Electrochemical potentials, optical transitions, and frontier orbitals of non-bridged and bridged bent sandwich zirconocene complexes

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A linear correlation between the electrochemical gap values ($G = E_{ox} - E_{red}$) and the energies of optical transition in the UV-vis region was found and justified for a series of non-bridged and bridged bent-sandwich zirconocene complexes with the general formula $R(\eta^5\text{-L})_2ZrX_2$, where L = cyclopentadienyl (Cp), indenyl (Ind), fluorenyl (Flu); X = Cl, Me; the bridging group R = $SiMe_2$, $(CH_2)_2$.

Key words: metallocene complexes, *ansa-* and bent sandwich dichloride and dimethyl zirconocenes; frontier molecular orbitals, redox properties, electrochemical gap, cyclic voltammetry; electron transitions, electronic spectra, correlations.

The frontier orbitals (HOMO and LUMO) determine the reactivity of compounds in various reactions.[1] Relative energies of these orbitals may be either calculated by quantum chemistry or determined empirically, *e.g.*, by spectral and electrochemical methods. In the present paper we show and justify the existence of linear correlation between electrochemical and optical characteristics of bridged and non-bridged dichloride and dimethyl zirconocene complexes, which are precursors of the highly efficient homogeneous Ziegler—Natta catalysts.[2] The thermodynamic correlation found is an graphic example of a combination of electronic and spectroscopic approaches.

Results and discussion

16-Electron (16e) dichloride and dimethyl zirconocene complexes (**1**—**8**, see Table 1, where Cp is η^5-cyclopentadienyl; Ind is η^5-indenyl; Flu is η^5-fluorenyl) un-

Table 1. Reduction and oxidation potentials (CH_2Cl_2/0.05 *M* Bu_4NF_6, glassy carbon electrode, 0.2 V s^{-1}) and absorption bands of the first LMCT optical transition for complexes **1**—**8** (solvent CH_2Cl_2)

Complex	E^0_{red}	E_{ox}	G/V	λ/nm	ν = 1/λ /cm^{-1}	Reference
	V (s. c. e.)					
Cp_2ZrCl_2 (**1**)	−1.63	1.86	3.49	338	29586	4
$Me_2SiCp_2ZrCl_2$ (**2**)	−1.53	1.80	3.33	360	27778	—[a]
Ind_2ZrCl_2 (**3**)	−1.59	1.48	3.07	390	25641	4
$C_2H_4Ind_2ZrCl_2$ (**4**)	−1.57	1.36	2.93	435	22989	—[a]
$Me_2SiInd_2ZrCl_2$ (**5**)	−1.54	1.38	2.92	454	22026	—[a]
$Ph_2C(CpFlu)ZrCl_2$ (**6**)	−1.49	1.21	2.70	500[b]	20000[b]	—[a]
Cp_2ZrMe_2 (**7**)	−(2.72)[c] −2.59[f]	1.41	(4.13)[c] 4.00[f]	278[d,e]	35971[d,e]	4
Ind_2ZrMe_2 (**8**)	−(2.46)[c] −2.33[f]	1.30	(3.76)[c] 3.63[f]	315[b]	31746[b]	4

[a] Present work.

[b] Toluene as solvent.

[c] THF as solvent.

[d] Cyclohexane as solvent.

[e] A shoulder.

[f] Potential of hypothetical reduction or the difference of redox potentials of redox processes in dichloromethane (the reduction of dimethyl circonocenes in CH_2Cl_2 is beyond reach) assuming that between THF and CH_2Cl_2 it holds that $\Delta E^0_{red} \sim 0.130$ V.

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dergo reversible or *quasi*-reversible one-electron reduction to the corresponding radical anions, which is characterized by the formal standard potential (E^0_{red}), and irreversible oxidation.[4,4a,5] We have previously obtained typical cyclic voltammograms of the reduction and oxidation of such complexes for compounds **3** and **8** as the examples.[4a] The irreversible character of the oxidation is caused by instability of 15e-radical anionic zirconocenes,[4a,5] which primarily ensue from one-electron oxidation. Nevertheless, the values of the oxidation potentials (E_{ox}) of complexes **1**—**8** may be employed in the calculation of electrochemical gap values ($G = E_{ox} - E^0_{red}$), which determine the difference of energies of redox orbitals, *i.e.*, HOMO and LUMO, in a given solvent.[6—10] On the other hand, the charge transfer band in electronic absorption spectra also characterizes the difference between the acceptor (LUMO) and donor (HOMO) orbitals. Though optical electron transition leads to the formation of excited states and, unlikely, electrochemical reduction/oxidation produces ground states, previously[11] the linear correlations between G values and optical electron HOMO → LUMO transfer energies have been found for some inorganic complexes.

In the case of metallocene complexes,[12] the first low-energy electron transition attributed to the charge transfer from aromatic ligand to the metal (LMCT) corresponds to optical transfer HOMO → LUMO.[13] The LMCT type HOMO → LUMO electron transition in the zirconocene complexes can be formally presented as $Zr^{4+}(\eta^5\text{-}L_2)^{2-} \rightarrow Zr^{3+}(\eta^5\text{-}L_2)^{-}$. In the redox processes we have, correspondingly, $Zr^{4+}(\eta^5\text{-}L_2)^{2-} + e^- \rightarrow Zr^{3+}(\eta^5\text{-}L_2)^{2-}$ (E_{red}) and $Zr^{4+}(\eta^5\text{-}L_2)^{2-} \rightarrow Zr^{4+}(\eta^5\text{-}L_2)^{-} + e^-$ (E_{ox}).

We investigated a dependence between experimentally measurable values, *viz.*, the energies of optical electron transition from HOMO to LUMO and the differences of redox potentials:

$$E_{ox}\left[\frac{Zr^{4+}(\eta^5\text{-}L_2)^{2-}}{Zr^{4+}(\eta^5\text{-}L_2)^{-}}\right] - E_{red}\left[\frac{Zr^{4+}(\eta^5\text{-}L_2)^{2-}}{Zr^{3+}(\eta^5\text{-}L_2)^{2-}}\right].$$

Data plotted on Fig. 1 testify in favor of a linear character of the dependence. The following conditions most probably hold: the difference of solvation energies of redox pairs in their ground states is small or comparable with the difference of the solvation enthalpies of the ground and excited states in electron transition; geometric distortions of considered redox components are small (difference of the entropies → 0); vibrational-type optical transition takes place.

Notably the same linear dependence holds for non-bridged (**1** and **3**) as well as for bridged (**2**, **4**, and **6**) dichlorides, and also for dimethylzirconocenes (**7** and **8**) lying within a wide range of variation of electrochemical and optical parameters (see Table 1). This is most likely caused by the fact that, first, reduction and oxidation of the complexes **1**—**8** proceed *via* principally similar mechanisms, second, solvation energy changes for $\eta^5\text{-}L_2ZrX_2^{0/\cdot-}$ and $\eta^5\text{-}L_2ZrX_2^{0/\cdot+}$ redox pairs components for the compounds studied between neutral and reduced or oxidated states, as well as between the ground and optically excited states, make approximately equal contributions to E^0_{red} and E_{ox}, and, third, the sequence and the character of frontier (redox) orbitals remains in general the same whatever non-bridged and bridged dichloride or dimethyl complexes are given.

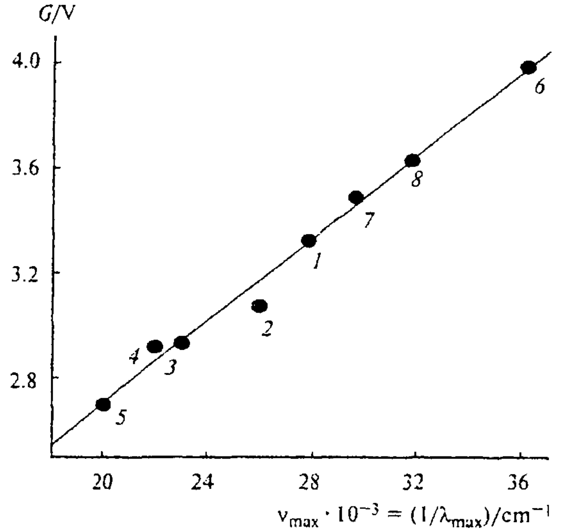

Fig. 1. The linear correlation between electrochemical gap G values and wave numbers of the first optical transition ν for the complexes **1**—**8** ($r = 0.992$): $Me_2SiCp_2ZrCl_2$ (*1*), Ind_2ZrCl_2 (*2*), $(CH_2)_2Ind_2ZrCl_2$ (*3*); $Me_2SiInd_2ZrCl_2$ (*4*); $Ph_2CCpFluZrCl_2$ (*5*); Cp_2ZrMe_2 (*6*); Cp_2ZrCl_2 (*7*); Ind_2ZrMe_2 (*8*).

According to the data obtained[3—6,14,15] the above-stated conditions generally hold, and this fact does lead to the linear relationship between the energies of optical and electrochemical electron transfers.

In distinction to E^0_{red} values, which are rather easily determinable by cyclic voltammetry, *e.g.*, in THF or CH_2Cl_2 medium, the measurement of the oxidation potentials (E_{ox}) for many zirconocene complexes is frequently unfeasible. This is caused by relatively high positive E_{ox} values and kinetic instability of the primarily generated radical cationic forms of the complexes. The latter rapidly decompose yielding very reactive radicals and cations,[4a,5] which react with a solvent, block the electrode surface, *etc.*[4a,5] As a result, on the cyclic voltammograms one can often see blurred, hump-shaped anodic peaks that encumber exact determination of E_{ox}. The linear dependence allows us to find a G value from the energy of the first optical transition (ν) and, measuring only E^0_{red}, to calculate E_{ox} without direct experimental determination of this value.

Experimental

For spectral studies, toluene (special purity) and cyclohexane (Aldrich, 99.9%, HPLC) were distilled over $LiAlH_4$, degassed *in vacuo*, and stored over the eutectic alloy Na + K; dichloromethane (Aldrich, 99.9%, A.C.S. HPLC) was dried successively over CaH_2 and P_2O_5. All preparative procedures for the zirconocene complexes were carried out in an atmosphere of pure dry argon using the standard Schlenk technique or in a dry box filled with helium.[16] Electronic absorption spectra of the complexes were recorded in 0.25, 0.5, 1.0, and 3.0 cm evacuated quartz cells on a Hewlett—Packard 8451A Diode Array spectrophotometer.

Voltammetric measurements were carried out in a dry inert atmosphere (Ar) in THF (Aldrich, 99.9%, A.C.S. HPLC) and CH_2Cl_2 pre-purified using standard procedures[17] and distilled directly in an evacuated and filled with argon electrochemical cell of a special construction according to previously described procedure.[4,18,19] An 0.05 *M* solution of tetrabutylammonium hexafluorophosphate pre-dehydrated by melting *in vacuo* (Aldrich) was used as the supporting electrolyte.

All potentials are presented relative to an aqueous saturated calomel electrode (SCE) by referring the potential of the reference electrode (Ag/AgCl/4 *M* aqueous solution of LiCl), which was separated from the solution under study in the cell by a solution of the supporting electrolyte, to the potentials of redox transition of ferrocene$^{0/+}$ (E^0 = 0.44 and 0.43 V *vs.* SCE in THF and CH_2Cl_2, respectively).

A glassy-carbon disk electrode sealed into glass and polished with a diamond paste (grain size ≤1 μm) was used as the working electrode. Voltammetric measurements were carried out using a PAR 175 signal generator and a PAR 173 potentiostat with drop compensation of ohmic losses.

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