

Homolysis of the Ln–N bond: Synthesis, characterization and catalytic activity of organolanthanide(II) complexes with 2-pyridylmethyl and 3-pyridylmethyl-functionalized indenyl ligands

Shaowu Wang^{a,b,*}, Yan Feng^a, Lili Mao^a, Enhong Sheng^a, Gaosheng Yang^a,
Meihua Xie^a, Shaoyin Wang^a, Yun Wei^a, Zixiang Huang^c

^a Anhui Key Laboratory of Functional Molecular Solids, Institute of Organic Chemistry, School of Chemistry and Materials Science, Anhui Normal University, Wuhu, Anhui 241000, China

^b State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

^c Fujian Institute of Research on the Structure of Matters, Chinese Academy of Sciences, Fuzhou 350002, China

Received 8 September 2005; received in revised form 28 November 2005; accepted 1 December 2005

Available online 5 January 2006

Abstract

Two series of new organolanthanide(II) complexes with general formula $\{\eta^5\text{-}\eta^1\text{-}[1\text{-R-3-(2-C}_5\text{H}_4\text{NCH}_2\text{)C}_9\text{H}_5]\}_2\text{Ln(II)}$ (R = H–, Ln = Yb (3), Eu (4); R = Me₃Si–, Ln = Yb (5), Eu (6)), and $\{\eta^5\text{-}\eta^1\text{-}[1\text{-R-3-(3-C}_5\text{H}_4\text{NCH}_2\text{)C}_9\text{H}_5]\}_2\text{Ln(II)}$ (R = H–, Ln = Yb (9), Eu (10); R = Me₃Si–, Ln = Yb (11), Eu (12)) were synthesized by silylamine elimination with one-electron reductive reactions of lanthanide(III) amides $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (Ln = Yb, Eu) with 2 equiv. 1-R-3-(2-C₅H₄NCH₂)C₉H₆ (R = H (1), Me₃Si– (2)) or 1-R-3-(3-C₅H₄NCH₂)C₉H₆ (R = H (7), Me₃Si– (8)) in good yields. All the complexes were fully characterized by elemental analyses and spectroscopic methods. Complexes 3 and 5 were additionally characterized by single-crystal X-ray diffraction study. The catalytic activities of the complexes for MMA polymerization were examined. It was found that complexes with 3-pyridylmethyl substituent on the indenyl ligands could function as single-component MMA polymerization catalysts with good activities, while the complexes with 2-pyridylmethyl substituent on the indenyl ligands cannot catalyze MMA polymerization. The temperatures and solvents effect on the MMA polymerization have also been examined.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Homolysis; Catalyst; Organolanthanide(II) complexes; Polymerization; Synthesis

1. Introduction

Organolanthanide chemistry is continuous one of the most attractive fields of chemistry for the potential applications of organolanthanide complexes as catalysts in olefins transformation and in organic synthesis [1]. Lanthanide complexes with the Ln–N bond has been proved having a diverse chemistry including catalytic reactivity and selectivity for hydroamination of olefins and alkynes [1e,2], hydrosilylation of olefins [3], hydrophosphination of olefins and alkynes [4], olefin polymerization, ring-opening polymeri-

zation of ϵ -caprolactone, δ -valerolactone and lactide [1a,1b,1c,1d,5], insertion reactions [6]. Homolytic reactivity of the Ln–N bond has been recently developed [7].

Lanthanide(II) complexes, which are normally prepared by metathesis reaction of alkaline metal salts of a ligand with LnI₂ or by reductive reaction of lanthanide(III) halides with metallic atoms [8], are one of the families of the lanthanide complexes which showed reductive chemistry to organic and inorganic compounds [9], N₂ [10], CO and CO₂ [11], as well as for olefin polymerization catalysts [1a,1b,1c,1d,7].

We have demonstrated that the interactions of (dimethylamino)ethyl-functionalized or methoxyethyl-substituted indene compounds with the lanthanide(III) amides

* Corresponding author. Tel.: +86 553 3869310; fax: +86 553 3883517.
E-mail address: swwang@mail.ahnu.edu.cn (S. Wang).

$[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ ($\text{Ln} = \text{Yb}, \text{Eu}$) produced organolanthanide(II) complexes [7a,7b,7c]. The formation pathway of the organolanthanide(II) complexes is proposed to proceed through a tandem silylamine elimination/homolysis of the Ln-N bonds, thus it provides a new methodology for the preparation of the lanthanide(II) complexes [7]. Extension of our study on the reaction of heterocyclic-functionalized indene compounds $\text{C}_9\text{H}_6\text{-1-R-3-CH}_2\text{SiMe}_2\text{NC}_4\text{H}_8$ ($\text{R} = \text{H}, \text{Me}$) with europium(III) amide $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Eu}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ has led to the isolation and characterization of the unexpected novel triple-decker tetranuclear europium(II) complex with linked indenyl ligands, and findings of a series of new single-site MMA and ϵ -caprolactone polymerization catalysts [7d,7e]. These results promoted us to extend our work on studying the reactivity of other heterocyclic-substituted indene compounds with the lanthanide(III) amides $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ ($\text{Ln} = \text{Yb}, \text{Eu}$), and to develop new catalysts for olefin transformations.

In this paper, we will report the interaction of pyridyl-methyl-functionalized indene compounds with the lanthanide(III) amides $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ ($\text{Ln} = \text{Yb}, \text{Eu}$) leading to preparation and characterization of two series of new organolanthanide(II) complexes, and the catalytic activities of the complexes as single-component MMA polymerization catalysts were also examined. The effects of polymerization conditions on the catalytic activities of the complexes will be discussed in this paper.

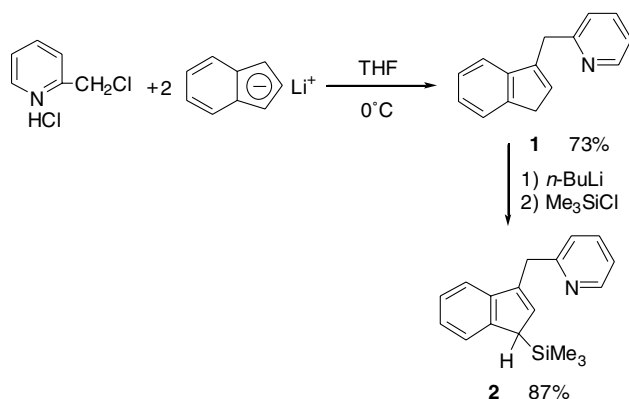
2. Results and discussion

2.1. Synthesis of the ligands

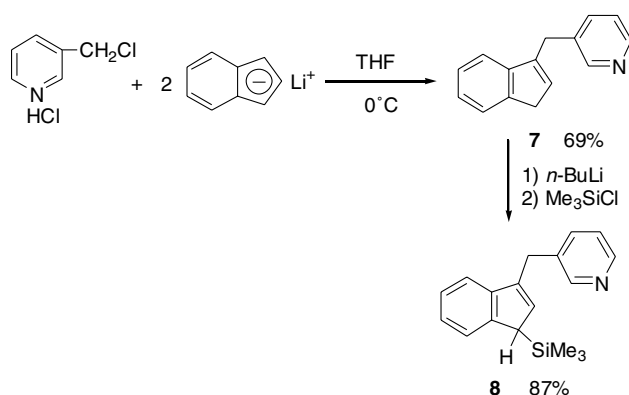
The indene compounds were synthesized by the reactions of lithium indenide with 2-pyridylmethyl or 3-pyridylmethyl chlorides by using the reported procedures with slightly modifications [12]. The silyl-substituted indene compounds were prepared by treatments of 3-(2- $\text{C}_5\text{H}_4\text{NCH}_2$) C_9H_7 or 3-(3- $\text{C}_5\text{H}_4\text{NCH}_2$) C_9H_7 with $n\text{-BuLi}$, followed by reactions with excess Me_3SiCl , the synthetic routes were outlined in Schemes 1 and 2. All the indene compounds were fully characterized by elemental analyses and spectroscopic methods. ^1H NMR spectra analyses showed that the pyridylmethyl substituents connect to the sp^2 carbon at 3-position of the indene ring, the silyl group connects to the sp^3 carbon of the indenyl ring.

2.2. Reaction of the indene compounds with lanthanide(III) amides $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ ($\text{Ln} = \text{Yb}, \text{Eu}$). Synthesis and characterization of ytterbium(II) and europium(II) complexes

Treatments of lanthanide(III) amides $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ ($\text{Ln} = \text{Yb}, \text{Eu}$) with 2 equiv. of 1-R-3-(2- $\text{C}_5\text{H}_4\text{NCH}_2$) C_9H_6 ($\text{R} = \text{H}$ (1), $\text{Me}_3\text{Si-}$ (2)) in hot toluene produced, after workup, the lanthanide(II) complexes with general formula $\{\eta^5\text{-}\eta^1\text{-}[1\text{-R-3-(2-}\text{C}_5\text{H}_4\text{NCH}_2\text{)C}_9\text{H}_5]\}_2\text{Ln}(\text{II})$



Scheme 1.

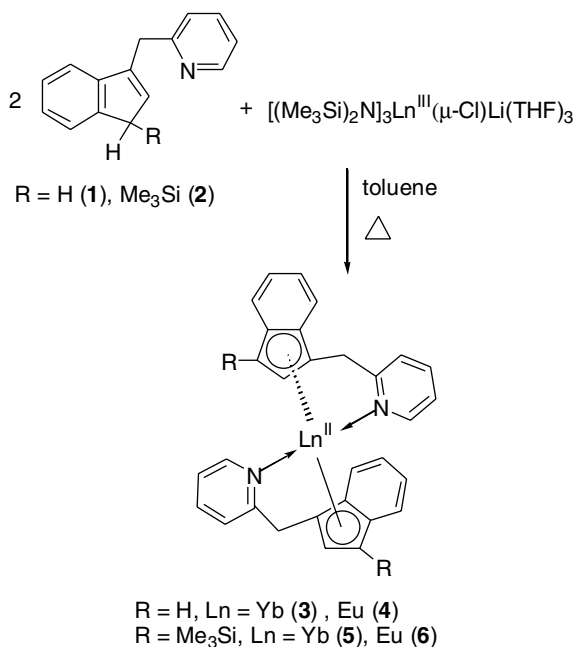


Scheme 2.

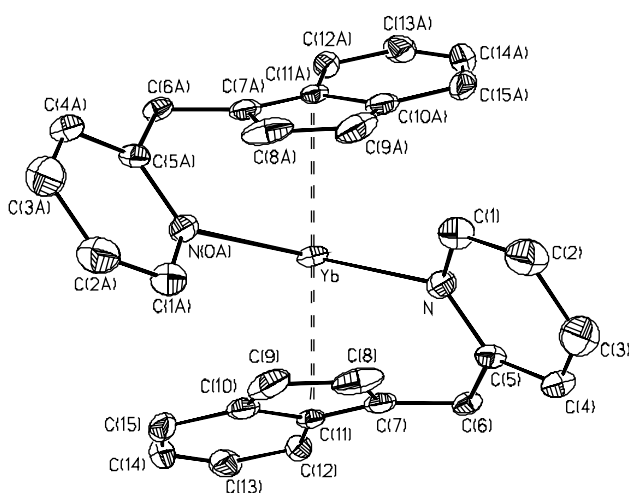
($\text{R} = \text{H-}$, $\text{Ln} = \text{Yb}$ (3), Eu (4); $\text{R} = \text{Me}_3\text{Si-}$, $\text{Ln} = \text{Yb}$ (5), Eu (6)) (Scheme 3). The complexes were air- and moisture-sensitive solid, they are soluble in THF, DME and pyridine, and are soluble in hot toluene, but they are insoluble in n -hexane. All complexes were fully characterized by elemental analyses and spectroscopic methods. NMR analyses of complexes 3 and 5 showed that they behaved diamagnetic properties, indicating that the oxidation state of the central ytterbium metal be in the oxidation state of +2. NMR spectra of complexes 4 and 6 are not informative for lacking of locking signals due to the paramagnetic properties of the complexes. In order to get further information about the reaction, and to determine the structures of the complexes, the structures of the complexes 3 and 5 were determined by single-crystal X-ray diffraction study.

Although the quality of the X-ray analyses data of complex 5 is not good enough for the severe thermally disorder of the carbon atoms of the Me_3Si groups, we can still deduce from the data that the central ytterbium ions of the complexes are in the oxidation state of +2. This result suggested that the formation of the lanthanide(II) complexes goes through one-electron reductive process.

From Figs. 1 and 2, we can see that the ytterbium(II) ion is coordinated by two indenyl ligands in an η^5 -mode, and two nitrogen atoms of the pyridine rings on the indenyl side-arm in an η^1 -fashion, thus the coordination chemistry

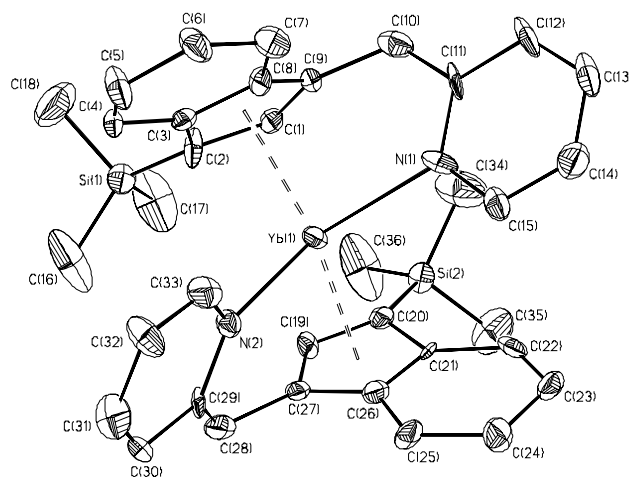


Scheme 3.

Fig. 1. Molecular structure of $[\eta^5:\eta^1-(2-C_5H_4NCH_2)C_9H_6]_2Yb$ (3). The hydrogen atoms are omitted for clarity.

of the ytterbium(II) metal can be described as a distorted tetrahedron.

The Yb–C distances range from 2.666(11) to 2.769(14) Å in **3** (Table 1), with an average distance of 2.723(14) Å. This distance is shorter than the corresponding values of 2.806(12) Å in $[Me_2Si(Me_2NCH_2CH_2C_9H_5)(t-BuNH)]_2Yb^{II}$ [7a], 2.782(8) Å in $[\eta^5:\eta^1-(2-C_5H_4NCH_2)C_9H_6]_2Yb^{II}$ (THF) [12], 2.778(14) Å in $(Me_2NCH_2CH_2C_9H_5SiMe_3)_2Yb$ [7a], is close to 2.722(10) Å in $(Me_2NCH_2CH_2C_9H_6)_2Yb$ [7a]. The average distance of 2.723(14) Å in **3** is longer than those of 2.683(5) Å, 2.68(1) Å, and 2.68(2) Å found in $(Me_2NCH(Me)CH_2C_5H_4)_2Yb$ [13], $Yb(Cp^{Py})_2$ [14], and $Yb(Cp^{Py(s)})_2$ [14], respectively. The Yb–N distance of 2.561(7) Å in **3** is shorter than the corresponding values

Fig. 2. Molecular structure of $[\eta^5:\eta^1-1-Me_3Si-3-(2-C_5H_4NCH_2)C_9H_5]_2Yb$ (5). The hydrogen atoms and LiCl in the unit cell are omitted for clarity.Table 1
Selected bond lengths (Å) and angles (°) for **3**

Yb–N	2.561(7)
Yb–C(7)	2.666(11)
Yb–C(8)	2.707(13)
Yb–C(9)	2.769(14)
Yb–C(10)	2.768(12)
Yb–C(11)	2.705(10)
Yb–C _{av}	2.723(14)
N(2)–Yb–N(1)	106.7(4)

of 2.587(7) Å in $[\eta^5:\eta^1-(2-C_5H_4NCH_2)C_9H_6]_2Yb^{II}$ (THF) [12], 2.673(11) Å in $[Me_2Si(Me_2NCH_2CH_2C_9H_5)(t-BuNH)]_2Yb^{II}$, 2.650(12) Å in $(Me_2NCH_2CH_2C_9H_5SiMe_3)_2Yb$, 2.588(7) Å in $(Me_2NCH_2CH_2C_9H_6)_2Yb$ [7a], and 2.603(4) Å in $(Me_2NCH(Me)CH_2C_5H_4)_2Yb$ [13]. But, the Yb–N distance of 2.561(7) Å in **3** is longer than those of 2.48(1) Å found in $Yb(Cp^{Py})_2$ [14], and $Yb(Cp^{Py(s)})_2$ [14], respectively. The differences of the average Yb–C and the Yb–N distances in these ytterbium(II) complexes may be attributed to the steric effects of the complexes, ionic radii differences [15] for the different coordination number of the ytterbium metal, and different hybridization of the nitrogen atoms.

The N–Yb–N angle of 106.7(4)° found in **3** is smaller than the corresponding value of 159.8° in $[\eta^5:\eta^1-(2-C_5H_4NCH_2)C_9H_6]_2Yb^{II}$ (THF) [12] for different coordination geometry, but the N–Yb–N angle of 106.7(4)° found in **3** is larger than those of 95.1(1)° in $[Me_2Si(Me_2NCH_2CH_2C_9H_5)(t-BuNH)]_2Yb^{II}$, 92.8(5)° in $(Me_2NCH_2CH_2C_9H_5SiMe_3)_2Yb$, 103.7(2)° in $(Me_2NCH_2CH_2C_9H_6)_2Yb$ [7a], 103.1(2)° in $(Me_2NCH(Me)CH_2C_5H_4)_2Yb$ [13], 100.8(2)° in $Yb(Cp^{Py})_2$, and 84.04(4)° in $Yb(Cp^{Py(s)})_2$ [14] due to steric effects.

In order to compare the catalytic activity between complexes with 2-pyridylmethyl-substituted indenyl ligands and complexes with 3-pyridylmethyl-functionalized indenyl ligands. Reactions of 1-R-3-(3-C₅H₄NCH₂)C₉H₆ (R = H

(7), Me₃Si– (8)) with lanthanide(III) amides [(Me₃Si)₂N]₃Ln(μ-Cl)Li(THF)₃ (Ln = Yb, Eu) were studied.

The reactions of [(Me₃Si)₂N]₃Ln(μ-Cl)Li(THF)₃ (Ln = Yb, Eu) with 2 equiv. of 1-R-3-(3-C₅H₄NCH₂)C₉H₆ (R = H (7), Me₃Si– (8)) in hot toluene produced, after workup, lanthanide(II) complexes with general formula {η⁵:η¹-[1-R-3-(3-C₅H₄NCH₂)C₉H₅]}₂Ln(II) (R = H–, Ln = Yb (9), Eu (10); R = Me₃Si–, Ln = Yb (11), Eu (12)) (Scheme 4). They were extremely air- and moisture-sensitive solid. All complexes were fully characterized by elemental analyses and spectroscopic methods. Elemental analyses data of the complexes are in agreement with the general formula of lanthanide(II) complexes with 3-pyridylmethyl-substituted indenyl ligands. It is found that complexes with 3-pyridylmethyl-functionalized indenyl ligand cannot be dissolved in hot toluene and *n*-hexane, but they are soluble in donor solvents such as THF, DME and pyridine. NMR analyses indicated that complexes 9 and 11 behave diamagnetic properties, suggesting that the oxidation state of the ytterbium metal be +2. NMR spectra of complexes 10 and 12 were not informative for lack of locking signals due to the paramagnetic properties of the complexes. All the attempts to grow crystals for determination the structure of the complexes failed for the poor solubility of the complexes in toluene, and severe twin problems of crystals growing in THF or diethyl ether.

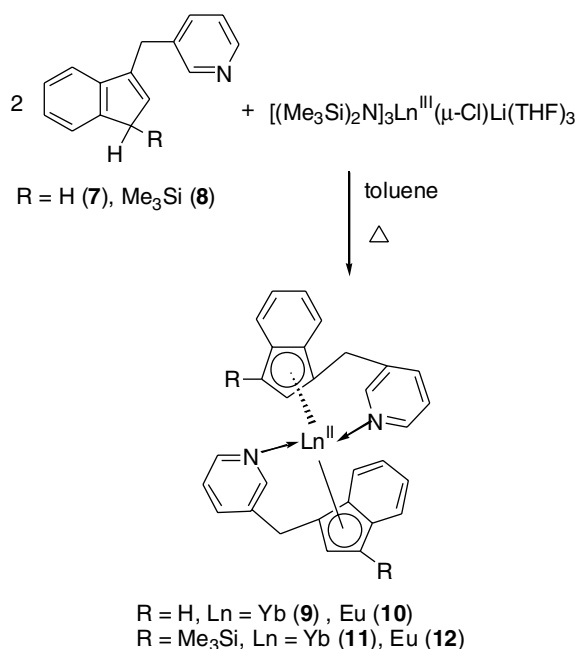
We have proved that the interactions of indene compounds without donor substituted groups on the indene ring with lanthanide(III) amides [(Me₃Si)₂N]₃Ln(μ-Cl)Li(THF)₃ (Ln = Yb, Eu) produced lanthanide(III) amides (Ind')₂LnN(SiMe₃)₂ (Ind' = indenyl or ethylene bridged indenyl ligands), while the interactions of the heteroatom side-arm functionalized indene compounds with

[(Me₃Si)₂N]₃Ln(μ-Cl)Li(THF)₃ (Ln = Yb, Eu) produced lanthanide(II) complexes, the formation pathway of the lanthanide(II) complexes have been proposed via a tandem silylamine elimination/homolysis of the Ln–N bond (Ln = Yb, Eu) based on the experimental results [7]. On the basis of these evidences, we can deduced that the interactions of 2-pyridylmethyl or 3-pyridylmethyl-functionalized indene compounds with lanthanide(III) amides [(Me₃Si)₂N]₃Ln(μ-Cl)Li(THF)₃ (Ln = Yb, Eu) produced the lanthanide(II) complexes via silylamine elimination to give (Indenyl')₂Ln^{III}N(SiMe₃)₂ (Indenyl' = pyridylmethyl-functionalized indenyl) as intermediates, coordination of the heteroatom on the indenyl side-arm to the central metal led to the homolysis of the Ln–N bond, and lanthanide(II) complexes and coupled product [N(SiMe₃)₂]₂ thus produced.

2.3. Catalytic activity of the complexes on MMA polymerization

We have examined the catalytic activity of the complexes as single-component MMA polymerization by performing the polymerization procedures in series of solvents at different temperatures. The polymer products were obtained by quenching with acidified methanol after a fixed interval and analyzed by ¹H NMR spectra for the microstructures, and by GPC for the molecular weight and molecular weight distribution. The results are summarized in Table 2 and 3.

It is found that complexes 3–6 with 2-pyridylmethyl-substituted indenyl ligands showed very poor catalytic activity on MMA polymerization (with no more than 1% conversion of monomer in 1 h), these results are similar to those of the THF-coordinated complexes with 2-pyridylmethyl-substituted indenyl ligands [12]. It is of interesting found that the lanthanide(II) complexes 9, 10 and 12 with 3-pyridylmethyl-functionalized indenyl ligands showed moderate to good catalytic activities on MMA polymerization in THF and DME, but they showed very poor catalytic activities when the polymerization procedures were performed in toluene, this phenomenon may be attributed to the poor solubility of the complexes in toluene at low temperatures. The dramatic differences in catalytic activities of between complexes with 2-pyridylmethyl indenyl ligand and complexes with 3-pyridylmethyl-substituted indenyl ligand may be explained by the different coordination bonding strengths between the central metal and the pyridylmethyl side-arm. The coordination bond of the 2-pyridylmethyl-substituted group with the central metal atom may be more stronger than that of the 3-pyridylmethyl-substituted group with the central metal atom, which in turn to affect the initiation and propagation process of polymerization, a dimeric enolate polymerization mechanism upon the MMA coordinating to the central metal proposed by Boffa and Novak [16]. The strong coordination bonding between the metal center and the 2-pyridylmethyl-substituted groups may prevent the enolate being formed. The catalytic



Scheme 4.

Table 2
Data for the polymerization of methyl methacrylate (MMA)

Catalyst	Solution	T_p (°C)	t_p (min)	Stereochemistry (%)			$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	M_w/M_n	Conv. (%)	Activity $\times 10^{-4}$
				mm	mr	rr					
4	THF	0	15	6	30	64	13.02	8.00	1.63	8	1.61
	THF	20	15	7	32	61	5.62	3.77	1.49	6	1.74
	DME	0	15	12	32	56	6.17	3.69	1.67	5	0.81
	DME	20	15	9	37	54	3.00	1.90	1.57	6	1.13
9	THF	0	20	9	36	55	7.64	5.15	1.48	23	2.7
	THF	−20	20	10	33	57	11.80	7.33	1.60	61	7.3
	THF	−40	15	6	30	64	12.61	8.42	1.50	76	12.1
	THF	−60	5	8	29	63	22.40	17.44	1.28	59	28.3
	DME	−20	20	13	34	53	7.12	4.09	1.73	27	3.2
	DME	−40	20	9	29	62	11.32	6.59	1.71	36	4.3
	DME	−60	15	8	30	62	20.14	13.06	1.54	53	8.4
10	THF	0	20	8	33	59	7.37	4.39	1.60	32	3.8
	THF	−20	20	8	35	58	17.42	10.29	1.69	39	4.6
	THF	−40	1	9	33	58	14.49	9.75	1.48	71	170.6
	THF	−60	0.5	5	31	64	18.80	14.27	1.31	85	408.4
	DME	0	20	10	33	57	3.78	2.63	1.43	10	1.2
	DME	−20	20	11	30	59	6.73	4.17	1.61	28	3.3
	DME	−40	15	5	28	67	9.96	5.91	1.68	55	88.1
	DME	−60	10	8	24	68	18.07	11.01	1.64	55	132.1
12	THF	0	20	8	34	58	3.94	2.99	1.31	21	6.1
	THF	−20	20	5	31	64	13.64	7.11	1.91	36	10.9
	THF	−40	5	8	30	62	17.79	9.72	1.82	37	44.5
	THF	−60	0.5	5	28	67	20.60	12.76	1.20	64	768.9
	DME	0	20	16	35	49	3.43	2.33	1.47	18	2.4
	DME	−20	20	14	34	52	5.94	3.68	1.61	52	6.8
	DME	−40	1.5	10	30	60	10.00	5.77	1.73	69	110.5
	DME	−60	0.5	12	37	51	14.73	9.01	1.63	95	457.8

Conditions: MMA/solvent (v/v) = 1:5 for catalysts **4**, **9** and **10** either in THF or in DME, and **12** in DME, MMA/solvent (v/v) = 1:2.5 (v/v) for catalyst **12** in THF; MMA/Cat. (mol ratio) = 500:1 for catalyst **4**; MMA/Cat. (mol ratio) = 400:1 for catalysts **9** and **10** either in THF or in DME, and **12** in DME; MMA/Cat. (mol ratio) = 1000:1 for catalyst **12** in THF; activity g PMMA mol^{−1}(cat) h^{−1}, stereochemistry is based on ¹H NMR spectroscopic analyses; T_p : polymerization temperature; t_p : polymerization time.

Table 3
MMA/catalyst mole ratio effects on the MMA polymerization

Catalyst	Ratio	Solvent/MMA (v/v)	Solution	t_p (min)	Stereochemistry (%)			$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n	Conv. (%)	Activity ($\times 10^{-4}$)
					mm	mr	rr					
10	400:1	5:1	THF	1	9	33	58	9.75	14.49	1.48	71	170.6
	600:1		THF	3	—	34	66	14.51	21.06	1.45	65	78.1
	800:1		THF	20	5	24	71	11.27	21.25	1.88	35	8.4
	1000:1		THF	20	6	29	65	18.58	22.96	1.23	11	3.3
	200:1		DME	10	8	27	65	4.76	8.29	1.74	61	7.3
	400:1		DME	15	36	22	42	5.91	9.96	1.68	55	8.8
	600:1		DME	20	11	30	59	10.92	17.25	1.57	45	8.1
	800:1		DME	20	3	10	87	8.87	15.52	1.75	28	6.7
	1000:1		DME	20	8	28	64	8.08	14.43	1.78	5	1.5
12	400:1	2.5:1	THF	0.5	30	33	37	6.86	9.61	1.39	73	350.8
	600:1		THF	0.5	13	33	54	10.33	15.10	1.46	77	555.0
	800:1		THF	0.5	51	18	31	11.62	19.69	1.21	66	634.3
	1000:1		THF	0.5	5	28	67	12.76	20.60	1.20	64	768.9
	1200:1		THF	0.5	16	28	56	16.08	23.39	1.45	62	893.8
	400:1		DME	1.5	10	30	60	5.77	10.00	1.73	69	110.5
	600:1	DME	5	28	29	43	10.00	15.21	1.52	45	32.4	
	800:1	DME	15	11	31	58	9.88	14.66	1.48	29	9.2	
	1000:1	DME	20	10	29	61	7.76	14.39	1.85	27	8.1	
	1200:1	DME	20	8	3	89	10.61	17.30	1.62	14	5.0	

Conditions: polymerization temperature: −40 °C for catalysts **10** either in THF or in DME, and **12** in DME, −60 °C for catalyst **12** in THF, ratio: MMA:catalyst mole ratio; activity: g PMMA mol^{−1}(cat) h^{−1}, stereochemistry is based on ¹H NMR spectroscopic analyses; t_p : polymerization time.

activities of the complexes **9**, **10** and **12** can be comparable to those of lanthanide(II) complexes with indenyl ligands having donor atoms on the substituent [7], but is only slightly lower than that of $(C_5Me_5)_2Sm(THF)_2$ [16].

It is found that the catalytic activities of the complexes are temperatures dependent. The catalytic activities of the complexes increase as the temperature decreases (Table 2), this phenomenon is similar to those of lanthanide complexes with 1,1'-(3-oxapentamethylene) bridged indenyl ligands [5d] and those of lanthanide(II) with different heteroatom substituted side-arms [7]. Complexes **9**, **10** and **12** generally exhibited moderate catalytic activities in the temperature ranges of 0 to $-20^\circ C$, they showed very good catalytic activities in the temperature ranges of -40 to $-60^\circ C$, for example, complex **12** has catalytic activities of 6.1×10^4 and 10.9×10^4 g polymer $mol^{-1}(cat) h^{-1}$ in THF at 0 and $-20^\circ C$, respectively, it showed catalytic activities of 44.5×10^4 and 768.9×10^4 g polymer $mol^{-1}(cat) h^{-1}$ in THF at -40 and $-60^\circ C$ (Table 2).

The microstructures of the polymers were analyzed by 1H NMR spectral analyses. The spectra showed that mostly syndiotactic polymers were obtained in all catalyst systems (Tables 2 and 3). The co-existence of different tacticity polymers may be due to the *rac/meso* interconversion. The interconversion is commonly promoted by the donor solvents such as THF, DME and Li^+ salt. Such conversion has also been observed in the ether-bridged lanthanidocene chlorides [5d].

The molecular weights of the polymers were analyzed by GPC; we found that the molecular weights of the polymers were dependent on the choice of catalysts, solvent, and polymerization temperatures. The molecular weight of polymers generally increase as the polymerization temperatures decrease, for example, the molecular weight is 5.15×10^4 (M_n) when catalyst **9** was used and the polymerization reaction was performed at $0^\circ C$ in THF, the molecular weight (M_n) can reach as high as 17.44×10^4 when the same catalyst **9** was used and the polymerization reaction temperature was lowered to $-60^\circ C$ in THF. The narrow molecular weight distributions ($M_w/M_n = 1.20$ to 1.88) were observed in all catalytic systems. The polymerization mechanism may follow the supposition that initiation with a divalent lanthanidocene complex occurs through reductive dimerization of MMA to form a bis-initiator, comprising two lanthanide(III) enolates joined through their double-bond termini [16]. The fact that the M_w/M_n values are far from unity may be explained by the effect of partial chain termination caused by deactivation of the catalysts with trace amounts of impurities present in the system for the lanthanide(II) complexes and the intermediates formed during the polymerization process are very sensitive to these impurities.

For the catalysts generally showed good catalytic activity on MMA polymerization at low temperatures, the influences of the MMA/catalyst mole ratio on the MMA polymerization were studied when the polymerization temperatures were fixed at $-40^\circ C$ for catalysts **10** either in

THF or in DME, for **12** in DME; and at $-60^\circ C$ for **12** in THF (Table 3). It is found that catalytic activities of the catalysts decrease as the MMA/catalyst mole ratio increase for catalyst **10** either in THF or in DME and **12** in DME. But the catalytic activity of the catalysts increases as the MMA/catalyst mole ratio increases for catalyst **12** in THF. The highest catalytic activity (as high as 893.8×10^4 g polymer $mol^{-1}(cat) h^{-1}$) of the catalyst has been observed. It is also found the molecular weight (M_n) increase as the MMA/catalyst mole ratio increase. These results indicated that the propagation process will be favored as the MMA concentration increase. The highest syndiotactic polymers 87% and 89% can be obtained when the MMA/catalyst mole ratio is 800:1 for catalyst **10** in DME, and the MMA/catalyst mole ratio is 1200:1 for catalyst **12** in DME, respectively.

3. Conclusion

Two series of new organolanthanide(II) complexes with general formula $\{\eta^5:\eta^1-[1-R-3-(2-C_5H_4NCH_2)C_9H_5]\}_2Ln(II)$ ($R = H-, Me_3Si-, Ln = Yb, Eu$) and $\{\eta^5:\eta^1-[1-R-3-(3-C_5H_4NCH_2)C_9H_5]\}_2Ln(II)$ ($R = H-, Me_3Si-, Ln = Yb, Eu$) were synthesized by silylamine elimination with one-electron reductive elimination reactions. They were fully characterized by elemental analyses and spectroscopic methods. This work demonstrated that the methodology for the synthesis of organolanthanide(II) complexes via a tandem silylamine elimination/homolysis of the $Ln-N$ bonds reaction can be extended to reactions of unsaturated heterocyclic pyridylmethyl functionalized indene compounds with tetracoordinated lanthanide(III) amides. The studies on the catalytic activities of the complexes showed that the pyridylmethyl-substituted group on the indenyl ligands have great influences on the catalytic activities of the complexes. Complexes with 3-pyridylmethyl-substituted group on the indenyl ligands exhibited moderate to good catalytic activities on MMA polymerization, while complexes with 2-pyridylmethyl functionalized groups on the indenyl ligands behaved very poor catalytic activities on MMA polymerization. These differences may be attributed to bonding strength between the substituted groups and the central metals. It is found that the catalytic activities of complexes with 3-pyridylmethyl groups are dependent on the choice of polymerization conditions and the lanthanide metals. The catalytic activities of the complexes generally increase as the polymerization reaction temperatures decrease. The highest molecular weight (as high as 17.44×10^4) and highest syndiotactic polymers (89%) can be obtained by choosing catalysts and controlling polymerization conditions.

4. Experimental

4.1. Materials and methods

All the syntheses and manipulations of air- and moisture-sensitive materials were carried out on the flamed

Schlenk-type glassware on a Schlenk line. All solvents were refluxed and distilled over finely divided LiAlH_4 or sodium benzophenone ketyl under argon prior to use unless otherwise noted. CDCl_3 was dried over activated 4 Å molecular sieves. MMA was dried over finely divided CaH_2 , distilled before use. 3-(2- $\text{C}_5\text{H}_4\text{NCH}_2$) C_9H_7 [12], $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (Ln = Yb [7a], Eu [5g]) were prepared according to the reported procedures with slightly modifications. Elemental analyses data were obtained on a Perkin–Elmer 2400 Series II Elemental Analyzer. IR spectra were recorded on a Perkin–Elmer 983(G) spectrometer (CsI crystal plate, Nujol and Fluoroble mulls). Melting points were determined in the sealed capillaries without corrections. GC–MS analyses were carried out on an Agilent 6890/Micromass GCT-MS instrument. ^1H and ^{13}C NMR spectra for analyses of the compounds were recorded on a Bruker AV-300 NMR spectrometer in $\text{C}_5\text{D}_5\text{N}$ (pyridine- d_5) for lanthanide complexes and in CDCl_3 for polymers and indene compounds. The chemical shifts for ^1H and ^{13}C NMR spectra were recorded to internal solvent resonances. Gel permeation chromatography (GPC) analyses of polymer samples were carried out at 30 °C using THF as eluent on a Waters-150C instrument and calibrated using monodispersed polystyrene standards at flow rate of 1.0 mL min^{-1} . Number-average molecular weight and polydispersities of polymers were given relative to PS standards. The polymers were analyzed according to the literature [17].

4.2. Synthesis of 1- Me_3Si -3-(2- $\text{C}_5\text{H}_4\text{NCH}_2$) C_9H_6 (2)

To a solution of 3-(2- $\text{C}_5\text{H}_4\text{NCH}_2$) C_9H_7 (1) (7.53 g, 36.3 mmol) in 50.0 mL of THF was slowly added a 1.55 M *n*-BuLi solution (23.4 mL, 36.3 mmol) at 0 °C. The reaction mixture was stirred at room temperature overnight, it was then cooled to 0 °C. To the mixture was added a freshly distilled Me_3SiCl (10.0 mL, 78.3 mmol) in one portion. The reaction temperature was gradually raised to room temperature, and was stirred at the temperature overnight. The solvents and excess Me_3SiCl were evaporated under vacuum, 80.0 mL of *n*-hexane was added, and the precipitate was filtered off. The solvent was pumped off affording the pure product as a pale yellow oil identified by NMR (8.62 g, 85%). ^1H NMR (CDCl_3): δ_{H} 8.58 (s, 1H) ($\text{C}_5\text{H}_4\text{N}$), 7.09–7.57 (m, 7H) ($\text{C}_9\text{H}_7 + \text{C}_5\text{H}_4\text{N}$), 6.43 (m, 1H) (C_9H_7), 4.21 (s, 2H) ($\text{C}_5\text{H}_4\text{NCH}_2$), 3.48 (s, 2H) (C_9H_7 , saturated CH), 0.02 (s, 9H) ($\text{Si}(\text{CH}_3)_3$) ppm. IR (Nujol and Fluoroble mulls, cm^{-1}): ν 3067 (s), 3014 (s), 2898 (s), 1930 (m), 1715 (w), 1690 (s), 1469 (s), 1429 (s), 1363 (m), 1250 (s), 1187 (w), 1145 (m), 1088 (w), 1028 (s), 989 (s), 877 (s), 840 (s), 764 (s), 689 (s), 608 (s), 566 (m). Anal. Calc. for $\text{C}_{18}\text{H}_{21}\text{NSi}$: C, 77.36; H, 7.57; N, 5.01. Found: C, 77.10; H, 7.70; N 4.99%.

4.3. Synthesis of $[\eta^5:\eta^1\text{-}(2\text{-C}_5\text{H}_4\text{NCH}_2)\text{C}_9\text{H}_6]_2\text{Yb}^{\text{II}}$ (3)

To a toluene (30.0 mL) solution of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Yb}^{\text{III}}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (1.10 g, 1.2 mmol) at room temperature was

slowly added a toluene (10.0 mL) solution of 3-(2- $\text{C}_5\text{H}_4\text{NCH}_2$) C_9H_7 (1) (0.50 g, 2.4 mmol). After the reaction was stirred at room temperature for 6 h, the mixture was then refluxed for 24 h. the color of the solution was changed from yellow to purple-red. The solvent was evaporated under reduced pressure. The residue was washed with *n*-hexane (10.0 mL). The resulting solid was extracted with toluene (2×10.0 mL). The toluene solution was combined and concentrated to 15.0 mL. Purple-red crystals were obtained by cooling the concentrated solution at 0 °C for several days (0.47 g, 59%). M.p. 108–110 °C. ^1H NMR (pyridine- d_5): δ_{H} 9.08 (s, 2H) ($\text{C}_5\text{H}_4\text{N}$), 7.78–7.92 (m, 6H) ($\text{C}_5\text{H}_4\text{N}$), 7.18–7.55 (m, 13H) ($\text{C}_9\text{H}_6 + \text{C}_6\text{H}_5\text{CH}_3$), 6.60–6.52 (m, 4H) (C_9H_6), 3.61 (s, 4H) ($\text{C}_5\text{H}_4\text{NCH}_2$), 2.31 (s, 3H) ($\text{C}_6\text{H}_5\text{CH}_3$) ppm. IR (Nujol and Fluoroble mulls, cm^{-1}): ν 2929 (w), 2854 (w), 2726 (m), 2678 (m), 1689 (w), 1456 (s), 1380 (s), 1304 (m), 1150 (w), 1081 (w), 970 (w), 724 (s). Anal. Calc. for $\text{C}_{30}\text{H}_{24}\text{N}_2\text{Yb} + \text{C}_7\text{H}_8$: C, 65.57; H, 4.76; N, 4.13. Found: C, 65.21; H, 5.10; N, 4.18%.

4.4. $[\eta^5:\eta^1\text{-}(2\text{-C}_5\text{H}_4\text{NCH}_2)\text{C}_9\text{H}_6]_2\text{Eu}^{\text{II}}$ (4)

To a toluene (30.0 mL) solution of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Eu}^{\text{III}}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (1.25 g, 1.4 mmol) at room temperature was slowly added a toluene (10.0 mL) solution of 3-(2- $\text{C}_5\text{H}_4\text{NCH}_2$) C_9H_7 (1) (0.58 g, 2.8 mmol). After the reaction was stirred at room temperature for 6 h, the temperature was raised to 50 °C, and the reaction mixture was stirred at the temperature for 12 h. The solvent was evaporated under reduced pressure. The residue was washed with *n*-hexane (10.0 mL). The resulting solid was extracted with toluene (2×10.0 mL). The toluene solution was combined and concentrated to 15.0 mL to give a green powder upon standing the solution at –15 °C for several days (0.58 g, 70%). M.p. 120–121 °C. NMR (pyridine- d_5) spectra of the compound were not informative due to the strong paramagnetic property of the europium(II) complex. IR (Nujol and Fluoroble mulls, cm^{-1}): ν 2955 (w), 2858 (w), 2729 (m), 2676 (m), 1588 (m), 1455 (s), 1378 (s), 1300 (w), 1153 (w), 1089 (w), 971 (w), 720 (m). Anal. Calc. for $\text{C}_{30}\text{H}_{24}\text{-N}_2\text{Eu} + 1/4\text{C}_7\text{H}_8$: C, 64.90; H, 4.46; N, 4.77. Found: C, 64.97; H, 4.65; N, 5.01%.

4.5. $[\eta^5:\eta^1\text{-}1\text{-Me}_3\text{Si-}3\text{-}(2\text{-C}_5\text{H}_4\text{NCH}_2)\text{C}_9\text{H}_5]_2\text{Yb}^{\text{II}} \cdot (\text{LiCl})_{0.5}$ (5)

This compound was prepared as a purple-red crystals in 60% yield from reaction of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Yb}^{\text{III}}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (1.10 g, 1.2 mmol) and 1- Me_3Si -3-(2- $\text{C}_5\text{H}_4\text{NCH}_2$) C_9H_6 (2) (0.67 g, 2.4 mmol) following the procedures similar to those used for the preparation of complex 3. M.p. 142–143 °C. ^1H NMR (pyridine- d_5): δ_{H} 9.08 (s, 2H) ($\text{C}_5\text{H}_4\text{N}$), 7.78–7.92 (m, 6H) ($\text{C}_5\text{H}_4\text{N}$), 7.18–7.55 (m, 8H) (C_9H_5), 6.60 (s, 2H) (C_9H_5), 3.61 (s, 4H) ($\text{C}_5\text{H}_4\text{NCH}_2$), 0.02 (s, 18H) ($\text{Si}(\text{CH}_3)_3$) ppm. IR (Nujol and Fluoroble mulls, cm^{-1}): ν 2921 (w), 2729 (m), 1597 (w), 1454 (s), 1381 (s), 1301 (m), 1251 (w), 1162 (w), 1072 (w), 1027

(w), 968 (w), 889 (w), 836 (w), 724 (m). Anal. Calc. for $C_{36}H_{40}N_2Si_2Yb + 1/2LiCl$: C, 57.56; H, 5.37; N, 3.73. Found: C, 57.15; H, 5.48; N, 3.73%.

4.6. $[\eta^5:\eta^1-1-Me_3Si-3-(2-C_5H_4NCH_2)C_9H_5]_2Eu^{II}$ (**6**)

This compound was prepared as a yellow solid in 54% yield from reaction of $[(Me_3Si)_2N]_3Eu^{III}(\mu-Cl)Li(THF)_3$ (1.25 g, 1.4 mmol) and $1-Me_3Si-3-(2-C_5H_4NCH_2)C_9H_6$ (**2**) (0.78 g, 2.8 mmol) following the procedures similar to those used for the preparation of complex **4**. M.p. 140–142 °C. NMR (pyridine- d_5) spectra of the compound were not informative due to the paramagnetic property of the europium(II) complex. IR (Nujol and Fluoroble mulls, cm^{-1}): ν 3061 (m), 2955 (m), 2726 (m), 1590 (w), 1454 (s), 1379 (s), 1306 (w), 1155 (w), 1081 (w), 969 (w), 887 (w), 835 (w), 718 (m) cm^{-1} . Anal. Calc. for $C_{36}H_{40}N_2Si_2Eu + C_7H_8$: C, 64.48; H, 6.04; N, 3.50. Found: C, 64.07; H, 5.80; N, 3.79%.

4.7. Synthesis of $3-(3-C_5H_4NCH_2)C_9H_7$ (**7**)

To a THF (120.0 mL) solution of indene (12.0 mL, 104.0 mmol) was slowly added a 1.55 M *n*-BuLi solution (67.0 mL, 104.0 mmol) at 0 °C. The reaction mixture was stirred at room temperature overnight and was then cooled to 0 °C. To $3-(ClCH_2)C_5H_4N \cdot HCl$ (10.2 g, 62.0 mmol) in 50.0 mL of THF was slowly added the reaction mixture. The reaction mixture was stirred at room temperature overnight and then it was hydrolyzed. The organic layer was separated and the aqueous layer was extracted with diethyl ether (2×15.0 mL). The organic fractions were combined and dried with anhydrous $MgSO_4$, filtered, and evaporated under vacuum. The pale yellow oily product (8.9 g, 69%) was obtained after distillation under reduced pressure. 1H NMR ($CDCl_3$): δ_H 8.61 (s, 1H) (C_5H_4N), 8.50 (d, 1H, $J = 6.3$ Hz) (C_5H_4N), 7.57 (m, 1H) (C_5H_4N), 7.50 (d, 1H, $J = 6.9$ Hz) (C_5H_4N), 7.20–7.30 (m, 4H) (C_9H_7), 6.15 (m, 1H) (C_9H_7), 3.92 (s, 2H) ($C_5H_4NCH_2$), 3.41 (s, 2H) (C_9H_7 , saturated CH) ppm. IR (Nujol and Fluoroble mulls, cm^{-1}): ν 3024 (s), 2897 (s), 2774 (m), 1916 (w), 1796 (w), 1709 (m), 1608 (m), 1578 (s), 1478 (m), 1461 (s), 1419 (m), 1393 (m), 1193 (m), 1027 (s), 977 (m), 920 (m), 838 (m), 775 (s), 712 (s), 621 (m). Anal. Calc. for $C_{15}H_{13}N$: C, 86.92; H, 6.32; N, 6.67. Found: C, 86.78; H, 6.23; N, 6.65%.

4.8. $1-Me_3Si-3-(3-C_5H_4NCH_2)C_9H_6$ (**8**)

To a solution of $3-(3-C_5H_4NCH_2)C_9H_7$ (**7**) (7.53 g, 36.3 mmol) in 50.0 mL of THF was slowly added a 1.61 M *n*-BuLi solution (22.5 mL, 36.3 mmol) at 0 °C. The reaction mixture was stirred at room temperature overnight and was then cooled to 0 °C. To the mixture was added freshly distilled Me_3SiCl (5.0 mL, 39.9 mmol) in one portion. The reaction temperature was gradually raised to room temperature and stirred at the temperature overnight. The solvents and excess Me_3SiCl were evapo-

rated under vacuum. 30.0 mL of *n*-hexane was added and the precipitate was filtered off. The solvent was pumped off affording the product as a pale yellow oil (8.81 g, 87%). 1H NMR ($CDCl_3$): δ_H 8.59 (s, 1H) (C_5H_4N), 8.47 (d, 1H, $J = 4.7$ Hz) (C_5H_4N), 7.59 (m, 1H) (C_5H_4N), 7.45 (d, 1H, $J = 6.7$ Hz) (C_5H_4N), 7.33–7.17 (m, 4H) (C_9H_6), 6.27 (s, 1H) (C_9H_6), 3.98 (s, 2H) ($C_5H_4NCH_2$), 3.45 (s, 1H) (C_9H_7 , saturated CH), 0.07 (s, 9H) ($Si(CH_3)_3$) ppm. IR (Nujol and Fluoroble mulls, cm^{-1}): ν 3036 (m), 2859 (s), 2900 (m), 1943 (w), 1683 (w), 1588 (m), 1569 (m), 1481 (m), 1451 (m), 1422 (m), 1367 (w), 1252 (s), 1184 (w), 1103 (w), 1029 (s), 992 (m), 876 (m), 829 (s), 758 (m), 710 (m), 608 (m). Anal. Calc. for $C_{18}H_{21}SiN$: C, 77.36; H, 7.57; N, 5.01. Found: C, 77.20; H, 7.71; N, 4.80%.

4.9. Synthesis of $[\eta^5:\eta^1-(3-C_5H_4NCH_2)C_9H_6]_2Yb^{II}$ (**9**)

To a toluene (50.0 mL) solution of $[(Me_3Si)_2N]_3Yb^{III}(\mu-Cl)Li(THF)_3$ (1.09 g, 1.19 mmol) at room temperature was slowly added a toluene (10.0 mL) solution of $3-(3-C_5H_4NCH_2)C_9H_7$ (**7**) (0.49 g, 2.38 mmol). After the reaction was stirred at room temperature for 6 h, the temperature was raised to 75 °C and the reaction mixture was stirred at this temperature for 12 h. The color of the solution changed to dark-green. The solvent was evaporated under reduced pressure. The residue was washed with *n*-hexane (10.0 mL). The resulting solid was extracted with THF (2×10.0 mL). The THF solution was combined and concentrated to 10.0 mL. The dark-green solid complex was obtained by cooling the concentrated solution at 0 °C (0.64 g, 71%). M.p. 104–106 °C; 1H NMR (pyridine- d_5): δ_H 8.87–8.70 (m, 4H) (C_5H_4N), 7.72–7.34 (m, 17H) ($C_5H_4N + C_9H_6 + C_6H_5CH_3$), 7.08 (m, 2H) (C_9H_6), 6.23 (m, 2H) (C_9H_6), 4.98 (s, 4H) ($C_5H_4NCH_2$), 2.36 (s, 3H) ($C_6H_5CH_3$) ppm. IR (Nujol and Fluoroble mulls, cm^{-1}): ν 2958 (s), 2856 (s), 1185 (s), 1466 (s), 1306 (s), 964 (s), 771 (m), 718 (m), 593 (s). Anal. Calc. for $C_{30}H_{24}N_2Yb + C_7H_8$: C, 65.57; H, 4.76; N, 4.13. Found: C, 65.30; H, 4.65; N, 4.38%.

4.10. $[\eta^5:\eta^1-(3-C_5H_4NCH_2)C_9H_6]_2Eu^{II}$ (**10**)

To a toluene (50.0 mL) solution of $[(Me_3Si)_2N]_3Eu^{III}(\mu-Cl)Li(THF)_3$ (0.96 g, 1.09 mmol) at room temperature was slowly added a toluene (10.0 mL) solution of $3-(3-C_5H_4NCH_2)C_9H_7$ (**7**) (0.45 g, 2.18 mmol). After the reaction was stirred at room temperature for 6 h, the temperature was raised to 50 °C and the reaction mixture was stirred at this temperature for 12 h. The color of the solution changed to dark-green. The solvent was evaporated under reduced pressure. The residue was washed with *n*-hexane (10.0 mL). The resulting solid was extracted with THF (2×10.0 mL). The THF solution was combined and concentrated to 10.0 mL to give a dark-green powder (0.46 g, 65%). M.p. 89–91 °C; IR (Nujol and Fluoroble mulls, cm^{-1}): 2952 (s), 2851 (s), 1422 (m), 1306 (s), 1165 (s), 1042 (m), 970 (s), 837 (m), 698 (m), 595 (s). Anal. Calc.

for $C_{30}H_{24}N_2Eu$: C, 63.83; H, 4.30; N, 4.96. Found: C, 64.33; H, 4.45; N, 4.85%.

4.11. Synthesis of $[\eta^5:\eta^1-1-Me_3Si-3-(3-C_5H_4NCH_2)-C_9H_5]_2 Yb$ (**11**)

To a toluene (50.0 mL) solution of $[(Me_3Si)_2N]_3Yb^{III}(\mu-Cl)Li(THF)_3$ (1.34 g, 1.47 mmol) at room temperature was slowly added a toluene (10.0 mL) solution of 1- $Me_3Si-3-(3-C_5H_4NCH_2)C_9H_6$ (**8**) (0.82 g, 2.94 mmol). After the reaction was stirred at room temperature for 6 h, the temperature was raised to 75 °C and the reaction mixture was stirred at this temperature for 12 h. The color of the solution changed to dark-green. The solvent was evaporated under reduced pressure. The residue was washed with *n*-hexane (10.0 mL). The resulting solid was extracted with THF (2 × 10.0 mL). The THF solution was combined and concentrated to 10.0 mL. The dark-green solid complex was obtained by cooling the concentrated solution at 0 °C (1.07 g, 77%). M.p. 132–134 °C; 1H NMR (pyridine- d_5): δ_H 8.69–8.46 (m, 4H) (C_5H_4N), 7.53–7.16 (m, 12H) ($C_5H_4N + C_9H_5$), 6.02 (s, 2H) (C_9H_5), 4.04 (s, 4H) ($C_5H_4NCH_2$), 0.09 (s, 18H) ($Si(CH_3)_3$) ppm. IR (Nujol and Fluoroble mulls, cm^{-1}): ν 3067 (s), 2899 (s), 1484 (s), 1377 (m), 1309 (w), 1247 (w), 1151 (w), 1089 (w), 1028 (w), 837 (w), 721 (w). Anal. Calc. for $C_{36}H_{40}Si_2N_2Yb$: C, 59.24; H, 5.52; N, 3.84. Found: C, 58.94; H, 5.82; N, 3.88%.

4.12. Synthesis of $[\eta^5:\eta^1-1-Me_3Si-3-(3-C_5H_4NCH_2)-C_9H_5]_2 Eu$ (**12**)

To a toluene (50.0 mL) solution of $[(Me_3Si)_2N]_3Eu^{III}(\mu-Cl)Li(THF)_3$ (1.02 g, 1.15 mmol) at room temperature was slowly added a toluene (10.0 mL) solution of 1- $Me_3Si-3-(3-C_5H_4NCH_2)C_9H_6$ (**8**) (0.64 g, 2.29 mmol). After the reaction was stirred at room temperature for 6 h, the reaction temperature was raised to 50 °C and the reaction mixture was stirred at this temperature for 12 h. The color of the solution changed to dark-green. The solvent was evaporated under reduced pressure. The residue was washed with *n*-hexane (10.0 mL). The resulting solid was extracted with THF (2 × 10.0 mL). The THF solution was combined and concentrated to 10.0 mL to give a dark-green powder (0.82 g, 68%). M.p. 130–132 °C; IR (Nujol and Fluoroble mulls, cm^{-1}): ν 3067 (s), 2946 (s), 1730 (w), 1462 (s), 1374 (m), 1307 (w), 1248 (w), 1163 (w), 971 (w), 839 (w), 718 (w). Anal. Calc. for $C_{36}H_{40}Si_2N_2Eu$: C, 61.00; H, 5.97; N, 3.95. Found: C, 60.72; H, 6.19; N, 4.01%.

4.13. X-ray crystallography

Suitable crystals of the complexes **3** and **5** were mounted in sealed capillaries. Diffraction was performed on a Siemens SMART CCD-area detector diffractometer using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å), temperature 293(2) K, ψ and ω scan technique, SADABS effects and empirical absorption were applied in the

Table 4
Crystal and data collection parameters for **3**

Empirical formula	$C_{30}H_{24}N_2Yb$
Formula weight	585.55
Crystal system	Monoclinic
Space group	C2
<i>a</i> (Å)	16.805(3)
<i>b</i> (Å)	8.2129(13)
<i>c</i> (Å)	8.6129(14)
β (°)	91.34
<i>V</i> (Å ³)	1188.4(3)
<i>T</i> (K)	293(2)
<i>D</i> _{calcd} (g cm ⁻³)	1.636
<i>Z</i>	2
<i>F</i> (000)	576
No. refls. collected	1640
No. unique refls.	1468 (<i>R</i> _{int} = 0.032)
No. parameters	127
λ (Å) Mo $K\alpha$	0.71073
μ (mm ⁻¹)	3.955
θ range (°)	2.37–24.94
Goodness-of-fit	1.092
<i>R</i> (<i>I</i> > 2 σ (<i>I</i>))	0.046
<i>wR</i> ₂	0.116
Largest difference peak and hole (e Å ⁻³)	1.783 and -0.979

data corrections. All structures were solved by direct methods (SHELXS-97), completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares calculations based on *F*² (SHELXS-97) [18]. The crystal and data collection parameters are given in Table 4. The crystal data in CIF format has been deposited with CCDC No. 283147 for **3** and 283148 for **5**, this data can be obtained free of charge from the Cambridge Crystallographic Data Centre. deposit@ccdc.cam.ac.uk; Tel.: (44)01223 762910; or Postal address: CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

4.14. MMA polymerization

MMA polymerization reactions were performed in a 50.0 mL Schlenk flask, placed in an external temperature-controlled bath, on a Schlenk line or in a glovebox. In a typical procedure, the catalyst (20–50 mg) was loaded into the Schlenk flask and the solvent was added. After the external bath temperature was stabilized, MMA was added through a gastight syringe in one portion. The polymer product was precipitated into methanol (50.0 mL), washed with methanol, and then dried to a constant weight in a vacuum oven at 50 °C. The stereochemistry of the polymers and their molecular weights were analyzed by 1H NMR spectroscopy and GPC techniques, respectively.

Acknowledgments

We thank the National Natural Science Foundation (20271003, 20472001), the Program for NCET (NCET-04-0590), the Excellent Young Scholars Foundation of Anhui Province (04046079) and a grant from Anhui Education Department (2005hzb06) for financial support for

this work. Prof. Baohui Du and Jiping Hu's assistances in running IR and NMR spectra are also grateful.

References

- [1] (a) A.M. Kawaoka, T.J. Marks, *J. Am. Chem. Soc.* 127 (2005) 6311–6324;
(b) H. Yasuda, *J. Organomet. Chem.* 647 (2002) 128;
(c) Z. Hou, Y. Wakatsuki, *Coord. Chem. Rev.* 231 (2002) 1–22;
(d) Y. Nakayama, H. Yasuda, *J. Organomet. Chem.* 689 (2004) 4489;
(e) S. Hong, T.J. Marks, *Acc. Chem. Res.* 37 (2004) 673–686;
(f) G.A. Molander, J.A.C. Romero, *Chem. Rev.* 102 (2002) 2161–2186;
(g) L. Zhang, S. Wang, E. Sheng, S. Zhou, *Green Chem.* 7 (2005) 683–686.
- [2] (a) P.W. Roesky, T.E. Müller, *Angew. Chem. Int. Ed.* 42 (2003) 2708–2710;
(b) Y.K. Kim, T. Livinghouse, Y. Horino, *J. Am. Chem. Soc.* 125 (2003) 9560;
(c) P.N. O'Shaughnessy, P. Scott, *Tetrahedron: Asymmetry* 14 (2003) 1979–1983;
(d) Y.K. Kim, T. Livinghouse, J.E. Bercaw, *Tetrahedron Lett.* 42 (2001) 2933;
(e) S. Tian, V.M. Arredondo, C.L. Stern, T.J. Marks, *Organometallics* 18 (1999) 2568;
(f) J.S. Ryu, T.J. Marks, F.E. McDonald, *Org. Lett.* 3 (2001) 3091;
(g) V.M. Arredondo, F.E. McDonald, T.J. Marks, *Organometallics* 18 (1999) 1949;
(h) V.M. Arredondo, S. Tian, F.E. McDonald, T.J. Marks, *J. Am. Chem. Soc.* 121 (1999) 3633;
(i) M.R. Gagne, C.L. Stern, T.J. Marks, *J. Am. Chem. Soc.* 114 (1992) 275;
(j) K.C. Hultsch, D.V. Gribkov, F. Hampel, *J. Organomet. Chem.* (2005), available online;
(k) T.K. Panda, A. Zulys, M.T. Gamer, P.W. Roesky, *Organometallics* 24 (2005) 2197–2202.
- [3] Y. Horino, T. Livinghouse, *Organometallics* 23 (2004) 12–14.
- [4] (a) M.R. Douglass, T.J. Marks, *J. Am. Chem. Soc.* 122 (2000) 1824–1825;
(b) M.R. Douglass, M. Ogasawara, S. Hong, M.V. Metz, T.J. Marks, *Organometallics* 21 (2002) 283–292;
(c) A.M. Kawaoka, M.R. Douglass, T.J. Marks, *Organometallics* 22 (2003) 4630–4632.
- [5] (a) F. Bonnet, A.C. Hillier, A. Collins, S.R. Dubberley, P. Mountford, *Dalton Trans.* (2005) 421–423;
(b) R.M. Gauvin, A. Mortreux, *Chem. Commun.* (2005) 1146–1148;
(c) F.M. Kerton, A.C. Whitwood, C.E. Williams, *Dalton Trans.* (2005) 2237–2244;
(d) C.T. Qian, G. Zuo, Y.F. Chen, J. Sun, *Organometallics* 20 (2001) 3106;
(e) C. Boisson, F. Barbotin, R. Spitz, *Macromol. Chem. Phys.* 200 (1999) 1163;
(f) C.T. Qian, W.L. Nie, J. Sun, *Organometallics* 19 (2000) 4134;
(g) S. Zhou, S. Wang, G. Yang, X. Liu, E. Sheng, K. Zhang, L. Cheng, Z. Huang, *Polyhedron* 22 (2003) 1019–1024;
(h) E. Martin, P. Dubois, R. Jerome, *Macromolecules* 33 (2000) 1530;
(i) B.J. O'Keefe, M.A. Hillmyer, W.B. Tolman, *Dalton Trans.* (2001) 2215–2224;
(j) C.X. Cai, A. Amgoune, C.W. Lehmann, J.-F. Carpentier, *Chem. Commun.* (2004) 330–331;
(k) M.T. Gamer, M. Rastätter, P.W. Roesky, A. Steffens, M. Glanz, *Chem. Eur. J.* 11 (2005) 3165–3172.
- [6] (a) J. Zhang, R. Cai, L. Weng, X. Zhou, *Organometallics* 23 (2004) 3303–3308;
(b) J. Zhang, R. Cai, L. Weng, X. Zhou, *Organometallics* 22 (2003) 5385–5391;
(c) H.R. Li, Y.M. Yao, Q. Shen, L.H. Weng, *Organometallics* 21 (2002) 2529–2532;
(d) L.S. Mao, Q. Shen, M.Q. Xue, *Organometallics* 16 (1997) 3711;
(e) J. Zhang, R. Cai, L. Weng, X. Zhou, *J. Organomet. Chem.* 672 (2003) 94–99;
(f) J. Zhang, X. Zhou, R. Cai, L. Weng, *Inorg. Chem.* 44 (2005) 716–722.
- [7] (a) E. Sheng, S. Wang, G. Yang, S. Zhou, L. Cheng, K. Zhang, Z. Huang, *Organometallics* 22 (2003) 684–692;
(b) K. Zhang, W. Zhang, S. Wang, E. Sheng, G. Yang, M. Xie, S. Zhou, Y. Feng, L. Mao, Z. Huang, *Dalton Trans.* (2004) 1029–1037;
(c) E. Sheng, S. Zhou, S. Wang, G. Yang, Y. Wu, Y. Feng, L. Mao, Z. Huang, *Eur. J. Inorg. Chem.* (2004) 2923–2932;
(d) S. Wang, S. Zhou, E. Sheng, G. Yang, M. Xie, K. Zhang, L. Cheng, Y. Feng, L. Mao, Z. Huang, *Organometallics* 22 (2003) 3546–3552;
(e) Y. Wu, S. Wang, C. Qian, E. Sheng, M. Xie, G. Sheng, Q. Feng, L. Zhang, X. Tang, *J. Organomet. Chem.* 690 (2005) 4139–4149.
- [8] M.N. Bochkarev, *Coord. Chem. Rev.* 248 (2004) 835–851, and references therein.
- [9] (a) M. Schuktz, J.M. Boncella, D.J. Berg, T.D. Tilley, R.A. Andersen, *Organometallics* 21 (2002) 460;
(b) D.J. Berg, J.M. Boncella, R.A. Andersen, *Organometallics* 21 (2002) 4622;
(c) A. Zalkin, D.J. Berg, *Acta Crystallogr., Sect. C* 44 (1988) 1488;
(d) D.J. Berg, C.J. Burns, R.A. Andersen, A. Zalkin, *Organometallics* 8 (1989) 1865;
(e) Z. Hou, T.-a. Koizumi, M. Nishiura, Y. Wakatsuki, *Organometallics* 20 (2001) 3323, and references therein.
- [10] (a) W.J. Evans, T.A. Ulibarri, J.W. Ziller, *J. Am. Chem. Soc.* 110 (1988) 6877;
(b) J. Jubbs, S. Gambarotta, *J. Am. Chem. Soc.* 116 (1994) 4477;
(c) E. Campazzi, E. Solari, C. Floriani, R. Scopelliti, *Chem. Commun.* (1998) 2603;
(d) T. Dube, S. Conoci, S. Gambarotta, G.P.A. Yap, G. Vasapollo, *Angew. Chem. Int., Ed. Engl.* 38 (1999) 3657;
(e) T. Dube, M. Ganesan, S. Conoci, S. Gambarotta, G.P.A. Yap, *Organometallics* 19 (2000) 3716;
(f) M. Ganesan, M.P. Lalonde, S. Gambarotta, G.P.A. Yap, *Organometallics* 20 (2001) 2443;
(g) W.J. Evans, N.T. Allen, J.W. Ziller, *J. Am. Chem. Soc.* 123 (2001) 7927;
(h) W.J. Evans, N.T. Allen, J.W. Ziller, *Angew. Chem. Int. Ed.* 41 (2002) 359;
(i) W.J. Evans, G. Zucchi, J.W. Ziller, *J. Am. Chem. Soc.* 125 (2003) 10.
- [11] (a) W.J. Evans, J.W. Grate, L.A. Hughes, H. Zhang, J.L. Atwood, *J. Am. Chem. Soc.* 107 (1985) 3728;
(b) W.J. Evans, C.A. Seibel, J.W. Ziller, *Inorg. Chem.* 37 (1998) 770.
- [12] J. Cheng, D. Cui, W. Chen, N. Hu, T. Tang, B. Huang, *J. Organomet. Chem.* 689 (2004) 2646–2653.
- [13] G.A. Molander, H. Schumann, E.C.E. Rosenthal, J. Demtschuk, *Organometallics* 15 (1996) 3817.
- [14] J.R. Van den Hende, P.B. Hitchcock, M.F. Lappert, T.A. Nile, *J. Organomet. Chem.* 472 (1994) 79.
- [15] R.D. Shannon, *Acta Crystallogr., Sect. A* 32 (1976) 751.
- [16] (a) L.S. Boffa, B.M. Novak, *Macromolecules* 27 (1994) 6993–6995;
(b) E. Ihara, M. Morimoto, H. Yasuda, *Macromolecules* 28 (1995) 7886–7892.
- [17] F.A. Bovey, P.A. Mirau, *NMR of Polymers*, Academic Press, San Diego, 1996.
- [18] G.M. Sheldrick, *SHELXTL*, version 5.10, Bruker Analytical X-ray Systems Inc., Madison, WI, 1997.