

Electrochemical versus optical insight in frontier orbitals of Ti(IV), Zr(IV), and Hf(IV) bent metallocenes

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Abstract

The linear relationship between the redox and optical HOMO-to-LUMO electron transitions are reported for complex molecules with π -ligands for the first time. Linear correlations between electrochemical (redox) gaps and absorption charge-transfer energies have been noted for Ti(IV), Zr(IV), and Hf(IV) bis(cyclopentadienyl) dichlorides. A similar correlation was also observed for the fourth ionization potentials of the corresponding Group IVB metals. The correlation between absorption charge-transfer energies and redox gaps was justified for a series of *ansa*- and unbridged zirconocene dichlorides and dimethyls with variable sandwich ligands. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Comprehensive models and empirical correlation schemes have enabled organic chemists to establish viable reaction mechanisms and design new species with specific properties [1]. The situation is less well defined for organometallic chemistry, in fact, a lack of comprehensive models and systematic empirical analyses may have hindered the advancement of the field [2]. Chemical reactivity is determined largely by the relative frontier orbital energies [3]. It is logical to estimate relative valence electronic structures of organometallic molecules applying direct independent observations, thus drawing correspondences between the information gained with each of the techniques. Interrelationships between broad electrochemical and spectroscopic data, enable one to rationalize frontier molecular orbital (HOMO and LUMO) trends and reactivities of complex molecules, particularly sandwich species [4a], nevertheless, the limited comprehensive knowledge has been transmitted.

We have previously described [4] a well defined relationship, between the electrochemical potentials E_j° ($j = 1-4$) of the metal-centered redox processes and gas-phase

ionization potentials of the corresponding free atomic metal (IP_j) viz.

$$E_j^\circ = \sum a_i + 0.1IP_j \quad (1)$$

in sandwich organometallic species; where $\sum a_i$ ($i = 1-2$) and values of the constants a_i were reported for common sandwich ligands. Later, applying the ligand electrochemical parametrization approach to the sandwich complexes, the electrochemical parameters E_L (L) for over 200 π -ligands were derived [5]. For many first row transition metal complexes, we first reported correlations between the formal redox potential (E°) and the $\sum E_L$ (L) for each metal couple; the E_L (L) values of the substituted π -ligands were correlated with Hammett substituent constants (σ_p).

2. Results and discussion

In this first analysis we do not attempt to provide an exhaustive survey, rather, we focus on the Group IVB bent sandwich complexes, specifically, the first representative bis(cyclopentadienyl) triad Cp_2MCl_2 [$M = Ti(IV), Zr(IV), Hf(IV)$] and a series of *ansa*- and unbridged bent zirconocenes $\eta-L_2ZrX_2$ [where $L=Cp$ (cyclopentadienyl), Ind (indenyl), Flu (fluorenyl); $X=Cl, Me$], being common

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precursors for cationic metallocene catalysts [6], to further arrive at a comprehensive electronic model for organometallic compounds. The linear relationships observed between the frontier orbitals gaps (HOMO-to-LUMO electron transition energies), and the difference in redox potentials (the redox gap G is the difference between oxidation and reduction potentials [7]), the fourth gas-phase ionization potentials of the corresponding metal (IP_4 [8]) ($r^2 = 1.000$), and also the lowest absorption ligand-to-metal charge-transfer (LMCT) energies¹ ($r^2 = 0.995$) are indeed excellent. Furthermore they provide an important means of probing the variations in the frontier molecular orbitals. Next, we have explored the extension of this correlation analysis to a series of the related bent zirconocenes. Specifically, the relationship between the redox gap, G , and the optical HOMO-to-LUMO electron transition energies is also excellent ($r^2 = 0.992$)². To our knowledge, these are the first fundamental correlations between electrochemical and optical parameters of the relative HOMO and LUMO energies, and the gaps between them, reported for a variety of organometallic molecules with π -ligands.

The Group IVB bent metallocenes [11a] are formally closed-shell d^0 complexes and the lowest energy excited states involve transfer of electron density from the ligands to the metal (LMCT) [11]. The sets of the frontier (redox and optical) orbitals involved are closely related within the whole series of complexes. The HOMO is ligand-based [11]; and the electrochemical oxidation is irreversible [4a,12c–f]. The LUMO is unoccupied has mainly d metal character; and the metal-centered electrochemical reduction is reversible or quasi-reversible [4a,12a,b,f]. The UV–vis absorption spectra of the samples show shifts of the band maxima by changing the microscopic environment around the metal (progressive red shift of charge-transfer absorp-

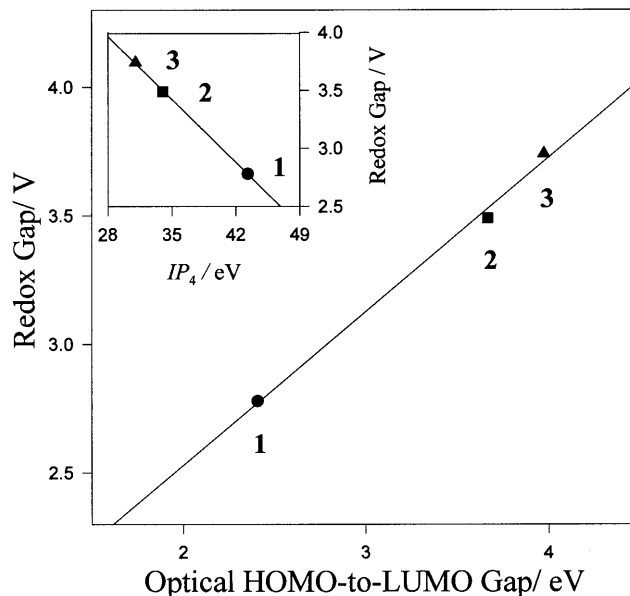


Fig. 1. Linear relationships between the electrochemical gaps (G) in the titanium 1, zirconium 2, and hafnium 3 bis(cyclopentadienyl) dichlorides and the fourth gas-phase ionization potentials of the corresponding metal, $r^2 = 1.000$ (inset), also the lowest LMCT energies in the complexes 1–3, $r^2 = 0.995$.

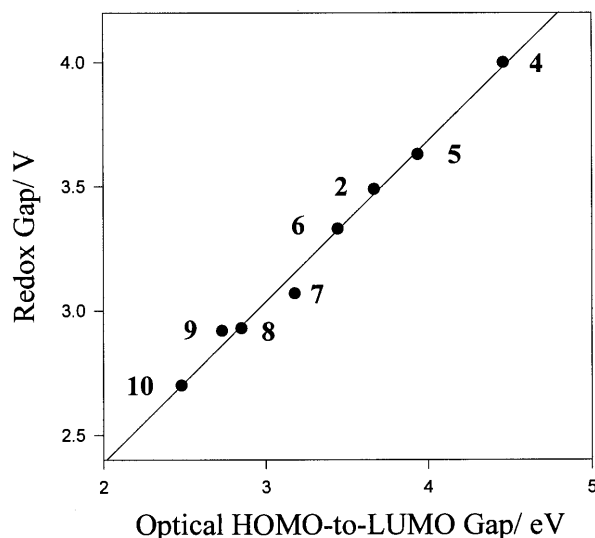


Fig. 2. Linear correlation between the electrochemical gaps (G) and the absorption LMCT energies in the related *ansa*- and unbridged zirconocene dichlorides and dimethyls 2, 4–10, $r^2 = 0.992$. Complexes appear in the numerical order given in the Table 1.

¹ The logic here is that the metal is formally reduced in the LMCT excited states: $(M^- - L^+)^*$. The correlations between the charge transfer absorption energies and the reduction/oxidation potentials are based on the fact that the energy of an optical transition is, in one-electron approximation, given by the difference between the energy of the orbital from which the electron is being transferred and the energy of the orbital accepting the electron [9a]. The difference is related to the difference in the redox potentials for the oxidation and reduction of the compound in its ground state [9b]. Therefore, the pair of orbitals involved in the optical and redox processes must be the same. Charge-transfer properties are compared, the frontier orbitals involved in these processes will be primarily localized on different fragments of the molecule [9b,c,d].

² (a) The best fit value is derived; all points data are shown on the regression lines in the Figs. 1 and 2 to demonstrate accuracy of the fit. Errors: the experimental values are subject to some error and the scatter in the lines may reflect experimental limitations rather than breakdown in ligand additivity. (b) The approach is based on ligand additivity made possible by Koopmans' theorem allowing prediction of orbital energies [10].

tion as the η -ligands become larger and more electron-rich, see Table 1). With reference to the ligand effects upon the energetics of metal-based LUMO, we have seen potential shifts are caused by two factors. First, the replacement of a sandwich ligand with another changes the overall electron density at the metal center (i.e. its effective charge), this yields energetic shifts in

Table 1
Electrochemical gaps, the fourth ionization potentials, and the related lowest absorption LMCT energies of the bent sandwich complexes

Complex	E_{red}° (V) ^a	E_{ox} (V) ^b	G (V) ^c	IP_4 (eV)	λ_{LMCT} (nm)	E_{LMCT} (eV)
Cp ₂ TiCl ₂ (1)	−0.82	1.96	2.78	43.30	515 ^{d,j}	2.407
Cp ₂ ZrCl ₂ (2)	−1.63 (−1.78) ^{e,f}	1.86	3.49	33.97	338 ^g	3.668
Cp ₂ HfCl ₂ (3)	−1.93	1.81	3.74	31.00	312 ^g	3.974
Cp ₂ ZrMe ₂ (4)	(−2.72) ^{e,f} −2.59 ^h	1.41 ^f	(4.13) 4.00 ^h		278 ^{i,k}	4.460
Ind ₂ ZrMe ₂ (5)	(−2.46) ^{e,f} −2.33 ^h	1.30 ^f	(3.76) 3.63 ^h		315 ^{d,k}	3.936
Me ₂ SiCp ₂ ZrCl ₂ (6)	−1.53	1.80	3.33		360 ^f	3.444
Ind ₂ ZrCl ₂ (7)	−1.59 (−1.71) ^{e,f}	1.48	3.07		390 ^f	3.179
(CH ₂) ₂ Ind ₂ ZrCl ₂ (8)	−1.57	1.36	2.93		435 ^f	2.850
Me ₂ SiInd ₂ ZrCl ₂ (9)	−1.54	1.38	2.92		454 ^f	2.731
Ph ₂ CCpFluZrCl ₂ (10)	−1.49	1.21	2.70		500 ^d	2.480

^a $E_{\text{red}}^{\circ} = (E_{\text{p}}^{\text{red}} + E_{\text{p}}^{\text{ox}})/2$.

^b Oxidation is irreversible.

^c The term $G = E_{\text{ox}} - E_{\text{red}}^{\circ}$ tends to cancel some of the errors in the individual potentials.

^d Solvent: toluene.

^e Solvent: THF.

^f Taken from ref. [12f].

^g Solvent: CH₂Cl₂.

^h The subtracted average value of 0.13 V is referred to the hypothetical reduction in CH₂Cl₂ owing to a greater solvating effect of THF.

ⁱ Solvent: cyclohexane.

^j Spin-forbidden transition.

^k Shoulder.

frontier HOMO and LUMO levels. For sandwich complexes with the donor methyl ligands, the metal-based LUMO is destabilized by antibonding interaction with the methyl fragments. Apparently, the complexes do not undergo significant structural changes. The variations in hapticity, inner-sphere solvent coordination should be approximately constant or scale, in both redox and optical electron transition processes, within the sequence of the isostructural bent complexes Cp₂MCl₂ and L₂ZrX₂. The latter property is of significance because optical transitions being a Franck–Condon process bring a molecule into thermally non-equilibrated excited states. The timescales of the extremely fast decomposition of the primary cationic complex, at oxidation, should scale throughout the series of metallocene complexes.

The associated electrochemical and spectroscopic model has evident applications for: (i) designing organometallic molecules with particular frontier orbital energies; (ii) understanding fundamental metal–ligand binding as a function of the metal ion and core environment change; (iii) predicting redox potentials; (iv) elucidation of the mechanism of electrochemical reactions; (v) enabling design of complexes with particular excited-state potentials [13]; and (vi) checking assignment of the observed charge-transfer energies in optical spectroscopy. The latter spectral property has been applied in the selection of the Group IV metallocenes for potentially active polymerization catalysts

[14a] and study of the multi-component catalyst successors [14b,c]. Clearly, a broader database of complexes is required before a full discussion can be made. Deviations from straight-line relationship are already a measure of possible interligand coupling, distinct structural changes, electronic effects, and stereochemical constraints introduced by substituents and the bridging group.

3. Experimental

All preparative manipulations and cyclic voltammetry experiments were carried out under prepurified Ar atmosphere in flame-dried glassware on a double-manifold high-vacuum line with use of standard Schlenk techniques; the handling of solid materials was performed in a He-filled dry box. All solvents (reagent grade) were rigorously dried over appropriate drying agents and vacuum distilled prior to use. Basic apparatus and electrochemical set-up were similar to that reported [4,12f]. Reduction and oxidation were carried out at a glassy carbon electrode (GC) in CH₂Cl₂–0.05 M Bu₄NPF₆, otherwise noted. All potentials were measured versus the ferrocenium–ferrocene redox couple (Fc^{+ / 0}, $E^{\circ} = 0.43$ V in CH₂Cl₂ and 0.44 V in THF) and given versus a saturated calomel electrode (SCE). Electronic absorption spectra for the Group IVB metal complexes were recorded in CH₂Cl₂, toluene, and cyclo-

hexane. On the basis of our study and the available spectroscopic data ([14a] and references therein) absorption spectra were approximately solvent-independent in these solvents.

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References

- [1] (a) P.R. Wells, *Linear Free Energy Relationships*, Academic Press, New York, 1968. (b) L.P. Hammett, *Physical Organic Chemistry*, McGraw-Hill, New York, 1970. (c) R.W. Taft, *Prog. Phys. Org. Chem.* 14 (1983) 247. (d) T.H. Lowry, K.S. Richardson, *Mechanism and Theory in Organic Chemistry*, third ed., Harper and Row, New York, 1987, Chapters 3 and 4. (e) J. March, *Advanced Organic Chemistry*, Wiley Interscience, New York, 1985.
- [2] J.R. Pugh, T.J. Meyer, *J. Am. Chem. Soc.* 114 (1992) 3784.
- [3] (a) I. Fleming, *Frontier Orbitals and Organic Chemical Reactions*, Wiley, New York, 1976. (b) K. Fukui, *Top. Curr. Chem.* 15 (1970) 1. (c) G. Klopman, *J. Am. Chem. Soc.* 90 (1968) 223.
- [4] (a) V.V. Strelets, *Coord. Chem. Rev.* 114 (1992) 1. (b) V.V. Strelets, S.V. Kukharensko, *Dokl. Akad. Nauk SSSR*, 275 (1984) 894. (c) V.V. Strelets, S.V. Kukharensko, *Nouv. J. Chim.* 8 (1985) 785. (d) V.V. Strelets, S.V. Kukharensko, *Organomet. Chem. USSR (Engl. Transl.)* 1 (1988) 385. (e) A.B. Gavrilov, S.V. Kukharensko, V.V. Strelets, *Organomet. Chem. USSR (Engl. Transl.)* 3 (1990) 199.
- [5] S. Lu, V.V. Strelets, M.F. Ryan, W.J. Pietro, A.B.P. Lever, *Inorg. Chem.* 35 (1996) 1013.
- [6] (a) F.S. Dyachkovskii, A.K. Shilova, A.E. Shilov, *J. Polym. Sci. Part C* 16 (1967) 2333. (b) H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. Waymouth, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 1143.
- [7] (a) K.P. Butin, R.D. Rakhimov, O.A. Reutov, *Zh. Org. Khim.* 23 (1987) 905 (*Russ. J. Org. Chem. (Engl. Transl.)*). (b) R.G. Pearson, *Chemistry in Britain*, 1991, pp. 444.
- [8] A.A. Radtsig, B.N. Smirnov, *Atomic and Molecular Physics Guide*, Atomizdat, Moscow, 1980, p. 68.
- [9] (a) C.C. Roothaan, *J. Rev. Mod. Phys.* 14 (1942) 112. (b) A.A. Vlcek, *Electrochim. Acta* 13 (1968) 1063. (c) K. Kalyanasudaram, M. Gratzel, E. Pelizzetti, *Coord. Chem. Rev.* 69 (1986) 57. (d) A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewski, *Coord. Chem. Rev.* 84 (1988) 85.
- [10] T. Koopmans, *Physica (Utrecht)* 1 (1934) 104.
- [11] (a) P.C. Wailes, R.S.P. Coutts, H. Weigold, *Organometallic Chemistry of Titanium, Zirconium, and Hafnium*, Academic Press, New York, 1974. (b) R.W. Harrigan, G.S. Hammond, H.B. Gray, *J. Organomet. Chem.* 81 (1974) 79. (c) J.W. Lauher, R. Hoffmann, *J. Am. Chem. Soc.* 98 (1976) 1729. (d) Z.-T. Tsai, C.H. Brubaker Jr., *J. Organomet. Chem.* 166 (1979) 199. (e) C. Cauletti, J.P. Clark, J.C. Green, S.E. Jackson, I.L. Fragala, E. Ciliberto, A.W. Coleman, *J. Electron Spectrosc. Relat. Phenom.* 18 (1980) 61. (f) M.R.M. Bruce, A. Sciafani, D.R. Tyler, *Inorg. Chem.* 25 (1986) 2546.
- [12] (a) M.G. Connely, W.E. Geiger, *Adv. Organomet. Chem.* 23 (1984) 1. (b) E. Samuel, D. Guery, J. Vedel, F. Basile, *Organometallics* 4 (1985) 1073. (c) M.J. Burk, W. Tumas, M.D. Ward, D.R. Wheeler, *J. Am. Chem. Soc.* 112 (1990) 6133. (d) J.E. Anderson, S.M. Sawtelle, *Inorg. Chem.* 31 (1992) 5345. (e) M. Schmittel, R. Söllner, *Chem. Commun.* (1998) 565. (f) G.V. Loukova, O.N. Babkina, T.A. Bazhenova, N.M. Bravaya, V.V. Strelets, *Russ. Chem. Bull.* 119 (2000) 60.
- [13] A.A. Vlcek, E.S. Dodsworth, W.J. Pietro, A.B.P. Lever, *Inorg. Chem.* 34 (1995) 1906.
- [14] (a) P.J.J. Pieters, J.A.M. van Beek, M.F.H. van Tol, *Macromol. Rapid Commun.* 16 (1995) 463. (b) J. Kim, K.H. Kim, J.C. Cho, S. Kwak, K.U. Kim, W.H. Jo, H.S. Yoon, D.S. Lim, *J. Polym. Sci., Part A* 36 (1998) 1733. (c) J.-N. Pedeutour, D. Coevoet, H. Cramait, A. Deffieux, *Macromol. Chem. Phys.* 200 (1999) 1215.