Macromolecules **1997,** *30,* 3477−3483

Homogeneous α-Olefin Polymerizations over Racemic Ethylene-Bridged *ansa*-Bis(2-(*tert*-butyldimethylsiloxy)-1-indenyl) and *ansa*-Bis(2-(*tert*-butyldimethylsiloxy)-4,5,6,7-tetrahydro-1-indenyl) Metallocene Dichlorides

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Received January 15, 1997; Revised Manuscript Received March 18, 1997[⊗]

ABSTRACT: Ethylene and propylene were polymerized over the siloxy-substituted bis(indenyl) *ansa*-metallocenes, *rac*-[ethylenebis(2-(*tert*-butyldimethylsiloxy)indenyl)]zirconium dichloride (**1**), *rac*-[ethylenebis(2-(*tert*-butyldimethylsiloxy)-4,5,6,7-tetrahydroindenyl)]zirconium dichloride (**2**), and *rac*-[ethylenebis(2-(*tert*-butyldimethylsiloxy)indenyl)]hafnium dichloride (**3**), using methylaluminoxane (MAO) and trityl tetrakis(pentafluorophenyl)borate as cocatalysts. Especially complex **1** forms a highly active catalyst precursor for the polymerization of α-olefins. Synthesis and characterization of **2** and **3** are described. The **1**/MAO and **3**/MAO catalyst systems show high polymerization activities at exceptionally low [Al]:[Zr] ratios [(100−250):1]. For both catalysts, extensive chain transfer to aluminum is observed as the predominant chain-transfer mechanism. Preliminary results from copolymerization of ethylene with 1-hexene and 1-hexadecene over **1**/MAO indicate a good comonomer response.

Introduction

Chiral group IV *ansa*-metallocenes are precursors to highly active catalysts for stereoselective polymerization of α-olefins.[1] Especially racemic C_2 symmetric bis(indenyl) complexes have received considerable interest in isospecific polymerization of propylene. Dimethylsilylene-bridged 2,2′-dimethyl-4,4′-diaryl-substituted bis(indenyl) zirconocenes developed by Brintzinger and coworkers[2] and Spaleck et al.[3] produce isotactic polypropylenes with catalyst activities and polymer properties comparable to those obtained with conventional Ziegler−Natta catalysts. The stereoselectivity and activity of the catalyst, and the molecular weight of the polymer are determined by steric and electronic effects induced by the size and positions of the substituents.

The area of electronically altered group IV bis(indenyl) complexes has remained relatively unexplored. Halogen or alkoxy substitution in the indenyl six-membered rings reduces the catalytic activity and molecular weight of the polymer.[4] Bis(indenyl) zirconocenes with 2-amino-functionalized ligands have been reported by several groups.[5] The bridged complexes show somewhat lower catalytic activities compared with their unsubstituted bis(indenyl) zirconocene analogues.[5a,c] Interestingly, an induction period of 2−3 h is required before the formation of polypropylene takes place.[5c]

Recently, we reported the synthesis of the first 2-siloxy-substituted bis(indenyl) *ansa*-zirconocene, *rac*-[ethylenebis(2-(*tert*-butyldimethylsiloxy)indenyl)]zirconium dichloride (**1**), and its preliminary application in the polymerization of α-olefins.[6] It was shown that **1**, in combination with methylaluminoxane (MAO), forms an active catalyst system for homopolymerization of ethylene and isospecific polymerization of propylene. As a continuation of the previous paper, we present here a detailed report on the polymerization behavior of **1**, its hydrogenated congener, *rac*-[ethylenebis(2-(*tert*-butyldimethylsiloxy)-4,5,6,7-tetrahydroindenyl)]zirconium dichloride (**2**), and the hafnocene, *rac*-[ethylenebis(2-(*tert*-butyldimethylsiloxy)indenyl)]hafnium dichloride (**3**).

Results and Discussion

Synthesis and Molecular Structure. Hydrogenation of **1** gave the tetrahydroindenyl complex **2** in 80% yield (Scheme 1). The hafnocene **3** was prepared by mixing the dry dilithium salt of bis(2-(*tert*-butyldimethylsiloxy)indenyl)ethane[6,7] with $HfCl_4$, followed by addition of precooled CH_2Cl_2 at −80 °C (Scheme 2). Workup and crystallization gave the pure racemic diastereomer of **3** in 13% yield. The molecular structure of **2** is displayed in Figure 1 with selected bond distances and angles in Table 1. Complex **2** adopts the expected monomeric bent metallocene structure and is in all essential features isostructural with its non-hydrogenated congener **1**.[6] The Zr atom lies on a crystallographic twofold rotation axis that bisects the Cl−Zr−Cl angle and the C(10)−C(10)* bond. The centroid−Zr−centroid angle (125.24°), Cl−Zr−Cl angle (98.16°), Zr−centroid bond length (2.2307 Å), and average Zr−C bond length (2.532 Å) of **2** deviate only slightly from those of **1** (Cen−Zr−Cen, 125.90°; Cl−Zr−Cl, 99.28°; Zr−Cen, 2.254 Å; Zr−C, 2.559 Å).[6] The η-carbon−oxygen bond (1.376 Å) is comparable to those of **1** (1.362 Å)[6] and *rac*-[ethylenebis(2-(thexyldimethylsiloxy)indenyl)]zirconium dichloride (**4**) (1.355 Å),[8] indicating partial double-bond character. Similar orbital overlap has been observed recently in the η-carbon−nitrogen bonds of bis(2-aminoindenyl) zirconocenes.[5] Complex **2** crystallizes in the indenyl-backward conformation first described by Brintzinger,[9] and recently observed

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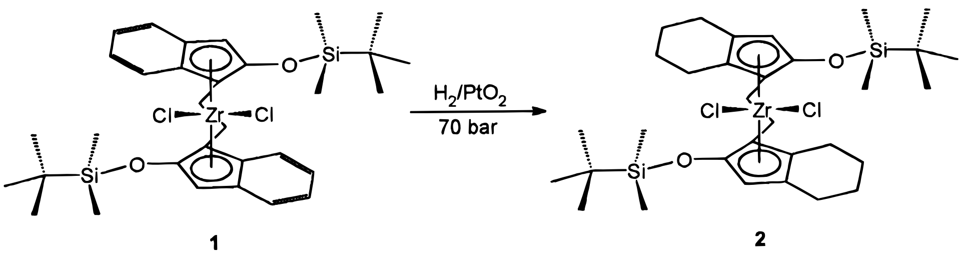
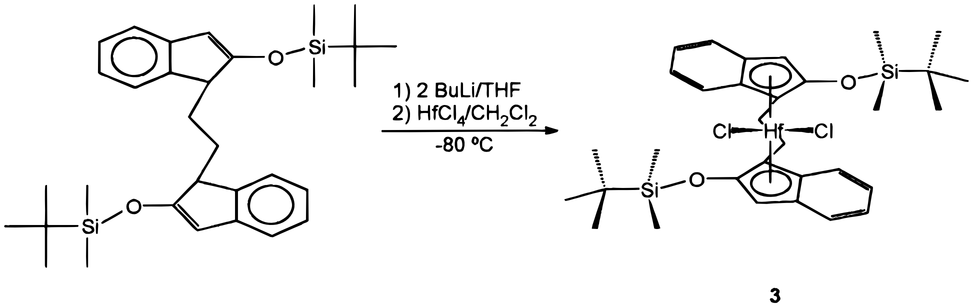
[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1997.

S0024-9297(97)00041-7 CCC: $14.00

Scheme 1



Scheme 2



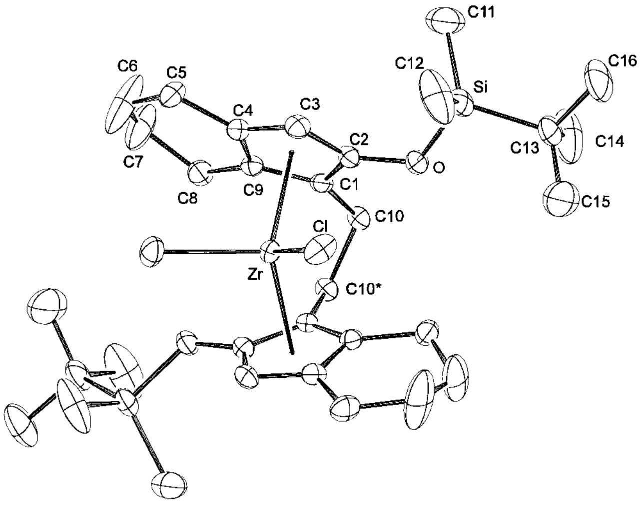


Figure 1. Molecular structure of **2**. Thermal ellipsoids are drawn at 30% probability.

Table 1. Selected Intramolecular Distances (Å) and Angles (deg) for 2[a–c]

	Intramolecular Distances		
Zr−Cl	2.439(1)	C(1)−C(2)	1.411(5)
Zr−C(1)	2.502(4)	C(2)−C(3)	1.408(6)
Zr−C(2)	2.531(4)	C(3)−C(4)	1.403(6)
Zr−C(3)	2.534(4)	C(4)−C(9)	1.410(5)
Zr−C(4)	2.581(4)	C(9)−C(1)	1.423(5)
Zr−C(9)	2.512(4)	C(1)−C(10)	1.497(5)
Si−O	1.679(3)	Zr−Cen	2.2307
C(2)−O	1.376(4)		
	Intramolecular Angles		
Cl−Zr−Cl*	98.16(6)	C(2)−O−Si	125.1(2)
Cen−Zr−Cen*	125.24	O−Si−C(13)	103.6(2)
Cp−Cp*[c]	58.56		

[a] Symmetry transformations used to generate equivalent atoms: *, $1 - x, y, 1\frac{1}{2} - z$. [b] Cen refers to the centroids of the C$_5$ rings and * denotes an atom or centroid related by the crystallographic twofold axis. [c] Angle between the cyclopentadienyl planes.

by Jordan and co-workers,[10] and by us for complexes **1** and **4**.[6,8]

Propylene Polymerization. Precursors **1** and **2** were activated with MAO for homogeneous polymerization of propylene.[11] The results are presented in Table 2. Table 3 shows the propylene polymerization activities of several *ansa*-zirconocene/MAO catalyst systems under similar polymerization conditions. The activity of **1**/MAO shows a strong temperature dependence, increasing linearly to a maximum value at T_p = 40 °C. The activity is essentially independent of the MAO concentration at [Al]:[Zr] = (250−10000):1.[12] In general, considerably higher [Al]:[Zr] ratios are required to achieve high catalyst activities.[1−3] The high activity of **1**/MAO at low [Al]:[Zr] ratios indicates a stable active species. Electron donation from the siloxy group may decrease the local Lewis acidity of the Zr atom, facilitating the alkylation and/or ionization of the neutral metallocene precursor, and weaken the coordination of the MAO counterion. Furthermore, through-bond stabilization of the generated zirconocene cation can increase the lifetime of active sites. Unlike the 2-amino-substituted bis(indenyl) *ansa*-zirconocenes,[5c] the **1**/MAO catalyst does not exhibit any induction period.

The molecular weights of the PPs obtained with **1**/MAO show a steady decrease of M_w with increasing polymerization temperature. Molecular weight distributions (MWDs) vary from 1.9 to 2.9, which is in accordance with the Schulz−Flory distribution for a single-site catalyst.[1a] The increase of MWD with increasing T_p indicates that the active species become partially nonuniform. This may result from the fluctionality of the ethylene bridge between the indenyl-forward (Π) and indenyl-backward (Y) conformers.[13] The M_w of the PP produced with **1**/MAO shows an unprecedented correlation with the [Al]:[Zr] ratio, *decreasing* from M_w = 27700 at [Al]:[Zr] = 50:1 to M_w = 4600 at [Al]:[Zr] = 10000:1. Typically, the molecular weight of polyolefins obtained with MAO-activated zirconocenes *increases* with the concentration of MAO, parallel with increased rates of chain growth.[1] The opposite behavior of **1**/MAO supports our previous hypothesis based on ^{13}C NMR,[6] that for this catalyst system, extensive transfer to aluminum is the main reason for the low molecular weight of the produced polypropylene. The low activity of **2**/MAO toward propylene is apparently due to steric hindrance at the catalytic site. Thermal motion of the hydrogenated six-membered rings, in

Table 2. Polymerization of Propylene over 1/MAO and 2/MAO Catalyst Systems[a]

cat.	T_p (°C)	P (bar)	[Al]:[Zr]	A (kg of PP/mol of Zr/h)	[*mm*][b] (%)	[*mmmm*][b] (%)	$10^{-3}M_w$[c]	M_w/M_n	T_m (°C)	X_c[d] (%)
1	0	1.30	3000:1	500	94.9	93.7	33.1	1.9	155	46
1[e]	20	2.00	3000:1	5300	94.7	92.3	19.0	2.4	148	45
1	40	2.70	3000:1	9000	90.5	86.6	9.2	2.7	138	35
1	60	3.40	3000:1	7000	85.4	78.9	7.0	2.9	130	24
1	80	4.10	3000:1	3500	71.5	61.7	3.4	2.6	110	8
1	40	2.70	50:1	200	91.8	86.2	27.7	1.8	147	43
1	40	2.70	250:1	8500	90.2	86.2	17.7	2.1	139	34
1	40	2.70	500:1	9900	88.7	84.7	15.9	2.2	137	37
1	40	2.70	1000:1	9400	88.4	85.0	13.5	2.4	137	36
1	40	2.70	10000:1	10200	94.4	85.5	4.6	2.3	137	37
2	20	2.00	3000:1	20	93.8	91.1	123.2	2.1	150	35
2	40	2.70	3000:1	150	90.5	85.3	37.8	1.8	136	30
2	60	3.40	3000:1	500	atactic		12.6	1.8	98	12
2	40	2.70	500:1	410	n.d.[f]	n.d.	48.0	1.9	129	27
2	40	2.70	10000:1	160	n.d.	n.d.	25.7	1.9	131	29

[a] Polymerization time = 60 min; [metallocene] = 11 μmol/200 mL of toluene. [b] By ^{13}C NMR. [c] By GPC vs polystyrene standards. [d] Crystallinity by DSC. [e] Reference 6. [f] Not determined.

Table 3. Comparison of Different *ansa*-Zirconocene/MAO Catalyst Systems in Polymerization of Propylene under Similar Conditions[a]

metallocene	A (kg of PP/mol of Zr/h)	$10^{-3}M_w$[b]	M_w/M_n	T_m (°C)
rac-$Me_2Si(4,5\text{-benzo-2-MeInd})_2ZrCl_2$	7200	98.5	2.1	150
rac-$Et(Ind)_2ZrCl_2$	5400	27.9	2.2	131
rac-$Et(2\text{-}(t\text{-}BuMe_2SiO)Ind)_2ZrCl_2$ (**1**)[c]	5300	19.1	2.4	148
rac-$Me_2Si(Ind)_2ZrCl_2$	4400	54.2	1.8	142
rac-$Et(2\text{-}(thexylMe_2SiO)Ind)_2ZrCl_2$ (**4**)[d]	2700	16.1	2.1	146
rac-$((1,4\text{-butanediyl})Si)Me_2Si(IndH_4)_2ZrCl_2$[c]	2400	54.8	2.1	145
rac-$Me_2Si(IndH_4)_2ZrCl_2$[c]	2300	53.2	2.0	146
$Me_2C(Flu)(Cp)ZrCl_2$	1700	97.1	1.8	141
rac-$Et(IndH_4)_2ZrCl_2$	800	33.0	2.0	138
rac-$Et(2\text{-}(t\text{-}BuMe_2SiO)IndH_4)_2ZrCl_2$ (**2**)	20	123.2	2.1	150

[a] T_p = 20 °C; $P(C_3H_6)$ = 2.0 bar; polymerization time = 60 min; [metallocene] = 11 μmol/200 mL of toluene. [b] By GPC vs polystyrene standards. [c] Reference 6. [d] Reference 8.

combination with the bulky siloxy groups, can interfere with the course of the propylene insertion, and decrease the rate of chain termination, thus leading to lower activities but higher molecular weights.

The stereochemical composition of the PPs was determined by ^{13}C NMR. The configurational microstructure suggests that the propagation step is mainly enantiomorphic site controlled.[14] 2,1-Insertion was observed for **1**/MAO at T_p = 20 °C.[6] At higher temperatures 1,3-addition is the predominant stereoerror. Figure 2 shows the methyl and methylene carbon regions of a ^{13}C NMR spectrum of PP produced with **1**/MAO (T_p = 40 °C; [Al]:[Zr] = 10000:1). In addition to the normal *n*-propyl end groups, strong signals corresponding to isopropyl end groups are observed at 25.8, 23.8, 22.7, and 21.2 ppm. Similar observations were reported by Brintzinger and co-workers for the 2-amino-substituted $Me_2Si[2\text{-}(Me_2N)Ind]_2ZrCl_2$/MAO catalyst system.[5c] The isopropyl end groups are consistent with chain termination by exchange of methyl groups and polymer chains between the aluminum centers of MAO and the Zr center of the catalyst. The isopropyl/*n*-propyl signal ratio increases with the [Al]:[Zr] ratio from 0.7–1 at [Al]:[Zr] = (250–1000):1 to 5–8 at [Al]:[Zr] = 3000:1 and 10000:1 (T_p = 40 °C). In conclusion, the low M_w of the PPs obtained with **1**/MAO indeed results from strong chain transfer to aluminum. As shown previously, the barrier to methyl exchange between dimethylzirconocenes and MAO is reduced with increased electron density at the metal center.[5c,15] Chain transfer to Al has also been observed with some sterically congested metallocene catalysts.[16] However, for **1**/MAO the reasons are likely to be electronic, since similar end-group signals are not detected in the spectra of the PPs obtained with **2**/MAO. The stabilized resting state of **1**/MAO may exhibit low barriers to both chain propagation, and chain termination by transfer to aluminum, thus explaining the high activities but low molecular weights.

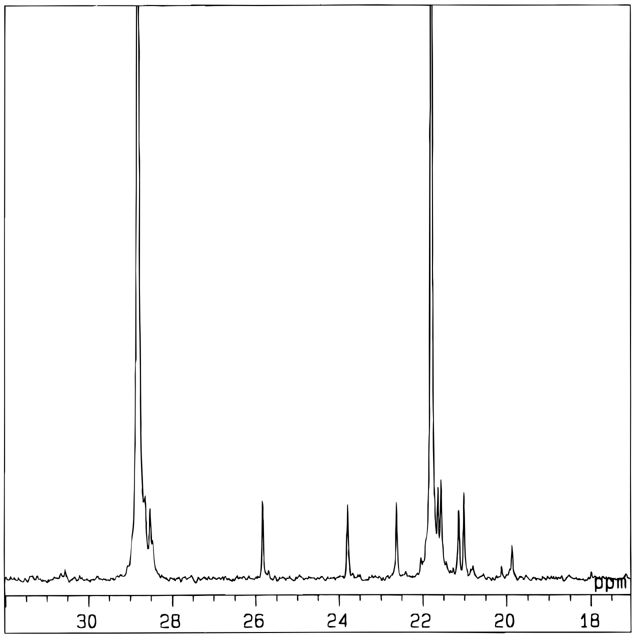


Figure 2. ^{13}C NMR methyl and methylene regions of iPP obtained with **1**/MAO at [Al]:[Zr] = 10000:1.

The *in situ* alkylated complex **1** was activated with the MAO free cocatalyst $[C(C_6H_5)_3]^+[B(C_6F_5)_4]^-$ for polymerization of propylene. The activity of [*rac*-$Et(2\text{-}(t\text{-}BuMe_2SiO)Ind)_2ZrR]^+[B(C_6F_5)_4]^-$ exceeds those of the reference catalyst systems under similar polymerization conditions (Table 4).

Table 4. Polymerization of Propylene over Cationic *ansa*-Zirconocene Catalyst Systems[a]

metallocene	A (kg of PP/mol of Zr/h)	$[mm]^b$ (%)	$[mmmm]^b$ (%)	$10^{-3}M_w{}^c$	M_w/M_n	T_m (°C)	$X_c{}^d$ (%)
$[\mathbf{1}]^+[B(C_6F_5)_4]^-$	7500	96.0	95.3	30.1	2.2	153	51
$[rac\text{-}Et(Ind)_2ZrR]^+[B(C_6F_5)_4]^-$	4600	94.9	93.7	36.4	2.3	146	43
$[rac\text{-}Me_2Si(Ind)_2ZrR]^+[B(C_6F_5)_4]^-$	4600	95.7	94.9	116.0	2.6	148	38

[a] $T_p = -20$ °C; $P(C_3H_6) = 2.0$ bar; polymerization time = 20 min; [metallocene] = 5 μmol/50 mL of toluene. [b] By ^{13}C NMR. [c] By GPC vs polystyrene standards. [d] Crystallinity by DSC.

Table 5. Polymerization of Ethylene over 1−3/MAO Catalyst Systems[a]

cat.	T_p (°C)	[Al]:[Zr]	A (kg of PE/mol of Zr/h)	$10^{-3}M_w{}^b$	M_w/M_n	T_m (°C)	$X_c{}^c$ (%)
1	20	3000:1	2900	260	3.2	134	59
1	40	3000:1	1800	240	4.1	134	66
1	60	3000:1	2700	84	4.9	134	68
1	80	3000:1	5900	24	2.9	130	85
1	40	100:1	2700	420	4.1	132	66
1	40	250:1	2300	310	4.3	133	67
1	40	500:1	2300	270	3.9	134	61
1	40	10000:1	2100	200	3.2	134	62
2	20	3000:1	900	>1000	∼2−3	136	47
2	40	3000:1	3700	>1000	∼3−4	135	49
2	60	3000:1	3700	880	3.0	135	50
2	80	3000:1	3000	37	2.3	133	63
2	40	100:1	700	1100	3.1	136	47
2	40	250:1	1100	980	2.8	135	46
2	40	500:1	3300	>1000	∼2−4	135	52
2	40	10000:1	2500	>1000	∼2−4	136	47
3	20	3000:1	0				
3	40	3000:1	500	500	3.5	135	54
3	60	3000:1	2100	240	2.9	133	58
3	80	3000:1	3400	63	2.3	131	73
3	40	100:1	500	>1000	∼2−4	132	42
3	40	250:1	1300	550	2.9	134	55
3	40	500:1	1000	660	3.1	135	54
3	40	10000:1	200	280	3.3	135	48

[a] $P(C_2H_4) = 2.5$ bar; polymerization time = 30 min; [metallocene] = 3 μmol/200 g of toluene. [b] By GPC vs polystyrene standards. [c] Crystallinity by DSC.

Ethylene Polymerization. Ethylene polymerization results obtained with **1**−**3**/MAO are presented in Table 5.[17,18] The bis(indenyl) complexes **1** and **3** show maximum activities at very low [Al]:[M] ratios (100:1 and 250:1). The results are in accordance with those obtained for **1**/MAO in the polymerization of propylene. The activity of the tetrahydroindenyl complex **2**/MAO shows an inverse behavior, increasing with the [Al]:[Zr] ratio to a maximum value at [Al]:[Zr] = 3000:1. Apparently, the hydrogenation of the indenyl six-membered rings considerably changes the steric and electronic properties of this metallocene, and for **2**, a higher excess of MAO is required to generate the activated catalyst. The activity of **2**/MAO exceeds that of **1**/MAO at $T_p = 40$ °C when [Al]:[Zr] ≥ 500:1, and at $T_p = 60$ °C when [Al]:[Zr] = 3000:1, suggesting that the low activity of **2**/MAO in the polymerization of propylene has a steric, rather than electronic, origin.

The M_w of the PE produced with **1**/MAO shows a similar correlation with the [Al]:[Zr] ratio, as observed earlier in the polymerization of propylene. At [Al]:[Zr] = 100:1 the M_w is twofold compared with the M_w at [Al]:[Zr] = 10000:1. For **3**/MAO the effect is less distinct at higher ratios. The MWDs are unusually broad for all catalyst systems, indicating that more than one type of active site is present in the polymerization reaction. We suggest that the Π and Υ conformers of these catalysts may have sufficiently different propagation rate coefficients in the polymerization of ethylene. If each population contributes to a significant amount of the total polymer production, high polydispersities will result. The rate of interconversion between the conformers may be decreased by the siloxy groups, leading to increased lifetimes of both conformers on the monomer coordination time scale. Narrowing of the MWDs at $T_p = 80$ °C can result from the temperature dependent predominance of the other indenyl conformer. The GPC curves of the PE samples produced with **1**/MAO show traces of bimodality at lower polymerization temperatures. The phenomena decreases with increasing temperature and increasing [Al]:[Zr] ratio. Since narrow MWDs were observed in the polymerization of propylene with **1**/MAO and **2**/MAO, it is possible that the steric hindrance at the Zr center in the indenyl-forward conformation to some extent blocks the coordination of propylene but not that of ethylene. Ethylene would, therefore, be polymerized by both of the conformers, whereas propylene predominantly by a single conformer, tentatively the indenyl-backward conformation, of the catalyst.

Table 6. Copolymerization of Ethylene with 1-Hexene and 1-Hexadecene over 1/MAO Catalyst System[a]

comonomer	[comon] (mmol/L)	A (kg of P/mol of Zr/h)	$10^{-3}M_w{}^b$	M_w/M_n	T_m (°C)	density (g/cm^3)
	0	3 700	158	3.8	134	0.944
1-hexene	36	16 900	130	2.9	116	0.921
1-hexene	90	14 300	73	2.2	99	n.d.[c]
1-hexene	180	16 300	56	2.2		0.892
1-hexadecene	36	12 400	100	2.8	116	0.917
1-hexadecene	90	15 600	69	2.2	92/104	n.d.[c]
1-hexadecene	180	19 900	56	2.1		0.891

[a] $T_p = 60$ °C; $P(C_2H_4) = 2.5$ bar; polymerization time = 30 min; [metallocene] = 1.5 μmol/230 g of toluene; [Al]:[Zr] = 2000:1. [b] By GPC vs polystyrene standards. [c] Not determined.

Ethylene Copolymerization. Preliminary results from copolymerization of ethylene with 1-hexene and 1-hexadecene over **1**/MAO are presented in Table 6. A comonomer effect is observed, which is typical for Ziegler−Natta catalysts and has been reported previously for other MAO-activated zirconocenes.[19] The copolymerization activities are 3−5 times higher compared with those of the homopolymerizations. The large decrease in the melting points of the polymers with increasing initial comonomer reactor concentration indicates a good comonomer response. Figure 3 shows the aliphatic region of the ^{13}C NMR spectrum of an ethylene−1-hexene copolymer prepared with **1**/MAO at [1-hexene] = 180 mmol/L. The concentration of bound comonomer is approximately 5.4 mol %. The NMR signals were assigned according to Randall.[20]

Summary and Conclusions

We have demonstrated that 2-siloxy-substituted bis(indenyl) and bis(tetrahydroindenyl) *ansa*-metallocenes form a new class of highly active stereoselective catalyst precursors for homo- and copolymerization of α-olefins.

Complex **1**, in combination with MAO or other activators, polymerizes propylene and ethylene with very high activity. The siloxy group probably has a stabilizing effect on the cationic active site of the catalyst. The low molecular weights of the PPs obtained with **1**/MAO are due to extensive chain transfer to aluminum, which may

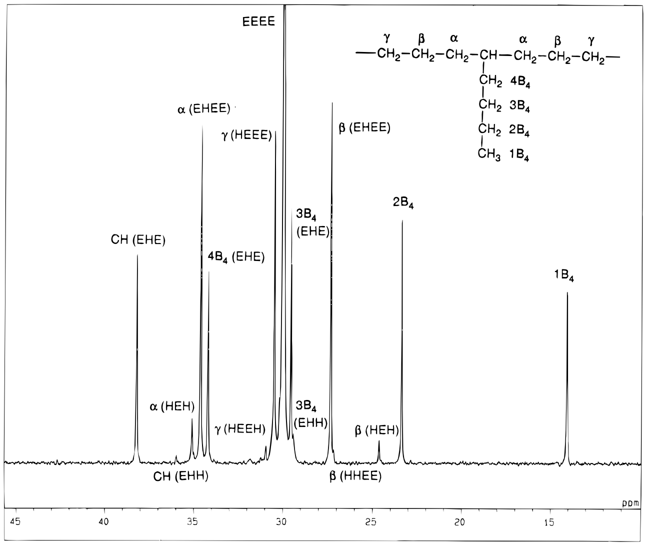


Figure 3. ^{13}C NMR spectrum of an ethylene−1-hexene copolymer prepared with **1**/MAO at [1-hexene] = 180 mmol/L. Concentration of bound comonomer is approximately 5.4 mol %.

be facilitated by electron donation from the siloxy group. Both non-hydrogenated catalyst precursors **1** and **3** require considerably reduced amounts of MAO compared with the conventional bis(indenyl) *ansa*-zirconocenes. The tetrahydroindenyl catalyst system **2**/MAO produces PE and PP with very high M_w. Its low activity in polymerization of propylene is apparently due to steric hindrance at the catalytic site. The ethylene polymerization activity of **2**/MAO is, however, comparable to that of **1**/MAO at elevated T_p. In copolymerization of ethylene with higher α-olefins, the **1**/MAO catalyst system shows good comonomer response.

Although the exact role of the siloxy group in these catalysts is unclear at present, we suggest that its influence is electron donating in nature. We are currently investigating the function of the heteroatom.

Experimental Section

General Considerations. All operations were carried out in an argon or nitrogen atmosphere using standard Schlenk, vacuum, or glovebox techniques. Solvents were dried and distilled under argon prior to use. Analytical grade toluene (Merck) was used in the ethylene polymerizations and purified over a series of columns containing molecular sieves, CuO, and Al_2O_3. Grade 3.5 ethylene (AGA), 1-hexene (Aldrich) and 1-hexadecene (Merck) were purified prior to use in a similar way. High-purity propylene (99.5%) was obtained from Neste Oy. Methylaluminoxane (10 or 30% w/w) and trityl tetrakis(pentafluorophenyl)borate were supplied by Witco and used as received. *rac*-Et(Ind)$_2$ZrCl$_2$ (Strem) was used as received. *rac*-Et(IndH$_4$)$_2$ZrCl$_2$,[21] *rac*-Me$_2$Si(Ind)$_2$ZrCl$_2$,[22] *rac*-Me$_2$Si(2-MeBenz[*e*]Ind)$_2$ZrCl$_2$,[3a] *rac*-C$_4$H$_8$Si(IndH$_4$)$_2$ZrCl$_2$,[23] and *i*-Pr-(Cp)(Flu)ZrCl$_2$,[24] were prepared according to the literature procedures.

The ^{1}H and ^{13}C NMR spectra were recorded in CDCl$_3$ or CD$_2$Cl$_2$ solutions using a JEOL JNM-LA400 or JEOL JNM-A500 NMR spectrometer and referenced against tetramethylsilane (TMS) or the residual protons of the deuterated solvents. Direct inlet electron ionization mass spectra (EIMS) were obtained at 70 eV on a Varian VG-7070E mass spectrometer.

***rac*-[Ethylenebis(2-(*tert*-butyldimethylsiloxy)-4,5,6,7-tetrahydro-1-indenyl)]zirconium Dichloride (2).** A mixture of **1** (1.00 g, 1.47 mmol) and PtO$_2$ (20 mg) in CH$_2$Cl$_2$ (150 mL) was hydrogenated at 70 bar in a stirred reactor for 16 h. The light green suspension was filtered through Celite and the solvent evaporated. The residue was dissolved in hexane (50 mL), and the solution was cooled to 0 °C to provide 0.80 g (79.2%) of light green microcrystalline **2**. In the EIMS mass spectrum of **2**, parent ions of composition $C_{32}H_{52}Si_2O_2ZrCl_2^+$ were observed at $m/e = 684-692$ in the appropriate isotope ratios. ^{1}H NMR (CDCl$_3$, δ): 5.69 (s, 2H), 3.39−3.29 (m, AA′, 2H), 3.04−2.97 (m, 2H), 2.85−2.77 (m, 2H), 2.73−2.64 (m, BB′, 2H), 2.48−2.34 (m, 4H), 1.90−1.70 (m, 4H), 1.59−1.42 (m, 4H), 0.92 (s, 18H), 0.20 (s, 6H), 0.16 (s, 6H). ^{13}C NMR (CDCl$_3$, δ): 142.24, 127.66, 117.29, 114.18, 106.45, 25.46, 24.46, 23.80, 22.05, 21.92, 21.75, 18.10, −4.09, −4.65.

***rac*-[Ethylenebis(2-(*tert*-butyldimethylsiloxy)-1-indenyl)]hafnium Dichloride (3).** To a solution of bis(2-(*tert*-butyldimethylsiloxy)indenyl)ethane (10.38 g, 20.0 mmol) in THF (80 mL) at 0 °C was added dropwise *n*-BuLi (16.1 mL of a 2.5 M solution in hexane, 40.2 mmol), and the reaction mixture was stirred overnight at room temperature. The solvents were removed *in vacuo*, and the resulting off-white powder was mixed with HfCl$_4$ (6.41 g, 20.0 mmol). The mixture was cooled to −80 °C, and precooled CH$_2$Cl$_2$ (150 mL) was added. The light yellow suspension was gradually warmed to room temperature, stirred overnight, and filtrated through Celite to remove lithium chloride. Concentration and cooling to −30 °C gave 1.96 g (12.8%) of **3** as a light yellow microcrystalline solid. In the EIMS mass spectrum of **3**, parent ions of composition $C_{32}H_{44}Si_2O_2HfCl_2^+$ were observed in the appropriate isotope ratios at $m/e = 760-774$. ^{1}H NMR (CD$_2$Cl$_2$, δ): 7.64 (dq, J = 8.5 Hz, 1.8 Hz, 1.0 Hz, 2H), 7.34−7.25 (m, 4H), 7.05−7.01 (m, 2H), 5.86 (d, ^4J = 0.7 Hz, 2H), 4.02−3.92 (AA′, 2H), 3.71−3.61 (BB′, 2H), 1.02 (s, 18H), 0.22 (s, 6H), 0.21 (s, 6H). ^{13}C NMR (CD$_2$Cl$_2$, δ): 148.64, 126.19, 124.97, 124.35, 124.30, 123.49, 115.47, 105.37, 96.46, 25.84, 25.52, 18.62, −3.92, −4.26.

Crystal Structure Determination. Single crystals of **2** for X-ray structure determination were obtained by crystallization from a concentrated toluene solution at −15 °C. The data set was collected on a Rigaku AFC5S diffractometer using Mo Kα radiation (λ = 0.710 69 Å) at 293 K. The experimental absorption correction (ψ-scan) was carried out. The structure was solved by direct methods and refined by least-squares techniques to the $R1$ value of 0.039, w$R2$ value of 0.034 [($I > 3\sigma(I)$], and GOF = 1.91 for all independent reflections. Heavy atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with fixed displacement parameters (1.2× that of the host atom), except the hydrogen of the five-membered ring and the hydrogens of the ethylene bridge which were found from the Fourier map and were refined with isotropic displacement parameters. All refinements were performed using SHELXL93 software.[25] Figures were plotted on ORTEPII.[26]

Propylene Polymerization Procedures. The polymerizations with the metallocene/MAO catalyst systems were carried out in a 0.5-L Büchi glass autoclave in 200 mL of toluene. In a typical run, half of the MAO/toluene solution was added to the reactor and stirred for 5 min in order to reduce any impurities in the reactor. In a parallel procedure, 11 μmol of the metallocene was dissolved in the remaining half of the MAO/toluene solution and preactivated for 5 min by standing at room temperature. The catalyst/activator mixture was charged into the reactor, and the polymerization was started by introducing the monomer. The pressure was maintained by controlling the monomer feed. The polymerization was interrupted after 60 min by addition of MeOH. The polymer was analyzed after being washed with MeOH/HCl.

The polymerizations with the cationic catalyst systems were carried out at −20 °C and 2.0 bar propylene pressure using triethylalumina (TEA) or triisobutylalumina (TIBA) as impurity scavenger and alkylating agent. The alkylated catalyst precursors were generated *in situ*. In a typical run 0.3 g of TEA was stirred with 50 mL of toluene followed by the addition of 5 μmol of the metallocene. The cation-forming agent (14 mmol) was added via a syringe. The polymerization was interrupted after 60 min by addition of EtOH. The polymer was analyzed after being washed with EtOH/HCl.

Ethylene Polymerization Procedures. The homo- and copolymerizations of ethylene were carried out in a 0.5-L stainless steel autoclave in 200 and 230 g of toluene, respectively. In a typical run, toluene and MAO were added to the reactor and stirred for 10 min in order to reduce any impurities in the reactor. In the copolymerizations, the comonomer was added batchwise after addition of the cocatalyst. Feeding of the ethylene was started, and the pressure was regulated to 2.5 bar. In the homopolymerizations 3.0 μmol, and in the copolymerizations 1.5 μmol, of the catalyst in toluene solution was pumped into the reactor to start the polymerization. The pressure was maintained by controlling the monomer feed. The polymerization was interrupted after 30 min by addition of EtOH. The polymer was analyzed after being washed with EtOH/HCl. The ethylene−1-hexadecene copolymers were further washed with acetone in order to remove the comonomer residuals.

Polymer Characterization. The melting temperatures and enthalpies of the polymers were determined using a Polymer Laboratories DSC instrument. The samples were heated twice (heating rate 10 °C/min), and the second heating curve was analyzed. The crystallinities were calculated from the heat of fusion using the equation $X_c = \Delta H_f/\Delta H_f^0$, where ΔH_f is the heat of fusion of the sample as determined from the DSC curve and ΔH_f^0 is the heat of fusion of folded-chain polyolefin crystals (293 J/g for PE[27] and 208 J/g for PP).[28] Molecular weights and molecular weight distributions were determined by gel permeation chromatography on a Waters 150-C ALC GPC instrument equipped with Waters Styragel or PL gel MIXEDB columns (exclusion limits for polystyrene 10^3, 10^4, and 10^6 Å) in 1,2,4-trichlorobenzene at 135 °C (flow rate 1 mL/min). The basic calibration was made by using polystyrene standards with narrow molecular weight distributions and the universal calibration using linear low-density polyethylene. Densities were determined according to the method D of ISO 1183 standard using a gradient column filled with water and EtOH at 23 °C. Quantitative ^{13}C NMR spectra of the polypropylene and ethylene−1-hexene copolymer samples were recorded from solutions of 70−90 mg of polymer in 0.4 mL of $C_2D_2Cl_4$ or 1,2,4-trichlorobenzene at 120 °C. The [*mmmm*] methyl signal of polypropylene was used as an internal standard and was given the chemical shift $\delta = 21.8$ ppm. The spectra were recorded using a 45° pulse by applying single pulse excitation with gated decoupling to suppress NOE. The spectral width was 8000 Hz, aquisition time 4 s, and pulse delay 8 s.

Acknowledgment. The authors thank the Finnish Technology Development Center (TEKES) for financial support and Mr. Markku Reunanen and Mrs. Päivi Pennanen for their assistance in characterizing the products, and Mrs. Outi Härkki for her help in the polymer analysis.

Supporting Information Available: Listings of crystal data and structure refinement, atomic coordinates, bond distances and angles, and thermal parameters and ORTEP views (5 pages). Ordering information is given on any current masthead page.

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(18) The activity of **1**/MAO decreases from 20 to 40 °C (2900 vs 1800 kg of PE/mol of Zr/h). The reason may originate from the mass transfer limitations of the polymerization system. The high-molecular-weight PE produced at 20 °C has a poor solubility in toluene and thus has no significant effect in the viscosity of the system. The PE produced 40 °C has a lower M_w and a higher solubility, which may increase the viscosity and decrease the diffusion rate of the monomer. The observations are in accordance with the rates of ethylene consumption at different polymerization temperatures. In the beginning of the polymerizations, the monomer consumption decreases with decreasing T_p (60 °C > 40 °C > 20 °C); however, after a few minutes the polymerization rate at 40 °C drops under the rate at 20 °C.

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MA970041O