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Spectral studies of bridged bisindenylmetallocenes and products of their reactions with polymethylalumoxane in toluene and dichloromethane in the visible region

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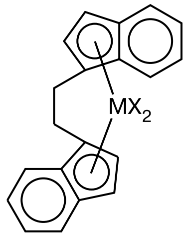
Quantitative characteristics of changes in the energy of charge transfer from π-bonded ligands to metal are presented for the series of structurally similar *ansa*-metallocene complexes of IVB Group elements. The changes are caused by the solvation effect, replacement of σ-bonded chlorine ligands by methyl groups and of bridging ethylene groups by dimethylsilylene moieties, introduction of the methyl substituent into position 2 and phenyl substituent into position 4 of the indenyl system, variation of the transition metal in metallocene, and formation of complexes with polymethylalumoxane (MAO) at different Al_{MAO}/Zr ratios. These effects are found to be additive.

Key words: *ansa*-metallocene complexes of IVB Group elements, UV-Vis spectroscopy, ligand to metal charge transfer, polymethylalumoxane, activation, metallocene catalysts.

The influence of substituents on the catalytic properties of metallocene complexes of the $(\pi\text{-L}^R)_2MX_2$ type (π-L is cyclopentadienyl (Cp), indenyl (Ind), fluorenyl (Flu); R is a substituent or substituents in the π-system; X = Cl, Me) in olefin polymerization is often analyzed at the qualitative level.[1,2] Reasonable quantitative characteristics of ligands, for instance, Tolman solid angles,[1,3] can be used to estimate the influence of steric parameters of a substituent during approaching and coordination of olefin to the active site. However, quantitative estimations of the electron-donor or electron-acceptor influence of substituents on a change in the effective charge and electron density on the metal seem difficult to perform mainly due to a complicated interrelation between the overlap of the frontier molecular orbitals and metallocene geometry,[4] influence of substituents in π-bonded ligands,[5] and several other factors. In recent time, researchers are interested in possibilities of obtaining the corresponding information using UV-Vis spectroscopy.[5—15] The experimentally observed long-wave absorption band (AB) in spectra of solutions of metallocenes or metallocene—activator catalytic systems reflects the charge transfer from the π-ligand to the transition metal (LMCT).[6] An increase in the positive charge on the metal is accompanied by the bathochromic shift of the AB and *vice versa*. For instance, the replacement of the electron-withdrawing σ-bonded chlorine ligands by electron-releasing methyl groups results in a noticeable hypsochromic shift of the AB, while the formation of cationic complexes in the presence of an activator leads to a noticeable bathochromic shift of the AB.



1

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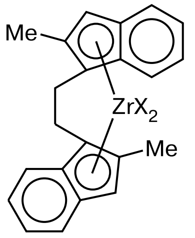
X = Cl, Me



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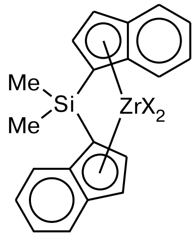

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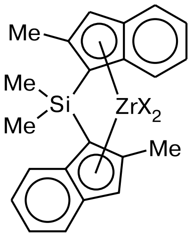
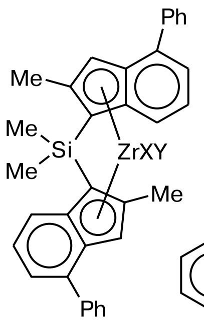


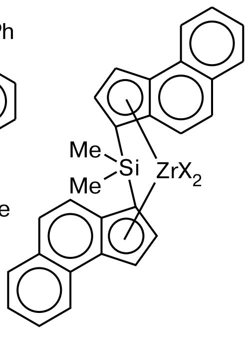
4

X = Cl, Me



5

X = Y = Cl;
X = Cl, Y = Me;
X = Y = Me



6[14]

X = Cl, Me

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In this work, we compared the UV-Vis spectra of solutions of the series of structurally similar metallocenes and products of their reactions with polymethylalumoxane (MAO) and showed that the spectroscopic data in the visible region can be used for analysis of qualitative effects and also for quantitative estimation of the electronic influence of substituents, bridges, solvation, type of transition metal, and type of complexes formed in the reaction with an activator on the LMCT energy. Solutions of the series of structurally similar bridged complexes in toluene and methylene dichloride were studied for quantitative analysis of these effects: *rac*-$(CH_2)_2Ind_2MX_2$ (M = Ti, Zr, Hf; X = Cl, Me) (**1**), *rac*-$(CH_2)_2(2\text{-}MeInd)_2ZrX_2$ (**2**), *rac*-$Me_2SiInd_2ZrX_2$ (**3**), *rac*-$Me_2Si(2\text{-}MeInd)_2ZrX_2$ (**4**), and *rac*-$Me_2Si(2\text{-}Me,4\text{-}PhInd)_2ZrXY$ (X = Y = Cl; X = Cl, Y = Me; X = Y = Me) (**5**).

The changes in the LMCT energy for the **5** (X, Y = Cl)/MAO catalytic system at different Al_{MAO}/Zr molar ratios were quantitatively analyzed. The results were compared with experimental data of other authors for structurally similar MAO-activated zirconocenes .

Experimental

Toluene and CH_2Cl_2 (spectroscopic purity grade), which were dried over molecular sieves 4Å, were used to prepare solutions of the complexes under study. Toluene was additionally distilled over $LiAlH_4$. All procedures on preparing solutions and filling cells were carried out in a special box with a dry inert gas (helium or argon) atmosphere. Spectra were recorded on a Specord UV–Vis M-40 spectrophotometer.

Metallocene dichlorides and compounds **1** (M = Ti, Hf; X = Me) are available from Boulder Sci. Other zirconocenes were dimethylated according to a procedure described previously.[16]

Dimethyl[ethylenebis(2-methylinden-1-yl)]zirconium (2, M = Zr). ^1H NMR (CD_2Cl_2), δ: –1.26 (s, 6 H, Me—Zr); 1.93 (s, 6 H, Me—Ind); 3.19—3.64 (m, 4 H, C_2H_4); 6.35 (s, 2 H, Ind); 6.98, 7.18 (both t, 2 H each, Ind, *J* = 7.8 Hz); 7.42 (d, 2 H, Ind, *J* = 8.3 Hz); 7.52 (d, 2 H, Ind, *J* = 7.8 Hz).

Dimethyl[dimethylsilylenebis(inden-1-yl)]zirconium (3, M = Zr). ^1H NMR (toluene-d_8), δ: –0.98 (s, 6 H, Me—Zr); 0.63 (s, 6 H, Me_2Si); 5.92, 6.73 (both d, 2 H each, Ind, *J* = 2.9 Hz); 6.89 (t, 2 H, Ind, *J* = 7.8 Hz); 7.20 (d, 2 H, Ind, *J* = 9.3 Hz); 7.23 (t, 2 H, Ind, *J* = 9.3 Hz); 7.50 (d, 2 H, Ind, *J* = 8.3 Hz).

Dimethyl[dimethylsilylenebis(2-methylinden-1-yl)]zirconium (4, M = Zr). ^1H NMR (CD_2Cl_2), δ: –1.31 (s, 6 H, Me—Zr); 1.08 (s, 6 H, Me_2Si); 2.05 (s, 6 H, Me—Ind); 6.74 (s, 2 H, Ind); 6.93, 7.24 (both t, 2 H each, Ind, *J* = 8.0 Hz); 7.52 (d, 4 H, Ind, *J* = 9.3 Hz).

Dimethyl[dimethylsilylenebis(2-methyl-4-phenylinden-1-yl)]zirconium (5, M = Zr). ^1H NMR (CD_2Cl_2), δ: –1.22 (s, 6 H, Me—Zr); 1.14 (s, 6 H, Me_2Si); 2.10 (s, 6 H, Me—Ind); 6.97 (s, 2 H, Ind); 7.00—7.64 (m, 16 H, Ph—Ind, Ind).

[Dimethylsilylenebis(2-methyl-4-phenylinden-1-yl)](methyl)zirconium chloride (5, M = Zr, X = Me, Y = Cl) was synthesized by the reaction of the dichloride complex with $AlMe_3$ at the molar ratio Al/Zr = 150 by analogy to a described procedure.[17] After $AlMe_3$ was removed, the reaction product contained ~90 mol.% monomethyl monochloride and 10 mol.% starting dichloride complex. ^1H NMR (CD_2Cl_2), δ: –0.76 (s, 3 H, Me—Zr); 1.20, 1.26 (both s, 3 H each, Me_2Si); 2.11, 2.26 (both s, 3 H each, Me—Ind); 6.80, 7.03 (both s, 1 H each, Ind); 7.06—7.72 (m, 16 H, Ph—Ind, Ind).

Absorbance in the visible region of solutions of products of the reaction between the dichloride complexes with MAO was measured as follows. Weighing samples of metallocenes were dissolved in a toluene solution of MAO at a specified Al_{MAO}/Zr molar ratio, the reaction mixture was stored for 1 h, and the spectra were recorded in 0.5-cm quartz cells. In all experiments, the concentration of metallocene was $\sim 1 \cdot 10^{-3}$ mol L^{-1}.

^1H NMR spectra of dimethylated zirconocenes were recorded on a Bruker DPX-200 spectrometer under the following conditions: spectral width 4 kHz, relaxation delay 4 s, and number of acquisitions 16. To calculate chemical shifts, signals of residual protons of the Ph ring in the toluene-d_8 molecule were used (δ 7.06, 7.10, and 7.18).

Results and Discussion

Solvation effect. The M—Cl bond in zirconocene dichlorides is more polar than that in dimethylated analogs. This difference determines effects of solvents with different polarities on the energy values of the LMCT process in the series of structurally similar zirconocene dichlorides and dimethylated zirconocenes and make it possible to estimate the solvation influence on the LMCT energy (Table 1). Comparison of the absorption spectra of zirconocene dichlorides in toluene and CH_2Cl_2 shows that the differences in polarities of the solvents (ε is 2.4 and 8.9 for toluene and CH_2Cl_2, respectively) result in the difference between the LMCT energies up to 0.06 eV and depend on the structure of *ansa*-zirconocene. The maximum effect of solvation by methylene dichloride is observed for the most spatially open unsubstituted *ansa*-zirconocene dichloride with the bridging ethylene group. The presence of the Me substituent in position 2 or Ph substituent in position 4 decreases the solvation effect, probably, due to steric factors. The solvation effect either is absent or much lower for the respective dimethylated zirconocenes.

Methylation effect. The energy effect of dialkylation is presented by a comparison of the LMCT energy for the series of structurally similar *ansa*-zirconocene dichlorides and dimethylated *ansa*-zirconocenes (see Table 1). Taking into account the solvation effect, we can conclude that the replacement of two chlorine ligands by methyl groups increases the LMCT energy by 0.40 eV on the average. It is of interest that analogous energy effects of dialkylation can be obtained by analysis of the data of other authors for structurally similar complexes **3** (X = Cl)[14] ($\Delta E_{Cl_2 \to Me_2}$ = 0.42 eV) and *rac*-$Me_2Si(2\text{-}Me,Benz[e]Ind)_2ZrCl_2$ (**6**, X = Cl)[14] ($\Delta E_{Cl_2 \to Me_2}$ =

Table 1. Positions of a maximum of the LMCT band (λ_{max}) and corresponding LMCT energies (E_{LMCT}) for solutions of *ansa*-zirconocenes and energy effects of solvation (ΔE_1), alkylation (ΔE_2), introduction of the Me substituent into position 2 and Ph substituent into position 4 of the indenyl system (ΔE_3), and bridging ligands (ΔE_4)

Complex	Solvent	λ_{max}/nm	E_{LMCT}	ΔE_1	ΔE_2	ΔE_3	ΔE_4
			eV				
1 (M = Zr, X = Cl)	Toluene	429	2.89	—	—	—	—
1 (M = Zr, X = Cl)	CH_2Cl_2	438	2.83	−0.06	—	—	—
1 (M = Zr, X = Me)	Toluene	369	3.36	—	0.47	—	—
1 (M = Zr, X = Me)	CH_2Cl_2	371	3.34	−0.02	—	—	—
1 (M = Ti, X = Cl)	Toluene	648	1..91	—	—	—	—
1 (M = Ti, X = Cl)	CH_2Cl_2	661	1.88	−0.03	—	—	—
1 (M = Ti, X = Me)	Toluene	432	2.87	—	0.96	—	—
1 (M = Ti, X = Me)	CH_2Cl_2	434	2.86	−0.01	0.98	—	—
1 (M = Hf, X = Cl)	Toluene	394	3.15	—	—	—	—
1 (M = Hf, X = Cl)	CH_2Cl_2	399	3.11	−0.04	—	—	—
1 (M = Hf, X = Me)	Toluene	359	3.45	—	0.30	—	—
2 (X = Cl)	Toluene	435	2.85	—	—	—	—
2 (X = Cl)	CH_2Cl_2	442	2.81	−0.04	—	—	—
2 (X = Me)	Toluene	378	3.28	—	0.43	−0.08	—
2 (X = Me)	CH_2Cl_2	382	3.25	−0.03	—	—	—
3 (X = Cl)	Toluene	446	2.78	—	—	—	—
3 (X = Cl)	CH_2Cl_2	452	2.74	−0.04	—	—	—
3 (X = Me)	Toluene	385	3.22	—	0.44	—	−0.14
3 (X = Me)	CH_2Cl_2	387	3.20	−0.02	—	—	—
4 (X = Cl)	Toluene	450	2.76	—	—	—	—
4 (X = Cl)	CH_2Cl_2	456	2.72	−0.04	—	—	—
4 (X = Me)	Toluene	394	3.15	—	0.39	−0.07	−0.13
4 (X = Me)	CH_2Cl_2	394	3.15	0	—	—	—
5 (X = Cl)	Toluene	464	2.67	—	—	—	—
5 (X = Y = Cl)	CH_2Cl_2	468	2.65	−0.02	—	—	—
5 (X = Cl, Y = Me)	Toluene	432	2.87	—	0.20	—	—
5 (X = Y = Me)	Toluene	404	3.07	—	0.40	−0.08	—

0.38 eV). Thus, the dimethylation effect for structurally similar zirconocenes increases the LMCT energy by ~0.4 eV.

To analyze the additivity of the influence of stepwise alkylation on the LMCT energy, we synthesized the monomethyl and dimethylated analogs of complex **5** (X = Cl). Complex **5** is characterized by the lowest shift of the LMCT band when toluene is replaced by CH_2Cl_2. As can be seen from the data in Table 1, the energy change upon the replacement of one chlorine ligand by methyl is half a change in the LMCT energy upon dialkylation.

Effects of introduction of 2-Me and 4-Ph substituents into the indenyl system and effect of the bridging group. The introduction of the electron-releasing Me substituent into position 2 of the indenyl system for two dimethylated *ansa*-zirconocenes, which are less sensitive to the solvation effect, resulted in an insignificant bathochromic shift of the LMCT AB by ~0.08 eV compared to the unsubstituted analogs (see Table 1). A lower bathochromic shift ($\Delta E = 0.02$ eV) is observed for the dichloride analogs (see Table 1). Such an insignificant change in the LMCT energy upon the introduction of an electron-releasing substituent into the indenyl system seems unusual. One could expect an opposite effect due to a decrease in the positive charge on the transition metal, because the electron density is donated through a system of π-bonds. Note that a low LMCT energy decrease (by 0.04 eV per each Me substituent) of 3.72, 3.68, and 3.54 eV was also observed[6] for toluene solutions of the cyclopentadienyl non-bridged complexes Cp_2ZrCl_2, $(MeCp)_2ZrCl_2$, and $(Me_4Cp)_2ZrCl_2$, respectively. The effect of the phenyl substituent in position 4 of the indenyl system on the LMCT energy is similar to that of the Me substituent in position 2. The additivity of the effects of the 2-Me and 4-Ph substituents follows from a comparison of the LMCT energies for **3** (X = Me) and **5** (X, Y = Me) (see Table 1).

The replacement of the bridging ethyl ligand by the dimethylsilyl fragment results in a noticeable bathochromic shift of the AB by 0.13—0.14 eV (see Table 1).

Effect of transition metal. The data on the energy effect of transition metal on LMCT for the series of *rac*-forms of the ethynyl-bisindenyl dichloride and dimethylated titanium, zirconium, and hafnium complexes are presented in Table 2. It is seen that the highest LMCT

Table 2. Positions of a maximum of the LMCT band (λ_{max}) and corresponding LMCT energies (E_{LMCT}) for solutions of *ansa*-metallocenes in toluene and CH_2Cl_2 and the influence of transition metal replacement on the energy effects of solvation (ΔE_{solv}) and alkylation ($\Delta E_{Cl_2 \to Me_2}$)

Complex **1**		Solvent	λ_{max}/nm	E_{LMCT}	ΔE_{solv}	$\Delta E_{Cl_2 \to Me_2}$
M	X			eV		
Ti	Cl	Toluene	648	1.91	—	—
Ti	Cl	CH_2Cl_2	661	1.88	−0.03	—
Ti	Me	Toluene	432	2.87	—	0.96
Ti	Me	CH_2Cl_2	434	2.86	−0.01	0.98
Zr	Cl	Toluene	429	2.89	—	—
Zr	Cl	CH_2Cl_2	438	2.83	−0.06	—
Zr	Me	Toluene	369	3.36	—	0.47
Zr	Me	CH_2Cl_2	371	3.34	−0.02	0.51
Hf	Cl	Toluene	394	3.15	—	—
Hf	Cl	CH_2Cl_2	399	3.11	−0.04	—
Hf	Me	Toluene	359	3.45	—	0.30

energy is observed for toluene solutions of dimethylated and dichloride hafnocenes (3.45 and 3.15 eV, respectively), and solutions of the respective titanocenes are characterized by the lowest values (2.87 and 1.91 eV). The solvation effect is most pronounced for zirconocene.

Quantitative estimation of LMCT energy changes in products of the reactions of metallocene dichlorides with polymethylalumoxane. The reactions of metallocene dichlorides with MAO are accompanied by complicated transformations in the LMCT spectra of the metallocene complexes.[7,9,10,12,14] As a rule, hypsochromic shifts of AB occur at low molar ratios. These shifts are attributed to the alkylation of the starting dichloride in the presence of MAO. An increase in the catalyst/cocatalyst molar ratio results in the formation of products, whose AB are shifted to the long-wave region compared to those of the alkylation products. Considerable bathochromic shifts of the LMCT AB are observed under conditions of high molar cocatalyst excess, indicating a considerable decrease in the electrooptic gap for the cationic complex that formed. These reactions are presented in Scheme 1.

Scheme 1

$$L_2ZrCl_2 + MAO \longrightarrow L_2ZrMeCl \qquad (1)$$

$$(Al_{MAO}/Zr \approx 10 \text{ mol mol}^{-1})$$

$$L_2ZrMeCl + MAO \rightleftharpoons L_2Zr^{\delta+}MeCl \cdot MAO^{\delta-} \qquad (2)$$

$$(Al_{MAO}/Zr \approx 10^2 \text{ mol mol}^{-1})$$

$$L_2ZrMeCl + MAO \rightleftharpoons L_2Zr^{+}Me...ClMAO^{-} \qquad (3)$$

$$(Al_{MAO}/Zr \approx 10^3\text{—}10^4 \text{ mol mol}^{-1})$$

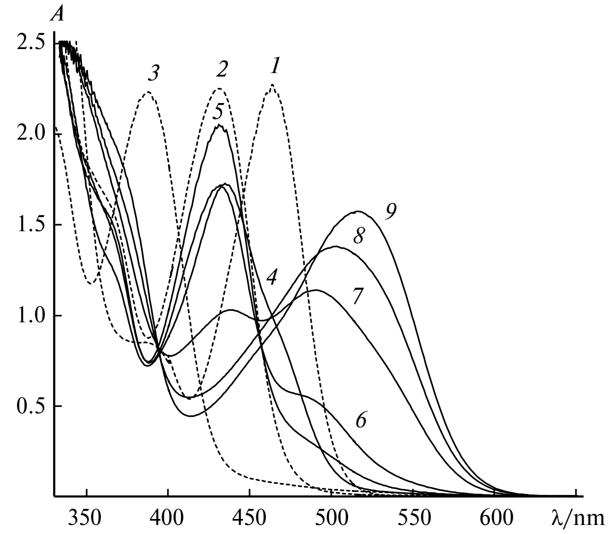

Fig. 1. Absorption spectra (*A*) of solutions of **5** (X = Y = Cl (*1*); X = Me, Y = Cl (*2*); X = Y = Me (*3*)) and products of the reaction of **5** (X = Y = Cl) with MAO (*4—9*) at the Al_{MAO}/Zr molar ratios equal to 10 (*4*), 20 (*5*), 120 (*6*), 240 (*7*), 500 (*8*), and 2000 (*9*); solvent toluene; [Zr] = $8.0 \cdot 10^{-4}$ mol L^{-1}.

The transformation of the absorption spectra for the **5** (X = Y = Cl)/MAO system at different Al_{MAO}/Zr molar ratios is shown in Fig. 1.

To obtain quantitative characteristics of the LMCT energy change in products of the reaction of metallocene dichloride with the activator, we analyzed the spectral data in the visible region for toluene solutions of the products of the reaction of **5** (X = Y = Cl) with MAO. Among the series of zirconocenes studied by us, this complex is characterized by AB with maximum shifts to the long-wave part of the spectrum compared to the spectrum of **1** (M = Zr, X = Cl) due to the combined influence of the Me and Ph substituents and bridging dimethylsilyl group.

The positions of maxima of the AB of toluene solutions of the dichloride complex, dimethylated analog, and products of the reaction with MAO are compared in Table 3. At the Al_{MAO}/Zr ratios equal to 10 and 20 mol mol^{-1}, a complex is formed, whose spectrum contains the AB with a maximum at 432 nm corresponding to the reference monoalkyl monochloride zirconocene (see Fig. 1, spectra *2*, *4*, and *5*, respectively). This shift corresponds to an increase in the LMCT energy by 0.2 eV upon monoalkylation (see Table 1). This fact asserts that zirconocene dichloride is monoalkylated at a low Al_{MAO}/Zr molar ratio. The hypsochromic shift of the absorption band of **1** (M = Zr, X = Cl) by 0.29 and 0.27 eV was observed in the reactions with MAO at low molar ratios Al_{MAO}/Zr = 10—50 in toluene[9] (see Table 3) and methylene dichloride,[10] respectively. The hypsochromic shifts of the AB by 0.25 and 0.20 eV corresponding to monoalkylation were also detected for products of the reactions of **3** (X = Cl) and **6** (X = Cl) with MAO in

Table 3. Positions of a maximum of the LMCT band (λ_{max}) and corresponding LMCT energies (E_{LMCT}) for solutions of *ansa*-zirconocenes in toluene and products of their reactions with MAO in toluene

System (M = Zr)	Al_{MAO}/Zr	λ_{max}/nm	E_{LMCT}/eV	Ref.
1 (X = Cl)	_	429	2.89	This work, 9
1 (X = Me)	_	369	3.36	This work, 9
1 (X = Cl) + MAO	30	390	3.18	9
1 (X = Cl) + MAO	400	440	2.82	9
1 (X = Cl) + MAO	2000	470	2.64	9
1 (X = Cl) + MAO	4000	470	2.64	9
3 (X = Cl)	_	446	2.78	This work, 14
3 (X = Me)	_	387	3.20	This work, 14
3 (X = Cl) + MAO	20	409	3.03	14
3 (X = Cl) + MAO	120	456	2.72	14
3 (X = Cl) + MAO	2500	496	2.50	14
5 (X = Y = Cl)	_	464	2.67	This work
5 (X = Y = Me)	_	404	3.07	This work
5 (X = Y = Cl) + MAO	50	432	2.87	This work
5 (X = Y = Cl) + MAO	120	432, 491 (sh)	2.87, 2.53	This work
5 (X = Y = Cl)+ MAO	500	491	2.53	This work
5 (X = Y = Cl)+ MAO	2000	524	2.37	This work
6 (X = Cl)	_	433	2.86	14
6 (X = Me)	_	383	3.24	14
6 (X = Cl) + MAO	20	406	3.05	14
6 (X = Cl) + MAO	160	448	2.77	14
6 (X = Cl) + MAO	4000	484	2.56	14

toluene at $Al_{MAO}/Zr \le 20$ mol mol^{-1} (see Table 3).[14] These data suggest that zirconocene dichloride is monoalkylated in the reactions with MAO at low Al_{MAO}/Zr ratios for at least structurally similar complexes (see Scheme 1, reaction (1)), which increases the LMCT energy by 0.20—0.27 eV.

An increase in the Al_{MAO}/Zr molar ratio to 120 mol mol^{-1} in the **5** (X = Y = Cl)/MAO system is accompanied by the appearance of a shoulder at 491 nm (see Fig. 1, spectrum *6*), while at the ratio $Al_{MAO}/Zr = 500$ the complex, whose spectrum exhibits the AB at 491 nm, predominates in the reaction products (see Fig. 1, spectrum *8*). The decrease in the LMCT energy of the complex, whose spectrum has an absorption maximum at 491 nm, relatively to that of dimethylated zirconocene (in this case, the latter acts as a reference) is 0.54 eV (see Table 3). This change in the LMCT energy exactly corresponds to the shift of the AB relatively to the reference dimethylated zirconocene when an intermediate is formed in the **1** (M = Zr, X = Cl)/MAO system[9] at Al_{MAO}/Zr = 400 (see Table 3). At the ratios $Al_{MAO}/Zr \approx 100$ for the **3** (X = Cl)/MAO and **6** (X = Cl)/MAO systems, we also observed the equilibrium formation of products, whose spectra had AB with the bathochromic shifts by 0.48 and 0.47 eV compared to those of the dimethylated analogs (see Table 3).[14] Probably, polarized complexes of the $L_2Zr^{\delta+}MeCl \cdot MAO^{\delta-}$ type are formed at the molar ratios $Al_{MAO}/Zr \approx 100$ (see Scheme 1, reaction (2)), which is manifested as a decrease in the LMCT energy by ~0.5 eV in these complexes compared to the dimethylated analogs.

The further increase in Al_{MAO}/Zr to 2000 mol mol^{-1} in the **5** (X = Cl)/MAO system is accompanied by the appearance of new products, whose spectra have an absorption maximum at 524 nm (see Fig. 1, spectrum *9*). The decrease in the LMCT energy relatively to that of the dimethylated complex is 0.70 eV (see Table 3), which is very close to a value of 0.69 eV of the LMCT energy changes for the formation of the polymerization-active complexes in the **1** (M = Zr, X = Cl)/MAO system[9] using the dimethylated complex as a reference (see Table 3). A similar decrease in the LMCT energy by 0.70 and 0.68 eV is also observed for two other structurally similar zirconocene dichlorides in the reactions with MAO at high molar cocatalyst excess[9] (see Table 3). It can be assumed that at high molar cocatalyst excess the chlorine ligand is displaced to MAO to form a cationic complex of the $L_2ZrMe^+...ClMAO^-$ type (see Scheme 3, reaction (3)), which appears as a decrease in the LMCT energy by ~0.7 eV relatively to that of dimethylated zirconocene. It should be noted that the qualitative changes observed in these systems correspond to the commonly accepted concepts (confirmed by numerous experimental data) about the nature of catalytic intermediates. These concepts consider active sites in catalytic metallocene systems as cationic species more or less bound with the counterion (see, *e.g.*, Refs. 18—23). It is important that we observed no formation of the dimethylated derivative, whose spectrum has an absorption maximum at 404 nm, for none of the Al_{MAO}/Zr values (see Fig. 1, spectrum *3*), which indicates that dimethylation in the presence of MAO does not occur.

Thus, it can be asserted that the series of structurally single-type bridged zirconocenes in the presence of MAO and at different Al_{MAO}/Zr molar ratios are characterized by similar reactions, which have approximately similar quantitative expressions for the charge transfer from the π-bonded ligand to metal in the complexes formed. For the molar ratios Al_{MAO}/Zr = 10—100, zirconocene is monoalkylated, which is accompanied by an increase in the LMCT energy by ~0.2 eV with an accuracy of an order of the solvation effect. The further increase in the Al_{MAO}/Zr ratio to 10^2—10^3 results in the equilibrium formation of catalytic intermediates, which are probably polarized ZrMeCl•MAO complexes in which a decrease in the LMCT energy relatively to those of the starting dimethylated zirconocenes is ~0.5 eV. The equilibrium formation of the polarized complexes is preceded by the formation of catalytically active cationic species, whose LMCT energy decrease relatively to those in the dimethylated analogs is ~0.7 eV.

This study shows that a change in the LMCT energy by various factors, such as solvation, the electronic effect of the π-system or bridging groups and σ-bonded ligands, the nature of transition metal, and formation of complex precursors of the catalytic system and cationic complexes, has a quantitative energy expression and is additive for at least the series of structurally similar metallocenes. Thus, UV-Vis spectral studies of solutions of metallocenes and products of their reactions with activators of the catalytic system can be useful for analytical purposes when studying metallocene-containing catalytic systems.

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