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Synthesis and application of pendant phenyl cyclopentadienyl lanthanide chlorides as catalyst precursors for methyl methacrylate polymerization

Xiaomin Xie and Jiling Huang*

Laboratory of Organometallic Chemistry, East China University of Science and Technology, 130 Meilong Road, PO Box 310, Shanghai 200237, People's Republic of China

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The synthesis and characterization of a series of new pendant phenyl substituted cyclopentadienyl lanthanide chlorides are reported. The analytical data of 3a–3e point to the formation of monomeric and unsolvated complexes, $(PhCMe_2C_5H_4)_2LnCl$ (Ln = Er (3a), Sm (3b), Gd (3c), Y (3d), Nd (3e)); and the analytical data of 4a–4d point to the formation of the dimeric and unsolvated complexes, $[(PhCH_2CMe_2C_5H_4)_2LnCl]_2$ (Ln = Gd (4a), Y (4b), Sm (4c), Er (4d)). The X-ray crystallographic structure of 4d indicates that the pendant phenyl substituent is not coordinated to the central metal. The nine complexes are efficient catalysts for the polymerization of methyl methacrylate in conjunction with $Al(Et)_3$ or NaH. As NaH was used as a new co-catalyst, the catalytic systems show highly catalytic activity at room temperature. In the $[(PhCH_2CMe_2C_5H_4)_2ErCl]_2/Al(Et)_3$ catalyst system, the effects of the concentration of catalyst, and the temperature and time of polymerization were studied. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: pendant phenyl-cyclopentadiene; organolanthanide chloride; co-catalyst; polymerization; methyl methacrylate

INTRODUCTION

Organolanthanide complexes possess unique properties in homogeneous catalysts. They are used as catalysts in many organic reactions and polymerization.[1–7] The cyclopentadienyl lanthanide alkyl (hydride) complexes have high catalytic activity as a single-component catalyst for the polymerization of polar monomers and non-polar monomers.[4–7] However, the synthesis of the complexes must be carried out under rigorously anaerobic conditions, and they are easy to inactivate in the polymerization. So, the corresponding chlorides, which are usually easy to synthesize, are used as catalyst precursors for the polymerization, and an alkyl aluminum, methylaluminoxane (MAO) or alkali (alkaline earth) metal alkyl is used as the co-catalyst to form the active species.[8–11]

The synthesis of cyclopentadienyl lanthanide chlorides has been extensively studied over a period of years, particularly those containing strong donor atoms on the pendant ligands,[12–15] since the donor-functionalized substituents increase the stability of the organolanthanide complexes by forming an intramolecular chelating coordination with the central lanthanide metal. In this regard, it is of special interest to investigate whether the pendant phenyl cyclopentadienyl lanthanide chloride is stable enough to be used as a catalyst to form the labile intramolecular coordination between the pendant phenyl substituents and the central lanthanide metal, and whether it shows catalytic activity. In the cationic Group 4 cyclopentadienyl complexes, the electrophilic metal centers can be stabilized by π-coordination of aryl substituents on the pendant group, and the labile intramolecular coordination can control catalytic activity and polymer molecular weight.[16–18] Here, we will report the synthesis of nine new organolanthanide complexes with pendant phenyl substituted cyclopentadienyl ligands and their catalytic behaviors for the polymerization of methyl methacrylate (MMA). In the polymerization, a new co-catalyst, NaH, was

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*Correspondence to: Jiling Huang, Laboratory of Organometallic Chemistry, East China University of Science and Technology, 130 Meilong Road, PO Box 310, Shanghai 200237, People's Republic of China.
E-mail: qianling@online.sh.cn
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used to activate these chlorides; the catalytic systems show highly catalytic activity at room temperature.

EXPERIMENTAL

All manipulations with air-sensitive compounds were carried out under an inert atmosphere of argon using standard Schlenk techniques. Solvents were refluxed over sodium and benzophenone and distilled under argon prior to use. (1-Phenyl)1-methylethyl-cyclopentadiene (**1**), 2-phenyl-1,1-dimethylethyl-cyclopentadiene (**2**), and anhydrous lanthanide trichloride (Ln = Y, Sm, Gd, Nd, Er) were prepared according to published procedures.[18,19] The methods for purifying MMA were carried out according to Ref. 11. Mass spectra were recorded on an HP 5989A spectrometer (electron impact (EI), 70 eV). IR spectra were obtained on a Nicolet 5 SXC spectrometer in the form of KBr pellets. Element analyses were performed on an EA1106 CHN spectrometer.

Synthesis of $(PhCMe_2C_5H_4)_2LnCl$

The general synthetic procedure for the complexes $(PhCMe_2C_5H_4)_2LnCl$ is similar. Typically, a solution of (1-phenyl)1-methylethyl-cyclopentadiene (**1**; 10.0 g, 54.3 mmol) in tetrahydrofuran (THF; 20 ml) was added dropwise to a suspension of potassium metal (3.0 g, 76.9 mmol) in 80 ml THF at −20 °C. The mixture was allowed to warm up to room temperature and stirred overnight. The excess potassium was separated from the solution; the suspension was then filtered, leaving a white solid that was washed several times with *n*-hexane (20 ml), and dried under reduced pressured to obtain a white powder of **1a** in 65% yield. To a solution of $ErCl_3$ (1.10 g, 4.05 mmol) in THF (40 ml) was added $PhC(Me)_2C_5H_4K$ (**1a**; 1.89 g, 8.52 mmol) at room temperature, and the reaction mixture was stirred for 24 h. The precipitate was separated and the solvent was removed under reduced pressure. The residue was extracted with diethyl ether (70 ml). The ethereal solution was concentrated and a small amount of *n*-hexane was added. A pink solid was precipitated, and the crude product was recrystallized from toluene to give 1.12 g (49%) of pink crystalline solid (**3a**). The complexes were characterized by elemental analyses, mass spectrometry (MS) and IR spectroscopy. Analytical data are presented below:

$(PhCMe_2C_5H_4)_2ErCl$ (**3a**) is a pink crystalline solid (yield: 49%); m.p. 194 °C. Anal. Found: C, 59.09; H, 5.47. Calc. for $C_{28}H_{30}ClEr$: C, 59.04; H, 5.31%. EIMS m/z (fragment, relative intensity %): 569 ($[M]^+$, 2), 534 ($[M - Cl]^+$, 1), 386 ($[M - L]^+$, 30), 184 ($[L]^+$, 70), 169 ($[L - CH_3]^+$, 100), 167 ($[Er]^+$, 17). IR (cm^{-1}): 3084(w), 3058(m), 2963(s), 2926(m), 1656(w), 1380(w), 1359(w), 1031(s), 784(s), 697(s), 550(s).

$(PhCMe_2C_5H_4)_2SmCl$ (**3b**) is a yellow powder (yield: 30%); m.p. 189 °C. Anal. Found: C, 60.11; H, 5.21. Calc. for $C_{28}H_{30}ClSm$: C, 60.89; H, 5.47%. EIMS m/z (fragment, relative intensity %): 553 ($[M]^+$, 1), 518 ($[M - Cl]^+$, 1), 369 ($[M - L]^+$, 1), 184 ($[L]^+$, 55), 169 ($[L - CH_3]^+$, 100), 152 ($[Sm]^+$, 16). IR (cm^{-1}): 3083(w), 3055(w), 2968(s), 2870(m), 1748(w), 1383(w), 1361(s), 1029(s), 773(s), 670(s), 551(s).

$(PhCMe_2C_5H_4)_2GdCl$ (**3c**) is a white crystalline solid (yield: 29%); m.p. 190 °C. Anal. Found: C, 59.61; H, 5.70. Calc. for $C_{28}H_{30}ClGd$: C, 60.14; H, 5.41%. EIMS m/z (fragment, relative intensity %): 559 ($[M]^+$, 1), 524 ($[M - Cl]^+$, 1), 422 ($[M - C_6H_5 - 4CH_3]^+$, 100), 376 ($[M - L]^+$, 17), 184 ($[L]^+$, 30), 158 ($[Gd]^+$, 1), 169 ($[L - CH_3]^+$, 66). IR (cm^{-1}): 3085(w), 3057(w), 2966(s), 2867(m), 1658(m), 1382(w), 1360(s), 1032(s), 782(s), 698(s), 551(m).

$[PhC(Me)_2C_5H_4]_2YCl$ (**3d**) is a white crystalline solid (yield: 62%); m.p. 195 °C. Anal. Found: C, 68.51; H, 6.16. Calc. for $C_{28}H_{30}ClY$: C, 68.46; H, 6.30%. EIMS m/z (fragment, relative intensity %): 490 ($[M]^+$, 3), 455 ($[M - Cl]^+$, 3), 306 ($[M - L]^+$, 61), 184 ($[L]^+$, 46), 169 ($[L - CH_3]^+$, 100), 89 ($[Y]^+$, 3). IR (cm^{-1}): 3085(w), 3058(w), 2966(s), 2930(m), 1750(w), 1381(w), 1360(m), 1031(s), 782(s), 698(s), 551(m).

$(PhCMe_2C_5H_4)_2NdCl$ (**3e**) is a blue solid (yield: 25%); m.p. 185 °C. Anal. Found: C, 60.97; H, 5.23. Calc. for $C_{28}H_{30}ClNd$: C, 61.56; H, 5.54%. EIMS m/z (fragment, relative intensity %): 543 ($[M]^+$, 1), 508 ($[M - Cl]^+$, 2), 359 ($[M - L]^+$, 16), 184 ($[L]^+$, 48), 143 ($[Nd]^+$, 6), 169 ($[L - CH_3]^+$, 100). IR (cm^{-1}): 3083(w), 3057(w), 2967(s), 2870(m), 1748(m), 1382(w), 1361(s), 1029(s), 770(s), 699(s), 549(m).

Synthesis of $[(PhCH_2CMe_2C_5H_4)_2LnCl]_2$

The general synthetic procedure for the complexes $[(PhCH_2CMe_2C_5H_4)_2LnCl]_2$ is similar. Typically, a solution of 2-phenyl-1,1-dimethylethyl-cyclopentadiene (**2**; 7.3 g, 36.9 mmol) in THF (20 ml) was added dropwise to a suspension of potassium chips (2.1 g, 53.8 mmol) in 80 ml THF at −20 °C. The mixture was allowed to warm to room temperature and stirred overnight and filtered. A solution of $PhCH_2C(Me)_2C_5H_4K$ (**2a**) in THF was obtained. To a solution of $GdCl_3$ (1.39 g, 5.28 mmol) in THF (20 ml) was added 37 ml (0.2896 mol L^{-1}, 10.64 mmol) $PhCH_2C(Me)_2C_5H_4K$ (**2a**) in THF at room temperature, and the reaction mixture was stirred for 24 h. After removal of the solvent under vacuum, the residue was extracted with diethyl ether (80 ml). The ethereal solution was concentrated to 15 ml, then 1.42 g (46%) of a white crystalline solid (**4a**) was precipitated at room temperature. The complexes were characterized by elemental analyses, MS and IR spectroscopy. Analytical data are presented below:

$[(PhCH_2CMe_2C_5H_4)_2GdCl]_2$ (**4a**) is a white crystalline solid (yield: 46%); m.p. 110 °C. Anal. Found: C, 61.02; H, 5.84. Calc. for $C_{60}H_{68}Cl_2Gd_2$: C, 61.35; H, 5.84%. EIMS m/z (fragment, relative intensity %): 552 ($[M/2 - Cl]^+$, 1), 389 ($[M/2 - L]^+$, 6), 198 ($[L]^+$, 21), 107 ($[C_8H_{11}]^+$, 100), 91 ($[C_7H_7]^+$, 44). IR (cm^{-1}): 3062(w), 3026(m), 2950(s), 2923(s), 1382(w), 1362(m), 1033(m), 743(s), 701(s), 497(w).

$[(PhCH_2CMe_2C_5H_4)_2YCl]_2$ (**4b**) is a white crystalline solid (yield: 24%); m.p. 148 °C. Anal. Found: C, 69.29; H, 6.73. Calc. for $C_{60}H_{68}Cl_2Y_2$: C, 69.43; H, 6.60%. EIMS m/z (fragment, relative intensity %): 483 ($[M/2 - Cl]^+$, 14), 321 ($[M/2 - L]^+$, 52), 198 ($[L]^+$, 20), 107 ($[C_8H_{11}]^+$, 100), 91 ($[C_7H_7]^+$, 51). IR (cm^{-1}): 3062(w), 3027(w), 2961(s), 2925(m), 1653(m), 1382(w), 1363(m), 1033(m), 783(w), 743 (s), 701(s), 497(w).

[(PhCH$_2$CMe$_2$C$_5$H$_4$)$_2$SmCl]$_2$ (**4c**) is a yellow solid (yield: 32%); m.p. 120 °C. Anal. Found: C, 61.93; H, 6.07. Calc. for $C_{60}H_{68}Cl_2Sm_2$: C, 62.08; H, 5.90%. EIMS m/z (fragment, relative intensity %): 547 ([M/2 − Cl]$^+$, 1), 384 ([M/2 − L]$^+$, 1), 198 ([L]$^+$, 24), 152 ([Sm]$^+$, 2), 107 ([C$_8$H$_{11}$]$^+$, 100), 91 ([C$_7$H$_7$]$^+$, 61). IR (cm^{-1}): 3062(w), 3027(w), 2962(s), 2925(m), 1382(w), 1382(w), 1364(m), 1364(m), 724(m), 702 (s), 681(m), 496(w).

[(PhCH$_2$CMe$_2$C$_5$H$_4$)$_2$ErCl]$_2$ (**4d**) is a pink crystal, the crystal is suitable for X-ray diffraction (yield: 24%); m.p. 160 °C. Anal. Found: C, 60.11; H, 6.02. Calc. for $C_{60}H_{68}Cl_2Er_2$: C, 60.33; H, 5.74%. EIMS m/z (fragment, relative intensity %): 560([M/2 − Cl]$^+$, 1), 319 ([C$_{13}$H$_9$Er]$^+$, 30), 166 ([Er]$^+$, 4), 107 ([C$_8$H$_{11}$]$^+$, 45), 91 ([C$_7$H$_7$]$^+$, 100). IR (cm^{-1}): 3081(w), 3026(m), 2959(s), 2921(s), 1601(m), 1382(w), 1363(m), 1035(m), 784(s), 701(s), 498(w).

X-ray structure determination

A single crystal was sealed in a thin-walled glass capillary under argon. Data were collected on a Bruker SMART diffractometer with graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation using the ω–2θ technique at 293 K. Crystal data and details of data collection and structure refinement are given in Table 1 and selected structural data are given in Table 2. The crystal structures were solved by direct methods and expanded using the Fourier technique. The non-hydrogen atoms were refined anisotropically by full-matrix least squares. All hydrogen atoms were included in calculated positions. All calculations were performed using the SHELXS-97 crystallographic software package.

Table 1. Crystal data and structure refinement for complex **4d**

Compound	[(PhCH$_2$C(Me)$_2$C$_5$H$_4$)$_2$ErCl]$_2$
Empirical formula	$C_{60}H_{68}Cl_2Er_2$
Formula weight	1194.56
Crystal color	Red
Crystal dimensions (mm^3)	0.468 × 0.457 × 0.411
a (Å)	25.454(2)
b (Å)	10.8054(7)
c (Å)	22.3774(8)
Volume (Å^3)	5239.2(7)
Z value	4
D (g cm^{-3})	1.514
Absorption coefficient (mm^{-1})	3.320
F(000)	2392
θ range for data collected (deg)	1.88–28.31
Refections collected	15507
Data/restraints/ parameters	5965/0/293
Goodness-of-fit on F^2	1.005
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0405$, $\omega R_2 = 0.0985$
R indices (all data)	$R_1 = 0.0487$, $\omega R_2 = 0.1013$
$\rho_{max/min}$ (e$^-$ Å^{-3})	2.204 and −1.2333

Table 2. Selected bond lengths (Å) and bond angles (°) for complex **4d**

Er–Cl(A)	2.6527(11)	Cl(A)–Er–Cl	80.84(4)
Cl–Er(A)	2.6527(11)	C(2)–Er–C(17)	102.6(2)
Er–C(2)	2.538(5)	C(2)–Er–C(18)	133.2(2)
Er–C(17)	2.564(5)	C(2)–Er–C(3)	31.41(2)
Er–C(18)	2.581(5)	C(18)–Er–C(3)	163.6(2)
Er–C(3)	2.590(5)	C(18)–Er–C(1)	111.8(2)
Er–C(1)	2.606(5)	C(17)–Er–C(1)	81.9(2)
Er–C(16)	2.619(5)	C(2)–Er–C(4)	51.32(19)
Er–C(19)	2.637(5)	C(2)–Er–Cl(A)	134.84(15)
Er–C(4)	2.646(6)	C(17)–Er–Cl(A)	106.87(15)
Er–C(5)	2.673(5)	C(1)–Er–Cl(A)	122.28(12)
Er–C(20)	2.690(6)	C(4)–Er–Cl(A)	83.56(13)
Er–Cl	2.6771(11)	C(2)–Er–Cl	100.10(14)
C(6)–C(7)–C(8)	116.1(4)	C(16)–Er–Cl	116.90(12)

Polymerization of MMA catalyzed by the (PhCMe$_2$C$_5$H$_4$)$_2$LnCl/Al(Et)$_3$ or [(PhCH$_2$CMe$_2$C$_5$H$_4$)$_2$LnCl]$_2$/Al(Et)$_3$ system

Al(Et)$_3$ (10% in toluene) was added to the corresponding lanthanide complexes (20–40 mg) in 10 : 1 molar ratio, then the required amount of monomer MMA was charged. Polymerization was carried out at a constant temperature for a selected period of time, and quenched by the addition of acidified ethanol (5% HCl). The polymer was washed twice with ethanol and dried to constant weight at 50 °C in a vacuum oven.

Polymerization of MMA catalyzed by the (PhCMe$_2$C$_5$H$_4$)$_2$LnCl/NaH or [(PhCH$_2$CMe$_2$C$_5$H$_4$)$_2$LnCl]$_2$/NaH system

To a suspension of the required amount of NaH (Ln : Na = 1 : 50) in 5 ml toluene, the corresponding lanthanide complex was added, and the mixture was stirred for several hours at 50 °C. After cooling to 20 °C, the required MMA (MMA : Ln (molar ratio) = 400 : 1) was added. The reaction mixture was stirred for a selected period of time at room temperature, and quenched by the addition of acidified ethanol (5% HCl). The polymer was washed twice with ethanol and dried *in vacuo*.

Characterization of the polymer

The inherent viscosity of poly(MMA) in CHCl$_3$ was determined at 30 °C with an Ubbelohde-type viscometer. Viscosity average molecular weight was calculated using the Mark–Houwink equation $[\eta] = 5.5 \times 10^{-3} M_\eta^{0.79}$ (cm^3/g) (where M_η is the viscosity average molecular weight). The tacticity of poly(MMA) obtained under different polymerization conditions was determined by ^{1}H NMR spectra (from the peak of α-methyl; mm, mr, and rr at 1.17, 0.98 and 0.78 δ respectively).[20] The ^{1}H NMR spectra were recorded in a Bruker AVANCE 500 MHz NMR spectrometer at room temperature in $CDCl_3$.

RESULT AND DISCUSSION

Synthesis and characterization

Cyclopentadienyl ligands with $-CMe_2Ph$ (**1**) or $-CMe_2CH_2Ph$ (**2**) substituent were readily synthesized according to the published procedures,[18] then the substituted cyclopentadiene was deprotonated with potassium in THF. The metathetic reaction of the substituted cyclopentadienyl anion (**1a**, **2a**) with $LnCl_3$ (Ln = Er, Nd, Sm, Gd, Y) in a 2 : 1 molar ratio in THF at room temperature gave the solvent-free complexes $[PhC(Me)_2C_5H_4]_2LnCl$ (Ln = Er (**3a**), Sm (**3b**), Gd (**3c**), Y (**3d**), Nd (**3e**)) and $[(PhCH_2CMe_2C_5H_4)_2LnCl]_2$ (Ln = Gd (**4a**), Y (**4b**), Sm (**4c**), Er (**4d**)) as shown in Scheme 1. All the nine complexes are sensitive towards air and moisture, and they are soluble in THF and toluene, but are insoluble in hexane. In contrast, the complexes of $[(PhCH_2CMe_2C_5H_4)_2LnCl]_2$ are soluble in Et_2O, whereas the complexes of $(PhCMe_2C_5H_4)_2LnCl$ are insoluble in Et_2O.

All complexes were characterized by elemental analysis, mass spectra and IR spectroscopy. The IR spectra of all nine complexes show similar patterns and display the characteristic absorptions of the mono-substituted phenyl group at 3030, 1600, 830, 780, 700 cm^{-1}. The molecular ion peak is detected in the MS spectra of **3a**–**3e**, and in combination with the IR and elemental analysis data, the complexes of **3a**–**3e** are presumed to be monomeric and unsolvated complexes and to have the general formula $(PhCMe_2C_5H_4)_2LnCl$. The X-ray data of complex **4d** indicates a dimeric structure, so the complexes of **4a**–**4d** may be dimeric and unsolvated complexes, and have the general formula $[(PhCMe_2C_5H_4)_2LnCl]_2$, even though in the MS spectra of **4a**–**4d** the $[M/2 - Cl]^+$ peak is the largest fragment among the fragments observed.

A crystal of **4d** suitable for X-ray structure determination was recrystallized from diethyl ether. The complex **4d** belongs to the monoclinic space group C2/2 with four crystallographically independent molecules in the asymmetric unit. The structure is shown in Fig. 1. The crystallographic data are given in Table 1 and selected structural data are given

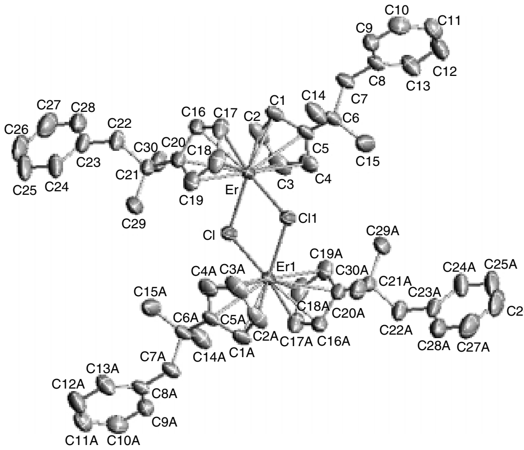
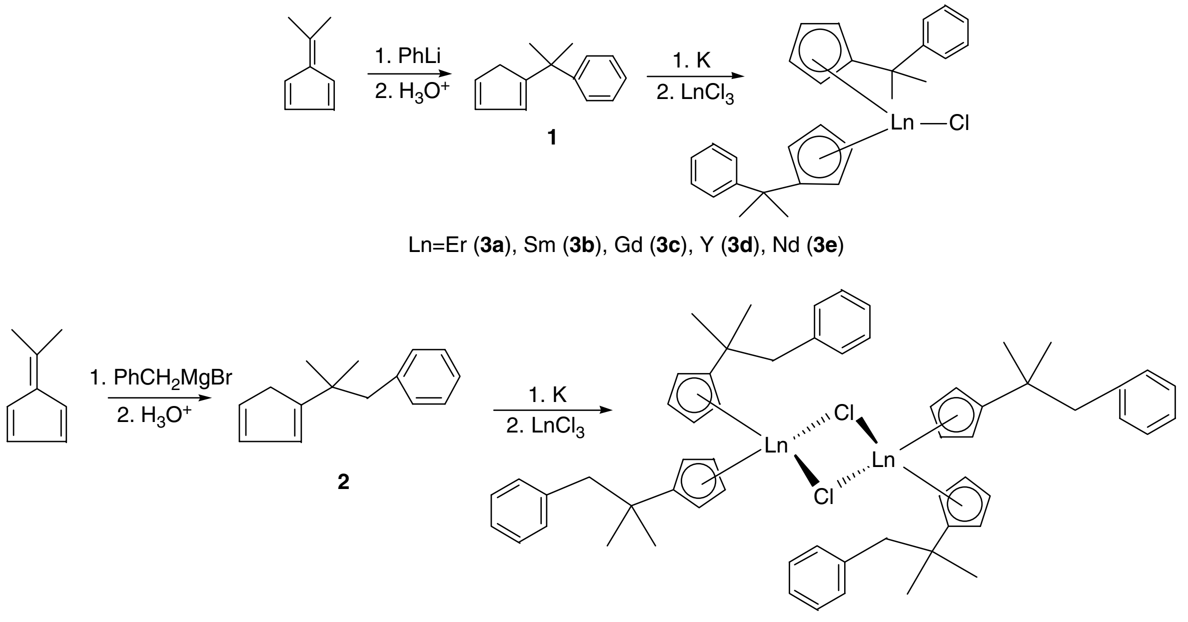


Figure 1. ORTEP diagram of the molecular structure of $[(PhCH_2CMe_2C_5H_4)_2ErCl]_2$ (**4d**).



Ln=Er (**3a**), Sm (**3b**), Gd (**3c**), Y (**3d**), Nd (**3e**)

Ln = Gd (**4a**), Y (**4b**), Sm (**4c**), Er (**4d**).

Scheme 1. Synthetic route to pendant phenyl cyclopentadienyl lanthanide chloride.

in Table 2. The complex is an unsolvated eight-coordinate dimeric complex, in which two $(PhCH_2CMe_2C_5H_4)_2Er^+$ units are bridged by two chloride ions. There is no coordination of the pendant phenyl substituent to the erbium center. In the dimeric complex, the two Er–Cl bridges are basically symmetrical, and the lengths of Er–Cl are longer than those of $(C_6H_5CH_2C_5H_4)_2ErCl(THF)$. The main reason for the difference is that $(C_6H_5CH_2C_5H_4)_2ErCl(THF)$ is monomeric having a smaller steric hindrance.[21] Similarly, the steric hindrance of the phenylalkyl substituent decreases the angle of Cl–Er–Cl compared with the structure of $[(C_5H_5)_2ErCl]_2$.[22]

Polymerization of MMA catalyzed by the $(PhCMe_2C_5H_4)_2LnCl/Al(Et)_3$ or $[(PhCH_2CMe_2C_5H_4)_2LnCl]_2/Al(Et)_3$ system

The synthesized cyclopentadienyl lanthanide complexes, which were activated by adding a 10-fold molar excess of $Al(Et)_3$, were used in the homogeneous polymerization of MMA. The results of polymerization are listed in Table 3. All the complexes have activity for the polymerization of MMA. The results indicate that the central lanthanide ionic radius and the structure of the ligands influence the catalytic activity. Complexes **3a** and **4d**, in which the central metal ionic radius is the smallest, show the highest catalytic activity among all complexes. The probable reason may be that the combination of a sterically bulky ligand in association with a small metal center stabilizes active centers such as Cp'_2LnR or Cp'_2LnH which are more active than $Cp'_2Ln(\mu\text{-}R)_2AlR_2$.[4] In complexes with the same central metal (Er), the catalytic activity increases with the increase in chain length of the alkylidene spacer located between the cyclopentadiene and the phenyl group. The reason may be that the increasing spacer chain length decreases the steric shielding of the catalytic center by the phenyl group.

In the catalyst system of $[(PhCH_2CMe_2C_5H_4)_2ErCl]_2/Al(Et)_3$, the effects of such factors as temperature, time of polymerization and variation in catalyst concentration were studied. The results are presented in Table 4. For the same concentration of the catalyst (MMA : Ln = 400 : 1), the yield of poly(MMA) increases with increase in temperature, while the molecular weight and tacticity of the polymer decline as temperature increases (the tacticity is shown in Table 5). Schwecke and Kaminsky[23] noted that the benzyl group also acts by competing with the monomer for the available coordination site during polymerization. The benzyl group coordinates to the active site for a short period (labile behavior), thereby blocking the free coordination

Table 3. Polymerization[a] of MMA catalyzed by the $PhCMe_2C_5H_4)_2LnCl/Al(Et)_3$ or $[(PhCH_2CMe_2C_5H_4)_2LnCl]_2/Al(Et)_3$ system

Lanthanide complex	Yield (%)	$M_\eta \times 10^{-3}$
$(PhCMe_2C_5H_4)_2ErCl$ (**3a**)	43.6	38
$(PhCMe_2C_5H_4)_2SmCl$ (**3b**)	32.5	101
$(PhCMe_2C_5H_4)_2GdCl$ (**3c**)	24.7	31
$(PhCMe_2C_5H_4)_2YCl$ (**3d**)	27.8	27
$(PhCMe_2C_5H_4)_2NdCl$ (**3e**)	25.9	37
$[(PhCH_2CMe_2C_5H_4)_2GdCl]_2$ (**4a**)	15.8	61
$[(PhCH_2CMe_2C_5H_4)_2YCl]_2$ (**4b**)	25.3	42
$[(PhCH_2CMe_2C_5H_4)_2SmCl]_2$ (**4c**)	21.4	113
$[(PhCH_2CMe_2C_5H_4)_2ErCl]_2$ (**4d**)	64.5	68

[a] Conditions: MMA/Ln = 400 (molar ratio), Al/Ln = 10 (molar ratio), 60 °C, 24 h, MMA 1 ml.

Table 4. Polymerization[a] of MMA catalyzed by the $[(PhCH_2CMe_2C_5H_4)_2ErCl]_2/Al(Et)_3$ catalyst system

MMA/Ln (molar ratio)	Temp. (°C)	Time (h)	Yield (%)	$M_\eta \times 10^{-3}$
200 : 1	60	24	47.3	44
400 : 1	60	24	64.5	68
800 : 1	60	24	55.5	285
1200 : 1	60	24	41.6	103
400 : 1	20	24	6.4	109
400 : 1	40	24	11.5	79
400 : 1	80	24	66.7	53
400 : 1	60	8	17.5	62
400 : 1	60	12	32.4	90
400 : 1	60	32	97.5	26

[a] Conditions: Ln/co-catalyst (molar ratio) = 1 : 10, MMA 1 ml.

Table 5. Tacticity of PMMA obtained under different polymerization conditions[a]

Catalyst system	Temp. (°C)	Time (h)	Yield (%)	$M_\eta \times 10^{-3}$	Tacticity (%)		
					mm	mr	rr
$[(PhCH_2CMe_2C_5H_4)_2ErCl]_2/Al(Et)_3$[b]	20	24	6.4	109	5	31	64
$[(PhCH_2CMe_2C_5H_4)_2ErCl]_2/Al(Et)_3$[b]	60	24	64.5	68	8	36	56
$[(PhCH_2CMe_2C_5H_4)_2ErCl]_2/NaH$[c]	20	24	71.9	190	45	36	19
$(PhCMe_2C_5H_4)_2ErCl/NaH$[c]	20	24	83.9	77	36	46	18

[a] Conditions: MMA/Ln = 400 (molar ratio), MMA 1 ml.
[b] Al/Ln = 10 (molar ratio).
[c] Na/Ln = 50 (molar ratio).

site to incoming monomer. This may be responsible for the fall in molar mass and syndiotactic selectivity. The influence of variation in MMA/catalyst molar ratio is that the molecular weight of the polymer obtained increases as the catalyst concentration decreases, and records a maximum of molecular weight ($M : 2.85 \times 10^5$) at a yield of 55.5%. The inverse dependence of molecular weight on initiator concentration indicates that the active center has high activity. The polymerization rate increases with the increase in concentration of monomer, whereas the rate of chain transfer to monomer is relatively slow, so the molecular weight increases with increasing concentration of monomer.

Polymerization of MMA catalyzed by the $(PhCMe_2C_5H_4)_2LnCl/NaH$ or $[(PhCH_2CMe_2C_5H_4)_2LnCl]_2/NaH$ system

In the polymerization of MMA, NaH was used as a new co-catalyst to activate the synthesized cycolpentadienyl lanthanide chloride. The results are listed in Table 6. The catalytic systems exhibit high catalytic activity even at room temperature. In the $[(PhCH_2CMe_2C_5H_4)_2ErCl]_2/NaH$ system, the yield of poly(MMA) reaches 74.9% with high molecular weight ($M_\eta = 190\,000$) at room temperature. It is presumed that the active center of these catalytic systems may be cyclopentadienyl lanthanide hydride, since the cyclopentadienyl lanthanide hydride can be synthesized by reducing the cyclopentadienyl lanthanide chloride with NaH,[24] and the cyclopentadienyl lanthanide hydride shows high catalytic activity for the living polymerization of MMA.[4] However, the polymerization in the present case is not totally the same as the living polymerization catalyzed by cyclopentadienyl lanthanide hydride. In the catalytic system, the tacticity of the resultant polymers is low (see in Table 5), and the molecular weight distribution (M_w/M_n) of poly(MMA) is rather broad. The gel-permeation chromatography (GPC) curve (Fig. 2) of polymer obtained with the $[(PhCH_2CMe_2C_5H_4)_2ErCl]_2/NaH$ catalyst system is bimodal, indicating the production of heterogenous products: the first peak comprises the higher molecular weight fraction and the second peak comprises the lower molecular weight fractions. The molecular weight distribution is narrow ($M_w/M_n = 1.28$) for the high-molecular-weight fraction, and $M_w/M_n = 2.8$ for the low-molecular-weight fraction. The reason for this is not clear yet, but it may be due to the presence of a solid-phase co-catalyst inducing the chain transfer of the polymerization chain.

Table 6. Polymerization[a] of MMA catalyzed by the $(PhCMe_2C_5H_4)_2LnCl/NaH$ or $[(PhCH_2CMe_2C_5H_4)_2LnCl]_2/NaH$ system

Lanthanide complex	Temp. (°C)	Time (h)	Yield (%)	$M_\eta \times 10^{-3}$
$[(PhCH_2CMe_2C_5H_4)_2GdCl]_2$ (**4a**)	25	24	99.9	60
$[(PhCH_2CMe_2C_5H_4)_2YCl]_2$ (**4b**)	25	24	30.1	84
$[(PhCH_2CMe_2C_5H_4)_2ErCl]_2$ (**4d**)	25	24	71.9	190
$(PhCMe_2C_5H_4)_2ErCl$ (**3a**)	25	24	83.9	77
$(PhCMe_2C_5H_4)_2SmCl$ (**3b**)	25	24	74.9	46
$(PhCMe_2C_5H_4)_2ErCl$ (**3a**)	25	10	38.0	60

[a] Conditions: MMA/Ln = 400 (molar ratio), Na/Ln = 50, MMA 1 ml, toluene 5 ml.

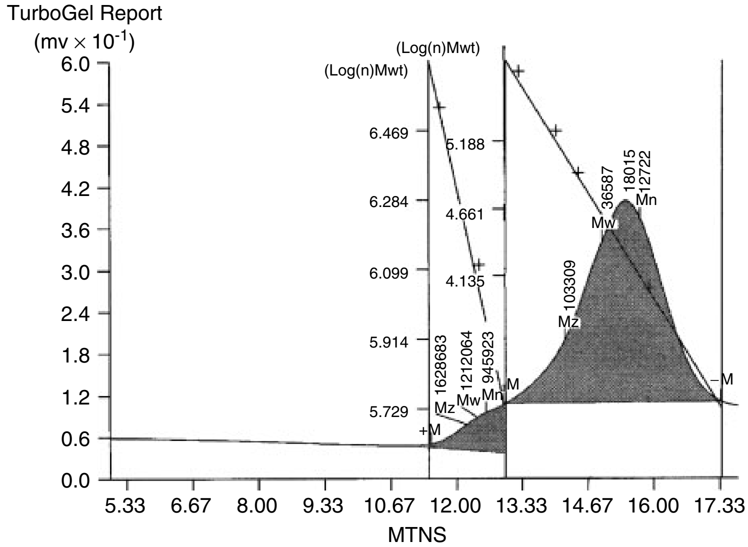


Figure 2. GPC curve for polymerization of MMA catalyzed by the $(PhCMe_2C_5H_4)_2ErCl/NaH$ system.

CONCLUSION

We have synthesized nine new pendant phenyl substituted cyclopentadienyl lanthanide chloride complexes. X-ray structure analysis of complex **4d** shows that the pendant phenyl substituent is not coordinated with the central metal. In conjunction with $Al(Et)_3$ or NaH as co-catalyst, the lanthanide complexes synthesized can catalyze the polymerization of MMA. The catalyst system $(PhCH_2CMe_2C_5H_4)_2ErCl/NaH$ shows high activity even at room temperature, but the tacticity of the polymers obtained is low.

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