Homolysis of the Ln−N (Ln = Yb, Eu) Bond − Synthesis, Structure, and Catalytic Activity of Ytterbium(II) and Europium(II) Complexes Having (Dimethylamino)propyl- and (Dimethylamino)ethyl-Functionalized Indenyl Ligands

Enhong Sheng,[a] Shuangliu Zhou,[a] Shaowu Wang,*[a,b] Gaosheng Yang,[a] Yongyong Wu,[a] Yan Feng,[a] Lili Mao,[a] and Zixiang Huang[c]

Dedicated to Professor Changtao Qian on the occasion of his 70th birthday

Keywords: Catalyst / Homolysis / Organometallics / Polymer / Polymerization

We have synthesized a new series of ytterbium(II) and europium(II) complexes by tandem silylamine elimination/homolysis of Ln–N (Ln = Yb, Eu) bonds. The interaction of 2 equiv. of $C_9H_7CH_2CH_2CH_2NMe_2$ (**1**) with $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Yb, Eu) in toluene under reflux produced lanthanide(II) complexes $[(\eta^5{:}\eta^1\text{-}C_9H_6CH_2CH_2CH_2NMe_2)_2\text{-}Ln]$ [Ln = Yb (**2**), Eu(**3**)] in 67 and 74% yields, respectively. Treatment of 2 equiv. of $Me_2Si(Me_2NCH_2CH_2C_9H_6)(NHtBu)$ with $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$ in toluene at 80 °C afforded a europium(II) complex $[\eta^5{:}\eta^1\text{-}Me_2Si(Me_2NCH_2\text{-}CH_2C_9H_5)(NHtBu)]_2Eu{\cdot}(OC_4H_8)_{0.5}$ (**4**) in 46% yield. The interaction of 2 equiv. of $Me_2NCH_2CH_2C_9H_6SiMe_3$ with $[(Me_3\text{-}Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$ produced a europium(II) compound $[\eta^5{:}\eta^1\text{-}(Me_2NCH_2CH_2C_9H_5SiMe_3)]_2Eu$ (**5**) in 49% yield. Treatment of 2 equiv. of $Me_2NCH_2CH_2C_9H_7$ with $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$ in toluene gave a europium(II) complex $(\eta^5{:}\eta^1\text{-}Me_2NCH_2CH_2C_9H_6)_2Eu$ (**6**) in 57% yield. All the compounds were fully characterized by spectroscopic methods and elemental analyses. The structures of the complexes **4**, **5**, and **6** were determined by single-crystal X-ray analyses. The catalytic activities of organometallic complexes were examined; we found that all of the complexes can function as single-component MMA polymerization catalysts with good activity. We studied the effects of solvent and temperature on the catalytic activities and the stereochemistries of the polymers.

Introduction

Organolanthanide complexes have attracted much attentions for their potential applications as catalysts for olefins transformations.[1] The Ln−N bonds in lanthanide complexes have been demonstrated to exhibit unique reactivity and selectivity for chemo-, regio-, and enantioselective hydroamination of olefins and alkynes,[2] hydrosilylations of olefins,[3] and hydrophosphinations of olefins and alkynes,[4] as well as for olefin polymerization,[5] Tishchenko reactions,[6] ring opening polymerization of ε-caprolactone and δ-valerolactone,[7] and insertion reactions.[8] All of these reactions occur because of the heterolytic reactivity of Ln−N bonds.

We have reported that the interactions of (dimethylamino)ethyl-functionalized indene compounds with ytterbium(III) amide $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$ lead to the isolation and characterization of a new class of ytterbium(II) complexes having indenyl ligands; the interactions of methoxyethyl-functionalized indene compounds with $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Yb, Eu) results in the synthesis of a new series of ytterbium(II) and europium(II) complexes.[9] On the basis of a mechanistic study, the pathway for the formation of the ytterbium(II) and europium(II) complexes is believed to proceed through tandem silylamine elimination[10]/homolysis of the Ln−N (Ln = Yb, Eu) bonds; this reaction provides a new methodology for the preparation of lanthanide(II) complexes. Extension of the process of homolysis of the Yb−N bond to europium chemistry, by studying the interactions of the indene compounds C_9H_6-1-R-3-$CH_2SiMe_2NC_4H_8$ (R = H, Me) with europium(III) amide $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$, has led to the isolation and characterization of novel europium(II) complexes.[11] The formation of different kinds

[a] Institute of Organic Chemistry, School of Chemistry and Materials Science, Anhui Normal University,
Wuhu, Anhui 241000, China
Fax: (internat.) + 86-553-3883517
E-mail: swwang@mail.ahnu.edu.cn
[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry,
Shanghai 200032, China
[c] Fujian Institute of Research on the Structure of Matters, Chinese Academy of Sciences,
Fuzhou 350002, China

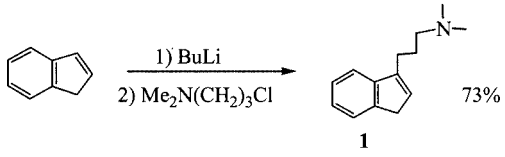
of lanthanide(II) complexes presumably is due to the ligands' effects on the reactivity. As part of our continued interest in the effects of ligands on the homolytic reactivity of Ln−N bonds, we have turned our attention to the interactions of (dimethylamino)propyl-functionalized indene compounds with $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Yb, Eu) and the interactions of (dimethylamino)ethyl-functionalized indene compounds with europium(III) amide $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$.

Herein, we report that interacting (dimethylamino)propyl- and (dimethylamino)ethyl-functionalized indene compounds with $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Yb, Eu) results in the isolation of a new series of ytterbium(II) and europium(II) complexes, which we have characterized. We propose that the pathway for the formation of the lanthanide(II) complexes proceeds through tandem silylamine elimination/homolysis of the Ln−N (Ln = Yb, Eu) bonds. The catalytic activity of the ytterbium(II) and europium(II) complexes as single-component MMA polymerization catalysts is also reported.

Results and Discussion

Synthesis of $Me_2NCH_2CH_2CH_2C_9H_7$ (1)

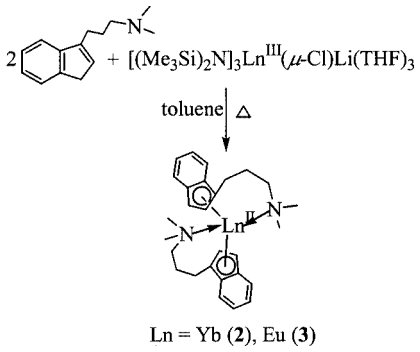
The interaction of C_9H_7Li with $Me_2NCH_2CH_2CH_2Cl$ in THF produced, after workup, the indene compound $Me_2NCH_2CH_2CH_2C_9H_7$ (**1**) in good yield (Scheme 1). The compound was fully characterized by spectroscopic methods and elemental analysis; the ^1H NMR spectrum showed that the substituent group connects to the sp^2-hybridized carbon atom of the five-membered ring of the indene compound.



Scheme 1

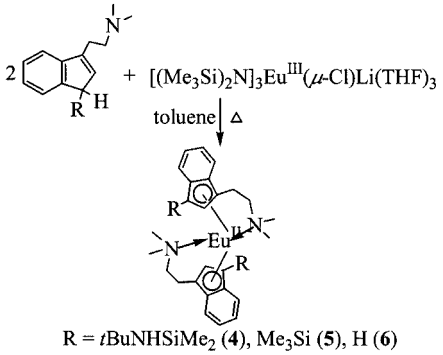
Reactions of the Indene Compounds with $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Yb, Eu). Synthesis of Ytterbium(II) and Europium(II) Complexes

The interaction of 2 equiv. of $Me_2NCH_2CH_2CH_2C_9H_7$ (**1**) with lanthanide(III) amides $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Yb, Eu) in toluene afforded, after workup, ytterbium(II) and europium(II) compounds $[(\eta^5{:}\eta^1\text{-}C_9H_6CH_2CH_2CH_2NMe_2)_2Yb]$ (**2**) and $[(\eta^5{:}\eta^1\text{-}C_9H_6CH_2CH_2CH_2NMe_2)_2Eu]$ (**3**) in 67 and 74% yields, respectively (Scheme 2). The complexes are sensitive to air and moisture, and they are soluble in THF, DME, and toluene. The complexes were fully characterized by spectroscopic methods and elemental analyses. A ^1H NMR spectroscopic study of complex **2** indicated the diamagnetic property of the complex and the +2 oxidation state of the ytterbium center. The results of elemental analyses are in agreement with the formulas of the ytterbium(II) and europium(II) complexes, which indicates that the reactions occur through a reductive process. All attempts to grow crystals suitable for X-ray analyses to confirm the structures of the complexes failed as a result the severe twinning problems. To overcome this difficulty and to extend the reaction chemistry, we studied the following reactions.



Scheme 2

Treatment of 2 equiv. of $Me_2Si(Me_2NCH_2CH_2C_9H_6)(NHtBu)$ with $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$ in toluene at 80 °C afforded, after workup, a europium(II) complex $[\{\eta^5{:}\eta^1\text{-}Me_2Si(Me_2NCH_2CH_2C_9H_5)(NHtBu)\}_2Eu]\cdot(OC_4H_8)_{0.5}$ (**4**) in 46% yield (Scheme 3). The complex is sensitive to air and moisture, and is soluble in THF, DME, pyridine, and toluene, but only slightly soluble in *n*-hexane. The compound was fully characterized by spectroscopic methods and elemental analysis. NMR spectra are not informative because of a lack of locking signals for the paramagnetic solutions of this compound. The elemental analysis of the product is in agreement with the formula of europium(II) complex being $Me_2Si(Me_2NCH_2CH_2C_9H_5)(NHtBu)]_2Eu$, which indicates that the reaction occurs through a reductive process. The structure of the europium(II) complex was confirmed by X-ray analysis. To extend the chemistry, we investigated the interaction of $Me_2NCH_2CH_2C_9H_6SiMe_3$ with $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$.



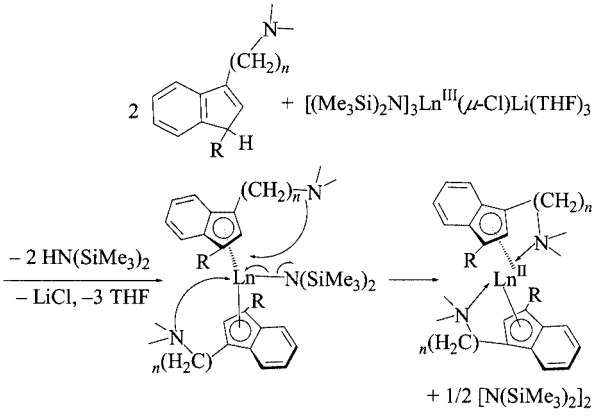
Scheme 3

Treatment of 2 equiv. of $Me_2NCH_2CH_2C_9H_6SiMe_3$ with $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$ produced a europium(II) compound $[\{\eta^5{:}\eta^1\text{-}(Me_2NCH_2CH_2C_9H_5SiMe_3)\}_2Eu]$ (**5**) in 49% yield (Scheme 3). The compound is sensitive to air and moisture, and is soluble in THF, DME, pyridine, and toluene, but is only slightly soluble in *n*-hexane. The complex was fully characterized by spectroscopic method and elemental analysis. Although NMR spectra are not informative because of the paramagnetic property of the complex, the elemental analysis of the complex is in agreement with the formula above; details of the structure were further confirmed by an X-ray diffraction study. These results suggest that the formation of the europium(II) complex occurs through a reductive reaction process. To probe the effects of the silyl substituent and the ligands on the reaction, we studied the interaction of $Me_2NCH_2CH_2C_9H_7$ with $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$.

Treatment of 2 equiv. of $Me_2NCH_2CH_2C_9H_7$ with $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$ in toluene gave the europium(II) complex $[(\eta^5{:}\eta^1\text{-}Me_2NCH_2CH_2C_9H_6)_2Eu]$ (**6**) in 57% yield (Scheme 3). The complex is sensitive to air and moisture; it is soluble in THF, DME, and pyridine, but it is only slightly soluble in toluene and insoluble in *n*-hexane. The complex was fully characterized by spectroscopic methods and elemental analysis. Although NMR spectra are not informative because of the paramagnetic property of the complex, the results of elemental analysis are in agreement with a monomeric europium(II) complex; the structure of this europium(II) complex was further confirmed by a X-ray diffraction study. The fact that a triple-decker tetranuclear europium(II) complex was not isolated as the product of the reaction between $C_9H_7CH_2SiMe_2NC_4H_8$ and europium(III) amide $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$ [11] may be due to the ligands' effects on the reactivity.

The formation of all of the ytterbium(II) and europium(II) complexes above is believed to occur through a reductive process. Several experiments were initiated to probe the reaction mechanism. The indene compounds, the amine $HN(SiMe_3)_2$, and the coupling product $[N(SiMe_3)_2]_2$ were detected by GC-MS analyses of the reaction mixtures after hydrolysis. The formation of the coupling product may be due to homolysis of the $Ln-N(SiMe_3)_2$ bond to produce the radical $N(SiMe_3)_2$, which then couples to give the coupling product; it should be noted, however, that the amount of coupling product $[N(SiMe_3)_2]_2$ is less than that expected, probably as a result of the free radical abstraction of a hydrogen atom from solvent. Homolysis of the Ln−N bond has not been observed, however, when heating the corresponding lanthanide(III) amides $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Yb, Eu) in toluene under reflux for 2 days or when subliming the lanthanide(III) amides $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Yb, Eu) at 100 °C and 10^{-4} Torr; instead, $[(Me_3Si)_2N]_3Ln$ was isolated,[5] indicating that homolysis of the $Ln-N(SiMe_3)_2$ bond occurs after the interaction of the indene compounds with $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Yb, Eu). Our previous work has indicated that the interaction of 1,2-bis(indenyl)ethane with $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$ does not produce the ytterbium(II) compound: the ytterbium(III) amides, *meso*-$(EBI)Yb^{III}N(SiMe_3)_2$, were isolated,[9] which suggests an effect of the heteroatom on the reductive reaction.

On the basis of the evidence above, we propose the following pathway for the formation of the lanthanide(II) complexes: The interactions of the (dimethylamino)propyl- or (dimethylamino)ethyl-functionalized indene compounds with $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Yb, Eu) produces the lanthanide(III) amides $(Indenyl')_2LnN(SiMe_3)_2$ [Indenyl' = (dimethylamino)ethyl- or (dimethylamino)propyl-functionalized indenyl ligands] as intermediates and $HN(SiMe_3)_2$ by a silylamine elimination reaction.[10] Coordination of the nitrogen atoms of the (dimethylamino)ethyl or (dimethylamino)propyl groups to the central lanthanide metal ions promotes homolysis of the Ln−N (Ln = Yb, Eu) bonds to give the lanthanide(II) complexes and the radical $N(SiMe_3)_2$, which then couples to form the coupling product (Scheme 4).



n = 3, R = H, Ln = Yb (**2**), Eu (**3**);
n = 2, Ln = Eu, R = *t*BuNHSiMe$_2$ (**4**), Me$_3$Si (**5**), H (**6**),

Scheme 4. Proposed mechanism for the reductive reaction

Molecular Structures of Complexes 4, 5, and 6

The structures of lanthanide(II) complexes **4** (Figure 1), **5** (Figure 2), and **6** (Figure 3) were determined by X-ray diffraction studies. X-Ray analyses revealed that the central metal ion of each complex exists in a +2 oxidation state. We found that there are two independent molecules in the unit cell of complex **6** that differ by the effects of the substituent groups of the indenyl ligands upon crystallization. The selected bond lengths and angles are listed in the Table 1. Some of the important structural parameters are compiled in Table 2 for a comparison of the structural parameters.

From Table 1 and 2, we see that the Eu−C bond lengths range from 2.827(10) to 2.944(11) Å, with an average of 2.883(11) Å in **4**; this distance is slightly different to those found in **5** [2.873(10) Å] and in **6** [2.841(7) Å]. Similarities are found in the average Eu−N bond lengths of **4** [2.748(9) Å], **5** [2.744(8) Å], and **6** [2.711(6) Å], which indicate the effect of the substituent groups on the bonding between the

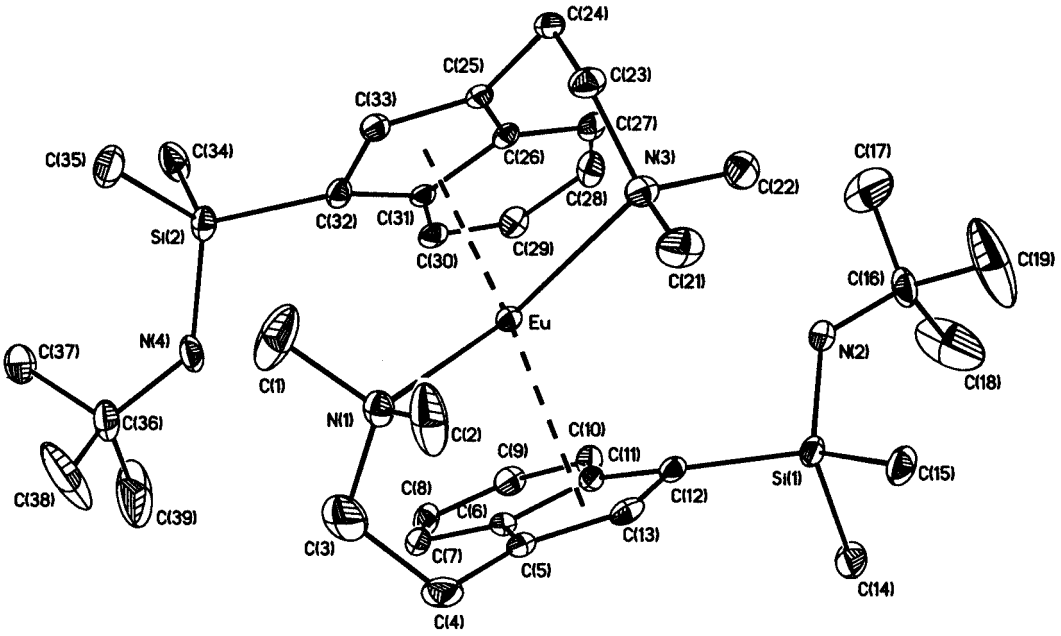


Figure 1. Molecular structure of complex **4**; hydrogen atoms and the solvated THF molecule have been omitted for clarity

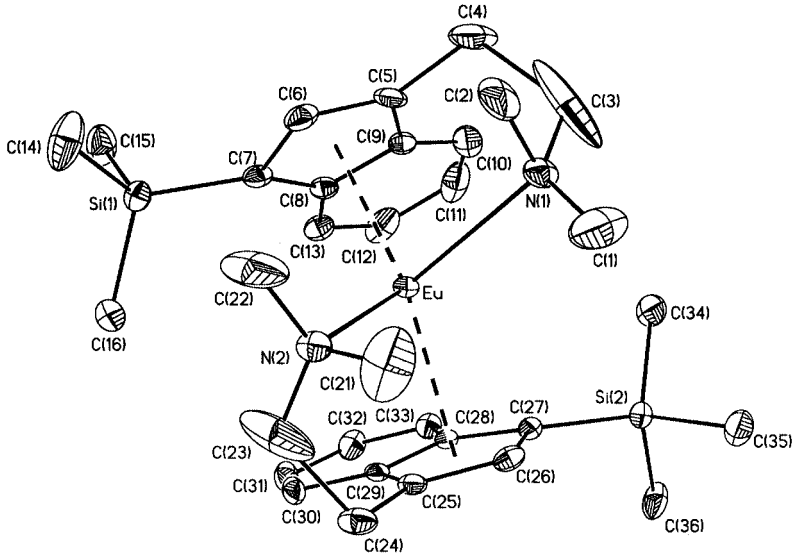


Figure 2. Molecular structure of complex **5**; hydrogen atoms have been omitted for clarity

ligands and the central metal ions. The N−Eu−N angle of 96.1(3)° in **4** is larger than the corresponding angle [92.9(3)°] in **5**, but it is smaller than these angles [102.1(2)° and 107.3(2)°] in **6**. Similar results have been found in the ytterbium(II) analogues (Table 2), suggesting an effect of the substituent groups on the configuration of the ytterbium(II) and europium(II) complexes. From Table 2, we see that, as the substituent groups on the indenyl rings change from *t*BuNHSiMe$_2$ to Me$_3$Si to H, the differences of either the average Ln−C or the average Ln−N bond lengths between **4** and **5**, **4** and **6**, and **5** and **6** are smaller than those values found in their ytterbium(II) analogues, which suggests that the effect of the substituent groups on the bonding between the ligands and the central metal ion becomes weaker as the ionic radii[12] of the central metal ion increases.

The average Eu−C distances found in **4** [2.883(11) Å], **5** [2.873(10) Å], and **6** [2.841(7) Å] are smaller than the corresponding value of 2.911(18) Å found in [(η^5:η^1-C$_9$H$_5$-1-Me-3-CH$_2$SiMe$_2$NC$_4$H$_8$)$_2$Eu], but are longer than the corresponding average values found in [{η^5:η^1-(MeOCH$_2$CH$_2$C$_9$H$_5$SiMe$_3$)}$_2$Yb] [**10**; 2.741(14) Å],[9b] [{η^5:η^1-Me$_2$Si(MeOCH$_2$CH$_2$C$_9$H$_5$)(NH*t*Bu)}$_2$Eu] [**11**; 2.858(8) Å],[9b] and [{η^5:η^1-(MeOCH$_2$CH$_2$C$_9$H$_5$-SiMe$_3$)}$_2$Eu] [**12**; 2.857(11) Å][9b] (Table 2); these difference may be due to steric effects and the different ionic radii. The average Eu−N distances found in **4** [2.748(9) Å], **5** [2.744(8) Å], and **6** [2.711(6) Å] are also smaller than the corresponding value of 2.754(16) Å found in [(η^5:η^1-C$_9$H$_5$-1-Me-3-CH$_2$SiMe$_2$NC$_4$H$_8$)$_2$Eu],[11] but are longer than the corresponding Ln−O bond lengths found in [η^5:η^1-(Me-

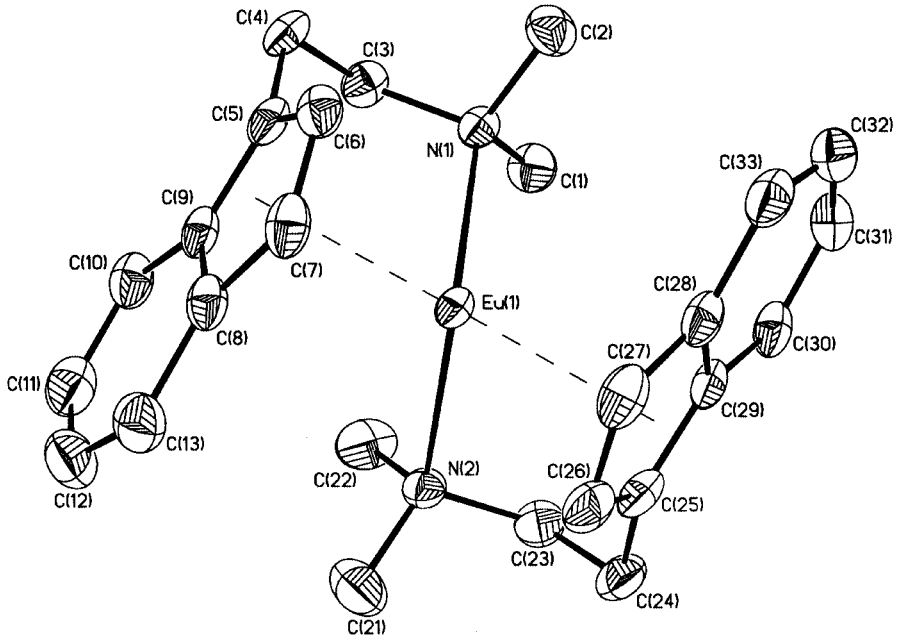


Figure 3. One of the molecular structures of complex **6** in the unit cell; hydrogen atoms have been omitted for clarity

Table 1. Selected bond lengths (Å) and angles (°) for **4**, **5**, and **6**

4		**5**		**6**			
Eu−N(1)	2.789(9)	Eu−N(1)	2.765(8)	Eu(1)−N(1)	2.726(6)	Eu(2)−N(3)	2.677(5)
Eu−N(3)	2.707(9)	Eu−N(2)	2.724(8)	Eu(1)−N(2)	2.742(5)	Eu(2)−N(4)	2.700(5)
Eu−C(5)	2.827(10)	Eu−C(5)	2.817(10)	Eu(1)−C(5)	2.820(6)	Eu(2)−C(45)	2.836(6)
Eu−C(6)	2.870(10)	Eu−C(6)	2.856(10)	Eu(1)−C(6)	2.823(7)	Eu(2)−C(46)	2.786(6)
Eu−C(11)	2.911(10)	Eu−C(7)	2.940(9)	Eu(1)−C(7)	2.822(7)	Eu(2)−C(47)	2.797(6)
Eu−C(12)	2.918(11)	Eu−C(8)	2.913(8)	Eu(1)−C(8)	2.859(7)	Eu(2)−C(48)	2.888(6)
Eu−C(13)	2.829(11)	Eu−C(9)	2.848(10)	Eu(1)−C(9)	2.850(6)	Eu(2)−C(49)	2.887(6)
Eu−C(25)	2.832(10)	Eu−C(25)	2.832(8)	Eu(1)−C(25)	2.821(7)	Eu(2)−C(65)	2.820(6)
Eu−C(26)	2.881(9)	Eu−C(26)	2.852(8)	Eu(1)−C(26)	2.814(7)	Eu(2)−C(66)	2.800(6)
Eu−C(31)	2.911(9)	Eu−C(27)	2.903(8)	Eu(1)−C(27)	2.837(7)	Eu(2)−C(67)	2.846(6)
Eu−C(32)	2.944(11)	Eu−C(28)	2.900(7)	Eu(1)−C(28)	2.864(6)	Eu(2)−C(68)	2.911(6)
Eu−C(33)	2.908(11)	Eu−C(29)	2.867(7)	Eu(1)−C(29)	2.853(6)	Eu(2)−C(69)	2.885(6)
N(1)−Eu−N(3)	96.1(3)	N(1)−Eu−N(2)	92.9(3)	N(1)−Eu(1)−N(2)	102.1(2)	N(3)−Eu(2)−N(4)	107.3(2)

Table 2. A comparison of the structural parameters of the ytterbium(II) and europium(II) complexes incorporating (dimethylamino)ethyl- and methoxyethyl-functionalized indenyl ligands

Complex[a]	Ln−C(av.)	Ln−A(av.)	A−Ln−A	Ref.
4 (Ln = Eu, A = N)	2.883(11)	2.748(9)	96.1(3)	this work
5 (Ln = Eu, A = N)	2.873(10)	2.744(8)	92.9(3)	this work
6 (Ln = Eu, A = N)	2.836(7); 2.846(6)	2.734(6); 2.688(5)	102.1(2); 107.3(2)	this work
7 (Ln = Yb, A = N)	2.806(12)	2.673(11)	95.1(4)	[9a]
8(Ln = Yb, A = N)	2.778(14)	2.650(12)	92.8(5)	[9a]
9(Ln = Yb, A = N)	2.722(10)	2.588(7)	103.7(2)	[9a]
10(Ln = Yb, A = O)	2.741(14)	2.462(9)	84.5(3), 86.3(3)	[9b]
11(Ln = Eu, A = O)	2.858(8)	2.559(6)	88.6(2)	[9b]
12(Ln = Eu, A = O)	2.857(11)	2.588(8)	88.1(3), 83.3(3)	[9b]

[a] **7**: $[\eta^5{:}\eta^1\text{-}Me_2Si(Me_2NCH_2CH_2C_9H_5)(NHtBu)]_2Yb$; **8**: $[\eta^5{:}\eta^1\text{-}(Me_2NCH_2CH_2C_9H_5SiMe_3)]_2Yb$; **9**: $(\eta^5{:}\eta^1\text{-}Me_2NCH_2CH_2C_9H_6)_2Yb$; **10**: $[\eta^5{:}\eta^1\text{-}(MeOCH_2CH_2C_9H_5SiMe_3)]_2Yb$; **11**: $[\eta^5{:}\eta^1\text{-}Me_2Si(MeOCH_2CH_2C_9H_5)(NHtBu)]_2Eu$; **12**: $[\eta^5{:}\eta^1\text{-}(MeOCH_2CH_2C_9H_5SiMe_3)]_2Eu$.

$OCH_2CH_2C_9H_5SiMe_3)]_2Yb$ [**10**; 2.462(9) Å],[9b] [{η^5:η^1-$Me_2Si(MeOCH_2CH_2C_9H_5)(NHtBu)$}$_2$Eu] [**11**; 2.559(6) Å],[9b] and [{η^5:η^1-$(MeOCH_2CH_2C_9H_5SiMe_3)$}$_2$Eu] [**12**; 2.588(8) Å][9b] (Table 2); these values reflect are steric and ionic radii effects on the bonding. The N−Eu−N angles in **4** [96.1(3)°], **5** [92.9(3)°], and **6** [102.1(2)° and 107.3(2)°] are smaller than the value of 110.19(15)° found in [η^5:η^1-C_9H_5-1-Me-3-$CH_2SiMe_2NC_4H_8)_2$Eu],[11] but are larger than the O−Ln−O (Ln = Yb, Eu) angles found in the methoxyethyl-functionalized (indenyl)ytterbium(II) and -europium(II) complexes[9b] (Table 2); these observations indicate that the substituent groups have an influence on the configuration of complexes having indenyl ligands.

MMA Polymerization

We have studied the activity of the complexes as single-component MMA polymerization catalysts by performing polymerizations in a series of solvents. The polymer products were quenched with acidified methanol after a fixed time and analyzed by obtaining ^{1}H NMR spectra of the microstructures.[13] We found that some polymers cannot be dissolved in THF or passed through GPC columns. We also found that all of the complexes can function as single-component MMA polymerization catalysts and that each has good catalytic activity. It is interesting to note that solvents influence the catalytic activity of the complexes: complexes **2** and **3** display catalytic activity in DME, THF, and toluene; complex **4** exhibits catalytic activity in THF; complexes **5** and **6** possess catalytic activity only in DME. The results are listed in Table 3.

We also examined the effects of temperature on the catalytic activities of the complexes. The catalytic activity of the complexes is temperature dependent: the catalytic activity of the complexes increases as the polymerization temperatures decrease; they possess poor catalytic activities in the temperature range 0−30 °C and exhibit relative higher catalytic activity at lower temperatures. These results are similar to those found when using other ytterbium(II) and eu-

Table 3. Data for the polymerizations of methyl methacrylate (MMA)

Entry[a]	Catalyst	Solvent	t_p (min)	T_p (°C)	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n	Conv. (%)	Activity ($\times 10^{-5}$)	Stereochemistry (%) *rr*	*rm*	*mm*
1	**2**	DME	40	30				6	0.04	51	35	14
2		DME	30	0	48.13	20.63	2.33	24	0.24	59	31	10
3		DME	3	−30	69.50	23.85	2.91	6143	3.70	62	28	10
4		DME	5	−60	88.26	37.73	2.34	1743	2.50	67	25	8
5		DME	6	−80	102.30	38.57	2.65	50	2.20	68	24	8
6	**2**	THF	30	0	88.46	38.41	2.30	38	0.38	55	32	13
7		THF	20	−30	85.31	33.34	2.56	23	0.36	60	28	12
8		THF	6	−60	106.30	56.88	1.87	67	3.30	66	27	7
9		THF	2	−80	185.50	75.09	2.47	60	8.90	73	21	6
10	**2**	toluene	40	30				44	0.34	58	28	14
11		toluene	2	0	33.48	9.95	3.36	63	9.50	67	25	8
12		toluene	8	−30				93	3.40	68	26	6
13		toluene	30	−60	69.84	48.41	1.44	5	0.05	65	23	12
14	**3**	DME	30	30	38.21	15.49	2.47	15	1.40	34	36	30
15		DME	30	0	50.96	20.79	2.45	23	3.40	35	43	22
16		DME	2	−30	93.55	42.57	2.20	51	7.70	37	31	32
17		DME	2	−60	109.40	55.28	1.98	84	13.0	42	33	25
18	**3**	THF	30	30	49.86	23.17	2.15	24	0.25	40	30	30
19		THF	2	0	47.46	23.76	2.00	48	7.20	41	31	28
20		THF	2	−30	109.50	55.01	1.96	34	5.10	44	40	16
21		THF	2	−60	154.80	86.12	1.80	63	9.40	47	35	18
22	**3**	toluene	2	30	56.18	25.71	2.18	23	3.40	8	15	77
23		toluene	5	0	93.27	39.52	2.36	13	0.83	10	18	72
24		toluene	30	−30	104.60	46.09	2.27	8	0.09	14	23	63
25	**4**	THF	10	0	40.12	20.42	1.96	12	0.27	29	37	34
26		THF	10	−15	53.58	24.79	2.16	44	1.06	28	33	39
27		THF	10	−30	58.81	27.33	2.15	100	4.82	33	39	28
28		THF	10	−45	96.92	40.46	2.40	100	5.18	40	42	18
29		THF	10	−60	131.19	72.09	1.82	72	1.72	51	37	12
30	**5**	DME	5	0				18	0.88	32	32	36
31		DME	5	−15				16	0.78	32	32	36
32		DME	5	−30	174.21	62.14	2.80	50	2.40	36	35	29
33		DME	5	−45				6	0.32	50	34	16
34	**6**	DME	5	−30				2	0.09	58	27	15
35		DME	5	−45				77	3.59	64	25	11
36		DME	5	−60				18	0.87	75	19	6

[a] Conditions: MMA/solvent = 1:3 (v/v) for catalysts **2** and **3**; MMA/solvent = 1:2 (v/v) for catalysts **4**, **5**, and **6**; cat./MMA (mole ratio) = 1:500 for catalysts **2** and **3**; cat/MMA (mole ratio) = 1:400 for catalysts **4**, **5**, and **6**; activity: g PMMA·mol^{-1}(cat)·h^{-1}; stereoregularity is based on ^{1}H NMR spectroscopic analyses. T_p: Polymerization temperature.

ropium(II) catalyst systems.[9,11] We also found that the catalytic activity increases as the ionic radii of the catalysts' central metal ion increases; for example, the ytterbium(II) catalyst **2** displayed an activity of 2.5×10^5 g PMMA·mol^{-1}(cat)·h^{-1} in DME at −60 °C, but the europium(II) catalyst **3** bearing the same indenyl ligand exhibited an activity of 13.0×10^5 g PMMA·mol^{-1}(cat)·h^{-1} in the same solvent at the same temperature. These results also support the conclusion that the larger the substituent group of the indenyl ligand, the higher the catalytic activity of the catalyst.

The microstructures of the polymers were studied by ^{1}H NMR spectral analyses.[13] The spectra showed that a mostly syndiotactic polymers were obtained when using the ytterbium catalyst **2** in either polar (THF, DME) or nonpolar (toluene) solvents and when using the europium(II) catalyst **6** in the polar solvent DME. Almost a 1:1:1 ratio of isotactic, syndiotactic, and atactic polymers were obtained, however, when applying the europium(II) catalysts **3**, **4**, and **5** in polar solvents (DME, THF); in contrast, isotactic polymers dominated when using the europium(II) catalyst **3** in toluene. These findings indicate that the donor solvents have an effect on the stereochemistry of the polymers and that this phenomenon may arise from the donor solvents' effects on the epimerization process of the catalysts.[4b,14] The different tacticities of the polymers obtained when using the ytterbium(II) and europium(II) catalysts probably is due to the different ionic radii of the ytterbium(II) and europium(II) ions; these differences affect the epimerization process of the catalysts during the polymerization process.

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 catalyst, solvent, and polymerization temperature. The molecular weights of the polymers generally increase as the polymerization temperature decreases. The results of the polymer molecular mass studies support the supposition that initiation with a divalent lanthanidocence complex occurs through reductive dimerization of MMA to form a bis-initiator, comprising two lanthanide(III) enolates joined through their double-bond termini.[15] The fact that the values of M_w/M_n (1.80 to 3.36) 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: lanthanide(II) complexes and their intermediates formed during the polymerization process are very sensitive to these impurities.

Conclusion

The interactions of the indene compound $Me_2NCH_2CH_2CH_2C_9H_7$ (**1**) with lanthanide(III) amides $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Yb, Eu) and indene compounds $Me_2Si(Me_2NCH_2CH_2C_9H_6)NHtBu$, $Me_2NCH_2CH_2C_9H_6SiMe_3$, and $Me_2NCH_2CH_2C_9H_7$ with europium(III) amide $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$ resulted in the isolation of a series of new europium(II) complexes, which we characterized. The formation of the lanthanide(II) complexes is proposed to proceed through tandem silylamine elimination/homolysis of the Ln−N (Ln = Yb, Eu) bonds, as deduced by a mechanistic study. The lanthanide(II) complexes obtained from the reactions function as single-component MMA polymerization catalysts. We examined the effects of temperature, solvent, and substituent groups on the catalysts' activities and the polymers' stereochemistries, molecular weights, and molecular weight distributions.

Experimental Section

General Remarks: All the syntheses and manipulations of air- and moisture-sensitive materials were carried out using flamed Schlenk-type glassware on a Schlenk line. All the solvents were refluxed over and distilled from finely divided $LiAlH_4$ or sodium benzophenone ketyl under argon prior to use, unless otherwise noted. $CDCl_3$ was dried with activated 4-Å molecular sieves. MMA was dried with finely divided CaH_2 and distilled before use. $Me_2Si(Me_2NCH_2CH_2C_9H_6)NHtBu$,[9] $Me_2NCH_2CH_2C_9H_6SiMe_3$,[9] $Me_2NCH_2CH_2C_9H_7$,[16] and $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Yb,[9] Eu[5h]) were prepared according to reported procedures. Elemental analyses were obtained with a Perkin−Elmer 2400 Series II Elemental Analyzer. IR spectra were recorded with a Perkin−Elmer 983(G) spectrometer (CsI crystal plate, Nujol and fluoroble mulls). Melting points were determined using sealed capillaries and uncorrected. GC-MS analyses were carried out with an Agilent 6890/Micromass GCT-MS instrument. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker AV-300 NMR spectrometer in C_5D_5N (pyridine-d_5) for lanthanide complexes and in $CDCl_3$ for polymers and indene compounds; the chemical shifts are listed relative to the internal solvent resonances. Gel permeation chromatography (GPC) analyses of polymer samples were performed at 30 °C using THF as the eluent on a Waters-150C instrument that was calibrated using monodisperse polystyrene (PS) standards at a flow rate of 1.0 mL·min^{-1}. Number-average molecular weights and polydispersities of polymers are given relative to PS standards. The polymers were analyzed according to the literature.[13]

$C_9H_7CH_2CH_2CH_2NMe_2$ (1): A 1.57 M hexane solution of *n*BuLi (54.0 mL, 85.2 mmol) was added slowly at 0 °C to a solution of indene (10.0 mL, 85.2 mmol) in THF (80.0 mL). The reaction mixture was stirred at room temperature overnight and then the solution was cooled to 0 °C and $Me_2NCH_2CH_2CH_2Cl$ (10.4 g, 85.2 mmol) was added in one portion. The reaction mixture was stirred at room temperature for 10 h 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 to dryness. The colorless oily product (12.5 mg, 73%) was obtained after distillation under reduced pressure. ^{1}H NMR (300.17 MHz, $CDCl_3$, 295 K): δ = 7.50 (d, J = 7.23 Hz, 1 H), 7.44 (d, J = 7.38 Hz, 1 H), 7.34 (m, 1 H), 7.24 (m, 1 H), 6.26 (s, 1 H) 3.36 (s, 2 H), 2.62 (m, 2 H), 2.42 (m, 2 H), 2.30 (s, 6 H), 1.94 (m, 2 H) ppm. ^{13}C NMR (75.48 MHz, $CDCl_3$, 295 K): δ = 145.55, 144.55, 144.38, 127.76, 126.76, 126.07, 124.58, 123.79, 119.04, 59.80, 45.66, 37.77, 26.25, 25.62 ppm. IR (Nujol and Fluroble mulls): $\tilde{\nu}$ = 3065 (m), 3017 (m), 2942 (s), 2857 (s), 2764 (s), 1881 (w), 1790 (w), 1682 (w), 1609 (m), 1460 (s), 1377 (m), 1264 (m), 1169 (m), 1097 (w), 1042 (m), 963 (m), 827 (w), 718 (m), 617 (w),

504 (w) cm^{-1}. $C_{14}H_{19}N$ (201.31): calcd. C 83.53, H 9.51, N 6.96; found C 83.15, H 9.45, N 7.02.

[(η⁵:η¹-$C_9H_6CH_2CH_2CH_2NMe_2$)$_2$Yb] (2): A solution of $C_9H_7CH_2CH_2CH_2NMe_2$ (**1**; 490 mg, 2.40 mmol) in toluene (10.0 mL) was added slowly to a solution of $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$ (1100 mg, 1.20 mmol) in toluene (50.0 mL) . The reaction mixture was stirred at room temperature for 6 h and then under reflux for 24 h. The color of the reaction mixture gradually changed from yellow to blue and finally to dark red. The solvent was evaporated to give a red solid that was washed with *n*-hexane (10.0 mL). The solid was extracted with toluene (2 × 15.0 mL); the extracts were combined and concentrated to ca. 15.0 mL. A red crystalline solid was obtained after cooling the solution to −10 °C. Yield: 460 mg (67%). M.p. 143−144 °C. ^{1}H NMR (300.17 MHz, C_5D_5N, 295 K): δ = 7.55 (m, 4 H), 7.35 (m, 4 H), 7.18 (m, 2 H), 6.16 (m, 2 H, C_9H_6), 3.24 (m, 4 H), 2.57 (m, 4 H), 1.81 (m, 4 H, $CH_2CH_2CH_2$), 2.13 [s, 12 H, $N(CH_3)_2$] ppm. IR (Nujol and Fluroble mulls): $\tilde{\nu}$ = 2947 (m), 2821 (m), 2777 (m), 1612 (m), 1461 (m), 1262 (m), 1152 (m), 1097 (m), 1042 (m), 965 (m), 914 (m), 769 (s), 719 (m), 411 (m) cm^{-1}. $C_{28}H_{36}N_2Yb$ (573.65): calcd. C58.63, H 6.33, N 4.88; found C 58.79, H 5.99, N 4.82.

[(η⁵:η¹-$C_9H_6CH_2CH_2CH_2NMe_2$)$_2$Eu] (3): This compound was prepared as a yellow crystalline solid in 74% yield from the reaction of $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$ (1.250 g, 1.40 mmol) and $C_9H_7CH_2CH_2CH_2NMe_2$ (570 mg, 2.80 mmol) in toluene at 50 °C by employing procedures similar to those used for the preparation of **2**. NMR spectra were not informative because of the lack of locking signals that arises from the paramagnetic property of the europium(II) complex. M.p. 335−337 °C (dec.). IR (Nujol and Fluroble mulls): $\tilde{\nu}$ = 3065 (m), 2954 (m), 2859 (m), 1789 (m), 1531 (m), 1460 (s), 1402 (s), 1265 (m), 1151 (m), 1042 (m), 963 (m), 847 (m), 769 (s), 719 (s), 412 (w) cm^{-1}. $C_{28}H_{36}EuN_2$ (552.57): calcd. C 60.86, H 6.57, N 5.07; found C 60.58, H 6.42, N 5.06.

[{η⁵:η¹-$Me_2Si(Me_2NCH_2CH_2C_9H_5)(NHtBu)$}$_2$Eu]·$(OC_4H_8)_{0.5}$ (4): This compound was prepared as yellow crystals in 46% yield from the reaction of $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$ (3.010 g, 3.38 mmol) and $Me_2Si(Me_2NCH_2CH_2C_9H_6)(NHtBu)$ (2.140 g, 6.76 mmol) in toluene at 60 °C by employing procedures similar to those used for the preparation of **2**. M.p. 252−254 °C. ^{1}H NMR (300.17 MHz, C_5D_5N, 295 K): δ = 7.54 (br. s, 4 H), 7.19 (br. s, 4 H), 6.57 (m, 2 H, C_9H_5), 4.00 (m, 4 H), 2.88 (m, 4 H, CH_2CH_2), 3.63 (s, 2 H, N*H*), 2.22 [br. s, 12 H, $N(CH_3)_2$], 1.18 [br. s, 18 H, $C(CH_3)_3$], −0.001 [br. s, 12 H, $Si(CH_3)_2$] ppm. IR (Nujol and Fluroble mulls): $\tilde{\nu}$ = 3377 (w), 3063 (w), 2963 (s), 2765 (m), 1600 (m), 1461 (s), 1377 (s), 1249 (s), 1097 (s), 1021 (vs), 864 (s), 764 (s), 721 (m), 615 (m), 435 (w) cm^{-1}. $C_{38}H_{60}EuN_4Si_2$ (**4**·0.5THF) (781.05): calcd. C 58.44, H 7.74, N 7.17; found C 58.05, H 7.76, N 6.90.

[{η⁵:η¹-$(Me_2NCH_2CH_2C_9H_5SiMe_3)$}$_2$Eu] (5): This compound was prepared as yellow crystals in 49% yield from the reaction of $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$ (6.870 g, 7.72 mmol) and $Me_2NCH_2CH_2C_9H_6SiMe_3$ (4.000 g, 15.44 mmol) in toluene at 60 °C by using procedures similar to those used for the preparation of **2**. ^{1}H NMR (300.17 MHz, C_5D_5N, 295 K): δ = 7.55 (br. s, 4 H), 7.18 (br. s, 4 H), 6.48 (m, 2 H, C_9H_5), 4.30 (m, 4 H), 2.90 (m, 4 H, CH_2CH_2), 2.24 [br. s, 12 H, $N(CH_3)_2$], 0.57 (br. s, 6 H), −0.03 [br. s, 12 H, $Si(CH_3)_3$] ppm. IR (Nujol and Fluroble mulls): $\tilde{\nu}$ = 3066 (w), 2954 (s), 1628 (m), 1455 (s), 1374 (m), 1260 (m), 1247 (vs), 1070 (m), 1018 (m), 838 (vs), 765 (m), 719 (m), 431 (w) cm^{-1}. $C_{32}H_{48}EuN_2Si_2$ (668.86): calcd. C 57.45, H 7.23, N 4.19; found C 57.02, H 6.93, N 4.02.

[(η⁵:η¹-$Me_2CH_2CH_2C_9H_6$)$_2$Eu] (6): This compound was prepared as yellow crystals in 57% yield from the reaction of $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$ (1.29 g, 1.91 mmol) and $Me_2NCH_2CH_2C_9H_7$ (720 mg, 3.82 mmol) in toluene under reflux by employing procedures similar to those used for the preparation of **2**. NMR spectra were not informative because of the lack of locking signals that arises from the paramagnetic property of the compound. IR (Nujol and Fluroble mulls): $\tilde{\nu}$ = 3180 (m), 2919 (vs), 1609 (m), 1459 (vs), 1375 (vs), 1265 (m), 1073 (m), 1018 (m), 863 (m), 769 (s), 718 (m), 386 (w) cm^{-1}. $C_{26}H_{32}EuN_2$ (524.50): calcd. C 59.54, H 6.15, N 5.34; found C 59.30, H 6.10, N 5.38.

Table 4. X-ray experimental data of compounds **4**, **5** and **6**

	4	**5**	**6**
Empirical formula	$C_{40}H_{66}EuN_4O_{0.5}Si_2$	$C_{32}H_{48}EuN_2Si_2$	$C_{26}H_{32}EuN_2$
Molecular mass	819.11	668.86	524.50
Crystal system	orthorhombic	tetragonal	monoclinic
Space group	*Fdd*2	$I\bar{4}$	$P2_1/n$
a (Å)	32.70000(10)	21.2723(5)	16.8056(2)
b (Å)	35.6054(7)	21.2723(5)	15.77160(10)
c (Å)	14.8446(4)	15.9895(5)	18.84910(10)
β (deg)			110.4200(10)
V (Å^3)	17283.5(6)	7235.4(3)	4682.03(7)
Temperature (K)	293(2)	293(2)	293(2)
$D_{calcd.}$ (g cm^{-3})	1.259	1.228	1.488
Z	16	8	8
F(000)	6864	2760	2120
No. of refls. collected	10029	8853	16822
No. of unique refls.	4793 (R_{int} = 0.047)	5426 (R_{int} = 0.024)	8219 (R_{int} = 0.035)
No. of parameters	416	334	523
λ (Å); Mo-K_α	0.71073	0.71073	0.71073
μ (mm^{-1})	1.538	1.820	2.693
Theta limits (deg)	2.39/25.04	2.89/25.06	1.40/25.04
GOF	1.064	1.102	1.140
R [$I > 2\sigma(I)$]	0.048	0.039	0.042
wR_2	0.100	0.085	0.083
Largest diff. peak and hole (e·Å^{-3})	0.687 and −0.411	0.562 and −0.334	0.788 and −0.861

High-Resolution GC-MS Analyses: Small portions of the reaction mixtures of the preparations of **2** to **6** were hydrolyzed and analyzed by GC-MS techniques. In addition to the corresponding indene compounds and $HN(SiMe_3)_2$, a small amount of coupling product $[(Me_3Si)_2N]_2$ was detected in each component. Retention time for $[(Me_3Si)_2N]_2$: 15.57 min; calcd. $[\{(Me_3Si)_2N\}_2 - Me]^+$ m/z = 306.1799; found 306.1838.

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 had stabilized, MMA was added through a gastight syringe. The polymerization was terminated by the addition of acidic methanol after a measured interval. 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.

X-Ray Crystallography: Suitable crystals of the complexes **4**, **5**, and **6** were each mounted in a sealed capillary. Diffraction was performed on a Siemens SMART CCD-area detector diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å); temperature 293(2) K; φ and ω scan technique; SADABS effects and empirical absorption were applied in the data corrections. All structures were solved by direct methods (SHELXS-97),[17] completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares calculations based on F^2 (SHELXS-97).[17] See Table 4 for crystallographic data.

CCDC-229706 (for **4**), -195752 (for **5**), and -195751 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was cosponsored by the National Natural Science Foundation of China (Project Nos. 20271003 and 20072001), the Excellent Young Scholars Foundation of Anhui Province, and a grants from the Anhui Education Department and the Anhui Normal University. We are grateful to Professors Jiping Hu and Baohui Du for their help in obtaining NMR and IR spectra.

[1] [1a] H. Schumann, J. A. Meese-Martscheffel, L. Esser, *Chem. Rev.* **1995**, *95*, 865. [1b] G. Bombieri, G. Paolucci, in *Handbook on the Physics and Chemistry of Rare Earths 25* (Eds.: K. A. Gschneidner, L. Eyring, Jr.), Elsevier, Amsterdam, **1998**, p. 265. [1c]W. J. Evans, *Polyhedron* **1987**, *6*, 803. [1d] W. J. Evans, *Coord. Chem. Rev.* **2000**, *206−207*, 263. [1e] W. J. Evans, *J. Organomet. Chem.* **2002**, *652*, 61. [1f] T. G. Wetzel, S. Dehnen, P. W. Roesky, *Angew. Chem. Int. Ed.* **1999**, *38*, 1086−1088. [1g] M. R. Bürgstein, P. W. Roesky, *Organometallics* **2003**, *22*, 1372−1375. [1h] F. Estler, G. Eickerling, E. Herdtweck, R. Anwander, *Organometallics* **2003**, *22*, 1212−1222.

[2] [2a] Y. K. Kim, T. Livinghouse, Y. Horino, *J. Am. Chem. Soc.* **2003**, *125*, 9560. [2b] P. N. O'Shaughnessy, P. Scott, *Tetrahedron: Asymmetry* **2003**, *14*, 1979−1983. [2c] Y. K. Kim, T. Livinghouse, J. E. Bercaw, *Tetrahedron Lett.* **2001**, *42*, 2933. [2d] S. Tian, V. M. Arredondo, C. L. Stern, T. J. Marks, *Organometallics* **1999**, *18*, 2568. [2e] J. S. Ryu, T. J. Marks, F. E. McDonald, *Org. Lett.* **2001**, *3*, 3091. [2f] V. M. Arredondo, F. E. McDonald, T. J. Marks, *Organometallics* **1999**, *18*, 1949. [2g] V. M. Arredondo, S. Tian, F. E. McDonald, T. J. Marks, *J. Am. Chem. Soc.* **1999**, *121*, 3633. [2h] M. R. Gagne, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1992**, *114*, 275. [2i] M. R. Gagne, L. Brard, V. P. Conticello, M. A. Giardello, C. L. Stern, T. J. Marks, *Organometallics* **1992**, *11*, 2003. [2j] M. A. Giardello, V. P. Conticello, L. Brard, M. R. Gagne, T. J. Marks, *J. Am. Chem. Soc.* **1994**, *116*, 10241X. [2k] P. N. O'Shaughnessy, P. D. Knight, C. Morton, K. M. Gillespie, P. Scott, *Chem. Commun.* **2003**, 1770−1771. [2l] P. W. Roesky, T. E. Müller, *Angew. Chem. Int. Ed.* **2003**, *42*, 2708−2710. [2m] M. R. Bürgstein, H. Berberich, P. W. Roesky, *Eur. J. Chem.* **2001**, *7*, 3078−3085.

[3] Y. Horino, T. Livinghouse, *Organometallics* **2004**, *23*, 12−14.

[4] [4a] M. R. Douglass, T. J. Marks, *J. Am. Chem. Soc.* **2000**, *122*, 1824−1825. [4b] M. R. Douglass, M. Ogasawara, S. Hong, M. V. Metz, T. J. Marks, *Organometallics* **2002**, *21*, 283−292. [4c] A. M. Kawaoka, M. R. Douglass, T. J. Marks, *Organometallics* **2003**, *22*, 4630−4632.

[5] [5a] H. Yasuda, in *Lanthanides: Chemistry and Use in Organic Synthesis* (Ed.: S. Kobayashi), Springer-Verlag, Heidelberg, **1999**, p. 255. [5b]H. Yasuda, *J. Organomet. Chem.* **2002**, *647*, 128. [5c] Z. Hou, Y. Wakatsuki, *Coord. Chem. Rev.* **2002**, *231*, 1. [5d] M. A. Giardello, Y. Yamamoto, L. Brard, T. J. Marks, *J. Am. Chem. Soc.* **1995**, *117*, 3276. [5e] C. T. Qian, G. Zuo, Y. F. Chen, J. Sun, *Organometallics* **2001**, *20*, 3106. [5f] C. Boisson, F. Barbotin, R. Spitz, *Macromol. Chem. Phys.* **1999**, *200*, 1163. [5g] C. T. Qian, W. L. Nie, J. Sun, *Organometallics* **2000**, *19*, 4134. [5h] S. Zhou, S. Wang, G. Yang, X. Liu, E. Sheng, K. Zhang, L. Cheng, Z. Huang, *Polyhedron* **2003**, *22*, 1019−1024. [5i] Y. Yao, Y. Zhang, Z. Zhang, Q. Shen, K. Yu, *Organometallics* **2003**, *22*, 2876−2882. [5j] Y. Yao, Y. Luo, J. Chen, Z. Zhang, Y. Zhang, Q. Shen, *J. Organomet. Chem.* **2003**, *679*, 229−237.

[6] [6a] H. Berberich, P. W. Roesky, *Angew. Chem. Int. Ed.* **1998**, *37*, 1569. [6b] M. R. Bürgstein, H. Berberich, P. W. Roesky, *Eur. J. Chem.* **2001**, *7*, 3078. [6c] G. B. Deacon, A. Gitlits, P. W. Roesky, M. R. Bürgstein, K. C. Lim, B. W. Skelton, A. H. White, *Chem. Eur. J.* **2001**, *7*, 127−138.

[7] [7a] K. C. Hultsch, T. P. Spaniol, J. Okuda, *Organometallics* **1997**, *16*, 4845. [7b] E. Martin, P. Dubois, R. Jerome, *Macromolecules* **2000**, *33*, 1530. [7c] H. Noss, M. Oberthür, C. Fischer, W. P. Kretschmer, R. Kempe, *Eur. J. Inorg. Chem.* **1999**, 2283−2288. [7d] Y. Luo, Y. Yao, Q. Shen, J. Sun, L. Weng, *J. Organomet. Chem.* **2002**, *662*, 144−149.

[8] [8a] J. Zhang, R. Cai, L. Weng, X. Zhou, *Organometallics* **2003**, *22*, 5385−5391. [8b] H. R. Li, Y. M. Yao, Q. Shen, L. H. Weng, *Organometallics* **2002**, *21*, 2529−2532. [8c] L. S. Mao, Q. Shen, M. Q. Xue, *Organometallics* **1997**, *16*, 3711. [8d] J. Zhang, R. Cai, L. Weng, X. Zhou, *J. Organomet. Chem.* **2003**, *672*, 94−99.

[9] [9a] E. Sheng, S. Wang, G. Yang, S. Zhou, L. Cheng, K. Zhang, Z. Huang, *Organometallics* **2003**, *22*, 684−692. [9b] K. Zhang, W. Zhang, S. Wang, E. Sheng, G. Yang, M. Xie, S. Zhou, Y. Feng, L. Mao, Z Huang, *J. Chem. Soc., Dalton Trans.* **2004**, 1029−1037.

[10] [10a] J. Eppinger, M. Spiegler, W. Hieringer, W. A. Herrmann, R. Anwander, *J. Am. Chem. Soc.* **2000**, *122*, 3080. [10b] W. A. Herrmann, J. Eppinger, M. Spiegler, O. Runte, R. Anwander, *Organometallics* **1997**, *16*, 1813. [10c] R. Anwander, O. Runte, J. Eppinger, G. Gerstberger, M. Spiegler, E. Herctweck, *J. Chem. Soc., Dalton Trans.* **1998**, 847.

[11] S. Wang, S. Zhou, E. Sheng, G. Yang, M. Xie, K. Zhang, L. Cheng, Y. Feng, L. Mao, Z. Huang, *Organometallics* **2003**, *22*, 3546−3552.

[12] R. D. Shannon, *Acta Crystallogr., Sect. A* **1976**, *32*, 751−767.

[13] F. A. Bovey, P. A. Mirau, *NMR of Polymers*, Academic Press, San Diego, **1996**.

[14] [14a] M. A. Giardello, V. P. Conticello, L. Brard, M. Sabat, A. L. Rheingold, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1994**,

116, 10212X. [14b] C. M. Haar, C. L. Stern, T. J. Marks, *Organometallics* **1996**, *15*, 1765. [14c] K. C. Hultzsch, T. P. Spaniol, J. Okuda, *Organometallics* **1997**, *16*, 4845. [14d] J. C. Yoder, M. W. Day, J. E. Bercaw, *Organometallics* **1998**, *17*, 4946. [14e] S. Wang, Q. Yang, T. C. W. Mak, Z. Xie, *Organometallics* **2000**, *19*, 334−343.
[15] L. S. Boffa, B. M. Novak, *Macromolecules* **1994**, *27*, 6993.
[16] C. Qian, G. Zuo, J. Sun, *J. Organomet. Chem.* **1999**, *585*, 59−62.
[17] G. M. Sheldrick, *SHELXTL*, Version 5.10; Bruker Analytical X-ray Systems, Inc., Madison, WI, **1997**.

Received January 30, 2004
Early View Article
Published Online June 1, 2004

