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Theoretical Study on the Factors Controlling the Accessibility of Cationic Metal Centers in Zirconocene Polymerization Catalysts

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ABSTRACT: The influence of the ligand structure of zirconocene polymerization catalysts on the accessibility of the active reaction center was studied by an ab initio Hartree−Fock method. The variations in the accessibility were elucidated by comparing molecular structures and relative stabilities of 54 bridged zirconocene catalysts with 19 different bridging units, 18 ancillary Cp′ ligands, and 18 ligand substituents. Ligand variations gave rise to various steric and electronic effects affecting both the nature and the concentration of active metal centers in the system, such as steric blocking or shielding of the metal center, and stabilization or destabilization of the active cationic species. Comparisons to experimental work demonstrated clear correlations between accessibility of the active reaction center and observed polymerization activity. Furthermore, interactions between the Lewis acidic aluminum centers and Lewis basic functionalities were observed. The consequences of such interactions are discussed.

Introduction

The most important application of metallocenes is currently the homogeneous polymerization of olefins by group IV metallocene catalysts.[1] In comparison with traditional heterogeneous Ziegler−Natta catalysts, metallocenes have several advantages. They can be used to polymerize a wide variety of monomers, they are able to produce very uniform polymers with narrow molecular weight distribution, and they are highly stereospecific in producing isotactic and syndiotactic polymer. Polymerization activities of the best metallocene/MAO catalysts are orders of magnitude higher than with heterogeneous Ziegler−Natta catalysts. Furthermore, the single site nature of the metallocene catalysts makes correlations between the catalyst structure and polymerization properties possible. Experimental work in the field has been extensively reviewed recently.[2]

The number of theoretical studies on olefin polymerization catalysts has been growing steadily for the last 10 years. The majority of this work has concerned mechanistic details of ethylene polymerization and stereospecificity of propylene polymerization.[3−9] These studies have provided valuable supporting information on many aspects of the polymerization process, such as understanding the reaction mechanisms as well as control of the polymer tacticity. On the basis of earlier theoretical and experimental studies it is, however, difficult to elucidate reasons for observed trends in polymerization activities due to a wide variety of influential parameters. In addition to the reaction conditions, the nature and amount of the cocatalyst, combined with simultaneous steric and electronic effects of the ligand framework, have a crucial influence on the catalytic process.

Regardless of the complexity of metallocene-catalyzed polymerization reactions in the whole, a fundamental prerequisite for the process is the existence of active reaction centers. The active center is generated by the cocatalyst, such as MAO, which first alkylates the metallocene precursor and in the next stage abstracts the methyl group resulting in a contact ion pair with the 14-electron cation being the catalytic active species[10] (Figure 1). Nevertheless, the existence of the catalytic active species merely is insufficient if the cationic center cannot be reached by the monomer. In the present work, the structures and stabilities of 54 zirconocene catalysts are computed by the Hartree−Fock method. The variations in the accessibility of active centers are concluded as a function of the ligand framework, and the observed correlations with experimental polymerization results are discussed.

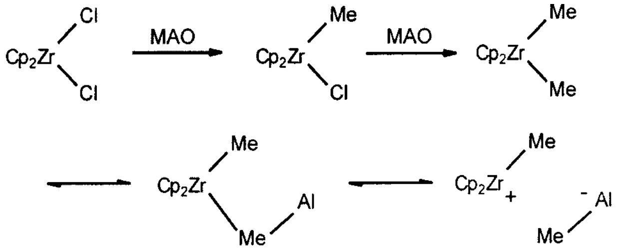

Figure 1. Activation of a zirconocene dichloride precursor by methylalumoxane.

Computational Aspects

The treatment of transition metal complexes by ab initio molecular orbital methods is generally difficult, mainly due to near-degeneracy and relativistic effects.[11,12] In this regard, zirconium is an exceptional metal. Because of its location at the beginning of the second transition row, both near-degeneracy and relativistic effects are small. As a consequence, relatively low level ab initio methods produce reasonably accurate geometries for zirconocenes. This has been demonstrated by comparing the geometry parameters of 62 HF/3-21G*-optimized bridged zirconocene dichlorides to the corresponding crystal structures.[13] Although the method showed systematic overestimation in the metal−ligand distances, the important ligand−metal−ligand bond angles were predicted with considerable accuracy. Furthermore, an essential feature of the HF/3-21G* method was its capability of generally reproducing the right trends in the changes of the geometry parameters for the whole series of molecules.

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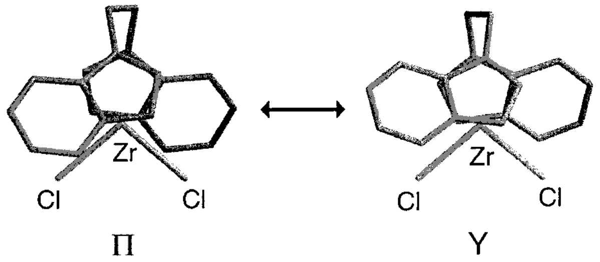


Figure 2. Top view of indenyl-forward (Π) and indenyl-backward (Y) conformations. Hydrogens are omitted for clarity.

In addition to the difficulties in the treatment of transition metal complexes in general, another computationally complicating factor is the possibility of large molecules going through structural isomerism. As a consequence, the equilibrium structures of the complexes cannot be unambiguously defined. The freedom of movements can be reduced by introducing a bridge between the cyclopentadienyl (Cp) ligands. In general, one-atom-bridged metallocenes are rigid, whereas two- or more-atom-bridged metallocenes are fluctional. A special case of fluxionality occurs when a two-atom bridge is combined with a bis(indenyl)- or bis(tetrahydroindenyl)-based ligand. Such configurations give rise to two distinct conformations, indenyl-forward (Π) and indenyl-backward (Y) (Figure 2). These conformations are separated by a small rotation barrier, and the conformational energy differences are generally small.[14] In this work, the zirconocenes of this type are studied in the Y-conformation.

Reported calculations were carried out by the Gaussian 94 program package.[15] Geometry optimizations and relative stability calculations were performed by ab initio Hartree−Fock method at the 3-21G* level. Furthermore, the reliability of the stability calculations was estimated by comparing the HF/3-21G* level results with higher level Hartree−Fock, MP2, or hybrid density functional B3LYP[16] methods. The relative stabilities at the HF/3-21G* level were found similar to those obtained by B3LYP/6-31G* and MP2/6-31G* methods.[17] The Gaussian 94 program includes standard basis sets only up to 3-21G* for zirconium. Therefore, when a larger basis set than 3-21G* was utilized for the rest of the molecule, zirconium was described by Huzinaga's extra basis (Zr, 433321/433/421).[18]

Results and Discussion

The Factors Controlling the Accessibility of the Active Reaction Center. In the beginning, two distinct properties of the active reaction center should be separated; structural and electronic properties and concentration, of which both are ruled by the ligand framework. The properties of the reaction centers are naturally also influenced by the reaction conditions and other components in the system, such as the cocatalyst or the solvent. These other variables were kept constant, and the focus was on the influence of the ligand framework.

The Reaction Center−Steric Influence of the Ligand Framework. The basic geometry parameters of zirconocenes are given in Figure 3. On the basis of steric parameters, the accessibility of the reaction center is improved by increasing the Zr−Cp′ (Cp′ = centroid of the five-ring for any η^5-based ligand) distance, increasing the Cp′−Cp′ plane angle, and also to a lesser degree by decreasing the Cp′−Zr−Cp′ angle. Furthermore, ligand substituents oriented toward the reaction site make the reaction center less accessible. The steric influence of the ligand framework has been presented by one parameter. The coordination gap aperture[19] was utilized by Janiak et al.[20] to estimate the activity order of methyl-substituted zirconocenes. The apertures were measured from the X-ray structures of dichloride precursors.

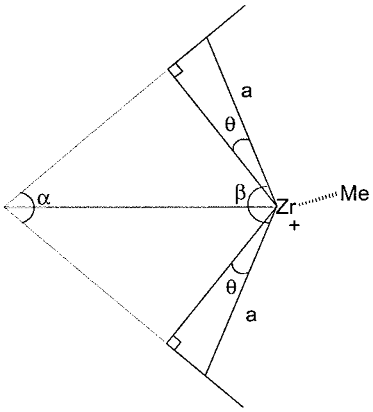


Figure 3. Cross-section of a zirconocene. a = Zr−Cp′ distance, α = Cp′−Cp′ plane angle, β = Cp′−Zr′−Cp′ angle, and θ = ring slippage angle; displacement of the ring centroid from the normal to the ring plane = $^1/_2(\alpha + \beta) - 90$.

The Reaction Center−Electronic Influence of the Ligand Framework. Since the coordination gap aperture measures the accessibility of the reaction center only from a steric point of view, its successful utilization in structure−polymerization property predictions requires a uniform group of catalysts with similar electronic properties. This requirement is rarely fulfilled when dealing with a large group of metallocenes. This is not only because of variations in the ancillary ligands, ligand substituents, and the bridging units with dissimilar electronic properties but also due to changes in geometry parameters, which have electronic effects as well.

In addition to steric requirements, the Zr−Cp′ distance is influenced by the electron-donating capability of the Cp′ ligand. The donated electron is transferred from the occupied Cp′-based bonding orbital to the empty d orbital of Zr.[21] Consequently, the electron is more easily detached if the Zr−Cp′ bond is weak and thus longer. On the other hand, the stronger electron donor the Cp′ ligand is, the more easily an electron is detached from the bonding ligand orbital, and transferred to the empty d orbital of the metal. Therefore, in the absence of steric as well as other electronic influences given rise by the ligand substituents, the Zr−Cp′ distance should be directly proportional to the electron-donating capability of the Cp′ ligand. Likewise, the changes in the Cp′−Zr−Cp′ angle and in the Cp′−Cp′ plane angle have both steric and electronic consequences. First, a combination of these parameters defines the ring slippage angle, which represents the displacement of the ring centroid from the normal to the ring plane. The change in the ring slippage angle has an influence on the electron-donating nature of the Cp′ ligand, because it affects the bonding between the metal and the ligand. Increasing ring slippage angle results in less optimal overlap of metal and ligand orbitals and weakens the bond. Again, the weaker the bond, the more easily an electron is detached, and transferred from the ligand to the empty d orbital of the metal. Hence, neglecting other simultaneous effects, an increase in the ring slippage angle should be directly proportional to the electron-donating capability of the Cp′ ligand.

The second combination of steric and electronic effects given rise by the angle parameters, is mainly due to the Cp′−Zr−Cp′ angle. As was mentioned above, the accessibility of the reaction center is, from a steric point of view only, slightly reduced by increasing the Cp′−Zr−Cp′ angle. However, increasing the Cp′−Zr−Cp′ angle provides more shielding for the metal (Figure 4). This shielding complicates the blocking of the reaction center by the cocatalyst, which would make the active center less accessible for the monomer. Likewise, increasing the Cp′−Zr−Cp′ angle complicates the interaction between two cationic catalyst centers, which in turn would result in dimerization of the cations and deactivation of the catalyst.

Electron deficiency of the metal is another important matter having an influence on the accessibility of the reaction center, while its influence is not straightforward. Increased electron deficiency results in increased tendency for reaction, not only with the monomer but also with other components in the system such as the cocatalyst, other cationic centers, and impurities. With this in mind, its influence can be considered similar to the Cp′−Zr−Cp′ angle. Decreased cationicity of zirconium provides shielding for the reaction center. Naturally, the increased electron-donating capability of the Cp′ ligand should decrease the cationicity of the metal.

Concentration of the Reaction Centers. So far the effect of the nature of a cationic center on its accessibility has been discussed. In addition to that, the quantity of these active metal centers in the system has a large improving influence on their accessibility. The active center is generated by sequential reactions between the metallocene and the cocalyst, according to eqs 1 and 2:

Methylation:

$$\underset{\mathbf{a}}{L_2ZrCl_2{\cdot}MAO} \leftrightarrow \underset{\mathbf{b}}{L_2Zr(CH_3)Cl} + MAO \leftrightarrow \underset{\mathbf{c}}{L_2Zr(CH_3)_2} + MAO{-}Cl \quad (1)$$

Activation:

$$\underset{\mathbf{c}}{L_2Zr(CH_3)_2} + MAO \leftrightarrow \underset{\mathbf{d}}{[L_2Zr(CH_3)]^+} + [MAO{-}CH_3]^- \quad (2)$$

The quantity of active metal centers in the system corresponds to the concentration of species **d** in eq 2. Hence, to improve the accessibility of cationic metal centers by increasing their quantity, the equilibrium of sequential reactions should be shifted as far right side of eq 2 as possible. To do this, a cocatalyst is necessary, and to do this properly, a large excess of MAO is usually required.

In addition to the nature and amount of the cocatalyst, the equilibrium **a** ↔ **d** of eqs 1 and 2 is strongly influenced by the stability of cation **d**. The relative stability of **d** can be determined as a function of the ligand structure, L_2. The simpliest way to do this is to consider the reaction without the presence of the cocatalyst (eq 3):

$$\underset{\mathbf{a}}{L_2ZrCl_2} + CH_3^+ \leftrightarrow \underset{\mathbf{d}}{L_2ZrCH_3^+} + Cl_2 \quad (3)$$

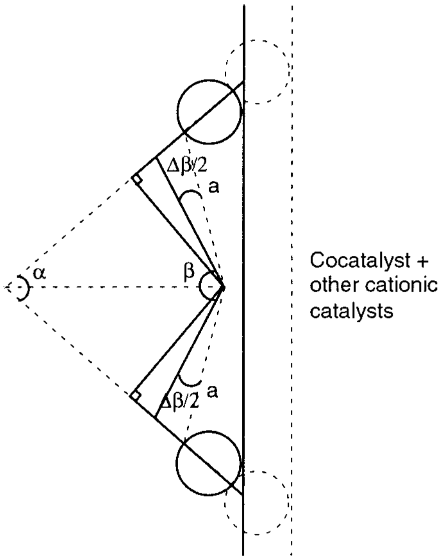


Figure 4. Shielding of the metal center by increasing the Cp′−Zr−Cp′ angle.

To determine the relative stability of **d** as a function of the ligand structure, one ligand needs to be selected for a reference (L_0), to which all the other ligands ($L_\mathbf{x}$) are compared. The energies of free CH_3^+ and Cl_2 fragments cancel out because they are independent of L_2 and constant. Hence, the relative stability of **d** having a ligand **x** can be written as in eq 4:

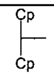
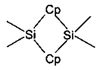
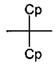
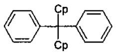
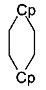
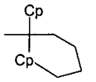
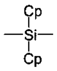
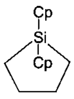
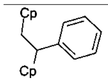
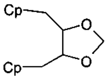
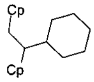
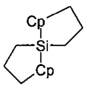
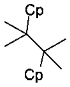
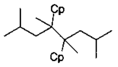
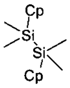
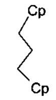
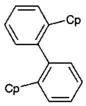
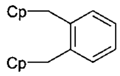
$$\Delta E_\mathbf{x} = [E_\mathbf{d}(L_0) - E_\mathbf{a}(L_0)] - [E_\mathbf{d}(L_\mathbf{x}) - E_\mathbf{a}(L_\mathbf{x})] \quad (4)$$

The Influence of the Ligand Structure on the Accessibility of the Active Reaction Center. Both the nature and the concentration of the reaction centers apparently affect the accessibility of the metal. However, the estimation of relative strengths of these factors on controlling the accessibility, and especially their relative consequences on polymerization results, is less obvious. Comparisons to experimental activity data are further complicated because of dissimilar reaction conditions in various sources. In the following, the influences of nature and concentration of the active reaction centers on their accessibility are reported as a function of the ligand structure. Comparisons to experimental polymerization results are performed as well. Because of the aforementioned reason, these comparisons will be limited mainly to general trends reported for the catalysts in the literature reviews.[2]

The Effect of the Bridge Structure. The influence of the bridging unit on structure of the catalyst and relative stability of the cation is presented in Table 1. The studied bridge structures were selected on the basis of a systematic search of bridged zirconocene dichlorides from the Cambridge Structural Database.[22] To eliminate simultaneous effects from the rest of the ligand, all bridges were attached to the Cp ligands. Geometry parameters in the tables are given for the dichloride structures throughout the results section. Since similar trends in geometry changes are generally observed for both forms,[23] the choice of the model system is indifferent in this sense.

The effect of the bridging unit on the Zr−Cp distance is generally small, wheras the angle parameters are strongly influenced. Short bridges open up the Cp−Cp plane angle, resulting in decreased steric hindrance of the ligand. Increasing Cp−Cp plane angle is accompa-

Table 1. Influence of the Bridging Unit on Structure of the Catalyst and Relative Stability of the Cationic Methyl Form in Increasing Order of Relative Stability

Bridge		ΔE_x (kJ/mol)	Zr-Cp (Å)	Cp-Cp (°)	Cp-Zr-Cp (°)	Ring slippage angle (°)
	B1	0	2.24	73	115	4
	B2	2	2.25	73	119	6
	B3	3	2.24	73	115	4
	B4	11	2.23	72	115	3
	B5	14	2.23	65	120	2
	B6	18	2.25	74	115	4
	B7	19	2.26	62	124	3
	B8	19	2.26	62	124	3
	B9	19	2.25	59	124	1
	B10	21	2.26	59	125	2
	B11	25	2.25	51	130	1
	B12	26	2.24	59	124	1
	B13	26	2.25	62	125	3
	B14	29	2.24	58	124	1
	B15	33	2.24	58	124	1
	B16	37	2.25	51	132	1
	B17	39	2.25	50	131	0
	B18	40	2.25	50	131	0
	B19	136	2.28	51	133	2

nied by decreasing Cp−Zr−Cp angle. Hence, the ring slippage angle remains relatively constant throughout the whole series of bridging units.

The general range of relative stabilities of the cations is 40 kJ/mol. All structures below the ethylene bridge (**B9**) in the stability of the cation are either one-atom bridges or double bridges. Both of these bridge types also have a strong tendency to open the Cp−Cp plane angle and at the same time to decrease the Cp−Zr−Cp angle. Most of the bridges above the ethylene bridge in the stability of the cation are three- or more-atom bridges. Common to these bridge types is a small Cp−Cp plane angle and a large Cp−Zr−Cp angle. Apparently, the stability of the cation is related to the capability of the Cp ligand to provide shielding for the cationic metal.

The dichloride and cationic methyl forms of **B19** with very high stability of the cation are presented in Figure 5. Considerably higher stability compared to all other bridging units in Table 1 is due to electron donation from an aromatic carbon to the electron-deficient metal, resulting in blocking of the metal center.

Comparisons with Experimental Observations. 1. Of two of the most commonly utilized bridging units, one-atom-bridged **B7** is slightly more active than the two-atom-bridged **B9**.[2b,c,f,g]

The relative stabilities of the cations are equal for these zirconocenes. Small differences in polymerization activities are possibly due to larger Cp−Cp plane angle in **B7**, resulting in improved accessibility of the cationic center because of reduced steric hindrance of the ligand.

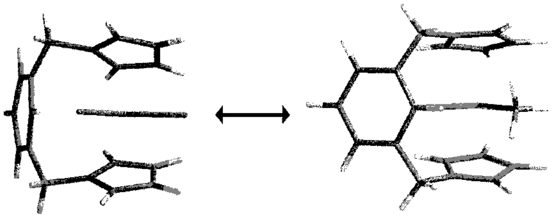


Figure 5. Formation of a highly stable cation by electron donation from an aromatic carbon to the electron-deficient metal.

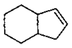
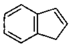
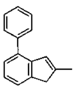
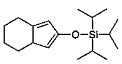
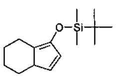
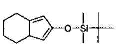
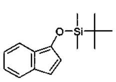
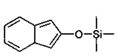
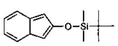
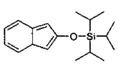
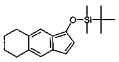
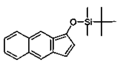
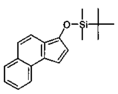
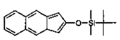
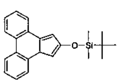
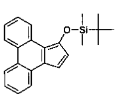
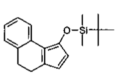
2. Three- or more-atom-bridged complexes are practically inactive in propylene polymerization but not in ethylene polymerization.[2b]

A long bridge decreases the Cp−Cp plane angle and therefore increases steric hindrance of the ligand. Propylene as a larger monomer is more strongly affected by steric effects than a small ethylene. Regardless of high stability of the cation, the accessibility of the reaction center remains low, because of steric congestion.

3. Double-bridged complexes are practically inactive.[2b,g]

A double bridge is an efficient way to decrease steric effects of the ligand by increasing the Cp−Cp plane angle. However, decreased steric hindrance is accompanied by lowering stability of the cation, which in turn reduces the accessibility of the metal.

Table 2. Influence of the Ancillary Cp′-Ligand on the Structure of the Catalyst and Relative Stability of the Cationic Methyl Form in Increasing Order of Relative Stability[a]

Ligand		ΔE_x (kJ/mol)	Zr-Cp' (Å)	Cp'-Cp' (°)	Cp'-Zr-Cp' (°)	Ring slippage angle (°)
	L1	0	2.25	59	124	1
	L2	30	2.25	59	125	2
	L3	48	2.27	60	126	3
	L4	48	2.27	60	127	4
	L5	54	2.26	59	125	2
	L6	55	2.26	62	126	4
	L7	55	2.25	58	125	1
	L8	71	2.28	65	128	7
	L9	72	2.27	61	127	4
	L10	74	2.27	61	127	4
	L11	77	2.27	61	126	4
	L12	85	2.27	65	128	7
	L13	85	2.29	69	130	10
	L14	85	2.27	63	127	5
	L15	90	2.28	62	128	5
	L16	94	2.27	56	127	2
	L17	97	2.27	61	127	4
	L18	100	2.27	63	127	5

[a] The parameters are given for ethylene-bridged zirconocenes.

4. The silicon-bridged complex (**B7**) produces higher activities than the corresponding carbon-bridged complex (**B3**).[2c,g]

B3 has a larger Cp−Cp plane angle than **B7**. On the other hand, stability of the cation, as well as shielding of the metal by the Cp ligand, is higher in **B7**. Apparently, the latter effects surpass the increased steric hindrance by the ligand.

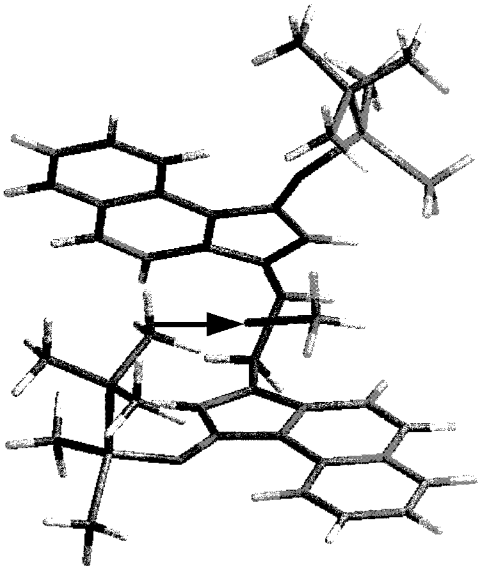


Figure 6. Stabilization of the cation by interaction between the siloxy group and zirconium in **L18**.

Overall, to reach high activities, compromises in the selection of the bridging unit seem to be inevitable. The high stability of the cation, indicating large concentration of active species in the system, is insufficient alone if the reaction site is sterically crowded. Conversely, despite of the absence of steric hindrance, the accessibility of the active center remains poor if the stability of the cation is low. The cationic center cannot be reached by the monomer if this center does not exist.

The Effect of the Ancillary Cp′ Ligand. The influence of various Cp′ ligands on structures of the catalysts and stabilities of the cations is presented in Table 2. Structures and stabilities are given for ethylene-bridged zirconocenes in the Y-conformation, if applicable. Most of the studied molecules are siloxy substituted. This is only due to our general interest in siloxy substituted zirconocenes. In the present section the attention should be focused on the type of the Cp′ ligand.

The Zr−Cp′ distances and ring slippage angles are related to the electron-donating capability of the ligand. The reason for this is the facilitation of the detachment of the electron from the bonding ligand orbital and its transfer to the empty d orbital of the metal, as discussed earlier. Unlike with the bridging units, changes in geometry parameters are minor compared to changes in relative stabilities of the cations. Zr−Cp′ distances range from 2.25 to 2.29 Å, and variations in angle parameters are generally within 10°. At the same time, the difference in relative stability of the cation is as considerable as 100 kJ/mol.

The stability of the cation is strongly dependent on the aromaticity of the ancillary ligand. Zirconocenes with the same number of aromatic carbons in Cp′ ligand produce nearly identical stabilities (**L5**−**L7**, **L8**−**L11**, **L13**−**L15**, **L16**, **L17**). The increase in the stability as a function of aromaticity of the ligand is equally systematic. The only exception is **L18**, which is further stabilized by an interaction between the siloxy group and the cationic metal center (Figure 6). On the basis of Table 2 it could be estimated that, at the HF/3-21G* level, the energy of such an interaction is 10−15 kJ/mol.

Comparisons with Experimental Observations. 1. It is well demonstrated that the polymerization

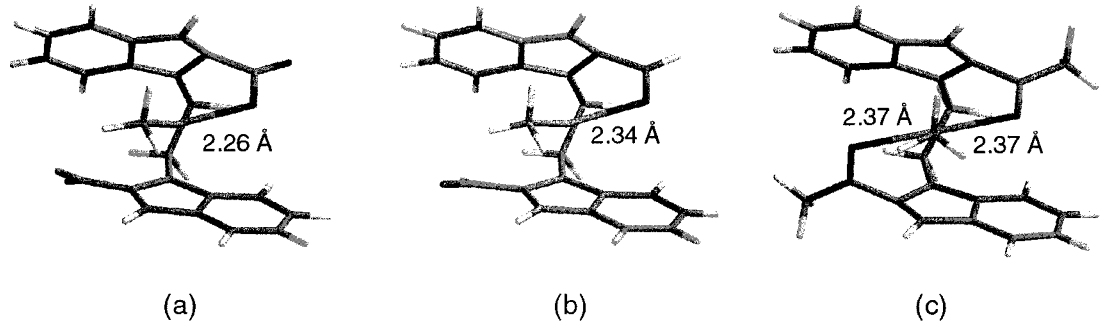


Figure 7. Stabilization of zirconocene cations by interaction between the metal and the oxygen of the ligand substituent. Relative stabilities compared to hydrogen: (a) 2-NO_2, $\Delta E_x = 37$ kJ/mol; (b) 2-CHO, $\Delta E_x = 43$ kJ/mol; (c) 2-$COCH_3$, $\Delta E_x = 140$ kJ/mol.

activity generally follows the order Cp (**L1**) < Thind (**L2**) < Ind (**L3**).[2a,c,e−g]

Variations in stericity are too small to provide explanation for this general trend. Instead, relative stability of the cation, and hence the concentration of active species in the system, increases in the same order.

2. Introduction of further annealated aromatic rings results in a considerable increase in polymerization activity.[2b,f,24]

On the basis of earlier observations, this is also what could have been predicted from Table 2. The relative stability of the cation is systematically increased by the addition of further annealated aromatic rings. It is also very interesting to note that the highest catalytic activities ever reported for zirconocenes are based on annealated ligands similar to those in **L16** and **L17**.[24c]

3. A catalyst based on 2-Me-4-Ph-substituted ligand (**L4**) is much more active in the polymerization of propylene than the corresponding unsubstituted **L3**.[2d,f]

The superiority of **L4** is due to combination of the 2- and 4-substituents as well as due to the shielding effect of aromatic substituent. The β-hydrogen transfer with the monomer is suppressed by the 2-substituent, whereas the 4-substituent reduces 2,1-misinsertions. This results in increased activity, as discussed in ref 2d.

The Effect of the Ligand Substituent. The earlier observations on how the stability of the zirconocene cation varies as a function of the bridge and the ancillary ligand do provide expectations on the influence of the ligand substituents. First, the electron-deficient metal center accepts readily electrons from its vicinity. This can be demonstrated by attaching oxygen containing substituents to a substitution site close to the cationic metal center (Figure 7). The direct interaction between the metal and oxygen stabilizes the cation, and presumably prevents the olefin coordination due to blocking of the reaction site.

Second, in the absence of direct interaction between the metal and the ligand substituent, electron-donating groups should generally stabilize and electron-withdrawing groups destabilize the cation. The former is due to electron donation from the substituent to the Cp′ ligand, which increases the electron-donating capability of the ligand. The influence of the latter is naturally opposite. To demonstrate this effect, the selection of the model systems has to be first examined.

The required absence of direct interaction between the metal and the ligand substituent cannot be fulfilled with a Cp ligand only, because of short intramolecular distances. Computationally the next practical ancillary ligand is Indenyl, which already provides substitution sites far off the metal center, when combined with an ethylene bridge (positions 6 and 7 in Figure 8). Position 6 was selected for the study due to its location at a distance from both the metal and the bridge. Structural parameters and stabilities of the cations are given in Table 3 for ethylene-bridged bis(indenyl)-type zirconocenes with various 6-substituents.

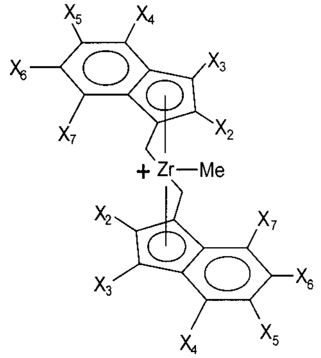


Figure 8. Substitution sites of ethylene-bridged bis(indenyl)-type zirconocenes.

As demonstrated in Table 3, the 6-substituents have in practice no influence on structural parameters of the catalyst. The situation is ideal for the investigation of substituent effects on relative stability of the cation. The nitro group (**S1**), which is the strongest known electron-withdrawing group, has the lowest stability of the cation, −75 kJ/mol, compared to hydrogen (**S10**). It is followed by another very strongly withdrawing group, the cyano group (**S2**). Aldehyde, (**S3**), halogens (**S4**, **S5**), carboxylic acid (**S6**), ketone (**S7**), and ester (**S8**) are also electron withdrawing and therefore destabilize the cation. The last substituent in Table 3 is *N*,*N*-dimethylamine (**S19**). It is one of the strongest known electron donors, and as a result the stability of the cationic form is increased by 52 kJ/mol. Also electron-donating alkyl groups (**S11**, **S12**, **S15**, **S17**), silyl group (**S16**), methoxy group (**S13**), and siloxy group (**S14**) stabilize the cationic form. Apparently, the magnitude of relative stability can be used to estimate the electron-donating ability of the Cp′ ligand.

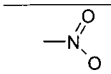
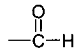
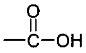
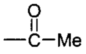
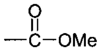
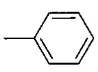
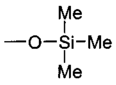
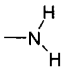
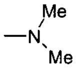
Comparisons with Experimental Observations. 1. Electron-withdrawing substituents have a decreasing effect on polymerization activity.[2a,g]

This is a clear indication on the importance of stability of the cation. To be accessible for the monomer, active reaction centers must be available. To be available, the cation must be stable.

2. The effect of electron-donating substituents is less clear.

While the stability of the cation is an important prerequisite, the process is influenced by many other

Table 3. Influence of Ligand Substituents on Structure of the Catalyst and Relative Stability of the Cationic Methyl Form in Increasing Order of the Relative Stability[a]

Ligand		ΔE_x (kJ/mol)	Zr-Cp (Å)	Cp-Cp (°)	Cp-Zr-Cp (°)	Ring slippage angle (°)
 $-NO_2$	S1	-75	2.28	61	126	3
$-C\equiv N$	S2	-57	2.27	60	126	3
 $-C(=O)H$	S3	-36	2.27	60	126	3
$-F$	S4	-33	2.27	60	126	3
$-Cl$	S5	-31	2.27	60	126	3
 $-C(=O)OH$	S6	-27	2.27	60	126	3
 $-C(=O)Me$	S7	-26	2.27	60	126	3
 $-C(=O)OMe$	S8	-18	2.27	61	126	3
$-OH$	S9	-3	2.26	60	126	3
$-H$	S10	0	2.27	60	126	3
$-Me$	S11	2	2.27	60	126	3
	S12	9	2.27	60	126	3
$-OMe$	S13	10	2.26	60	126	3
 $-O-SiMe_3$	S14	11	2.26	60	126	3
$-iPr$	S15	11	2.27	60	126	3
$-SiMe_3$	S16	17	2.27	60	126	3
$-tBu$	S17	19	2.27	60	126	3
 $-NH_2$	S18	35	2.26	59	126	3
 $-NMe_2$	S19	52	2.26	60	126	3

[a] The parameters are given for ethylene-bridged bis(indenyl)-type zirconocenes with substituents attached to position 6 of the indenyl ring.

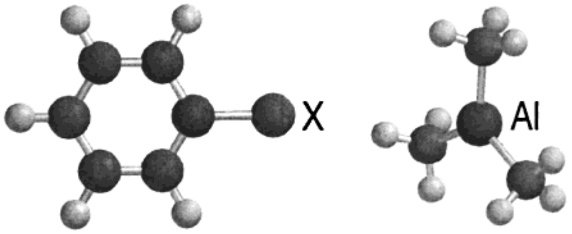


Figure 9. Model for investigation of the interaction between the ligand substituent (X) and the Lewis acidic aluminum.

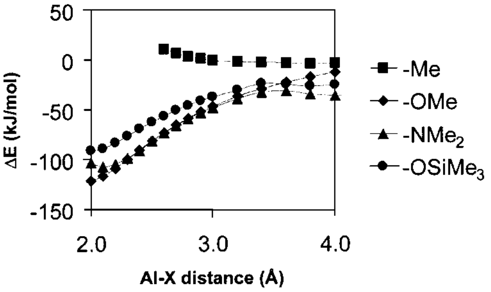


Figure 10. Coordination of TMA to methyl, methoxy, amino, and siloxy substituents. X represents the Lewis basic atom (C, N, or O). Energies are given relative to the sum of free species.

factors, too. High stability of the naked cation alone is insufficient to produce an active catalyst.

2.1. The influence of alkyl groups is small.[2a,c,e,g]

Alkyl groups are weak electron donors and therefore only slightly stabilize the cation. Bulkier alkyl groups stabilize the cation more effectively, still at the cost of increased steric hindrance. Hence, the improved accessibility of metal centers due to their higher concentration is balanced by worsened accessibility because of steric blocking by the ligand substituent.

2.2. Methoxy substitution (**S13**) results in considerably decreased activity,[25] whereas siloxy substitution (**S14**) provides highly active catalysts at low cocatalyst concentration.[26]

Both substituents are electron donating and therefore stabilize the cation. To understand the large difference of these fairly similar substituents, the effects of the cocatalyst have to be considered.

2.3. Activity of amino-substituted catalysts (**S19**) is modest.[27]

As above with the methoxy substituent, also the strongly electron-donating amino group decreases the polymerization activity, despite the increased stability of the cation. An explanation requires consideration of the cocatalyst effects.

The Effect of Lewis Acidic Aluminum Centers. While the primary function of the cocatalyst is methylation and activation of the catalyst precursor, the Lewis acidic aluminum center may also interact with other Lewis basic sites of the catalyst. Such interaction between the alumoxane and the methoxy group has been detected and confirmed by ^{1}H NMR experiments.[25a] This coordination leads to inductive electron withdrawal, and as a consequence, the methoxy group acts as an electron-withdrawing substituent. This results in decreased polymerization activity due to reduced concentration of active species, which originates from destabilization of the cationic catalyst.

The coordination of a Lewis acidic aluminum center to various ligand substituents was studied qualitatively using a model system of Figure 9. Since our interests were solely on the interaction between the substituent and the Lewis acidic aluminum, the presence of the central metal was neglected. Instead of the negatively charged indenyl ligand, the very similar neutral benzene ring was selected for the base system to be substituted with various Lewis basic functionalities. The Lewis acidic aluminum center was described by a 3-coordinated trimethylaluminum (TMA). Al−X (X = center of the Lewis basic functionality) coordination energies are presented in Figure 10.

Distinct dissimilarities between hard and soft Lewis basic substituents can be observed in Figure 10. Hard Lewis acidic TMA reacts readily with hard Lewis basic methoxy, amino, and siloxy groups but not with the soft Lewis basic methyl group. Coordination to the methoxy group proceeds spontaneously, whereas low activation

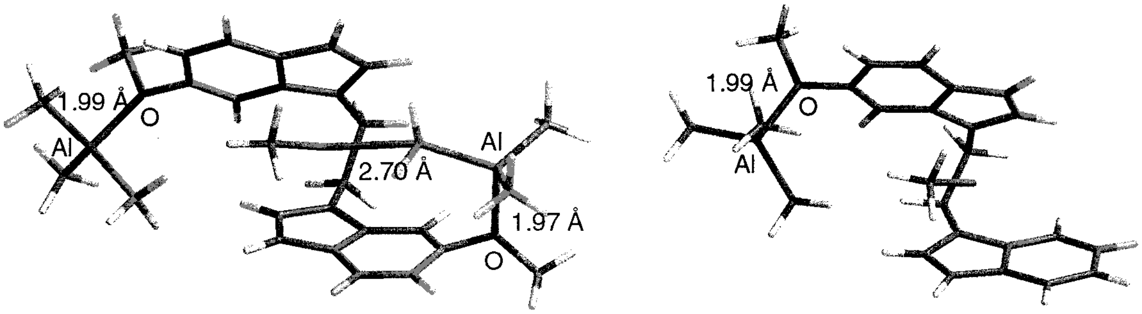


Figure 11. Coordination of TMA to the methoxy substituent (**S13**).

barriers are obtained for both amino and siloxy substituents. These disparities can be explained by steric effects. In methoxy substituent, the small methyl group in front of the oxygen donor atom does not have noticeable influence on the Al−O coordination. Instead, two methyl groups around the nitrogen in the amino substituent and the $SiMe_3$ fragment around the oxygen in the siloxy substituent somewhat complicate the Al−O coordination by providing steric shielding for the donor atom.

To demonstrate the inductive electron withdrawal as concluded by Piccolrovazzi et al., TMA was brought into close contact with the 6-OMe substituted **S13**. The other 6-OMe substituent was removed, because coordination of TMA to the methoxy group close to the vacant coordination site of cationic zirconocene results in simultaneous coordination of the methyl group to the metal (Figure 11). This stabilizes the structure due to electron donation from the methyl group to the electron-deficient metal, and complicates interpretation of the influence of Al−O coordination.

The coordinations of TMA to the methoxy group are similar with and without the presence of zirconium, the distance between oxygen and aluminum being in both cases approximately 2.0 Å. In the absence of Al−O coordination, the relative stability of methoxy substituted **S13** is 10 kJ/mol higher than that of the unsubstituted **S10**. The stabilizing effect of one methoxy group is thus 5 kJ/mol. The relative stability of the monomethoxy-substituted complex with Al−O coordination becomes 11 kJ/mol lower compared to the corresponding unsubstituted **S10**. Therefore, the total decrease in relative stability of the cation is 5 kJ/mol + 11 kJ/mol = 16 kJ/mol. However, the C_2 symmetry is normally retained by a substitution to both indenyl ligands, which would lead to destabilization of the cation by 2 × 16 kJ/mol = 32 kJ/mol. Apparently, this decrease in relative stability of the active cationic species is due to inductive electron withdrawal caused by Al−O coordination, resulting in a decreased electron-donating capability of the indenyl ligand.

In the preceding comparisons concerning the influence of the ligand substituents on polymerization activities, the effects of electron-donating substituents were not comprehensively analyzed. The following questions can now be discussed.

1. Why do electron-donating alkyl groups generally provide high polymerization activities, while other electron-donating substituents like methoxy, siloxy, and amino, generally do not?

Alkyl groups do not react with the cocatalyst, whereas all the other mentioned groups do (see Figure 10). The resulting inductive electron withdrawal destabilizes the active cationic species and decreases the concentration of active metal centers in the system, thereby reducing the accessibility of the metal center for the monomer. The final outcome is decreased activity.

2. Why does the siloxy group provide considerably higher polymerization activities than the methoxy group, even though their electron-donating properties are similar?

The siloxy group is much bulkier than the methoxy group. In actual siloxy-substituted catalysts the siloxy group is even larger than $-OSiMe_3$, which is used in Figure 10 to study the Al−O interaction. As a consequence, the unfavorable coordination of the cocatalyst to the oxygen donor atom is complicated by the siloxy group but not by the methoxy group. The same applies for the highly electron-donating amino group as well. Two methyl groups can provide some steric shielding for the nitrogen, but not enough to prevent the nitrogen−cocatalyst coordination. The inductive electron withdrawal and resulting destabilization of the active cation lower the accessibility of the metal center and polymerization activity.

3. Why do the siloxy-substituted catalysts provide high polymerization activities at unusually low cocatalyst concentrations? Maximum activities are observed even at as low cocatalyst concentrations as [Al]:[Zr] = 150:1.[26]

Siloxy groups increase the electron-donating capability of the Cp′ ligand, which stabilizes the cationic species. Because of this high stability, lower amounts of cocatalyst are required to complete the activation step. In other words, the equilibrium of eqs 1 and 2 can be more easily shifted toward the right side of eq 2. Increasing the amount of the cocatalyst further facilitates the activation step. However, it also increases the possibility of the cocatalyst−oxygen coordination. Steric shielding of the donor atom by the bulky siloxy group can prevent this unfavorable coordination at low cocatalyst concentration, but not if the amount of Lewis acidic aluminums is considerably increased. Hence, at high cocatalyst concentrations, the cocatalyst coordinates to the oxygen atom of the siloxy group. The consequence of this is inductive electron withdrawal, which converts the otherwise electron-donating siloxy group to an electron-withdrawing substituent, resulting in destabilization of the active cation and decreased polymerization activity due to reduced accessibility of the cationic metal center.

Conclusions

The consequences of the ligand structure of zirconocene polymerization catalysts on accessibility of active cationic metal centers are far from straightforward due to simultaneous steric and electronic effects of the ligand. The influence of both nature and concentration of the metal centers is significant. The ligand structure of the catalyst controls the accessibility of the cationic center in numerous ways. Influential factors include blocking or shielding of the metal center by the ligand framework, varying the electrophilicity of the metal affecting the reactions between the catalyst and other components in the system, and changes in the stability of the active cationic species. The last accounts for the concentration of active reaction centers as well as for the feasibility of the activation step.

A systematic study on changes in the accessibility of the reaction center as a function of the ligand structure was performed by an ab initio Hartree–Fock method. Modifications on the bridging unit have both steric and electronic influences. Short bridges provide decreased steric hindrance of the ligand framework, but also reduced shielding for the cationic metal resulting in decreased stability of the cation. The influence of long bridges is opposite, with lowered steric hindrance, but increased shielding and stability of the cation. Modifications on the Cp′ ligand have for the most part electronic consequences. Increased aromaticity of the Cp′ ligand improves its capability of donating electrons for the electron-deficient metal, which stabilizes the cation. The increase in relative stability of the cation as a function of the number of aromatic carbons is systematic. Furthermore, the improved accessibility of the cationic metal due to the increased relative stability of the cation shows clear correlations with experimental activity data.

Without exceptions, electron-withdrawing substituents attached to the Cp′ ligand were demonstrated to destabilize the cation due to the decreased electron-donating capability of the Cp′ ligand. The resulting reduced concentration of active catalyst centers can be seen in decreased polymerization activities. The opposite influence of electron-donating substituents is equally evident. However, increased stability of the cation, obtained by increased electron-donating capability of the Cp′ ligand, does not inevitably provide highly active catalysts. The electronic nature of the ligand is further influenced by coordination of the hard Lewis acidic cocatalyst to the hard Lewis basic ligand substituents. The consequence of this coordination is inductive electron withdrawal which converts electron-donating substituents to electron-withdrawing ones, resulting in reduced electron-donating capability of the Cp′ ligand, decreased stability of the active cation, worsened accessibility of the reaction center, and decreased polymerization activity. This unfavorable coordination of the cocatalyst to hard Lewis basic substituents can be complicated by introducing steric bulk around the donor atom. A uniform group of such catalysts is formed by siloxy-substituted metallocenes, which reach high polymerization activities at considerably lower cocatalyst concentrations than metallocenes in general.

Acknowledgment. Financial support from the Finnish Technology Development Center (TEKES) is gratefully acknowledged.

Supporting Information Available: Figures showing the dependence of the relative stability of the cation on methods and basis sets, and comparison of HF/3-21G* calculated geometry parameters of dichloride and cationic methyl forms for zirconocenes with various bridging units. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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