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Homoleptic lanthanide metallocenes and their derivates: syntheses, structural characterization and their catalysis for ring-opening polymerization of ε-caprolactone

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Homoleptic lanthanide metallocenes Cp'_3Ln [Cp' = methylcyclopentadienyl, Ln = Y (1), Er (2), Sm (3); Cp' = cyclopentadienyl, Ln = Er (4) and Sm (5)] have been found to be a novel type of initiators for the ring-opening polymerization (ROP) of ε-caprolactone (ε-CL). Among them, complex 1 shows the highest catalytic activity for ROP of ε-CL. In addition, a novel neutral trifluoroethoxo yttrium complex $[(MeC_5H_4)_2Y(\mu\text{-}OCH_2CF_3)]_2$ (6) has been synthesized by the reaction of 1 with trifluoroethanol in 1:1 molar ratio in toluene and characterized by single-crystal X-ray structural analysis. Preliminary study shows that the catalytic activity of tris(methylcyclopentadienyl)yttrium complex 1 is higher than that of bis(methylcyclopentadienyl)yttrium complex 6. The mechanism of the present polymerization was studied by NMR spectra. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: cyclopentadienyl; organolanthanide; trifluoroethoxo ligand; ring-opening polymerization; ε-caprolactone

INTRODUCTION

In recent years, considerable interest has been focused on developing structurally well-characterized lanthanide complexes (which includes scandium, yttrium and lanthanoid[1]) as single-component homogeneous polymerization catalysts.[2,3] To date, the organolanthanide initiators developed so far usually include Ln–H, Ln–C, Ln–O, and Ln–N bond, or divalent species. For example, organolanthanide complexes such as Cp^*_2LnR ($Cp^* = \eta^5\text{-}C_5Me_5$, R = hydride, alkyl, alkoxy and amide, etc.) have been found to be highly active catalysts for the polymerization of ethylene,[4,5] α-olefin,[5–8] methyl methacrylate,[7,9] alkyl acrylate,[7,10,11] alkyl isocyanate[7] as well as the ring-opening polymerization (ROP) of ε-caprolactone (ε-CL).[12–15] In general, cyclopentadiene and its derivatives are commonly used as typically inert ancillary ligands, which stabilize and solubilize organolanthanides but do not participate in catalytic reactions. Therefore, the homoleptic organolanthanides of Cp'_3Ln (Cp' = cyclopentadienyl or substituted cyclopentadienyl) have been developed exclusively as precursors or from a structural point of view; meanwhile, their catalytic chemistry has been little investigated. Very recently, Evans *et al.* found that the C_5Me_5 ring of sterically crowded complexes Cp^*_3Ln had unusual reactivity which similar to alkyl ligands,[16] i.e. Cp^*_3Sm for polymerization of ethylene and ROP of ε-CL.[17] Subsequent structural studies indicate that the sterically induced $\eta^5\text{-}C_5Me_5 \leftrightarrow \eta^1\text{-}C_5Me_5$ equilibrium occurred, hence, Cp^*_3Sm can react like a bulky alkyl complex, i.e. $Cp^*_2Sm\text{-}R$.[18] However, to date, no such catalytic reactivity is known with another type of simple Cp'_3Ln complexes, in which Cp' has been expected for an η^5-type ring in general.

Considering the fact that the disruption enthalpy for the Ln–Cπ bond is lower than that of Ln–O bond and a number of lanthanide alkoxides are capable of catalyzing the ROP of ε-CL,[19] it is reasonable that the Ln–Cπ bond might also react with lactone. Therefore, we synthesized a series of homoleptic lanthanide metallocenes of Cp'_3Ln [Cp' = methylcyclopentadienyl, Ln = Y (**1**), Er (**2**),

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Sm (**3**); Cp′ = cyclopentadienyl, Ln = Er (**4**) and Sm(**5**)] and examined their catalytic activity for ROP of *ε*-CL. It is found that these complexes can efficiently initiate the ROP of *ε*-CL. We report the results in this article. To the best of our knowledge, this is the first example of the catalytic activity of the η^5-type Cp′ ring presented in Cp'_3Ln complexes. In comparison, a novel trifluoroethoxo yttrium complex, $[(MeC_5H_4)_2Y(\mu\text{-}OCH_2CF_3)]_2$ (**6**), has been synthesized by the reaction of **1** with trifluoroethanol and structurally characterized. Preliminary study shows that the catalytic activity of tris(methylcyclopentadienyl)yttrium complex **1** is higher than that of bis(methylcyclopentadienyl)yttrium complex **6**.

EXPERIMENTAL

Materials and methods

All manipulations were carried out under pure argon, using standard Schlenk techniques. *ε*-CL was dried over CaH_2 for 4 days, then distilled in vacuum, and stored over molecular sieves before use. Toluene and THF were purified by distillation from sodium benzophenone ketyl prior to use. C_6D_6 was dried over sodium and distilled before use. $HOCH_2CF_3$ was dried over activated 4 Å molecular sieves for more than 5 days. Anhydrous lanthanide chlorides were synthesized as described in the literature.[20] Complexes **1–5** were prepared according to published procedures.[21] All other chemicals were commercially available and used as received. Elemental analyses for carbon and hydrogen were performed on a Carlo Erba 1110 analyzer. Metal analyses were accomplished using the literature method.[22] Melting points were determined in sealed capillaries filled with argon and not corrected. Infrared spectra were obtained on a Magna-500 spectrometer. ^1H NMR and ^{19}F NMR spectra were recorded on an INOVA 400 spectrometer. The molecular weights of the isolated polymers were determined by gel permeation chromatography at room temperature using THF as the eluent and a universal calibration relative to polystyrene standards.

Synthesis of $[(MeC_5H_4)_2Y(\mu\text{-}OCH_2CF_3)]_2$ (1)

To a slurry of YCl_3 (1.59 g, 8.04 mmol) in 20 ml THF, a THF solution of MeC_5H_4Na (17.6 ml, 24.1 mmol) was added by syringe. After the mixture was stirred at room temperature for 48 h, the NaCl was separated from the reaction mixture by centrifugation. The THF was completely removed in vacuum and the residue was extracted with 30 ml toluene. To the toluene extracts (28.5 ml, 5.97 mmol), a toluene solution of $HOCH_2CF_3$ (8.78 ml, 5.97 mmol) was added by syringe. After the mixture was stirred for 24h at room temperature, the solution was concentrated and cooled at −20 °C. Colorless crystals were then obtained (0.754 g, 35.9%) suitable for elemental analysis, m.p. 180–184 °C. Anal. Calcd for $C_{28}H_{32}O_2F_6Y_2$: C, 48.57; H, 4.63; Y, 25.70. Found: C, 47.84; H, 4.73; Y, 25.29. IR absorptions (KBr pellet, cm^{-1}): 3090(w), 2935(s), 2870(s), 1460(w), 1377(w), 1288(s), 1180(s), 1095(s), 1049(m), 956(s), 779(s). ^1H NMR (400 MHz, C_6D_6): 2.0 (6H, $-CH_3$), 3.5 (2H, $-CH_2-$), 6.0 (8H, $-C_5H_4-$).

X-ray structure determination

A single crystal was sealed under argon in a thin-walled glass capillary. Diffraction data were collected at 25 °C on a Rigaku AFC7R diffractometer with graphite monochromated Mo-K*α* radiation (0.71073 Å). A total of 2822 intensities within the range $2.24^\circ < \theta < 25.00^\circ$ were collected by the *ω*−scan technique. The intensity was corrected for Lorentz-polarization effects and empirical absorption. A summary of crystallographic data is given in Table 1 and selected structural data are given in Table 2. The structure was solved by the heavy-atom method and expanded using the Fourier technique. H atoms were placed in calculated positions and assigned isotropic thermal parameters. Further refinement led to final convergence at $R = 0.0319$. All calculations were performed on an IRIS INDIGO computer using DIRDIF92 programs.

Polymerization of *ε*-CL

A typical polymerization procedure is as follows: to a toluene solution of *ε*-CL was added at once the toluene solution of **1**

Table 1. Crystal data and experimental parameters for **6**

	6		**6**
Empirical formula	$C_{28}H_{32}O_2F_6Y$	*Z*	4
Formula weight	692.36	D_{calcd} (g/cm^3)	1.646
Temperature (K)	291(2)	Absorption cofficent (mm^{-1})	4.196
λ (Mo K*α*), Å	0.71073	*F* (000)	696
Crystal system	Monoclinic	*θ* range for data collection (°)	2.24–25.00
Space group	$P2_1/C$	Reflections collected	2822
Unit cell dimensions		Independent reflections	2430
a (Å)	9.324 (2)	Goodness-of-fit on F^2	0.699
b (Å)	14.863(4)	Final *R* indices $[I > 2\sigma(I)]$	$R_1 = 0.0319$, $wR_2 = 0.0427$
c (Å)	10.334(3)	Extinction coefficient	0.0010(2)
V $(Å^3)$	1397.2(6)	CCDC deposition number	272 341

Table 2. Selected bond lengths (Å) and angles (deg) for complex **6**

Bond lengths (Å)			
Y–O	2.275(2)	Y–O	2.270(2)
Y–C(7)	2.615(4)	Y–C(13)	2.617(4)
Y–C(6)	2.641(4)	Y–C(12)	2.647(4)
Y–C(14)	2.651(4)	Y–C(8)	2.661(4)
Y–C(11)	2.676(4)	Y–C(5)	2.680(4)
Y–C(10)	2.686(4)	Y–C(4)	2.695(4)
Y–Cent(1)[a]	2.3862	Y–Cent(2)[a]	2.3786
Angles (deg)			
O–Y–O	72.18(9)	Cent(1)–Y–Cent(2)	126.58
Y–O–C(2)	122.2(2)	Y–O–Y	107.83(1)

[a] Cent(1) is the centroid of the C(4)–C(8) ring and Cent(2) is the centroid of the C(10)–C(14) ring.

Table 3. Polymerization of ε-CL with complexes **1–5**[a]

Run	Initiator	T (°C)	t (h)	Yield (%)	M_n ($\times 10^{-3}$)	M_w/M_n
1	**1**	0	1	39	—	—
2	**1**	25	1	98	44.7	2.08
3	**1**	60	1	100	25.3	2.51
4[b]	**1**	60	1	98	28.6	2.42
5[c]	**1**	60	1	87	19.0	2.26
6	**2**	25	1	83	19.8	1.99
7	**3**	25	1	54	—	—
8	**4**	25	4.5	70	18.6	2.00
9	**5**	25	14	16	—	—

[a] Conditions: [ε-CL]/[Ln] = 500, [ε-CL] = 1.89 mol/l, toluene.
[b] Conditions: [ε-CL]/[Ln] = 1000, others are the same as run 2.
[c] Conditions: [ε-CL]/[Ln] = 2000, others are the same as run 2.

with vigorous magnetic stirring at the desired temperature. After the polymerization was held for a determined time, ethanol containing 5% HCl solution was quickly added to terminate the reaction, and then the mixture was poured into a large excess of petroleum ether. The polymer was isolated, washed with petroleum ether three times, and dried at 30 °C in vacuum overnight. The polymer yield was determined gravimetrically.

Oligomerization of ε-CL

A typical oligomerization procedure is as follows: at 25 °C, in a 5 mm NMR tube (with a Teflon valve), complex **1** (10–15 mg) was dissolved in C_6D_6 (0.6 ml). ε-CL (2–5 equivalents) was placed at the upper end of the NMR tube to prevent early mixing. The NMR tube was closed and vigorously shaken.

RESULTS AND DISCUSSION

Polymerization of ε-CL catalyzed by Cp'_3Ln

The synthesized homoleptic lanthanide metallocenes of Cp'_3Ln [Cp′ = methylcyclopentadienyl, Ln = Y (**1**), Er (**2**), Sm (**3**); Cp′ = cyclopentadienyl, Ln = Er (**4**) and Sm(**5**)] are used as single-component initiators for the ROP of ε-CL in toluene at 25 °C. The results are summarized in Table 3. All of these complexes have catalytic activity for the ROP of ε-CL. These results indicate that the structure of Cp′ ligand and the central lanthanide ionic radius have great influence on the catalytic activity of these complexes. For example, when different complexes with the same central metal [Er(III)] were used as initiators, the polymer yield reached to 83% in about 1 h for complex **2** (Table 3, run 6), but only 70% even after 4.5 h for complex **4** (Table 3, run 8). The increasing order is cyclopentadienyl < methylcyclopentadienyl, in agreement with the order of the ligand's bulk. The suggested reason might be that the increasing steric bulk of the five-member ring induced a more unsymmetric η^5 coordination. On the other hand, the influence of the metal on polymerization activity is observed. For instance, in the case of $(MeCp)_3Ln$, the ROP of ε-CL with yttrium(III) complex **1** gives the highest polymer yield of 98% using 0.2 mol% initiator concentration (Table 3, run 2); in comparison, polymer yields of 83 and 54% are obtained with erbium(III) complex **2** (Table 3, run 6) and samarium(III) complex **3** (Table 3, run 7), respectively, under the same polymerization conditions. The increasing activity order, Sm < Er < Y, is approximately opposite to the order of nine-coordinate ionic radii Sm (0.96 Å) > Er (0.88 Å) ≈ Y (0.89 Å).[23] This behavior is also observed in polymerization of methyl methacrylate initiated by $Cp^*_2Ln\text{-}CH_3$.[24] The reason may be that the combination of a sterically bulky ligand with a small metal center is of benefit to form a more unsymmetric η^5 coordination of the five-membered ring as well as to stabilize active centers.

In the initiator of $(MeCp)_3Y$, the effects of polymerization temperature and variation in initiator concentration were studied. The results are also presented in Table 3. It is observed that the temperature has great influence on the present polymerization. For the same concentration of $(MeCp)_3Y$ ([ε-CL]:[Ln] = 500 : 1), the polymer yield increases from 39% to ca. 100% with increase in temperature from 0 to 60 °C (Table 3, runs 1–3); however, the number-average molecular weight of obtained polymer shows a trend of decrease and the corresponding molecular weight distribution becomes broader. This suggests that there occur more side reactions such as transesterifications under the higher temperature during the polymerization. In addition, the yttrium(III) complex $(MeCp)_3Y$ is really a highly effective initiator for the ROP of ε-CL at 60 °C. The polymerization gives a high yield of 87% even by use of 0.07 mol% initiator concentration (Table 3, run 5); meanwhile, the number-average molecular weight of obtained polymer increases as the initiator concentration decreases, and records a maximum of 28.6×10^3 at a yield of 98%.

Polymerization of ε-CL catalyzed by $[(MeC_5H_4)_2Y(\mu\text{-}OCH_2CF_3)]_2$ (6)

Recently, Novak *et al.* reported that the titanium(IV) complex ($TiCl_3OCH_2CF_3$) containing trifluoroethoxo ligand can realize 'living' polymerization of alkyl isocyanates, and found that there is a close relationship between the Lewis-acidity of the ligand and its catalytic behavior.[25] We notice that, although a series of lanthanide(III) alkoxides have been reported to catalyze the ROP of ε-CL efficiently and some of them show the living character,[19] the lanthanide(III) alkoxide whose alkoxo ligand contains a strong electro-attracting group such as —CF_3 has not been investigated so far for the same polymerization. Therefore, in order to further evaluate the catalytic characteristics of the homoleptic lanthanide metallocenes of Cp'_3Ln, a novel trifluoroethoxo yttrium(III) complex of $[(MeC_5H_4)_2Y(\mu\text{-}OCH_2CF_3)]_2$ (**6**) has been synthesized in turn.

The method of liberating methylcyclopentadiene from a $(MeC_5H_4)_3Ln$ moiety by action of protonic acid stronger than MeC_5H_5 was adopted. When YCl_3 was reacted with three equivalents of MeC_5H_4Na in THF, followed by treatment with $HOCH_2CF_3$ in toluene at room temperature, neutral trifluoroethoxo yttrium(III) complexes were obtained as crystals, as shown in Scheme 1

The yttrium(III) complex **6** was characterized by elemental analysis, IR, ^1H NMR spectroscopy and the X-ray structural determination. It was observed that complex **6** has a dimeric structure. As shown in Fig. 1, the coordinated geometry around the yttrium atom can be described as a distorted tetrahedral geometry in which the yttrium ion is coordinated to two methylcyclopentadienyl rings and two oxygen atoms of the trifluoroethoxo ligands. The formal coordination number of the central metal is 8 if the MeC_5H_4 group is regarded as occupying three coordinated sites. In complex **6**, the Y–O and Y–O* distances are 2.275(2) and 2.270(2) Å, respectively. The very small disparity (ca. 0.005 Å) between the Y–O and Y–O* bond lengths suggests that their bonding modes are just the same. The Y–O and Y–O* bond distances are very similar to those in previously characterized binuclear bis-cyclopentadienyl lanthanide alkoxides $[(Me_3SiC_5H_4)_2Y(\mu\text{-}Ome)]_2$ [2.217(3) and 2.233(3) Å][26] and $[(MeC_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$ [2.275(3) and 2.290(3) Å].[27] The Y–C_{ring} distances of these complexes range from 2.615(4) to 2.695(4) Å, with an average value of 2.657 Å for **1**. When the difference in ionic radii is considered, the average value of the Y–C_{ring} distance for **1** is compatible with those found in corresponding $[Cp_2Ln(\mu\text{-}OR)]_2$ structures such as 2.670(1) Å for $[(Me_3SiC_5H_4)_2Y(\mu\text{-}OMe)]_2$[26] and 2.651(5) Å for $[(MeC_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$[27] and so on. The (ring centroid)–Y–(ring centroid) angle of 126.58° in complex **1** is much larger than the O–Y–O* angle of 72.18°, and shows the large deviation from the ideal tetrahedral geometry.

$$YCl_3 + 3MeC_5H_4Na \xrightarrow[\text{r.t.}]{\text{toluene}} (MeC_5H_4)_3Y(THF) + 3NaCl$$

$$(MeC_5H_4)_3Y(THF) + CF_3CH_2OH \xrightarrow[\text{r.t.}]{\text{toluene}} \underset{(\mathbf{6})}{[(MeC_5H_4)_2Y(\mu\text{-}OCH_2CF_3)]_2}$$

Scheme 1.

On the basis of well-defined structure of complex **6**, we tested its catalytic behavior for the ROP of ε-CL. The results are summarized in Table 4. It was found that, within 2 h, the polymerization proceeded rapidly up to a polymer yield of 100% at room temperature. It is also worth noting that the catalytic activity of trifluoroethoxo yttrium(III) complex **6** is somewhat lower than that of the homoleptic trimethylcyclopentadienyl yttrium(III) complex **1**. For example, the 500 : 1 reaction of ε-CL with **6** gave poly(ε-caprolactone) (PCL) with $M_n = 9.2 \times 10^3$ in 95% yield over a period of 1 h at 25 °C (Table 4, run 4), while under the same ratio of ε-CL to initiator **1** gave PCL of $M_n = 44.7 \times 10^3$ in 98% yield over a same period of polymerization at 25 °C. However, both of the molecular weight distributions (M_w/M_n) obtained with **1** or **6** are relatively broad, i.e. 2.08 for **1** and 2.80 for **6**. This phenomenon might be caused either by multiactive species in these polymerizations or by transesterifications in the present polymerization.

Compared with Cp^*_3Sm,[16] we suggest that the present ROP of ε-CL with $(MeC_5H_4)_3Y$ should be initiated by

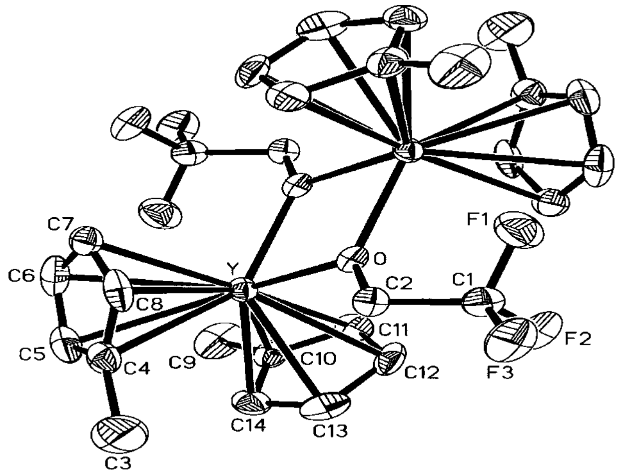

Figure 1. The molecular structure of $[(MeC_5H_4)_2Y(\mu\text{-}OCH_2CF_3)]_2$ (**6**).

Table 4. Polymerization of ε-caprolactone with $[(MeC_5H_4)_2Y(\mu\text{-}OCH_2CF_3)]_2$ (**6**)[a]

Run	Time (min)	Yield (%)	$M_n \times 10^{-3}$	M_w/M_n
1	15	55	8.0	2.26
2	30	75	/	/
3	60	95	9.6	2.61
4	120	100	12.0	2.80

[a] Conditions: [ε-CL]/[**1**] = 500, [ε-CL] = 1.89 mol/l, toluene, 25 °C.

the yttrium(III) alkoxide which is generated *in situ* by the reaction of $(MeC_5H_4)_3Y$ with ε-CL, and proceed via a 'coordination addition, acyl-oxygen cleavage' mechanism. In fact, such a polymerization mechanism has been popular accepted for the ROP of ε-CL initiated by various lanthanide complexes containing Ln−C and Ln−H bonds, which are similar to the mechanism of the ROP of ε-CL initiated by lanthanide alkoxides.[19] According to this mechanism, the methylcyclopentadienyl moiety should be present at the end of the PCL chain. Herein, the polymerization of ε-CL with **1** is recorded by ^{1}H NMR spectra. For example, complex **1** was treated with ε-CL in the range from 2 to 5 equivalents in an NMR tube. The ^{1}H NMR spectrum recorded after 10 min shows that the signals attributed to PCL ($\delta = 4.0, 2.3, 1.6$ and 1.4 ppm) appeared accompanied by the gradual disappearance of the signals attributed to ε-CL ($\delta = 3.5, 2.2, 1.2$ and 1.0 ppm). Meanwhile the chemical shifts of the methylcyclopentadienyl protons in **1** changed from the high field to the low field, which might be due to the connection of the methylcyclopentadienyl moiety to the end of the oligomer. However, the signals attributed to the protons of methylcyclopentadienyl ligand could not be observed in the ^{1}H NMR spectrum of the oligomer of PCL, which was synthesized by the reaction of **1** with ε-CL in 1: 5 molar ratio. This phenomenon is just the same as the results observed in the ROP of ε-CL with $Cp^*{}_3Sm$.[17] Similarly, the mechanism of ROP of ε-CL with **6** is investigated by NMR spectra in turn. The ^{1}H NMR spectrum recorded after 10 min shows a new quartet peak appeared at 4.3 ppm, which did not exist either in the spectrum of complex **6** or in that of ε-CL. This signal should be due to methylene protons of trifluoroethoxy group, which connects to the end of PCL. Furthermore, the ^{19}F NMR spectra of PCL obtained with **6** show that the $—OCH_2CF_3$ group is present. Obviously, the $—OCH_2CF_3$ group existing in the PCL must come from the initiator used.

CONCLUSION

In conclusion, homoleptic lanthanide metallocenes of Cp'_3Ln [Cp′ = methylcyclopentadienyl, Ln = Y (**1**), Er (**2**), Sm (**3**); Cp′ = cyclopentadienyl, Ln = Er (**4**) and Sm(**5**)] act as a novel type of single-component initiators for the ROP of ε-CL. The catalytic property of these metallocenes is related to the structure of Cp′ ligand and the central lanthanide ionic radius. Among these complexes, the yttrium(III) complex of $(MeC_5H_4)_3Y$ (**1**) shows the highest catalytic activity for the ROP of ε-CL, and a polymer with $M_n = 25.3 \times 10^3$ in ca. 100% yield is obtained over a period of 1 h at 25 °C by using 0.2 mol% initiator concentration. Furthermore, the catalytic activity of **1** is higher than that of **6**, a novel trifluoroethoxo yttrium(III) complex of $[(MeC_5H_4)_2Y(\mu\text{-}OCH_2CF_3)]_2$ synthesized by the reaction of **1** with trifluoroethanol and structurally characterized. The study investigated by the ^{1}H NMR and ^{19}F NMR spectra indicates that the Ln−Cπ bond presented in Cp'_3Ln could act as the Ln−Cσ bond in $Cp'_2Ln\text{-}R$, and the polymerization with **1** could be initiated by the *in situ* generated yttrium(III) alkoxide and proceed via a 'coordination addition, acyl-oxygen cleavage' mechanism.

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