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Reactivity of Zirconium Complexes Incorporating Asymmetrically Substituted *ansa* Ligands and Their Use as Catalysts in Olefin Polymerization. X-ray Crystal Structures of [$Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R)$]$ZrCl_2$ (R = Et, ^{i}Pr)

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The synthesis and use of the *ansa*-zirconocene complexes [$Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R)$]-$ZrCl_2$ (R = H (**5**), Me (**6**), Et (**7**), ^{i}Pr (**8**), ^{t}Bu (**9**), $SiMe_3$ (**10**)) as catalysts in the polymerization of ethylene and propylene has been studied. The alkyl complexes [$Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R)$]-$ZrMe_2$ (R = H (**11**), Me (**12**), Et (**13**), ^{i}Pr (**14**), ^{t}Bu (**15**), $SiMe_3$ (**16**)) have also been prepared. The reaction of **11**−**16** with $B(C_6F_5)_3$ gave the cationic species [{$Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R)$}-$ZrMe$]$^+$ (R = H (**17**), Me (**18**), Et (**19**), ^{i}Pr (**20**), ^{t}Bu (**21**), $SiMe_3$ (**22**)). In the absence of cocatalyst, **17**−**22** have been shown to act as catalysts in the polymerization of ethylene. The molecular structures of **7** and **8** have been determined by single-crystal X-ray diffraction studies.

Introduction

The use of *ansa*-cyclopentadienyl ligands has received wide attention in the chemistry of group 4 metals,[1] due mainly to their ability to impart to their complexes a selective degree of catalytic activity.[2] Recent studies have demonstrated that the incorporation of the *ansa* bridge may have a profound influence on the behavior of the metallocene system.[3] Furthermore, the use of substituted *ansa*-cyclopentadienyl ligands in the stereoselective synthesis of group 4 metal complexes and their importance in catalysis is receiving special attention.[4] Simple ligand design, as in $Me_2Si(C_5H_3Me\text{-}3)_2$, has been shown to lead to stereoselective catalysts, e.g. *rac*-[$Me_2Si(C_5H_3Me)_2$]$ZrCl_2$.[5] Some examples of asymmetric *ansa*-zirconocene complexes have been described,[6] although the great majority contain indenyl or fluorenyl systems.[7]

It has been shown that steric effects in the transition-metal catalyst greatly effect the polymerization of olefins and that bulky ligands, such as substituted *ansa* ligands, would therefore aid stereospecific olefin coor-

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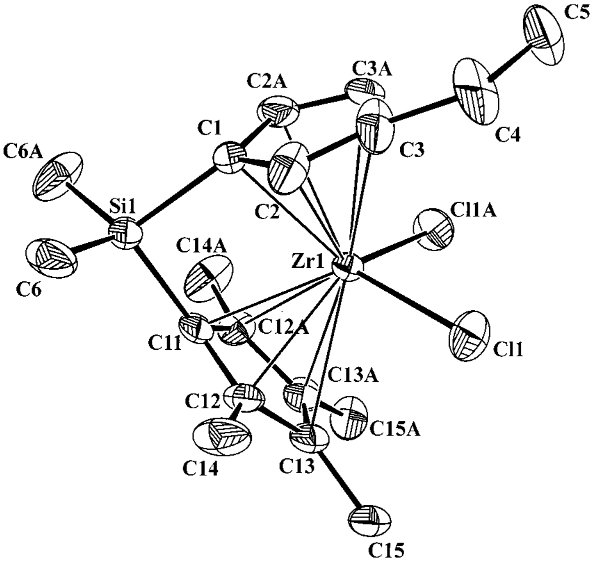

Figure 1. Molecular structure and atom-labeling scheme for $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Et)]ZrCl_2$ (**7**), with thermal ellipsoids at the 20% probability level.

dination and the stereoregularity of the polymers obtained using these metallocene catalysts.[8] In addition, the chiral nature of these ligands would also strongly influence stereoselectivity.[9] An extensive review regarding selectivity in propylene polymerization with metallocene catalysts has recently been published.[10]

We have previously described the preparation of niobocene complexes containing *ansa* ligands[11,12] and, following from this, the synthesis of niobium and zirconium systems with symmetrically and asymmetrically substituted *ansa* ligands.[12,13] As an extension of this work we report here, first, the synthesis, structure, and reactivity of other zirconocene complexes which incorporate *ansa* ligands with two distinctly substituted cyclopentadienyl rings and, second, the role as catalysts of these zirconocene species in the polymerization of ethylene and stereoselective polymerization of propylene.

Results and Discussion

The synthesis and characterization of $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R)]ZrCl_2$ (R = H (**5**), Me (**6**), ^{i}Pr (**8**), $SiMe_3$ (**10**)) have previously been described by us.[13] In addition we have prepared, in a similar manner, the *ansa* ligands $(C_5Me_4H)SiMe_2(C_5H_4R)$ (R = Et (**1**), ^{t}Bu (**2**)), their dilithium derivatives $[Me_2Si(C_5Me_4)(C_5H_3R)]Li_2$ (R = Et (**3**), ^{t}Bu (**4**)), and the *ansa*-zirconocene complexes $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R)]ZrCl_2$ (R = Et (**7**), ^{t}Bu (**9**)) (see Experimental Section for further details).

The molecular structures of **7** and **8** were established by X-ray crystal studies. The molecular structures and atomic numbering schemes are shown in Figures 1 and 2, respectively. Selected bond lengths and angles for **7** and **8** are given in Table 1.

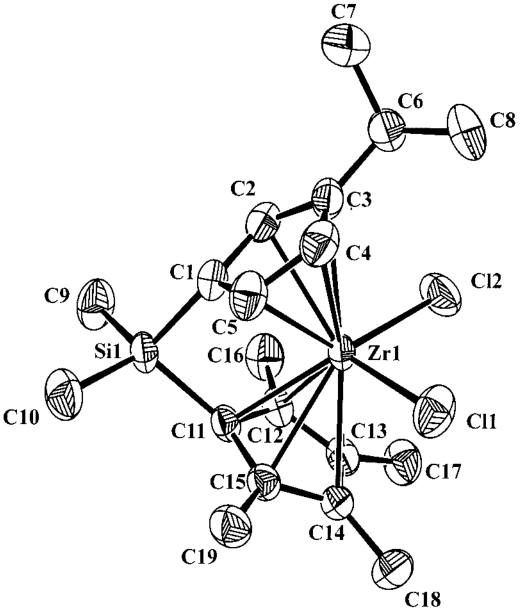

Figure 2. Molecular structure and atom-labeling scheme for $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3iPr)]ZrCl_2$ (**8**), with thermal ellipsoids at the 50% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 7 and 8

	7[a]	**8**[b]
Zr(1)−Cent(1)	2.214	2.223
Zr(1)−Cent(2)	2.207	2.230
av Zr(1)−C(Cent(1))[c]	2.504	2.529
av Zr(1)−C(Cent(2))[c]	2.514	2.531
Zr(1)−Cl(1)	2.429(4)	2.431(2)
Zr(1)−Cl(2)		2.426(2)
Cent(1)−Zr(1)−Cent(2)	126.5	126.9
Si(1)−C(1)−Cent(1)	162.7	162.8
Si(1)−C(11)−Cent(2)	165.1	163.3
C(1)−Si(1)−C(11)	93.3(7)	94.2(2)
Cl(1)−Zr(1)−Cent(1)	106.1	105.6
Cl(1)−Zr(1)−Cent(2)	107.4	107.2
Cl(2)−Zr(1)−Cent(1)		107.9
Cl(2)−Zr(1)−Cent(2)		107.3
Cl(1)−Zr(1)−Cl(1A)	100.4(2)	98.2(1)

[a] For **7**, Cent(1) and Cent(2) are the centroids of C(1)−C(3) and C(11)−C(13), respectively. [b] For **8**, Cent(1) and Cent(2) are the centroids of C(1)−C(5) and C(11)−C(15), respectively. [c] Refers to the average bond distance between Zr(1) and the carbon atoms of the C_5 ring of the corresponding cyclopentadienyl moiety.

The structures of **7** and **8** show the typical bent-metallocene conformation observed in zirconocene dichlorides. The *ansa* ligand chelates the zirconium atom, and both cyclopentadienyl rings are bound to the metal in an η^5 mode. A comparison of **7** and **8** with related zirconocene and *ansa*-zirconocene complexes is given in Table 2 and shows that the molecular structures of all these complexes are essentially the same. The Cent−Zr−Cent angles of **7** and **8** are of values between those of $[Me_2Si(\eta^5\text{-}C_5H_4)_2]ZrCl_2$ and $[Me_2Si(\eta^5\text{-}C_5Me_4)_2]ZrCl_2$ and less than that observed for the non-*ansa* complexes $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)ZrCl_2$ and $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ (see Table 2).

We have previously reported that **5**, **6**, **8**, and **10** are catalytically active in the polymerization of ethylene.[13]

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Table 2. Selected Structural Data of Zirconocene Complexes

complex	Zr−Cp (Å)[a]	Zr−Cl (Å)	Cp−Zr−Cp (deg)	Cl−Zr−Cl (deg)	C_{Cp}−Si−C_{Cp} (deg)	ref
$(\eta^5\text{-}C_5H_5)_2ZrCl_2$	2.21(1)	2.441(5)	129	97.1(2)		14
$(\eta^5\text{-}C_5H_4Me)_2ZrCl_2$	2.206(5)	2.443(1)	128.9(2)	95.10(5)		15
$(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)ZrCl_2$	2.209 (Cp) 2.219 (Cp*)	2.442	130.01	97.78		16
$[Me_2Si(\eta^5\text{-}C_5H_4)_2]ZrCl_2$	2.197(6)	2.452	125.4(3)	97.98(4)	93.2(2)	17
$[Me_2Si(\eta^5\text{-}C_5Me_4)_2]ZrCl_2$	2.329	2.4334(7)	128.6	92.28	95.7(1)	18
$[EtMeSi(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]ZrCl_2$	2.219(2) (Cp) 2.218(2) (Cp*)	2.4336(8)	126.70(4)	101.17(5)	93.82(14)	6d
$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]ZrCl_2$	2.198(4) (Cp*) 2.202(3) (Cp)	2.451(1)	128.10(2)	104.60(7)	95.2(2)	13
$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Me)]ZrCl_2$	2.184(6) (Cp*) 2.194(2) (Cp)	2.414(4)	126.25(6)	101.1(2)	93.1(8)	13
$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Et)]ZrCl_2$ (**7**)	2.207 (Cp*) 2.214 (Cp)	2.429(4)	126.5	100.4(2)	93.3(7)	this work
$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3{}^i\text{Pr})]ZrCl_2$ (**8**)	2.230 (Cp*) 2.223 (Cp)	2.431(2) 2.426(2)	126.90(6)	98.22(7)	94.2(2)	this work

[a] Cp refers to the C_5H_4 or C_5H_3R moiety; Cp* refers to the C_5Me_4 moiety.

Table 3. Ethylene Polymerization Results for $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R)]ZrCl_2$ (R = H (5), Me (6), Et (7), ^{i}Pr (8), ^{t}Bu (9), $SiMe_3$ (10)), $(\eta^5\text{-}C_5H_5)_2ZrCl_2$, and $[Me_2Si(\eta^5\text{-}C_5H_4)_2]ZrCl_2$[a]

catalyst	activity[b]	M_w	M_w/M_n
$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]ZrCl_2$ (**5**)	4500	174 000	4.8
$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Me)]ZrCl_2$ (**6**)	4333	178 000	5.2
$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Et)]ZrCl_2$ (**7**)	3700	248 000	9.6
$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3{}^i\text{Pr})]ZrCl_2$ (**8**)	4300	114 000	3.8
$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3{}^t\text{Bu})]ZrCl_2$ (**9**)	3460	119 500	7.7
$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3SiMe_3)]ZrCl_2$ (**10**)	3400	136 000	9.1
$(\eta^5\text{-}C_5H_5)_2ZrCl_2$	5000	281 000	8.3
$[Me_2Si(\eta^5\text{-}C_5H_4)_2]ZrCl_2$	4480	183 200	6.2

[a] Conditions: 25 °C, 1.5 bar of monomer pressure, 150 mL of toluene, $[MAO] = 2 \times 10^{-2}$ mol L^{-1}, $[Zr] = 4 \times 10^{-5}$ mol L^{-1}, t_{polymer} = 30 min. [b] In kg of polymer ((mol of Zr) h)$^{-1}$.

This initial study was carried out using a low MAO:Zr catalyst ratio of 125:1 and gave relatively poor catalytic activities and low polymer weights.[13] To improve these results, we have carried out the polymerization of ethylene by increasing the MAO/Zr catalyst ratio to 500:1, and in addition, we have included as catalysts compounds **7** and **9**, which were absent from the initial report. The polymerization experiments were carried out at 25 °C and at an olefin pressure of 1.5 bar over 30 min. The results of the experiments are given in Table 3.

Besides the electronic and steric influence of the silylene bridge itself, the linkage of the two cyclopentadienyl ligands changes the structure and energy of the metal orbitals and also the angle between the ring planes, with the latter factor influencing the space available for reactions at the metal center.[19] Differences in the relative activities in the process of ethylene polymerization should therefore be the consequence of changes in the metallocene complex geometry.

In all cases very much higher activities and polymer molecular weights were achieved when the polymerization of ethylene was carried using a MAO:Zr catalyst ratio of 500:1 instead of the ratio of 125:1 used in the previously described experiments.[13] This behavior is not unexpected, as MAO, in addition to its role as an alkylating agent, acts as a moisture scavenger and thus an increase in its concentration increases the efficiency of the metallocene catalyst.

In general, it was found that the catalytic activities of **5**−**10** were slightly lower than that recorded for $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ but comparable to that of the unsubstituted *ansa* complex $[Me_2Si(\eta^5\text{-}C_5H_4)_2]ZrCl_2$. This same trend was observed for the molecular weights of the polymers obtained. Molecular weight distributions recorded for **5**−**10**, $[Me_2Si(\eta^5\text{-}C_5H_4)_2]ZrCl_2$, and $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ were all of a high order (probably due to the experimental conditions employed in the polymerization process).

The asymmetric nature of the *ansa*-zirconocene complexes **5**−**10** (chiral in the cases **6**−**10**) should lead to the stereoselective polymerization of asymmetric olefins such as propylene. We have therefore tested **5**−**10** as catalysts in the polymerization of propylene. The experiments were carried out at 25 °C in the presence of the zirconium complex and MAO cocatalyst (ratio 1:1000) and at an olefin pressure of 2 bar during 30 min. The results of the experiments are given in Table 4.

The catalytic activities for **5**−**10** were lower than those recorded for $[Me_2Si(\eta^5\text{-}C_5H_4)_2]ZrCl_2$ and $(\eta^5\text{-}C_5H_5)_2ZrCl_2$, although in the case of **8** this value was comparable. Polymer molecular weights obtained were all similar to those achieved for $[Me_2Si(\eta^5\text{-}C_5H_4)_2]ZrCl_2$ and $(\eta^5\text{-}C_5H_5)_2ZrCl_2$. In the case of **8** the highest polymer molecular weight was recorded; however, it also gave the highest molecular weight distribution. In general the asymmetric *ansa*-metallocene catalysts gave polymer molecular weight distribution values comparable to those recorded for $[Me_2Si(\eta^5\text{-}C_5H_4)_2]ZrCl_2$ and $(\eta^5\text{-}C_5H_5)_2ZrCl_2$.

For **5** the C_s symmetry should make the metallocene catalyst syndiospecific in the polymerization of propylene. However, Morokuma and co-workers have predicted, via theoretical studies, that catalytic systems based on the C_s symmetric $H_2Si(C_5Me_4)(C_5H_4)$ ligand will be substantially non enantioselective, due to repulsive interactions between the methyl group of the

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Table 4. Propylene Polymerization Results for $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R)]ZrCl_2$ (R = H (5), Me (6), Et (7), ^{i}Pr (8), ^{t}Bu (9), $SiMe_3$ (10)), $(\eta^5\text{-}C_5H_5)_2ZrCl_2$, and $[Me_2Si(\eta^5\text{-}C_5H_4)_2]ZrCl_2$[a]

catalyst	activity[b]	M_w	M_w/M_n	[*mmmm*] (%)	mp (°C)
$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]ZrCl_2$ (**5**)	3100	201 300	13.9	*c*	107
$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Me)]ZrCl_2$ (**6**)	4120	188 300	10.8	*c*	110
$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Et)]ZrCl_2$ (**7**)	3333	215 000	12.6	85	153
$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3{}^iPr)]ZrCl_2$ (**8**)	4812	238 000	20.3	88	145
$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3{}^tBu)]ZrCl_2$ (**9**)	2333	191 100	14.1	87	155
$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3SiMe_3)]ZrCl_2$ (**10**)	4323	171 100	15.0	84	143
$(\eta^5\text{-}C_5H_5)_2ZrCl_2$	4920	205 200	13.1	*c*	30
$[Me_2Si(\eta^5\text{-}C_5H_4)_2]ZrCl_2$	4915	183 000	12.2	*c*	30

[a] Conditions: 25 °C, 2.0 bar of monomer pressure, 150 mL of toluene, [MAO] = 4×10^{-2} mol L^{-1}, [Zr] = 4×10^{-5} mol L^{-1}, $t_{polymer}$ = 30 min. [b] In kg of polymer ((mol of Zr) h)$^{-1}$. [c] ^{13}C NMR spectra showed essentially atactic polymers.

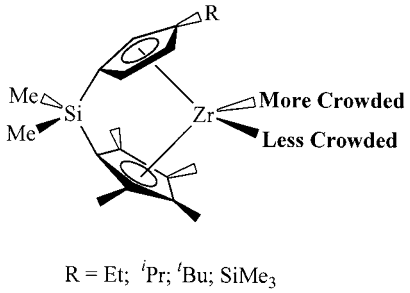

Figure 3. Steric conditions in the metallocene catalyst.

propylene and the methyl groups of the C_5Me_4 ligand.[20] Our results concur with this affirmation, with the polypropylene obtained using **5** as catalyst being of low stereospecificity (as observed by ^{13}C NMR spectroscopy of the polymer). This is in agreement with a previous study conducted on this metallocene complex, where this phenomenon was explained by the assumption that the polymer chain experiences counterbalanced steric forces exerted by the monomer methyl group on one hand and from the β-methyl cyclopentadienyl (C_5*Me*$_4$) substituents on the other.[21]

The zirconocene complexes **6**−**10** exhibit C_1 symmetry. The stereospecificity of the polypropylene obtained when using **6**−**10** as catalysts is directly related to the β-alkyl cyclopentadienyl (C_5H_3*R*) substituent. In C_1 symmetric catalysts the two available coordination positions are nonequivalent. In this case, the stereoselectivity of the catalytic systems depends on the energy difference between structures corresponding to propylene coordination on the two nonequivalent, more and less crowded, coordination sites (see Figure 3).

If we assume that a chain migratory insertion mechanism is taking place and that the two coordination positions are of similar energy, then these catalysts will be isospecific or syndiospecific if propylene coordination at the two coordination positions are enantioselective in favor of the same or opposite propylene enantiofaces, respectively. If propylene coordination is enantioselective in only one of the coordination positions, then the corresponding catalytic system will be *hemi*-isospecific.

If the two coordination positions have distinct energies, a different scenario can be proposed. According to Morokuma, the presence of a bulky alkyl cyclopentadienyl β-substituent forbids the growing polymer chain to be located in the more crowded position. In particular, in the absence of monomer molecule, as probably occurs at the end of each insertion step, the steric pressure of the ligand skeleton may force the growing chain to skip back to the less crowded position. Hence, insertion always occurs with the same relative disposition of the monomer and the growing polymer chain and thus leads to an isospecific polymer (see Figure 4).[20] An example of this back-skip mechanism in the polymerization of propylene has recently been reported.[22]

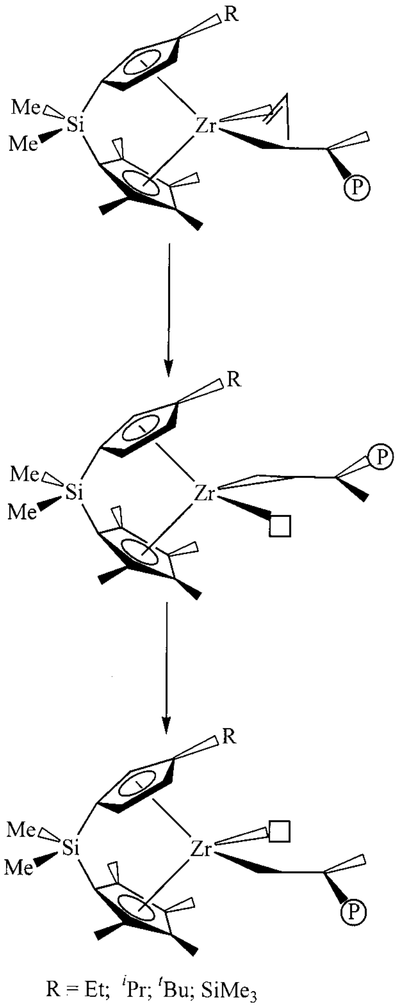

Figure 4. Proposed polymer chain back skip mechanism in the *ansa*-zirconocene complexes **7**−**10**.

In the case of $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Me)]ZrCl_2$ (**6**) the catalyst is only enantioselective in one of the two coordination positions, due to the fact that the β-alkyl

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(20) Kawamura-Kuribayashi, H.; Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1992**, *114*, 8687.

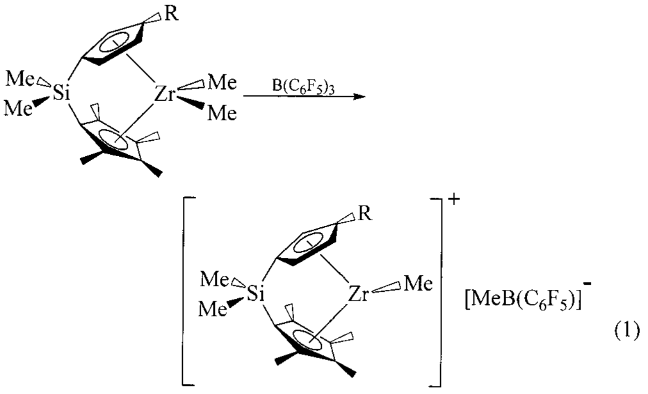
(21) Ewen, J. A.; Elder, M. J.; Jones, R. L.; Haspeslagh, L.; Atwood, J. L.; Bott, S. G.; Robinson, K. *Makromol. Chem., Macromol. Symp.* **1991**, *48*/*49*, 253.

(22) Kukral, J.; Lehmus, P.; Feifel, T.; Troll, C.; Rieger, B. *Organometallics* **2000**, *19*, 3767.

cyclopentadienyl substituents oriented toward the more crowded position are both identically sized methyl groups. **6** should therefore produce hemi-isotactic polypropylene. However, we were unable to verify this, as the ^{13}C NMR spectrum of the polymer was complicated by the high atactic nature of these types of plastics. When the alkyl group of the monosubstituted cyclopentadienyl moiety is larger than methyl, as in the case of **7**−**10**, the catalysts produce isotactic polymers. This was confirmed by characterizing the polymers formed by ^{13}C NMR spectroscopy. This technique also permitted us to measure the level of isotacticty (% mmmm) of the plastic (see Table 4).

The alkyl derivatives [$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_3R)$]$ZrMe_2$ (R = H (**11**), Me (**12**), Et (**13**), ^{i}Pr (**14**), ^{t}Bu (**15**), $SiMe_3$ (**16**)) were prepared via the reaction of 2 equiv of the Grignard reagent MeMgCl with the corresponding dihalide *ansa*-zirconocene complexes **5**−**10**. **11**−**16** were characterized by spectroscopic methods (see Experimental Section). The difference in symmetry of **11** (C_s) with regard to **12**−**16** (C_1) is clearly observed in NMR spectroscopy. In **11** only one signal was recorded for the two metal−methyl groups in both ^{1}H and ^{13}C NMR spectroscopy. However, for **12**−**16** two signals were recorded, confirming the inequivalency of the two alkyl groups.

The reaction of **11**−**16** with $B(C_6F_5)_3$ gave the cationic species [{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_3R)$}ZrMe]$^+$ (R = H (**17**), Me (**18**), Et (**19**), ^{i}Pr (**20**), ^{t}Bu (**21**), $SiMe_3$ (**22**)), with $MeB(C_6F_5)_3$ as the counteranion (see eq 1). **17**−**22** were characterized by ^{1}H NMR spectroscopy. This revealed the disappearance of one methyl peak and a shifting of the remaining peak resonances. The Me−B signal is generally difficult to observe, due to the relaxation time of the boron nucleus.

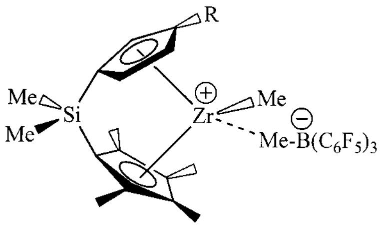


(1)

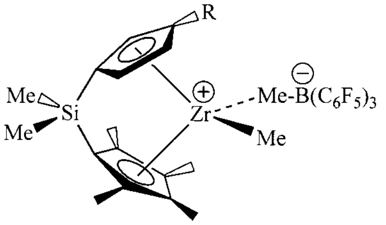
R = H (**17**), Me (**18**), Et (**19**),
^{i}Pr (**20**); ^{t}Bu (**21**), $SiMe_3$ (**22**)

In the case of **17** the symmetry of the molecule changes from C_s to C_1 and the lack of symmetry leads to four multiplets being observed for the cyclopentadienyl ring protons in the ^{1}H NMR spectrum.

There are two possible isomers for **18**−**22** (Figure 5). For isomer A the metal−methyl group is positioned below the β-substituent of the monosubstituted cyclopentadienyl moiety. In isomer B the β-substituent of the monosubstituted cyclopentadienyl ligand situates itself above the boron-coordinated methyl group. ^{1}H NMR spectroscopy revealed in all cases the presence of only one of the possible isomers, and it appears likely that this isomer corresponds to A on the grounds of steric effects.



Structure A



Structure B

Figure 5. Two possible isomers for [{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_3R)$}ZrMe][$MeB(C_6F_5)_3$] (R = Me (**18**), Et (**19**), ^{i}Pr (**20**), ^{t}Bu (**21**), $SiMe_3$ (**22**)).

Table 5. Ethylene Polymerization Results for [{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_3R)$}ZrMe][$MeB(C_6F_5)_3$] (R = H (17), Me (18), Et (19), ^{i}Pr (20), ^{t}Bu (21), $SiMe_3$ (22)), [$(\eta^5$-$C_5H_5)_2$ZrMe][$MeB(C_6F_5)_3$], and [{$Me_2Si(\eta^5$-$C_5H_4)_2$}ZrMe][$MeB(C_6F_5)_3$]^a

catalyst	activity^b	M_w	M_w/M_n
[{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_4)$}ZrMe]$^+$ (**17**)	1520	245 100	13.3
[{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_3Me)$}ZrMe]$^+$ (**18**)	1215	183 200	14.2
[{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_3Et)$}ZrMe]$^+$ (**19**)	1613	166 300	9.4
[{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_3{}^iPr)$}ZrMe]$^+$ (**20**)	1288	125 000	8.7
[{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_3{}^tBu)$}ZrMe]$^+$ (**21**)	1183	171 200	8.5
[{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_3SiMe_3)$}ZrMe]$^+$ (**22**)	1172	197 000	8.3
[$(\eta^5$-$C_5H_5)_2$ZrMe]$^+$	2012	89 000	5.2
[{$Me_2Si(\eta^5$-$C_5H_4)_2$}ZrMe]$^+$	1912	193 000	7.4

^{a} Conditions: 25 °C, 1.5 bar of monomer pressure, 250 mL of toluene, [Zr] = 1.5×10^{-5} mol L^{-1}, [TIBA] = 8×10^{-3} mol L^{-1}, $t_{polymer}$ = 30 min. ^{b} In kg of polymer ((mol of Zr) h)$^{-1}$.

The use of the cationic species as a catalyst without the need of cocatalysts such as MAO has been previously reported.[21] Complexes **17**−**22** also proved to be catalytically active in the polymerization of ethylene (see Table 5). The activities obtained were slightly lower than that for [$(\eta^5$-$C_5H_5)_2$ZrMe][$MeB(C_6F_5)_3$] under the same conditions and overall much lower than those obtained with the parent dichloro complexes and MAO.

Conclusions

We have prepared new *ansa*-zirconocene complexes, two of which have been characterized by single-crystal X-ray diffraction studies. We have tested *ansa*-zirconocene complexes with asymmetrically substituted cyclopentadienyl rings as catalysts in the polymerization of olefins. We have found in the case of ethylene that the catalytic activities are high, although a little lower than for $(\eta^5\text{-}C_5H_5)_2ZrCl_2$. For propylene it has been shown that changing the β-substituent of the cyclopentadienyl moiety has a marked influence on the stereospecificity of the polymerization. We have also shown that the cationic *ansa*-zirconocene species in the absence of cocatalyst are catalytically active in the polymerization of ethylene.

Experimental Section

General Procedures. All reactions were performed using standard Schlenk tube techniques under an atmosphere of dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use.

$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R)]ZrCl_2$ (R = H (**5**), Me (**6**), ^{i}Pr (**8**), $SiMe_3$ (**10**)) were prepared as described earlier.[13] MeMgCl, $Mg(C_5H_4Et)_2$, $Li(C_5H_4tBu)$, $ZrCl_4$, $ClMe_2Si(C_5Me_4H)$, and $B(C_6F_5)_3$ were purchased from Aldrich and used directly. ^1H and ^{13}C spectra were recorded on a Varian FT-300 spectrometer and referenced to the residual deuterated solvent. Microanalyses were carried out with a Perkin-Elmer 2400 microanalyzer. Mass spectroscopic analyses were preformed on a VG Autospec instrument or a Hewlett-Packard 5988A (*m/z* 50−1000) (electron impact). Polymer isotacticity was calculated from ^{13}C NMR spectra of polymer samples dissolved in 1,2,4-trichlorobenzene and C_6D_6 (1:1). Polymer molecular weights were determined by GPC in $o\text{-}C_6H_4Cl_2$ at 135 °C.

$(C_5Me_4H)SiMe_2(C_5H_4Et)$ (1). $ClMe_2Si(C_5Me_4H)$ (2.50 g, 11.64 mmol) in THF (50 mL) was added to a solution of $Mg(C_5H_4Et)_2$ (1.23 g, 5.82 mmol) in THF (50 mL) at −78 °C. The reaction mixture was warmed to room temperature and stirred for 15 h. Solvent was removed in vacuo, and hexane (150 mL) was added to the resulting orange oil. The mixture was filtered and solvent removed from the filtrate under reduced pressure to yield the title compound as a dark orange oil (3.01 g, 95%). ^1H NMR (300 MHz, C_6D_6; for the predominant isomer): δ −0.20 (s, 6H, $SiMe_2$), 1.12 (m, 3H, CH_2CH_3), 1.78 (6H), 1.90 (6H) (s, C_5Me_4), 2.37 (m, 2H, CH_2CH_3), 2.74 (1H), 3.30 (1H) (m, HC_5), 6.02 (1H), 6.36 (1H), 6.51 (1H) (m, C_5H_3). MS electron impact (*m/e* (relative intensity)): 272 (85) (M^+, $(C_5Me_4H)SiMe_2(C_5H_4Et)^+$), 257 (100) ($M^+ - Me$), 179 (75) ($M^+ - C_5H_4Et$), 151 (72) ($M^+ - C_5Me_4H$).

$(C_5Me_4H)SiMe_2(C_5H_4{}^tBu)$ (2). The preparation of **2** was carried out in a manner identical with that for **1**, using $ClMe_2Si(C_5Me_4H)$ (2.50 g, 11.64 mmol) and $Li(C_5H_4{}^tBu)$ (1.49 g, 11.64 mmol). Yield: 3.35 g, 96%. ^1H NMR (300 MHz, C_6D_6; for the predominant isomer): δ −0.20 (s, 6H, $SiMe_2$), 1.20 (s, 9H, $C_5H_3{}^tBu$), 1.79 (6H), 1.90 (6H) (s, C_5Me_4), 2.86 (1H), 3.26 (1H) (m, HC_5), 6.00 (1H), 6.36 (1H), 6.64 (1H) (m, C_5H_3). MS electron impact (*m/e* (relative intensity)): 300 (13) (M^+, $(C_5Me_4H)SiMe_2(C_5H_4{}^tBu)^+$), 285 (15) ($M^+ - Me$), 179 (100) ($M^+ - C_5H_4Me$).

$[Me_2Si(C_5Me_4)(C_5H_3Et)]Li_2$ (3). ^{n}BuLi (1.6 M in hexane) (13.8 mL, 22.10 mmol) was added via syringe to a solution of **1** (3.01 g, 11.05 mmol) in Et_2O (50 mL) at −78 °C. The mixture was warmed to 25 °C and stirred for 15 h. Solvent was removed in vacuo to give a white solid, which was washed with hexane (2 × 50 mL) and dried under vacuum to yield a free-flowing white solid of the title complex (2.76 g, 88%). Anal. Calcd for $C_{18}H_{26}Li_2Si$: C, 76.03; H, 9.22. Found: C, 75.76; H, 9.11.

$[Me_2Si(C_5Me_4)(C_5H_3{}^tBu)]Li_2$ (4). The preparation of **4** was carried out in a manner identical with that for **3**, using **2** (3.35 g, 11.14 mmol) and ^{n}BuLi (1.6 M in hexane) (13.9 mL, 22.28 mmol). Yield: 2.82 g, 81%. Anal. Calcd for $C_{20}H_{30}Li_2Si$: C, 76.89; H, 9.68. Found: C, 76.71; H, 9.66.

$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Et)]ZrCl_2$ (7). THF (50 mL) was added to a solid mixture of $ZrCl_4$ (1.00 g, 4.29 mmol) and $[Me_2Si(C_5Me_4)(C_5H_3Et)]Li_2$ (**3**; 1.22 g, 4.29 mmol). The resulting pale yellow solution was stirred for 15 h. Solvent was removed in vacuo and toluene added (75 mL) to the resulting solid. The mixture was filtered and the filtrate concentrated (10 mL) and cooled to −30 °C to yield white crystals of the title complex (0.89 g, 48%). ^1H NMR (300 MHz, C_6D_6): δ 0.33 (3H), 0.36 (3H) (s, $SiMe_2$), 1.14 (m, 3H, CH_2CH_3), 1.61 (3H), 1.69 (3H), 1.97 (3H), 1.99 (3H) (s, C_5Me_4), 2.68 (1H), 2.82 (1H) (m, CH_2CH_3), 5.06 (1H), 5.37 (1H), 6.67 (1H) (m, C_5H_4). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ −0.6, −0.5 ($SiMe_2$), 12.3, 12.4, 14.9, 15.0 (C_5Me_4), 14.1 (CH_2CH_3), 23.4 (CH_2CH_3), 96.9 (C^{ipso}), 105.7 (C^{ipso}), 112.0, 113.2, 125.6 (C_5H_4), 124.9, 125.0, 135.2, 135.3, 143.8 (C_5Me_4). Anal. Calcd for $C_{18}H_{26}Cl_2SiZr$: C, 49.97; H, 6.06. Found: C, 49.79; H, 6.00.

$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3tBu)]ZrCl_2$ (9). The synthesis of **9** was carried out in a manner identical with that for **7**, using $ZrCl_4$ (1.12 g, 4.80 mmol) and $[Me_2Si(C_5Me_4)(C_5H_3tBu)]Li_2$ (**4**; 1.50 g, 4.80 mmol). Yield: 1.04 g, 47%. ^1H NMR (300 MHz, C_6D_6): δ 0.34 (3H), 0.38 (3H) (s, $SiMe_2$), 1.42 (s, 9H, ^{t}Bu), 1.68 (3H), 1.69 (3H), 1.93 (3H), 1.94 (3H) (s, C_5Me_4), 5.43 (1H), 5.52 (1H), 6.86 (1H) (m, C_5H_3). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ −1.0, −0.2 ($SiMe_2$), 12.2, 12.4, 15.0, 15.1 (C_5Me_4), 30.8 (CMe_3), 33.7 (CMe_3), 97.6 (C^{ipso}), 104.5 (C^{ipso}), 110.2, 113.7, 126.5 (C_5H_3), 123.8, 125.6, 129.2, 135.0, 151.4 (C_5Me_4). Anal. Calcd for $C_{20}H_{30}Cl_2SiZr$: C, 52.14; H, 6.56. Found: C, 51.98; H, 6.52.

$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]ZrMe_2$ (11). A 3 M solution of ClMgMe in THF (0.66 mL, 1.98 mmol) was added to a stirred solution of $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]ZrCl_2$ (**5**; 0.40 g, 0.99 mmol) in THF (25 mL) at −78 °C. The solution was warmed to room temperature and stirred for 4 h. Solvent was removed in vacuo and the remaining solid extracted in hexane (30 mL). A white crystalline solid was obtained by concentrating (5 mL) and cooling (−30 °C) the solution (0.27 g, 75%). ^1H NMR (300 MHz, C_6D_6): δ −0.32 (s, 6H, CH_3), 0.31 (6H, s, $SiMe_2$), 1.58 (6H), 1.89 (6H) (s, C_5Me_4), 5.27 (2H), 6.77 (2H) (m, C_5H_4). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ −0.4 ($SiMe_2$), 11.6, 14.4 (C_5Me_4), 31.8 (CH_3), 100.0 (C^{ipso}), 111.7, 120.2 (C_5H_3), 121.9, 122.4, 126.7 (C_5Me_4). Anal. Calcd for $C_{18}H_{28}ZrSi$: C, 59.44; H, 7.76. Found: C, 59.27; H, 7.73.

$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Me)]ZrMe_2$ (12). The synthesis of **12** was carried out in a manner identical with that for **11**, using a 3 M solution of MgMeCl in THF (0.67 mL, 2.00 mmol) and $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Me)]ZrCl_2$ (**6**; 0.42 g, 1.00 mmol). Yield: 0.22 g, 76%. ^1H NMR (300 MHz, C_6D_6): δ −0.44 (3H), −0.34 (3H) (s, CH_3), 0.32 (3H), 0.33 (3H) (s, $SiMe_2$), 1.55 (3H), 1.64 (3H), 1.91 (3H), 1.92 (3H) (s, C_5Me_4), 2.20 (s, 3H, C_5H_3Me), 4.97 (1H), 5.25 (1H), 6.47 (1H) (m, C_5H_3). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ −0.3, −0.2 ($SiMe_2$), 11.6, 11.7, 14.3, 14.5, 15.0 (C_5Me_4, C_5H_3Me), 31.0, 35.5 (CH_3), 99.1 (C^{ipso}), 111.1 (C^{ipso}), 112.3, 112.5, 120.9 (C_5H_3), 122.4, 124.5, 125.2, 126.5, 129.6 (C_5Me_4). Anal. Calcd for $C_{19}H_{30}SiZr$: C, 60.41; H, 8.00. Found: C, 60.19; H, 7.90.

$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Et)]ZrMe_2$ (13). The synthesis of **13** was carried out in a manner identical with that for **11**, using a 3 M solution of MgMeCl in THF (0.59 mL, 1.76 mmol) and $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Et)]ZrCl_2$ (**7**; 0.38 g, 0.88 mmol). Yield: 0.28 g, 79%. ^1H NMR (300 MHz, C_6D_6): δ −0.44 (3H), −0.33 (3H) (s, CH_3), 0.33 (3H), 0.35 (3H) (s, $SiMe_2$), 1.20 (m, 3H, CH_2CH_3), 1.58 (3H), 1.65 (3H), 1.92 (3H), 1.93 (3H) (s, C_5Me_4), 2.63 (m, 2H, CH_2CH_3), 5.06 (1H), 5.27 (1H), 6.56 (1H) (m, C_5H_4). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ −0.3, −0.2 ($SiMe_2$), 11.6, 11.7, 14.4, 14.5 (C_5Me_4), 15.4 (CH_2CH_3), 23.2 (CH_2CH_3), 31.3, 34.9 (CH_3), 99.1 (C^{ipso}), 106.5 (C^{ipso}), 111.1, 112.2, 119.4 (C_5H_4), 122.2, 126.8, 128.8, 136.4, 143.1 (C_5Me_4). Anal. Calcd for $C_{20}H_{32}SiZr$: C, 61.31; H, 8.23. Found: C, 61.22; H, 8.24.

$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3{}^iPr)]ZrMe_2$ (14). The synthesis of **14** was carried out in a manner identical with that for **11**, using a 3 M solution of MgMeCl in THF (0.60 mL, 1.80 mmol) and $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3iPr)]ZrCl_2$ (**8**; 0.40 g, 0.90 mmol). Yield: 0.26 g, 72%. ^1H NMR (300 MHz, C_6D_6): δ −0.40 (3H), −0.31 (3H) (s, CH_3), 0.32 (3H), 0.36 (3H) (s, $SiMe_2$), 1.21 (3H), 1.31 (3H) (d, $HCMe_2$) ($^3J(^1H-^1H)$ 6.8 Hz), 1.60 (3H), 1.65 (3H), 1.92 (3H), 1.94 (3H), (s, C_5Me_4), 3.06 (sep, 1H, $HCMe_2$), 5.16

(1H), 5.25 (1H), 6.65 (1H) (m, C_5H_3). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ −0.4, −0.1 (Si*Me*$_2$), 11.6, 11.7, 14.4, 14.5 (C_5Me_4), 22.4, 25.5 (HC*Me*$_2$), 28.6 (H*C*Me$_2$), 31.4, 34.6 (CH_3), 91.4 (C^{ipso}), 98.9 (C^{ipso}), 110.2, 111.6, 117.9 (C_5H_3), 121.9, 122.5, 126.8, 129.0, 141.5 (C_5Me_4). Anal. Calcd for $C_{21}H_{34}SiZr$: C, 62.15; H, 8.44. Found: C, 62.00; H, 8.38.

[Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$^{t}Bu)]ZrMe$_2$ (15). The synthesis of **15** was carried out in a manner identical with that for **11**, using a 3 M solution of MgMeCl in THF (0.54 mL, 1.60 mmol) and [Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$*t*Bu)]ZrCl$_2$ (**9**; 0.38 g, 0.80 mmol). Yield: 0.24 g, 72%. ^1H NMR (300 MHz, C_6D_6): δ −0.28 (3H), −0.27 (3H) (s, CH_3), 0.34 (3H), 0.37 (3H) (s, Si*Me*$_2$), 1.38 (s, 9H, ^{t}Bu), 1.64 (3H), 1.65 (3H), 1.87 (3H), 1.89 (3H) (s, C_5Me_4), 5.27 (1H), 5.46 (1H), 6.72 (1H) (m, C_5H_3). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ −0.6, 0.2 (Si*Me*$_2$), 11.6, 11.7, 14.5, 14.6 (C_5Me_4), 31.3 (C*Me*$_3$), 33.5 (*C*Me$_3$), 31.8, 33.4 (CH_3), 92.0 (C^{ipso}), 98.4 (C^{ipso}), 108.7, 112.6, 118.9 (C_5H_3), 121.5, 123.1, 127.0, 145.7, 148.6 (C_5Me_4). Anal. Calcd for $C_{22}H_{36}SiZr$: C, 62.94; H, 8.64. Found: C, 62.69; H, 8.55.

[Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$SiMe$_3$)]ZrMe$_2$ (16). The synthesis of **16** was carried out in a manner identical with that for **11**, using a 3 M solution of MgMeCl in THF (0.56 mL, 1.68 mmol) and [Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$SiMe$_3$)]ZrCl$_2$ (**10**; 0.40 g, 0.84 mmol). Yield: 0.30 g, 81%. ^1H NMR (300 MHz, C_6D_6): δ −0.31 (s, 6H, CH_3), 0.35 (3H), 0.38 (3H) (s, Si*Me*$_2$), 0.36 (s, 9H, Si*Me*$_3$), 1.62 (3H), 1.63 (3H), 1.85 (3H), 1.87 (3H) (s, C_5Me_4), 5.46 (1H), 5.66 (1H), 6.96 (1H) (m, C_5H_3). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ −0.6, 0.2 (Si*Me*$_2$), 0.0 (Si*Me*$_3$), 11.6, 11.7, 14.5, 14.6 (C_5Me_4), 32.0, 32.6 (CH_3), 92.1 (C^{ipso}), 103.8 (C^{ipso}), 115.7, 117.5, 127.3 (C_5H_3), 121.4, 123.0, 127.0, 127.1, 127.2 (C_5Me$_4$). Anal. Calcd for $C_{21}H_{36}Si_2Zr$: C, 57.86; H, 8.32. Found: C, 57.61; H, 8.21.

[{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}ZrMe][MeB(C$_6$F$_5$)$_3$] (17). A solution of B(C$_6$F$_5$)$_3$ (0.28 g, 0.55 mmol) in toluene (25 mL) was added to a stirred solution of **11** (0.20 g, 0.55 mmol) in toluene (25 mL) at −78 °C. The mixture was warmed to room temperature and stirred for 30 min. Solvent was removed in vacuo to give a red oil, which was identified as the title complex. ^1H NMR (300 MHz, $C_6D_5CD_3$): δ 0.21 (s, 3H, CH_3), 0.06 (3H), 0.18 (3H) (s, Si*Me*$_2$), 1.14 (3H), 1.29 (3H), 1.48 (3H), 1.68 (3H) (s, C_5Me_4), 4.59 (1H), 5.26 (1H), 6.27 (1H), 6.53 (1H) (m, C_5H_4).

[{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$Me)}ZrMe][MeB(C$_6$F$_5$)$_3$] (18). The synthesis of **18** was carried out in a manner identical with that for **17**, using B(C$_6$F$_5$)$_3$ (0.27 g, 0.53 mmol) and **12** (0.20 g, 0.53 mmol). ^1H NMR (300 MHz, $C_6D_5CD_3$): δ 0.18 (s, 3H, CH_3), 0.08 (3H), 0.12 (3H) (s, Si*Me*$_2$), 1.11 (3H), 1.30 (3H), 1.50 (3H), 1.72 (3H) (s, C_5Me_4), 2.09 (s, 3H, C$_5$H$_3$*Me*), 4.33 (1H), 5.28 (1H), 6.00 (1H) (m, C_5H_3).

[{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$Et)}ZrMe][MeB(C$_6$F$_5$)$_3$] (19). The synthesis of **19** was carried out in a manner identical with that for **17**, using B(C$_6$F$_5$)$_3$ (0.24 g, 0.47 mmol) and **13** (0.20 g, 0.47 mmol). ^1H NMR (300 MHz, $C_6D_5CD_3$): δ 0.22 (s, 3H, CH_3), 0.03 (3H), 0.08 (3H) (s, Si*Me*$_2$), 0.97 (m, 3H, CH$_2$C*H*$_3$), 1.09 (3H), 1.30 (3H), 1.47 (3H), 1.69 (3H) (s, C_5Me_4), 2.32 (1H), 2.45 (1H) (m, C*H*$_2$CH$_3$), 4.40 (1H), 5.29 (1H), 6.02 (1H) (m, C_5H_4).

[{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$*i*Pr)}ZrMe][MeB(C$_6$F$_5$)$_3$] (20). The synthesis of **20** was carried out in a manner identical with that for **17**, using B(C$_6$F$_5$)$_3$ (0.25 g, 0.49 mmol) and **14** (0.20 g, 0.49 mmol). ^1H NMR (300 MHz, $C_6D_5CD_3$): δ 0.23 (s, 3H, CH_3), 0.02 (3H), 0.05 (3H) (s, Si*Me*$_2$), 0.91 (3H), 0.97 (3H) (d, HC*Me*$_2$) ($^3J(^1H-^1H) = 6.7$ Hz), 1.09 (3H), 1.39 (3H), 1.49 (3H), 1.69 (3H) (s, C_5Me_4), 2.70 (sep, 1H, *H*CMe$_2$), 4.51 (1H), 5.34 (1H), 6.11 (1H) (m, C_5H_3).

[{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$*t*Bu)}ZrMe][MeB(C$_6$F$_5$)$_3$] (21). The synthesis of **21** was carried out in a manner identical with that for **17**, using B(C$_6$F$_5$)$_3$ (0.24 g, 0.48 mmol) and **13** (0.20 g, 0.48 mmol). ^1H NMR (300 MHz, $C_6D_5CD_3$): δ 0.30 (s, 3H, CH_3), 0.09 (3H), 0.29 (3H) (s, Si*Me*$_2$), 1.07 (s, 9H, ^{t}Bu), 1.23 (3H), 1.47 (3H), 1.59 (3H), 1.74 (3H) (s, C_5Me_4), 5.01 (1H), 5.44 (1H), 6.15 (1H) (m, C_5H_3).

Table 6. Crystal Data and Structure Refinement Details for 7 and 8

	7	**8**
formula	$C_{18}H_{28}Cl_2SiZr$	$C_{19}H_{28}Cl_2SiZr$
fw	218.79	446.62
T (K)	293(2)	250(2)
cryst syst	orthorhombic	monoclinic
space group	*Pnma*	$P2_1/n$
a (Å)	10.997(2)	9.799(6)
b (Å)	13.416(2)	13.677(1)
c (Å)	13.218(1)	15.625(3)
β (deg)		102.244(9)
V (Å^3)	1950.1(3)	2046.4(13)
Z	8	4
D_c (g cm^{-3})	1.470	1.450
μ (mm^{-1})	0.894	0.855
F(000)	884	920
cryst dimens (mm)	0.4 × 0.3 × 0.2	0.3 × 0.3 × 0.2
θ range (deg)	2.16−24.97	2.26−28.00
hkl ranges	$0 \le h \le 13$, $0 \le k \le 5$, $0 \le l \le 15$	$-12 \le h \le 12$, $0 \le k \le 18$, $0 \le l \le 20$
no. of data/params	1793/112	4918/208
goodness of fit on F^2	1.191	1.109
final R indices ($I > 2\sigma(I)$)^a	R1 = 0.0960 wR2 = 0.2981	R1 = 0.0549 wR2 = 0.1429
largest diff peak (e Å^{-3})	1.798/−1.295	1.661/−1.01

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$.

[{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$SiMe$_3$)}ZrMe][MeB(C$_6$F$_5$)$_3$] (22). The synthesis of **22** was carried out in a manner identical with that for **17**, using B(C$_6$F$_5$)$_3$ (0.23 g, 0.46 mmol) and **16** (0.20 g, 0.46 mmol). ^1H NMR (300 MHz, $C_6D_5CD_3$): δ 0.09 (s, 3H, CH_3), 0.10 (s, 9H, SiMe$_3$), 0.25 (3H), 0.29 (3H) (s, Si*Me*$_2$), 1.20 (3H), 1.45 (3H), 1.57 (3H), 1.71 (3H) (s, C_5Me_4), 5.17 (1H), 5.61 (1H), 6.42 (1H) (m, C_5H_3).

Polymerization of Ethylene with 5−10. The *ansa*-zirconocene catalyst (6 μmol), MAO (10% in toluene; 3000 μmol), and toluene (150 mL) were mixed together in a Schlenk tube. The N$_2$ pressure inside the Schlenk tube was reduced by applying vacuum. An ethylene pressure of 1.5 bar was then applied to the Schlenk tube, and stirring of the mixture commenced. After exactly 30 min, stirring was halted and the ethylene pressure was released. Excess MAO was then destroyed by adding cautiously a mixture of methanol and HCl (90:10). The polymer formed was isolated by filtration, washed with ethanol, and dried under vacuum at 60 °C for 12 h.

Polymerization of Propylene with 5−10. The *ansa*-zirconocene catalyst (6 μmol), MAO (10% in toluene; 6000 μmol), and toluene (150 mL) were mixed together in a Schlenk tube. The N$_2$ pressure inside the Schlenk tube was reduced by applying vacuum. A propylene pressure of 2.0 bar was then applied to the Schlenk tube, and stirring of the mixture commenced. After exactly 30 min, stirring was halted and the propylene pressure was released. Excess MAO was then destroyed by adding cautiously a mixture of methanol and HCl (90:10). The polymer formed was isolated by filtration, washed with ethanol, and dried under vacuum at 60 °C for 12 h.

Polymerization of Ethylene with 17−22. The *ansa*-zirconocene cationic catalyst (6 μmol), [TIBA] (scavenger; 16 μmol), and toluene (150 mL) were mixed together in a Schlenk tube. The N$_2$ pressure inside the Schlenk tube was reduced by applying vacuum. An ethylene pressure of 1.5 bar was then applied to the Schlenk tube, and stirring of the mixture commenced. After exactly 30 min, stirring was halted and the ethylene pressure was released. The polymer formed was isolated by filtration, washed with ethanol, and dried under vacuum at 60 °C for 12 h.

X-ray Structure Determinations for [Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$R)]ZrCl$_2$ (R = Et (7), ^{i}Pr (8)). Intensity data were collected on a NONIUS-MACH3 diffractometer equipped with a graphite monochromator (Mo Kα radiation; $\lambda = 0.710\ 73$ Å), using an $\omega/2\theta$ scan technique. For **7**, the specimen diffracted weakly. The final unit cell parameters were determined from 25 well-centered reflections and refined by least-squares methods. Data were corrected for Lorentz and polarization effects but not for absorption. The space group was determined from the systematic absences, and this was vindicated by the success of the subsequent solutions and refinements. The structures were solved by direct methods using the SHELXS computer program[24] and refined on F^2 by full-matrix least squares (SHELXL-97).[25] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in calculated positions and were refined with an overall isotropic temperature factor using a riding model. Weights were optimized in the final cycles. In **7**, the ethyl group is in a disordered position. Crystallographic data are given in Table 6.

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Supporting Information Available: Details of the data collection and refinement, atom coordinates, anisotropic displacement parameters, and bond lengths and angles for complexes **7** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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