A REVIEW ON MOLECULAR ELECTROCHEMISTRY OF METALLOCENE DICHLORIDE AND DIMETHYL COMPLEXES OF GROUP 4 METALS: REDOX PROPERTIES AND RELATION WITH OPTICAL LIGAND-TO-METAL CHARGE TRANSFER TRANSITIONS

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This article is dedicated to Professor Antonín A. Vlček, whose personal contribution to the advancement of physical inorganic chemistry and electrochemistry is invaluable. We recognise that the term "molecular electrochemistry" was invented by Prof. Vlček.

Emphasis is given to redox, photophysical, and photochemical properties of homologous bent metallocenes of group 4 transition metals. Comparative analysis of a variety of electron-transfer induced transformations and ligand-to-metal charge-transfer excited states is performed for bent metallocene complexes upon systematic variation of the identity of the metal ion (Ti, Zr or Hf), ancillary π- and monodentate σ- (Cl, Me) ligands. For such organometallic π-complexes, linear correlations exist between energies of optical and redox HOMO-to-LUMO electron transitions. It is suggested that combination of spectroscopic and electrochemical techniques provides important diagnostics to determine "ionisation potential" and "electron affinity" in solution (relative energies of frontier molecular orbitals obtained as redox potentials) and the energy gap in metallocene complexes. Some of earlier instructive cases of direct relationship between optical transition energies and differences in redox potentials revealed for inorganic and coordination compounds are discussed.

Keywords: Metallocenes; Titanocenes; Zirconocenes; Redox behaviour; Charge transfer; Electron transition; Frontier orbitals; Electrochemistry; EPR spectroscopy; Substituent effects; Cyclopentadienyl ligands.

1. INTRODUCTION

First bent metallocenes [Cp$_2$M^{IV}Cl$_2$] (Cp stands for η^5-C$_5$H$_5$ anion)[1–3] have provided impetus for a new generation of a large family of highly reactive organometallics, for years successfully used in the fields of homogeneous and heterogeneous catalysis. In the recent years, considerable effort has been devoted to fundamental understanding of factors that govern chemical reactivity of bent π-complexes of group 4 metals (Ti, Zr, Hf). In this respect, particular emphasis has been placed on metallocene-mediated (catalytic) transformations of various substrates, such as activation of small molecules (N$_2$ (refs[4,5]), CO (ref.[6]), CO$_2$ (ref.[7])), and olefin polymerisation (for most recent reviews, see refs[8–13]). It has become clear that the nature of the metal site and the ligand structures of the bent π-complex precursors dramatically affect performance of the catalyst as well as physico-chemical and mechanical properties of final products (*e.g.*, polymers) of catalytic processes.

Our most recent and other systematic studies were aimed at understanding electronic and steric patterns of the bent metallocenes (π-L)$_2$MX$_2$ *via* substituting the metal core, introducing functionalities and a bridging group to ancillary π-ligands. In this contribution, we wish to briefly review knowledge gained in electrochemical and spectroscopic experiments, of electronic properties of bent π-complexes of group 4 metals and of the nature of possible intermediates formed in "pure" electron-transfer reactions, such as one- or two-electron reduction and oxidation. The complete survey of such a broad organometallic family, successively developed in the past four decades, is almost impossible; rather, we intend to emphasise some explicit examples of innovation in this rapidly growing area.

2. ELECTROCHEMICAL REDUCTION OF BENT SANDWICH COMPLEXES

2.1. Metallocene Dichlorides

The highest occupied orbital levels of d^0 bent complexes [Cp$_2$MCl$_2$] are closely related along the group 4 metal triad (Ti, Zr, Hf), as suggested by a number of experimental (*e.g.*, photoelectron spectroscopy[14–16]) and theoretic investigations[16–20]. Dominant contribution of the metal d orbitals to non-bonding LUMO and that of aromatic ligands to π-type HOMO are retained along the metallocene dichloride series. This will be discussed in more detail hereinafter. The mechanism of reduction/oxidation of the bent metallocenes of group 4 metals is not elucidated in detail and continue re-

ceiving special attention. First, we proceed from the redox chemistry of the bent metallocene dichlorides.

Among the group 4 bent π-complexes, substituted and bridged titanocenes with variable π- or σ-bound ligands have been thoroughly studied[21,22]. Thus, the two successive one-electron reductions of $[Cp_2TiCl_2]$ produce a solvated monohalide complex $[Cp_2Ti^{III}Cl]$ and the unidentified "titanocene" $[Cp_2Ti^{II}]$, respectively. The latter species is capable of accepting additional electron[23–25]. However, it has been also proposed[23] that the product of $[Cp_2Ti^{III}Cl]$ reduction is a dimeric titanium(II) complex and not the "titanocene". Combined electrolysis – EPR studies have revealed[26] that reduction of dihalides $[Cp_2TiX_2]$ (X = Cl, Br, I) only yields stable monohalide complexes $[Cp_2Ti^{III}X]$.

Among heavier homologues of the bent titanocene, zirconocene[25,27–30] and hafnocene[25,28,30] were studied electrochemically. Thus, the metallocene dichlorides $[Cp_2MX_2]$ are reversibly reduced to corresponding radical anions $[Cp_2MX_2]^{\bullet-}$, that have been characterised *in situ* by EPR spectroscopy[28–31]. Subsequent one-electron reduction of the radical anions $[Cp_2ZrX_2]^{\bullet-}$ and $[Cp_2HfX_2]^{\bullet-}$ in the region of extremely cathodic potentials (*ca* –3 V *vs* SCE) produces unstable dianions that convert to the corresponding "metallocene" species $[Cp_2M^{II}]$ (ref.[25]). At room temperature, the radical anions $[Cp_2MX_2]^{\bullet-}$ readily dehalogenate. The rate of the dehalogenation diminishes in the order Ti > Hf > Zr; in opposite, the rate of the reverse reaction then increases in the order Hf ≤ Zr << Ti (ref.[22]). A possibility of sandwich cleavage in the radical anions $[Cp_2MX_2]^{\bullet-}$ (M = Zr, Hf) and elimination of the cyclopentadienyl anion has also been suggested.

Electrochemical reduction of $[Cp_2TiCl_2]$ was studied in $AlCl_3$/1-butylpyridinium chloride melts[32]. The product of the first reversible one-electron uptake is the heterometallic complex $[Cp_2Ti\{Al_2Cl_7\}]$.

The $[Cp_2TiCl]$ complex generated *in situ* reacts with 9,10-diazaphenanthrene (RN=NR) to form dinuclear species $[[Cp_2Ti(Cl)N(R)N(R)(Cl)TiCp_2]$. The reaction was chosen[33] as a model for the N=N double bond activation process.

The two-electron reduction of the bent-sandwich dichloride complexes of the group 4 metals is accompanied by elimination of two chloride ligands to form a short-lived metallocene species. The intermediate formation of titanocene, zirconocene, and hafnocene was detected during reduction of the corresponding pentamethyl and *tert*-butyl substituted bis(cyclopentadienyl) dichloride complexes[34]. We have further revealed electron-transfer induced transformation in other bent zirconium(IV) and hafnium(IV) com-

plexes. Thus, the metastable species $[PhInd_2M^{II}]$ (PhInd = η^5-(2-phenyl)-indenyl) were generated *via* two successive electron additions and elimination of two chloride ligands from the zirconium(IV) and hafnium(IV) dichlorides $[(PhInd)_2MCl_2]$ (refs[35,36]). The correctness of the assignment was additionally supported by linear dependence of the E^0 (or E_p) values for the redox couples $[PhInd_2Ni]^{+/0/-}$ (see refs[34,35]) and $[PhInd_2M]^{0/-}$ (M = Zr, Hf) on ionisation potentials of a corresponding metal (IP_j) in gas phase, *viz.* $E^0 = -3.95 + 0.11\ IP_j$.

The uniform mechanism, proposed on the basis of linear correlation $E_{1/2}$ *vs* IP_j (refs[22,25]), generally operates in the electrochemical reduction of the groups 4–6 bent metallocene dichlorides. Pathway A in Scheme 1 applies to molecules with M = Zr, Hf at low temperatures, pathway B to M = Ti, V, Zr, and Hf at room temperature, and pathway C to M = Mo and W.
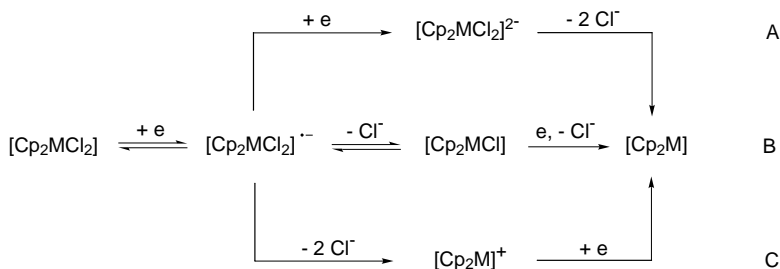
SCHEME 1

Substituent effect. A broad variety of catalytic and other physico-chemical properties, such as stability of the related closed-shell π-complexes, originate from the nature of transition metal centre, specific character of metal–ligand bonding, and "ligand" and "substituent" effects. The introduction of substituents and bridging moieties to the aromatic five-membered ring systems changes not only electronic and steric properties but also decreases the symmetry from C_{2v} (pseudo-tetrahedral structure) to lower C_2 and C_s (distorted tetrahedral arrangement); although, these symmetries do not necessarily persist in solution and owing to intramolecular dynamics. The substituent effect can have a tremendous influence on the course and products of inorganic chemical reactions, the influence being predominantly steric in origin. Substituent effects are generally considered smaller in electronic sense than ligand effects. Will successive ligand or substituent replacement possess an additive effect on the electronic changes at the metal core? To the best of our knowledge, the question cannot be answered unequivocally.

Among all, aliphatic substituents on aromatic ancillary ligands, in contrast to polar groups, usually enhance activity of the corresponding metallocene-based catalysts[8–13]. The electrochemical behaviour of *ansa*-titanocene dichlorides $[\{R(\eta^5-C_5H_4)_2\}TiCl_2]$ (R is a bridging group) and substituted bent titanocenes has been studied extensively by a number of research groups. For example, in the methyl substituted bent zirconocenes $[(\eta^5-C_5H_{5-n}Me_n)_2ZrCl_2]$ ($n = 0–4$) and titanocenes $[(\eta^5-C_5H_{5-n}Me_n)_2TiCl_2]$ ($n = 0–3$) standard reduction potentials were shown to shift negatively with increasing the substituent number by 0.071 and 0.093 V per one methyl substituent, respectively[36,37]. Here the effect of breakdown of the linear potential dependence for $[(\eta^5-C_5Me_5)_2ZrCl_2]$ has been assigned to bulkiness of the two ancillary ligands C_5Me_5 (ref.[37]). It should be noted that the more sterically more demanding the alkyl substituents on the Cp π-ligands, the greater breakdown in the symmetrical bonding to the transition metal ion can be observed.

The presence of the bridging group in ancillary aromatic ligands introduces several significant changes with regard to the electrochemical reduction of the corresponding titano- and zirconocene dichlorides[38,39]. The observed decrease in reduction potentials of the first electron uptake, most pronounced for the related zirconocenes (supported by available ^{13}C NMR data), was attributed by the authors[39] to the net withdrawing effect of the bridge. It has been suggested in other studies[38] that the influence of the bridging group on the reduction potentials compared to those of unbridged analogues originates entirely from steric effects.

It has been shown that reduction potentials make it possible to distinguish electronic and steric effects of functionalities expressed in the form of the two-parameter Taft equation. For instance, for the substituted zirconocenes $[Cp'_2ZrCl_2]$ ($Cp' = \eta^5-C_5R'_5$), the values $\Delta E = E_1^0 – E_3$, characterising the region of the redox stability of the radical anion $[Cp'_2ZrCl_2]^{\bullet-}$, obey the Taft equation $E^{R'} = E^H + \rho^*\sigma^*$ ($\rho^* = 0.203$; $r^2 = 0.999$, $s = 0.05$); the steric effects are therefore negligible[40]. The reduction potentials of the series $[Cp'_2ZrCl_2]$ ($R' = H$, Me, Et, $SiMe_3$) were shown to linearly correlate with increasing influence of the electron-donating substituent[41]. The half-wave reduction potentials increase in the order $Me_3Si < H < Me < Et$, which suggests that the trimethylsilyl group has a poor inductive influence as mediated by the Cp rings on the metal. Another study has revealed negative shifts of reduction potentials upon multiple Me_3Si substitution in the metallocene series $[\{\eta^5-Cp(SiMe_3)_n\}_2MCl_2]$ (M = Ti, $n = 2$; M = Zr, $n = 0–2$; M = Hf, $n = 2$)[42], (M = Zr, $n = 0–3$)[36].

Furthermore, the transfer of electron density from different substituents, mostly alkyl groups, on the Cp ligands to the metal core was also probed by other suitable experimental methods, such as photoelectron spectroscopy (PES), NMR, and electron spectroscopy for chemical analysis (ESCA). The trend of an decrease in positive charge on the metal core with increasing the number of methyl substituents was revealed in shifts of the binding energies of inner-shell electrons (for the C_5H_5 and C_5Me_5 ancillary π-ligands)[43], [91]Zr down-field chemical shifts (for the C_5H_5, C_5H_4Me, and C_5Me_5 π-ligands)[44], downfield chemical shifts of acetylenic carbon atoms in ^{13}C NMR spectra of the $[(\eta^5\text{-}C_5H_{5-n}Me_n)_2Zr(Me_3SiC{\equiv}CSiMe_3)]$ (n = 0–5) series[45], *etc.* The latter quality has been discovered for a number of methyl substituted hafnocene[46] and titanocene dichlorides[37]. From X-ray photoelectron spectroscopy studies (XPS), effect of the replacement of hydrogen with methyl in the cyclopentadienyl ligands on the binding energy of a metal core of bent titano-, zircono-, and hafnocene dihalides results in lowering the metal core orbital binding energies by 0.06–0.08 eV per every methyl group[43,46,47]. The trialkylsilyl group R_3Si was found to be slightly more electron-donating than methyl[48]. Replacement of all hydrogen atoms with alkyl groups in the Cp ligands was shown to result in a *ca* 1 eV decrease in the binding energy of the metal core. Therefore, it may be assumed that the metal core is "reduced"[49]. In another study, the linear correlation of the binding energy with the number of methyl substituents was evidenced. This fact implies that the electronic influence of methyl groups on the metal centre in $[(\eta^5\text{-}C_5H_{5-m}Me_m)(\eta^5\text{-}C_5H_{5-n}Me_n)TiCl_2]$ is additive[50]. Remarkably, XPS studies have suggested that the relative electronic differences essentially retained in olefin polymerisation catalysts derived from these bent sandwich complexes[51].

Another problem associated with a possible difference in redox properties of the *syn*- and *anti*-conformers of a bent metallocene should be emphasised. Specifically, single-crystal asymmetric units of isostructural complexes $[PhInd_2MCl_2]$ (M = Zr, Hf) incorporate two rotational isomers (*syn* and *anti*) relative to the metal–π-ligand bond[35,36]. Both isomers undergo redox reactions at the same potential within the accuracy of the measurements (±0.01 V). The energies of the frontier orbitals (HOMO and LUMO) are assumed to be very close for the two conformers.

2.2. Dialkyl Metallocenes

As we demonstrate below, bent dimethyl metallocenes of group 4 metals show unusual behaviour on electrochemical reduction. The quasi-reversible

one-electron reduction of dialkyl titano- and zirconocenes $[Cp_2MR_2]$ (M = Ti, Zr; R = Me or $PhCH_2$) has been proposed to produce the respective radical anions, decomposing upon the elimination of either R^- or Cp^- anion[28,52–54]. In a recent contribution[55], a voltammetric response essentially identical to that in Fig. 1a was recorded in the case of the one-electron reduction of related $[Ind_2Ti^{IV}Me_2]$ (Ind = η^5-indenyl). For $[Cp_2TiMe_2]$ and $[Ind_2TiMe_2]$, the one-electron reduction was thought to induce cleavage of the metal–carbon σ-bond and fast elimination of the very reactive anion CH_3^-. Based on this assumption, the irreversible anodic peak on the reverse voltammetric scan (O2 in Fig. 1a; for $[Ind_2TiMe_2]$ at *ca* –0.6 V *vs* SCE) was attributed[55] to the oxidation of the intermediate $[Ind_2Ti^{III}Me]$. In our related experiments, however, a seven-fold excess of indene (IndH) was added to $[Ind_2Zr^{IV}Me_2]$ test solutions in THF. As a result, the current intensity of this irreversible anodic peak O2 (Fig. 1a, potentials in Table I) sharp increased after a forward potential scan to the cathodic region where the Ind^- anion is produced (the same situation applies for CpH). Reported data on the $Ind^-/Ind^\bullet$ and $Cp^-/Cp^\bullet$ redox couples[56], together with our voltammetric evidence[57], therefore advocate just the opposite idea, *i.e.* reductive cleavage of the sandwich skeleton in the bent sandwich dimethyl titano- and zirconocenes, and elimination of the solvated aromatic anion (Ind^-, Cp^-, *etc.*). From the viewpoint of the electronic interaction of the ligands, it is
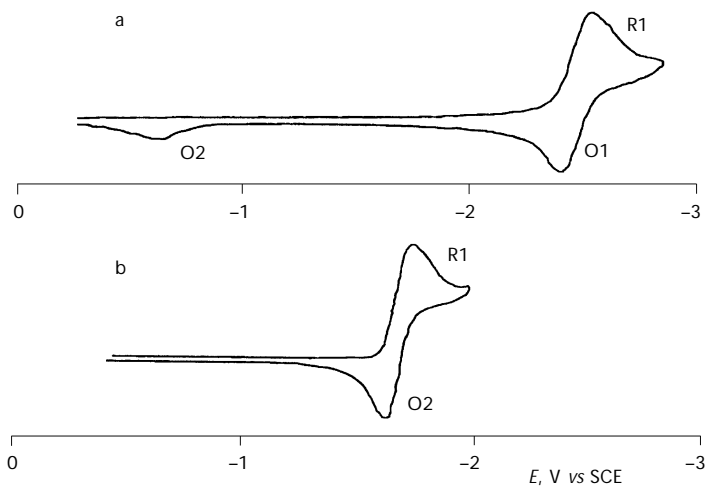

Fig. 1
Cyclic voltammograms of $[(\eta^5\text{-Ind})_2ZrMe_2]$ (a) and $[(\eta^5\text{-Ind})_2ZrCl_2]$ (b). Experimental conditions: THF/5 · 10^{-2} M Bu_4NPF_6, glassy carbon electrode, T = 265 K, scan rate 0.2 V s^{-1}

reasonable to assume that electron density on electron-withdrawing aromatic π-ligands increases upon coordination of electron-rich σ-donor ligands, such as methyl group(s). One-electron reduction of such an electron-rich neutral complex activates and may even induce cleavage of the metal–ligand π-bond. The latter process occurs on the time scale of cyclic voltammetry defined by moderate scan rates. One-electron reduction of a *dimethyl metallocene*, in contrast to the corresponding *metallocene dichloride*, thus leads to *destruction of the sandwich skeleton* (Scheme 2). Dependent on the choice of the electron-withdrawing or -releasing constituents of the ligand framework, electron transfer induces different transformations in the bent sandwich complexes.
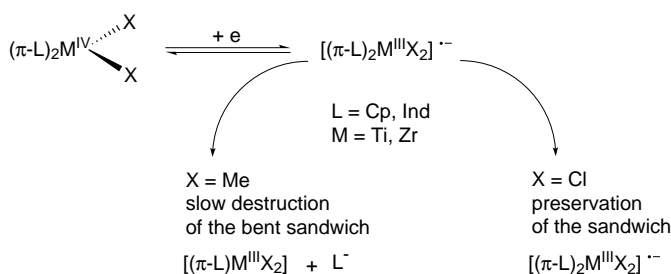
SCHEME 2

TABLE I
Electrode potentials of selected bent zirconocenes (in V *vs* SCE), recorded in THF/$5 \cdot 10^{-2}$ M Bu_4NPF_6 at a GC electrode and scan rate 0.2 V s^{-1}

Bent zirconocene	Peak	$E^{0a}, E_p^{\ b}$
$[Ind_2ZrMe_2]$	R1/O1	-2.46^a
	O2	-0.64^b
$[Ind_2ZrCl_2]$	R1/O1	-1.71^a
	np^c	
$[Cp_2ZrMe_2]$	R1/O1	-2.72^a
	O2	-0.47^b
$[Cp_2ZrCl_2]$	R1/O1	-1.78^a
	np^c	

^{a} $E^0 = \{E_{p,a}(O1) + E_{p,c}(R1)\}/2$. ^{b} Potential of the irreversible anodic peak O2 recorded on the reverse potential scan. ^{c} np, no peak O2 detected.

The stable radical anion $[Cp_2TiR_2]^{\bullet-}$ (R = C≡CPh) is obtained upon one-electron reduction of parent $[Cp_2TiR_2]$ at –30 °C. Upon warming up to room temperature, it starts to decompose into the paramagnetic complex $[CpTi^{III}R_2]$ and the aromatic anion Cp^- (ref.[58]). As another instructive case, the radical anion of {2,3-dimethylidenebicyclo[2.2.2.]octane}zirconocene is relatively stable at room temperature (as was proved by EPR spectroscopy), but decomposes *via* the zirconocene–diene bond cleavage at higher temperatures[59]. Other examples of the reduction of dialkyl metallocenes can be found in literature[60,61].

3. ELECTROCHEMICAL OXIDATION OF BENT SANDWICH COMPLEXES

Oxidation of d^0 bent sandwich complexes was first reported in the past decade. Ligand-localised oxidation, as an entry point into cationic bent sandwich group 4 metal complex chemistry, is reached at reasonable anodic potentials, in particular oxidation of molecules bearing electron-donating ligands (*e.g.*, alkyls). The pioneering formation of the metallocenium cation $[Cp_2TiCl(CH_3CN)]^+$ by one-electron oxidation of $[Cp_2TiCl_2]$ has pointed to direct electron abstraction from the Ti–Cl bond, resulting in release of the neutral radical $Cl^{\bullet}$ and coordination of the solvent (CH_3CN)[62].

The dialkyl titanocenes have been shown to react with one-electron oxidants[63–65] to species arising from the alkyl radical expulsion or formal reductive elimination[66]. This oxidative chemistry closely parallels electrochemical oxidation of such organometallic d^0 complexes. In fact, bulk electrochemical oxidation of titanacyclobutanes $[Cp_2TiCH_2CR^1(R^2)CH_2]$, where R^1, R^2 are different combinations of H, Me, iPr, *t*-Bu, results in the formation of the corresponding cyclopropanes. Oxidation of stereospecifically deuterated titanacyclobutanes produces cyclopropanes with a high degree of retention of the stereospecific configuration (>15/1 retention/inversion). This stereoselectivity requires that either oxidatively induced reductive elimination is concerted or, if stepwise, the consecutive cleavage pathways leading to the product are faster than the C–C bond rotation, if any intermediates are formed by the Ti–C bond homolysis. The plausible mechanism of oxidation of bent d^0 metallocenes involves M–C$_{sp^3}$ bond homolysis after removal of one-electron, giving the radical–cation pair (transient **A** in Scheme 3).

The observed reaction products would then result from a competition between the intramolecular SN2 coupling and the intermediate cage escape (paths *a* and *b* in Scheme 3, respectively).
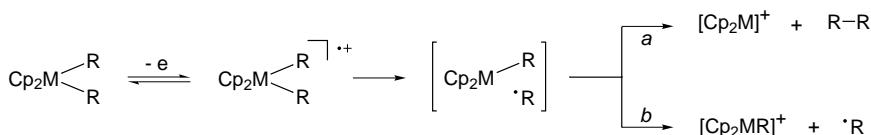
Scheme 3

Diphenyl zirconocene oxidises with the formation of biphenyl, while the corresponding diphenyl titanocene predominantly gives rise to benzene and some biphenyl under similar conditions. Thus, the authors proposed[66] important synthetic application of the reaction as a novel route from Ti(IV) and Zr(IV) metallacycles to hetero- and carbocycles.

Bent titanocene and zirconocene methyl (or chloride) enolate radical cations $[Cp_2MR^1\{O(R^2)C=CMes_2\}]^{\bullet+}$ (R^1 = Me, Cl; Mes = mesityl) were shown to undergo transformation of the C–C bond to 1,4-diketones, even in a stereoselective fashion. The radical cations were characterised with fast-scan cyclic voltammetry. Lifetimes of the bent zirconocene methyl (or chloride) enolate radical cations (1–2 ms at room temperature) were estimated from the apparent rates of concomitant Zr–O(enolate) bond cleavage[67].

Irreversible outer-sphere oxidation of bent d^0 metallocenes is therefore a superposition of two processes (either ECE or EC$_{ir}$ scheme). Release of the first electron from the 16-electron neutral complex yields a kinetically unstable 15-electron radical cation undergoing fast heterolysis of the M–X bond in $[(\pi\text{-L})_2M^{IV}X_2]^{\bullet+}$ (X = Me, Cl), giving rise to the corresponding radical $X^\bullet$ and cation $[(\pi\text{-L})_2M^{IV}X]^+$, and further oxidation of the radical $X^\bullet$. Generally speaking, oxidative homolysis of the M–X bond yielding the neutral complex $[(\pi\text{-L})_2M^{III}X]$ and the cation X^+ is unfavourable owing to much stronger reducing power of the former complex in this redox pair[57]. In fact, other available data unequivocally suggest oxidation of the related bis(cyclopentadienyl)zirconium(III) monomethyl complex $[Cp_2Zr^{III}Me]$ at –1.9 V in MeCN (*vs* Fc/Fc$^+$)[67], the potential of the Me$^\bullet$/Me$^+$ couple being –0.5 V (ref.[68]). At sufficiently positive potentials the radical $X^\bullet$ should be oxidised in the electrode vicinity immediately when produced (ECE scheme). Certainly, the proposed oxidation scheme is not exhaustive since highly reactive intermediates participate in parallel reactions and passivation of the electrode surface[57,66]. Concluding mechanistic discussion, the extremely reactive d^0 cationic species $[(\pi\text{-L})_2MR]^+$ (R = alkyl) has been recognised[69] as a key intermediate in olefin polymerisation catalysis.

Substituent effect. The measurements of oxidation potentials for a series of $[(\eta^5\text{-C}_5H_{5-n}Me_n)_2TiCl_2]$ complexes (*n* = 0, 3–5) suggested that successive hy-

drogen replacement with the methyl groups decreased the binding energies of valence and inner-shell electrons due to the hyperconjugative effect of the substituents[70].

Thus, the redox activation of the organometallics with closed-shell 16-electron (16e) configuration expands the mechanistic knowledge and synthetic applications for the modification of the sandwich complexes and derivated metal complex catalysts. The high reactivity of 15e and 17e complexes (compared to the 16e species) is caused by both thermodynamic and kinetic reasons. If the excitation of 16e organometallics is associated with electron transfer between bonding and non- or antibonding frontier orbitals, the excitation of odd-electron (15e, 17e) complexes then involves electron transfer between bonding (15e species) and non- or antibonding (17e species) orbitals. Thus the excitation energy and the difference in the reactivity for the ground and excited states of the intermediate odd-electron complexes are lower than for their 16e analogues. Due to this high reactivity, the 15e and 17e complexes undergo some characteristic transformations that hardly occur with their 16e precursors. After giving of representative examples of the electron-transfer-induced reactions of bent sandwich complexes of the group 4 metals, we further advocate the combined electrochemical and spectroscopic approach to obtaining fundamental energetic quantities of frontier molecular orbitals of the closed-shell organometallics based on the group 4 transition metals.

4. FRONTIER MOLECULAR ORBITALS AND HOMO-TO-LUMO ENERGY GAP FROM THE VIEWPOINT OF THE REDOX AND OPTICAL ELECTRON TRANSITION PARADIGM

4.1. Combined Spectroscopic and Electrochemical Approach to Probing Frontier Molecular Orbitals

Limited comprehensive knowledge has been gained on thermodynamic and other properties of organometallic, inorganic, and coordination compounds allowing full characterisation of the structure–property relationship, aimed at predictable properties of untested or hitherto unknown molecules. As a general case, frontier (high-lying occupied and low-lying vacant) orbitals govern the chemical reactivity of a molecule. Relative energies of the frontier molecular orbitals can be estimated by quantum-chemical calculations or derived experimentally, using techniques monitoring the electronic changes located on valence and occupied orbitals of a molecule. For decades, both revealing electrochemical and optical experi-

ments have been successfully applied to probe the metal–ligands electronic coupling, the ionic or covalent nature of bonding in the metal–ligand framework, and also to the interplay between ligands in homologous series of inorganic and coordination compounds. The idea behind the studies has been based on the assumption, that the oxidation/reduction potential of a molecule corresponds to a "solution ionisation potential", and that there should be a direct relationship between oxidation/reduction potentials and HOMO/LUMO energies. Thermodynamic correlations between optical transition energies in complex molecules and the reduction/oxidation potentials, or differences thereof, were advocated over the past forty years in diverse reports (for some elegant studies, see refs[71–87]). The most extensive correlations of differences in redox potentials and energies of optical transitions have been derived for a number of Rh, Ru, Os, and Fe complexes. The correlation analysis has been based on the classical work of A. A. Vlček[88–91].

The correlations arise from the fact that energy of an optical transition is given by the difference between the energy of the donor orbital, which the electron is to be transferred from, and the energy of the orbital accepting the electron in the excited state[92]. Configuration interaction between the charge-transfer excited state and other nearby states must be weak or preferably negligible. Energy of an optical transition is related to the difference in the redox potentials for the oxidation and reduction of a molecule in its ground state[91]. Obviously, the pair of orbitals involved in the optical and redox processes must be the same. As a rule, the orbitals involved in these processes are localised on different fragments of a molecule[91,93,94]. The approach is based on ligand additivity made possible by Koopmans' theorem[95] ($I + E$ = const.), allowing prediction of energies of the frontier molecular orbitals. Last, extensive comparison can be made for a class or a series of related molecules, where the electronic structures of the involved states remain the same throughout the target molecular sequence.

A number of authors have evidenced the linear relationship between optical ($E_{h\nu}$) and electrochemical (ΔE_{redox}) gap energies, approximated as $E_{h\nu} = a\Delta E_{redox} + \Sigma b_i$, where the slope a may differ from unity and the constant Σb_i denotes solvation, reorganisation, and configuration interaction energies. The inner-sphere χ_i (vibrational) and outer-sphere χ_o (solvent, vibrational in nature) reorganisation energies are of importance. Solvatochromic molecules (*e.g.*, in ref.[75]) may not obey a general relationship $E_{h\nu} \propto \Delta E_{redox}$ owing to large values of χ_o within the target molecular series. The inner-sphere reorganisation χ_i is expected to vary markedly even for structurally related molecules possessing strong configurational interaction, interligand coupling, *etc.* The structural changes are generally expected in molecules ex-

posed to (i) photoexcitation or (ii) electron-transfer reactions, *i.e.* when proceeding from (i) thermally non-equilibrated (a vertical electron transition) to equilibrium excited states or (ii) from a neutral molecule to the respective reduced/oxidised species.

There are other known intriguing cases of linear fit ($E_{h\nu}$ *vs* $E_{red/ox}$) involving optical transition energies and *one* (E_{red} or E_{ox}) from the two redox potentials (for a large number of complexes with low-lying metal-to-ligand CT excited states this concerns metal oxidation)[85,96–99]. In principle, a linear correlation between energies of "optical" and "redox" frontier molecular orbitals should exist *a priori* for any given series of closely related complex molecules. Lack of the correlation[100], any fine exceptions, deviations from a linear relationship, all indicating anomalies in ligand additivity, interligand coupling, distinct electronic and structural alterations or even a qualitative reversal of higher occupied or/and low unoccupied orbitals in a molecule[101], may appear even more informative in analysing sequences of homologous complex molecules. In particular, in view of a pure charge-transfer transition (labelled as MLCT or LMCT) involving transfer of electron density from a metal to a ligand (or *vice versa*), the description of the transitions is arbitrary and loses the meaning whenever the excited states cannot fit adequately to the localised orbital configuration model. For example, extensive metal–ligand d_π-π orbital mixing leads to the occurrence of relatively high-lying electronic transitions having little charge-transfer character. The lack of charge-transfer character is then nicely evidenced by breakdown of the linear relationship between electrochemical and optical HOMO-to-LUMO energy gaps[101]. For mixed-ligand and other complexes, data points deviating significantly from the key relationship $E_{h\nu} \propto \Delta E_{redox}$ may be taken as a more quantitative evidence of the difference between "optical" and "redox" frontier MOs involved in photophysical (absorption, emission) and redox, or electrochemical processes[77]. A great body of data from earlier studies are referred specifically to a *metal-to-ligand* charge-transfer transition. The most striking aspect is that the redox and optical electron transition paradigm arithmetically simplified as $E_{h\nu} \propto \Delta E_{redox}$, must be quite general. This conclusion has led us to a division of the paradigm into the strategy of studying *ligand-to-metal* CT excited states and, more specifically, photophysics and electrochemistry of a special class of highly reactive coordination compounds, the organotransition metal π-complexes. This aspect is further elaborated in the next section.

4.2. Ligand-to-Metal Charge-Transfer Excited States of Bent Sandwich Complexes

In a large number of organometallics, ligand-to-metal charge-transfer transitions occur at rather high energies, typically overlapping with metal-to-ligand, ligand-field, d–d and other electronic transitions[102–104]. For this reason, relatively little knowledge has been gained on photophysical properties of organometallics having pure ligand-to-metal charge-transfer excited states.

The group 4 bent metallocenes $[(\pi\text{-L})_2MX_2]$ (X = *e.g.*, halide or alkyl) are complexes tailored of a d^0 transition metal and multiply- and η^1-bonded ligands, that comply with a "localised" molecular orbital approach. These complexes belong to the C_{2v} and lower symmetry point groups and the symmetry treatment provides readily labelling of the molecular orbitals according to their transformation properties, but without assignment of a relative order of the energy levels. Molecular orbital calculations, mostly at semiempirical level, are indicative in this regard, but so far they have only been performed on a few representatives of this organometallic family, specifically for bent bis(η^5-cyclopentadienyl)metal complexes.

The high-lying occupied and low-lying vacant molecular orbitals of bent metallocenes have been a subject of numerous studies and will be noted herein briefly. The HOMO of each $[(\pi\text{-L})_2M^{IV}X_2]$ complex is predominantly ligand-localised, and the low-lying unoccupied orbitals are associated mainly with the metal d orbitals; the LUMO is an essentially non- bonding orbital (Fig. 2).

Low-lying electronic excited states of closed-shell d^0 metal complexes will be charge transfer in nature. Figure 2 shows simplified representation of the HOMO-to-LUMO charge-transfer transition in a bent metallocene $[(\pi\text{-L})_2MX_2]$. Visible-light absorption in the group 4 bent metallocenes leads to the population of ligand→M CT excited states that correspond to the promotion of an electron from a ligand-centred (electron-rich either π-L or σ-X) to the low-lying vacant MOs of largely metal d character. The occurrence of LMCT transitions in the low-energy region is expected, at least, from the viewpoint of 6e-donor ability of (non)functionalised five-membered sandwich π-ligands. According to the current models for LMCT transitions, the energy and intensity of the CT absorption band are related to (i) energy separation and extent of mixing of the involved ligand-centred and metal-centred orbitals; (ii) the average separation of the electron promoted into the metal centre and the hole left on the ligand of the π- or σ-type. In one-electron approximation, the primary photophysical

process is the generation of the d^1 metal species $M^{IV} \rightarrow M^{III}$ and one-electron oxidation of the better electron-releasing ligand (π-L or σ-X), which may induce homolysis of the respective metal–ligand bond and produce the paramagnetic metal-centred species and free (organic) radical.

The HOMO-to-LUMO energy difference (gap) depends on the nature of the transition metal and the strength of the ligand field, which is related to the molecular structure of ligands (electron-withdrawing and electron-donating substituents, *etc.*). Photolysis in the UV-VIS region has been applied as a neat probe to the bonding character of metal–ligand framework. The relative energetic ordering of the high-lying occupied MOs based on different π-L and σ-X ligands may vary (*e.g.*, π-L orbitals drop in energy and the σ-X orbitals rise in energy), resulting in different HOMO characters. The character and relative ordering of the high-lying occupied MOs and assignment of long-wavelength absorptions have been a subject of controversy[105–119]. The question, whether the excited electrons come from HOMO extending predominantly over multiply-bound π- or monodentate σ-ligands remains to be solved. A more flexible, rather than unified MO scheme is therefore desirable. Thus, the ligand-based HOMO changes in character when electron-withdrawing σ-ligands (*e.g.*, X = F, Cl) are substituted for electron-donating σ-ligands (*e.g.*, X = Me, I); consistent with this is the different photochemistry observed for the bent sandwich complexes
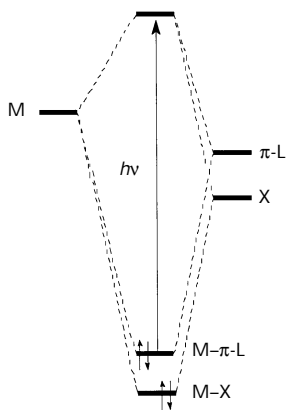

FIG. 2

Simplified MO diagram for bent group 4 metal complexes $[(\pi\text{-L})_2 MX_2]$, showing the interaction of a π-ligand (L) orbital and a σ-ligand (X) orbital with a metal (M) orbital and the HOMO-to-LUMO electronic transition (X ligand is more electronegative)

[$(\pi\text{-L})_2\text{MX}_2$]. Recall that in the case of dichloride complexes [$(\pi\text{-L})_2\text{MCl}_2$], when only sandwich π-ligands are varied, the character of the lowest energy charge-transfer excited states [$(\pi\text{-L})_2$-based HOMO] is not changed, and the primary photoprocess remains the metal–π-ligand bond cleavage. It appears that introduction of methyl or iodide σ-ligands reverses the HOMO character and population of the lowest energy X→M charge-transfer excited state results in M–σ-ligand bond cleavage as the primary photoprecess. After photodissociation in the absence of scavengers (radical traps, oxidants), the two paramagnetic species may recombine. The latter process is responsible for the photoracemisation of the *meso*- and *rac*-isomers in the case of bridged metallocene dichlorides[119–126]. Together with electrochemistry, the photochemical data clearly demonstrate the extent of possible fine tuning of the redox and photophysical/-chemical properties by simple substitution of the ligand sphere and the transition metal ion. Additional experimental information about electronic structure of the target organometallic complexes [$(\pi\text{-L})_2\text{MX}_2$] has been also obtained by means of photoelectron spectroscopy[14–16].

During on-going studies, we have revealed linear correlations[127,128] between the frontier MO gap in the redox processes (the redox gap G as the difference between the oxidation and reduction potentials[129,130]) and the fourth gas-phase ionisation potentials of the corresponding transition metal [IP_4: $\text{M}^{IV} \rightarrow \text{M}^{III}$] ($r^2 = 1.000$) as well as the lowest LMCT transition energies, for the first bent metallocene triad [Cp_2MCl_2] (M = Ti, Zr, Hf) ($r^2 = 0.995$) (Fig. 3). We explored the extension of this correlation analysis to a broad series of the related bent zirconocenes [$(\pi\text{-L})_2\text{MX}_2$] with variable multiply-bound π-ligands (π-L = Cp (C_5H_5), Ind (C_9H_{13}), Flu (C_{13}H_9)) and monodentate σ-ligands (X = Cl, Me) of different electronegativity. The linear relationships between the redox gaps G (2.7 up to 4 V) and optical electron transition energies E_{hv} (2.5 up to 4.5 eV) are also very good (Fig. 3; $r^2 = 0.992$) and provide important means to probe the frontier levels of these d^0 organometallics. Among all, this is associated with retention of the dominant metal d contribution to the redox and optical LUMO throughout the whole series.

With increasing electron-donor character of aromatic π- or monodentate σ-ligand the electron-donating ability of high occupied levels is enhanced and this effect is also transmitted to the non-bonding or antibonding metal d orbitals[127,128]. The standard reduction potentials data suggest that there is significant shift to negative potentials (0.8 up to 1.0 V) for a metal-centre reduction from M^{IV} to M^{III}, *e.g.*, when chloride ligands are replaced with the effective σ-donor methyl groups. Metal centre has a pronounced electronic

effect, which results, for example, in systematically increasing intensity of the lowest LMCT transition in absorption spectra and in lowering the standard reduction potential along the group 4 transition metals. Comparison of the spectroscopic properties of the bent metallocenes along the metal triad (Ti, Zr, Hf) indicates a large blue shift and increase in the charge-transfer intensity[131] for heavier metals, thus actually confirming that photoexcitation leads to the electron promotion from the ligand framework to the transition metal ion.

The heteroligand sandwich complexes are similar in their electrochemical behaviour with respect to the parent homoligand analogues. They are also characterised by (quasi)reversible reduction and irreversible oxidation steps that formally proceed with a change of the metal and ligand oxidation states, respectively. With these similarities in electronic structure and molecular architecture and on the basis of energetic correlations $E_{h\nu} \propto \Delta E_{redox}$, we may argue that *sets of the frontier orbitals (named "redox" and "optical") retain virtually the same character*. The molecules undergo similar structural

FIG. 3
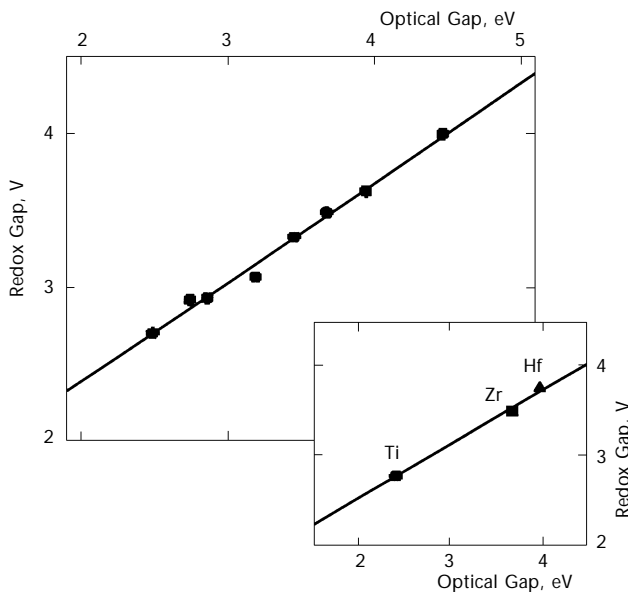Two linear correlations between the differences in oxidation and reduction potentials (electrochemical, or redox gaps) and energies of the lowest LMCT transition (optical gaps) for the closely related series of the (non)bridged dichloride and dimethyl zirconocenes [(π-L)$_2$ZrX$_2$] (r^2 = 0.992) and bis(cyclopentadienyl)metal dichloride complexes [Cp$_2$MCl$_2$] (M = Ti, Zr, Hf) (r^2 = 0.995)

changes in the redox and electron-transfer processes. Inner- and outer-sphere solvent coordination changes in these processes should be approximately constant or scale[131]. The lifetimes of the extremely unstable primary oxidation products $[(\pi\text{-}L)_2MX_2]^{\bullet+}$ should scale for oxidation along the metallocene series.

The combined redox and spectroscopic approach is employed for designing coloured organometallic species with desired energies of frontier orbitals, understanding the character of metal–ligand binding coordination bonds, predicting redox potentials, elucidation of mechanisms of the redox and electrochemical reactions, designing complex molecules with appropriate excited state potentials[87], checking assignment of CT bands in optical spectra, *etc.*

In conclusion, fundamental experimental correlations between energetic separations of the frontier optical and redox levels (HOMO, LUMO) are reported in our preceding communications. Recently, there have been much doubts with regard to mechanisms of photochemical and redox (or electrochemical) electron transfer reactions of these compounds. The use of solvents stable in regions of extreme anodic and cathodic potentials, cryoelectrochemistry and ultramicroelectrode techniques have greatly expanded our knowledge of electrochemistry and electron-transfer-induced reactions of bent metallocene complexes. Unambiguously, in the near future much attention will be focused on understanding the "structure–property" relationship principle, using correlation of the redox potentials and electrochemical and/or photochemical properties and reactivity of various groups of organometallics.

REFERENCES

1. Wailes P. C., Coutts R. S. P., Weigold H.: *Organometallic Chemistry of Titanium, Zirconium, and Hafnium*. Academic Press, New York 1974.
2. Bottrill M., Gavens P. D., Kelland J. W., McMeeking J.: *Comprehensive Organometallic Chemistry* (G. Wilkinson, F. G. A. Stone and E. W. Abel, Eds), p. 271. Pergamon Press, Oxford 1982.
3. Cardin D. L., Lappert M. F., Raston C. L., Riley P. I. in: Ref.[2], p. 549.
4. Volpin M. E., Shur V. B.: *Advances in Chemical Nitrogen Fixation*. Mir, Moscow 1983.

5. Shilov A. E.: *Metal Complexes in Biomimetic Chemical Reactions*. CRS Press, Boca Raton, New York 1997.
6. Wolczanski P. T., Bercaw J. E.: *Acc. Chem. Res.* **1980**, *13*, 121.
7. Silver M. E., Einsenstein O., Fay R. C.: *Inorg. Chem.* **1983**, *22*, 759.
8. Kaminsky W.: *J. Chem. Soc., Dalton Trans.* **1998**, 1413.
9. Bochmann M.: *Top. Catal.* **1999**, *1–4*, 9.
10. Resconi L., Cavallo L., Fait A., Piemontesi F.: *Chem. Rev. (Washington D. C.)* **2000**, *100*, 1253.
11. Alt H. G., Köppl A.: *Chem. Rev. (Washington D. C.)* **2000**, *100*, 1205.
12. Fink G., Steinmetz B., Zechlin J., Przybyla C.: *Chem. Rev. (Washington D. C.)* **2000**, *100*, 1377.
13. Chen E. Y.-X., Marks T. J.: *Chem. Rev. (Washington D. C.)* **2000**, *100*, 1391.
14. Cauletti C., Clark J. P., Green J. C., Jackson S. E., Fragala I. L., Ciliberto E., Coleman A. W.: *J. Electron Spectrosc. Relat. Phenom.* **1980**, *18*, 61.
15. Condorelli G., Fragala I., Centineo A., Tondello E.: *J. Organomet. Chem.* **1975**, *87*, 311.
16. Petersen J. L., Lichtenberg P. L., Fenske R., Dahl L. F.: *J. Am. Chem. Soc.* **1975**, *97*, 6433.
17. Lauher J. W., Hoffmann R.: *J. Am. Chem. Soc.* **1976**, *98*, 1729.
18. Eisenstein O., Hoffmann R.: *J. Am. Chem. Soc.* **1981**, *103*, 4308.
19. Bruce M. R. M., Kenter A., Tyler D. R.: *J. Am. Chem. Soc.* **1984**, *106*, 639.
20. Rabaâ H., Saillard J.-H., Hoffmann R.: *J. Am. Chem. Soc.* **1986**, *108*, 4327.
21. Connely M. G., Geiger W. E.: *Adv. Organomet. Chem.* **1984**, *23*, 1.
22. Strelets V. V.: *Coord. Chem. Rev.* **1992**, *114, 1*.
23. Mugnier Y., Fakhr A., Fauconet M., Moise C., Laviron E.: *Acta Chim. Scand., Ser. B* **1983**, *37*, 423.
24. Losada J., Moran M.: *J. Organomet. Chem.* **1984**, *276*, 13.
25. Kukharenko S. V., Soloveichik G. L., Strelets V. V.: *Izv. Akad. Nauk SSSR, Ser. Khim.* **1985**, 1020.
26. Samuel E., Vedel J.: *Organometallics* **1989**, *8*, 237.
27. El Murr N., Chaloyard A., Tirouflet J.: *J. Chem. Soc., Chem. Commun.* **1980**, 446.
28. Samuel E., Guery D., Vedel J., Basile F.: *Organometallics* **1985**, *4*, 1073.
29. Fakhr A., Mugnier Y., Gautheron B., Laviron E.: *J. Organomet. Chem.* **1986**, *302*, C7.
30. Fakhr A., Mugnier Y., Gautheron B., Laviron E.: *Nouv. J. Chim.* **1986**, *10*, 601.
31. Da Rold A., Mugnier Y., Broussier R., Gautheron B., Laviron E.: *J. Organomet. Chem.* **1989**, *362*, C27.
32. Gale R. J., Job R.: *Inorg. Chem.* **1981**, *20*, 42.
33. Kukharenko S. V., Soloveichik G. L., Strelets V. V.: *Metalloorg. Khim.* **1989**, *2*, 395.
34. Babkina O. N., Bazhenova T. A., Bravaya N. M., Strelets V. V., Antipin M. Yu., Lissenko K. A.: *Izv. Akad. Nauk, Ser. Khim.* **1996**, 1529 (*Russ. Chem. Bull. (Engl. Transl.)* **1996**, *45*, 1458).
35. Bazhenova T. A., Antipin M. Yu., Babkina O. N., Bravaya N. M., Lissenko K. A., Strelets V. V.: *Izv. Akad. Nauk, Ser. Khim.* **1997**, 2161 (*Russ. Chem. Bull. (Engl. Transl.)* **1997**, *46*, 2048).
36. Langmaier J., Samec Z., Varga V., Horáček M., Chouktroun R., Mach K.: *J. Organomet. Chem.* **1999**, *584, 323*.
37. Langmaier J., Samec Z., Varga V., Horáček M., Mach K.: *J. Organomet. Chem.* **1999**, *579, 348*.

38. Strelets V. V., Soloveichik G. L., Sizov A. I., Bulychev B. M., Rusina A., Vlček A.: *Izv. Akad. Nauk SSSR, Ser. Khim.* **1983**, 2493.

39. Bajgur C. S., Tikkanen W. R., Petersen J. L.: *Inorg. Chem.* **1985**, *24*, 2539.

40. Soloveichik G. L., Gavrilov A. B., Strelets V. V.: *Metalloorg. Khim.* **1989**, 431.

41. Lappert M. F., Pickett C. J., Riley P. I., Yarrow P. I. W. P.: *J. Chem. Soc., Dalton Trans.* **1981**, 805.

42. Winter C. H., Zhou X.-X., Dobbs D. A., Heeg M. J.: *Organometallics* **1991**, *10*, 210.

43. Gassman P. G., Macomber D. W., Hershberger J. W.: *Organometallics* **1983**, *2*, 1470.

44. Bühl M., Hopp G., von Philipsborn W., Beck S., Prosenc M.-H., Rief U., Brintzinger H. H.: *Organometallics* **1996**, *15*, 778.

45. Hiller J., Thewalt U., Polášek M., Petrusová L., Varga V., Sedmera P., Mach K.: *Organometallics* **1996**, *15*, 3752.

46. Gassman P. G., Winter C. H.: *Organometallics* **1991**, *10*, 1592.

47. Gassman P. G., Campbell W. H., Macomber D. W.: *Organometallics* **1984**, *3*, 385.

48. Gassman P. G., Deck P. A., Winter C. H., Dobbs D. A., Cao D. H.: *Organometallics* **1992**, *11*, 959.

49. Feltham R. D., Brant P.: *J. Am. Chem. Soc.* **1982**, *104*, 641.

50. Bursten B. E., Callstrom M. R., Jolly C. A., Paquette L. A., Sivik M. R., Tucker R. S., Martchow C. A.: *Organometallics* **1994**, *13*, 127.

51. Gassman P. G., Callstrom M. R.: *J. Am. Chem. Soc.* **1987**, *109*, 7875.

52. Chaloyard A., Darmond A., Tirouflet J., El Murr N.: *J. Chem. Soc., Chem. Commun.* **1980**, 214.

53. Etienne M., Choukroun R., Gervais D.: *J. Chem. Soc., Dalton Trans.* **1984**, 915.

54. Lappert M. F., Pickett C. J., Riley P. I., Yarrow P. I. W.: *J. Chem. Soc., Dalton Trans.* **1981**, 805.

55. Samuel E., Hénique J.: *J. Organomet. Chem.* **1996**, *512*, 183.

56. Lochert P., Federlin P.: *Tetrahedron Lett.* **1973**, *13*, 1109.

57. Loukova G. V., Babkina O. N., Bazhenova T. A., Bravaya N. M., Strelets V. V.: *Izv. Akad. Nauk, Ser. Khim.* **2000**, 59 (*Russ. Chem. Bull. (Engl. Transl.)* **2000**, *49*, 60).

58. Koch L., Fakhr A., Mugnier Y., Roullier R., Moise C., Laviron E.: *J. Organomet. Chem.* **1986**, *314*, C17.

59. Erker G., Engel K., Kruger C., Tsay Y.-H., Samuel E., Vogel P.: *Z. Naturforsch., B* **1985**, *40*, 150.

60. Pickett C. J.: *Electrochemistry* **1983**, *8*, 81.

61. Pickett C. J.: *Electrochemistry* **1984**, *9*, 162.

62. Anderson J. A., Sawtelle S. M.: *Inorg. Chem.* **1992**, *31*, 5345.

63. Jordan R. F., LaPointe R. E., Bajgur C. S., Echols S. F., Willett R. J.: *J. Am. Chem. Soc.* **1987**, *109*, 4111.

64. Jordan R. F., Echols S. F.: *Inorg. Chem.* **1987**, *26*, 383.

65. Jordan R. F., Dasher W. E., Echols S. F.: *J. Am. Chem. Soc.* **1986**, *108*, 1718.

66. Burk M. J., Tumas W., Ward M. D., Wheeler D. R.: *J. Am. Chem. Soc.* **1990**, *112*, 6133.

67. Schmittel M., Söllner R.: *J. Chem. Soc., Chem. Commun.* **1998**, 565.

68. Benderskii V. A., Krivenko A. G., Kurmaz V. A., Simbirceva G. V.: *Elektrokhimiya* **1988**, *24*, 158.

69. a) Dyachkovskii F. S., Shilova A. K., Shilov A. E.: *J. Polym. Sci., Part C: Polym. Symp.* **1967**, *16*, 2333; b) Dyachkovskii F. S., Grigoryan E. A., Babkina O. N.: *Int. J. Chem. Kinet.* **1981**, *13*, 603.

70. Mach K., Varga V.: *J. Organomet. Chem.* **1989**, *347*, 85.
71. Ford P. C., Rudd De F. P., Gaunder R., Taube H.: *J. Am. Chem. Soc*. **1968**, *90*, 1187.
72. Saji T., Aoyagui S.: *J. Electroanal. Chem. Interfacial Electrochem.* **1975**, *58*, 401.
73. Saji T., Aoyagui S.: *J. Electroanal. Chem. Interfacial Electrochem.* **1975**, *60*, 1.
74. Crutchley R. J., Lever A. B. P.: *Inorg. Chem.* **1982**, *21*, 2276.
75. Curtis J. C., Sullivan B. P., Meyer T. J.: *Inorg. Chem.* **1983**, *22*, 224.
76. Rillema D. P., Allen G., Meyer T. J., Conrad D.: *Inorg. Chem.* **1983**, *22*, 1617.
77. Ohsawa Y., Hanck K. W., DeArmond M. K.: *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *175*, 229.
78. Dodsworth E. S., Lever A. B. P.: *Chem. Phys. Lett.* **1985**, *119*, 61.
79. Rottia S., Paradisi C., Bignozzi C. A.: *J. Electroanal. Chem. Interfacial Electrochem*. **1986**, *200*, 105.
80. Barigelletti F., Juris A., Balzani V., Belser P., von Zelewsky A.: *Inorg. Chem.* **1987**, *26*, 4115.
81. Sandrini D., Maestri M., Balzani V., Maeder U., von Zelewsky A.: *Inorg. Chem.* **1988**, *27*, 2640.
82. Campagna S., Denti G., De Rossa G., Sabatino L., Ciano M., Balzani V.: *Inorg. Chem.* **1989**, *28*, 2565.
83. Bianchini C., Peruzzini M., Ottaviani M. F., Laschi F., Zanobini F.: *Organometallics* **1989**, *8*, 893.
84. Bianchini C., Meli A., Peruzzini M., Vacca A., Laschi F., Zanello P.: *Organometallics* **1990**, *9*, 360.
85. Steel P. J., Constable E. C.: *J. Chem. Soc., Dalton Trans.* **1990**, 1389.
86. Nazeeruddin M. K., Zakeeruddin S. M., Kalyanasundaram K.: *J. Phys. Chem.* **1993**, *97*, 9607.
87. Vlček A. A., Dodsworth E. S., Pietro W. J., Lever A. B. P.: *Inorg. Chem.* **1995**, *34*, 1906.
88. Vlček A. A.: *Z. Anorg. Allg. Chem.* **1960**, *304*, 109.
89. Vlček A. A.: *Prog. Inorg. Chem.* **1963**, *5*, 211.
90. Vlček A. A.: *Coord. Chem. Rev.* **1982**, *43*, 39.
91. Vlček A. A.: *Electrochim. Acta* **1968**, *13*, 1063.
92. Roothaan C. C.: *Rev. Mod. Phys.* **1942**, *14*, 112.
93. Kalyanasudaram K., Grätzel M., Pelizzetti E.: *Coord. Chem. Rev.* **1986**, *69*, 57.
94. Juris A., Balzani V., Barigelletti F., Campagna S., Belser P., von Zelewsky A.: *Coord. Chem. Rev.* **1988**, *84*, 85.
95. Koopmans T.: *Physica* **1934**, *1*, 104.
96. Malouf G., Ford P. C.: *J. Am. Chem. Soc*. **1974**, *96*, 601.
97. Malouf G., Ford P. C.: *J. Am. Chem. Soc*. **1977**, *99*, 7213.
98. Figard J. E., Petersen J. D.: *Inorg. Chem.* **1978**, *17*, 1059.
99. Haga M., Sato G. P., Matsumura T., Shimizu K.: *J. Chem. Soc., Dalton Trans*. **1989**, 371.
100. Mak S. T., Yam V. W. W., Che C. M., Mak T. C. W.: *J. Chem. Soc., Dalton Trans.* **1990**, 2555.
101. Gorelsky S. I., Dodsworth E. S., Lever A. B. P., Vlček A. A.: *Coord. Chem. Rev.* **1998**, *174*, 469.
102. Geoffroy G. L., Wrighton M. S.: *Organometallic Photochemistry*. Academic Press, New York 1979.
103. Roundhill D. M.: *Photochemistry and Photophysics of Metal Complexes*. Academic Press, New York 1994.

104. Balzani V., Scandola F.: *Supramolecular Photochemistry*. Horwood, Chichester 1994.
105. Harrigan R. W., Hammound G. S., Gray H. B.: *J. Organomet. Chem.* **1974**, *81, 79*.
106. Vitz E., Brubaker C. H., Jr.: *J. Organomet. Chem.* **1974**, *84*, C16.
107. Alt H., Rausch M. D.: *J. Am. Chem. Soc.* **1974**, *96*, 5936.
108. Vitz E., Wagner P. J., Brubaker C. H., Jr.: *J. Organomet. Chem.* **1976**, *107, 301*.
109. Vitz E., Brubaker C. H., Jr.: *J. Organomet. Chem.* **1976**, *104*, C33.
110. Samuel E., Alt H. G., Hrncir D. C., Rausch M. D.: *J. Organomet. Chem.* **1976**, *113, 331*.
111. Rausch M. D., Boon W. H., Alt H. G.: *J. Organomet. Chem.* **1977**, *141, 299*.
112. Lee J. C., Brubaker C. H., Jr.: *Inorg. Chim. Acta* **1977**, *25, 181*.
113. Samuel E., Maillard P., Giannotti C.: *J. Organomet. Chem.* **1977**, *142, 289*.
114. Peng M., Brubaker C. H., Jr.: *Inorg. Chim. Acta* **1978**, *26*, 231.
115. Bamford C. H., Puddephatt R. J., Slater D. M.: *J. Organomet. Chem.* **1978**, *159*, C31.
116. Tsai Z.-T., Brubaker C. H., Jr.: *J. Organomet. Chem.* **1979**, *166*, 199.
117. Pankowski M., Samuel E.: *J. Organomet. Chem.* **1981**, *221*, C21.
118. Bruce M. R. M., Sciafani A., Tyler D. R.: *Inorg. Chem.* **1986**, *25*, 2546.
119. Barbieri A., Doghetti A., Sostero S., Traverso O.: *J. Photochem. Photobiol., A* **1999**, *129, 137*.
120. Wild F. R. W. P., Zolnai L., Huttner G., Brintzinger H. H.: *J. Organomet. Chem.* **1982**, *232, 233*.
121. Wild F. R. W. P., Wasiucionek M., Huttner G., Brintzinger H. H.: *J. Organomet. Chem.* **1985**, *288, 63*.
122. Schäfer A., Karl E., Zolnai L., Huttner G., Brintzinger H. H.: *J. Organomet. Chem.* **1987**, *328*, 87.
123. Krutko D. P., Borzov M. V., Churakov A. V., Lemenovskii D. A.: *Izv. Akad. Nauk, Ser. Khim.* **1998**, 2351.
124. Kaminsky W., Schauwienold A. M., Freidanck F.: *J. Mol. Catal.* **1996**, *112, 37*.
125. Rheingold A. L., Robinson N. P., Whelan J., Bosnich B.: *Organometallics* **1992**, *11*, 1869.
126. Schmidt K., Reinmuth A., Rief U., Diebold J., Brintzinger H. H.: *Organometallics* **1997**, *16*, 1724.
127. Loukova G. V., Strelets V. V.: *J. Organomet. Chem.* **2000**, *606, 203*.
128. Loukova G. V., Strelets V. V.: *Izv. Akad. Nauk, Ser. Khim.* **2000**, 1043 (*Russ. Chem. Bull. (Engl. Transl.*) **2000**, 49, 1037).
129. Butin K. P., Rakhimov R. D., Reutov O. A.: *Zh. Org. Khim.* **1987**, *23*, 905.
130. Pearson R. G.: *Chem. Br.* **1991**, 444.
131. Loukova G. V., Smirnov V. V.: Unpublished results.