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Propylene Polymerization with *ansa*-Metallocene Amide Complexes

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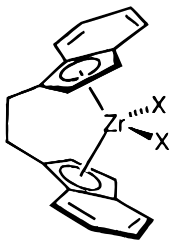
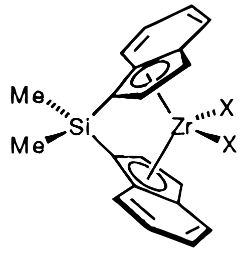
Catalysts derived from chiral C_2-symmetric *ansa*-metallocenes, such as *rac*-(EBI)ZrCl$_2$ (**1**, EBI = C$_2$H$_4$(indenyl)$_2$) and *rac*-(SBI)ZrCl$_2$ (**2**, SBI = Me$_2$Si(indenyl)$_2$), have been studied extensively for the stereoselective polymerization of propylene and other olefins.[1] The active species in these catalysts are ^{ch}Cp$_2$Zr(R)$^+$ cations (^{ch}Cp$_2$Zr = chiral *ansa*-metallocene framework), which are generated by alkylation and ionization of neutral metallocene precursors.[2] Standard activation procedures include (i) treatment of ^{ch}Cp$_2$ZrX$_2$ (X = Cl, R, OR) with excess methylaluminoxane (MAO), (ii) reaction of ^{ch}Cp$_2$ZrR$_2$ complexes with ammonium salts (e.g., [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]), oxidizing agents (e.g., Ag$^+$, Cp$_2$Fe$^+$), or alkyl abstraction reagents (e.g., CPh$_3$$^+$, B(C$_6F_5$)$_3$), or (iii) *in situ* alkylation of ^{ch}Cp$_2$ZrX$_2$ complexes with AlR$_3$ or other reagents followed by ionization as in (ii).[1,2]



1, X = Cl
3, X = NMe$_2$
5, X = Me



2, X = Cl
4, X = NMe$_2$
7, X = Me

Practical application of *ansa*-metallocene catalysts is limited by the fact that the racemic (*rac*) isomers required for isotactic α-olefin polymerization are difficult to prepare.[3] However, we recently reported that the amide complex *rac*-(EBI)Zr(NMe$_2$)$_2$ (**3**) can be prepared efficiently via an amine elimination route, which we have since extended to *rac*-(SBI)Zr(NMe$_2$)$_2$ (**4**) and other *ansa*-metallocenes.[4] These amide derivatives can be converted to the corresponding dichloride (**1**, **2**) or dimethyl (**5**, **7**) complexes, which can then be used in polymerization reactions using standard procedures. However, the efficiency of the amine elimination route would be more fully exploited if the amide derivatives could be used directly in catalyst formulations. This paper describes our initial studies of this possibility. It was reported earlier that the achiral metallocene amide complex Cp$_2$Zr(NEt$_2$)$_2$ is activated for ethylene polymerization by excess MAO.[5]

Results and Discussion. To determine if **3** and **4** could be activated for propylene polymerization by MAO, we compared the activities of **3**/MAO and **4**/MAO catalysts with conventional catalysts **1**/MAO and **2**/MAO under the same conditions (48 °C, 1 atm of propylene, Al/Zr ca. 1000/1, toluene; Table 1, runs 1−5). The amide-derived catalysts are significantly less active than the chloride-derived catalysts under these conditions, although the stereoselectivity is comparable.[6] GPC results for the polymer produced by **3**/MAO are consistent with single-site behavior.

One possible reason for the lower activities observed for the catalysts based on **3** and **4** is that these amide complexes are not efficiently alkylated by MAO (or the AlMe$_3$ contained therein).[7] In an effort to circumvent this potential problem, **3** and **4** were pretreated with excess AlR$_3$ prior to activation with MAO, such that the total Al/Zr ratio was maintained in the range 800/1 to 1300/1. The results of these experiments using AlMe$_3$ or Al(^{i}Bu)$_3$ are summarized in runs 6−11. This procedure produces catalysts with activities and stereoselectivities which are comparable to those of the **1**/MAO or **2**/MAO catalysts under the conditions studied. The prealkylation procedure can also be used with CPh$_3$$^+$ and HNR$_3$$^+$ cocatalysts, as illustrated by runs 12−22. GPC results for representative examples are characteristic of single-site behavior.

The reactions of **3** and **4** with AlMe$_3$ and selected cocatalysts from Table 1 were studied by NMR spectroscopy in an effort to elucidate the chemical steps in the catalyst activation process. Treatment of a CD$_2$Cl$_2$ solution of **3** with 2.5 equiv of Al$_2$Me$_6$ results in an immediate color change from red to yellow and quantitative formation of *rac*-(EBI)ZrMe$_2$ (**5**) and a mixture of Al$_2$Me$_5$(NMe$_2$), Al$_2$Me$_4$(NMe$_2$)$_2$, and unreacted Al$_2$Me$_6$, as determined by ^{1}H NMR (Scheme 1).[8,9] Subsequent addition of 1 equiv of [CPh$_3$][B(C$_6$F$_5$)$_4$] results in immediate conversion to [*rac*-(EBI)Zr(μ-Me)$_2$AlMe$_2$]$^+$ (**6**), the adduct of the base-free *rac*-(EBI)ZrMe$^+$ cation and AlMe$_3$ which was previously identified by Bochmann as the principal component in mixtures of these species.[10] Complex **6** presumably undergoes loss or displacement of AlMe$_3$, ultimately leading to active *rac*-(EBI)Zr(Me)$^+$ or *rac*-(EBI)Zr(Me)(propene)$^+$ species. Similarly, sequential reaction of **3** with 2.5 equiv of Al$_2$Me$_6$ and 1 equiv of [HNMePh$_2$][B(C$_6$F$_5$)$_4$] in CD$_2$Cl$_2$ results in formation of **6** (>90% NMR). In this case, the resonances of **6** and the Al amide species are broadened, presumably due to reversible formation of NMePh$_2$ adducts. In an analogous series of experiments, complex **4** was converted to *rac*-(SBI)ZrMe$_2$ (**7**, >95% NMR) upon treatment with 2.5 equiv of Al$_2$Me$_6$ and then to [*rac*-(SBI)Zr(μ-Me)$_2$AlMe$_2$]$^+$ (**8**) by subsequent reaction with [CPh$_3$][B(C$_6$F$_5$)$_4$] or [HNMePh$_2$][B(C$_6$F$_5$)$_4$].[11] The reactions of **3** and **4** with MAO and AlR$_3$/MAO are still under investigation.

Conclusions. The metallocene amide derivatives **3** and **4** are activated for propylene polymerization by initial alkylation with AlR$_3$ reagents and subsequent reaction with MAO or other activators which generate ^{ch}Cp$_2$Zr(R)$^+$ species. Thus these easily prepared metallocenes can be used directly in catalyst formulations without conversion to dichloride complexes **1** and **2**. More thorough studies of the influence of the nature and concentration of the AlR$_3$ reagent and the polymerization conditions on the catalyst performance and polymer properties are in progress. The simplicity of the alkylation reactions of **3** and **4** may prove advantageous in studies of the solution structure and reactivity of MAO and the presumed ^{ch}Cp$_2$M(R)$^+$ (MAO−X)$^-$ active species.

Experimental Section. Propylene (99.5%, polymer grade, Matheson) was purified by passage through a Matheson 6410 gas purification column. Toluene was distilled from sodium under nitrogen. The following

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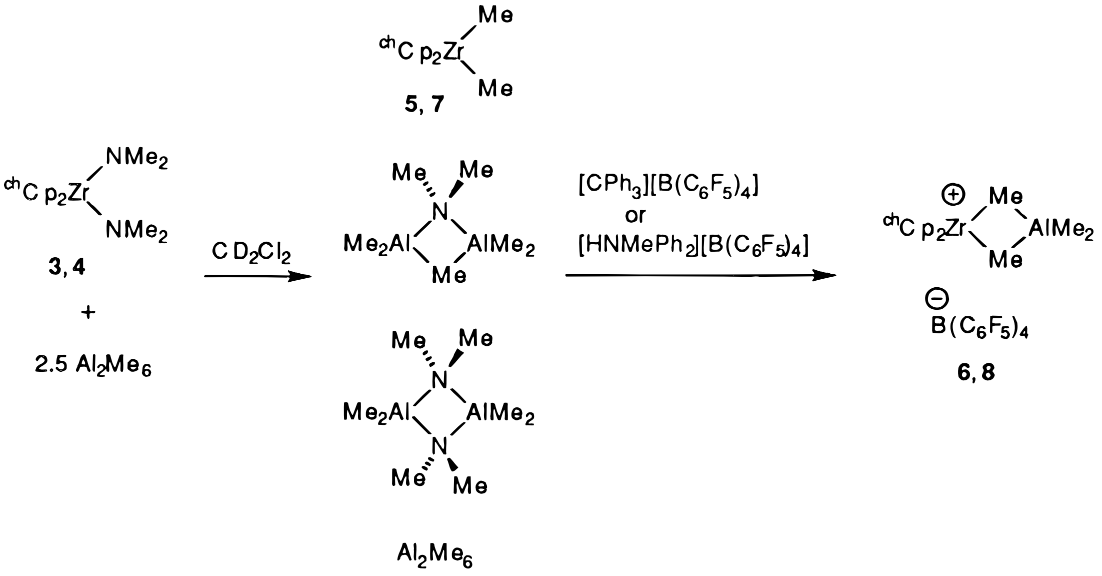
Table 1. Propylene Polymerization Results (Toluene, P = 1 atm, T = 48 °C)

run	cat.[a]	µmol of cat.	AlR_3	µmol of AlR_3	cocat.[b,c]	µmol of cocat	time (min)	yield (g)	activity [10^6 g (mol of Zr)$^{-1}$ h^{-1}]	% mmmm	T_m (°C)	$M_w \times 10^{-3}$	M_w/M_n
1	**3**	5.7			MAO	5600	60	1.6	0.27	74.9			
2	**3**	5.7			MAO	5800	60	1.5	0.26		135.1	29.4	1.9
3	**4**	5.4			MAO	5200	60	5.2	0.97	79.0			
4	**1**	5.9			MAO	5800	96	63.2	6.7	73.4			
5	**2**	5.5			MAO	4300	106	64.5	6.6	81.5			
6	**3**	5.7	$AlMe_3$	520	MAO	4300	90	50.5	5.9	79.8			
7	**3**	5.7	$AlMe_3$	2080	MAO	5000	60	34.8	6.1		128.8	11.9	1.9
8	**3**	5.7	$Al(^iBu)_3$	200	MAO	4300	90	56.8	6.6	76.9			
9	**3**	5.7	$Al(^iBu)_3$	2000	MAO	5000	60	46.2	8.1		134.8	25.4	2.1
10	**4**	5.4	$AlMe_3$	2080	MAO	4300	90	70.8	8.7	82.9			
11	**4**	5.4	$Al(^iBu)_3$	790	MAO	4200	60	34.2	6.3		135.9	33.9	2.2
12	**3**	5.7	$AlMe_3$	520	CPh_3^+	5.7	126	31.3	2.6	82.1			
13	**3**	5.7	$Al(^iBu)_2H$	280	CPh_3^+	5.4	85	50.3	6.3	69.2			
14	**3**	5.7	$AlPr_3$	260	CPh_3^+	5.4	100	51.5	5.4	72.2			
15	**3**	5.7	$AlMe_3$	520	$HNMe_2Ph^+$	5.7	96	19.6	2.1	80.0			
16	**3**	5.7	$AlMe_3$	520	$HNMePh_2^+$	5.7	66	30.0	4.8	76.2			
17	**3**	5.7	$Al(^iBu)_2H$	560	$HNMePh_2^+$	5.7	150	30.5	2.1				
18	**4**	5.6	$AlMe_3$	2080	CPh_3^+	6.3	66	60.9	9.9	78.8			
19	**4**	5.4	$AlPr_3$	260	CPh_3^+	5.4	60	32.3	5.9	86.3			
20	**4**	5.4	$Al(^iBu)_3$	1000	CPh_3^+	6.0	90	49.1	6.1	79.6			
21	**4**	5.4	$AlMe_3$	2080	$HNMe_2Ph^+$	7.5	77	53.1	7.5	81.5			
22	**4**	5.3	$AlMe_3$	1000	$HNMePh_2^+$	5.2	60	44.2	8.5		141.3	29.4	1.9

[a] **1** = *rac*-(EBI)$ZrCl_2$; **2** = *rac*-(SBI)$ZrCl_2$; **3** = *rac*-(EBI)$Zr(NMe_2)_2$; **4** = *rac*-(SBI)$Zr(NMe_2)_2$. [b] mmol of MAO = mmol of Al, of which 82 wt % = "AlMeO" and 18 wt % = $AlMe_3$. [c] Anion = $B(C_6F_5)_4^-$ for CPh_3^+ and HNR_3^+ cocatalysts.

Scheme 1



compounds were synthesized by literature procedures: *rac*-(EBI)$ZrCl_2$ (**1**),[4] *rac*-(SBI)$ZrCl_2$ (**2**),[12] *rac*-(EBI)$Zr(NMe_2)_2$ (**3**),[4] *rac*-(SBI)$Zr(NMe_2)_2$ (**4**),[4] $[HNMe_2Ph][B(C_6F_5)_4]$,[13] and $[HNMePh_2][B(C_6F_5)_4]$.[13] Methylaluminoxane (MAO) was donated by Albemarle as a 10% solution in toluene, which contained 1.85 wt % $AlMe_3$ and 8.15 wt % MAO (4.49 wt % total Al). $AlMe_3$ and $Al(^iBu)_3$ were obtained from Aldrich and used without further purification. $[Ph_3C][B(C_6F_5)_4]$ was donated by Asahi Glass Co., Ltd.

Propylene polymerizations were performed in a 250 mL Fisher–Porter reactor equipped with a mechanical stirrer and a temperature probe. In a drybox the reactor was charged with toluene (120 mL), and the prescribed amount of alkyl aluminum reagent was added. The metallocene compound (2.5 mg) was then added. After the metallocene dissolved, the activator ($[Ph_3C][B(C_6F_5)_4]$, $[HNMe_2Ph][B(C_6F_5)_4]$ or $[HNMePh_2][B(C_6F_5)_4]$) was added. The reactor was immersed in a constant-temperature bath previously set to the desired temperature, and the stirrer was turned on. When the reactor temperature had equilibrated to the bath temperature, polymerization was initiated by pressurizing the reactor with propylene (1 atm). The pressure was maintained at 1 atm. Polymerization was quenched by addition of EtOH (ca. 200 mL) followed by concentrated HCl (20 mL). The polypropylene was isolated by filtration, washed several times with EtOH, and dried (70 °C, vacuum oven, overnight).

Molecular weights and molecular weight distributions were measured by GPC (Waters 150-C) at 135 °C in 1,2-dichlorobenzene. Polymer melting points were measured with a Perkin-Elmer DSC-4 system at a heating rate of 10 °C/min. ^{13}C NMR spectra were recorded on a Bruker AMX-360 spectrometer at 120 °C. NMR samples were prepared by dissolving 100 mg of polymer in 0.5 mL of C_6D_6/1,2,4-trichlorobenzene (1/5) in a 5 mm tube. Regiochemical errors (1–3 insertion) were detected (ca. 1.0–1.8% for (EBI)Zr catalysts and 0.7–1.2% for (SBI)Zr catalysts).[6k,14]

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(9) ^{1}H NMR data (CD_2Cl_2, 25 °C): *rac*-(EBI)$ZrMe_2$ δ 7.48 (d, J = 8, 2H), 7.43 (d, J = 8, 2H), 7.19 (pseudo t, J = 7, 2H), 7.05 (pseudo t, J = 7, 2H), 6.55 (d, J = 3, 2H), 6.00 (d, J = 3, 2H), 3.3 (m, 4H), -1.42 (s, 6H); *rac*-(SBI)$ZrMe_2$ δ 7.63 (d, J = 8, 2H), 7.38 (d, J = 8, 2H), 7.27 (pseudo t, J = 8, 2H), 6.98 (pseudo t, J = 8, 2H), 6.84 (d, J = 3, 2H), 5.92 (d, J = 3, 2H), 0.91 (s, 6H), -1.43 (s, 6H).

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(11) (a) In the CPh_3^+ reaction, $[rac\text{-}(SBI)Zr(\mu\text{-}Me)_2AlMe_2]^+$ (**8**) is formed in >80% NMR yield; the dinuclear cation $\{rac\text{-}(SBI)Zr(Me)\}_2(\mu\text{-}Me)^+$ (two isomers)[10] and an as yet unidentified species are also formed. (b) In the $HNMePh_2^+$ reaction, **8** is formed in >90% NMR yield and exhibits broadened resonances, most likely due to reversible formation of $NMePh_2$ adducts. Trace amounts of $\{rac\text{-}(SBI)Zr(Me)\}2(\mu\text{-}Me)^+$ (two isomers) are also observed in this case.

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