Journal of Organometallic Chemistry, 121 (1976) 261—264
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

ELECTROCHEMISTRY OF COORDINATION COMPOUNDS

XII. ELECTROCHEMICAL STUDIES OF d^8 σ-ORGANOMETALLIC RHODIUM AND IRIDIUM COMPLEXES

GILBERTO SCHIAVON *, SANDRO ZECCHIN, GIUSEPPE PILLONI
Consiglio Nazionale delle Ricerche, Laboratorio di Polarografia ed Elettrochimica Preparativa, C.P. 1075, 35100 Padova (Italy)

and MARIO MARTELLI
Consiglio Nazionale delle Ricerche, Centro di Studio sulla Stabilità e Reattività dei Composti di Coordinazione, Instituto di Chimica Analitica dell'Università, Via Marzolo 1, 35100 Padova (Italy)

(Received May 9th, 1976)

Summary

The electrochemical behaviour of d^8 organometallic rhodium and iridium complexes, $M(R)(CO)(PPh_3)_2$ (R = alkyl, aryl), has been investigated with a mercury electrode in acetonitrile. The reduction proceeds via a single two-electron step, no (or only small) differences in the reduction potential being noted between rhodium and iridium. The comparison with previous findings suggests that this unusual result is related to a specific influence of the organic ligand in promoting the reduction process in such a way that the actual redox molecular orbital can be mainly of ligand-orbital character.

Since (i) specific medium effects could not be studied and (ii) studies of the effects of substituents in the benzene ring of some rhodium organometallic complexes were inconclusive, it was not possible to establish the pathways for the electron uptake.

Introduction

In studying the influence of the anionic ligand on the polarographic behaviour of d^8 rhodium and iridium complexes, we found that the differences in the half-wave reduction potential values between these two metals became progressively larger as the electron donor properties of the anionic ligand (EDP) increased [1].

---

* To whom correspondence should be addressed.

Since experimental data support the idea that organic groups are very strong donors in comparison with most common anionic ligands [2], we extended the investigation to the d^8 organometallic derivatives of the same complexes.

The aims of this study were: (a) to check whether the previously found trend [1] occurred also with a series of formally anionic ligands, R and (b) to obtain information about the effect of the "charged" ligand on the reduction potential of metal complexes.

Results and discussion

All the complexes examined show a single, two-electron, irreversible and diffusion controlled wave which is not affected by addition of free PPh_3. Exhaustive controlled potential electrolysis carried out in the potential range of the plateau requires two moles of electrons per mole of complex leading to the formation of $[M(CO)(PPh_3)_3]^-$ [3]. In these experiments a five-fold excess of PPh_3 was used to stabilize the anionic derivative. The fate of the organic group was investigated by gas-liquid chromatographic analysis of the electrolyzed solution, which showed the presence of an equimolar amount of RH. These findings and the almost identical charge transfer coefficients, α (about 0.5), indicate a common reduction mechanism at the electrode (eq. 1).

$$M(R)(CO)(PPh_3)_2 + 2\,e \xrightarrow[+\text{proton donor}]{+PPh_3} [M(CO)(PPh_3)_3]^- + RH \qquad (1)$$

The half-wave potentials and the ν(CO) stretching frequencies of the complexes are collected in Table 1 and indicate that for both metals: (i) the uptake of electrons is more difficult in the order $CH_3 > Ph > CPh_3 > C_6F_5$ and (ii) the reduction potentials for all ligands are either identical or show small differences.

The first result is commonplace [2], the second is quite unusual. All our previous studies and in particular those on the closely related complexes $M(CO)(PPh_3)_2X$ (M = Rh, Ir; X = univalent anionic ligand), showed the ease of reduction to run parallel to the ν(CO) stretching frequency of the complexes, which is lower in the iridium compounds than in the corresponding rhodium compounds [1]. While the ν(CO) values of corresponding organometallic iridium and rhodium derivatives show the expected differences, the reduction potentials of both metals are almost identical.

It is known, however, that the heavier metals generally give kinetically more stable compounds than the lighter elements if the ligands are the same [4], and this result would be expected to influence the irreversible half-wave potentials values which are related to kinetic parameters [5].

Furthermore, we previously found that the differences in the reduction half-wave potentials between rhodium and iridium increased with the electron donor ability of the anionic ligand and an analogous trend was also expected with organic groups, which are very strong electron donors [2].

In contrast to these expectations, there is no apparent effect of the metal in the series of organometallic derivatives, indicating that either the differences between the metals are minimized or the actual redox orbitals are different from those which determine the behaviour of the anionic ligands. We favour the latter hypothesis, because the previously found relationship between the lowest energy

TABLE 1

HALF WAVE POTENTIALS (VOLTS VS. Ag/Ag$^+$ 0.1 *M* ACETONITRILE SOLUTION) AND I.R. (cm^{-1}) DATA

Complex	$E_{1/2}$	ν(CO)[a]
$Rh(Me)(CO)(PPh_3)_2$	—2.65	1950
$Rh(p\text{-methoxyphenyl})(CO)(PPh_3)_2$	—2.59	1960
$Rh(p\text{-tolyl})(CO)(PPh_3)_2$	—2.58	1960
$Rh(Ph)(CO)(PPh_3)_2$	—2.53	1965
$Rh(p\text{-chlorophenyl})(CO)(PPh_3)_2$	—2.47	1965
$Rh(m\text{-chlorophenyl})(CO)(PPh_3)_2$	—2.46	1965
$Rh(p\text{-trifluoromethylphenyl})(CO)(PPh_3)_2$	—2.45	1965
$Rh(Ph_3C)(CO)(PPh_3)_2$	—2.27	1970
$Rh(C_6F_5)(CO)(PPh_3)_2$	—2.27	1970
$Ir(Me)(CO)(PPh_3)_2$	—2.66	1935
$Ir(Ph)(CO)(PPh_3)_2$	—2.53	1940
$Ir(Ph_3C)(CO)(PPh_3)_2$	—2.35	1955
$Ir(C_6F_5)(CO)(PPh_3)_2$	—2.31	1960

[a] Recorded in acetonitrile/chloroform solution.

transition of the electronic spectra of the iridium complexes is not obeyed in this case. Thus, the unusual behaviour must be related to a specific influence of the organic group in promoting the reduction process. It is known that the organic group is able to increase the electron availability at the central metal so that the electronic charge on the metal might be close to that of a lower oxidation state [2]. Consequently, the location of the added electrons could be on a molecular orbital mainly of ligand orbital character. In other words, the experimental findings are compatible with the differing abilities of the "halogeno" and "organo" ligands to accommodate electrons such that, on going to the transition state, the metal—halogeno bond could be preferably weakened compared to the metal—organo bond. We cannot discuss at present the possible pathways for the uptake of electrons because the very negative reduction potentials prevented us evaluating medium effects (e.g. a change of supporting electrolyte from Et_4NClO_4 to $LiClO_4$) which would be indicative of an electron transfer carried by the liganc

Hoping to get additional information we prepared some rhodium complexes with substituents in the benzene ring (see Table 1). The reduction potentials are related to the Hammett substituent constants, the most negative σ-values being associated with the most negative half-wave potentials. In line with previous interpretations of the mechanism of the electrolytic reduction of carbon—halogen bond [6], this last result indicates that the carbon of the metal—carbon bond is becoming negative as the system moves to the transition state of the potential-determining step. This does not provide support for any particular mechanism, and further investigations are needed.

Experimental

Chemicals and reagents

The d^8 organometallic rhodium and iridium complexes $M(R)(CO)(PPh_3)_2$ (R = alkyl, aryl) were prepared by electrochemical reduction of the parent d^6 dihalogeno derivatives $M(R)X_2(CO)(PPh_3)_2$ or via oxidative addition of the appropriate organic halide on the d^{10} anionic complex $[M(CO)(PPh_3)_3]^-$ [8].

The acetonitrile, benzene, tetraethylammonium perchlorate and triphenylphosphine were treated as previously described [3].

Apparatus and procedure

The apparatus and the techniques involved in the use of the polarographic apparatus and the controlled-potential coulometry have also been described previously [7]. Owing to the poor solubility of the complexes in acetonitrile, all measurements were carried out in acetonitrile/benzene (75—25 V/V) with 0.1 *M* TEAP as supporting electrolyte.

Infrared spectra were recorded in acetonitrile/chloroform (75—25 V/V) solution on a Perkin—Elmer Model 457 grating spectrometer. All the experiments were carried out at 25.0 ± 0.1°C, under argon.

References

1 G. Schiavon, S. Zecchin, G. Pilloni and M. Martelli, J. Inorg. Nucl. Chem., in press.
2 G. Costa, Fifth Int. Conf. on Organometallic Chemistry, Moscow, August 1971, p. 335 and references therein.
3 G. Pilloni, S. Valcher and M. Martelli, J. Electroanal. Chem., 40 (1972) 63.
4 J. Chatt, B.L. Shaw, J. Chem. Soc., (1960) 1718. J. Chatt, B.L. Shaw ibid. (1959) 705.
5 M. Martelli, G. Zotti and G. Pilloni, J. Electroanal. Chem., 63 (1975) 421.
6 J.W. Sease, F.G. Burton and S.L. Nickol, J. Amer. Chem. Soc., 90 (1968) 2595.
7 M. Martelli, G. Schiavon, S. Zecchin and G. Pilloni, Inorg. Chim. Acta, 15 (1975) 217.
8 S. Zecchin, G. Schiavon, G. Pilloni and M. Martelli, J. Organometal. Chem., 110 (1976) C45.