4980 *Organometallics* **2004,** *23,* 4980−4986

Selective Synthesis, Structure, and Catalytic Behavior of *meso*-Divalent 1,1′-(3-Oxapentamethylene)-Bridged Bis(indenyl)lanthanidocenes[†]

Changtao Qian,[*] Gang Zou,[‡] Weihua Jiang, Yaofeng Chen, Jie Sun, and Nan Li

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Science, 354 Fenglin Road, Shanghai 200032, People's Republic of China

Received April 6, 2004

Mesomeric divalent 1,1′-(3-oxapentamethylene)-bridged bis(indenyl)lanthanidocenes, *meso*-$[O(CH_2CH_2C_9H_6)_2]Ln\cdot(DME)$ (Ln = Sm (**2**),Yb (**3**)), have been synthesized by reduction of a mixture of *rac*/*meso*-$[O(CH_2CH_2C_9H_6)_2]LnCl\cdot THF$ (Ln = Sm, Yb) with Na or reaction of LnI_2 (Ln = Sm, Yb) with $[O(CH_2CH_2C_9H_6K)_2]$ in THF followed by recrystallization in DME. The structures of these *meso*, *ansa*-lanthanidocenes were determined by X-ray diffraction analysis. The factors that dictated the *rac*/*meso* selectivity are discussed. Nonbridged divalent lanthanide complexes $(CH_3OCH_2CH_2C_9H_6)_2Ln^{II}$ (Ln = Sm (**4**), Yb (**5**)) were also synthesized for comparison by the reaction of LnI_2 (Ln = Sm, Yb) with $(CH_3OCH_2CH_2C_9H_6)_2K$ in THF. Stereoselective polymerization of methyl methacrylate with these divalent lanthanide complexes as single-component catalysts was preliminarily investigated.

Introduction

In the past two decades, organolanthanide complexes have drawn much attention.[1] However, the research of divalent lanthanides is far less in-depth than that of trivalent ones,[2] although the divalent lanthanides can effect various reactions,[3] such as activation of small molecules containing multiple bonds, N_2,[4] CO,[5] alkene,[6] alkyne,[7] and carbonyl,[8] as well as polymerization of ethylene, styrene,[9] acrylonitrile,[10] and methyl methacrylate (MMA).[11] Samarium, europium, and ytterbium are the only lanthanide elements that exhibit an extensive chemistry in the oxidation state +II, among which samarium and ytterbium have more negative reduction potential and more extensive reducing ability.[12] Cyclopentadienyl and its sterically demanding derivatives, especially $C_5Me_5^-$, have represented the most successful supporting ligand for stabilization of divalent organolanthanide complexes.[13] In addition, cyclopentadienyl ligands modified with functional groups, in particular ether, have also been used to stabilize divalent lanthanidocenes.[14] The indenyl ligand, as an

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[†] This paper is dedicated to Professor Lixin Dai on the occasion of his 80th birthday.

[*] To whom correspondence should be addressed. Fax: 0086-21-64166128. E-mail: qianct@pub.sioc.ac.cn.

[‡] Present address: Department of Chemistry, East China Normal University, 3663 North Zhongshan Rd., Shanghai 200062, China.

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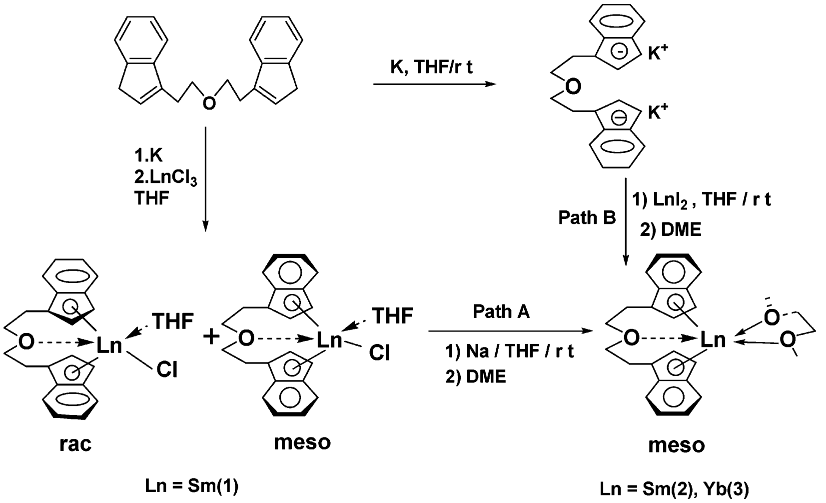
Scheme 1



aromatic derivative of cyclopentadienyl, has recently found increasing applications in organolanthanide chemistry.[15] In our previous work, we have introduced the 1,1′-(3-oxapentamethylene)-bridged bis(indenyl) ligand for planar chiral lanthanidocenes and found direct amidation or alkylation of the *rac*/*meso* (ca. 6:1) mixture of $[O(CH_2CH_2C_9H_6)_2]LnCl\cdot THF$ provided solely pure racemic *ansa*-lanthanidocene amides $[O(CH_2CH_2C_9H_6)_2]LnN(TMS)_2$ or hydrocarbyls $[O(CH_2CH_2C_9H_6)_2]LnCH_2TMS$.[16] We suggested that interconversion of racemic and mesomeric *ansa*-lanthanidocenes took place during the reaction through equilibrium in solution between *rac* and *meso* isomers of the above *ansa*-lanthanidocenes with the bridged indenyl ligand and the σ-ligand probably controlling the stereochemistry of $[O(CH_2CH_2C_9H_6)_2]LnX(sol)_n$; that is bulky σ-ligands favored *rac* isomers, while *meso* isomers would form favorably with small σ-ligands. We report here the results that substantiated the proposal by formation of mesomeric divalent complexes via reduction of the *rac*/*meso* mixture of the lanthanidocene chlorides $[O(CH_2CH_2C_9H_6)_2]LnCl\cdot THF$ with Na.[17] Polymerization of MMA using these *ansa*-lanthanidocenes and bis(2-methoxyethylindenyl) lanthanide(II) complexes as single-component catalysts was also investigated.

Results and Discussion

Synthesis. The divalent *ansa*-1,1′-(3-oxapentamethylene)-bridged bis(indenyl)lanthanidocenes were synthesized as described in Scheme 1. $[O(CH_2CH_2C_9H_6)_2]SmCl\cdot THF$ (**1**) was synthesized by reaction of $SmCl_3$ with $[O(CH_2CH_2C_9H_6K)_2]$ in THF following our previously reported procedure for the synthesis of $[O(CH_2CH_2C_9H_6)_2]YbCl\cdot THF$.[16] Complexes of *meso*-$[O(CH_2CH_2C_9H_6)_2]Ln\cdot(DME)$ (Ln = Sm (**2**), Yb (**3**)) were synthesized by reduction of the mixture of *rac*/*meso*-$[O(CH_2CH_2C_9H_6)_2]LnCl\cdot THF$ with Na in THF and purified by recrystallization in DME in 75−80% yields (Scheme 1, path A). In sharp contrast to alkylation or amidation of these *ansa*-lanthanide chlorides, divalent *meso*-complexes, *meso*-$[O(CH_2CH_2C_9H_6)_2]Ln\cdot(DME)$, were obtained. To examine the effect of the synthetic route on the stereostructure of the resulting divalent *ansa*-lanthanidocenes **2** and **3**, both of them were also prepared by reaction of LnI_2 with $O(CH_2CH_2C_9H_6)_2K$ in THF and recrystallized in DME in 35−42% yields (Scheme 1, path B). These results unmistakably confirmed that synthetic procedures did not affect the stereochemistry of *ansa*-lanthanidocenes with the 1,1′-(3-oxapentamethylene)-bridged bis(indenyl) ligand, supporting our suggestion that the bulk of the σ-ligand controlled the stereoselectivity of the *ansa*-lanthanidocenes through an equilibrium between *rac* and *meso* isomers in solution and the interconversion of *rac* and *meso* *ansa*-lanthanidocenes took place during the reaction. Dimethoxyethane (DME) satisfied the coordination requirement of the central lanthanide but did not lead to strong steric interactions with indenyl moieties. Thereby, mesomeric complexes *meso*-$[O(CH_2CH_2C_9H_6)_2]Ln\cdot(DME)$ (Ln = Sm, Yb) were afforded.

Similar to path B, nonbridged complexes $(CH_3OCH_2CH_2C_9H_6)_2Ln$ (Ln = Sm (**4**), Yb (**5**)) were prepared by the reaction of LnI_2 with $(CH_3OCH_2CH_2C_9H_6)K$ and recrystallized in THF (Scheme 2). By this way, $(CH_3OCH_2CH_2C_9H_6)_2Yb$ (**5**) is an oil material. To facilitate the handling, it was treated with 2,2′-bipyridine in THF solution, and a black solid $[(CH_3OCH_2CH_2C_9H_6)_2Yb]_2(bipy)_3$ (**6**) was obtained in 56% yield.

All these complexes are air and moisture sensitive. Complexes **2** and **3** are soluble in THF, but just slightly soluble in toluene, while nonbridged complexes (**4** and **5**) are very soluble in THF, DME, and toluene and sparingly soluble in hexane. Elemental analyses and spectroscopic data indicated complexes **4**, **5**, and **6** are solvent-free.

Spectroscopic Properties. The electronic impact mass spectrum of complex **1** showed the parent molec-

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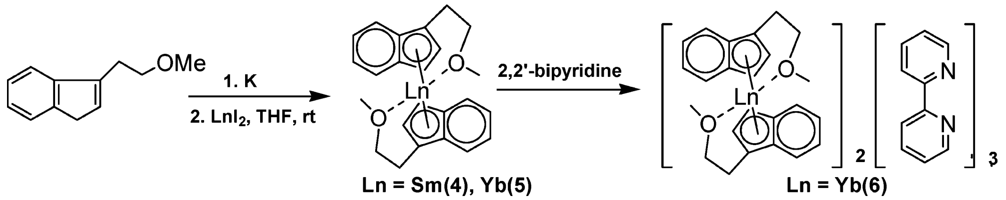
Scheme 2



ular ion [M − thf]$^+$ and relative fragments such as [M − thf − Cl]$^+$ and 142 [$C_{11}H_{10}$]$^+$, while complexes **2** and **3** gave no fragment containing metal. ^{1}HNMR spectra of the diamagnetic complexes **3**, **5**, and **6** were recorded in THF-d_8. For **3**, the protons on the six- and five-membered rings of the indenyl groups were found at 7.45 and 6.75 ppm and 6.55, 6.00, and 5.85 ppm as broad signals, respectively, indicating a flexible solution structure, in sharp contrast to the unsymmetric structure of the corresponding trivalent lanthanide complexes, in which two sets of signals were found for the protons of bridged indenyls. For complex **5**, the protons of the six-membered ring of the indenyl moieties were found at 7.2−7.45 ppm, with those of five-membered ring at 6.78 and 5.70 ppm as broad signals, showing a symmetric and flexible structure as expected. The ^{1}HNMR spectrum of **6** is similar to that of **5**, although the signals of bipy are partly overlapped with signals of the aromatic ring of indenyl groups at 7.2−7.45 ppm, implying that their structures were essentially identical. The signals at 8.68, 8.57, and 7.88 ppm in the ^{1}HNMR of **6** were assigned to the bipyridyl protons. In FT-IR and Raman spectra, all these complexes **1**−**5** showed the typical indenyl absorptions at 3073, 1441, 1000, and 741 cm^{-1}.

Molecular Structures. The molecular structures of **1**, **2**, and **3** were determined by single-crystal X-ray diffraction. ORTEP drawings are shown in Figures 1, and 3, respectively. The crystallographic data and refinements are given in Table 1, and selected structural data are listed in Table 2.

X-ray analysis revealed that complex **1** is racemic in the solid state and crystallizes in the monoclinic system with the *P*2/*n* space group, while complexes **2** and **3** are mesomeric isomers and in the orthorhombic system with the $P2_12_12_1$ space group. The intramolecular coordination between oxygen and the central metal ion was observed in all the above complexes. The distance between oxygen in the bridge and the metal ion in **1** is 2.531(5) Å, significantly shorter than that in **2** (2.626(5) Å). However, there is only a slight difference if the ionic radii of Sm^{2+} (1.10 Å) and Sm^{3+} (0.96 Å) were taken into account. Similarly, the Yb−O distance in **3** (2.506(6) Å) is longer than that in [$O(CH_2CH_2C_9H_6)_2$]YbCl(THF) (2.407(4) Å)[16c] without consideration of the ionic radii of Yb^{2+} (0.90 Å) and Yb^{3+} (0.86 Å).

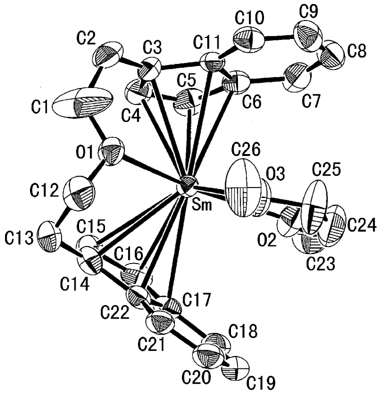


Figure 2. ORTEP diagram of *meso*-[$O(CH_2CH_2C_9H_6)_2$]Sm·DME (**2**).

The X-ray structure analysis showed an unsymmetric structure for **1** with two indenyl groups coordinating the metal ion in a *trans* orientation and forming a racemic structure. Both indenyl groups showed a η^5-coordination to the metal ion with a normal distance ranging from 2.724(6) to 2.871(6) Å and 2.751(6) to 2.793(5) Å, respectively. Similar to that observed in the series of complexes [$O(CH_2CH_2C_9H_6)_2$]LnCl(THF), the gradient degree of two indenyl groups is different in complex **1**. One indenyl ring slipped more, with the Δ_{Ln-C} defined as the difference of the longest and the shortest bond lengths between the lanthanide ion and the indenyl ligand, reaching 0.15 Å, while only 0.04 Å for the other

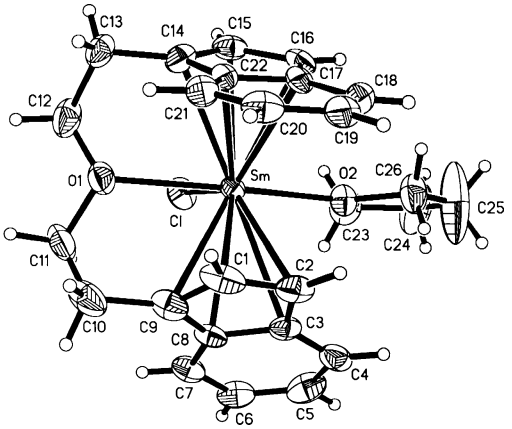


Figure 1. ORTEP diagram of *rac*-[$O(CH_2CH_2C_9H_6)_2$]SmCl·THF (**1**).

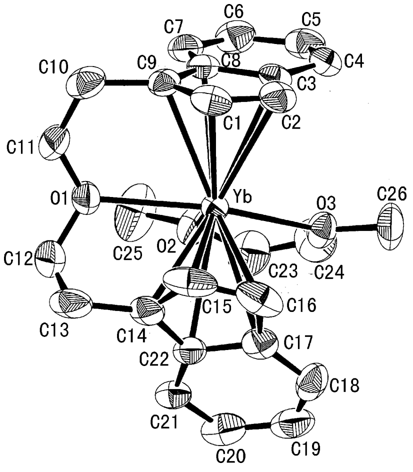


Figure 3. ORTEP diagram of *meso*-[$O(CH_2CH_2C_9H_6)_2$]Yb·DME (**3**).

Table 1. Details of the Crystallographic Data and Refinements

	1	**2**	**3**
formula	$C_{26}H_{28}ClO_2Sm$	$C_{26}H_{30}O_3Sm$	$C_{26}H_{30}O_3Yb$
fw	558.28	540.92	563.56
cryst size, mm	0.2 × 0.2 × 0.3	0.2 × 0.2 × 0.3	0.2 × 0.2 × 0.3
color	red	red	red
cryst syst	monoclinic	orthorhombic	orthorhombic
space group	$P2(1)/n$	$P2_12_12_1$(#19)	$P2_12_12_1$(#19)
a, Å	11.180(4)	14.872(5)	14.767(4)
b, Å	10.331(4)	17.124(4)	16.988(3)
c, Å	20.759(8)	9.095(2)	8.994(3)
α, deg	90	90	90
β, deg	98.739(6)	90	90
γ, deg	90	90	90
V, Å^3	2369.9(16)	2316(1)	2256(1)
Z	4	4	4
D_{calcd}, Mg/m^3	1.565	1.551	1.659
F(000)	1116	1088.00	112.
μ, cm^{-1}	26.09	25.64	41.69
θ range (deg)	1.96−26.00	2.25−27.45	2.3−27.5
no. of refins collected	12 128	2852	2956
no. of ind reflns	4630	2852	2956
no. of obsd data	3979 ($I > 2\sigma(I)$)	2527 ($I > 2\sigma(I)$)	2531 ($I > 2\sigma(I)$)
no. of params	272	272	272
GOF	1.087	1.49	1.23
final R, R_w[a]	0.0577 0.1518	0.030, 0.037	0.032, 0.037
$\nabla\rho_{max,min}$, e·Å^{-3}	1.853, −2.221	0.86, −1.14	1.33, −0.69

indenyl group. However, for divalent complex **2**, the two bridged indenyl groups coordinated the lanthanide ion with a *cis* orientation in a η^5-coordination form and almost overlapped. The angles O(1)−Sm−O(2), O(1)−Sm−O(3), and O(2)−Sm−O(3) are 150.1(2)°, 85.4(2)°, and 64.8(2)°, respectively, showing the atoms of O(1), O(2), O(3), and Sm are coplanar. The coordination polyhedron of Sm in **2** can be described as a distorted triangle bipyramid. The bond distances of the lanthanide ion to the fused carbon atoms in the indenyl groups (Sm−C$_{fused}$) are 2.920(6)−2.962(7)Å and 2.886(7)−2.902(6) Å, respectively, longer than the remaining three Sm−C bonds, 2.832(7), 2.839(6), 2.899(7) Å and 2.836(7), 2.862(7), 2.860(7) Å. The Δ_{Ln-C} values for the two bridged indenyl groups are 0.13 and 0.07 Å, respectively. A significant difference between C(1)−C(2) (1.40(1) Å) and C(12)−C(13) (1.54(1) Å) was observed, which has not been observed in the trivalent lanthanide complexes bearing the same bridged indenyl ligand. It was concluded that minimization of nonbonded repulsion between the indenyl ring and the DME molecule could be attributed not only to adopting a mesomic structure but also to the distortion of the ether bridge chain. From the crystal structure of **2**, the coordinated DME approached the Sm ion from the open side of the bent *ansa*-lanthanidocene structure. Interestingly, the coordinated DME was oriented *parallel* to the indenyl moiety, indicating the repulsive interactions between the six-membered portion of the indenyl groups and the DME frame are small, if one could not say the interactions are attractive. The bond angles of O(1)−Sm−O(2) (150.1(2)°) and O(1)−Sm−O(3) (85.4(2)°) are consistent with a *parallel* orientation of DME and the bridged indenyl groups. If the divalent complex **2** adopted a racemic structure, i.e., a *trans* orientation for the bridged indenyl groups, the coordinated DME frame would have a strong repulsive interaction with at least one of the indenyl groups. Complex **3** has a structure similar to **2**, but the Δ_{Ln-C} values are 0.23 and 0.11 Å for the two bridged indenyl groups, respectively, bigger than those in **2**, indicating the indenyl gradient degree in **3** is larger than that in **2** due to the smaller metal ion size that leads to the more crowed coordination environment around the ytterbium ion. However, in **3**, the distances of three Yb−O bonds are 2.468(6), 2.447(7) Å (DME) and 2.506(6) Å ($(CH_2CH_2)_2O$), respectively, similar to those observed in $[O(CH_2CH_2C_5H_4)_2Yb(DME)]$ (2.468, 2.494 Å (DME), 2.488 Å ($-CH_2CH_2)_2O$),[2a] owing to the so-called indene effect through the slippage of the indenyl group from the η^5 to η^3 coordination mode.

rac/meso **Selectivity for $O(CH_2CH_2C_9H_6)_2LnX$.** Control of the *rac/meso* selectivity in the synthesis of planar chiral *ansa*-metallocenes has been the subject of extensive research. With the 1,1′-(3-oxapentamethylene)-bridged bis(indenyl) ligand, we have previously obtained a *rac/meso* (ca. 6:1) mixture of $[O(CH_2CH_2C_9H_6)_2LnCl(THF)]$ in solution. Redissolving the pure *rac*-$[O(CH_2CH_2C_9H_6)_2LnCl(THF)]$ in THF led to the original *rac/meso* mixture, indicating an equilibrium between the racemic and mesomeric isomers in coordinative solvents such as THF. The formation of sole racemic *ansa*-lanthanidocene amides $[O(CH_2CH_2C_9H_6)_2]LnN(TMS)_2$ and hydrocarbyls $[O(CH_2CH_2C_9H_6)_2]LnCH_2TMS$ as well as *meso*-$[O(CH_2CH_2C_9H_6)_2]Ln^{II}(DME)$ (Ln = Sm (**2**), Yb (**3**)) from the same racemic and mesomeric mixture starting materials $[O(CH_2CH_2C_9H_6)_2LnCl(THF)]$ not only supported the equilibrium but also led to the conclusion that σ-ligands play a critical role in the stereochemistry of $[O(CH_2CH_2C_9H_6)_2LnX$. Bulkyl σ-ligands favored the racemic *ansa*-lanthanidocenes with a *trans* orientation for the two bridged indenyl moieties to minimize the repulsive interactions among them, while releasing the repulsive interactions between the indenyl and σ-ligands led to the conversion of racemic isomers to a mesomeric one, *meso*-$[O(CH_2CH_2C_9H_6)_2]Ln^{II}(DME)$ (Scheme 3).

Polymerization of Methyl Methacrylate. Lanthanidocenes have been found to efficiently catalyze highly stereospecific polymerization of MMA,[18] producing polymeric methyl methacrylate (PMMA), the widely used polymer. We have reported C_{2v}-, C_1-, and C_s-symmetric *ansa*-lanthanidocenes for MMA stereospecific polymerization and found that the structure of *ansa*-lanthanidocenes had a significant effect on polymerization.[16c,19] The above divalent *ansa, meso*-lanthanidocenes **2** and **3** were also found to be single-component catalysts for methyl methacrylate polymerization and displayed syndiotactic selectivity (Table 3), while the corresponding *ansa, rac*-lanthanidocene amides $[O(CH_2CH_2C_9H_6)_2]LnN(TMS)_2$ and hydrocarbyls $[O(CH_2CH_2C_9H_6)_2]LnCH_2TMS$ produced isotactic polymers. Polymerization of MMA with divalent lanthanidocenes was proposed to proceed via the formation of a bimetallic initiator of trivalent lanthanidocenes.[18f] However, the stereochemistry of the resulting PMMA using our mesomeric divalent 1,1′-(3-oxapentamethylene)-bridged

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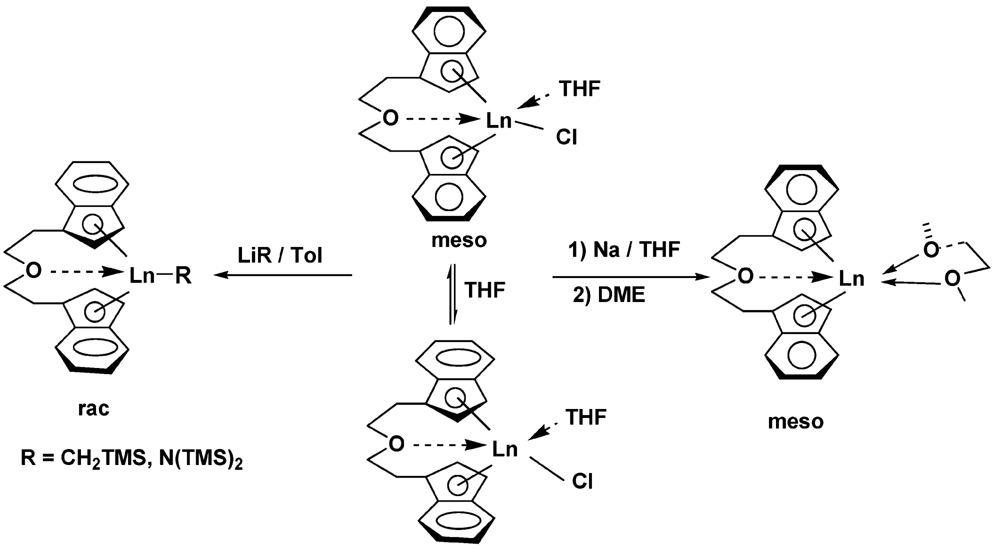
Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes 1, 2, and 3

1		2		3	
Sm–Cl	2.6697(17)	Sm–O(1)	2.626(5)	Yb–O(1)	2.506(6)
Sm–O(1)	2.531(5)	Sm–O(2)	2.575(5)	Yb–O(2)	2.447(7)
Sm–O(2)	2.514(5)	Sm–O(3)	2.578(6)	Yb–O(3)	2.468(6)
Sm–C(1)	2.724(6)	Sm–C(3)	2.839(6)	Yb–C(1)	2.704(9)
Sm–C(2)	2.742(6)	Sm–C(4)	2.832(7)	Yb–C(2)	2.752(9)
Sm–C(3)	2.871(6)	Sm–C(5)	2.899(7)	Yb–C(3)	2.818(9)
Sm–C(8)	2.863(6)	Sm–C(6)	2.962(7)	Yb–C(8)	2.806(9)
Sm–C(9)	2.780(7)	Sm–C(11)	2.920(6)	Yb–C(9)	2.719(8)
Sm–C(14)	2.751(6)	Sm–C(14)	2.862(7)	Yb–C(14)	2.744(8)
Sm–C(15)	2.751(7)	Sm–C(15)	2.836(7)	Yb–C(15)	2.69(1)
Sm–C(16)	2.767(6)	Sm–C(16)	2.860(7)	Yb–C(16)	2.78(1)
Sm–C(17)	2.789(5)	Sm–C(17)	2.902(6)	Yb–C(17)	2.92(1)
Sm–C(22)	2.793(5)	Sm–C(22)	2.886(6)	Yb–C(22)	2.88(1)
C(12)–C(13)	1.553(12)	O(1)–C(1)	1.32(1)	O(1)–C(11)	1.29(1)
C(11)–C(12)	1.518(13)	O(1)–C(12)	1.381(10)	O(1)–C(12)	1.38(1)
Cl–Sm–O(1)	80.01(12)	C(1)–C(2)	1.40(1)	O(2)–C(23)	1.38(1)
Cl–Sm–O(2)	83.21(10)	C(2)–C(3)	1.469(10)	O(2)–C(25)	1.43(1)
O(1)–Sm–O(2)	163.22(15)	C(12)–C(13)	1.54(1)	O(3)–C(24)	1.40(2)
		C(13)–C(14)	1.50(1)	O(3)–C(26)	1.43(1)
		O(2)–C(23)	1.39(1)	C(11)–C(10)	1.38(2)
		O(2)–C(24)	1.42(1)	C(12)–C(13)	1.53(2)
		O(3)–C(25)	1.35(1)	C(23)–C(24)	1.39(2)
		O(3)–C(26)	1.39(1)	C(10)–C(9)	1.52(1)
		C(24)–C(25)	1.37(2)	C(23)–C(24)	1.48(2)
		O(1)–Sm–O(2)	150.1(2)	O(1)–Yb–O(2)	81.3(2)
		O(1)–Sm–O(3)	85.4(2)	O(1)–Yb–O(3)	147.9(2)
		O(2)–Sm–O(3)	64.8(2)	O(2)–Yb–O(3)	66.6(2)

Scheme 3



bis(indenyl)lanthanidocenes as initiators was obviously different from the corresponding racemic trivalent ones, indicating that the true mechanism might not be that simple and needs further investigation.

The polymerization temperature has a great effect on the polymerization of MMA. Decreasing the reaction temperature from 0 to −78 °C, the conversion of MMA with **2** dramatically increased to 98% from almost 0%, while complex **3** completely lost its activity at −78 °C.

In DME and toluene, both **2** and **3** displayed some activity at 0 °C. However, the resulting PMMA was found to be insoluble in THF and failed to pass through the GPC columns, making it infeasible to measure the molecular weight and molecular weight distributions of these polymers. Nonbridged lanthanidocenes **4** and **5** showed higher activities than **2** and **3**, while all these complexes displayed syndiotactic selectivity in the polymerization of MMA under otherwise identical conditions. Decreasing the reaction temperature from 0 to −78 °C, the conversion of MMA with **5** increased from 88% to 98%, but the activity of **4** decreased. The molecular weight increased dramatically when the reaction temperature was lowered. Thus a high molecular weight ($M_w = 1.38 \times 10^5$) with a narrow molecular distribution (M_w/M_n = 1.68) and 78% syndiotactic polymer was produced with **5** at −78 °C.

Conclusion

In summary, we have shown that *meso*-[O(CH$_2$CH$_2$C$_9$H$_6$)$_2$]Ln^{II}(DME) lanthanidocenes could be obtained by direct reduction of the racemic and mesomeric mixture of lanthanidocene chlorides [O(CH$_2$CH$_2$C$_9$H$_6$)$_2$LnCl(THF)] or reaction of LnI$_2$ with [O(CH$_2$CH$_2$C$_9$H$_6$)$_2$K$_2$,

Table 3. Polymerization of MMA at Different Temperature and Solvent

catalyst	solvent	T (°C)	conversion (%)	microstructure rr	microstructure mr	microstructure mm	$M_w \times 10^4$	$M_n \times 10^4$	M_w/M_n
2	THF	0	inactive						
	THF	−78	98	40	53	7	48.1	13.3	3.60
	toluene[a]	0	12	59	21	20			
	DME[a]	0	46	41	22	37			
3	THF	0	40	61	27	12	9.43	3.51	2.69
	THF	−78	inactive						
	toluene[a]	0	26	58	25	16			
	DME[a]	0	26	61	26	13			
4	THF	0	98	31	56	13	6.75	3.44	1.96
	THF	−78	75	65	30	5	16.9	7.22	2.34
	toluene	0	94	29	46	25	8.81	3.07	2.87
	DME	0	89	40	50	10	3.34	1.71	1.95
5	THF	0	88	35	53	12	9.54	5.24	1.82
	THF	−78	98	78	20	2	13.8	8.19	1.68
	toluene[a]	0	69	32	32	36			
	DME	0	93	46	45	9	11.0	4.63	2.38

[a] Part of the PMMA was insoluble in THF, making the measurement of molecular weight and molecular weight distribution of these polymers infeasible.

indicating the stereochemistry of these *ansa*-lanthanidocenes obtained was independent of the synthesis procedures. The results presented here further substantiated the existence of an equilibrium and interconversion between the racemic and mesomeric isomers of *ansa*-lanthanidocenes $O(CH_2CH_2C_9H_6)_2LnX$. Polymerization of methyl methacrylate by the divalent *ansa*, *meso*-lanthanidocenes *meso*-$[O(CH_2CH_2C_9H_6)_2]Ln^{II}(DME)$ was briefly investigated, showing a syndiotactic selectivity that is in contrast to polymerization with the corresponding *ansa*, *rac*-$O(CH_2CH_2C_9H_6)_2LnR$ as catalysts. For comparison, nonbridged lanthanidocenes $[(CH_3OCH_2CH_2C_9H_6)_2Ln^{II}]$ were also synthesized and used as catalysts in the polymerization of methyl methacrylate and were found to be more active as single-component catalysts with a strong activity and tacticity dependence on temperature and solvents.

Experimental Section

General Procedures. All operations involving organometallics were carried out under an inert atmosphere of argon using standard Schlenk techniques. Tetrahydrofuran, toluene, and 1,2-dimethoxyethane were distilled under argon from sodium-benzophenone prior to use. Anhydrous lanthanide diiodides were prepared according to the literature.[20] The *rac*/*meso* mixture of $[O(CH_2CH_2C_9H_6)_2]LnCl$ (THF) and $[O(CH_2CH_2C_9H_6K)_2]$ was synthesized following the procedures previously reported.[16] $[^2H_8]$-Tetrahydrofuran was degassed and dried over Na/K alloy. IR and FT-Raman spectra were recorded using Perkin-Elmer 983 and Bio-Rad FT-Raman spectrometers. Mass spectra were recorded with a HP5989A spectrometer (50−400 °C, 1.3 kV). ^1H NMR spectra were performed on a Bruker Am-300 (300 MHz) spectrometer. Elemental and GPC analyses were performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry.

Synthesis of *rac*/*meso* Mixture of $[O(CH_2CH_2C_9H_6)_2]SmCl$ (THF) (1). To a suspension of $SmCl_3$ (1.32 g, 5.1 mmol) at room temperature was added by syringe a THF solution of $[O(CH_2CH_2C_9H_6K)_2]$ (2.0 g, 5.3 mmol in 40 mL). The mixture was stirred for 2 days. The precipitate was separated, and the resulting clear solution was concentrated until a solid appeared. The crude product was washed with cool THF (10 mL) and dried in vacuo at room temperature, affording 1.2 g (42%) of a *rac*/*meso* mixture of $[O(CH_2CH_2C_9H_6)_2]SmCl$ (THF). Anal. Calcd for $C_{26}H_{28}O_2ClSm$: C, 55.92; H, 5.02. Found: C, 55.76; H, 5.09. EI mass spectrum (70 ev, 50−400 °C, based on ^{152}Sm): m/z 487 ($[M - thf]^+$), 452 (1.55, $[M - thf - Cl]^-$), and 142 (100.0). IR (cm^{-1}): 3065 (m), 3030 (sh), 3018 (m), 2929 (s), 2857 (s), 1684 (w), 1653 (w), 1609 (m), 1576 (m), 1459 (m), 1439 (m), 1397 (m), 1380 (m), 1339 (m),1286 (m), 1205 (m), 1171 (m), 1120 (s), 1080 (w), 1055 (m), 1023 (m), 966 (m), 918 (m), 873 (m), 772 (m), 746 (m), 721 (m), 673 (m), 439 (m), 330 (m). FT-Raman (cm^{-1}): 3080 (sh), 3038 (m), 2966 (m), 2910 (m), 1526 (m), 1338 (m), 1001 (s), 1440 (m), 871 (m), 740 (s). *rac*-$[O(CH_2CH_2C_9H_6)_2]SmCl$ (THF) (**1**) was obtained by recrystallization of a *rac*/*meso* mixture of $[O(CH_2CH_2C_9H_6)_2]SmCl$-(THF) in THF.

Synthesis of *meso*-$[O(CH_2CH_2C_9H_6)_2]Sm^{II}(DME)$ (2). Path A. To a suspension of 1.10 g (1.97 mmol) of a mixture of *rac*- and *meso*-$[O(CH_2CH_2C_9H_6)_2]SmCl$ (THF) in 70 mL of THF was added 0.18 g (7.8 mmol) of Na at room temperature under stirring. The color changed from red to black-red. The resulting suspension was stirred for 3 days under an atmosphere of argon. The precipitate was separated by centrifugation, and the resulting clear solution was concentrated. The residue foamy solid was extracted with THF (4 × 5 mL). Then, hexane was added to the THF solution until a solid appeared. The precipitate was isolated and recrystalized in 20 mL of DME at −30 °C. A total of 0.79 g (75%) of **2** was obtained as black-red crystals. Anal. Calcd for $C_{26}H_{30}O_3Sm$: C, 57.74; H, 5.55. Found: Path A: C, 56.92; H, 5.59. Path B: C, 57.93; H, 4.97. FT-Raman (cm^{-1}): 3080 (m), 3040 (m), 2940 (m), 2890 (m), 1520 (m), 1480 (m), 1460 (m), 1440 (m), 1330 (m), 1142 (m), 742 (m).

Path B. To a suspension of SmI_2 (0.990 g, 2.45 mmol in 10 mL of THF) was added a solution of $[O(CH_2CH_2C_9H_6K)_2]$ (0.926 g, 2.45 mmol in 10 mL of THF) at room temperature. The mixture was stirred for 2 days. The precipitate was separated by centrifugation. The resulting clear solution was concentrated to 10 mL, and hexane was added until a solid appeared. The precipitate was isolated and recrystallized in 10 mL of DME at −30 °C. A total of 0.40 g (36%) of **2** was obtained as black-red crystals.

Synthesis of *meso*-$[O(CH_2CH_2C_9H_6)_2]Yb^{II}(DME)$ (3). Procedures similar to those for complex **2** were adopted for reduction of a mixture of *rac*/*meso*-$[O(CH_2CH_2C_9H_6)_2]YbCl\cdot$(THF) (0.96 g, 1.65 mmol) with Na(0.15 g, 6.5 mmol) or reaction of $[O(CH_2CH_2C_9H_6K)_2]$ (0.990 g, 2.62 mmol in 21.1 mL) with YbI_2 (1.12 g, 2.62 mmol), respectively, and both afforded **3** as red crystals (0.74 g, 80%, and 0.52 g, 42%). Anal. Calcd for $C_{26}H_{30}YbO_3$: C, 55.42; H, 5.33. Found: Path A: C, 54.51; H, 5.16. Path B: C, 55.27; H, 4.61. ^1H NMR (300 MHz, C_4D_8O, 25 °C): δ (ppm) 7.45(m, 4H, aromatic), 6.75 (m, 4H, aromatic), 6.55 (m, 2H, indenyl), 6.00 and 5.85 (v br, over-

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lapped, s, 2H, indenyl), 4.30−3.95 (m, 4H, OCH_2 (bridge)), 3.35 (s, 6H, CH_3O (DME)), 3.20 (s, 4H, OCH_2 (DME)), 3.10−2.90 (m, 4H, CH_2CH_2O (bridge)). FT-Raman (cm^{-1}): 3073 (m), 3028 (m), 2942 (m), 2897 (m), 2845 (m), 1525 (m), 1482 (m), 1463 (m), 1441 (m), 1330 (s), 1285 (m), 1183 (w), 1153 (w), 1122 (w), 1080 (w), 1000 (m), 870 (w), 742 (m).

Synthesis of $(CH_3OCH_2CH_2C_9H_6)_2Sm^{II}$ (4). To a suspension of SmI_2 (1.35 g, 3.34 mmol in 20 mL of THF) was added a THF solution of $(CH_3OCH_2CH_2C_9H_6K)$ (2.798 g, 6.6 mmol in 20 mL) at −50 °C. The mixture was stirred for 2 days. The precipitate was separated by centrifugation. The resulting clear solution was concentrated, and hexane was added, followed by cooling to −30 °C to produce a black solid. The solid was isolated and dried in vacuo at room temperature, affording 0.59 g (36%) of **4**. Anal. Calcd for $C_{26}H_{30}SmO_3$: C, 57.74; H, 5.55. Found: C, 56.92; H, 5.59. EI mass spectrum (70 eV, 50−400 °C, based on ^{152}Sm): *m/z* 325 (0.21 $[M + 1 - L]^+$), 128 (100.0). FT-Raman (cm^{-1}): 3070 (m), 3027 (m), 1525 (m), 1482 (m), 1463 (m), 1440 (m), 1330 (s), 1000 (m), 742 (m).

Synthesis of $[(CH_3OCH_2CH_2C_9H_6)_2]Yb^{II}$ (5) and $[(CH_3OCH_2CH_2C_9H_6)_2Yb^{II}]_2(bipy)_3$ (6). A procedure similar to that for complex **4** was adopted for the reaction of $(CH_3OCH_2CH_2C_9H_6K)$ (2.267 g, 5.347 mmol in 22.5 mL) with YbI_2 (1.141 g, 2.673 mmol), which also afforded **5** as a red oil (0.73 g, 53%). EI mass spectrum (70 ev, 50−400 °C, based on ^{174}Yb): *m/z* 521 (0.01 $[M]^+$), 520 (0.04 $[M - 1]^+$), 347 (0.16 $[M - L]^+$), 142 (100.0). ^1H NMR (300 MHz, C_4D_8O, 25 °C): δ (ppm) 7.46−7.20 (m, 8H, aromatic), 6.77 (m, 2H, indenyl), 6.36 (br s, 1H, indenyl), 5.78 (v br, 1H, indenyl), 4.05 (m, 2H, OCH_2), 3.41 (s, 6H, OCH_3), 3.31 (s, 2H, CH_2), 3.12 (m, 2H, OCH_2), 2.91 (s, 2H, CH_2). FT-Raman (cm^{-1}): 3070 (m), 3029 (m), 2903 (m), 2843 (m), 1521 (m), 1460 (m), 1438 (m), 1328 (s), 999 (m), 738 (m). To obtain solid materials, 0.3 g (1.92 mmol) of 2,2′-bipyridine in 5 mL of THF was added to the THF solution of **5**. The color changed from red to black-red. The resulting suspension was stirred for 1 day under an atmosphere of argon. The precipitate was separated by centrifugation, and the clear solution was concentrated until a solid appeared. The precipitate was separated and recrystalized in THF, which afforded **6** as black solid (0.59 g, 56%). Anal. Calcd for $C_{39}H_{38}YbN_3O_2$: C, 61.97; H, 5.29; N, 5.64. Found: C, 62.01; H, 5.48; N, 5.51. ^1H NMR (300 MHz, C_4D_8O, 25 °C): δ (ppm) 8.68 (m, 2H, bipyridyl), 8.57 (pseudo doublet, 2H, bipyridyl), 7.88 (m, 2H, bipyridyl), 7.46−7.19 (m, 10H, aromatic), 6.80 (m, 2H, indenyl), 6.32 (br s, 1H, indenyl), 5.71 (v br, 1H, indenyl), 3.95 (m, 2H, OCH_2) 3.10 (m, 2H, OCH_2), 3.35 (s, 6H, OCH_3), 3.37 (br s, 2H, CH_2), 2.93 (br s, 2H, CH_2). FT-Raman (cm^{-1}): 3064 (m), 3025 (m), 2902 (m), 1593 (m), 1573 (m), 1483 (m), 1445 (m), 1328 (s), 1302 (m), 1236 (m), 1044 (w), 1018 (w), 995 (s), 762 (m).

X-ray Structure Determination. Single crystals of **1**, **2**, and **3** suitable for X-ray diffraction analysis were obtained by recrystallization in THF and DME, respectively. Owing to air- and moisture-sensitivity, the single crystals of **1**, **2**, and **3** were sealed in thin-walled glass capillaries. In the case of **1**, some mother liquor was added. Data were collected on a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation, $\lambda = 0.71.69$ Å, using the $\omega-2\theta$ technique at 20 °C. The data were corrected for Lorentz−polarization effects; an empirical absorption correction was applied using the program DIFABS for **1** or based on azimuthal scans of several reflections for **2** and **3**. The structures were solved by direct methods for **1** or heavy-atom Patterson methods for **2** and **3** and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically by full-matrix least squares. Hydrogen atoms were included but not refined. Scattering factors were taken from ref 17. All calculations were performed using the TFXSAN crystallographic software package.

Polymerization of MMA. All polymerization reactions were carried out under argon. MMA was added to the solution of the catalysts 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 50 °C.

Acknowledgment. We are grateful to Natural Science Foundation of China for financial support.

Supporting Information Available: X-ray crystallographic data for structure determination of **1**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049753A