Electrochemistry of bis(indenyl)dimethylzirconium complex — the precursor of the olefin polymerization catalyst*

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The reduction in THF and oxidation in CH_2Cl_2 of the bent-sandwich complex $(\eta^5\text{-Ind})_2ZrMe_2$ (**1**) (Ind = C_9H_7, indenyl) were studied by cyclic voltammetry. Complex **1** in THF undergoes one-electron reduction to radical anion $\mathbf{1}^{\cdot -}$, which partially decomposes with the liberation of the Ind^- anion. Even at −45 °C the one-electron oxidation leads to the formation of an unstable 15-electron radical cation undergoing fast heterolytic decomposition to the $Me^{\cdot}$ radical and $(\eta^5\text{-Ind})_2ZrMe^+$ cation, which is the key reaction center in the catalytic polymerization of olefins. Comparative analysis of electron-transfer-induced transformations of bent-sandwich dimethyl and dichloride zirconocenes of the general formula L_2ZrX_2 (L = η^5-Ind, η^5-Cp; X = Cl, Me) was performed.

Key words: bis(indenyl)dimethylzirconocene, polymerization catalysts, redox properties, cyclic voltammetry.

It is known that highly reactive catalytic systems for olefin polymerization based on metallocene complexes of Group IVB metals (Ti, Zr, Hf) with σ-bound alkyl ligands are prepared by their treatment with Lewis acids (organoaluminum compounds, polyalkylalumoxanes, perfluorophenylboranes, borates, and others).[2—7] The main function of cocatalysts of this type is the oxidative elimination of the alkyl ligand and generation of tetravalent cationic complexes of L_2MR^+ type (L is the η-coordinate ligand, R is alkyl).[2,8—14] A weak coordination of the cocatalyst in the form of a complex counterion is an important condition for providing for efficient insertion of a monomer molecule at the metal—carbon bond in the active center. The acting active center in these catalytic systems, a cationic particle with an active metal—carbon bond, is stabilized in the time scale of the polymer chain growth by weak interactions with a counterion, fragments of the macromolecular chain, solvent, *etc.* Processes leading to the formation of the active center (primary alkylation of metallocene dichloride, formation of the cationic species L_2MR^+) and its catalytic effect (insertion of the monomer, chain transfer, *etc.*) reflect the reactivity of the metal—alkyl σ-bond, which is affected by the nature of the η-bound ligands, substituents, and bridging groups.[14—17]

Direct experimental observation and identification of the cationic complexes and possible related intermediates are complicated due to their high reactivity. As a rule, the nature, evolution, and deactivation of active centers are determined from data of macroscopic studies using kinetic laws of the catalyzed polymerization process and structural analysis of individual components of a catalytic system, metallocenes. At the same time, one can attempt to generate an "individual" cationic particle by, *e.g.*, redox transformation of dialkyl metallocenes L_2MR_2 by varying conditions (temperature, medium) and to study its reactivity. We have previously applied a similar approach for studying the mechanism of reduction of bis(2-phenylindenyl) zirconium and hafnium dichloride complexes, and the approach was rather fruitful.[18,19]

In this work, low-temperature cyclic voltammetry (CV) was used to study the electron-transfer-induced heterolytic fragmentation of the $(\eta^5\text{-Ind})_2ZrMe_2$ complex (**1**) and related bent-sandwich zirconocenes L_2ZrX_2 (L = η^5-Ind, X = Cl (**2**); L = η^5-Cp, X = Me (**3**), Cl (**4**)).

Results and Discussion

Reduction of $(\eta^5\text{-Ind})_2ZrMe_2$ *(1)*

The symmetrical pair of peaks *A*/*A'* and the irreversible secondary anodic peak *B* are observed on the cyclic voltammograms of reduction of the 16-electron complex **1** in THF (Fig. 1, *a*). The potentials of these peaks are presented in Table 1. Peak currents *A*, *A'*, and *B* are diffusion-limited ($I_p \cdot v^{-1/2}$ = const, where I_p is the peak height and v is the scan rate).[20] Peaks *A* and *A'* correspond to one-electron transfers, which follows from comparison of their heights with that of the one-electron peak of reduction of $(\eta^5\text{-Cp})_2ZrCl_2$ under the same conditions.[15,21—23] The reduction of complex **1** is char-

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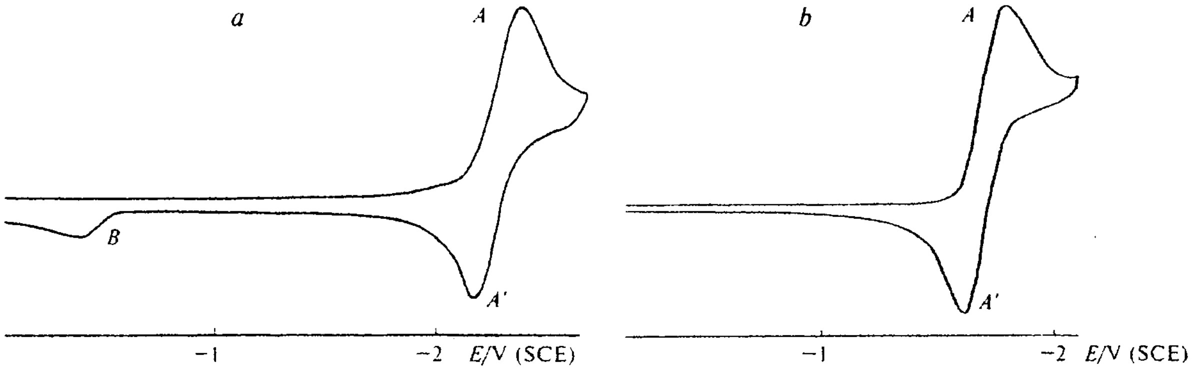


Fig. 1. Cyclic voltammograms of reduction: (*a*) complex **1** ($5 \cdot 10^{-4}$ mol L^{-1}, 8 °C); (*b*) complex **2** ($5 \cdot 10^{-4}$ mol L^{-1}, −15 °C) in THF in the presence of 0.05 *M* Bu_4NPF_6 on a glassy-carbon electrode at v = 0.2 V s^{-1}.

acterized by close values of peak currents *A*/*A'* ($I_p^a/I_p^c \approx 0.9$, where I_p^a and I_p^c are the heights of the anodic and cathodic peaks, respectively) and $\Delta E_p = E_p^a - E_p^c$ = 120 mV (E_p^a and E_p^c are the potentials of the anodic and cathodic peaks, respectively). The voltammograms of reduction of the dimethyl (**1**) and dichloride (**2**) complexes are presented in Fig. 1 for comparison.

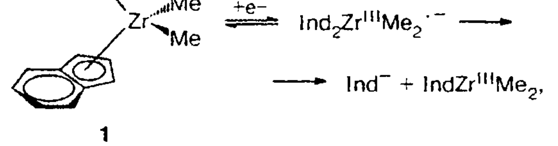
Change from the 16-electron configuration in the starting complex **1** to a 17-electron configuration in radical anion $\mathbf{1}^{\cdot -}$ is accompanied by a substantial increase in the reactivity of the zirconocene: the reverse scan allows one to detect a pronounced irreversible peak (*B*) attributed to solvated reduction products and indicating the kinetic instability of the primary radical anion $\mathbf{1}^{\cdot -}$ (Fig. 1, curve *a*). The temperature decrease from room temperature to −25 to −50 °C results only in a decrease in the peak height, but not its disappearance. Similar voltammograms were obtained for the one-electron reduction of bis(cyclopentadienyl)dimethylzirconium (**3**): peak *B* is shifted toward positive potentials, $E_{p,B}$ = −0.47 V.

Table 1. Potentials of peaks on cyclic voltammograms of bis(indenyl)- and bis(cyclopentadienyl)zirconium complexes ($5 \cdot 10^{-4}$ mol L^{-1}) during their reduction in THF and oxidation in CH_2Cl_2 (in the presence of 0.05 *M* Bu_4NPF_6, a glassy-carbon electrode, sweep rate 0.2 V s^{-1})

Complex	Solvent	*T*/°C	Peak	$E^{0\,a}$ ($E_p{}^b$)/V (SCE)
1	THF	8	*A*/*A'*	−2.46
			B	(−0.64)
	CH_2Cl_2	−45	*C*	1.30
2	THF	−15	*A*/*A'*	−1.71
	CH_2Cl_2	−45	*C*	1.45
3	THF	8	*A*/*A'*	−2.72
			B	(−0.47)
	CH_2Cl_2		*C* [c]	
4	THF	−40	*A*/*A'*	−1.78
	CH_2Cl_2		*C* [c]	

[a] $E^0 = (E_p{}^a + E_p{}^c)/2$.
[b] Potential of the irreversible peak.
[c] The oxidation potential was not measured.

The nature of a species oxidized at the potentials of peak *B* ($E_{p,B}$ = −0.64 V for complex **1**) is not reliably proved at the present time. Note that a similar species has recently been detected[24] upon the reduction of the related titanium complex $(\eta^5\text{-Ind})_2TiMe_2$ (**5**). The irreversible anodic peak at −0.6 V has been attributed[24] to the oxidation of the intermediate titanocene $(\eta^5\text{-Ind})_2Ti^{III}Me$ that originated at the reduction potentials of complex **5**. However, it can reasonably be assumed that when complexes bear electron-donating ligands of the methyl type, the density of negative charge on the electron-withdrawing ligands η^5-Cp and/or η^5-Ind increases and, therefore, electron transfer may induce cleavage of the metallocene skeleton with elimination of a stable aromatic anion (Cp^- or Ind^-). In fact, the addition of a sevenfold excess of indene (IndH) to a solution of complex **1** in THF results in an increase in the height of anodic peak *B* upon a forward potential scan to the region of formation of Ind^- anions. Taking into account this fact and the published data[25] on the potentials of the $Ind^-/Ind^{\cdot}$ redox pair, we can propose the following mechanism of reductive cleavage of zirconocene*:



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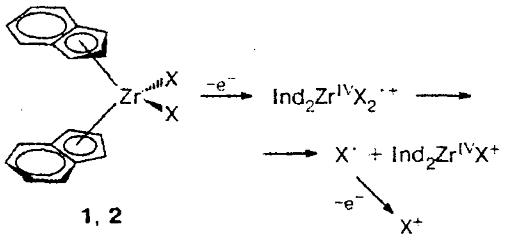
* We do not rule out parallel elimination of the highly reactive Me^- anion in dimethyl derivatives.

Oxidation of $(\eta^5\text{-L})_2ZrX_2$ complexes (L = Ind, Cp; X = Me, Cl)

Oxidation of zirconocenes **1**—**4** has a sophisticated irreversible mechanism (Fig. 2) and is a superposition of two processes: oxidative heterolysis of the Zr—X bond (X = Me, Cl) and oxidation of the X$^{\cdot}$ radical, the product of fragmentation of the primarily formed, kinetically unstable 15-electron radical cation $(\eta^5\text{-L})_2ZrX_2{}^{\cdot +}$. Oxidative homolysis of the Zr—X bond, resulting in the 15-electron complex $L_2Zr^{III}X$ and cation X^+, is improbable because $L_2Zr^{III}X$ is a stronger reducing agent in this redox pair.* d^0-Complexes containing ligands of the η^5-cyclopentadienyl type are characterized by an out-of-sphere oxidation *via* the *ECE* or EC_{ir} route (*E* and *C* are the electrochemical and chemical stages, respectively).[20] Note that the above proposed mechanism of two-electron electrooxidation of the 16-electron d^0-complexes $(\eta^5\text{-L})_2ZrX_2$ (X = Me, Cl) is not exhaustive,** because highly reactive intermediates participate in parallel reactions and passivation of the electrode surface.[28]



1, 2

In conclusion, we note that similar electrochemical processes occur in bent-sandwich cyclopentadienyl zirconocenes (**3**, **4**).

Catalytic activity of intermediate products of electrochemical reactions in olefin polymerization processes is of independent interest and will be discussed elsewhere.

Experimental

Toluene and pentane freshly distilled above $LiAlH_4$ were used for the synthesis of dimethylzirconocene **1**. All procedures were carried out in an atmosphere of purified dry argon using the Schlenk techniques. Bis(indenyl)zirconium dichloride (**2**) was prepared by a procedure described previously.[18]

Bis(indenyl)dimethylzirconocene, $(\eta^5\text{-Ind})_2ZrMe_2$ (1). A weighed sample of $(\eta^5\text{-Ind})_2ZrCl_2$ (**2**) (1.15 g, 3.3 mmol) was placed in a round-bottomed flask with a Teflon valve and a magnetic stirrer. Anhydrous toluene (20 mL) was frozen into the flask, and a 1.6 *M* solution (4.12 mL) of MeLi (6.6 mmol, Aldrich) in diethyl ether was added at −80 °C in a dry argon flow. The reaction mixture was slowly (for 0.5 h) heated to ~20 °C with continuous stirring, and the stirring was continued for 16 h. The precipitated LiCl was filtered off, toluene was removed by distillation *in vacuo*, and $(\eta^5\text{-Ind})_2ZrMe_2$ (**1**) was extracted from the solid residue with anhydrous pentane (4×40 mL). The pentane extracts were combined, and the solvent was removed by evacuation. Complex **1** was obtained in 80% yield (0.85 g). Found (%): C, 68.27; H, 5.80; Zr, 25.93. $C_{20}H_{20}Zr$. Calculated (%): C, 68.32; H, 5.73; Zr, 25.95.

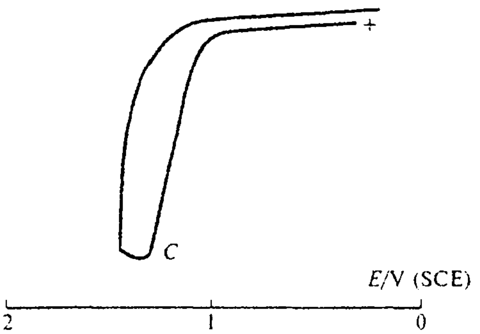


Fig. 2. Cyclic voltammogram of oxidation of complex **1** ($5 \cdot 10^{-4}$ mol L^{-1}, −45 °C) in CH_2Cl_2 in the presence of 0.05 *M* Bu_4NPF_6 on a glassy-carbon electrode at v = 0.2 V s^{-1}.

Voltammetric measurements were carried out in a dry inert atmosphere in CH_2Cl_2 and THF pre-purified and distilled directly to an evacuated and argon-filled electrochemical cell according to a previously described procedure[29]; THF (Aldrich) was purified by the ketyl method.[29] An 0.05 *M* solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, Aldrich) pre-dehydrated by melting *in vacuo* was used as the supporting electrolyte. Low-temperature electrochemical measurements were carried out in a cell thermostatted with isopropyl alcohol/liquid nitrogen in a Dewar flask.

All potentials were given *vs.* an aqueous saturated calomel electrode (SCE) and were obtained 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 bridge filled with a solution of the supporting electrolyte, to the potentials of redox transitions (0/+) for ferrocene or decamethylferrocene (E^0 = 0.44 and 0 V, respectively, relative to SCE in THF).

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

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* In MeCN—$NaBPh_4$, a related $Cp_2Zr^{III}Me$ complex is oxidized at −1.9 V *vs.* the Fc^+/Fc^0 pair,[26] whereas the potential of the $Me^{\cdot}/Me^+$ pair is −0.5 V.[27]

** The height of oxidation peak *C* (see Fig. 2) does not reach the two-electron level.

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