Articles

Amine Bis(phenolate) Zirconium Complexes: Influence of Ligand Structure and Cocatalyst on Copolymerization Behavior

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ABSTRACT: Five amine bis(phenolate)zirconium dibenzyl complexes, [ONDO]$ZrBn_2$, were investigated in ethylene/1-hexene copolymerization. The copolymerization behavior is sensitive both to the symmetry and connectivity of the ligand framework and to the nature of the cocatalyst. The C_s-symmetric [ONDO]$ZrBn_2$ complexes were more active and exhibited higher comonomer incorporations than the C_2-symmetric [ONDO]$ZrBn_2$ complexes. The nature of the cocatalyst was observed to have a significant effect on the amount of hexene incorporated into the copolymers. Activation of the C_s-symmetric [ONDO]$ZrBn_2$ complexes with MMAO yielded copolymers with 10% higher hexene incorporation than that observed upon activation with $[PhNMe_2H][B(C_6F_5)_4]$, $[B(C_6F_5)_3]$, or $[Ph_3C][B(C_6F_5)_4]$.

Introduction

Linear, low-density polyethylenes (LLDPE) are an important class of materials found in food and textile packaging films, injection-molded containers, blow-molded tanks, piping and tubing, and wire and cable insulation.[1] The physical properties and processing characteristics of these materials depend on the number and distribution of short-chain branches derived from alpha-olefin comonomers, and the development of catalysts to control these structural parameters remains an important objective in olefin polymerization.[2]

Considerable effort has been devoted to metallocene-based catalyst systems for ethylene/α-olefin copolymerization as these systems typically yield copolymers with higher comonomer incorporations and narrower molecular weight and compositional distributions than those obtained with conventional Zieger-Natta catalysts.[2,3] The modification of metallocene structure has a pronounced effect on copolymerization behavior including productivity, molecular weight, tacticity, and comonomer incorporation. The nature of the cocatalyst has also been shown to influence the activity, productivity and/or stereoselectivity of metallocene catalysts for homopolymerization[4−15] and copolymerization,[4,6−8,16−23] in some cases due to the formation of dinuclear active species.[6,8,17]

Recent efforts have focused on coordination complexes lacking cyclopentadienyl ligands to expand the range of catalysts for controlled polymerization reactions.[24,25] In 1996, McConville reported a class of diamido titanium complexes which exhibit characteristics of living polymerization.[26] Studies by Schrock, Sita, Coates, and Fujita have since expanded the scope of catalysts exhibiting living polymerization behavior.[27−32] Recently, Kol, Goldschmidt, and co-workers have introduced a family of tetradentate C_s-symmetric amine bis(phenolate) zirconium dibenzyl, [ONDO]$ZrBn_2$, complexes whose productivity in 1-hexene homopolymerization is significantly influenced by the nature of the pendant donor arm.[33−37] Related C_2-symmetric zirconium complexes gave living, isospecific polymerization of 1-hexene.[38,39]

Although olefin homopolymerizations have been extensively explored with nonmetallocene group 4 complexes, less is known about the relationship between ligand geometry or cocatalysts on ethylene/α-olefin copolymerization behavior.[40−45] The variety of structural modifications possible with amine bis(phenolate) complexes prompted us to initiate studies of ethylene/1-hexene copolymerization with this class of complexes to study the effects of ligand structure and the nature of the cocatalyst on ethylene/α-olefin copolymerization behavior. Herein, we report that the copolymerization behavior of these complexes is sensitive not only to the symmetry and connectivity of the ligand framework, but also to the nature of the cocatalyst.

Results/Discussion

Five amine bis(phenolate)zirconium dibenzyl complexes were prepared and investigated for ethylene/1-hexene copolymerization (Figure 1). The synthesis of **1a**, **2a**, **4a**, and **5a** have been previously reported.[35,36,38,39,46] To investigate the influence of different 2,4-aryl substituents in copolymerization, the 2,4-phenyl complex **3a** was synthesized (Figure 2) for comparison to 2,4-^{t}Bu- and Me-substituted complexes **2a** and **4a**, respectively. The 2,4-diphenylphenol ligand precursor was synthesized following a procedure from Yus.[47] Ligand **3** was synthesized in a one-step Mannich condensation between formaldehyde, *N*,*N*-dimethylethylenediamine, and 2,4-diphenylphenol according to literature procedures.[35,36,38] Reaction of **3** with zirconium tetrabenzyl at 65°C for 6 h gave the metal complex **3a**. Analysis of complex **3a** by ^{1}H NMR spectroscopy is consistent with C_s-symmetry as observed for complexes **2a**, **4a**, and **5a**.[35,36] Two singlets are observed for the benzyl protons,

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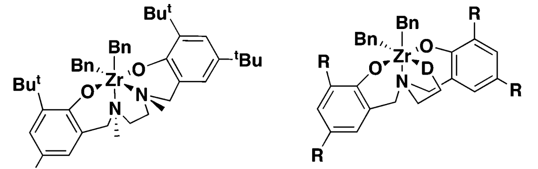
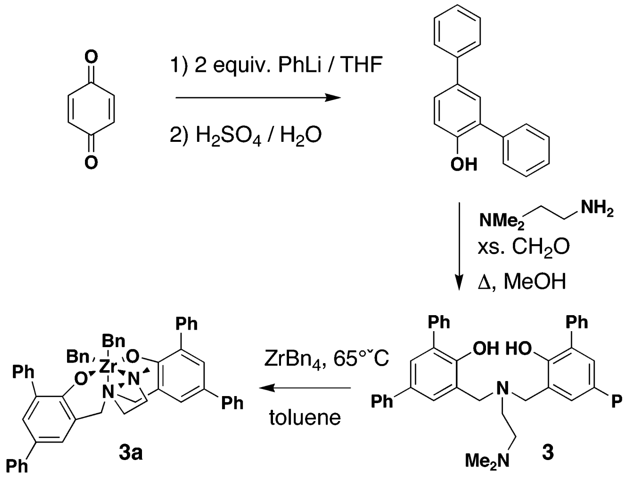


Complex 1a

R	D	Complex
^{t}Bu	NMe$_2$	**2a**
Ph	NMe$_2$	**3a**
Me	NMe$_2$	**4a**
^{t}Bu	OMe	**5a**

Figure 1. [ONDO]ZrBn$_2$ catalyst precursors used in ethylene/1-hexene copolymerization studies.



3a **3**

Figure 2. Synthesis of complex **3a**.

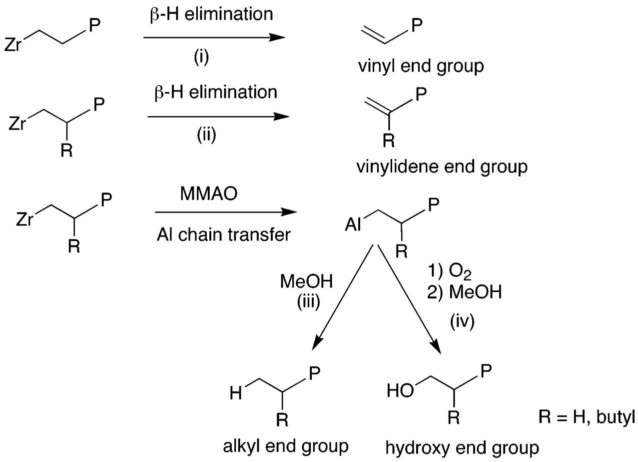


Figure 3. Possible chain transfer reactions for [ONDO]ZrBn$_2$ complexes.

CH_2−C$_6$H$_5$, as are two doublets for the diastereotopic Ar−CH_2−N protons.

Ethylene/hexene copolymerizations with complexes **1a**−**5a** were carried out under a variety of conditions in neat 1-hexene with varying overpressures of ethylene (20−200 psig). To investigate the influence of the cocatalyst, a variety of cocatalysts were studied, including modified methylaluminoxane (MMAO, Akzo Type 3A), *N,N*-dimethylanilinium tetrakis(pentafluorophenyl)borate ([PhNMe$_2$H][B(C$_6$F$_5$)$_4$], "anilinium borate", **B1**), tris(pentafluorophenyl)borane ([B(C$_6$F$_5$)$_3$], "borane", **B2**), or trityl tetrakis(pentafluorophenyl)borate ([Ph$_3$C][B(C$_6$F$_5$)$_4$], "trityl borate", **B4**) in the presence of triisobutylaluminum, TIBA, as a scavenger. To optimize the determination of the reactivity ratios for these systems, concentrations of both the catalyst precursor and cocatalyst were optimized to generate less than 2 g of polymer per run and conversions of 1-hexene were kept below 3%. Comonomer feed compositions were determined using empirical equations for the solubility of ethylene in 1-hexene reported by Spitz.[48] Conditions and results for copolymerizations with complexes **1a**−**5a** are reported in Tables 1−5.

The productivities of complexes **1a**−**5a** are an order of magnitude lower than those observed with indenyl-metallocene systems under similar conditions.[49] The productivity of the C_2-symmetric complex **1a** is less than those of C_s-symmetric complexes **2a**−**5a**. Among the C_s-symmetric series of complexes, methyl-substituted **4a** showed lower productivities than either **2a** or **3a** with *tert*-butyl or phenyl substituents, respectively. In the presence of larger amounts of MMAO activator, the productivity of complex **3a** decreased (vide infra).

Molecular weight data were obtained using Symyx Rapid GPC[50,51] in *o*-dichlorobenzene at 160 °C as described in the Experimental Section. M_w/M_n values are thus lower than would be obtained using conventional GPC methods.[50,51] For comparison, an ethylene/1-hexene copolymer (52.7% E) prepared using *rac*-ethylene bis(indenyl)zirconium dichloride/MMAO was analyzed using Rapid GPC and compared to results obtained using a Waters 150C instrument under conditions described previously.[52] Rapid GPC gave M_w = 94 000 and M_w/M_n = 2.0. Analysis using a Waters 150 °C gave M_w = 57 500 and M_w/M_n = 2.3. Copolymers produced with **1a**−**5a** all show monomodal, narrow molecular weight distributions consistent with single-site catalyst behavior. In general, molecular weights for copolymers derived from the C_s-symmetric [ONNO]ZrBn$_2$ complexes **2a**−**4a** were higher than those obtained from the C_2-symmetric complex **1a** or the C_s-symmetric [ONOO]ZrBn$_2$ complex **5a**.

In our initial screen of reaction conditions for catalysts **1a**−**5a**, we observed considerable variation in molecular weight as a function of MMAO concentration. For example, while molecular weights obtained from complex **3a** showed little sensitivity to the monomer feed ratio (run 13 vs 19 and run 15 vs 21) or zirconium concentration (run 19 vs 20), higher concentrations of MMAO led to lower molecular weight copolymers (run 13 vs 14 and run 17 vs 20).

To investigate the origin of the influence of MMAO on the molecular weights, we carried out end group analysis of copolymers derived from **5a**/MMAO. Two major chain termination processes observed in homogeneous zirconium-catalyzed polymerizations are β-hydride elimination and chain transfer to aluminum (Figure 3). Vinylidene end groups[53] were observed by ^{1}H NMR for the copolymer described in entry 30, suggesting that β-H elimination is favored after insertion of an α-olefin (path ii, Figure 3). Vinyl end groups, which would occur from β-H elimination after an ethylene insertion (path i, Figure 3), were not observed.

To provide evidence for chain transfer to aluminum with the amine bis(phenolate) zirconium dibenzyl complexes, a copolymerization under the conditions of entry 30 was repeated but, instead of being quenched with methanol (path iii, Figure 3), was quenched with air followed by hydrolysis. The air quenched sample showed the presence of both vinylidene and hydroxy-terminated polymer chains (path iv, Figure 3).[54,55] Integration of

Table 1. Ethylene/1-Hexene Copolymerization Results for [ONDO]ZrBn$_2$ Complexes 1a−5a Activated with MMAO at 20 °C

catalyst precursor	entry	[Zr] (μmol)	MMAO (mg)	P_{total} (psig)	X_e/X_h (mol/mol)	yield (g)	product (kg mol Zr^{-1} h^{-1})	(E)$_{\text{copolymer}}$ (mol %)	M_n (×10^3 g/mol)	M_w/M_n
1a	1	600	329	21	0.0416	1.801	150	71.5	12	1.6
	2	250	288	31	0.0540	1.103	221	79.2	8	1.5
	3	150	300	43	0.0692	0.707	236	84.5	7	1.5
	4	80	318	53	0.0822	0.241	151	88.5	5	1.5
	5	100	100	53	0.0822	0.240	120	87.6	50	1.6
	6	100	100	72	0.1079	0.330	165	91.3	48	1.7
2a	7	5	141	41	0.0666	0.085	798	50.1	209	1.7
	8	15	103	50	0.0783	0.817	2721	50.8	147	1.7
	9	15	100	54	0.0836	0.878	2927	51.5	229	1.6
	10	10	329	71	0.1065	0.553	2684	55.1	149	1.7
	11	10	100	100	0.1480	0.532	2660	59.9	105	1.8
	12	5	100	199	0.3164	0.223	2230	72.0	169	1.6
3a	13	15	100	52	0.0809	1.267	6335	42.3	239	1.7
	14	15	300	52	0.0809	0.347	1157	42.4	32	1.6
	15	80	300	85	0.1261	0.771	482	56.0	15	1.6
	16	5	100	102	0.1510	0.389	5835	60.8	196	1.8
	17	40	300	149	0.2256	0.553	691	70.1	29	1.6
	18	40	300	194	0.3067	0.533	666	77.1	21	1.7
	19	15	100	149	0.2256	1.497	7485	71.7	200	1.6
	20	40	100	149	0.2256	3.542	6641	70.9	228	1.7
	21	80	300	149	0.2256	1.037	648	71.4	35	1.6
4a	22	100	100	52	0.0809	0.919	460	35.9	114	1.6
	23	400	300	82	0.1219	0.124	16	50.6		
	24	100	100	100	0.1480	0.989	495	51.0	96	1.6
	25	400	300	135	0.2024	0.122	15	59.8		
	26	400	300	193	0.3048	0.178	22	68.8	9	1.9
5a	27	300	300	33	0.0565	1.557	260	49.9	9	1.6
	28	300	100	52	0.0809	1.230	205	57.1	18	1.7
	29	200	100	100	0.1480	0.742	186	72.8	13	1.8
	30	100	300	102	0.1510	0.440	220	73.1	5	1.3

Table 2. Ethylene/1-Hexene Copolymerization Results for Complex 1a Activated under Various Conditions at 20 °C

entry	activator	N_{exp}	[Zr] (μmol)	[activator] (μmol)	P_{total} (psig)	X_e/X_h (mol/mol)	yield (g)	product (kg mol Zr^{1-}hr^{-1})	(E)$_{\text{copolymer}}$ (mol %)
32	B1/TIBA[a]	1	80	82	100	0.1480	0.343	215	95.2
33	B2/TIBA[b]	1	80	80	100	0.1480	0.311	195	95.6
34	B4/TIBA[c]	1	80	80	100	0.1480	0.397	248	96.8
35	MMAO	2	80	*d*	100	0.1480	0.663	413	93.0
36	MMAO	2	80	*d*	50	0.0783	0.330	207	86.4

[a] B1/TIBA = anilinium borate, TIBA activation conditions. [b] B2/TIBA = borane, TIBA activation conditions. [c] B4/TIBA = trityl borate, TIBA activation conditions. [d] 100 mg of MMAO used.

Table 3. Ethylene/1-Hexene Copolymerization Results for Complex 2a Activated under Various Conditions at 20 °C

entry	activator	N_{exp}[b]	[Zr] (μmol)	[activator] (μmol)	P_{total} (psig)	X_e/X_h (mol/mol)	yield (g)	product (kg mol Zr^{-1} h^{-1})	mol % E	M_n (×10^3 g/mol)	M_w/M_n
37	B1/TIBA	1	39	40	40	0.0654	0.86	1097	58.2		
38	B2/TIBA	1	41	40	40	0.0654	1.23	1502	54.6		
39	B4/TIBA	1	40	41	40	0.0654	1.32	1661	59.2		
40	MMAO	1	42	*a*	40	0.0654	1.27	1505	48.4		
41	B1/TIBA	1	39	40	50	0.0783	1.01	1295	61.3		
42	B2/TIBA	1	41	40	50	0.0783	1.22	1485	61.1		
43	B4/TIBA	1	40	41	50	0.0783	2.18	2740	64.2		
44	MMAO	1	42	*a*	50	0.0783	1.59	1894	50.9		
45	B1/TIBA	4	16	15	100	0.1480	0.36	1165	71.6	142	1.8
46	B2/TIBA	3	30	30	100	0.1480	0.60	989	74.3	157	1.8
47	B4/TIBA	4	40	40	100	0.1480	1.47	1824	74.7	175	1.8
48	MMAO	2	41	*a*	100	0.1480	1.18	1459	63.3	110	1.8

[a] 100 mg of MMAO used. [b] N_{exp} = number of experiments.

the end group signals indicated that the ratio of β-H elimination to chain transfer to aluminum was approximately 20:80 for complex **5a** under these copolymerization conditions. These observations provide clear evidence for chain transfer to aluminum.[56]

The copolymerization behavior for **1a**−**5a** was analyzed according to first-order Markov statistics. To investigate the effect of copolymerization conditions on comonomer incorporation and sequence distribution, ^{13}C NMR spectra of the copolymers were acquired under quantitative conditions and characterized according to assignments by Randall.[57] Copolymer compositions and *n*-ad distributions were calculated following Cheng's method.[58] Reactivity ratios for first-order Markov statistics,[59] r_e and r_h, were calculated from the triad distributions for each run according to previously described methods[52] (Table 4).

Effect of Ligand Structure on Copolymerization Behavior. The symmetry of the [ONDO]ZrBn$_2$ complexes has a considerable influence on their copolym-

Table 4. Reactivity Ratios for Ethylene/1-Hexene Copolymerizations with [ONDO]ZrBn$_2$ Complexes 1a–5a

catalyst	N_{exp}[a]	X_e/X_h	$(E)_{copolymer}$ (mol %)	r_e	r_h	r_er_h	r_h/r_e ($\times 10^5$)
1a/MMAO	6	0.04–0.11	71.5–91.3	98 ± 7	0.026 ± 0.005	2.6 ± 0.3	28 ± 7
2a/MMAO	6	0.07–0.32	50.1–72.0	5.9 ± 0.3	0.031 ± 0.003	0.18 ± 0.02	530 ± 60
2a/B1/TIBA	4	0.07–0.15	58.2–71.6	12.5 ± 0.3	0.018 ± 0.001	0.22 ± 0.02	72 ± 6
2a/B2/TIBA	3	0.07–0.15	54.6–74.3	14.2 ± 1.3	0.020 ± 0.008	0.28 ± 0.09	74 ± 24
2a/B4/TIBA	4	0.07–0.15	59.2–74.7	15.1 ± 1.7	0.017 ± 0.001	0.26 ± 0.04	59 ± 15
3a/MMAO	6	0.08–0.31	42.3–77.1	9 ± 1	0.077 ± 0.006	0.67 ± 0.06	900 ± 200
4a/MMAO	5	0.08–0.30	35.9–68.8	6.1 ± 0.8	0.11 ± 0.02	0.63 ± 0.09	1800 ± 400
5a/MMAO	5	0.06–0.22	49.9–78.5	15 ± 1	0.039 ± 0.004	0.59 ± 0.05	270 ± 40

[a] N_{exp} = number of experiments.

Table 5. Diad and Triad Distributions for Ethylene/1-Hexene Copolymers from Complexes 1a–5a at ~70% Ethylene Incorporation

entry	catalyst	$(E)_{copolymer}$ (mol %)	HHH	HHE	HEH	EHE	EEH	EEE	HH	HE	EE
1	**1a**/MMAO	71.5	9.2	7.5	4.0	11.9	23.7	44.9	13.3	31.6	55.7
12	**2a**/MMAO	72.0	0.8	3.5	8.7	23.7	31.4	31.5	2.8	48.9	47.6
45	**2a**/B1/TIBA	71.6	0.7	4.7	8.1	23.1	33.4	30.4	2.8	49.5	46.8
46	**2a**/B2/TIBA	74.3	0.6	4.3	7.1	20.7	31.4	35.2	2.2	45.6	51.6
47	**2a**/B4/TIBA	74.7	0.3	4.6	7.1	20.4	30.1	37.5	2.6	44.3	52.6
17	**3a**/MMAO	70.1	2.4	8.9	6.6	18.6	29.3	33.7	8.1	42.5	48.8
26	**4a**/MMAO	68.8	3.7	8.1	7.9	19.4	29.6	31.8	8.0	45.4	46.1
29	**5a**/MMAO	72.8	1.6	7.6	6.6	18.0	30.0	36.0	5.1	43.1	51.2

erization behavior. The C_2-symmetric complex **1a** exhibits a much lower ability to incorporate 1-hexene than the C_s-symmetric complexes **2a**–**5a**; at approximately the same feed ratio of comonomers ($X_e/X_h = 0.1079$ and 0.1065, entries 4 and 9 respectively) complex **2a**/MMAO showed a significantly higher incorporation of 1-hexene (55.1% E) compared to **1a**/MMAO (91.3% E). This is manifested in the much higher value of r_e for **1a** compared to **2a** ($r_e = 98$ and 5.9, respectively) and their similar r_h values (Table 4). The higher 1-hexene selectivity for **2a** compared to **1a** is consistent with the general trend observed by Kol that the C_s-symmetric complexes show higher activity for 1-hexene in homopolymerization compared to the C_2-symmetric complexes (productivity = 860 kg mol^{-1} h^{-1} for **2a**[35] and 18 kg mol^{-1} h^{-1} for **1a**[38]), although homopolymerization activities are not necessarily a good indicator of copolymerization behavior.

The symmetry of the catalysts also has a significant effect on copolymer sequence distribution. Analysis of the copolymerization parameters (Table 4) reveals that the product of the reactivity ratios r_er_h for complex **1a** is higher than 1 ($r_er_h = 2.6$), indicative of either a blocky distribution of comonomers or of a broad short chain branching distribution,[18] whereas that for **2a** (r_er_h = 0.18) is indicative of a slightly alternating sequence distribution. The higher value of r_er_h for **1a** is reminiscent of that observed by Galimberti for the sterically hindered metallocene catalysts *rac*-[isopropylidenebis-(3-*tert*-butyl-1-indenyl]zirconium dichloride ($r_e = 14.0$, $r_p = 0.19$, $r_er_p = 2.7$) and *rac*-[ethylenebis(4,7,-dimethyl-4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride (r_e = 95.5, $r_p = 0.063$, $r_er_p = 6.3$).[60,61] The origin of this behavior is not clear for these sterically hindered systems and warrants further investigation. Nevertheless, these results illustrate the potential of both nonmetallocene and metallocene catalysts to generate copolymers with a range of sequence distributions.[62] As expected from their 1-hexene homopolymerization selectivities,[35,38] 1-hexene homosequences in the ethylene/1-hexene copolymers from **1a** were isotactic, whereas those from **2a** were atactic.

The slightly alternating sequence distributions for the C_s-symmetric catalysts **2a**–**5a** are similar to those observed for the C_s-symmetric metallocene catalysts of the Ewen–Razavi type,[63,64] although we note that the two coordination sites for the C_s-symmetric catalysts **2a**–**5a** are heterotopic and thus are more closely analogous to the C_1-symmetric catalyst systems which we and others have shown can yield quite highly alternating copolymers.[65–71]

The 1-hexene selectivity of the C_s-symmetric [ONDO]ZrBn$_2$ complexes increases in the order of decreasing steric bulk at the 2,4-aryl positions, ^{t}Bu < Ph < Me (**2a** < **3a** < **4a**, respectively). Specifically, the three complexes show similar r_e values while r_h values increase more than 3-fold going from a ^{t}Bu to Me substituent. In contrast to metallocene-based catalyst systems,[52,72] the addition of phenyl substituents near the metal coordination site (**3a**) did not result in enhanced 1-hexene incorporation compared to ^{t}Bu or Me substituents (complexes **2a** or **4a**, respectively). Complex **2a** (r_er_h = 0.18) showed a slightly higher tendency to produce copolymers with alternating sequence distributions than **3a** or **4a** (r_er_h = 0.67 (**3a**), 0.63 (**4a**)).

The influence of the pendant donor group has was investigated by comparison of the copolymerization behavior of complexes **2a** and **5a**, which differ both sterically and electronically (**2a**, Zr–N = 2.594 Å, two methyl substituents; **5a**, Zr–O = 2.447 Å, one methyl substituent).[35,36] The copolymerization selectivity varied little with the pendant donor group. Compared to complex **2a** ($r_h = 0.031$, $r_e = 5.9$, $r_er_h = 0.18$), complex **5a** showed a slightly higher tendency to incorporate ethylene ($r_e = 15$), and subsequently a less alternating sequence distribution ($r_er_h = 0.59$). The pendant donor had a large effect on the productivity: the productivity of **2a**/MMAO was several times higher than that of **5a**/MMAO. Kol observed an opposite trend for 1-hexene homopolymerization with $B(C_6F_5)_3$ cocatalyst.[36] This difference is likely the consequence of the steric bulk of the two methyl groups on the pendant amine of **2a** giving better protection of the donor compared to the methoxy group of **5a** against electrophilic attack by TMA (present from the MMAO). In contrast to catalyst systems **3a**/MMAO and **4a**/MMAO, productivities for **2a** and **5a** were not affected by the presence of different amounts of MMAO activator.

Influence of Cocatalyst on the Copolymerization Behavior of 2a. The activation conditions have a significant influence on the copolymerization behavior.[8,10,12,13,17−19] The activation of complex **2a** with anilinium borate, $[PhNMe_2H][B(C_6F_5)_4]$, trityl borate, $[Ph_3C][B(C_6F_5)_4]$, or borane, $[B(C_6F_5)_3]$, in the presence of triisobutylaluminum, TIBA, as a scavenger was carried out to examine the effect of different activation conditions on copolymerization productivity and selectivity (Table 3). At the same feed ratio of comonomers ($X_e/X_h = 0.0783$, entries 8 and 41−44; $X_e/X_h = 0.1480$, entries 11 and 45−48) complex **2a**/MMAO showed approximately 10% higher incorporation of 1-hexene compared to **2a**/$[PhNMe_2H][B(C_6F_5)_4]$/TIBA, **2a**/$[Ph_3C][B(C_6F_5)_4]$/TIBA, or **2a**/$B(C_6F_5)_3$/TIBA. The higher 1-hexene selectivity of **2a**/MMAO results from both higher r_e and lower r_h. The origin of this unprecedented difference in selectivity with different activators is unclear and is currently under investigation. As Kol has demonstrated that borane activation of **2a** or **5a** forms well-defined solvent-separated ion pairs,[36] one possibility is that the borate counterions interact more closely with the cationic metal center than the MMAO counterion, thus sterically hindering coordination and insertion of the bulkier α-olefin comonomer. Brintzinger and Landis have proposed that unassisted dissociation of the catalyst-counterion pair is unlikely; rather they propose that the olefin must displace the counterion in order to coordinate to the metal center.[5,73,74] This hypothesis raises the intriguing possibility that the ability of hexene or ethylene to displace the anion may vary as a function of different anions.

The ability of the different cocatalysts to influence the copolymerization behavior is sensitive to the catalyst structure. Compared to the C_s-symmetric complex **2a**, the C_2 complex **1a** demonstrated a smaller increase in ethylene incorporation (2−5%) when borane or borate activators were used (Table 2). This may be a consequence of the heterotopic coordination sites of complex **2a**. Further studies are warranted to evaluate the role of catalyst/cocatalyst structure and dynamics on copolymerization behavior.

Conclusions

The ethylene/1-hexene copolymerization behavior of a series of $[ONDO]ZrBn_2$ complexes was explored. A remarkable 10% variation in ethylene incorporation was observed when the C_s-symmetric complex **2a** was activated with MMAO as compared to activation with borane or borate cocatalysts. These results indicated that the nature of the cocatalyst can influence the copolymerization behavior of certain catalysts. As observed for metallocene catalysts, the copolymerization behavior of the amine bis(phenolate) complexes $[ONDO]ZrBn_2$ depends on the ligand geometry and substitution pattern: complexes with heterotopic coordination sites tend to give slightly alternating comonomer sequence distributions relative to those with homotopic coordination sites. Introduction of sterically hindering groups at the 2,4-positions of the aryl rings leads to an increase in productivity and a decrease in hexene incorporation.

Experimental Section

General Procedures. Standard Schlenk techniques and a Vacuum Atmospheres drybox were used to handle air- and moisture-sensitive compounds. Ligands **1**, **2**, **4**, and **5** and the complexes **1a**, **2a**, **4a**, and **5a** were prepared according to the procedures described by Kol.[35,36,38] Polymerization grade ethylene (supplied by Matheson) and toluene were prepared by passage through columns containing Q5 and alumina. Modified methylaluminoxane (MMAO type 4) was supplied as a toluene solution by Akzo Nobel and dried under vacuum to remove solvent and residual trimethylaluminum prior to use. Anilinium borate was obtained from Albemarle and recrystallized from methylene chloride/pentane before use. 1-Hexene (97%) was purchased from Aldrich, dried over sodium, distilled, degassed, and stored over alumina prior to use. All other chemicals were obtained from Aldrich unless otherwise noted.

Ligand Synthesis. 2,4-Diphenylphenol. This compound was prepared following the literature procedure.[47] Phenyllithium (28 mL, 2.0 M in cyclohexane/diethyl ether, 56 mmol) was added dropwise at −78 °C to a stirred solution of benzoquinone (2.039 g, 18.9 mmol) in THF. The resulting light brown solution was stirred for 4 h allowing the temperature to rise to 20 °C. The reaction was hydrolyzed with 40 mL of water, and the resulting orange solution was acidified with sulfuric acid (if the reaction is not acidified, the 1,4-diol will be isolated), extracted with diethyl ether (3 × 40 mL), and dried over magnesium sulfate. Purification by column chromatography (9:1 pentane/ethyl acetate) and recrystallization from hexanes gave the desired product as a pale yellow crystalline solid (2.012 g, 43.3% yield). ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.42−7.59 (overlapping peaks, 11 H, Ar*H*), 7.31 (d, J = 8.4 Hz, 1H, 5,6-Ar*H*), 7.06 (d, J = 8.4 Hz, 1H, 5,6-Ar*H*), 5.25 (s, 1H, O*H*).

Ligand 3. 2,4-Diphenylphenol (0.5001 g, 2.03 mmol), *N*,*N*-dimethylethylenediamine (0.089 g, 1.02 mmol), and 37% formaldehyde in water (0.5 mL, 6.0 mmol) were dissolved in 4 mL of methanol and refluxed for 48 h. Upon cooling slowly to room temperature, a white precipitate formed. The precipitate was filtered, washed with cold methanol, and dried in a vacuum oven to yield 0.430 g of a white powder (70% yield). ^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.64 (d, J = 7.7 Hz, 4H), 7.52 (d, J = 7.7 Hz, 4H), 7.47 (d, J = 2.2 Hz, 2H), 7.37 (m, 8H), 7.31 (m, 2H), 7.26 (m, 4H), 3.82 (s, 4H), 2.77 (t, J = 5.9 Hz, 2H) 2.63 (t, J = 5.9 Hz, 2H), 2.29 (s, 6H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ (ppm) 153.8, 140.8, 138.7, 132.0, 129.7, 129.6, 129.3, 128.6, 128.1, 127.9, 126.7, 126.6, 126.5, 123.2, 56.5, 56.2, 49.6, 44.9. Anal. Found (Calcd) for $C_{42}H_{40}N_2O_2$: C, 83.57 (83.41); H, 6.89 (6.67); N, 4.67 (4.63).

Complex 3a. A solution of **3** (0.270 g, 0.44 mmol) in 10 mL of toluene was added dropwise to a solution of zirconium tetrabenzyl (0.204 g, 0.44 mmol) in 5 mL of toluene. After heating to 65 °C and stirring for 4 h, a bright yellow solution resulted. Upon removal of the toluene, 0.263 g of a bright yellow powder was isolated (68% yield). ^1H NMR (C_6D_6, 400 MHz): δ (ppm) 7.89 (d, J = 8 Hz, 4H), 7.73 (d, J = 2.4 Hz, 2H), 7.53 (m, 4H), 7.45 (t, J = 7.6 Hz, 4H), 7.26−7.06 (overlapping peaks, 15H), 7.00−6.97 (overlapping peaks, 4H), 6.70 (m, 1H), 3.88 (d, J = 13.6 Hz, 2H, Ar−C*H*$_2$), 2.66 (d, J = 13.6 Hz, 2H, Ar−C*H*$_2$), 2.26 (s, 2H, Ph−C*H*$_2$), 2.07 (s, 2H, Ph−C*H*$_2$), 1.90 (br s, 2H), 1.21 (b s, 8H). ^{13}C NMR (C_6D_6, 75.4 MHz): δ (ppm) 157.7, 151.3, 143.9, 141.0, 139.4, 132.7, 130.8, 130.1, 129.5, 129.4, 129.1, 126.9, 123.3, 120.4, 66.6, 64.4, 64.0, 60.0, 51.4, 46.6, 21.4. Anal. Found (Calcd) for $C_{56}H_{52}N_2O_2Zr$: C, 76.80 (76.76); H, 6.02 (5.98); N, 2.56 (3.20).

Ethylene/1-Hexene Copolymerization. MMAO Activation. Polymerizations were carried out in a 300 mL stainless steel Parr reactor. The reactor was evacuated on a vacuum line and then refilled and flushed 3 times with 100 psig of ethylene. MMAO (100−330 mg) was suspended in 35 mL of 1-hexene and equilibrated in the reactor under the desired pressure of ethylene for at least 30 min at a high stirring speed. A catalyst precursor stock solution was prepared by dissolving 10−50 mg of the zirconium complex in toluene (5−10 mL). The desired amount of stock solution was added to 5 mL of 1-hexene and injected into the reactor to start the polymerization. The polymerization temperature was maintained constant at 20 ± 1 °C via an ethylene glycol/water cooling loop. Methanol (15 mL) was injected after 20−30 min time to quench the polymerizations. The polymers were stirred in acidified methanol overnight, filtered, washed with additional methanol, and dried under vacuum at 40 °C for at least 6 h.

Borane or Borate Activation. The Parr reactor was evacuated on a vacuum line and then refilled and flushed 3 times with 100 psig of ethylene. A solution of 50 mg of TIBA in 35 mL of 1-hexene was injected into the reactor and stirred under the desired ethylene pressure for at least 30 min at a high stirring speed. The catalyst precursor stock solution was prepared by dissolving 10–50 mg of the zirconium complex in 1-hexene (25 mL); the desired amount of precatalyst was diluted in 2 mL total of 1-hexene. The activator stock solution was prepared by dissolving in toluene (1 mg/mL); the desired amount of activator stock solution was added to 3 mL of 1-hexene. Stirring on the reactor was stopped and the pressure was vented by 10 psig. The precatalyst solution was injected under ethylene pressure, the pressure was immediately vented again by 10 psig, the activator solution was injected under ethylene pressure using an aluminum-free injection tube, and stirring was resumed. The polymerization temperature was maintained constant at 20 ± 1 °C via an ethylene glycol/water cooling loop. After 30 min, the polymerization was quenched and worked up as described above for MMAO activation.

Copolymerization Quenched with O$_2$. Copolymerizations were carried out as described for MMAO activation. After 30 min, the ethylene feed was disconnected and a single-ended injection tube pressurized with 200 psig of air was connected to the reactor. The reaction exothermed slightly (+2 °C). After 2 min, the injection tube was pressurized again with 200 psig air and connected to the reactor. No additional exotherm was observed. After stirring for 30 min, 15 mL methanol pressurized with argon was injected into the reactor. The reactor contents were poured into acidic methanol, stirred for 2 h, and allowed to settle overnight. An oily polymer was isolated from the methanol and dried in a vacuum oven at 40 °C for 6 h.

Polymer Characterization. High-temperature GPC was performed using the automated Symyx Rapid GPC system.[50,51] Two 30 cm × 7.5 mm linear columns containing PLgel 10 μm, MixB and PLgel 5 μm, Mix C, respectively were used. *o*-Dichlorobenzene was used as an eluant at 1.5 mL/min at 160 °C. Polymer molecular weights were calibrated relative to linear polystyrene standards.

^{13}C {^{1}H} NMR spectra were recorded at 75.4 MHz on a Varian UI300 spectrometer at 100 °C. Samples were prepared by dissolving 50–200 mg of polymer in 2 mL of 90:10 *o*-dichlorobenzene/d_6-benzene containing approximately 5 mg of chromium(III) acetylacetonate to reduce T_1. Spectra were recorded using pulse repetition intervals of 5 s and gated proton decoupling.

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