APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 10, 761–771 (1996)

Synthesis of Lanthanide–Alkylaluminium Bimetallic Complexes and Studies on Their Catalytic Activities for Polymerization of Some Polar Monomers*

Fengfu Li,†‡ Yingtai Jin,§ Chunlei Song,§ Yonghua Lin,§ Fengkui Pei,§ Fosong Wang§ and Ninghai Hu§

‡ Institute of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China, and § Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

Three new lanthanide (Ln)–alkylaluminium (Al) bimetallic complexes with the formula $[(\mu\text{-}CF_3CO_2)_2Ln(\mu\text{-}CF_3CHO_2)AlR_2 \cdot 2THF]_2$ (Ln = Nd, Y, R = i-C_4H_9 (i-Bu); Ln = Eu, R = C_2H_5(Et); THF = tetrahydrofuran) were synthesized by the reaction of $Ln(CF_3CO_2)_3$ (Ln = Nd, Y) with HAl $(i\text{-}Bu)_2$ and of $Eu(CF_3CO_2)_3$ with $AlEt_3$, respectively. Their crystal structures were determined by X-ray diffraction at 233 K. $[(\mu\text{-}CF_3CO_2)_2Nd(\mu\text{-}CF_3CHO_2)Al(i\text{-}Bu)_2 \cdot 2THF]_2$ (Nd–Al) and $[(\mu\text{-}CF_3CO_2)_2Y(\mu\text{-}CF_3CHO_2)Al(i\text{-}Bu)_2 \cdot 2THF]_2$ (Y–Al) are isomorphous and crystallize in space group $P\bar{1}$ with $a = 12.441(3)$ Å [12.347(5) Å for Y–Al], $b = 12.832(3)$ Å [12.832(4) Å], $c = 11.334(3)$ Å [11.292(8) Å], $\alpha = 104.93\ (2)°$ [104.45(4)°], $\beta = 98.47(2)°$ [98.81(4)°], $\gamma = 64.60(2)°$ [64.30(3)°], $R = 0.519$ [0.113], $R_w = 0.0532$ [0.110], $Z = 1$ and $[(\mu\text{-}CF_3CO_2)_2Eu(CF_3CHO_2)AlEt_2 \cdot 2THF]_2$(Eu–Al) in space group $P2_1/n$ with $a = 11.913(6)$ Å, $b = 14.051(9)$ Å, $c = 17.920(9)$ Å, $\alpha = 101.88(11)°$, $\beta = \gamma = 90°$, $R = 0.0509$, $R_w = 0.0471$ and $Z = 2$. The six $CF_3CO_2^-$ (including $CF_3CHO_2^-$) of each complex, among which pairs are equivalent, coordinated to Ln and Al in three patterns: (A) the two oxygen atoms in one of the three $CF_3CO_2^-$ type coordinated to two different Ln; (B) the two oxygen atoms in the second of $CF_3CO_2^-$ type coordinated to Ln and Al, respectively; (C) one of the two oxygen atoms in the third $CF_3CO_2^-$ type bidentately coordinated to two Ln and another oxygen coordinated to Al and one of the two Ln, respectively. Unlike types A and B, in type C the carboxyl carbon with a hydrogen atom bonded to it was found to appear as an sp^3-hybridized configuration rather than an sp^2-one. 1D and 2D NMR results further confirmed the existence of such a disproportionated $CF_3CHO_2^-$ ligand. Methyl methacrylate (MMA) and epichlorohydrin (ECH) could be polymerized by Y–Al or Eu–Al as a single-component catalyst and highly syndiotactic poly(MMA) was obtained. THF could also be polymerized by Y–Al in the presence of a small amount of ECH.

Keywords: organolanthanide; alkylaluminium; bimetallic complex; NMR spectra; polymerization; single-component catalyst; epichlorohydrin; methyl methacrylate; tetrahydrofuran

INTRODUCTION

Recently, the homopolymerization or copolymerization of some monomers, such as ethylene, α-olefins, acrylate, methyl methacrylate (MMA), ethylene carbonate and ε-caprolactone, with well-defined organolanthanide compounds as single-component catalysts has become an interesting area.[1–12] Some of the above polymerization systems showed living polymerization features[5, 10] and the polymerization mechanisms were clearly elucidated.[5] However, these catalysts generally have either cyclopentadienyl (Cp) or substituted cyclopentadienyl (Cp*) coordi-

---

* Crystallographic data and structure factors for the synthesized complexes have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK.

† Author to whom correspondence should be addressed.

CCC 0268-2605/96/100761-11

Received 6 December 1995
Accepted 29 January 1996

nated to lanthanide ions. Other single-component organolanthanide catalysts without Cp or Cp* ligands have rarely been reported.[13] In our previous work, we reported two crystal structures of $[(CF_3CO_2)_3LnAl(C_2H_5)_2 \cdot 2THF]_2$ (Ln=Y, Nd; THF=tetrahydrofuran).[14] However, the reason for the non-coplanar configuration between the methyl carbon and the carboxylic atoms in one kind of $CF_3CO_2^-$ in these complexes was not elucidated, nor were the catalytic activities of these complexes reported. In this paper, three new Ln–Al complexes with the formula $[(CF_3CO_2)_2Ln(CF_3CHO_2)AlR_2 \cdot 2THF]_2$ (Ln=Nd, Y, R=i-Bu; Ln=Eu, R=Et) were synthesized by the reaction of $Ln(CF_3CO_2)_3$ with $R^1AlR^2_2$ (Ln=Nd, Y, R^1=H, R^2=i-Bu, Ln=Eu, R^1=R^2=Et) in THF, and characterized by elemental analysis, X-ray diffraction and 1D and 2D NMR techniques. The reason for the non-coplanar configuration mentioned above was clarified. Also, the catalytic activities of these complexes in polymerizing epichlorohydrin (ECH), MMA and THF were studied.

EXPERIMENTAL

Measurements

Lanthanide elements were determined by complexometric titration. 1D and 2D NMR spectra of the Y–Al complex were recorded on a Unity 400 MHz NMR spectrometer generally at 19.6 °C. Under argon, the Y–Al complex (30 mg) was added in a dry 5 mm NMR tube and THF-d_8 was added as solvent. Then the tube was sealed. The microstructures of poly(MMA) were analysed by the ^{13}C NMR technique with $CDCl_3$ as solvent according to the literature.[15]

Single crystals of Ln–Al complexes were selected under an atmosphere of nitrogen and sealed in quartz-glass capillaries. Intensity data were collected on a Nicolet R 3m/E four-circle diffractometer at 233 K using graphite-monochromated MoKα radiation (λ=0.71073 Å) in the ω scan mode. Empirical absorption corrections were applied to intensity data by the Ψ scan method. The structures were solved by the heavy-atom method and refined by block-diagonal least-squares techniques. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added to the structures in their theoretical positions and fixed in the final cycles of the refinements. All crystallographic calculations were performed using the SHELXTL program system.

Materials

THF and THF-d_8 (Aldrich) were refluxed over Na–K alloy and benzophenone under the atmosphere of purified argon and distilled before use. MMA and ECH were dried over CaH_2 and distilled prior to use. CF_3COOH (Merck), $AlEt_3$ (Fluka) and HAl $(i\text{-}Bu)_2$ (Schering) were used without further purification. Nd_2O_3, Y_2O_3 and Eu_2O_3 (99.9% purity) were purchased from the Chemistry Department of Beijing University. Lanthanide trifluoroacetates were prepared according to the reported method.[16]

Preparation of $[(\mu\text{-}CF_3CO_2)_2Y(\mu\text{-}CF_3CHO_2)Al(i\text{-}Bu)_2 \cdot 2THF]_2$

$Y(CF_3CO_2)_3$ (1.28 g, 3.0 mmol) was placed in a dry Schlenk-type glass vessel under argon and dissolved in 21.4 cm^3 THF. At −78 °C, HAl (i-Bu)$_2$ (2.68 cm^3, 15 mmol) was added dropwise and the reacting system was kept for 24 h at 0 °C. Then the solution was concentrated to about 5 cm^3 and kept at 0 °C for 24 h. Colourless crystals (Y–Al) (0.32 g) were obtained. Nd-Al (purplish) and Eu–Al (colourless) crystals were prepared by the same way. These three kinds of crystals decomposed before melting.

Analyses: $C_{22}H_{35}O_8AlF_9Y$, Calcd: Y, 12.47; Found: 12.79% $C_{22}H_{35}O_8AlF_9Nd$, Calcd: Nd, 18.77; Found: 18.45%. $C_{18}H_{27}O_8AlEuF_9$, Calcd: Eu, 21.11; Found: 21.56%.

Polymerization procedures

All polymerization procedures were carried out in dry glass polymerization bottles under argon in a thermostat. Catalysts were added to the polymerization bottles first, then monomers were added by syringe. Both THF and ECH polymerizations were terminated by adding water containing a small amount of hydrochloric acid. The polymers precipitated were washed with water and dried *in vacuo* at 50°C. The polymerization of MMA was terminated by adding ethanol containing a small amount of hydrochloric acid. The resulting polymer was washed with

Table 1 Crystal data and some data collection parameters for Nd–Al, Y–Al and Eu–Al complexes

Formula	$C_{44}H_{70}O_{16}Al_2F_{18}Nd_2$	$C_{44}H_{70}O_{16}Al_2F_{18}Y_2$	$C_{36}H_{54}O_{16}Al_2Eu_2F_{18}$
Formula weight	1539.4	1428.7	1442.6
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a, Å	12.441(3)	12.347(5)	11.913(6)
b,Å	12.832(3)	12.832(4)	14.051(9)
c,Å	11.334(3)	11.292(8)	17.920(9)
α, deg	104.9(2)	104.5(4)	90
β, deg	98.5(2)	98.8(4)	101.9(1)
γ, deg	64.6(2)	64.3(3)	90
V, Å^3	1577.7(7)	1561.1(0)	2935.0(2)
Crystal system	Triclinic	Triclinic	Monoclinic
Z	1 (dimer)	1 (dimer)	2 (dimer)
D_{calcd}, g cm^{-3}	1.713	1.577	1.690
2θ range, deg	3–48	3–42	3–46
Reflections collected	3530	4111	4006
$I>3\sigma(I)$	1044	1150	1888
R	0.0519	0.113	0.0509
R_w	0.0532	0.110	0.0471

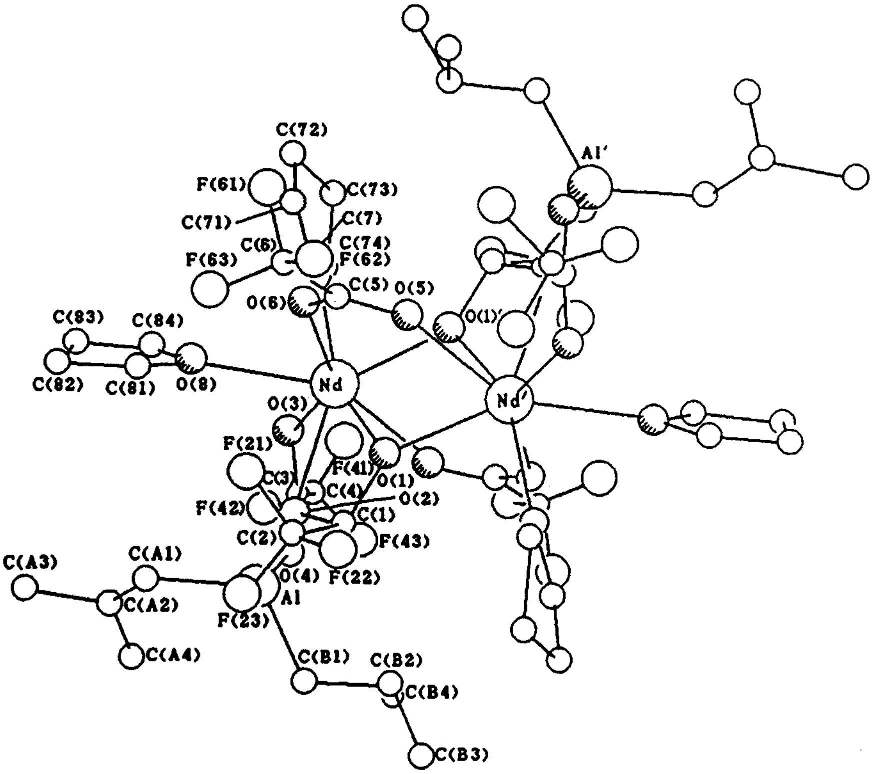


Figure 1 Perspective view of $[(\mu\text{-}CF_3CO_2)_2Nd\,(\mu\text{-}CF_3CHO_2)\,Al(i\text{-}Bu)_2\cdot 2THF]_2$ complex.

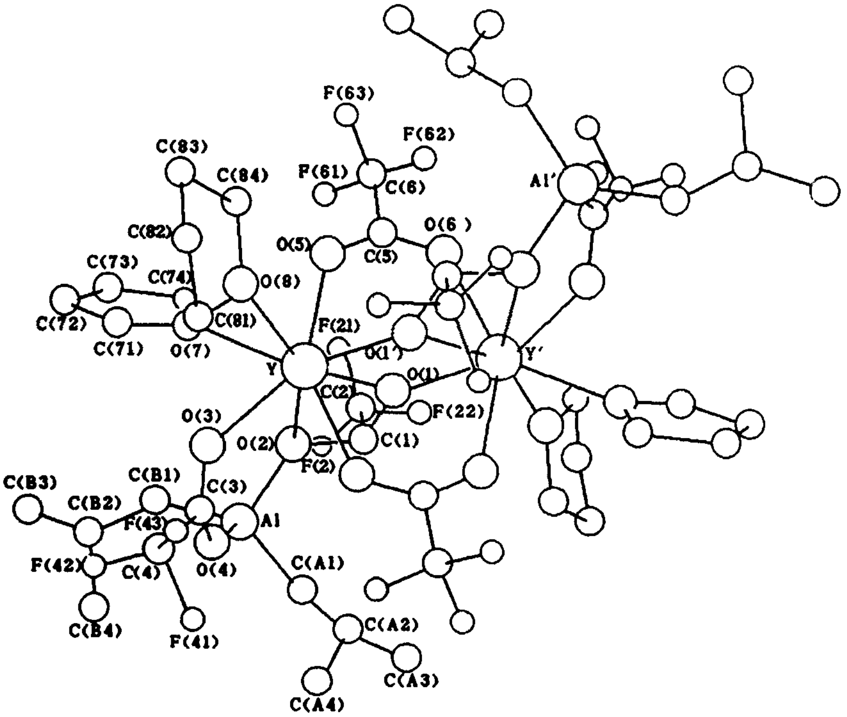


Figure 2 Perspective view of $[(\mu\text{-}CF_3CO_2)_2Y(\mu\text{-}CF_3CHO_2)Al(i\text{-}Bu)_2 \cdot 2THF]_2$ complex.

ethanol and dried under the same conditions as above. Conversions were calculated from the amount of polymer obtained versus the amount of monomers used.

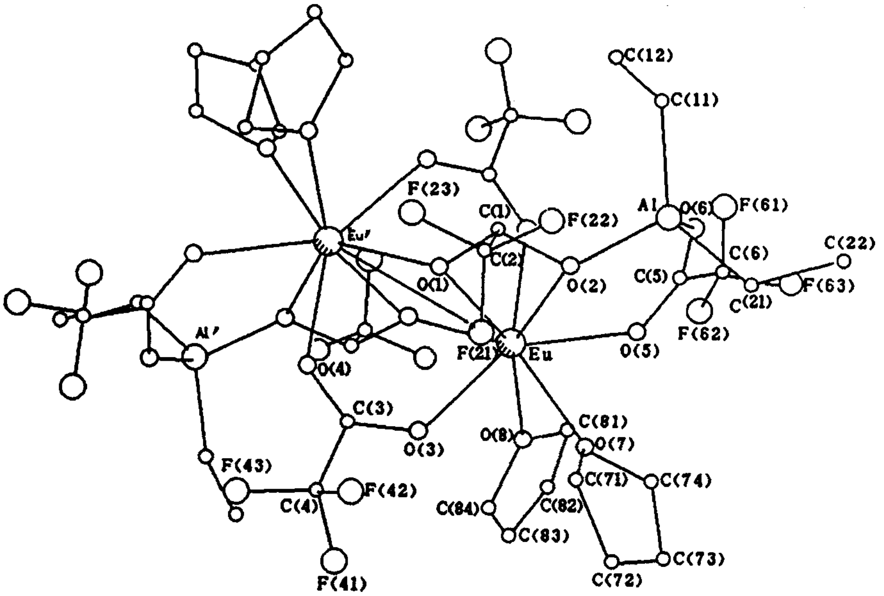


Figure 3 Perspective view of $[(\mu\text{-}CF_3CO_2)_2Eu(\mu\text{-}CF_3CHO_2)AlEt_2 \cdot 2THF]_2$.

Table 2 Selected bond distances and bond angles in the Nd–Al complex

Bond distances, Å					
Nd–Nd′	3.756(1)	C(1)–O(1)	1.382(8)	Al–O(2)	1.813(5)
Nd–O(1)	2.386(5)	C(1)–O(2)	1.429(8)	Al–O(4)	1.858(7)
Nd–O(2)	2.451(4)	C(3)–O(3)	1.234(11)	Al–C(A1)	1.940(12)
Nd–O(3)	2.462(5)	C(3)–O(4)	1.247(10)	Al–C(B1)	1.947(12)
Nd–O(5)	2.481(7)	C(5)–O(5)	1.218(12)		
Nd–O(6)	2.432(6)	C(5)–O(6)	1.254(9)		
Nd–O(7)	2.499(5)				
Nd–O(8)	2.547(7)				
Nd–O(1′)	2.319(5)				
Nd–C(1)	2.973(8)				
Bond angles, deg					
O(1)–C(1)–O(2)	107.0(6)				
O(1)–C(1)–C(2)	109.0(7)				
O(2)–C(1)–C(2)	107.1(2)				
O(3)–C(3)–C(4)	129.6(8)				
O(4)–C(3)–C(4)	114.9(8)				
O(3)–C(3)–C(4)	115.5(7)				
O(6)–C(5)–C(6)	114.7(9)				
O(6)–C(5)–O(5)	130.2(11)				
O(6)–C(5)–O(5)	115.0(7)				

RESULTS AND DISCUSSION

Synthesis of Ln–Al bimetallic complexes

The Nd–Al and Y–Al complexes were obtained according to Eqn [1] and the Eu–Al complex according to Eqn [2], in THF.

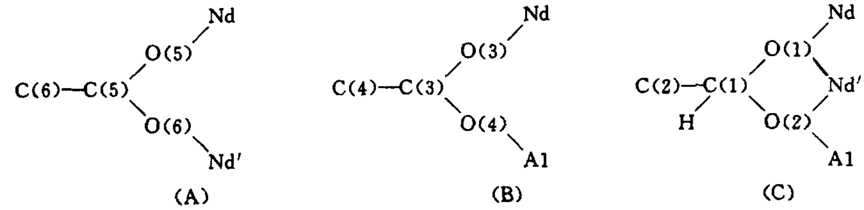
$$2\mathrm{Ln(CF_3CO_2)_3)+2HAl\,(i\text{-}Bu)_2+4THF}\rightarrow$$
$$\mathrm{[(CF_3CO_2)_2Ln(CF_3CHO_2)Al(i\text{-}Bu)_2\cdot 2THF]_2}$$
$$(\mathrm{Ln=Nd\ or\ Y})\quad [1]$$

$$2\mathrm{Eu(CF_3CO_2)_3+2AlEt_3+4THF}\rightarrow$$
$$\mathrm{[(CF_3CO_2)_2Eu(CF_3CHO_2)AlEt_2\cdot 2THF]_2}$$
$$+2\mathrm{C_2H_4}\uparrow\quad [2]$$

No gas, such as isobutene, was found to be released during the reaction of Ln $(\mathrm{CF_3CO_2})_3$ (Ln=Nd or Y) with $\mathrm{HAl(i\text{-}Bu)_2}$, but the evolution of ethylene was detected during the reaction of $\mathrm{Eu(CF_3CO_2)_3}$ with $\mathrm{AlEt_3}$. Obviously, the hydrogen in the $\mathrm{CF_3CHO_2^-}$ of the Nd–Al or Y–Al complex was from the hydrogen bonded to Al in $\mathrm{HAl(i\text{-}Bu)_2}$, while the hydrogen in the $\mathrm{CF_3CHO_2^-}$ of the Eu–Al complex was from the β-hydrogen elimination of ethyl in $\mathrm{AlEt_3}$. However, the detailed processes of formation of these complexes still need further investigation.

Crystallographic studies of Ln–Al complexes

Crystallographic data of Nd–Al, Y–Al and Eu–Al are listed in Table 1. Their crystal structures are shown in Figs 1, 2 and 3, respectively. As can be seen from Table 1, both Nd–Al and Y–Al crystals are triclinic with the Pi space group and have similar parameters. Obviously, the two complexes are isomorphous. However, the *R* factor for the Y–Al complex is quite high, which may be caused by the poor quality of the crystal selected.



Scheme 1 The coordination patterns of $\mathrm{CF_3CO_2^-}$ and $\mathrm{CF_3CHO_2^-}$ in the Nd–Al complex.

Table 3 Selected bond distances and bond angles in the Eu–Al complex

Bond distances, Å					
Eu–Eu′	3.691(2)	Eu–O(1′)	2.297(9)	C(3)–C(4)	1.538(21)
Eu–O(1)	2.364(10)	O(1)–C(1)	1.381(19)	C(5)–C(6)	1.535(24)
Eu–O(2)	2.429(10)	O(2)–C(1)	1.404(8)	Al–O(2)	1.823(11)
Eu–O(3)	2.408(9)	O(3)–C(3)	1.252(17)	Al–O(6)	1.863(11)
Eu–O(4)	2.443(8)	O(4)–C(3)	1.254(17)		
Eu–O(5)	2.402(9)	O(5)–C(5)	1.200(20)		
Eu–O(7)	2.457(9)	O(6)–C(5)	1.308(21)		
Eu–O(8)	2.456(11)	C(1)–C(2)	1.524(21)		

Bond angles, deg			
O(2)–C(1)–C(2)	108.0(12)	O(5)–C(5)–O(6)	129.2(14)
O(2)–C(1)–O(1)	107.6(12)	O(5)–C(5)–C(6)	117.8(16)
C(2)–C(1)–O(1)	106.9(12)	O(6)–C(5)–C(6)	112.9(14)
O(4)–C(3)–C(4)	120.0(13)		
O(4)–C(3)–O(3)	126.0(12)		
C(4)–C(3)–O(3)	113.9(13)		

The selected bond lengths and bond angles of the Nd–Al complex are summarized in Table 2. It is found that all the oxygen atoms in $CF_3CO_2^-$ or $CF_3CHO_2^-$ participated in forming bridge bonds in either of the three types of coordination patterns (Scheme 1).

Each Nd ion was coordinated by eight oxygens from one $CF_3CHO_2^-$, two $CF_3CO_2^-$ and two THF. The geometry around an Nd ion is a distorted bicapped prism. The average Nd–O ($CF_3CO_2^-$, $CF_3CHO_2^-$) distance, 2.422(5) Å, approximates to that of Pr–O ($CF_3CO_2^-$), 2.45(3) Å, found in $Pr(CF_3CO_2)_3(OH)(C_{10}H_{20}O_5)_2Pr(CF_3CO_2)_8$.[17] The average bond length of Nd–O (THF), 2.523(7) Å, is slightly shorter than that of La–O (THF), 2.57(1) Å, in $Cp_3La \cdot THF$.[18] Two oxygens separately from $CF_3CO_2^-$ and $CF_3CHO_2^-$ and two carbons from two i-Bu coordinated to Al form a distorted tetrahedron, where the average Al–O distance is 1.836(6) Å and Al–C is 1.944(12) Å. The average Al–C bond is shorter than that in $Cp_2Y(\mu\text{-}CH_3)_2Al(CH_3)_2$ (Al–C, 2.095 Å).[19]

It is interesting that the sum of O(1)–C(1)–O(2), O(1)–C(1)–C(2) and O(2)–C(1)–C(2) angles around C(1) is 323.1°, while angles

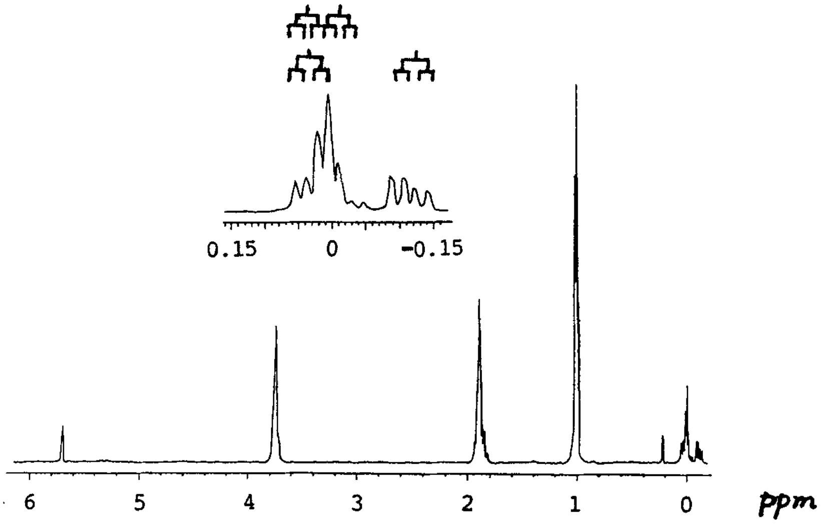


Figure 4 400 MHz ^1H NMR spectrum of $[(\mu\text{-}CF_3CO_2)_2Y(\mu\text{-}CF_3CHO_2)Al(i\text{-}Bu)_2 \cdot 2THF]_2$ complex.

Table 4 Chemical shifts of the Y–Al complex

		^{1}H NMR, δ^a (ppm)	^{13}C NMR, δ^b (ppm)
i-Bu	CH_3	1.00, 1.01, 1.02	28.69, 28.77, 29.10, 29.31
	CH	1.90	27.06, 27.09
	CH_2	-0.11, 0.03 ($^2J=16.0$ Hz, $^3J\approx6.5$ Hz)	21.32, 23.16
		-0.02, 0.03 ($^2J=16.0$ Hz, $^3J\approx6.0$ Hz)	
THF	OCH_2	3.78	68.69
	CH_2	1.90	26.87
CF_3CHO_2	HCO_2	5.68	93.47 ($^2J_{CF}=35.4$ Hz)
	CF_3		124.82 ($^2J_{CF}=286.9$ Hz)
CF_3CO_2	CO_2		164.17 ($^2J_{CF}=40.9$ Hz)
			164.83 ($^1J_{CF}=38.5$ Hz)
	CF_3		116.93 ($^1J_{CF}=285.7$ Hz)
			117.50 ($^1J_{CF}=288.8$ Hz)

[a] Referenced to the residual hydrogen of THF-d_8 at 1.90 ppm.

[b] Referenced to 25.8 ppm of THF-d_8.

around C(3) and C(5) are 360°, respectively (see Table 2). Obviously, the four atoms, C(1), C(2), O(1) and O(2) from $CF_3CHO_2^-$ lost coplanarity and C(1) appeared as an sp^3-hybridized configuration rather than an sp^2 one. The same happened to $[(CF_3CO_2)_3LnAlEt_2 \cdot 2THF]_2$ (Ln = Y, Nd).[14] Moreover, the average C(1)–O distance, 1.406(8) Å, is apparently longer than that of C(3)–O, 1.241(11) Å or C(5)–O, 1.236(11) Å. We assumed that C(1) was bonded by a hydrogen atom in addition to O(1), O(2) and C(2). The existence of such a special hydrogen atom was confirmed by studying the Y–Al complex with NMR techniques (see the NMR characterization section).

Unlike the Nd–Al or Y–Al complex, the crystal of Eu–Al is monoclinic with the $P2_1/n$ space group (Table 1). The coordination patterns of $CF_3CO_2^-$ and $CF_3CHO_2^-$ to Eu and Al atoms (Fig. 3) are the same as those in the Y–Al or Nd–Al complex. The selected bond distances and bond angles are listed in Table 3. As can be seen from Table 3, the sum of angles around C(1) is 322.5°, similar to that in the Nd–Al complex.

It is notable that the Ln–Ln distances are 3.756(1) Å (Nd–Nd), 3.639(7) Å (Y–Y) and 3.691(2) Å (Eu–Eu) in the corresponding complexes. The first two are 15% and 12% longer

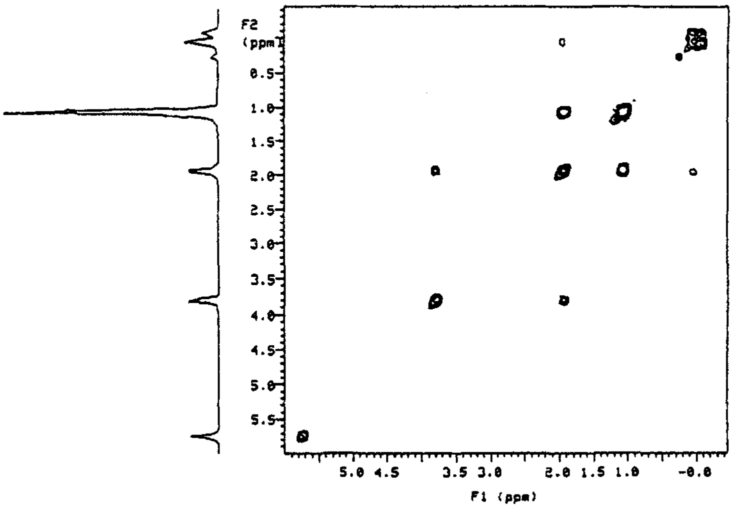


Figure 5 400 MHz ^{1}H–^{1}H COSY spectrum of $[(\mu\text{-}CF_3CO_2)_2Y(\mu\text{-}CF_3CHO_2)Al(i\text{-}Bu)_2 \cdot 2THF]_2$ complex.

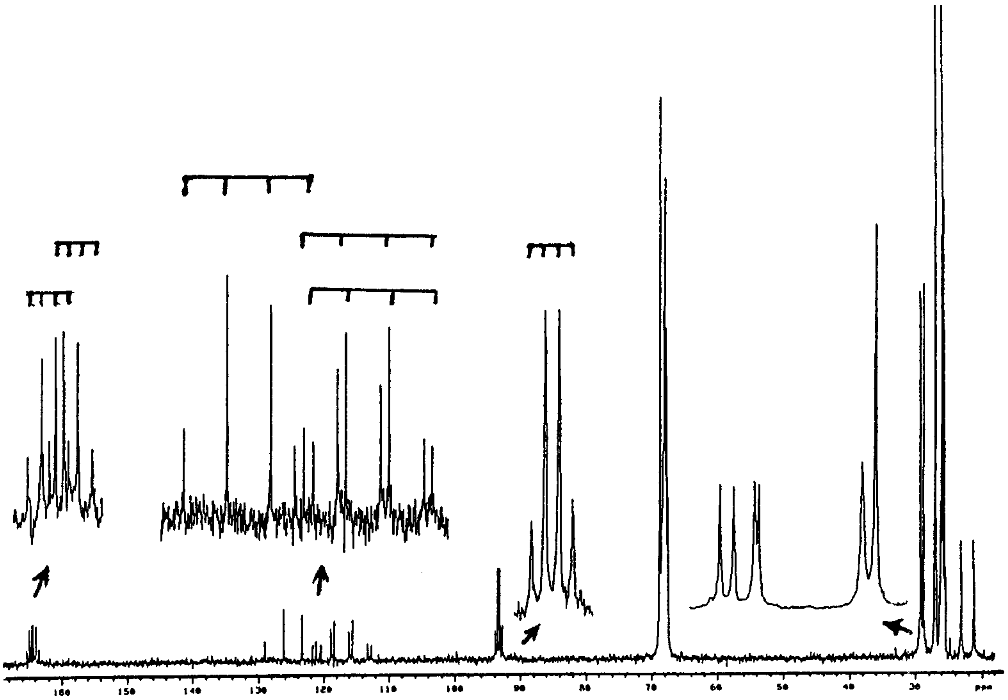


Figure 6 400 MHz ^{13}C NMR spectrum of $[(\mu\text{-}CF_3CO_2)_2Y(\mu\text{-}CF_3CHO_2)Al(i\text{-}Bu)_2 \cdot 2THF]_2$ complex.

than the sums of the corresponding covalent radius, 3.28 Å and 3.24 Å. Moreover, the Eu–Eu distance is nearly equal to the sum of the covalent radius of two Eu atoms, 3.70 Å. Such short distances between two lanthanide ions in organolanthanides have not been found in the literature.

NMR characterization of Ln–Al complexes

Because of the paramagnetic effects of Nd^{3+} and Eu^{3+} ions, the chemical shifts of ligands, generally being considerably broadened and shifted, were hard to analyse and assign, so we studied the Y–Al complex in detail by NMR. The ^{1}H NMR spectrum of the Y–Al complex at 50 °C is shown in Fig. 4. The ^{1}H and ^{13}C chemical shifts are shown in Table 4. In the range of −0.2 to 6.0 ppm, five groups of signals were observed. The chemical shifts at 1.90 and 3.78 ppm showing a strong correlating peak in the ^{1}H–^{1}H COSY spectrum (Fig. 5), are from CH_2 and CH_2O of the THF ligand and the corresponding residual hydrogens of THF-d_8. Moreover, the signal at 1.90 ppm, which correlates with two groups of multiplets at higher field, contains a strong singlet and a weak multiplet. These two multiplets also correlate with each other with an integration ratio of 3 : 1. The multiplet at 1.0 ppm results from two doublets overlapped. The weak signals in the range of −0.2 to 0.1 ppm can be considered as the combination of two AB spectra as part of two typical ABX spectra. Based on the above analyses, the weak multiplet at 1.90 ppm is assigned to the CH proton in two i-Bu, and the peaks at 1.0 ppm are assigned to the CH_3 protons in two i-Bu. The multiplets from −0.2 to 0.1 ppm are due to the CH_2 protons in i-Bu. It is obvious that the two i-Bu coordinating to one Al are magnetically non-equivalent because of steric hindrance.

It is interesting to know that a singlet with resonance at 5.68 ppm, not correlating with any other peaks in the ^{1}H–^{1}H COSY spectrum, was observed. The integration ratio of the singlet to the signals of CH_3 in i-Bu is 1 : 12. This signal is assigned to the CH proton from $CF_3CHO_2^-$ deriving from the hydrogen addition reaction of $CF_3CO_2^-$.

The ^{13}C NMR spectrum of the Y–Al complex is shown in Fig. 6. The chemical shifts are assigned by referencing the ^{13}C–^{1}H COSY spectrum (Fig. 7) and are listed in Table 4.

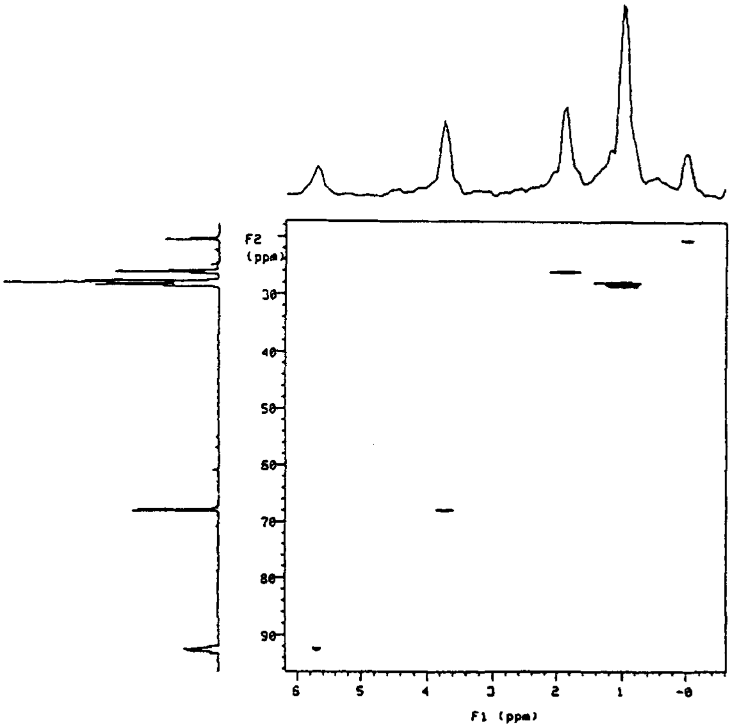


Figure 7 400 MHz ^{13}C-^{1}H COSY spectrum of $[(\mu\text{-}CF_3CO_2)_2Y(\mu\text{-}CF_3CHO_2)Al(i\text{-}Bu)_2 \cdot 2THF]_2$ complex.

Obviously, all the corresponding carbons from two i-Bu are non-equivalent. However, the two THF coordinating to one Y show no apparent difference, in either the ^{1}H NMR or ^{13}C NMR spectrum. Moreover, the peaks at 28.69 and 28.78 ppm coalesced at 50 °C, which indicated that there was slow exchange occuring between the two CH_3 in one i-Bu. This exchange can be accelerated by raising the temperature. However, the exchange between the two non-equivalent i-Bu ligands did not occur at higher temperatures.

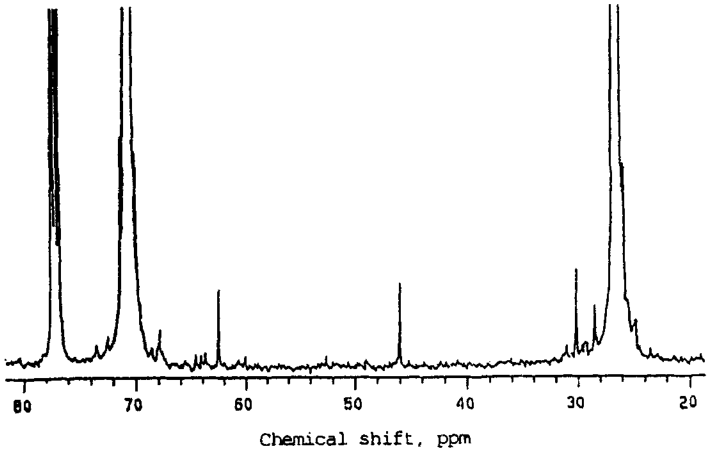
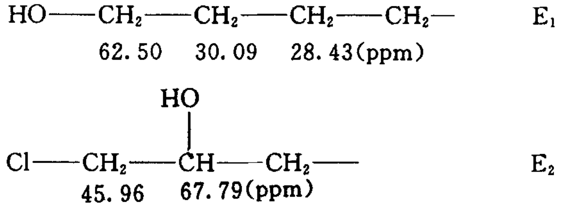


Figure 8 400 MHz ^{13}C NMR spectrum of poly(THF).

Table 5 Catalytic activities of Ln–Al complexes for bulk polymerization of some polar monomers

Ln–Al ($\times 10^5$ mol)	Monomer (g)	Polym. temp. (°C)	Polym. time (h)	Conversion (%)	Tacticity[b] (%) rr	mm
2.18 (Y–Al)	2.81 (MMA)	50	7	12.3	65.9	34.1
2.66 (Y–Al)	2.81 (MMA)	0	7	8.5	76.5	23.5
2.12 (Eu–Al)	2.81 (MMA)	50	4	17.8	67.3	32.7
2.12 (Eu–Al)	5.92 (ECH)	50	2	64.9		
2.17 (Y–Al)	3.55 (ECH)	50	1.3	59.2		
2.20 (Y–Al)	5.32 (THF)	50	24	0		
2.00 (Y–Al)	5.32 (THF)	50	24	7.5[a]		

[a] ECH/(Y–Al) (molar ratio) is 1 : 1. [b] rr; mm.



$$\mathrm{HO{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}} \qquad E_1$$

$$\mathrm{Cl{-}CH_2{-}\overset{\displaystyle HO}{\overset{|}{C}}H{-}CH_2{-}} \qquad E_2$$

Scheme 2 Polymer ends in poly(THF).

In the range of 90–170 ppm in the ^{13}C NMR spectrum, six groups of quartets could be found. The splitting between the two peaks of each quartet is the same. These chemical shifts are due to $CF_3CHO_2^-$ and two kinds of $CF_3CO_2^-$. Both chemical shifts and coupling constants are slightly different for the two kinds of $CF_3CO_2^-$ in coordination patterns A and B (Scheme 1), but apparently different from those in pattern C. In pattern C, the carbon chemical shift of CF_3 shifted to lower field by about 7.5 ppm, while the chemical shift of the carboxyl carbon shifted by about 71 ppm to higher field. Unlike in A or B, the carboxyl carbon in pattern C with $\delta = 93.47$ ppm lost the character of a common carboxyl carbon. As can be seen from the ^{13}C–^{1}H COSY spectrum (Fig. 7), the chemical shifts centred at $\delta = 93.47$ ppm correlate with the singlet at 5.68 ppm, which gives sound evidence that a hydrogen atom bonds to the carboxyl carbon in pattern C resulting in the non-coplanar configuration between the methyl carbon and the carboxyl atoms.

The NMR results mentioned above are consistent with those of X-ray diffraction of Nd–Al, Y–Al and Eu–Al complexes. The reason for the non-coplanar result among the corresponding atoms in Nd–Al, Eu–Al and the analogous complexes previously reported[14] could thus be elucidated here.

Catalytic activities of Ln–Al bimetallic complexes

The bulk polymerization results of MMA, ECH and THF with Y–Al and Eu–Al complexes are summarized in Table 5. Both Y–Al and Eu–Al were more active in the polymerization of ECH than that for MMA. Poly(MMA) with syndiotactic microstructures predominating was obtained at 0 °C. Moreover, the Y–Al complex could also initiate the ring-opening polymerization of THF with low activity in the presence of ECH as promoter. A single-component organolanthanide catalyst initiating the polymerization of ECH and THF has not been found in the literature to the present date.

In order to investigate the mechanism of THF polymerization, we studied the microstuctures of poly(THF) obtained as described above. The ^{13}C NMR spectrum of poly(THF) is shown in Fig. 8. Apart from the chemical shifts of 26.38 and 70.46 ppm produced by CH_2 and CH_2O carbons in the main chains of poly(THF), two polymer ends were found and identified as E_1 and E_2 (see Scheme 2).

Obviously, ECH first coordinated to Ln or Al with oxygen and formed the active oxonium by ring-opening, which initiated the polymerization of THF. E_1 and E_2 were from the termination of the polymerizing system by addition of water containing a small amount of hydrochloric acid. Investigations on more detailed mechanisms of polymerization of THF, ECH and MMA are in progress.

Acknowledgements We are grateful to the National Science Foundation of China and the Yanshan Petroleum Chemical Company for financial support for this research. We also thank professor Licheng Song (Nankai University) and Wenjian Shen for helpful discussions.

REFERENCES

1. P. L. Watson and T. Herskovitz, *ACS Symp. Ser.* **212**, 459 (1983).
2. G. Jeske, H. Lauke, H. Mauermann, P. N. Swepston, H. Schumann and T. J. Marks, *J. Am. Chem. Soc.* **107**, 8091 (1985).
3. P. J. Shapiro, E. Bunel, W. P. Schaefer and J. E. Bercaw, *Organometallics* **9**, 867 (1990).
4. H. Yasuda, H. Yamamoto, K. Yokota, S. Miyke and A. Nakamura, *J. Am. Chem. Soc.* **114**, 4908 (1992).
5. H. Yasuda, E. Ihara, M. Morimoto, M. Yamashita, M. Nodono and S. Yoshilka, *Polym. Prep.* **35**(2), 532 (1994).
6. H. Yasuda and E. Ihara, *Tetrahedron* **51**, 4563 (1995).
7. W. J. Evans, T. A. Ulibarri and J. W. Ziller, *J. Am. Chem. Soc.* **114**, 7606 (1992).
8. W. J. Evans and H. Katsumata, *Macromolecules* **27**, 2330 (1994).
9. W. J. Evans and H. Katsumata, *Macromolecules* **27**, 4011 (1994).
10. B. M. Novak and L. S. Boffa, *Polym. Prep.* **35**(2), 528 (1994).
11. C. J. Schaverien, *Organometallics* **13**, 69 (1994).
12. X. Yang, A. M. Seyam, P. Fu and T. J. Marks, *Macromolecules* **27**, 4625 (1994).
13. C. Shan, Y. Lin, J. Ouyang, Y. Fan and G. Yang, *Macromol. Chem.* **188**, 629 (1987).
14. Y. Jin, Y. Lin, S. Jin, G. Hu and X. Zhang, *Chin. J. Appl. Chem.* **6**, 67 (1989).
15. J. C. Rundall, *Polymer Sequence Determination Carbon-13 Method*, Academic Press, New York, 1977, p. 111.
16. E. J. Schimitshek and J. A. Trias, US Patent 3 699 211 (1972).
17. D. Harrison, A. Giorgetti and J. C. G. Bünzli, *J. Chem. Soc., Dalton Trans.* **5**, 885 (1985).
18. R. D. Rogers, J. L. Atwood, A. Emad, D. J. Sikora and M. D. Rausch, *J. Organomet. Chem.* **216**, 383 (1981).
19. J. Holton, M. F. Lappert, D. G. H. Ballard, R. Pearce, J. L. Atwood and W. E. Hunter, *J. Chem. Soc., Dalton Trans.* **1**, 45 (1979).