Activation of Racemic Ethylene-Bridged Bis(indenyl)-Type Siloxy-Substituted Zirconocenes with Methylaluminoxane. A Combined UV/vis Spectroscopic and ab Initio Hartree−Fock Study

Nora I. Mäkelä* and Hilkka R. Knuuttila

Borealis Polymers Oy, P.O. Box 330, FIN-06101 Porvoo, Finland

Mikko Linnolahti* and Tapani A. Pakkanen

Department of Chemistry, University of Joensuu, P.O. Box 111, FIN-80101 Joensuu, Finland

Markku A. Leskelä

Department of Chemistry, University of Helsinki, P.O. Box 55, FIN-00014 University of Helsinki, Finland

Received December 7, 2001; Revised Manuscript Received February 26, 2002

ABSTRACT: Lowest energy ligand-to-metal charge-transfer (LMCT) transitions of racemic siloxy-substituted ethylene-bridged bis(indenyl)-type zirconocenes reacted with methylaluminoxane (MAO) were studied using UV/vis spectroscopy in combination with the ab initio Hartree−Fock method. The LMCT absorptions were recorded at various [Al]/[Zr] ratios, representing dichloride, methylated, and cationic forms of the zirconocenes. The experimental LMCT absorption energies of each intermediate were compared to the calculated energies of the indenyl ligand-based HOMO and the zirconium-based LUMO. The lowest energy LMCT absorptions were directly proportional to the calculated LUMO−HOMO energy gaps. Furthermore, the LMCT absorption energies were demonstrated to correlate with ethylene polymerization activity of the siloxy-substituted complexes. This correlation was clarified by a frontier orbital analysis, suggesting that decreasing absorption energy is related to the feasibility of the activation of the catalyst.

Introduction

Several correlations between the catalyst and polyolefin structures have been found in earlier studies. However, successful catalyst structure−activity correlations at a general level have been unavailable for metallocene polymerization catalysts despite significant experimental and theoretical resources put into the field.[1] Although the metallocene catalysts have single-site nature that facilitates the understanding of catalyst structure−polymerization property relationships, the large number of components in the whole catalytic system has complicated the interpretations. In addition to the variable polymerization conditions, the identification of electronic effects has turned out to be a difficult task, mainly due to the presence of simultaneous steric factors.

UV/vis spectroscopy provides valuable information on electronic effects owing to its applicability for the detection of ligand-to-metal charge-transfer (LMCT) transitions.[2] The LMCT occurs between the frontier orbitals of which, for d^0 metallocenes, HOMO is mainly Cp′ ligand based (Cp′ = any η^5Cp- type ligand) while the LUMO is mostly of metal character.[3] Consequently, the lowest energy LMCT absorptions together with theoretical HOMO and LUMO energies are related to the electronic properties of the ligands as well as the metal center.[4]

The present work aims to clarify the role of charge transitions on the activation steps of the catalytic process. To do that, a selection of catalysts was activated by MAO. This selection consists of racemic ethylene-bridged bis(indenyl)-type siloxy-substituted zirconocene dichlorides,[5] together with the corresponding unsubstituted catalyst. We had two motives to select the siloxy-substituted catalysts for the study. First, they represent highly active catalysts at reduced cocatalyst concentrations and are therefore especially interesting and promising compounds. Second, they constitute an unusually uniform group of catalysts with similar steric surroundings at the vicinity of the metal center. The close similarity was a prerequisite for this study, since the structural changes, e.g., ligand orientation and bonding angles, influence the overlap between the metal and ligand orbitals, therefore affecting on the LMCT transition.[3,6] The changes in UV/vis spectra were recorded at the known steps of the activation process. The spectroscopic data were then compared to the ab initio Hartree−Fock level investigations[7] on the frontier orbitals of each step to qualitatively understand both the activation behavior and the observed consequences on the activities of the studied catalysts.

Experimental Section

Siloxy-substituted zirconocenes (Figure 1) were synthesized and characterized by Leino et al.[5a−e] Complex **6** was purchased from Witco. Dimethylation of complex **1** was performed in the following way: Methyllithium was added dropwise into the complex **1** in dry ether at −78 °C, and the mixture was stirred at ambient temperature for 2 h. Solvent was removed under vacuum, and the product was extracted into boiling hexane and filtered. The product was further purified by recrystallization from cold (−30 °C) hexane to afford the product as yellow needlelike crystals in 80% yield. All syntheses and measurements were carried out in inert conditions.

* Corresponding author. E-mail nora.makela@borealisgroup.com.

10.1021/ma012127u CCC: $22.00
Published on Web 03/22/2002

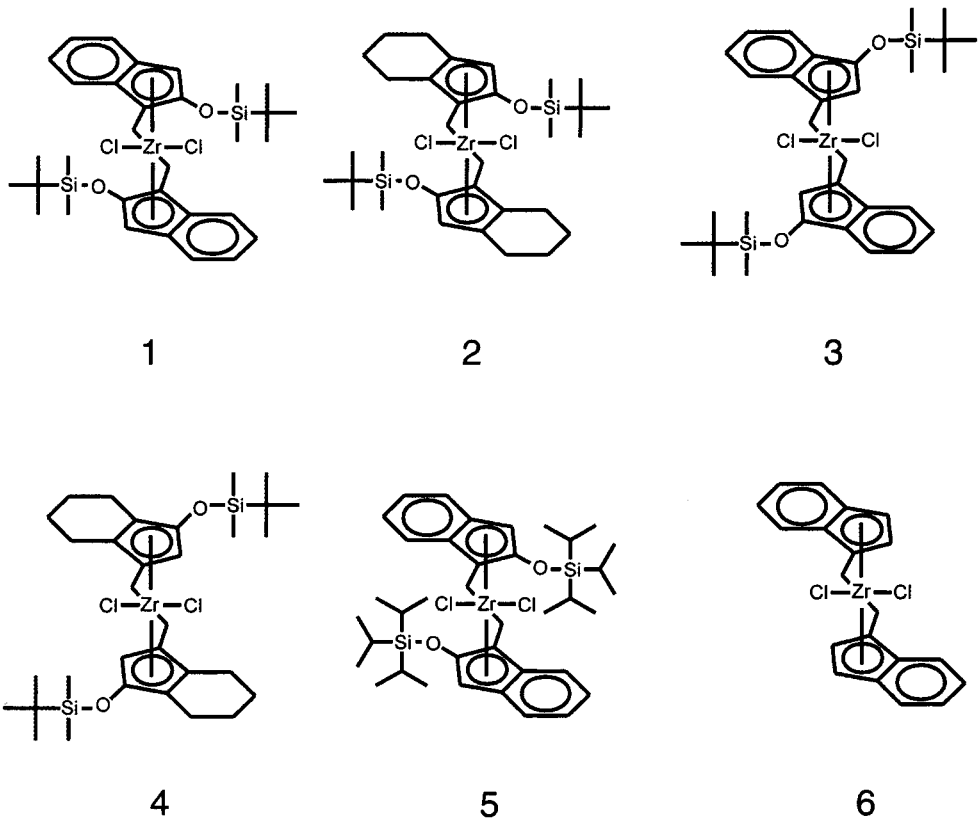

Figure 1. Schematic structures of the studied zirconocenes in the dichloride precursor form.

For the UV/vis measurements a required amount of 30 wt % MAO in toluene from Albemarle (optional) was added to the metallocene−toluene solution (8×10^{-4} mol/L Zr). All complexes were reacted with MAO. This solution was transferred to 1 cm path length quartz cells with Teflon stoppers, and the samples were analyzed with a Perkin-Elmer Lambda 11 spectrophotometer after 2 h reaction. The analysis was repeated after 6 h to verify the stability of the complex. Measurements were carried out in the wavelength range of 200−800 nm, scan speed 240 nm/min, and data interval 1 nm.

For the polymerization experiments the studied metallocenes were dissolved in MAO solution and allowed to react for 2 h before polymerization. The Al/Zr molar ratio used was 1000. The polymerizations of ethylene with 1-hexene were performed in *n*-pentane in a 2 L autoclave reactor equipped with a paddle stirrer. The ethylene partial pressure was 10 bar, the amount of 1-hexene 50 mL, polymerization time 30 min, and temperature 80 °C.

Computational Aspects

The performance of the Hartree−Fock method is generally unsatisfactory for transition-metal complexes, mainly due to near-degeneracy[8] and relativistic effects.[9] Zirconium is an exception because of its location at the beginning of the second transition row in the periodic table. Because of the absence of significant near-degeneracy and relativistic effects in several complexes of zirconium, the HF/3-21G* method is capable of producing realistic geometries for zirconocenes. This has been demonstrated by optimizing the structures of 62 crystallographically characterized zirconocene dichlorides.[10] The performance of the HF/3-21G* is consistent, and the accuracy is comparable to the more expensive MP2 and hybrid density functional B3LYP calculations.

For rigorous treatment of ligand-to-metal charge transitions, excited states of the complexes should be studied by configuration interaction (CI) calculations allowing mixing of the configurations. The 3-21G* basis set is apparently too small for the SCF calculations of the excited states, while the CI methods are beyond the practical limit of the large siloxy-substituted zirconocenes. For the qualitative purposes of the present work, the calculations of the excited states were not considered. The interest of the work is in the trends in LMCT absorptions, which are reproduced by the HF/3-21G*-derived LUMO−HOMO energy gaps.[3] Reported HF/3-21G* calculations were carried out with GAUSSIAN 94.[11]

A characteristic feature of racemic ethylene-bridged bis(indenyl)-type zirconocenes is conformational isomerism due to flexibility of the bridge, resulting in two distinct limit conformations, indenyl-forward (Π) and indenyl-backward (Y).[12] Since the siloxy-substituted complexes generally favor the Y-conformation[5,13] and the calculated LUMO−HOMO gaps are nearly identical for the conformers,[3] only the Y-conformations have been considered in this context.

Results and Discussion

Activation of the Zirconocene Complexes. Earlier theoretical[14] and luminescence[15] studies on titanocenes suggest that the HOMO orbitals of methylated intermediates are methyl-based unlike the dichloride precursors for which the HOMO is Cp′-based. The suggested orbital rearrangement does not, however, occur for the studied siloxy-substituted zirconocenes. On the basis of our calculations, the four highest occupied molecular orbitals of dimethyl species are Cp′-based and the fifth is the highest occupied methyl-based orbital (Figure 2).[16] The same applies for the cationic monomethyl forms as well, the four highest being Cp′-based, in this case followed by two siloxy-based orbitals, and the seventh

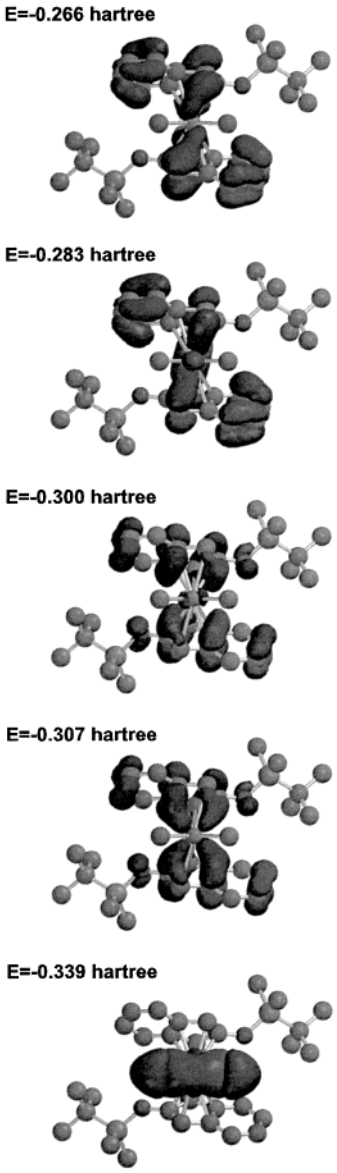

Figure 2. Five highest occupied molecular orbitals of complex **1** in dimethyl form. Hydrogens are omitted for clarity.

is the highest occupied methyl-based orbital. The lowest unoccupied orbitals of the dichloride, dimethyl, and cationic monomethyl forms of the studied zirconocenes are zirconium-based. Hence, lowest energy LMCT absorptions are due to Cp′ → Zr charge transitions for all intermediate structures of the activation step.

Deffieux et al. detected three successive transformations for $Et(Ind)_2ZrCl_2$/MAO with UV/vis spectroscopy: (1) generation of a neutral monomethyl monochloride zirconocene species at [Al]/[Zr] < 30, resulting in a LMCT band shift to higher energies (a hypsochromic shift), (2) with increasing [Al]/[Zr] ratio of 30−150 a shift to lower energies was observed (bathochromic shift), and (3) at even higher ratios ([Al]/[Zr] = 150−2000) a second bathochromic shift of the LMCT band was recorded. The bathochromic shift at [Al]/[Zr] ratio range of 30−150 was concluded to be an indication of cation formation and the second bathochromic shift at [Al]/[Zr] = 150−2000 an indication of cation dissociation.[4b−d]

In the present study, no further bathochromic shifts were observed beyond MAO concentration of [Al]/[Zr] = 1000 and with reaction times exceeding 2 h. This

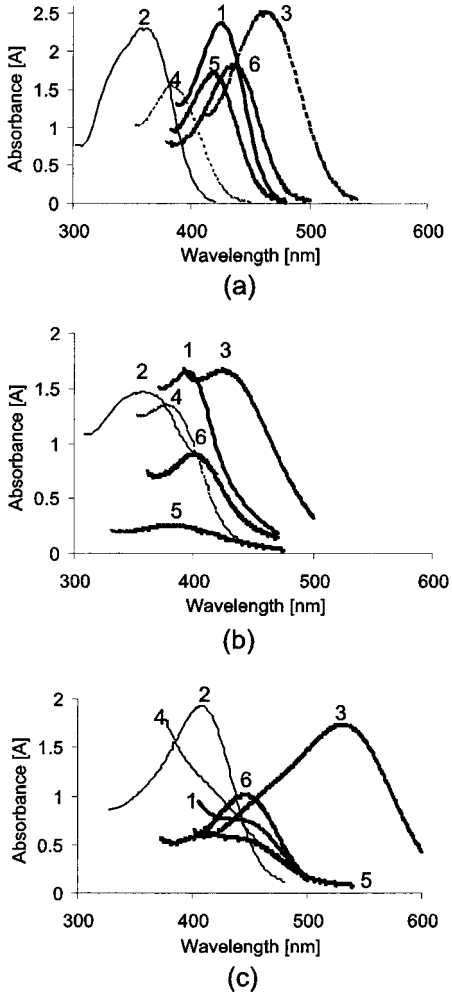

Figure 3. Lowest energy LMCT absorptions of the studied metallocenes: (a) in toluene; (b) reacted with MAO, [Al]/[Zr] = 20; (c) reacted with MAO, [Al]/[Zr] = 1000. Numbers refer to complexes in Figure 1.

indicates that the catalysts had reached their final activated forms at the specified conditions. In the following, the spectral changes caused by the addition of different amounts of MAO (i.e., [Al]/[Zr] = 0, 20, or 1000) are studied with the aid of frontier orbital calculations (Figure 3).

Dichloride Precursors (in Toluene). The lowest energy LMCT absorptions for dichloride forms of complexes **1**−**6** measured in toluene are presented in Figure 3a. The apparent trends between the molecular structures and absorption energies have been reported in a preceding study[3] and are shortly summarized:

The siloxy group itself has no or marginal effects on the absorption energy, due to almost equal destabilization of both HOMO and LUMO orbitals. Instead, indenyl ring hydrogenation as well as the position, while not the size, of the substituent affects the lowest energy LMCT markedly. Indenyl ring hydrogenation stabilizes the HOMO orbital and destabilizes the LUMO orbital, resulting in increased energy of LMCT absorption because of enlarged LUMO−HOMO energy gap. Moving the siloxy group from position 2 to 1, decreases the absorption energy due to the reduced LUMO−HOMO gap, which originates from destabilization of the HOMO combined with simultaneous stabilization of the LUMO.

Reaction of Zirconocene Complex and MAO, [Al]/[Zr] = 20. Previous NMR and UV/vis studies on

Table 1. Measured LMCT Energies (eV), Calculated HOMO and LUMO Orbital Energies (hartrees), and Calculated LUMO−HOMO Energy Gaps (Δ, eV) for Complexes 1−6 and Their Monomethyl Monochloride, Dimethyl, and Cationic Forms[a]

	Cp'_2ZrCl_2				$Cp'_2ZrMeCl$				Cp'_2ZrMe_2				Cp'_2ZrMe^+			
	LMCT	HOMO	LUMO	Δ	LMCT	HOMO	LUMO	Δ	LMCT	HOMO	LUMO	Δ	LMCT	HOMO	LUMO	Δ
1	2.9	−0.28	0.05	9.0	3.1	−0.27	0.07	9.3	3.3	−0.27	0.08	9.5	2.8	−0.40	−0.09	8.4
2	3.4	−0.31	0.06	10.0	3.5	−0.30	0.09	10.4		−0.29	0.10	10.6	3.1	−0.42	−0.09	9.1
3	2.7	−0.26	0.04	8.3	2.9	−0.26	0.06	8.7		−0.25	0.07	8.9	2.3	−0.38	−0.09	8.0
4	3.2	−0.30	0.06	9.6	3.3	−0.29	0.08	10.0		−0.28	0.10	10.3	3.1	−0.42	−0.09	8.9
5	3.0	−0.28	0.05	9.0	3.2	−0.27	0.07	9.3		−0.27	0.08	9.5	2.8	−0.40	−0.09	8.5
6	2.8	−0.28	0.04	8.7	3.1	−0.28	0.07	9.4		−0.27	0.07	9.2	2.6	−0.41	−0.11	8.3

[a] The monomethyl monochloride and cationic forms were prepared by contacting MAO ([Al]/[Zr] = 20) and MAO ([Al]/[Zr] = 200), respectively, with dichloride complex.

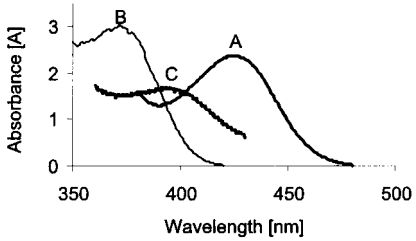

Figure 4. Spectra of complex **1**: (A) in toluene; (B) dimethyl form in toluene; (C) methylated with MAO, [Al]/[Zr] = 20.

Cp'_2ZrCl_2/MAO reaction systems uniformly indicate that Cl/Me exchange leads to a monomethyl monochloride species ($Cp'_2ZrClMe$) instead of a dimethyl species (Cp'_2ZrMe_2) at relatively low [Al]/[Zr] ratios of 10−20.[4b,17] The hypsochromic shifts observed with the addition of MAO have been reported to indicate the methylation of the dichloride precursors. These shifts are due to the replacement of the electron-withdrawing chloride ligands with the electron-donating methyl groups. Consequently, the electron density at the metal center is increased, which in turn raises the energy needed for the Cp → Zr charge transition.[4] We, as well, observed the monomethylation of the dichloride precursors at [Al]/[Zr] ratio of 20. This monomethylation is demonstrated in Figure 4, in which the spectrum of catalyst **1** is shown in three conditions. The conditions for the measured spectra (A, B, and C) were the following: The dichloride form of complex **1** in toluene (A), the isolated dimethyl form of complex **1** in toluene (B), and complex **1** reacted with MAO at [Al]/[Zr] = 20. Spectrum C, representing the methylated species of the catalysts, absorbs almost exactly in between the corresponding dichloride (A) and dimethyl (B) forms of the catalyst. As a consequence, it is meaningful to compare the experimental LMCT energies at a [Al]/[Zr] ratio of 20 with the theoretical HOMO−LUMO energy gaps of monomethyl monochloride species.

Frontier orbital calculations revealed that methylation of the dichloride precursor destabilizes both HOMO and LUMO (Table 1 and Figure 5). Destabilization of the LUMO occurs because of decreased electron deficiency at the metal center and is accompanied by increasing Zr−Cp′ distances.[18] This, in turn, destabilizes the HOMO due to less optimal overlap between the metal and ligand orbitals. Destabilization of the LUMO is generally more pronounced than destabilization of the HOMO, resulting in increased LUMO−HOMO energy gaps and LMCT absorption energies. The relative order of the LMCT absorption energies within the studied series of siloxy-substituted zirconocenes remains unaffected (Figure 7).

While hypsochromic shifts are observed for all of the studied complexes at low [Al]/[Zr], the shifts are smaller

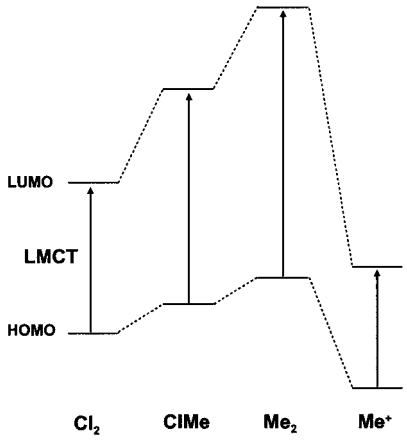

Figure 5. Schematic presentation of the relationship between the intermediate of the activation step, frontier orbital energies, and LMCT absorption energies.

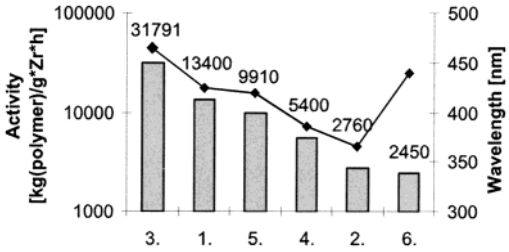

Figure 6. Correlation between the catalyst polymerization activity (activated with MAO, [Al]/[Zr] = 1000) and the lowest energy LMCT absorptions of the complexes in the dichloride form.

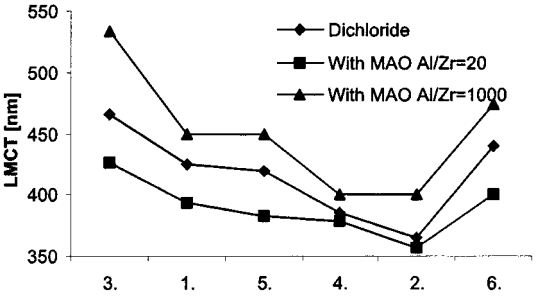

Figure 7. LMCT absorption energies of the studied complexes.

in the spectra of **2** and **4** (Figure 3b). A plausible explanation arises from the difference in the type of Cp′ ligand in these compounds. In the case of complexes **1**, **3**, and **5**, Cp′ ligand is indenyl-based, whereas for **2** and **4** Cp′ is tetrahydroindenyl-based. The main contributor to the hypsochromic shift at low [Al]/[Zr] is the destabilization of the Zr-based LUMO orbital. The LUMOs of hydrated **2** and **4** lie initially (in the dichloride

precursor) higher in energy than their nonhydrated indenyl-based congeners **1**, **3**, and **5** (Table 1). The destabilization of the LUMO is less pronounced for the hydrated compounds, which already possess more unstable LUMOs. Consequently, smaller hypsochromic shifts are observed for **2** and **4**.

Reaction of Zirconocene Complex and MAO, [Al]/[Zr] = 1000. The lowest energy LMCT absorptions of the complex−MAO reaction system ([Al]/[Zr] = 1000) are shown in Figure 3c. The significant bathochromic shifts, compared to both dichloride and monomethyl monochloride cases, suggest increased electron deficiency at the metal center due to formation of the monomethyl cation. Frontier orbital calculations (Table 1 and Figure 5) demonstrate a marked stabilization of both LUMO and HOMO. The changes in the energy of the LUMO are much stronger, leading to lower energy absorptions. The decreased electron density at the Zr atom stabilizes the Zr-based LUMO resulting in shortening of the Zr−Cp′ distances by approximately 0.1 Å, which stabilizes the HOMO due to better orbital overlap between the metal and the Cp′ ligand. The calculations of cationic monomethyl zirconocenes were performed of the free cation, not of the zirconocene cation−MAO anion ion pair. Naturally, in the experiments MAO was present. Since the experimental and theoretical results are in line with each other, it is probable that the LUMOs are not largely directly affected by MAO by for example MAO → Zr charge transfer.

MAO has its wide absorption band at the area 280−330 nm, therefore sometimes overlapping with the metallocene LMCT bands. The weak LMCT band of complex **4** is a result of such overlapping.

Correlation between the Polymerization Activity and the Lowest Energy LMCT Absorption. In earlier UV/vis spectroscopic studies, the catalyst activity in polymerization has been correlated to the position of the lowest energy absorption band of MAO-activated zirconocene when different forms of the same zirconocene catalyst are studied, e.g., different [Al]/[Zr] ratios.[4b−d] The correlation has been explained to arise from the relationship between the energy of the absorption band and the cationic nature of the metal center, lower energy, and thus higher electron deficiency, suggesting increased polymerization activity. In the present study a correlation between the polymerization activity and the LMCT transitions was observed for a group of siloxy-substituted zirconocenes. (Figure 6). Within the siloxy-substituted complexes **1**−**5**, the polymerization activity systematically decreases as a function of increasing lowest energy LMCT absorption. It is evident that the direct correlation is valid only for a uniform group of complexes with similar steric and electronic properties. The unsubstituted catalyst **6** does not belong to this uniform series because of the absence of the siloxy group. Furthermore, it is important to note that, within the series of complexes **1**−**5**, the trends in lowest energy LMCT absorptions are independent of the studied form of the zirconocene, i.e., dichloride, monomethyl monochloride, or cationic (Figure 7). This observation has two implications. First, it confirms that the identity of the lowest energy absorption is the same Cp′ → Zr for all catalyst states. Second, it enables correlations between polymerization activity and absorption energies independently of the form (Cl_2, MeCl, Me^+) of the catalyst in a series of similar complexes.

While the cationic nature of the metal undoubtedly contributes to the activity of the catalyst, its favorable influence is generally less straightforward. Higher electron deficiency at the metal center increases the reactivity of the complex, not only toward the monomer but also toward the other components in the system including cocatalyst, catalyst poisons, and other cationic catalyst centers. Each of these reactions should have unfavorable influence on the catalyst performance.[19]

If the catalytic activity is not directly proportional to the cationic nature of the metal center, where does the correlation between the catalytic activity and the lowest energy LMCT absorption band come from? An alternative explanation becomes evident in the frontier orbital investigations. The absorption energy is reduced by stabilization of the LUMO, which is mostly of metal character, as well as by destabilization of the Cp′ ligand-based HOMO. Stabilization of the LUMO favors the methylation step through facilitation of the charge transfer to the metal, which is more significant for electron donors (methyl) than electron acceptors (chlorine). On the other hand, destabilization of the HOMO favors the cation formation by methyl or chlorine abstraction. This is due to facilitation of the charge transfer from the ligand to the metal, which stabilizes the active cationic species. The lowest energy LMCT absorptions are consequently related to the facility of the whole activation step and therefore correlate with the catalytic activity for siloxy-substituted zirconocenes.

The cationization process of the proposed monomethyl monochloride zirconocene includes the chloride abstraction to give the cationic complex directly or methyl abstraction followed by methylation of the cationic halide complex. As discussed above, cation formation should be favored by the destabilized HOMO. Since the HOMO is more stable in monomethyl chloride zirconocenes than in their dimethyl congeners (Figure 5), we can expect that cationization of a dimethyl complex is more facile. To demonstrate this effect, the activation behavior of complex **1** was compared to the activation behavior of complex **1**−Me_2. Both of the catalysts reached the final cationic form in less than 5 min, suggesting that the kinetics of activation is similar in both catalysts. The reaction of the complexes with MAO (Al/Zr = 1000) resulted in LMCT bands at exactly same energy; i.e., the cationic species are the same, as expected. Although the LMCT energies of the complexes were same, the activated complex **1** absorbed at lower intensity than the activated complex **1**−Me_2, which according to Beer's law reveals lower concentration of active species. This was further supported by polymerization results—the activity of the dimethylated complex was higher (Figure 8).

Indenyl ring hydrogenation destabilizes the LUMO and stabilizes the HOMO, resulting in an increased LUMO−HOMO gap as well as in an increased LMCT absorption energy. As a consequence, the activities of hydrogenated **2** and **4** are much lower than those of the non-hydrogenated congeners **1** and **3**. Moving the siloxy group from position 2 to position 1 stabilizes the LUMO and destabilizes the HOMO, therefore reducing the energy of LMCT. Because of the facilitation of the activation step, 1-siloxy-substituted complexes **3** and **4** are more active than their 2-substituted congeners **1** and **2**, respectively. Complex **3**, combining both the favorable non-hydrogenated indenyl ligand and the 1-substituent, is the most active catalyst of the series

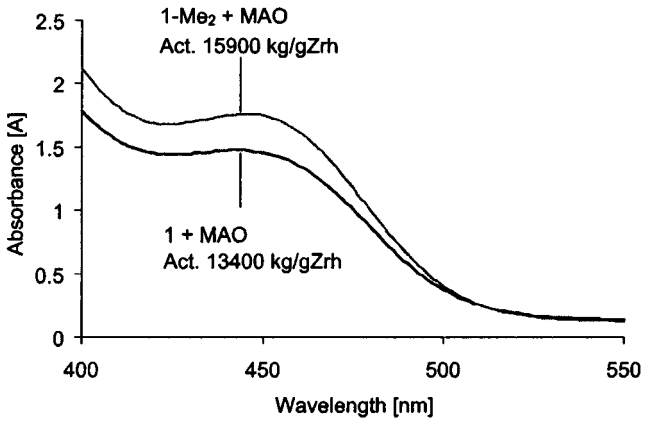

Figure 8. LMCT transitions and polymerization activities of **1** and **1**−Me_2 activated with MAO ([Al]/[Zr] = 1000, contact time 2 h).

by a great margin. The size of the siloxy group (**1** vs **5**) has no effect on orbital energies and LMCT absorptions. The changes in catalytic activities are small, slightly favoring the smaller substituent (**1**). Apparently, the bulky triisopropyl substituent in **5** increases the steric hindrance around the metal center, thus making the coordination site somewhat less accessible for the monomer.

Conclusions

The activation of racemic siloxy-substituted ethylene-bridged bis(indenyl)-type zirconocenes with MAO was studied by combining UV/vis spectroscopy with quantum chemical calculations. Independent of the activation step intermediate, i.e., Cp'_2ZrCl_2, $Cp'_2ZrMeCl$, or Cp'_2ZrMe^+, the lowest energy LMCT absorption band arises from the charge transition between the Cp′-based HOMO and the Zr-based LUMO. The correlation between the experimental absorption energies and LUMO−HOMO energy gaps calculated at the HF/3-21G* level is clear.

The formation of the active cationic species proceeds through monomethylated instead of dimethylated intermediate. Methylation destabilizes both frontier orbitals, while the destabilization is more pronounced for the LUMO, giving rise to the observed hypsochromic shifts in the spectra. Cationization of the complexes results in significant stabilization of both LUMO and HOMO. The LUMO is more strongly affected, causing the observed bathochromic shifts. The position of the lowest energy LMCT absorption band correlates with the polymerization activity of siloxy-substituted complexes. Frontier orbital investigations suggest that the correlation is due to increased facility of the activation step as a function of the decreasing absorption energy, which is achieved by stabilization of the LUMO and/or destabilization of the HOMO. Stabilization of the LUMO favors the methylation step, whereas destabilization of the HOMO facilitates the cation formation. Consequently, the non-hydrogenated 1-siloxy-substituted complex **3**, combining a low-lying LUMO with a high-lying HOMO, is clearly the most active catalyst of the series.

Acknowledgment. The authors thank Mr. Harri Hokkanen and Ms. Tarja-Tuulikki Turpeinen for providing the polymerization results, Mr. Janne Maaranen for the synthesis of the dimethylated complex, and Ms. Paula Oinonen for the spectroscopic measurements. Special thanks are due to Dr. Reko Leino and Dr. Hendrik Luttikhedde for the synthesis of siloxy-substituted zirconocenes. Financial support from the Finnish Technology Development Centre (TEKES) is gratefully acknowledged.

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MA012127U