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ELECTROCHEMICAL INVESTIGATION OF COORDINATION COMPOUNDS

I. THE OXIDATION—REDUCTION MECHANISM OF Co^I, Rh^I AND Ir^I SYSTEMS CONTAINING TRIVALENT PHOSPHORUS AND CARBONYL LIGANDS

D. de MONTAUZON and R. POILBLANC

Groupe d'étude et d'application des complexes métalliques, Laboratoire de Chimie de Coordination du C.N.R.S., 205 route de Narbonne, 31030 Toulouse Cédex (France)

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Summary

The polarographic reduction of complexes in the +I state, obtained by the reactions of phosphorus ligands with $[Co(CO)_4]_2$, $[RhCl(CO)_2]_2$ and $[Ir(CO)_3Cl]_n$, has been studied. The reduction has been shown to proceed in a two-electron step leading to anionic complexes in the —I state, which react with the starting materials to form zero-valent complexes. For the complexes $MX(CO)L_2$ (M = Rh, Ir) the $E_{1/2}$ values are more negative when the basicity of the ligand L and the electronegativity of X increase.

Introduction

Organometallic electrochemistry is keeping pace with the rapid developments in organic electrochemistry. Although this is only at the beginning of its development, there have already been an abundance of polarographic studies. Previous electrochemical reductions [1-6] (or oxidations) on organometallic complexes have shown that the electrochemical method affords, in many cases, the most suitable conditions for obtaining unusual oxidation states, and allows a more detailed study of the oxidation—reduction mechanism to be made. Electrochemical techniques have also been used in organometallic syntheses [6,9-11] for the clarification of structural questions about π-ligand metal complexes [12] and in kinetic studies [13].

In this paper special attention is given to the oxidation—reduction mechanism of complexes in the +I state derived from cobalt, rhodium and iridium carbonyls by substitution of CO groups with trivalent phosphorus ligands (phosphines or phosphites) [14].

Experimental

Solvent

Because of its resistance to reduction, tetrahydrofuran was chosen. Several methods have been suggested for preparing pure, anhydrous tetrahydrofuran (THF) for electrochemical purposes [15]. The transfer of the solvent into the cell, the use of an imperfectly anhydrous supporting electrolyte, and in general any contact with the atmosphere and the surroundings can raise the water content of solutions to a level considerably higher than the maximum acceptable. We have developed a purification procedure which gives a product of good purity starting from THF Prolabo (Technical grade) [14]. The solvent was successively percolated through a column containing activated alumina, stored 24 h over a molecular sieve (4 A), purified by refluxing over $LiAlH_4$ and distilled under a nitrogen atmosphere. The vessel containing the THF was then attached to a vacuum line, the THF degassed and its vapour transferred into a second solvent vessel which contained Na/K alloy (1/1 by weight). The solvent was then vapour-transferred into the elements constituting the electrochemical cell (vide infra).

Supporting electrolyte

Table 1 shows cathodic and anodic useable potential ranges under our experimental conditions. Lithium salts may be used as supporting electrolytes for reductions unless mercury electrodes are used (amalgam formation). Te-

TABLE 1

CATHODIC AND ANODIC USEABLE RANGES OF POTENTIALS OF ELECTROLYTES (CONCENTRATION 10^{-1} *M*) IN THF[a] (V vs. $Ag/AgClO_4$ 10^{-1} *M*) (measured for a limiting current: $i = 5$ μA)

Electrolyte	Cathode	Cathodic range and reduced species	Anodic range and oxidized species
$LiClO_4$	Hg	−2.60 $Li^+ + e \rightarrow Li(Hg)$	+0.10 $Hg\downarrow - 2e \rightarrow Hg^{2+}$
	Pt(or Au)	−3.60 $Li^+ + e \rightarrow Li$	+1.50 oxidation of THF
$NaB(C_6H_5)_4$	Hg	−2.60 $Na^+ + e \rightarrow Na(Hg)$	+0.20 $Hg\downarrow - 2e \rightarrow Hg^{2+}$
	Pt(or Au)	−3.60 $Na^+ + e \rightarrow Na$	+1.50 oxidation of THF
NMe_4Cl	Hg	−4.00 reduction of the cation or of THF	+0.10 $2Hg\downarrow + 2Cl^- - 2e \rightarrow Hg_2Cl_2\downarrow$
	Pt(or Au)	−4.00 reduction of the cation or of THF	+0.10 $2Cl^- - 2e \rightarrow Cl_2$
NBu_4ClO_4	Hg	−4.00 reduction of the cation or of THF.	+0.10 $Hg\downarrow - 2e \rightarrow Hg^{2+}$
	Pt(or Au)	−4.00 reduction of the cation or of THF	+1.50 oxidation of THF

[a] Water content not higher than 10^{-3} *M*.

traalkyl and especially tetrabutylammonium salts are more suitable for oxidations.

With regard to the potential range tetrabutylammonium perchlorate (TBAP) was used. It was prepared from the metathetical reaction between perchloric acid and tetrabutylammonium hydroxide (Fluka, 40% in water) in water, from which it precipitates. The perchlorate salt was washed with water, recrystallized twice from THF and dried in vacuo for 24 h at 70°C.

The water content of the solution TBAP—THF so obtained, checked by coulometric titration [16], was always less than 10^{-3} *M*.

Electrochemical cell

Polarographic and controlled potential electrolysis experiments were made in a cell adapted from Anderson's proposed model [17]. This cell was attached to a vacuum line; it was simple to use when once assembled. With the slight modifications introduced, coulometry and polarography may be carried out simultaneously without changing the auxiliary and dropping mercury electrodes.

Polarographic measurements were conducted using a dropping mercury electrode ($m^{2/3}t^{1/6}$ = 1.80 at 0 V) as cathode, a Pt wire as anode, and Ag/Ag^{I} ($AgClO_4$ 10^{-3} *M*, NBu_4ClO_4 10^{-1} *M*) as reference electrode. Unless otherwise stated all solutions for electrochemical studies were 10^{-3} *M*.

At low temperatures, the electrolysis was carried out with a Tacussel cell equipped with five glass joints; this cell was thermostatted by means of an external cryostat. In these conditions the area of the mercury pool electrode was about 10 cm^2 and a solution volume of 50 ml was employed.

Apparatus

A Soléa—Tacussel PRT 20-2X potentiostat (scan speed 333 mV/min), a Soléa—Tacussel S60 AS-R millivoltmeter and a Soléa—Tacussel MAR milliamperemeter coupled with a Servogor RE 511 recorder were used to obtain polarograms.

Controlled potential electrolysis was carried out using a Soléa—Tacussel ASA 10-100 potentiostat.

Infrared spectra were recorded on a Perkin—Elmer model 225 instrument using hexadecane solutions and NMR spectra were recorded on a Varian A60 instrument. Elemental analysis (C, H, Cl, I, P) was performed at the CNRS microanalysis laboratory.

Chemicals

The complexes $Co(CO)_2(PMe_3)_3^+BPh_4^-$ [18], $MX(CO)L_2$ [19] (M = Rh, Ir; X = Cl, Br, I; L = PR_3) were synthesized and purified according to methods already described.

Results and discussion

Oxidation—reduction mechanism of the complex $Co(CO)_2(PMe_3)_3^+BPh_4^-$

At 25°C the electrochemical reduction at the dropping mercury electrode

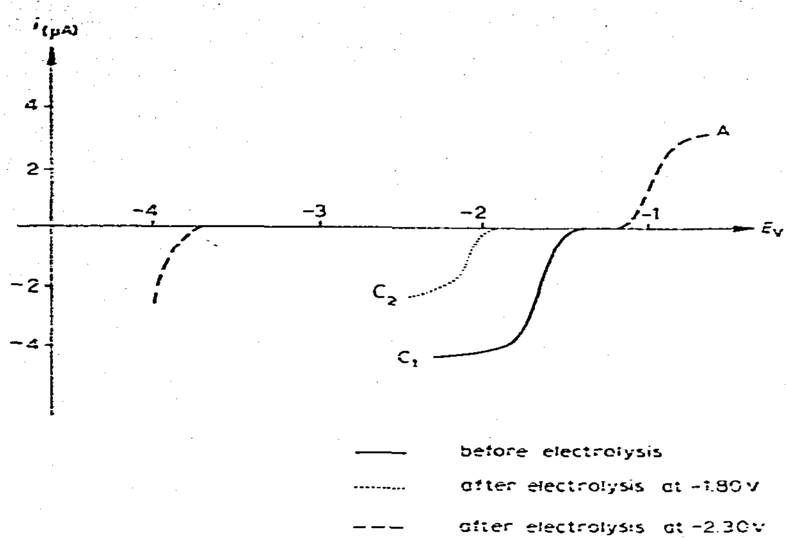

Fig. 1. Polarograms of 10^{-3} *M* $Co(CO)_2(PMe_3)_3^+ BPh_4^-$ in THF solutions (10^{-1} *M* Bu_4NClO_4; 10^{-1} *M* $AgClO_4/Ag$).

(DME) of $Co(CO)_2(PMe_3)_3^+BPh_4^-$ (10^{-3} *M*) in THF containing TBAP (10^{-1} *M*) occurs in a two-electron step (Fig. 1, wave C_1) with $E_{1/2} = -1.68$ V. The limiting current is consistent with a two-electron reduction (as ascertained by controlled-potential electrolysis), and the wave height varies as the square root of the head of the DME, indicating a diffusion-controlled process. The theoretical equation of the curve $\log i/i_d - i = f(E)$, for reversible systems, is not verified.

Exhaustive controlled-potential electrolysis carried out at —1.8 V leads to the formation of a wave C_2 at more negative potential ($E_{1/2} = -2.10$ V), the height at the end of the electrolysis being half that of the wave of the initial complex. The initially yellow solution became red and from it a crystalline dark red solid was isolated with pentane. This compound was identified as $[Co(CO)_2(PMe_3)_2]_2$ by means of its infrared and NMR spectrum, and elemental analysis, identical with those of an authentic sample prepared by Pegot's method [20] [ν(CO) 1939 m, 1919 s, 1739 m, 1719 s cm^{-1} in hexadecane solution; δ —1.00 ppm, *J*(P—H) 6.8 Hz in C_6H_6, TMS used as internal standard. (Found: C, 36.25; H, 6.80; P, 22.65. $C_8H_{18}O_2CoP_2$ calcd.: C, 36.09; H, 6.77; P, 23.31%.)

It may be noticed that this new complex $[Co(CO)_2(PMe_3)_2]_2$, characterized by the wave C_2 (the reduction of which corresponds to a process involving two electrons, but for two cobalt atoms), is not a mercury derivative (for example $Hg[Co(CO)_2(PMe_3)_2]_2$ [21]). Consequently it appears there is no reaction between the Hg pool cathode and the complex during electrolysis.

Nevertheless, if exhaustive controlled-potential electrolysis was carried out at more negative potential ($E = -2.3$ V, for example) or at low temperatures (—20°C) at any voltage on the wave C_1, wave C_2 does not appear, and a new unstable complex can be obtained, which has not been isolated or characterized. At the end of the electrolysis only an anodic wave A_1 ($E_{1/2} = -1.00$ V) remains, which corresponds to a process involving a number of electrons intermediate between one and two.

A controlled-potential electrolysis at —0.80 V requires a number of electrons intermediate between one and two, leading to a mixture of $Co(CO)_2(PMe_3)_3^+$ and $Co_2(CO)_4(PMe_3)_4$.

The above observations agree with the results previously reported by Valcher et al. [5] in an electrochemical study on $RhCl(CO)(PPh_3)_2$. From these results one can propose the following scheme as the oxidation—reduction mechanism of $Co(CO)_2(PMe_3)_3BPh_4$:

$$Co(CO)_2(PMe_3)_3^+BPh_4^- + 2e \xrightarrow[\text{slow}]{\text{wave } C_1} Co(CO)_2(PMe_3)_2^- + PMe_3 + BPh_4^- \quad (1)$$

At 25°C this reduction is followed by a chemical reaction with the starting material:

$$Co(CO)_2(PMe_3)_2^- + Co(CO)_2(PMe_3)_3^+BPh_4^- \rightarrow Co_2(CO)_4(PMe_3)_4 + PMe_3 + BPh_4^- \quad (2)$$

At —20°C the speed of reaction 2 is certainly so much reduced that reaction 1 only was observed.

The reduction of the dinuclear complex proceeds according to eqn. 3, wave C_2:

$$[Co(CO)_2(PMe_3)_2]_2 + 2e \xrightarrow{\text{wave } C_2} 2\ Co(CO)_2(PMe_3)_2^- \quad (3)$$

The wave A_1 can be explained by eqns. 4-6 in which both two-electron (4 + 5) and one electron (4 + 6) oxidations are operating:

$$Co(CO)_2(PMe_3)_2^- - 2e \xrightarrow{(4)} Co(CO)_2(PMe_3)_2^+$$

$$Co(CO)_2(PMe_3)_2^+ \xrightarrow[(5)]{+BPh_4^- + PMe_3} Co(CO)_2(PMe_3)_3BPh_4$$

$$Co(CO)_2(PMe_3)_2^+ \xrightarrow[+Co(CO)_2(PMe_3)_2^-]{(6)} [Co(CO)_2(PMe_3)_2]_2$$

Oxidation—reduction mechanism of the complex $MX(CO)L_2$

(a) Rhodium(I) complexes with different ligands L. Olson and Keim [6] have already studied the electrochemical reduction of $RhClL_3$ (L = PPh_3, $PMePh_2$), without establishing mechanistic details. Pilloni and Valcher [5] have investigated the electrochemical behaviour of *trans*-chlorocarbonylbis-(triphenylphosphine)rhodium and have proposed a reduction—oxidation mechanism accounting for the chemical and electrochemical results; the electrolysis was realized in an acetonitrile—toluene solution containing excess of ligand L.

In our present study, rhodium(I) complexes, with different ligands L (Table 2) and without ligands, were studied in THF—TBAP solutions. Under these conditions the polarograms obtained for the $RhCl(CO)L_2$ derivatives (10^{-3} *M*) showed a well-developed polarographic wave (C_1), identical to that previously observed for the Co^I complex, characterized by $E_{1/2}$ (see Table 2) and for which the limiting current is consistent with a two-electron reduction.

From the mechanism proposed by Pilloni and Valcher [5] (in toluene—acetonitrile solvent containing excess of L), and to account for the reduction of $RhCl(CO)L_2$ complexes in the absence of L, the following scheme can be proposed:

TABLE 2

ELECTROCHEMICAL AND INFRARED CHARACTERISTICS OF $RhCl(CO)L_2$ COMPLEXES (10^{-1} *M* Bu_4NClO_4, 10^{-1} *M* $AgClO_4/Ag$)

Compounds	$-E_{1/2}$ (V)	CO^a (cm^{-1})
$RhCl(CO)(PPh_3)_2$	2.43	1966
$RhCl(CO)[P(N(Me)_2)_3]_2$	2.70	1963
$RhCl(CO)(PMe_2Ph)_2$	2.83	1965
$RhCl(CO)(PMe_3)_2$	3.02	1962
$RhCl(CO)(PEt_3)_2$	3.00	1956

[a] In hexadecane solution.

$$RhCl(CO)L_2 + 2e \xrightarrow{\text{wave } C_1} Rh\,\square\,(CO)L_2^- + Cl^- \quad (7)$$

where □ depicts the existence of a lacuna, which suggests for the model with 16 electrons the ability to pick up a fourth ligand. With a donor solvent S (such as THF) this lacuna would be occupied by a solvent molecule; with an excess of ligand L in THF—TBAP solution the reduced species $Rh(CO)L_3^-$ can be obtained. At room temperature this electrochemical reduction is followed by a chemical reaction with the starting material:

$$Rh(S)(CO)L_2^- + RhCl(CO)L_2 \xrightarrow{+S} [Rh(S)(CO)L_2]_2 + Cl^- \quad (8)$$

This hypothesis was confirmed by exhaustive controlled-potential electrolysis on $RhCl(CO)(PMe_2Ph)_2$ at —3.00 V: $[Rh(S)(CO)(PMe_2Ph)_2]_2$ can be obtained. This compound was identified by means of its infrared spectrum (1965 and 1720 cm^{-1} in hexadecane solution), in agreement with those previously observed by Wilkinson [22] on $[Rh(S)(CO)(PPh_3)_2]_2$. Finally, in the presence of an excess of PMe_2Ph only the infrared frequency of the bridged carbonyl, characteristic of $[Rh(CO)(PMe_2Ph)_3]_2$ (1710 cm^{-1}) was seen.

The reduction of the dinuclear complex proceeds according to eqn. 9 (wave C_2, analogous to that of Co^I complex):

$$[Rh(S)(CO)L_2]_2 + 2e \rightarrow 2\,Rh(S)(CO)L_2^- \quad (9)$$

This reduction product has not been isolated nor characterized. But, by analogy with the Co^I system already described, and the similar compounds reported by Valcher, its formulation as $Rh(S)(CO)L_2^-$ can be inferred. In these conditions, the anodic wave A_1, obtained after controlled-potential electrolysis on the dinuclear complex, which corresponds to a process involving a number of electrons intermediate between one and two, agrees with the scheme:

$$Rh(S)(CO)L_2^- - 2e \rightarrow Rh(S)(CO)L_2^+$$

$$Rh(S)(CO)L_2^+ \xrightarrow[(10)]{+Cl^-,\,-S} RhCl(CO)L_2$$

$$Rh(S)(CO)L_2^+ \xrightarrow[+Rh(S)(CO)L_2^-]{(11)} [Rh(S)(CO)L_2]_2$$

By reference to the cases in which reduction of $RhCl(CO)(PPh_3)_2$ [5] or $Rh(DPE)_2Cl$ [23] gives respectively $[Rh(CO)L_3]_2$ or $Rh(DPE)_2H$, our present study leads to a third possibility.

TABLE 3

ELECTROCHEMICAL AND INFRARED CHARACTERISTICS OF $IrX(CO)(PPh_3)_2$ COMPLEXES (10^{-1} *M* Bu_4NClO_4, 10^{-1} *M* $AgClO_4/Ag$)

Compounds	$-E_{1/2}$ (V)	CO^a (cm^{-1})
$IrCl(CO)(PPh_3)_2$	2.60	1950
$IrBr(CO)(PPh_3)_2$	2.55	1955
$IrI(CO)(PPh_3)_2$	2.47	1975

^{a} In hexadecane solutions.

It is surprising to note that the $E_{1/2}$ values can be correlated with the basicity of the ligand L (Table 2). It is well known in organometallic carbonyl chemistry that the CO stretching frequency gives a measure of the force constant of the CO group bonded to the metal atom. It was observed that in general increasing basicity of the ligand L decreases the CO stretching frequency. The results summarized in Table 2 suggest that the electrode process can be regarded as a tool to investigate electron transfer in any organometallic carbonyl compound together with the shift of the CO stretching frequency. Further investigations are in progress in this field.

(b) Iridium(I) complexes. The same pattern as above can be observed for the iridium(I) analogues $IrX(CO)L_2$. The oxidation—reduction mechanism was studied with various halogens (X) as ligand (see Table 3).

It can first be noted that the reduction takes place at a more negative potential than for the rhodium analogue. This result can easily be explained in terms of "metal basicity" [24]. As the CO stretching frequency increases when the electron density on the central metal atom decreases from Ir^I to Rh^I, it is suggested that the $E_{1/2}$ value is more negative when the basicity of this atom increases.

Furthermore, although the variation of the $E_{1/2}$ values from Cl to I in $IrX(CO)(PPh_3)_2$ compounds is very small, its decrease reflects the increase in the infrared frequency.

In conclusion, the present study has shown that the polarographic reduction of rhodium and iridium d^8 complexes $RhCl(CO)L_2$ and $IrX(CO)L_2$ (L = PR_3; X = Cl, Br, I) proceeds in a two-electron step leading to the final d^{10} anionic species with no intermediate stable state. It is known that chemical reduction of the isoelectronic cobalt(I) complex with 1,2-diphenylphosphinoethane (DPE) as bidentate ligand gives the d^9 complex $Co(DPE)_2$ [25]. In the opposite, the isoelectronic cobalt(I) d^8 complex $Co(CO)_2(PMe_3)_2BPh_4$ which is electrochemically reduced into the d^{10} anionic species.

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