Ethylene Polymerization Using *β*-Diketimine Complexes of Zirconium

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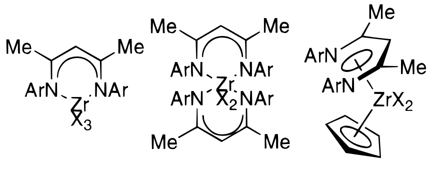
Ethylene polymerizations were conducted using *β*-diketimine complexes of Zr [$LZrX_3$ (**1**) and L_2ZrX_2 (**2**) with L = MeC(NAr)CHC(NAr)Me and X = Cl, R (R = Me, Bn)] as well as $Cp(L)ZrX_2$ (**3**) in the presence of MAO. Complexes **1** possess low polymerization activities (ca. 10^5 g PE/(mol Zr h)) and provide PEs with a trimodal, molecular weight distribution. Both **2** and **3** behave as single-site catalysts under these conditions, with the activity of the latter being considerably higher than the former (ca. 10^6−10^7 vs 10^5 g PE/(mol Zr h)). Induction periods of 10−20 min at 70 °C were observed in polymerizations involving **3** (Ar = Ph, X = Cl, Me) when activated by MAO. The use of $[Ph_3C][B(C_6F_5)_4]$ and **3b** (Ar = Ph, X = Me) in the presence of small amounts of MAO (ca. 100:1 Al:Zr) led to rapid monomer uptake and an increase in catalytic activity by about a factor of 4. Lower activities were observed in the presence of Me_3Al or $^iBu_3Al$. Little or no polymerization activity was observed when excess **3b** was used as a scrubbing agent (in the presence of $[Ph_3C][B(C_6F_5)_4]$), and rapid loss of activity was observed when excess **3b** was added to a catalyst system already producing PE. Complex **3b** reacts with $[Ph_3C][B(C_6F_5)_4]$ in chlorobenzene-*d*$_5$ solution at 25 °C to provide $[Cp(L)ZrMe][B(C_6F_5)_4]$ (**4**). Complex **4** is transformed on heating in chlorobenzene to a dicationic (μ-Cl)$_2$ complex $[(Cp(L)ZrCl)_2][B(C_6F_5)_4]_2$ (**5**), which was characterized by X-ray crystallography. Complex **4** forms dinuclear complexes with **3b** or Me_3Al in solution at room temperature. These complexes, $[Cp(L)Zr(\mu\text{-}Me)_2AlMe_2][B(C_6F_5)_4]$ (**6**) or $[(Cp(L)ZrMe)_2(\mu\text{-}Me)][B(C_6F_5)_4]$ (**7**), are fluxional in solution; at lower temperature, the solution NMR spectra are consistent with the structures shown. Complex **3b** is a potent inhibitor of ethylene polymerization by **4**, forming **7**, which is resistant to dissociation. The presence of $AlMe_3$ (or MAO) appears to reversibly displace **3b** from **7**, allowing the reaction of **3b** with $[Ph_3C][B(C_6F_5)_4]$ to proceed to completion.

Introduction

There is considerable interest in the development of early metal single-site polymerization catalysts not based on metallocene complexes of group 4. Two basic approaches can be identified based on the bonding mode of the ligands employed. Thus, a number of complexes that feature *π*-bound surrogates for Cp^- have been reported,[1] while an increasing number of systems feature *σ*-bound, heteroatom ligands in which there is a substantial *π*-donor component to the X−M bond.[2]

Chart 1



1 **2** **3**

It has occurred to us, based on the work of Jordan[2p] and Lappert,[3] that *β*-diketimine complexes of group 4 might prove to be interesting polymerization catalysts to study in view of the flexible, bonding modes possible for this ligand (i.e., 6*π* or 4*σ*, 2*π*, Chart 1). We have recently reported general synthetic routes to both mono- and disubstituted *β*-diketimine as well as mixed, cyclopentadienyl[*β*-diketimine] complexes of Zr (**1**−**3**, respectively, Chart 1) and have demonstrated that complexes **2** feature the 4*σ*, 2*π* bonding mode, while complexes **3** feature a *η*^{5}-*π*-bound ligand in the solid state.[4] In this paper, we describe the polymerization of ethylene using complexes **1**−**3**, some fundamental reactions of alkyl cations derived from **3**, and an interpretation of some of the unusual behavior of the latter compounds in ethylene polymerization.[5]

Results and Discussion

Polymerization of Ethylene Using 1−3 in the Presence of Methylaluminoxane (MAO). The polymerization of ethylene using complexes **1**−**3** was initially studied in toluene slurry at 70 °C, 75 psi C_2H_4, in the presence of MAO (1000:1 Al:Zr), and the results are summarized in Table 1. The monosubstituted com-

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(1) (a) Rodriguez, G.; Bazan, G. C. *J. Am. Chem. Soc.* **1997**, *119*, 343. (b) Kreuder, C. Jordan, R. F.; Zhang, H. *Organometallics* **1995**, *14*, 2993, and references therein. (c) Crowther, D. J.; Baenziger, N. C.; Jordan, R. F. *J. Chem. Soc., Chem. Commun.* **1994**, 2607. (d) Bazan, G. C.; Rodriguez, G.; Cleary, B. P. *J. Am. Chem. Soc.* **1994**, *116*, 2177. (e) Guan, R. W.; Bazan, G. C.; Kiely, A. F.; Schaefer, W. P.; Bercow, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4489.

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Table 1. Ethylene Polymerization Using Complexes 1−3 and MAO[a]

entry no.	catalyst	activity[b]	M_n (K)	M_w/M_n
1	**1a** (Ar = Ph, X = Cl)	0.185	13	17[c]
2	**1b** (Ar = Ph, X = Bn)	0.080	7	28[c]
3	**2b** (Ar = Ph, X = Cl)	0.300	27	2.6
4	**2c** (Ar = Ph, X = Me)	0.280	29	2.0
5	**2d** (Ar = Ph, X = Bn)	0.185	30	1.9
6	**3a** (Ar = Ph, X = Cl)	1.50	142	2.4
7	**3b** (Ar = Ph, X = Me)	1.10	130	2.0
8	**3c** (Ar = p-CF_3Ph, X = Cl)	11.0	81	2.8
9	**3d** (Ar = *p*-CF_3Ph, X = Me)	8.00	78	2.1

[a] Conditions: toluene slurry, 70 °C, 75 psi C_2, 1000 rpm, Al:Zr = 1000:1. [b] Activity is in 10^6 g PE/(mol Zr h). [c] Trimodal MWD, see text.

plexes **1** are not very active catalysts under these conditions ($A \approx 1 \times 10^5$ g PE/(mol Zr h)) and produce PEs with a very broad molecular weight distribution (MWD, Table 1, entries 1, 2). In fact, the MWD observed for both **1a** and **1b** was trimodal, indicating at least three different species present, capable of polymerizing ethylene.[6]

In contrast, complexes **2** behave as single-site catalysts under these conditions, producing PE with a narrower and unimodal MWD (PDI 2−3, Table 1, entries 3−5). Complexes **2** are marginally more active than monosubstituted systems **1** under these conditions (ca. 3×10^5 g PE/(mol Zr h)). Use of the dialkylated precursors (**2b**,**c**) provides PE with a narrower MWD (PDI ≈ 2.0) compared to use of the dichloride analogue (**2a**, PDI = 2.6). We suspect that slow alkylation of **2a** by MAO (or the Me_3Al in MAO) may be responsible for this difference; in earlier work, attempted alkylation of **2** (X = NMe_2) using Me_3Al was slow, even at elevated temperatures,[4] in contrast to the facile reactions observed for metallocene dialkylamido complexes.[7]

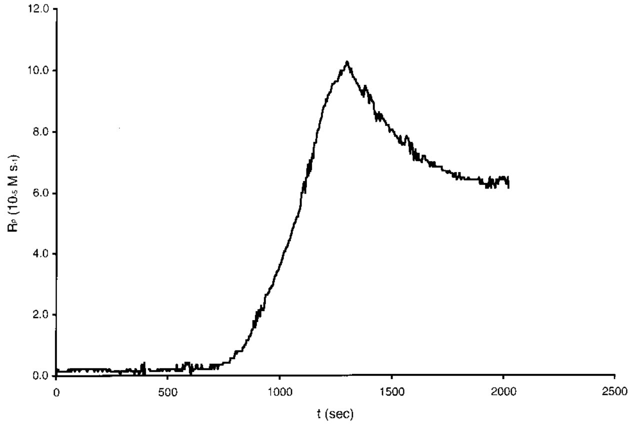

Figure 1. Polymerization flow profile [R_p (10^{-5} M s^{-1}) vs *t* (s)] for a polymerization using catalyst **3a** in the presence of MAO. For polymerization conditions, see Table 1.

Finally, the mixed complexes **3** were significantly more active that either **1** or **2** ($A = 10^6$−10^7 g PE/(mol Zr h), entries 6−9) with the more electron-deficient complexes **3c**,**d** (Ar = *p*-CF_3Ph) being about 7 times more active than the parent system (**3a**,**b**). Again, use of the dimethyl precursors afforded PE with a significantly narrower MWD (PDI ≈ 2.0) compared to the use of the dichloride complexes (PDI = 2.6−2.8), which may be related to slow alkylation of the latter, as suggested above for complexes **2**.

Having said that, the polymerization behavior of both **3a** and **3b** under these conditions was very unusual. Induction periods of up to 20 min duration at 70 °C were observed prior to measurable monomer consumption; this was particularly dramatic in the case of **3a**, as shown in Figure 1. The use of **3b** under these conditions led to similar results, although the length of the induction period was considerably shorter (<10 min), suggesting that alkylation of **3a** may also be slow under these conditions.

There are two obvious interpretations of this behavior: (1) the cationic alkyl derived from ionization of **3b** by MAO may be *inactive* in ethylene polymerization but is slowly transformed into an active species by some unknown process or (2) ionization of **3b** by MAO may be slow and the alkyl cation is active in ethylene polymerization. These explanations are not very compelling because one would have expected to observe a slow increase in ethylene consumption to a steady-state value for either of these two processes, rather than a period of very low monomer flow.[8] The observed behavior suggests that there must also be an *inhibitor* of ethylene polymerization present that is gradually consumed by some process.

Polymerization of Ethylene Using 3b in the Presence of Single-Component Cocatalysts. In view of the mechanistic complexity of MAO-activated systems, and the possibility that ionization might be slow and/or inefficient, we elected to study the use of single-component activators with complex **3b**, in the presence of various scrubbing agents.

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(2) (a) Warren, T. H.; Schrock, R. R.; Davis, W. M. *Organometallics* **1998**, *17*, 308. (b) Gibson, V. C.; Kimberley, B. S.; White, A. J. R.; Williams, D. J. *Chem. Commun.* **1998**, 313. (c) Schrock, R. R.; Schattenmann, F.; Aizenberg, M.; Davis, W. M. *Chem. Commun.* **1998**, 199. (d) Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Organometallics* **1997**, *16*, 4415. (e) Fokken, S.; Spaniol, T. P.; Okuda, J.; Serentz, F. G.; Mulhaupt, R. *Organometallics* **1997**, *16*, 4240. (f) Sarsfield, M. J.; Ewart, S. W.; Tremblay, T. L.; Roszak, A. W.; Baird, M. C. *J. Chem. Soc., Dalton Trans.* **1997**, 3097. (g) Tinkler, S.; Deeth, R. J.; Duncalf, D. J.; McCamley, A. *Chem. Commun.* **1996**, 2623. (h) Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008. (i) Duchateau, R.; Cornelis, T. W.; Meetsma, A.; van Duijnen, P. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2279. (j) Black, D. G.; Swenson, D. C.; Jordan, R. F.; Rogers, R. D. *Organometallics* **1995**, *14*, 3539. (k) Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Organometallics* **1995**, *14*, 5478. (l) Herskovics-Korine, D.; Eisen, M. S. *J. Organomet. Chem.* **1995**, *503*, 307. (m) Cozzi, P. G.; Gallo, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Organomet. Chem.* **1995**, *14*, 4994. (n) Gomez, R.; Green, M. L. H.; Haggitt, J. L. *Chem. Commun.* **1994**, 2607. (o) Brand, H.; Capriotti, J. A.; Arnold, J. *Organometallics* **1994**, *13*, 4469. (p) Uhrhammer, R.; Black, D. G.; Gardner, T. G.; Olsen, J. D.; Jordan, R. F. *J. Am. Chem. Soc.* **1993**, *115*, 8493.

(3) (a) Lappert, M. F.; Liu, D-S. *J. Organomet. Chem.* **1995**, *500*, 203. (b) Hitchcock, P. B.; Lappert, M. F.; Liu, D-S. *J. Chem. Soc., Chem. Commun.* **1994**, 2637.

(4) Rahim, M.; Taylor, N. J.; Xin, S.; Collins, S. *Organometallics* **1998**, *17*, 1315.

(5) While this work was in progress, the polymerization of ethylene using a Ti(III) complex analogous to **1** (in addition to some V and Cr diketimine complexes) in the presence of MAO was briefly reported; the activities of these systems are comparable to those reported here for **1** (ca. (3−6) × 10^5 g PE/(mol M h)). Kim, W-K.; Fevola, M. J.; Liable-Sands, L. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1998**, *17*, 4541.

(6) At least part of this behavior can be attributed to the thermal instability of the trialkyl complexes at elevated temperatures: Rahim, M. Unpublished results. For some recent work that sheds light on this phenomenon see: Qian, B.; Scanlon, W. J.; Smith, M. R., III; Motry, D. H. *Organometallics* **1999**, *18*, 1693.

(7) Kim, I.; Jordan, R. F. *Macromolecules* **1996**, *29*, 489.

(8) The mass flow meters used to monitor ethylene consumption in this work are accurate (and readable) from ca. 10−950 mL ethylene/min. Peak flows corresponded to ca. 160 mL ethylene/min under these conditions.

Table 2. Ethylene Polymerization Using Various Cocatalysts and 3b[a]

entry no.	cocatalyst[b]	scrubbing agent[c]	A[d]	M_n (K)	M_w/M_n
1	MAO	MAO (15.0 mM)	1.10	130	2.0
2	$B(Ar_F)_3$	TMA (30 μM)	low		
3	$B(Ar_F)_3$	MAO (1.5 mM)	0.140		
4	$[DMANH][B(Ar_F)_4]$	MAO (1.5 mM)	2.80	108	2.3
5	$[Ph_3C][B(ArF)_4]$	MAO (1.5 mM)	4.40	94	2.3
6	$[Ph_3C][B(ArF)_4]$	TIBAL (90 μM)	1.40	153	1.9
7	$[Ph_3C][B(ArF)_4]$	TMA (30 μM)	1.20	127	2.5
8	$[Ph_3C][B(ArF)_4]$	TMA (30 μM)	3.60[e]	140	1.9
9	$[Ph_3C][B(ArF)_4]$	**3b** (75 μM)	v. low		

[a] Conditions: toluene solvent, 70 °C, 75 psi C_2, 1000 rpm. [b] [Cocatalyst] = [**3b**] = 15 μM except where noted. [c] Impurity level in reactor ca. 60 μM. [d] Activity in 10^6 g PE/(mol Zr h). [e] MAO (1.0 mmol) added after 5 min at 70 °C.

Initially, small quantities of MAO were used as a scrubbing agent (Al:Zr = 100:1).[9] As shown in Table 2, high activities were observed when using combinations of $[PhNHMe_2][B(Ar_F)_4]$, or especially $[Ph_3C][B(ArF)_4]$, and complex **3b** under these conditions (Table 2, entries 4.5, 4 vs 1−3), and prolonged induction periods prior to monomer uptake were *not* observed. Substitution of MAO by other R_3Al scrubbing agents, using $[Ph_3C][B(Ar_F)_4]$ as a cocatalyst, led to a decrease in productivity, with the effect being somewhat more pronounced for $AlMe_3$ compared to Al^iBu_3 (Table 2, entries 6, 7). Interestingly, in the case of $AlMe_3$, activity could be restored to levels observed in the presence of MAO by *subsequent* addition of MAO (Table 2, entry 8).

As it is known that Me_3Al (and alkylaluminums in general) can have an inhibitory effect on ethylene polymerization using cationic, alkylmetallocenes, through the formation of stable $Cp_nZr(\mu\text{-}Me)_2AlMe_2$ complexes,[10] we also used an excess of complex **3b** as a scrubbing agent; under these conditions, measurable consumption of ethylene was *not* observed (Table 2, entry 9).

To gain further insight into the nature of these effects, a further series of polymerization experiments were conducted at lower temperature (30 °C) and monomer pressure (15 psi) to facilitate introduction of various compounds into the reactor during polymerization.

As shown in Figure 2a, addition of a mixture of **3b**/$[Ph_3C][B(Ar_F)_4]$ (ca. 1:1, total 10 μM) to a presaturated toluene solution of ethylene containing 30 μM $AlMe_3$ as scrubbing agent[11] does not result in significant monomer consumption; subsequent addition of 90 equiv of MAO leads to rapid monomer uptake and establishment of steady-state conditions. Under the same conditions (but without addition of MAO), addition of small quantities of $AlMe_3$ (2 equiv with respect to **3b**, in addition to that already present) into the reactor led to less pronounced uptake of ethylene; further addition of $AlMe_3$ led to a slight decline in activity (Figure 2b).

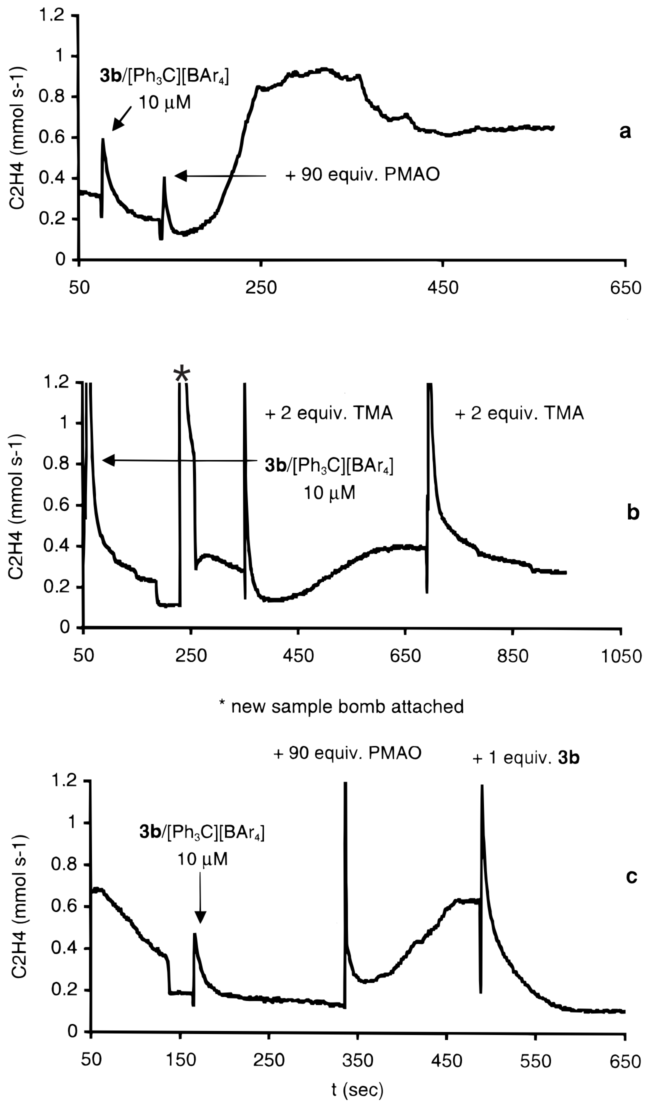

Figure 2. Polymerization flow profiles [mmol C_2H_4 s^{-1} vs *t* (s)] for polymerizations involving catalyst **3b** and $[Ph_3C][B(C_6F_5)_4]$ at 30 °C and 15 psi C_2H_4: (a) in the presence of MAO (90:1 Al:Zr); (b) in the presence of $AlMe_3$ (3:1 Al:Zr) to which $AlMe_3$ (2:1 Al:Zr) is subsequently added twice; (c) in the presence of MAO (90:1 Al:Zr) to which **3b** (1 equiv) is subsequently added. For further details see text.

As mentioned previously, activity can be restored from these lower levels by subsequent addition of MAO (Table 2, entry 8). In other words, $AlMe_3$ appears to be a "reversible" inhibitor of polymerization; the function of added MAO may be to reduce the concentration of free $AlMe_3$ to a lower level.[12]

Finally, addition of **3b** (1.0 equiv with respect to **3b** initially present) to the polymerizing system derived from **3b**/$[Ph_3C][B(Ar_F)_4]$/MAO (at 90:1 Al:Zr) led to *complete* inhibition of polymerization (Figure 2c). Evidently, **3b** (or possibly a compound derived from it) is an "irreversible" inhibitor of polymerization under these conditions.

However, none of these experiments demonstrate what is the active catalyst responsible for ethylene

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(9) Complex **3b** is essentially inactive for ethylene polymerization at this low loading of MAO.

(10) Bochmann, M.; Lancaster, S. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1634.

(11) The total impurity level in the reactor under these conditions is ∼60 μM. Previous work has shown that a 50% excess of $AlMe_3$ with respect to the total impurity level is optimal for use with, for example, $Cp_2ZrMe_2/B(Ar_F)_3$: Koehler, K.; Piers, W. E.; Jarvis, A. P.; Xin, S.; Collins, S.; Elsegood, M. J.; Clegg, W.; Marder, T. B. *Organometallics* **1998**, *17*, 3557.

(12) Commercially available MAO contains variable amounts of $AlMe_3$, some of which may be removed by drying in vacuo. While solid MAO was used for all of these experiments, it is known that this material will (reversibly) react with added $AlMe_3$ to provide MAO with lower degrees of oligomerization. For a review of the chemistry and structure of MAO see: *Makromol. Chem., Symp.* **1995**, *89*, and references therein.

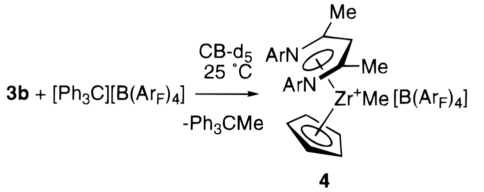
Table 3. ^{1}H and ^{13}C NMR Spectroscopic Data of Zirconium Complexes

cmpd	^{1}H NMR (δ, m)[a]	assign.	^{13}C NMR (δ)[b]	assign.
3b	7.1−6.7, m, 10H	ArH	113.1	Cp
	5.77, s, 5H	CpH	94.0	L-CH
	5.31, s, 1H	L-CH	27.0 (J_{CH} = 114 Hz)	ZrMe
	1.66, s, 6H	L-Me	22.4	L-Me
	−0.17, s, 6H	ZrMe		
4	7.12−6.83, m, 6H	*m*, *p*-ArH	116.6	Cp
	6.45, d, *J* = 7.7, 4H	*o*-ArH	97.9	L-CH
	5.49, s, 5H	CpH	43.2 (J_{CH} = 118 Hz)	ZrMe
	5.27, s, 1H	L-CH	22.5	L-Me
	1.65, s, 6H	L-Me		
	0.21, s, 3H	ZrMe		
6	7.18−6.85, m, 6H	*m*, *p*-ArH	117.9	Cp
	6.47, d, *J* = 7.4, 4H	*o*-ArH	85.69	L-CH
	5.66, s, 5H	CpH	9.15	ZrMe_2AlMe_2
	5.19, s, 1H	L-CH	21.68	L-Me
	1.65, s, 6H	L-Me	−7.55, −10.16	ZrMe_2AlMe_2
	−0.43, br s, 12H	Zr, AlMe		
7[c]	7.18−6.85 m, 12 H	*m*, *p*-ArH	114.6 (br)	Cp (major, minor)
	6.55, d, *J*= 7.6, 8H	*o*-ArH	89.4 (br)	L-CH (major, minor)
	5.74, s, 10 H	CpH	22.4, 22.1 (1:1 br)	L-Me (major, minor)
	5.42, s, 2 H	L-CH	26.5, 26.2 (~3:1, J_{CH} = 114 Hz)	ZrMe_t (major, minor)
	1.71, s, 12 H	L-Me	11.9, 11.0 (~3:1, J_{CH} = 140 Hz)	ZrMe_{br} (major,minor)
	−0.26, s, 9 H	ZrMe		

[a] ^{1}H NMR chemical shifts are reported for compounds in C_6D_5Cl at 298 K and 300 MHz, unless otherwise noted. [b] ^{13}C NMR chemical shifts are reported at 240 K in C_6D_5Cl and at 75.5 MHz, unless otherwise noted. [c] ^{13}C NMR data are reported at 225 K in C_6D_5Cl/toluene-d_8 (3:1) at 75.5 MHz.

polymerization. In other words, one can account for the induction periods observed in the presence of only MAO (vide supra) as resulting from the inhibitory presence of **3b**, *coupled* with slow ionization of this compound by MAO to form an alkyl cation (which is the active catalyst), *or* slow transformation of the alkyl cation (which is inactive) to another species, which is also inhibited by **3b**. In view of these uncertainties, we elected to study the fundamental chemistry of **3b** and the alkyl cation derived from it.

Preparation and Characterization of Cationic Alkyl Complex 4. Mixtures of **3b** and $[Ph_3C][B(Ar_F)_4]$ form oily, insoluble materials in toluene-d_8 (T-d_8) at room or at low temperature. A ^{1}H NMR spectrum of the supernatant reveals signals due to triphenylethane, but little else. More satisfactory results were obtained using chlorobenzene-d_5 (CB-d_5) solvent,[13] and under these conditions, a single new complex **4** is formed (eq 1). This compound is stable in CB-d_5 at room temperature for several hours, and the spectroscopic data (Table 3) are consistent with **4** being the cationic methyl complex shown, possibly ligated by chlorobenzene.



4 (1)

While **4** is surprisingly stable in CB-d_5 solvent at room temperature, decomposition of this material is observed at elevated temperatures, and crystals of a new complex **5** [as a tetra(chlorobenzene) solvate] separate from solution with complete disappearance of signals due to **4**. Complex **5** is insoluble/unstable in common solvents but was characterized by X-ray crystallography as being a centrosymmetric, dicationic, (μ-Cl)$_2$ dimer **5** (Figure 3, Tables 4, 5).

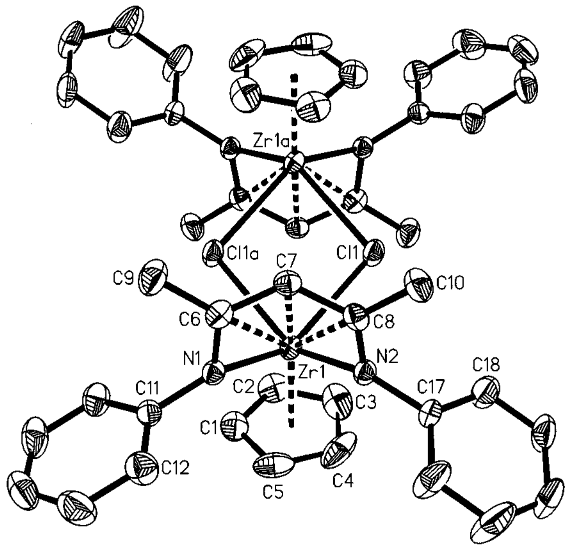


Figure 3. Molecular structure of complex **5** with 50% thermal probability ellipsoids depicted and H-atoms removed for clarity. For crystallographic and metrical data see Tables 4 and 5, respectively.

The metrical parameters associated with the π-bound, diketimine ligand are similar to those observed for a neutral complex characterized previously,[4] although the range of Zr−C distances to this ligand [i.e., Zr(1)−C(6), Zr(1)−C(7), and Zr(1)−C(8)] are considerably shorter (2.65−2.70 vs 2.70−2.75 Å), a reflection of the increased electrophilicity of the metal centers in **5**. The geometry of the Zr(μ-Cl)$_2$Zr core is reminiscent of a [Cp*-(benzamidinato)ZrCl]$_2$ dication characterized by Green and co-workers.[14] The Zr−Cl distances of 2.631(1) And 2.633(1) Å are significantly longer than those observed

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[13] For analogous studies involving metallocenium ions in bromobenzene solvent see: Horton, A. D.; Orpen, A. G. *Organometallics* **1991**, *10*, 3910, and references therein.

[14] Gomez, R.; Green M. L. H.; Haggitt, J. L. *J. Chem. Soc., Dalton Trans.* **1996**, 936.

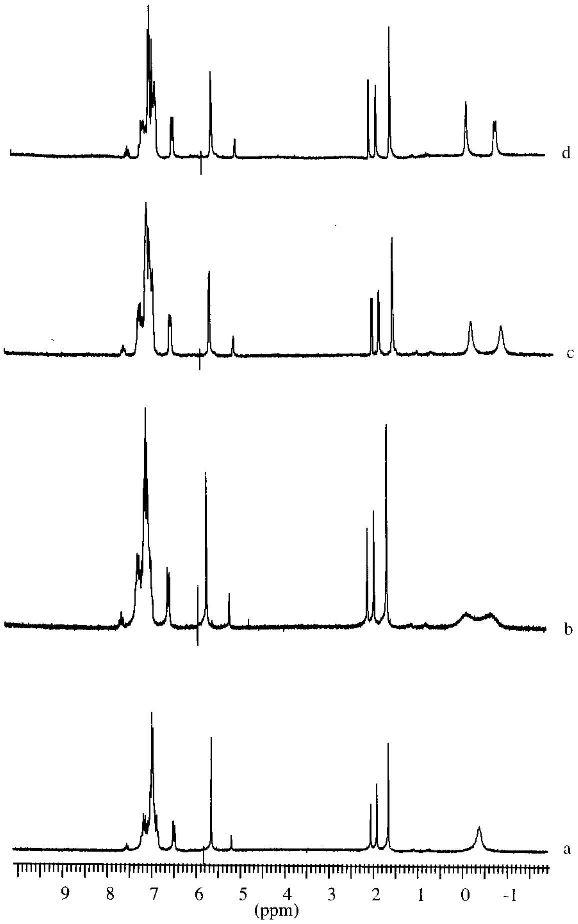
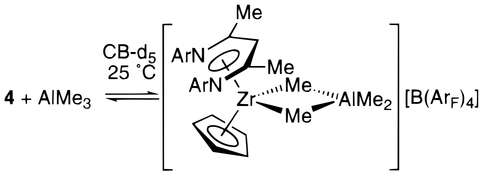


Figure 4. Variable-temperature ^{1}H NMR spectra of complex **6** in toluene-d_8/chlorobenzene-d_5 solution (1:3 v/v) at (a) 303, (b) 283, (c) 263, and (d) 243 K.

in the latter compound [2.552(1) and 2.563(1) Å, respectively], and the angles at the metal [76.9(1)° vs 80.70(4)°] and chlorine atom [103.1(1)° vs 99.30(4)°] are consistent with the longer Zr−Cl distances. Thus, the metal centers appear to be less electrophilic in **5** compared with those in the σ-bound, benzamidinato complex.

Reactivity of Cationic Alkyl Complex 4. Addition of 1 equiv of Me_3Al to solutions of compound **4** in CB-d_5 at room temperature led to the formation of a new species which exhibited a single set of resonances due to the Cp and diketimine ligands and a *single* signal corresponding to Zr and Al methyl groups, which is somewhat line broadened at this temperature (Figure 4a, spectroscopic data are summarized in Table 3). In mixed CB-d_5/T-d_8 solution (ca. 3:1), separate signals due to methyl groups at δ −0.24, −0.76, and −0.78 ppm were observed at 243 K in a ratio of 2:1:1 (Figure 4d). The low-temperature spectrum is consistent with this new complex (**6**, eq 2) being structurally analogous to similar metallocenium·AlR_3 species characterized by Bochmann and co-workers.[10]

Simulation of the spectra using the program DNMR version 4.0[15] was possible by assuming a mechanism in which terminal methyl groups exchange with bridging ones, but not directly with one another. Activation parameters of $\Delta H^{\ddagger}$ of 10.2 kcal mol^{-1} and $\Delta S^{\ddagger}$ of −11.3 cal mol^{-1} K^{-1} were obtained for the exchange process. The negative value of $\Delta S^{\ddagger}$ (although admittedly small) is inconsistent with exchange of methyl groups by a dissociative mechanism (i.e., by formation of **4** and $AlMe_3$). It is possible that the exchange is solvent mediated (i.e., displacement of $AlMe_3$ from **6** by CB in an associative process) or may involve an intramolecular reorganization process.



(2)

6

Addition of **3b** to solutions of **4** in CB-d_5 or mixed CB-d_5/T-d_8 solution (ca. 3:1) led to similar behavior; a single new species was formed that was also fluxional in solution and exhibited a single set of resonances due to the Cp and diketimine ligands and a single signal for the Zr−Me groups at room temperature (spectroscopic data in Table 3).

At low temperatures in mixed CB-d_5/T-d_8 solvent, partial decoalescence of the ZrMe, Me ligand, and Cp signals were observed. In particular, three separate resonances for Zr−Me groups were observed at δ −0.22, −0.29, and −0.34 in a ratio of 2.2:1:1.5, while two broadened resonances were observed for the diketimine Me protons at δ 1.83 and 1.74 in a ratio of 1:1.8 and two Cp resonances were observed at δ 5.96 and 5.90 in a ratio of 1: 2.4. The total integrals associated with these sets of resonances were consistent with the formation of a dinuclear complex (i.e., 9:12:10, respectively), and none of these signals correspond to either **3b** or **4** in this solvent mixture at the same temperature. The ^{1}H NMR data are consistent with the formation of two, isomeric, dinuclear complexes in a ratio of 1:2.4.

The low-temperature ^{13}C NMR spectrum was more revealing and also consistent with the presence of two dinuclear isomers. In mixed CB-d_5/T-d_8 solution at 225 K, two, major, line-broadened signals at δ 26.5 and 11.9 in a ~2:1 ratio were observed and could be assigned to ZrMe groups using a HMQC pulse sequence; two minor signals were present at δ 26.2 and 11.0, also in a 2:1 ratio, that could be similarly assigned (major:minor ca. 3:1). From a coupled, DEPT-135 spectrum, the signal at 11.9 ppm (due to one ZrMe group of the major isomer) had J_{CH} = 137 Hz, while that at 26.5 ppm (due to two ZrMe groups) had J_{CH} = 114 Hz. These values are consistent with bridging and terminal ZrMe groups, respectively.[10,16] In addition, two broadened resonances were observed for the β-diketimine Me groups at δ 22.6 and 22.3 in a 1:1 ratio, indicating inversion or 2-fold symmetry for these dinuclear complexes.

We tentatively attribute the behavior observed to formation of isomeric μ-Me complexes **7** (eq 3).[17] The structures of these complexes seem to be analogous to those formed on ionization of some metallocene dialkyls, although the latter complexes feature significantly different ^{1}H NMR chemical shifts for terminal and

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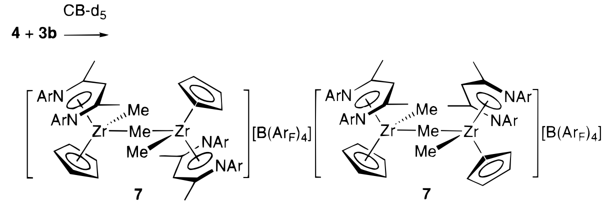
(15) Bushweller, C. H.; Letenare, L. J.; Brunelle, J. A.; Bilorsky, H. J.; Whalon, M. J.; Fiels, S. H. *Calculation of Chemically Exchanging Spectra (QCPE Program No. 466)*; Department of Chemistry, University of Vermont: Burlington, VT 05401.

(16) In support of the latter assignment, J_{CH} = 118 and 114 Hz for the terminal Zr−Me groups in **3b** and **4**, respectively.

bridging methyl groups ($\Delta\delta$ ca. 1−2 ppm vs only 0.12 ppm here).[18]



(3)

These complexes may interconvert either directly by intramolecular exchange of terminal and bridging Me groups or indirectly by dissociation into **3b** and **4**, possibly mediated by solvent (vide supra for **6**). At present, we have been unable to distinguish between these pathways.[19]

Interestingly, addition of Me_3Al to solutions of μ-Me complexes **7** led to the (partial) formation of compound **6** and **3b**, which could be separately detected at low temperatures. Evidently, Me_3Al can competitively stabilize **4** (through formation of **6**) under these conditions.

Finally, for the sake of completeness, the reaction of **4** with MAO (ca. 10:1 Al:Zr) was investigated. The only change observed on mixing these two compounds was the (partial) disappearance of the signal due to free Me_3Al (present in MAO) with formation of a species exhibiting a single set of resonances for the Cp, diketimine, and Zr−Me groups, whose chemicals shifts were intermediate between those of complex **4** and $AlMe_3$ adduct **6**. The spectrum can be interpreted as arising from a competition for $AlMe_3$ between MAO and complex **4** that is rapid on the NMR time scale at room temperature; in particular, the chemical shifts of the Cp and diketimine resonances were sensitive to the ratio of MAO:**4**.

There was no evidence for transformation of **4** into some new complex (other than **6**) on treatment with MAO at room temperature.[20] Given the high concentrations of both MAO and **4** under the conditions of the NMR experiment (i.e., ca. 0.5 and 0.05 M, respectively), we can conclude that the effect of added MAO in ethylene polymerization (where the absolute concentrations of both compounds are ~1000 times lower!), at least at room temperature, does not involve formation of some new complex from **4**.

At higher temperatures, complex **6** also decomposed to form **5** (and Me_3Al). The presence of MAO had little, if any, effect on the thermal stability of **6**, and no new Zr products (i.e., other than **5**) were formed on thermolysis of a mixture of **4**/MAO. While we cannot absolutely rule out that **4** might react with MAO in toluene at elevated temperatures to give some new species, the fact that no additional products were detected in CB solvent suggests that any putative side reaction cannot be very favorable.

Ethylene Polymerization Using 4. While complex **4** can be cleanly formed from **3b** and $[Ph_3C][B(Ar_F)_4]$ in CB solvent, we find that CB appears to also be an inhibitor of ethylene polymerization, as ethylene uptake is not observed at 30 °C when complex **4** is generated in CB prior to introduction to the reactor containing toluene (even in the presence of MAO or $AlMe_3$). We have also found that complex **4** can be prepared in CH_2Cl_2 solution at room temperature and is stable for short periods of time in this solvent. Removal of the CH_2Cl_2 in vacuo provides a 1:1 mixture of complex **4** and Ph_3CMe as an orange solid that contains small quantities of CH_2Cl_2 (ca. 0.5 equiv with respect to **4**).[21]

When this mixture is suspended in toluene and injected into a reactor containing MAO (100:1 Al:Zr), rapid polymerization is observed, following introduction of ethylene at 30 °C and 15 psi.[22] At identical Zr loadings (i.e., 10 μM), this mixture is about 2 times more active ($A = (1.8 \pm 0.2) \times 10^6$ g/(mol Zr h)) than when **3b** and $[Ph_3C][B(Ar_F)_4]$ are premixed in toluene and added to the reactor under the same conditions ($A = (0.9 \pm 0.1) \times 10^6$ g/(mol Zr h)). The polymer properties are also very similar under the two conditions ($M_n = 240$ K, $M_w/M_n = 1.94$ vs $M_n = 220$ K, $M_w/M_n = 1.95$).

On the basis of these results and the fact that **4** appears unreactive toward MAO at room temperature (vide supra), it seems clear that **4** is the active catalyst in these polymerizations. As mentioned previously, little or no ethylene uptake is observed when a mixture of **3b**/$[Ph_3C][B(Ar_F)_4]$ (1:1 or when **3b** is present in excess) in toluene is introduced into the reactor in the absence of MAO. Given the inhibitory nature of **3b** in ethylene polymerization (vide supra), it is reasonable to conclude that very little “free” **4** is present under these conditions, even at a 1:1 ratio of **3b**:$[Ph_3C][B(Ar_F)_4]$. That is, as **3b** reacts with $[Ph_3C][B(Ar_F)_4]$ in toluene solvent to form **4**, the latter is rapidly sequestered by **3b** to form dinuclear complexes **7**, which appear to be inactive and do not readily dissociate in toluene solvent (Scheme 1).

As noted previously, $AlMe_3$ reacts (reversibly) with complexes **7** to produce **6** and **3b**. In the presence of $[Ph_3C][B(Ar_F)_4]$, this would lead to further ionization of liberated **3b** and ultimately formation of **6** (Scheme 1) at $AlMe_3$ concentrations *above* those required to remove

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[17] Unfortunately, because the ^{1}H NMR spectra are exchange-broadened at the lowest accessible temperature, not all of the expected signals (i.e., four ketimine−Me and four Zr−Me resonances) are resolved, even at 500 MHz. However, the ^{1}H NMR spectrum can be interpreted as arising from two isomers (in a 1:2.4 ratio based on the intensities of the two Cp signals), if the diketimine Me signals at δ 1.83 and 1.74 are due to the major and major + minor isomers, respectively (calculated ratio 1:1.83 vs 1:1.77 observed) and the Zr−Me signals at δ −0.22, −0.29, and −0.34 are due to the terminal (major), terminal (minor), and bridging Me groups (major + minor) in the two isomers (calculated ratio 2.4:1:1.7 vs 2.2:1:1.5 observed).

[18] For spectroscopic and structural studies on $[CpM(Me)]_2(\mu\text{-}Me)$ complexes see ref 10 and: (a) Chen, Y.-X.; Stern, C. L.; Yang, S.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 12451. (b) Beck, S.; Prosenc, M.-H.; Brintzinger, H.-H.; Goretski, R.; Herfert, N.; Fink, G. *J. Mol. Cat. A: Chem.* **1996**, *111*, 67.

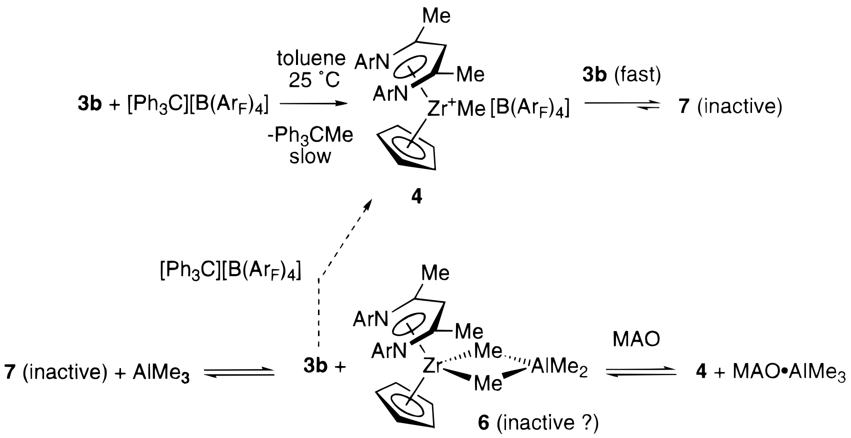
[19] Intramolecular exchange of the terminal and bridging Me groups of a given isomer involves conversion to the other isomer and back again and thus would occur at half the rate of, for example, exchange of terminal (or bridging) Me groups of different isomers. This difference would allow one to distinguish between this pathway and others involving, for example, dissociation where all Me groups would exchange at the same rate. Simulations reveal that significant differences in line-widths and intensities of individual peaks are only *clearly* evident at rates close to the slow exchange limit; at the lowest accessible temperature (i.e., 225 K in CB-d_5:T-d_8 3:1), the signals dues to terminal and bridging Me groups are still significantly exchange-broadened.

[20] Complex **3b** also appears unreactive toward MAO (10:1 Al:Zr) at room temperature in T-d_8 solution.

[21] Attempts to purify **4** by, for example, extraction of Ph_3CMe with toluene led to formation of intractable oils. Similarly, attempts to obtain complexes **6** and **7** in crystalline form by a variety of techniques from chlorobenzene/toluene, chlorobenzene/hexane, CH_2Cl_2/toluene, or CH_2Cl_2/hexane mixtures led to formation of oils and/or formation of complex **5**.

[22] This procedure had to be used, as opposed to the more usual method of presaturating with ethylene, because the syringe invariably plugged with PE when **4** was introduced using the latter technique.

Scheme 1



impurities in solvent and monomer. On the basis of the work of Bochmann and co-workers,[10] it is reasonable to expect that **6** is also inactive (or less active) in ethylene polymerization, and this would account for the lower activities seen in the presence of (excess) $AlMe_3$.

Highest activities are observed in the presence of MAO (with or without additional $AlMe_3$). Does MAO also assist with ionization of **3b** in the same manner as $AlMe_3$ and/or enhance the activity/stability of **4** in some fashion? This is difficult to determine; as mentioned previously, the only effect of MAO on **4** (by NMR spectroscopy) appears to be indirect in that there is competition for "free" $AlMe_3$ between **4** and MAO (Scheme 1). It would be useful to compare the activity of **4** in the absence of MAO to its activity in its presence to (partly) answer this question.

We have recently reported that $MeAl(BHT)_2$ (MAD, BHT = 2,6-di-*tert*-butyl-4-methylphenoxide), a monomeric aluminum alkyl,[23] is a useful scrubbing agent for olefin polymerizations in that it does not readily react with metallocenium ions and/or typical cocatalysts used to prepare metallocenium ions.[24] Also, it does not seem to form significant quantities of AlR_3-type adducts with metallocenium ions, as polymerization activity is not diminished in the presence of a large excess (e.g., 400:1 Al:Zr) of this material.[25]

We thought it would be useful to compare the polymerization behavior of complex **4** in the presence of MAD vs **4** in the presence of MAO (both at 100:1 Al:Zr). At 30 °C, 15 psi C_2H_4, the activity of **4** was essentially the same, within experimental error, in the presence of these two additives (i.e., 1.6×10^6 vs $(1.8 \pm 0.2) \times 10^6$ g PE/(mol Zr h)). This would seem to indicate that MAO *does not* play a role in enhancing the activity/stability of **4**. In other words, the function of MAO, at least during polymerization, would seem to be important but otherwise innocent; it serves to regulate "free" $AlMe_3$ levels in the reactor, which can inhibit **4** (by formation of **6**, Scheme 1). We suspect that it also serves an indirect role during ionization of **3b** by $[Ph_3C][B(Ar_F)_4]$ (i.e., as a source of $AlMe_3$, vide supra), but further work would be required to determine this.

Conclusions

β-Diketimine complexes **1**−**3** are active in ethylene polymerization, with the mixed complexes **3** being most active. Mechanistic work has revealed that the active species involved in polymerizations by **3** is the expected cationic alkyl (i.e., **4**) but that the polymerization activity of **4** is dramatically inhibited by excess **3** and to a lesser extent AlR_3. In the former case, it would appear that dinuclear complexes **7**, formed from **3** and **4**, are inactive in olefin polymerization and do not readily dissociate, at least at room temperature in toluene solvent. Thus, a 1:1 mixture of **3** and $[Ph_3C][B(Ar_F)_4]$ (i.e., a 1:1 mixture of complexes **7** and $[Ph_3C][B(Ar_F)_4]$) does not polymerize ethylene in the absence of additives such as $AlMe_3$, which serve to displace **3** from **7**. Highest activities are observed in the presence of small quantities of MAO, which appears to act as a reservoir for $AlMe_3$ under these conditions, allowing ionization of **3** by $[Ph_3C][B(Ar_F)_4]$ to proceed but sequestering excess $AlMe_3$ during polymerization.

While much of the chemistry of complex **4** mirrors that reported for metallocene complexes,[10,18] it is evident from the catalysis itself that the *quantitative* differences in behavior are significant. These studies point out the need for caution in interpreting the results of initial screening experiments using new catalysts, particularly if facilities for monitoring of monomer uptake are not available (i.e., polymerization activity is based on the *amount* of polymer formed in a given period of time). As illustrated here, the inhibitory effect of dialkyl **3b** on the polymerization activity of **4** is pronounced, and this type of behavior would generally be undetectable during initial screening experiments using MAO as cocatalyst (or even $[Ph_3C][B(Ar_F)_4]$).[26] We believe the complicating features identified here are more general than previously suspected; indeed another class of related catalysts currently under study shows very similar behavior.[27]

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(23) Healey, M. D.; Wierda, D. A.; Barron, A. R. *Organometallics* **1988**, *7*, 2543.

(24) Williams, C. V.; Dai, C.; Li, Z.; Collins, S.; Piers, W. E.; Elsegood, M. J.; Clegg, W.; Marder, T. B. *Angew. Chem., Int. Ed.* **1999**, *38*, 3695.

(25) NMR experiments indicate that MAD (1.0 equiv or a large excess) does not bind to complex **4** in CB-d_5 solution; the relevance of this observation to polymerizations conducted in toluene remains to be determined. Tomaszewski, R. Unpublished results.

(26) For example, complex **3a** (or **3b**) is *inactive* for olefin polymerization at room temperature (as opposed to 70 °C) in the presence of MAO (1000:1) for a period exceeding 4 h.

(27) Vollmerhaus, R.; Shao, P.; Taylor, N. J.; Collins, S. *Organometallics* **1999**, *18*, 2731.

Experimental Section

All solvents and chemicals were reagent grade and purified as required. All synthetic reactions were conducted under an atmosphere of dry nitrogen in dry glassware unless otherwise noted. Tetrahydrofuran, diethyl ether, hexane, toluene, and dichloromethane were dried and deoxygenated by passage through columns of A2 alumina and Q5 deoxo catalyst as described in the literature.[28] Compounds **1**−**3** were prepared as described previously,[4] or the dimethyl complexes **3** can be prepared by a more efficient procedure involving alkane elimination that is outlined below. Routine ^{1}H and ^{13}C NMR spectra were recorded in benzene-d_6 or $CDCl_3$ solution on either a Bruker AM-250, AC-200, or AC-300 spectrometer. Low-temperature NMR spectra were recorded using a AC-300 or AMX-500 spectrometer in toluene-d_8 or chlorobenzene-d_5 solution using a solution of methanol in CD_3OD for temperature calibration purposes. Elemental analyses were determined by M. H. W. Laboratories of Phoenix, AZ, and Oneida Research Services, Inc., New York.

Detailed polymerization procedures and methods for polymer characterization are described in the literature.[29] In the experiments summarized in Table 1, a solution of the catalyst precursor was added via a sample vessel, slightly overpressurized with dry nitrogen, to a solution of solid methylaluminoxane in toluene, presaturated with monomer at the desired temperature and pressure. A similar procedure was employed for the polymerizations summarized in Table 2; the catalyst precursor and cocatalyst were premixed in toluene solution just prior to delivery to the reactor containing scrubbing agent, solvent, and monomer. Polymerizations were conducted for various periods of time that corresponded to buildup to and attainment of steady-state conditions as revealed by mass-flow measurements; typically polymerizations were conducted for about 30 min after attaining steady-state conditions. Reactor fouling was common under these conditions; the activities quoted in Tables 1 and 2, which are based on the weight of polymer recovered, are probably only precise to ±20%.

Preparation of Complex 3b by Alkane Elimination. To a slurry of finely ground $CpZrCl_3$ (525 mg, 2.0 mmol) in 10 mL of toluene at −40 °C was added a solution of MeLi in diethyl ether (3.3 mL of 1.9 M, 6.2 mmol) via syringe. After stirring at this temperature for 10−15 min, a solution of 4-phenylamino-2-phenyliminopent-3-ene (500 mg, 2.0 mmol) in toluene (20 mL) was added via cannula over 5−10 min. Methane evolution occurred and was complete on warming the solution to room temperature. After 1 h, the mixture was filtered and washed with toluene; the filtrate was concentrated to dryness in vacuo and the crude product crystallized from isooctane to provide **3b** as an off-white solid (750 mg, 86%). For spectroscopic data see ref 4.

NMR Experiments. Stock solutions of **3b**, $[Ph_3C][B(C_6F_5)_4]$, and $AlMe_3$ (ca. 0.10 M) or MAO (ca. 1.0 M) were prepared in CB-d_5 or 3:1 (v/v) mixtures of CB-d_5:T-d_8 at room temperature in a glovebox.

Complex **4** was generated by adding a solution of **3b** in portions, via microliter syringe, to a solution of $[Ph_3C][B(C_6F_5)_4]$ in a 5 mm NMR tube equipped with a screw-top septum cap at room temperature. Proton NMR spectra were recorded after addition of ca. 0.8, 0.9, and 1.0 equiv of **3b** to verify stoichiometry. Attempts to crystallize (and thus purify) this material by liquid diffusion of hexane or toluene into these samples led to formation of oils at low temperature or competing decomposition to **5** using vapor or liquid diffusion of pentane or toluene at ambient temperature; hence only NMR spectroscopic data are provided (Table 3).

Table 4. Selected Crystallographic and Refinement Data for 5·$(C_6H_5Cl)_4$

emp. form., fw	$C_{92}H_{44}B_2Cl_2F_{40}N_4Zr_2 \cdot 4C_6H_5Cl$, 2690.4
cryst size	0.20{011} × 0.40{100} × 0.60 {110}{1$\bar{1}$0}
cryst syst, space group	triclinic, $P\bar{1}$
unit cell dimens	$a = 13.837(1)$, $b = 14.031(2)$, $c = 15.376(2)$ Å $\alpha = 81.729(8)°$, $\beta = 67.677(5)°$, $\gamma = 78.350(7)°$
volume	2697.1(1) Å^3
Z	1
density (calc)	1.656 g cm^{-3}
abs coeff	4.65 cm^{-1}
2θ range	4.0−52.0°
scan type	ω
scan speed	variable; 3.00−30.00 deg min^{-1}
scan range (ω)	1.20°
no. of reflns collected	11 034
no. of indep reflns	10 573 ($R_{int} = 2.88\%$)
no. of obs reflns	7723 [$F > 6.0\sigma(F)$]
R	3.25%
R_w	3.32%
GOF	1.97
data-to-param ratio	9.6:1
larg diff peak	0.54 e Å^{-3}
larg diff hole	−0.60 e Å^{-3}

Further addition of 1.0 equiv of **3b** to a solution of **4** provided a solution of complexes **7**, while addition of 1 equiv of $AlMe_3$ provided a solution of complex **6** (^{1}H and ^{13}C NMR data for these complexes are collected in Table 3). Similar comments concerning attempted purification of **4** also apply to **6** and **7**.

The addition of 10 equiv of MAO (containing ca. 1.0 equiv of free $AlMe_3$) to a solution of complex **4** and Ph_3CMe resulted in the disappearance of the signal due to free $AlMe_3$ in MAO (δ −0.5) and formation of a species with the following spectrum: ^{1}H NMR (300 MHz, C_6D_5Cl, 25 °C) δ 7.2−6.8, (m, NArH + Ph_3CMe), 6.46 (d, $J = 7.2$ Hz, o-ArH), 5.56 (s, 10 H, Cp) 5.23 (s, 1H, ligand−CH), 1.65 (s, 6H, ligand−Me), and a very broad signal at ca. 0 ppm. The chemical shifts of the Cp and ligand−CH resonances of this species are intermediate (i.e., ca. the numerical average) between those of **4** and complex **6** (see Table 3).

Preparation of Complex 5. The cleanest route to this compound involved reaction of **3b** with $[Ph_3C][B(C_6F_5)_4]$ (92 mg, 0.1 mmol) in the presence of excess $AlMe_3$ at elevated temperatures: To a solution of $[Ph_3C][B(C_6F_5)_4]$ (92 mg, 0.1 mmol) in chlorobenzene (1.0 mL) was added complex **3b** (44 mg, 0.1 mmol) in one portion followed by excess $AlMe_3$ (15 mg, 0.2 mmol). The solution was transferred to a clean tube and the tube immersed in an oil bath at 50 °C for several hours, over which time crystals of complex **5** separated. After decanting the mother liquor, some of the crystals were reserved for X-ray diffraction studies (vide infra), while the remainder were washed successively with chlorobenzene (1.0 mL), toluene (1.0 mL), and hexane (1.0 mL) to provide **5** as a colorless crystalline solid (250 mg, 93% yield as the tetrachlorobenzene solvate). An analytical sample, free of chlorobenzene, was obtained by grinding these crystals and drying under high vacuum (10^{-3} mmHg) for 24 h. Anal. Calcd for $C_{92}H_{44}B_2Cl_2F_{40}N_4Zr_2$: C, 49.32; H, 1.98; N, 2.50. Found: C, 48.97; H, 1.96; N 2.29.

X-ray Structural Determination of Complex 5. A crystal of dimensions 0.20{011} × 0.40{100} × 0.60 {110}-{1$\bar{1}$0} mm was glued to a glass fiber using epoxy resin, and the fiber was then mounted on a Siemens P4 diffractometer. Unit cell parameters were determined and refined from a set of 25 general reflections (20.0° < 2θ < 30.0°) well distributed in reciprocal space.

Intensity data were collected using graphite-monochromated Mo Kα radiation at 180 K by employing the ω-scan technique over the 2θ range 4.0−52.0° with variable scan speeds (3.00−30.00 deg min^{-1}) and a 1.20° scan width. Background mea-

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[28] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *13*, 1518.

[29] Bravakis, A. M.; Bailey, L. E.; Pigeon, M.; Collins, S. *Macromolecules* **1998**, *31*, 1000, and references therein.

Table 5. Selected Bond Distances and Angles for Compound 5[a]

Bond Lengths (Å)			
Zr(1)−Cl(1)	2.631(1)	Zr(1)−Cl(1A)	2.633(1)
Zr(1)−N(1)	2.110(3)	Zr(1)−N(2)	2.141(2)
Zr(1)−C(1)	2.469(3)	Zr(1)−C(2)	2.469(3)
Zr(1)−C(3)	2.479(4)	Zr(1)−C(4)	2.488(3)
Zr(1)−C(5)	2.468(3)	Zr(1)−C(6)	2.651(3)
Zr(1)−C(7)	2.657(3)	Zr(1)−C(8)	2.706(3)
N(1)−C(6)	1.342(3)	C(6)−C(7)	1.410(4)
C(7)−C(8)	1.422(3)	C(8)−N(2)	1.325(3)
Bond Angles (deg)			
Cl(1)−Zr(1)−Cl(1A)	76.9(1)	Zr(1)−Cl(1)−Zr(1A)	103.1(1)
N(1)−Zr(1)−N(2)	85.4(1)	Zr(1)−N(1)−C(6)	97.9(2)
N(1)−C(6)−C(7)	119.6(3)	C(6)−C(7)−C(8)	128.8(2)
C(7)−C(8)−N(2)	119.1(2)	C(8)−N(2)−Zr(1)	100.0(2)

[a] Bond lengths in angstroms and bond angles in degrees with estimated standard deviations in parentheses.

surements using the stationary crystal, stationary counter method were made at the beginning and end of each scan, each for 25% of the total scan time. Three standard reflections were measured after every 100 reflections and showed no significant loss in intensity during data acquisition.

Intensities were corrected for Lorentz and polarization effects. A face-indexed numerical method was employed to correct for adsorption effects in all cases. Collected, independent, and observed reflections [$F > 6.0\sigma(F)$] are summarized in Table 4, and the latter were used in the structure solution and refinement. The minimum and maximum transmission factors through the crystals were calculated to be 0.8328 and 0.9204, respectively.

The structure was solved by Patterson and Fourier methods and refined by full-matrix, least-squares techniques using the Siemens SHELXTL PLUS software. Anisotropic refinement of all non-H atoms allowed location of all hydrogen atoms from a difference map. In the final cycles of refinement, all hydrogens were included using a riding model, except for H(7), which was included at its found position [due to significant deviation from planarity at C(7)], and all were refined isotropically.

Scattering factors for non-hydrogen atoms were taken from the *International Tables*,[30] while the data of Stewart et al.[31] were used for hydrogen atoms. Full details of the crystallographic data, solution and refinement, and atomic coordinates, thermal parameters, and bond lengths and angles are included in the Supporting Information.

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Supporting Information Available: Tables of crystallographic data, atomic coordinates with isotropic thermal coefficients, bond lengths, bond angles, anisotropic thermal coefficients, H-atom coordinates, and isotropic thermal coefficients for compound **5**; experimental and simulated ^{1}H NMR spectra for complex **6** at various temperatures; ^{1}H and ^{13}C NMR spectra for compounds **4** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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