h at room temperature. All the volatiles were removed *in vacuo*. The residue was extracted with three portions of hexane (5 mL). The extraction was filtered, concentrated to *ca.* 5 mL and then kept under −30 ℃. Malachite green crystals of complex **1** were collected after several days. Yield: 0.385 g (69%). Anal. Calcd. for $C_{30}H_{54}OYb$ (%): C, 59.68; H, 9.01; O, 2.65. Found(%): C, 59.36; H, 9.13; O, 2.76. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 4.67 (t, 2H, CH, $^4J_{H\text{-}H}$=2.2 Hz), 4.32 (d, 4H, CH_2, $^4J_{H\text{-}H}$=2.3 Hz), 3.45 (br, 8H, CH_2, α-H in THF), 1.33 (br, 40H, $(CH_3)_3C$, β-H in THF).

Path B: From $YbCl_3$ and K(Pdl′)

To a slurry of $YbCl_3$ (0.14 g, 0.5 mmol) in 20 mL THF was added K (Pdl′) (0.33 g, 1.5 mmol), the stirring solution rapidly turned dark green, and the suspension was stirred for 2 h at room temperature. After removal of all the volatiles, the residue was extracted with three portions of hexane (5 mL). The extraction was filtered, concentrated to *ca.* 3 mL, and kept at −30 ℃ overnight to give the malachite green crystals. Yield: 0.08 g (26%). ^1H NMR data is consist with complex **1**.

1.3 Synthesis of (2,4-(^{t}Bu)$_2$-C_5H_5)$_2$Sm(DME) (2)

Path A: From $SmI_2(THF)_2$ and K(Pdl′)

To a slurry of $SmI_2(THF)_2$ (1.25 g, 2.29 mmol) in 50 mL THF was added K(Pdl′) (1 g, 4.58 mmol), the solution turned black immediately, and the suspension was stirred for 2 h at room temperature. All the volatiles were removed in vacuo. The residue was extracted with three portions of hexane (10 mL). The extraction was filtered, concentrated to *ca.* 8 mL. Addition of 0.5 mL DME to the solution afforded a large amount of black precipitate immediately. After removal of supernatant solution, the left black solid was washed with hexane, and dried under vaccum to give complex **2**. Yield: 1.0 g (80%). Single crystals of complex **2** suitable for X-ray analysis were grown from DME solution at −30 ℃. Anal. Calcd. for $C_{30}H_{56}O_2Sm$ (%): C, 60.14; H, 9.42; O, 5.34. Found(%): C, 60.50; H, 9.33; O, 5.21.

Path B: From $SmCl_3$ and K(Pdl′)

To a slurry of $SmCl_3$ (0.13 g, 0.5 mmol) in 20 mL THF was added 3 equivalent of K(Pdl′) (0.33 g, 1.5 mmol), the stirring solution rapidly turned black, and the suspension was stirred for 2 h at room temperature. After removal of all the volatiles, the residue was extracted with three portions of hexane (5 mL). The extraction was filtered, concentrated to *ca.* 3 mL. Addition of 0.5 mL DME to the solution afforded a large amount of black solid. Recrystallization from DME at −30 ℃ overnight gave the black brick crystals. Yield: 0.08 g (27%). X-Ray data analysis disclosed that the cell parameters are the same with complex **2**.

1.4 Ring-opening polymerization of *ε*-caprolactone

All polymerization reactions were carried out in the glovebox under N_2 atmosphere. In a typical procedure, *ε*-caprolactone was added to the toluene solution of the initiator **1** and **2** with vigorous magnetic stirring at the desired temperature. After a certain time, the polymerization was quenched with acidified methanol, and the polymer was precipitated. The resulting polymer was washed with methanol and dried in a vacuum at 35 ℃.

1.5 X-ray crystallographic studies

Crystals for X-ray analysis were obtained as described in the preparations. The crystals were manipulated in a glovebox. Data collections were performed at −88.5 ℃ on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromatic Mo $K\alpha$ radiation (λ=0.071 073 nm). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file[19]. The structures were solved by using the SHELXTL program[20]. Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. The methyl carbon atoms (C7, C8, C9 and C11, C12, C13) of tert-butyl groups and the carbon atoms (C27, C28, C29, C30) of THF fragment were disordered and were refined with 64%, 52% and 50% occupancy anisotropically respectively for all the atoms in complex **2**.

CCDC: 1045037, **1**; 1045038, **2**.

2 Results and discussion

2.1 Syntheses and crystal structures

As our expectation, the bulkier 2,4-^{t}Bu$_2$-Pdl could more efficiently stabilize Ln(Ⅱ) than the 2,4-Me$_2$-Pdl. Salt metathesis reactions of LnI_2 (Ln=Sm, Yb) with two equivalents of K(Pdl′) proceeded smoothly in THF to afford corresponding “open-metallocenes” (Pdl′)$_2$Sm (DME) and (Pdl′)$_2$Yb(THF) in moderate yields, respectively. Noteworthily, these two complexes showed higher solubility in hydrocarbon than the previous reported complex $Yb(2,4-C_7H_{11})_2(DME)$, which was insoluble in hexane[11b]. The introduction of DME afforded an improved stability of the Sm(Ⅱ) complex. After the addition of DME, the solubility of **2** in hexane decreased dramatically, and great amount of **2** precipitated from the solution. It could be assumed that the bi-coordinate sites of DME molecular stabilized the entire complex, and decreased the solubility of the coordinated Sm complex. The reactions of K(Pdl′) with $SmCl_3$ or $YbCl_3$ in a molar ratio of 3∶1, also afforded a blackish and a dark green solution, suggested that reductive ways rather than salt elimination reactions happened. The subsequent X-ray crystallographic studies of these single crystals product confirm the reductive path ways. This result is different from the previous reaction between the $K(C_7H_{11})$ and $SmCl_3$, which afforded the $Sm(C_7H_{11})_3$ complex. It could be inferred that sterically demanding ^{t}Bu enhanced the stabilization of the divalent samarium center.

Due to the striking similarity in the chemistry of Yb(Ⅱ) and Ca(Ⅱ) complexes, in the ^{1}H NMR spectrum of the complex **1**, the chemical shifts of Pdl fragments are almost the same as $(Pdl')_2Ca(THF)$, which suggested a η^5-U coordination of the 2,4-di-butyl-pentadienyl ligand[21]. However, the chemical shifts of coordinated THF move slightly low-field. The resonance of α-H and β-H of THF fragment occasionally overlaps with the prime carbon H (exo) resonance (δ 3.45) and the ^{t}Bu protons (δ 1.33) of Pdl′ ligands, respectively. Unfortunately, complex **2** could not be characterized by ^{1}H NMR spectra because of its paramagnetic property.

The molecular structures of **1** and **2** are shown in Fig.1, and the relevant bond distances and angles are listed in Table 1. In the pentadienyl fragments, the C-C distances show a distinct short-long-long-short pattern. The carbon atoms lie in a plane, adopting a η^5 coordination mode. The Yb-C distances of complex **1** are the same as the previous analog $(2,4\text{-}Me_2\text{-}C_5H_5)_2Yb(DME)$. The conformation angle χ of these two complexes, defined as the angle between the two planes (centroid (C1-C5)-C3-M) and (centroid(C14-C18)-C16-M), are all approximately 180°. This anti-eclipsed conformation, which displays the mutual orientations of the two pentadienyl moieties, are consistent with Ca, Cr and Fe pentadiene analog[17b], but in contrast with $(2,4\text{-}Me_2\text{-}C_5H_5)_2Yb$ (DME). The interaction of the bulkier ^{t}Bu determines the orientation of the pentadienyl to offer a rather flat potential energy surface with respect to the conformation angle χ.

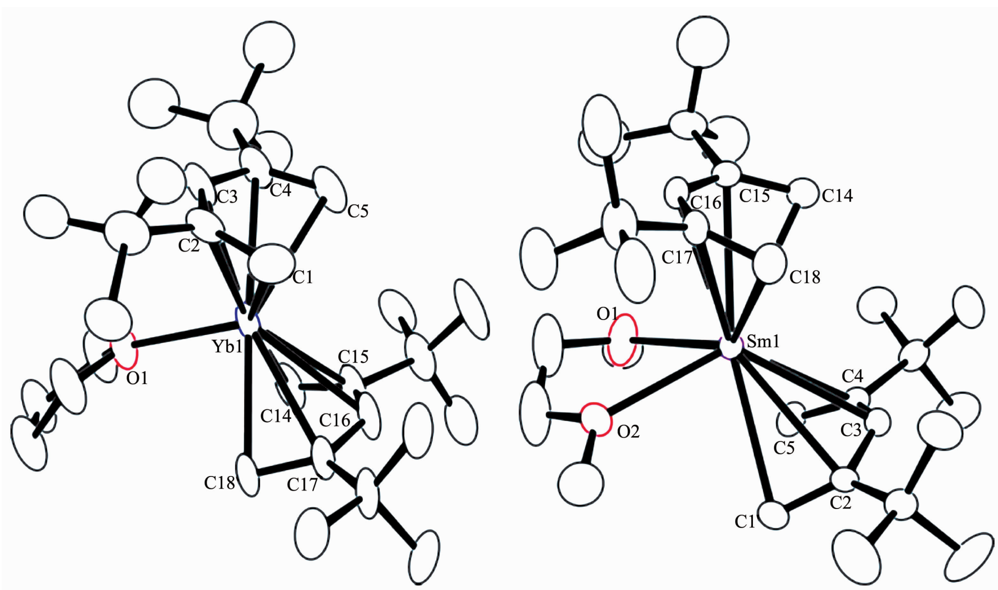


Fig.1 ORTEP diagrams of **1** and **2** (10% and 35% probability ellipsoids respectively)

Table 1　Selected bond distances (nm) and angles (°) of 1 and 2

Complex	**1**	**2**
M-C1, 5(Pdl′)	0.274 8(11), 0.278 0(12)	0.297 0(6), 0.288 1(6)
M-C2, 4(Pdl′)	0.273 8(14), 0.276 4(13)	0.300 6(6), 0.292 2(6)
M-C3(Pdl′)	0.267 6(15)	0.285 6(6)
M-C(Pdl′)[a]	0.274 1	0.292 7
M-Pdlp′[b]	0.217 7, 0.222 6	0.243 4, 0.243 8
M-Pdlc′[c]	0.228 5, 0.228 9	0.250 2, 0.250 5
M-O1, 2	0.242 3(6)	0.259 6(5), 0.264 8(5)
Pdlc′-M-Pdlc′	144.12	135.79
α[d]	31.50	44.61

[a] M-C (Pdl′) is the average distance between the center metal and the five C atoms of the Pdl′ framework; [b] Pdl_p' is the plane of the pentadienyl ligand; [c] Pdl_c' is the centroid of the pentadienyl ligand; [d] α is defined as the angle formed by the two dienyl planes

2.2　Polymerization of ε-caprolactone

Ring-opening polymerization of ε-caprolactone (ε-CL) under varying conditions was investigated by using complexes **1** and **2**. The representative polymerization results are summarized in Table 2. Complexes **1** and **2** both display high activity for the ring-opening polymerization of ε-CL in toluene at room temperature. As the monomer was introduced, the dark solution immediately faded to colorless due to an oxidation process, indicating the transformation of Ln^{2+} to Ln^{3+}. Complexes **1** and **2** showed much higher activity toward ε-CL polymerization than that of $(C_5Me_5)_2Sm(THF)_2$[15]. The monomer conversion could be achieved in 1 min rather than 1 h for $(C_5Me_5)_2Sm(THF)_2$ in the same condition. The molecular weights of the obtained polymers increase from 7 700 to 26 200 with monomer-to-initiator ratios increasing from 100 to 400 with a moderate PDI (1.24~1.62). One of the factors to explain such disparity is that these two seemingly similar ligands adopted different π-delocalization modes. Once the caprolactone introduced, a η^5-η^3-η^1 allyl transformation of the pentadienyl could take place more readily than cyclopetadienyl due to the small loss of resonance delocalization energy. These results are compared to the previous investigation of ethylene polymerization catalyzed by pentadienyl chromium complexes.

Table 2　Polymerization of ε-caprolactone by complexes 1 and 2[a]

Entry	Complex	c_{CL} / c_{Ln}	Yield[b] / %	M_n[c]	M_w / M_n
1	**1**	100	99	1.34×10^4	1.40
2	**2**	100	99	1.37×10^4	1.24
3	**2**	200	99	2.47×10^4	1.39
4	**2**	400	99	4.68×10^4	1.62

[a] Polymerization conditions: 5 mL of toluene, 10 μmol of Ln, 25 ℃, 1 min; [b] Yield: weight of polymer obtained/weight of monomer used; [c] Measured by GPC in THF at 40 ℃ using the polystyrene standard

3　Conclusions

Hydrocarbon soluable bis (2,4-^{t}Bu$_2$-pentadienyl) Sm and Yb complexes have been synthesized and crystallographically characterized. Crystal structures disclose the η^5-pentadienyl-metal bonding mode. The introduction of ^{t}Bu in the 2,4-position of pentadiene enhanced the sterically demanding, provided a promise for stabilized the divalent Yb and Sm centre. Compared with typical samarium metallocene, complexes **1** and **2** showed higher activities toward ε-caprolactone polymerization with narrow polydispersities.

Supporting information (The crystal data and structure refinement for complexes **1** and **2**, ^{1}H NMR of complexes **1**) is available at http://www.wjhxxb.cn

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