Journal of Organometallic Chemistry, 229 (1982) 43—47
Elsevier Sequoia, S.A., Lausanne — Printed in The Netherlands

A VOLTAMMETRIC STUDY OF THE METAL—LIGAND INTERACTION IN BIS(ARENE)CHROMIUM(I) COMPLEXES

NAOYUKI ITO, TETSUO SAJI *, KOSAKU SUGA and SHIGERU AOYAGUI

Department of Chemical Engineering, Tokyo Institute of Technology, Ohokayama, Meguro-ku, Tokyo 152 (Japan)

(Received July 16th, 1981; in revised form November 16th, 1981)

Summary

Cyclic voltammetric and ESR measurements are made on nine bis(arene)-chromium(I) (arene = hydrocarbons with condensed benzene rings) complexes. Every cyclic voltammogram exhibits a reversible one-electron reduction step. The half-wave potentials of these complexes are independent of the ligands and form a striking contrast with those of the complexes with alkyl- and aryl-substituted benzenes, which depend largely on the ligands. This finding suggests that the redox orbitals should be of pure σ-character which partly originates from ligand σ-orbitals. The ESR spectrum of each $[Cr(arene)_2]^+$ exhibits, besides ^{53}Cr hyperfine lines, only ^1H hyperfine lines due to a pair of benzene rings bonded to Cr, irrespective of the number of the rings. Consequently, the findings of previous workers concerning the bis(naphthalene) complexes of Cr^I and V^0 are also true of complexes with greater aromatic ring systems. Our experimental results support the conclusion of the previous ESR and NMR studies that the HOMO of $[Cr(arene)_2]^0$ is mainly composed of the metal $3d_{z^2}$ and the ligand σ-orbitals. However, the previously reported formation of $[Cr(naphthalene)_2]^-$ by chemical reduction is not substantiated by our voltammetric experiments.

Introduction

It was considered in earlier works that the ligand MO's which were responsible for the metal—ligand bonding in sandwich complexes were only π-orbitals. However, later theoretical and experimental studies concluded that ligand σ-orbitals played an important role in the metal—ligand bondings. According to the NMR, ESR and MO studies of Drago and coworkers [1—5] on the metallo-

---

* To whom correspondence should be addressed.

cenes and bis(benzene) complexes of the first-row transition metals, competing σ- and π-delocalizations of the unpaired electron are operative, the σ-mechanism being predominant in the earlier transition metals and the π-mechanism in the later ones. The ESR studies of Prins and coworkers [6,7] have led to the same conclusion.

Although sandwich complexes have also been subjects of many electrochemical investigations, especially voltammetric ones, they have been almost confined to metallocenes and their derivatives [8,9]. Gubin et al. [10] found that the introduction of electron-withdrawing substituents into the cyclopentadienyl rings caused a considerable anodic shift of the oxidation half-wave potentials of ruthenocenes, whereas electron-donating substituents had the reverse effect. They explained this in terms of the inductive effect of the substituents on the ruthenium atom and suggested, furthermore, that electron delocalization on the σ- rather than on the π-ring orbitals should take part.

It is likely that the inductive effect is also operative in the half-wave potential shifts found for $[Cr(substituted\ benzene)_2]^{+/0}$ with electron-withdrawing or -donating substituents [11—13]. The authors of refs. 10—12 considered that their conclusions were in accord with the theoretical prediction of Vlček [14] who worked out as early as in 1960 this first voltammetric approach to the nature of the metal—ligand bonding in sandwich complexes.

Among the little information available about sandwich complexes with arene ligands other than benzene, a finding of Dessy et al. [15] drew our attention, because it stated that the difference between the half-wave potentials for $[Cr(naphthalene)_2]^{+/0}$ [15] and $[Cr(benzene)_2]^{+/0}$ [16] was less than 0.1 V, despite the difference between the ligand half-wave potentials exceeding 1 V. The present paper deals with some sandwich complexes of an early transition metal, Cr^I, with condensed benzene rings, in order to examine the effect of the change of ligand π-frameworks on the reduction half-wave potentials of these complexes.

Experimental

Bis(benzene)chromium(I) iodide [17] and bis(arene)chromium(I) tetraphenylborates [18] ($[Cr(arene)_2]B(C_6H_5)_4$ with arene = fluorene, naphthalene, phenanthrene and anthracene) were prepared by the literature methods. The complexes of chrysene, pyrene, fluoranthene and bis(diphenylene)ethene were prepared in similar ways. Each reaction mixture was refluxed for 3 to 40 h until the violet solution of $CrCl_3$ turned brownish-yellow and viscous. 1,2-Dimethoxyethane (DMeE) and *N,N*-dimethylformamide (DMF) were used as solvents and tetra-n-butylammonium perchlorate (TBAP) as the supporting electrolyte. The solvents were treated with sodium anthracenide and distilled on a vacuum line, as described in a previous paper [19]. Therein are also described the purification of TBAP and the preparation of the test solutions.

The electrolysis cell used had a three-electrode arrangement with a platinum wire electrode as the working electrode and an $Ag/AgNO_3$(sat.) or a saturated calomel electrode (SCE) as the reference electrode. Cyclic voltammetric experiments were carried out at (21 ± 1)°C with a scan rate of 0.1 V s^{-1}.

A 6 m*M* solution of a Cr^I complex in DMF was used in the ESR experiments, which were carried out on a Varian E-22 ESR spectrometer operated at room temperature. Coupling constants were determined by using as a reference the nitrogen coupling constant of nitrobenzene radical anion, 0.979 mT [20].

Results

The ESR spectra of all the $[Cr(arene)_2]^+$ complexes studied were very similar to those of $[Cr(benzene)_2]^+$ [21,22], $[Cr(naphthalene)_2]^+$ [23] and $[Cr(biphenyl)_2]^+$ [24] in the literature. They exhibited respectively nine equally-spaced ^1H hyperfine lines, except for the spectrum of $[Cr(benzene)_2]^+$ which had eleven lines. A common ^1H coupling constant of (0.354 ± 0.004) mT was determined in the same way as used for $[Cr(naphthalene)_2]^+$ [23]. A pair of satellite lines were assigned to the ^{53}Cr hyperfine splittings, following refs. 7 and 22. The ^{53}Cr coupling constants ranged within (1.73 ± 0.01) mT, and the g-values within 1.9908 ± 0.0004.

On the basis of the reversibility criteria of the peak separation and the peak : height ratio in cyclic voltammetry, it is concluded that all the redox couples, $[Cr(arene)_2]^{+/0}$ and arene $^{0/-}$, undergo reversible one-electron processes, except for benzene $^{0/-}$ whose half-wave potential could not be obtained. Table 1 lists the reversible half-wave potentials for $[Cr(arene)_2]^{+/0}$ ($E_{1/2,C}$) and arene$^{0/-}$ ($E_{1/2,L}$) which were obtained by taking the half-wave potential as the midpoint between the anodic and the cathodic peak potentials. Strikingly, the $E_{1/2,C}$ values are invariable against the $E_{1/2,L}$ change over more than 1.7 V and presents a contrast to those of the $[Cr(arene)_2]^{+/0}$ couples with alkyl- and aryl-substituted benzenes as ligands [11], in which a change of ligands from mesitylene to biphenyl caused an $E_{1/2,C}$ change of 0.25 V. Very recently, Treichel et al. presented a more extensive change in $E_{1/2,C}$ which covered over a 1.15 V range [13]. Unfortunately, it is likely that their experiments were conducted under inappropriate conditions, because the peak separation for $[Cr(benzene)_2]^{+/0}$ in acetonitrile was as great as 144 mV against our value of 58 mV.

TABLE 1

THE HALF-WAVE POTENTIALS OF $[Cr(arene)_2]^{+/0}$ ($E_{1/2,C}$) IN 0.2 *M* TBAP-DMF AND IN 0.4 *M* TBAP-DMeE, THE HALF-WAVE POTENTIALS OF arene$^{0/-}$ ($E_{1/2,L}$) IN 0.4 *M* TBAP-DMeE AND THE PEAK SEPARATIONS OF CYCLIC VOLTAMMOGRAMS (ΔE_p) AT 21°C

TBAP: tetra-n-butylammonium perchlorate
DMF: *N,N*-dimethylformamide
DMeE: 1,2-dimethoxyethane

Arene	$-E_{1/2,L}$ (V) [a]	$-E_{1/2,C}$ (V) [a]	$-E_{1/2,C}$ (V) [b]	ΔE_p (mV) [b]
Benzene	—	1.39_7	0.74_0	58
Fluorene	3.37_2	1.38_1	0.72_8	60
Naphthalene	3.18_3	1.39_8	0.74_4	58
Phenanthrene	3.11_0	1.39_8	0.74_4	57
Chrysene	2.91_4	1.39_5	0.74_4	58
Pyrene	2.75_2	1.39_8	0.74_1	58
Anthracene	2.60_4	1.39_5	0.74_7	55
Fluoranthene	2.39_8	1.39_8	0.74_3	58
Bis(diphenylene)ethene	1.64_0	1.39_4	0.74_2	64

[a] In DMeE; vs. $Ag/AgNO_3$(sat.). [b] In DMF; vs. SCE.

Discussion

The feature of the ESR spectra can be understood following the explanations of Anderson and Drago [5] and Prins and coworkers [6,7], if it is assumed that the HOMO of $[\mathrm{Cr(arene)_2}]^0$ is the a_{1g} orbital composed of the $3d_{z^2}$ AO of Cr and the σ-frameworks of the benzene rings bonded to the central Cr atom. In this instance the results of Table 1 can be explained as follows. An alkyl and aryl substitution on benzene would give rise to a change in the σ- as well as the π-orbital energy of the complex, although the σ-effect may be mainly operative in the alkyl substitution. The σ-effect of electron-donating groups is responsible for the increase in the HOMO energy of $[\mathrm{Cr(arene)_2}]^0$ and, in turn, the negative shift of the $[\mathrm{Cr(arene)_2}]^{+/0}$ half-wave potential. Contrary to the alkyl and aryl substitution, a change in the number of condensed benzene rings should cause an appreciable change only in the π-orbital energy and, consequently, should not affect the HOMO energy of any $[\mathrm{Cr(arene)_2}]^0$ studied. This may be the reason for the constant $E_{1/2,\mathrm{C}}$ values in Table 1. The constancy of $E_{1/2,\mathrm{C}}$ within experimental error may imply that the redox orbital of $[\mathrm{Cr(arene)_2}]^{+/0}$ should be of pure σ-character. The fact that the alkyl or aryl substitution of ligand benzene causes a considerable shift in $E_{1/2,\mathrm{C}}$ suggests that the redox orbital is not a pure metal d_{z^2} orbital but that it involves some contribution of the ligand σ- orbitals. Consequently, the present voltammetric study reached the same conclusion as the previous spectroscopic studies that the σ-orbitals of the ligand and the central metal are responsible for the metal—ligand bonding of the $[\mathrm{Cr(arene)_2}]^+$ complexes.

It is worth noting that every $[\mathrm{Cr(arene)_2}]^+$ complex studied has only one reduction step. According to Anderson and Drago [5] and Prins and Reinders [7] the electronic configuration of $[\mathrm{Cr(benzene)_2}]^+$ is $\cdots(e_{2g})^4(a_{1g})^1(e_{2u})^0$, a_{1g} being a metal d orbital and e_{2u} a ligand π-orbital. Consequently, the redox orbital in the second reduction step of this complex may be a ligand π^*-orbital. If this applies to other $[\mathrm{Cr(arene)_2}]^+$ complexes, the finding above will imply that the π^*-orbital of the coordinated ligand is so high that the second reduction step of the complex may be located beyond −3.4 V vs. $\mathrm{Ag/AgNO_3}$(sat.), the negative break of the voltammogram. This orbital energy relative to the π^*-energy of the free ligand molecule is given by the following equation [25]:

$$A_\mathrm{C} - A_\mathrm{L} = e(E_{1/2,\mathrm{C}} - E_{1/2,\mathrm{L}}) + S_\mathrm{L} - S_\mathrm{C}$$

where A denotes the electron affinity of the oxidant, S the solvation energy of the reductant, and the suffixes C and L denote a complex and a free ligand, respectively. It may be safe to consider that $S_\mathrm{L} > S_\mathrm{C}$, since the excess electron of $[\mathrm{Cr(arene)_2}]^-$ may occupy a π^*-orbital which is delocalized over two ligand molecules. Hence, this equation shows that the ligand π^*-orbital of $[\mathrm{Cr(arene)_2}]^0$ should be higher than the π^*-orbital of the free ligand molecule by more than 1.7 eV, even in the case where the ligand is bis(diphenylene)ethene which has the most positive $E_{1/2,\mathrm{L}}$ value among the ligands used in this work. With respect to this destabilization, the $[\mathrm{Cr(arene)_2}]^0$ complexes form a striking contrast to the $[\mathrm{Cr(2,2'\text{-}bipyridine)_3}]^0$ complex whose ligand π^*-orbital is lower-lying than that of the free ligand [25].

Henrici-Olivé and Olivé reduced $[\mathrm{Cr(naphthalene)_2}]^+$ with lithium naphthalenide and suggested the formation of [Cr(naphthalene)$_2$]$^-$ on the basis of the ESR spectra [23]. If they are right, [Cr(naphthalene)$_2$]^0 should be reducible at a more positive potential than naphthalene, whose reduction half-wave potential is −3.18 V vs. Ag/AgNO$_3$(sat.) in DMeE. This is in disagreement with our observation that the second reduction step of [Cr(naphthalene)$_2$]$^+$ does not appear at potentials more positive than −3.4 V. Their reduction product must be identified on other bases than the ESR spectrum which cannot give definite evidence for [Cr(naphthalene)$_2$]$^-$.

Acknowledgement

The authors wish to thank Dr. Eiichi Ichikawa for his guidance in the synthesis of the complexes.

References

1 M.F. Rettig and R.S. Drago, J. Amer. Chem. Soc., 91 (1969) 1361.
2 M.F. Rettig and R.S. Drago, J. Amer. Chem. Soc., 91 (1969) 3432.
3 S.E. Anderson, Jr. and R.S. Drago, J. Amer. Chem. Soc., 91 (1969) 3656.
4 S.E. Anderson, Jr. and R.S. Drago, J. Amer. Chem. Soc., 92 (1970) 4244.
5 S.E. Anderson, Jr. and R.S. Drago, Inorg. Chem., 11 (1972) 1564.
6 R. Prins, J. Chem. Phys., 50 (1969) 4804.
7 R. Prins and F.J. Reinders, Chem. Phys. Lett., 3 (1969) 45.
8 C.K. Mann and K.K. Barnes, Electrochemical Reactions in Nonaqueous Systems, Marcel Dekker, New York, 1970.
9 J.D.L. Halloway and W.E. Geiger, Jr., J. Amer. Chem. Soc., 101 (1979) 2038.
10 S.P. Gubin, S.A. Smirnova, L.I. Denisovich and A.A. Lubovich, J. Organometal. Chem., 30 (1971) 243.
11 S. Valcher, G. Casalbore and M. Mastragostino, J. Electroanal. Chem., 51 (1974) 226.
12 H. Hsiung and G.H. Brown, J. Electrochem. Soc., 110 (1963) 1085.
13 P.M. Treichel, G.P. Essenmacher, H.F. Efner and K.J. Klabunde, Inorg. Chim. Acta, 48 (1981) 41.
14 A.A. Vlček, Z. anorg. allgem. Chem., 304 (1960) 109.
15 R.E. Dessy, R.B. King and M. Waldrop, J. Amer. Chem. Soc., 88 (1966) 5112.
16 R.E. Dessy, F.E. Stary, R.B. King and M. Waldrop, J. Amer. Chem. Soc., 88 (1966) 471.
17 E.O. Fischer in E.G. Rochow (Ed.), Inorg. Synth., Vol. VI, McGraw-Hill, New York, 1960, p. 132.
18 F. Hein and W. Kleinwächter, Monatsber. Deut. Akad. Wiss. Berlin, 2 (1960) 607; Chem. Abstr., 56 (1962) 4787g.
19 T. Saji, T. Yamada and S. Aoyagui, J. Electroanal. Chem., 61 (1975) 147.
20 T. Kitagawa, T.P. Lagoll and R.N. Adams, Anal. Chem., 35 (1963) 1086.
21 R.D. Feltham, P. Sogo and M. Calvin, J. Chem. Phys., 26 (1957) 1354.
22 R.D. Feltham, J. Inorg. Nucl. Chem., 16 (1961) 197.
23 G. Henrici-Olivé and S. Olivé, J. Amer. Chem. Soc., 92 (1970) 4831.
24 B. Elschner and S. Herzog, Z. Naturforsch., 12a (1959) 860.
25 T. Saji and S. Aoyagui, J. Electroanal. Chem., 63 (1975) 405.