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A New Cocatalyst for Metallocene Complexes in Olefin Polymerization

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Introduction

Activation of metallocene complexes for olefin polymerization reactions can only be achieved by a relatively short list of special cocatalysts: (1) dialkylaluminum chlorides, which work well only with titanocenes,[1,2] trialkylaluminum compounds being very poor cocatalysts for metallocene complexes);[3] (2) alkylalumoxanes;[4−6] (3) a combination of trimethylaluminum and dimethylaluminum fluoride;[7] (4) compounds or salts generating noncoordinative anions such as $[R_3NH]^+[B(C_6F_5)_4]^-$, $B(C_6F_5)_3$, $[CPh_3]^+[B(C_6F_5)_4]^-$, etc.[8−11]

We have discovered a new type of cocatalyst which is capable of activating metallocene complexes in olefin polymerization reactions. This cocatalyst has two components: (a) a haloorganoaluminum compound $Al_nR_mX_{3n-m}$, (for example, $AlEt_2Cl$, $AlMe_2Cl$, $Al_2Et_3Cl_3$, $AlEt_2F$, etc.) and (b) a dialkylmagnesium compound MgR'_2 ($R' =$ butyl, hexyl etc.). These compounds are used at a molar [Al]:[Mg] ratio of greater than 2. In the case of zirconocene complexes, each of the components, if used alone, does not produce an olefin polymerization catalyst. However, when these components are mixed, they readily activate metallocene complexes for polymerization reactions.

Experimental Section

Metallocene complexes were purchased from Boulder Scientific Co: bis(*n*-butylcyclopentadienyl)zirconium dichloride, $(n\text{-}BuCp)_2ZrCl_2$; *rac*-ethylenebis(1-indenyl)zirconium dichloride, $C_2H_4(Ind)_2ZrCl_2$; *rac*-dimethylsilylbis(1-indenyl)zirconium dichloride, $Me_2Si(Ind)_2ZrCl_2$; and dimethylsilyl(cyclopentadienyl)(9-fluorenyl)zirconium dichloride, $Me_2Si(Cp)(Flu)ZrCl_2$. They were used as diluted solutions in toluene. To facilitate dissolution of some bridged metallocene complexes, small quantities of $AlMe_3$ were added to toluene. Dialkylaluminum halides and dihexyl magnesium ($MgHex_2$) were purchased from Akzo Nobel Co.; dibutyl magnesium ($MgBu_2$) was purchased from FMC.

Supported metallocene catalysts were prepared in two steps. First, a metallocene complex dissolved in toluene was mixed with toluene solutions of $AlEt_2Cl$ and $MgBu_2$. The Al:Mg molar ratio in the mixtures was 3:1, and the Al:Zr ratio varied from 20:1 to 30:1. In the second step, the mixtures were combined with Davison-grade 955 silica (precalcined at 600 °C) at an Al:silica ratio of 3 mmol/g, and the liquid phase was removed in a nitrogen flow at 50−55 °C.

Polymerization experiments were carried out in 0.5- and 2.5-L stainless steel autoclaves equipped with magnet-driven propeller stirrers, manometers, electric heating jackets, and ports for addition of catalyst components. The reactor was dried in a nitrogen flow at 90 °C for 60−120 min, and then a liquid component (usually *n*-heptane) and, optionally, an α-olefin (1-hexene) were added to the reactor, followed by components of cocatalyst mixtures. After that, the reactor was heated to a desired reaction temperature and the polymerization reaction was started by adding a solution of a metallocene complex or the supported catalyst and pressurizing the reactor with ethylene. The reaction was monitored at a constant pressure for 60−120 min, after which polymers were recovered and dried overnight at 25 °C. Typical reaction conditions were as follows: temperature 60−90 °C; 1-hexene concentration from 20 to 40 vol %; total reaction pressure 1.0−1.4 MPa.

^{13}C NMR spectra of organometallic compounds were recorded at 100.4 MHz on a JEOL Eclipse 400 NMR spectrometer at 20 °C. ^{13}C NMR spectra of polymers were recorded using the same instrument at 130 °C under experimental conditions appropriate for acquiring quantitative spectra of polyolefins (pulse angle was 90° and the pulse delay was 15 s). Continuous ^1H decoupling was applied throughout. The samples were prepared as solutions in a 3:1 mixture of 1,3,5-trichlorobenzene and 1,2-dichlorobenzene-d_4. Copolymer compositions were measured by IR; they are reported as mol % of an α-olefin in the copolymers, C_{olef}^{copol}. Infrared spectra were recorded with a Perkin-Elmer Paragon 1000 spectrophotometer. X-ray diffraction patterns were recorded with Phillips PW 1877 automated powder diffractometer.

Results and Discussion

Cocatalyst Structure. Chloroorganoaluminum compounds and dialkylmagnesium compounds react rapidly with the formation of finely dispersed white solids. When this reaction is carried out in aliphatic solvents (*n*-heptane, isohexane), the precipitation is quite rapid and produces a white voluminous mass which is soluble in water, THF, and acetone. In aromatic solvents such as toluene, the same reaction is slower and produces finely dispersed solid particles which remain in a quasi-colloidal state for long periods of time. ^{13}C NMR analysis of liquid products formed in the reaction of $AlMe_2Cl$ and $MgBu_2$ at the [Al]:[Mg] molar ratio of 2 showed that both $AlMe_2Cl$ (based on the CH_3 signal at −6.5 ppm) and $MgBu_2$ (based on the α-CH_2 signal at +9.5 ppm) are fully consumed in the reaction and a new product, with a CH_3 signal at −8.0 ppm and the α-CH_2 signal at +10.8 ppm, is formed. Comparison with spectra of various organoaluminum compounds ($AlMe_3$ and $AlHex_3$) suggests that the most probable reaction is

$$2AlMe_2Cl + MgBu_2 \rightarrow MgCl_2 + 2AlMe_2n\text{-}Bu$$

X-ray analysis of the solid product formed in this reaction confirmed formation of finely dispersed $MgCl_2$;[15] its main broad reflections were at $2\theta = \sim16$, ∼31, 51, and ∼60°. However, chemical analysis of the precipitates revealed a more complex picture. The solid formed in the mixture of $AlEt_2Cl$ and $MgBu_2$ at an [Al]:[Mg] molar ratio of 2 (25 °C, overnight) has an empirical formula $MgCl_2{\cdot}0.4(AlR_2Cl)$ ($R \sim C_4$). Analysis of the solid produced in the mixture of $Al(i\text{-}Bu)_2Cl$ and $MgHex_2$ at an [Al]:[Mg] molar ratio of 1 (25 °C, overnight, reprecipitated from ethanol) also showed the presence of Al in the solid, $([Al]:[Mg])_{mol} \sim 0.13$. GC analysis of organic products generated during dissolution of the thoroughly washed solid in ethanol indicated the presence of isobutane and *n*-hexane in a 3:1 molar ratio. Similarly, a reaction between $AlMe_2Cl$ and $MgBu_2$ at an [Al]:[Mg] molar ratio of 2 produced a solid containing Al with $([Al]:[Mg])_{mol} \sim 0.07$.

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Table 1. Polymerization with Cp_2ZrCl_2 Activated with $AlR_2X-MgBu_2$ and $AlR_2X-LiBu$ Mixtures

cocatalyst	[Al]:[Mg], mmol/mmol	[Zr], mmol	temp, °C	P_E,[a] MPa	C_{Hex},[b] M	yield, g
$MgBu_2$	0/1.5	7×10^{-3}	60	1.24	0	0
$AlEt_2Cl$	7.5/0	1×10^{-3}	80	1.03	0	0
$AlEt_2Cl$	1.5/0	1.4×10^{-2}	60	0.82	3.2	~0.1[c]
$AlEt_2Cl/MgBu_2$	7.5/2.0	1.0×10^{-2}	80	1.03	0	56.3
$AlEt_2Cl/MgBu_2$	7.5/2.0	1.0×10^{-2}	80	1.03	2.7	45.7
$AlEt_2Cl/MgBu_2$	1.5/0.8	3.3×10^{-2}	80	0.82	3.9	55.8
$AlMe_2Cl/MgBu_2$	7.5/2.0	7×10^{-3}	80	1.24	3.2	23.1
$AlEt_2F/MgBu_2$	4.5/1.0	6×10^{-3}	60	1.24	3.2	15.6
$AlMe_2Cl$/*sec*-BuLi	2.0/1.0	3.4×10^{-3}	70	1.03	1.3	12.9

[a] P_E = partial pressure of ethylene. [b] C_{Hex} = molar concentration of 1-hexene in solution. [c] Cationic oligomers of 1-hexene.

Table 2. Ethylene/α-Olefin Copolymerization Reactions with Bridged Metallocene Complexes Activated with $AlEt_2Cl-MgBu_2$ and with $AlMe_2Cl-MgBu_2$ Mixtures ([Al]:[Mg] = 2.8−3.0)

catalyst	temp, °C	P_E,[a] (MPa)	α-olefin	C_{olef},[b] (M)	yield, g/mmol of Zr	C_{olef}^{copol}, mol %
$(n\text{-}BuCp)_2ZrCl_2$	80	1.03	1-hexene	1.38	6000 (0.5 h)	0.9
$C_2H_4(Ind)_2ZrCl_2$	80	0.41	propylene	0.23 MPa	1200 (1 h)	9.0
$C_2H_4(Ind)_2ZrCl_2$	80	1.25	1-hexene	1.66	12400 (0.5 h)	5.3
$C_2H_4(Ind)_2ZrCl_2$	80	1.25	1-hexene	1.38	18000 (2 h)	2.0
$C_2H_4(Ind)_2ZrCl_2$	80	1.26	1-hexene	0.80	5200 (2 h)	0.6
$C_2H_4(Ind)_2ZrCl_2$	90	1.30	1-hexene	1.75	6900 (1 h)	4.7
$Me_2Si(Ind)_2ZrCl_2$	80	1.26	1-hexene	0.90	6250 (2 h)	0.7
$Me_2Si(Cp)(Flu)ZrCl_2$	90	1.30	1-hexene	1.75	6700 (1 h)	3.4
			Silica-Supported Catalysts			
$C_2H_4(Ind)_2ZrCl_2$	90	1.30	1-hexene	1.75	7800 (1 h)	4.4
$C_2H_4(Ind)_2ZrCl_2$[c]	90	1.30	1-hexene	1.75	4900 (1 h)	2.4
$Me_2Si(Cp)(Flu)ZrCl_2$	90	1.30	1-hexene	1.75	750 (1 h)	-

[a] P_E = partial pressure of ethylene. [b] C_{olef} = molar concentration of 1-hexene in solution. [c] $AlMe_2Cl-Mg(n\text{-}Bu)_2$ combination was used as a cocatalyst.

Polymerization Reactions. When the products of the reaction between AlR_2Cl and MgR'_2 were combined with metallocene complexes of Ti, Zr, or Hf (either unsubstituted metallocenes or their ring-substituted analogues), they formed catalytically active systems for the polymerization of ethylene and α-olefins. The polymerization reactions were typically carried out in aliphatic hydrocarbons under the following conditions: an $[AlR_2X]:[MgR'_2]$ molar ratio from 2 to 5 and a temperature range from 20 to 90 °C. The [Al]:[transition metal] ratio in these experiments can vary from 500 to 2000. Table 1 presents some results of these polymerization reactions using the unsubstituted zirconocene complex Cp_2ZrCl_2. Neither $MgBu_2$ nor $AlEt_2Cl$, when used alone, activated the zirconocene complex (although $AlEt_2Cl$ initiated cationic polymerization of 1-hexene), but combinations of $AlEt_2Cl$ and $Mg(n\text{-}Bu)_2$ were quite effective cocatalysts. An [Al]:[Mg] molar ratio from 2 to 5 was needed for a catalytic effect; the same combinations at the [Al]:[Mg] ratio less than 1 were virtually inactive. In the case of ethylene copolymerization reactions, polymer yields ranged from 2500 to 10 000 g/mmol pf Zr. Comparison with MAO as a cocatalyst showed that $AlR_2Cl-MgR'_2$ combinations were 5−10 times less active (per mole of the zirconocene complex).

Two other combinations of organometallic compounds are also capable of activating metallocene complexes: (a) AlR_2F and MgR'_2 and (b) AlR_2Cl and LiR′ (see Table 1). However, none of the cocatalyst combinations was effective when $(C_5Me_5)_2ZrCl_2$ was used as a zirconocene complex, in contrast to MAO. Combinations of $AlEt_2Cl$ and $MgBu_2$ also readily activate metal-alkylated zirconocene complexes (Cp_2ZrMe_2), zirconocenes with alkyl-substituted cyclopentadienyl rings, as well as metallocene complexes with bridged cyclopentadienyl rings (Table 2). This table also shows results of ethylene/1-hexene copolymerization reactions using supported metallocene catalysts.

The $AlR_2Cl-MgR'_2$ combinations can also activate bridged metallocene complexes in stereospecific polymerization of α-olefins. Polymerization of propylene with $C_2H_4(Ind)_2ZrCl_2$ activated by $AlEt_2Cl-MgBu_2$ cocatalyst at the [Al]:[Mg] molar ratio of 2.8 at 50 °C and the propylene partial pressure of 0.48 MPa produced polypropylene (2 h yield ~200 g/mmol Zr) with a moderate degree of isotacticity; its melting point was 136−140 °C. Polymerization of 4-methyl-1-pentene with the same catalyst at 55 °C also produced crystalline isotactic poly(4-methyl-1-pentene) with a low yield.

3.3. Single-Site Catalysis. Based on GPC data, polymers prepared with metallocene complexes activated with AlR_2Cl and MgR'_2 have relatively broad molecular weight distributions, with M_w/M_n values in the range of 10−15. However, ethylene/α-olefin copolymers prepared with these catalysts have relatively narrow compositional distributions, an important indicator of single-site catalysis. Analysis of DSC melting curves of several ethylene/1-hexene copolymers prepared with unsubstituted and ring-substituted zirconocene complexes, activated with $AlEt_2Cl-MgBu_2$ at relatively high [Al]:[Zr] ratios (over 1500), showed two indicators of single-site catalysis. The copolymers containing from 3 to 5 mol % of 1-hexene had quite narrow melting peaks, and their melting points were relatively low, (100−125 °C), depending on composition. For example, the copolymer with the 1-hexene constant of 2.0 mol %, prepared with the $Cp_2ZrCl_2/AlEt_2Cl-MgBu_2$ catalyst, had T_m = 118.7 °C (crystallinity 67%), and the copolymer 1-hexene content 5.2 mol %, prepared with the $C_2H_2(Ind)_2ZrCl_2/AlEt_2Cl\text{-}MgBu_2$ catalyst, had T_m = 99.6 °C (crystallinity 26%). Supported catalysts activated with $AlR_2Cl-MgR'_2$ cocatalysts also produced ethylene copolymers with uniform compositional distributions. Their melting points are uniformly low:

C_{Hex}^{copol}, mol %	2.4	3.4	4.7	4.4
T_m, °C	114.7	106.9	106.6	105.1

Reaction Mechanism. Combinations of haloorganoaluminum compounds and dialkylmagnesium compounds are universal, very effective cocatalysts for various transition metal-based polymerization catalysts. For example, these binary cocatalysts activate $TiCl_4$,[16,17] supported Ti-based Ziegler−Natta catalysts,[18,19] $Ti(OR)_4$, and mono- and multidentate Ti complexes of various types.[20−22] As described above, these cocatalysts can also activate various metallocene complexes in olefin polymerization reactions. It is reasonable to assume similar activating mechanisms in all these cases. Such a mechanism, in the case of metallocene catalysis, should include at least two steps. The first one is alkylation of transition metal compounds. It is probably achieved by reactions involving the transition metal atom in a metallocene complex and AlR_2R' which is formed in the reaction between AlR_2Cl and MgR'_2. The second essential part of the catalysis is ionization of alkylated transition-metal species and the formation of cationic active centers. In the case of metallocene complexes, they are metallocenium species $[Cp_2Zr-R]^+$. By analogy with the role of MAO in metallocene-MAO pairs, we assume that the counterions, most probably derivatives of MgX_2 lattices, can abstract R^- or Cl^- from the alkylated transition-metal complexes and that the resulting anionic species have a broadly distributed negative charge. Such a mechanism of active center formation from $(CMe_5)_2ThMe_2$ in contact with $MgCl_2$ has been demonstrated by Hedden and Marks.[23] Similarly, combinations of $MgCl_2$ and AlR_3 were found to activate the monometallocene complexes $CpMCl_3$.[24]

Chain growth reactions with $AlR_2Cl-MgR'_2$-activated metallocene complexes proceed in the same manner as over MAO-activated metallocenes complexes. The principal chain termination reaction is β-hydrogen elimination. In the case of ethylene/1-hexene copolymerization reactions (products prepared with a $Cp_2ZrCl_2-AlEt_2Cl-MgBu_2$ system in toluene at 85 °C), it produces two chain-end double bonds: vinyl bonds when the last monomer unit in the chain is ethylene

$$Zr^+-CH_2-CH_2-R \rightarrow Zr^+-H + CH_2{=}CH-R$$

and vinylidene bonds when the last monomer unit in the chain is 1-hexene unit

$$Zr^+-CH_2\text{EnDash}-C(C_4H_9)H-R \rightarrow Zr^+-H + CH_2{=}C(C_4H_9)-R$$

Comparison of the chain-end composition with the overall copolymer composition (by IR) shows that the probability of the second reaction is ca. 20 times higher.

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