Journal of Organometallic Chemistry, 246 (1983) 61–71
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ELECTROCHEMISTRY OF COORDINATION COMPOUNDS

XX *. ELECTROGENERATED $Rh(CO)(PPh_3)_3$ AND $Ir(CO)(PPh_3)_3$

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(Received October 13th, 1982)

Summary

The redox behaviour of the d^8 complexes $[M(CO)(PPh_3)_3]^+$ (M = Rh, Ir) was studied on platinum electrode in 1,2-dimethoxyethane by cyclic voltammetry, differential pulse voltammetry, and potentiostatic coulometry. The complexes show two reversible one-electron reductions consistent with the formation of the rare zerovalent $M(CO)(PPh_3)_3$ and the anionic $[M(CO)(PPh_3)_3]^-$ derivatives, respectively. The reduced species were characterized by ESR and IR spectroscopy. A significant feature is that the one-electron reduced intermediates, in spite of their radical nature, react very easily with molecules capable of reacting as proton rather than H-atom sources to give the hydride species $HM(CO)(PPh_3)_3$. A tentative interpretation of this behaviour is suggested.

Introduction

Previous electrochemical studies on d^8 square-planar complexes of rhodium and iridium containing phosphorus ligands [1–7] showed that they commonly undergo a single two-electron reduction process. Even the one-electron reductions claimed by some authors to occur with $RhClL_3$ (L = PPh_3 or $PMePh_2$) [8] and $[M(DPE)_2]^+$ (M = Rh, Ir; DPE = $Ph_2PCH_2CH_2PPh_2$) [9,10] were shown to involve, respectively a primary two-electron transfer process [1] and an uncomplicated two-electron reversible reduction [2,11]. Two one-electron reductions were observed only in complexes containing highly delocalizing π-aromatic systems such as *N*-heterocyclic ligands [12]. Thus the production of monomeric d^9 species of rhodium and iridium with phosphorus ligands, which would be of much interest particularly in the field of homogeneous catalysis [13], appeared to be a fascinating but thus far unrealized objective.

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* For part XIX see ref. 34.

This paper deals with the production of the title compounds by electrochemical reduction of $[Rh(CO)(PPh_3)_3]^+$ and $[Ir(CO)(PPh_3)_3]^+$ in 1,2-dimethoxyethane. In view of the unusual nature of the reduced species, an electrochemical investigation of the d^8 precursors in acetonitrile, comparable to the earlier studies, was also made. The $[M(CO)(PPh_3)_3]^+$ system was principally chosen, to permit comparison with the $[M(DPE)_2]^+$ system, which exhibits a higher degree of structural constraint due to the chelating phosphines.

Results and discussion

1,2-Dimethoxyethane as solvent

Since several stable derivatives of $[M(CO)(PPh_3)_3]^+$ in which one phosphine is replaced by a coordinating solvent molecule are known [14,15], the complexes were investigated first in a poorly coordinating solvent such as 1,2-dimethoxyethane (DME). UV-VIS spectrophotometric measurements showed that in this medium the rhodium complex is so little dissociated that millimolar concentrations of free

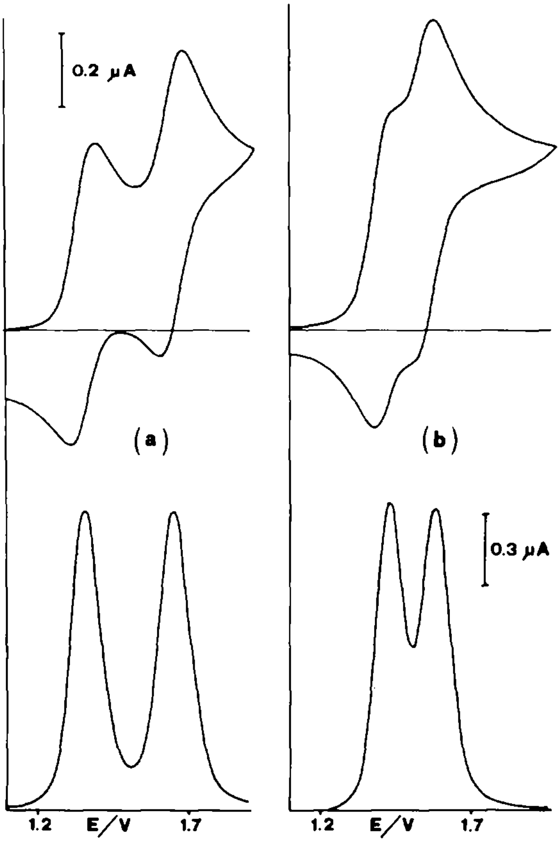

Fig. 1. Cyclic (upper) and differential pulse (lower) voltammograms for $[Rh(CO)(PPh_3)_3]^+$ (a) and $[Ir(CO)(PPh_3)_3]^+$ (b) $1.0 \times 10^{-3} M$ in DME 0.2 *M* TBAP at 25°C (Pt microelectrode; Ag/0.1 *M* $AgClO_4$ in CH_3CN as ref. electrode). Cyclic: scan rate 50 mV/s; Differential pulse: scan rate 2mV/s, pulse amplitude 10 mV, pulse frequency 13 Hz.

TABLE 1

CYCLIC AND DIFFERENTIAL PULSE VOLTAMMETRIC DATA FOR THE TWO-STEP REDUCTION OF $[M(CO)(PPh_3)_3]^+$ (M = Rh, Ir) IN DME 0.2 *M* TBAP AT 25°C (Pt microelectrode, Ag/0.1 *M* $AgClO_4$ in CH_3CN as reference electrode)

M	$E_{1/2}(I)$ (V)	$E_{1/2}(II)$ (V)	$1/2\{E_{1/2}(I)+E_{1/2}(II)\}$ (V)	$\Delta E_p(I)$ (mv)	$\Delta E_p(II)$ (mV)	$W_{1/2}(I)$ [a] (mV)	$W_{1/2}(II)$ [a] (mV)
Rh	−1.31	−1.56	−1.43	65	65	95	95
Ir	−1.36 [b]	−1.48 [b]	−1.42	–	–	100	100

[a] Peak half-width in differential pulse polarography. [b] Data from differential pulse voltammetry alone, owing to the reduced potential separation.

phosphine are more than enough to quench the process. The iridium compound is undissociated.

The voltammetric profile of $[M(CO)(PPh_3)_3]^+$ at 25°C consists of two one-electron diffusion controlled steps. The uncomplicated reversibility of the process is indicated by cyclic voltammetric and differential pulse voltammetric data (Fig. 1 and Table 1). Added triphenylphosphine does not influence the voltammetric parameters. In spite of the similar voltammetric behaviour, rhodium and iridium give different results in preparative electrolyses. In exhaustive electrolysis of $[Rh(CO)(PPh_3)_3]^+$ both in the absence and in the presence of PPh_3, at a potential corresponding to the mean of the two subsequent half-wave potentials, a dark brown colour develops immediately and one electron/mol is consumed. Afterwards the solution turns bright red with a conversion time, which was found to increase as the concentration of the phosphine was increased up to several hours. Apart from a one-electron shift of the current response, the voltammetric profile of the brown, highly air-sensitive catholyte corresponds to that of the unreduced solution, suggesting that the reduced species is $Rh(CO)(PPh_3)_3$. This formulation is supported by the following spectral data: (i) the ESR spectrum gives a strong signal centered at $g = 2.07$ with a poorly resolved hyperfine structure, probably due to the interaction of the unpaired electron with the phosphorus atoms and the nucleus (Fig. 2) *; (ii) a broad band is present in the NIR spectrum at 10100 cm^{-1} ($\varepsilon \simeq 130\ M^{-1}\ cm^{-1}$), which is a rather common feature of d^9 species in distorted tetrahedral geometry [16]; (iii) the IR spectrum shows a strong ν(CO) band at 1895 cm^{-1}, shifted by about 100 cm^{-1} towards lower frequencies relative to the d^8 precursor, as expected for a simple one-electron process [17].

The bright-red solution originating from the spontaneous decay of $Rh(CO)(PPh_3)_3$ shows a ν(CO) band in the IR spectrum at 1740 cm^{-1} with a shoulder at 1775 cm^{-1}, indicative of bridging carbonyl groups. The product was unambiguously identified as $[Rh(CO)(PPh_3)_2(DME)]_2$ by comparison of its infrared spectrum with that of an authentic sample [18], as well as by its reactions with H_2 and CO to yield $HRh(CO)(PPh_3)_3$ and $[Rh(CO)_2(PPh_3)_2]_2$, respectively.

To elucidate the mechanism of the dimerization reaction we measured the rate of decay of the d^9 complex both spectrophotometrically by following the disappearance of the band at 10100 cm^{-1} or that at 1895 cm^{-1}, and chronoamperometrically by

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* Unfortunately the hyperfine structure is completely lost in the isotropic solution.

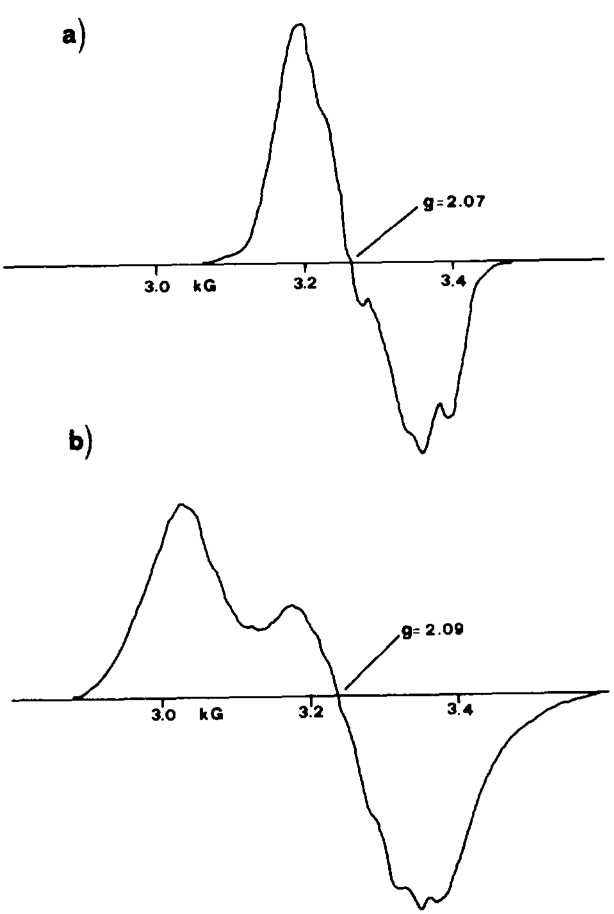

Fig. 2. ESR spectra of $Rh(CO)(PPh_3)_3$ (a) and $Ir(CO)(PPh_3)_3$ (b) in DME. Frozen samples at 100 K.

monitoring the decrease of the oxidation or reduction voltammetric waves as a function of time. In all the experiments excess triphenylphosphine (tenfold or more) was present. The results from the two techniques were in fairly good agreement. The rate was found to show a second order dependence on the complex concentration, and the observed rate constant, k_{obs}, was shown to be inversely proportional to the free ligand concentration in the range 10^{-2}–$1\ M$. A typical example is given in Table 2. The following rate law (eq. 1) thus applies:

$$-\mathrm{d}[Rh(CO)(PPh_3)_3]/\mathrm{d}t = k[Rh(CO)(PPh_3)_3]^2[PPh_3]^{-1} \qquad (1)$$

This can be accounted for in terms of the existence of a dissociative equilibrium preceding the dimer-producing rate-determining step (eq. 2, 3) with $k = 2Kk_2$ and $k_{obs} = k[PPh_3]^{-1}$.

$$Rh(CO)(PPh_3)_3 + DME \overset{K}{\rightleftarrows} Rh(CO)(PPh_3)_2(DME) + PPh_3 \qquad (2)$$

$$Rh(CO)(PPh_3)_2(DME) + Rh(CO)(PPh_3)_3 \xrightarrow{k_2} [Rh(CO)(PPh_3)_2(DME)]_2 + PPh_3 \qquad (3)$$

TABLE 2

DEPENDENCE ON TRIPHENYLPHOSPHINE CONCENTRATION OF THE RATE CONSTANT (k_{obs}) FOR THE DIMERIZATION REACTION OF $Rh(CO)(PPh_3)_3$ IN DME 0.2 *M* TBAP AT 25°C (Data from NIR measurements at λ 1000 nm in 1.0 cm cells. Total complex concentration = 5.0×10^{-3} *M*)

$[PPh_3]$ (*M*)	$k_{obs} \times 10^3$ ($M^{-1}\ s^{-1}$)	$k_{obs}[PPh_3] \times 10^4$ (s^{-1})
0.05	10.0	5.0
0.15	3.5	5.2
0.40	1.2	4.8
0.80	0.64	5.1

Furthermore equilibrium 2 must lie over to the left, as had already been indicated by the non-dependence of the half-wave potentials on the phosphine concentration (see above). It is to be noted that the proposed mechanism is in agreement with the smaller number of phosphorus ligands in the dimer. Furthermore, the observation that the rate of the dimerization is greatly enhanced when small amounts of a better coordinating solvent molecule such as acetonitrile are added, while supporting the pre-dissociative hypothesis, agrees with the well known lability of phosphine ligands in rhodium complexes.

Exhaustive electrolysis of $[Rh(CO)(PPh_3)_3]^+$ on the plateau of the second wave in the presence of excess PPh_3 to minimize the dimer formation requires two electrons/mol and leads to a stable red-orange solution with a voltammetric oxidation profile corresponding to the reduction pattern of the unreduced species. The formulation of the product as $[Rh(CO)(PPh_3)_3]^-$ is confirmed by the presence of a strong ν(CO) band at 1800 cm^{-1}, i.e. in the low-frequency region expected for anionic carbonyl species, and by the formation of $HRh(CO)(PPh_3)_3$ upon reaction with proton donors. Further support is provided by the reaction with carbon monoxide, which results in stepwise substitution of the phosphine ligands to $[Rh(CO)_2(PPh_3)_2]^-$ and $[Rh(CO)_3(PPh_3)]^-$, as inferred from a comparison of their infrared spectra (Table 3) with literature data [19].

The overall electrochemical pathway can thus be summarized as follows:

$$\begin{tikzcd}
{[Rh(CO)(PPh_3)_3]^+} \arrow[r, shift left, "e"] & Rh(CO)(PPh_3)_3 \arrow[l, shift left] \arrow[r, shift left, "e"] \arrow[d, "+DME"', "-PPh_3"] & {[Rh(CO)(PPh_3)_3]^-} \arrow[l, shift left] \\
 & \frac{1}{2}[Rh(CO)(PPh_3)_2(DME)]_2 &
\end{tikzcd} \qquad (4)$$

Exhaustive reduction of $[Ir(CO)(PPh_3)_3]^+$ at a potential mid-way between the two subsequent half-wave potentials requires one electron/mol. During the electrolysis a brown colour develops as in the case of rhodium, but finally a yellow solution is formed which contains the metal as $Ir(OH)(CO)(PPh_3)_2$ [20] and $HIr(CO)(PPh_3)_3$ [21] in 1/1 ratio, as evidenced by voltammetric measurements [7,22] and infrared spectra. When water is deliberately added, the same final products are obtained without even the appearance of the brown colour, suggesting the fast occurrence of the overall reaction of the one-electron reduction species with water *:

$$2Ir(CO)(PPh_3)_3 + H_2O \rightarrow Ir(OH)(CO)(PPh_3)_2 + HIr(CO)(PPh_3)_3 + PPh_3 \qquad (5)$$

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* The rhodium analogue reacts similarly, but at a much slower rate.

TABLE 3

SPECTRAL PROPERTIES OF $M(CO)(PPh_3)_3$ AND $[M(CO)_n(PPh_3)_{4-n}]^-$ ($M = Rh, Ir$; $n = 1,2,3$) IN DME 0.2 *M* TBAP

Complex	IR ν(CO)(cm^{-1})	NIR λ_{max}(nm)	ESR (g)
$Rh(CO)(PPh_3)_3$	1895	990	2.07
$[Rh(CO)(PPh_3)_3]^-$	1800		
$[Rh(CO)_2(PPh_3)_2]^-$	1855,1805		
$[Rh(CO)_3(PPh_3)]^-$	1930,1855		
$Ir(CO)(PPh_3)_3$	1886	910	2.09
$[Ir(CO)(PPh_3)_3]^-$	1775		
$[Ir(CO)_2(PPh_3)_2]^-$	1845,1795		
$[Ir(CO)_3(PPh_3)]^-$	1920,1845		

Consequently, relatively stable brown solutions of $Ir(CO)(PPh_3)_3$ could be obtained only when moisture was carefully avoided, even though the species is so reactive that it could not be preserved for more than a few hours. Only under these conditions the reduction of $[Ir(CO)(PPh_3)_3]^+$ at potentials on the plateau of the second reduction wave requires two electrons/mol and produces the orange anionic species $[Ir(CO)(PPh_3)_3]^-$. The identity of this anion is confirmed by the reaction with proton donors to give the hydride $HIr(CO)(PPh_3)_3$, and that with carbon monoxide to give $[Ir(CO)_2(PPh_3)_2]^-$ and $[Ir(CO)_3(PPh_3)]^-$ [19]. These reactions are much easier than in the case of rhodium, in keeping with the well known higher metal basicity of iridium. Thus the electrochemical pathway for iridium is simply:

$$[Ir(CO)(PPh_3)_3]^+ \overset{e}{\rightleftarrows} Ir(CO)(PPh_3)_3 \overset{e}{\rightleftarrows} [Ir(CO)(PPh_3)_3]^- \qquad (6)$$

As is apparent from Table 3, the spectral properties of the neutral and anionic iridium species are similar to those of the corresponding rhodium counterparts. The different shape of the ESR spectrum of iridium (Fig. 2), which is consistent with the expected axially symmetrical (C_{3v}) distribution of the ligands, must be attributed to a greater separation between the $g_{\parallel}$ and $g_{\perp}$ values.

It is to be noted that $Ir(CO)(PPh_3)_3$, in contrast to its rhodium analogue, shows no tendency towards dimerization, which is not unexpected in view of the well known higher stability of iridium complexes towards dissociation of phosphine ligands.

The unforeseen production of the relatively stable $M(CO)(PPh_3)_3$ species, a rare example of monomeric d^9 complexes of rhodium and iridium [12], prompted us to study their reactivity towards molecules of catalytic importance such as CO, H_2 and NO. Also, the unusually easy occurrence of the reaction of $M(CO)(PPh_3)_3$ with water (eq.5) called for a deeper investigation. The results are described below.

Reactions of $M(CO)(PPh_3)_3$ with NO, H_2 and CO

The d^9 species react immediately with one equivalent of nitric oxide to give $M(CO)(NO)(PPh_3)_2$, as inferred from a comparison of infrared solution spectra (ν(NO) 1665 (Rh) and 1650 (Ir) cm^{-1}; ν(CO) = 1960 (Rh) and 1940 (Ir) cm^{-1}) with literature data [23,24]. Dihydrogen reacts in a few minutes with $M(CO)(PPh_3)_3$ to give $HM(CO)(PPh_3)_3$. In the absence of free phosphine, the iridium complex also gives a considerable amount of $H_3Ir(CO)(PPh_3)_2$ [25]. The reaction with excess carbon monoxide produces $[Rh(CO)_2(PPh_3)_2]_2$ [18] and $[Ir(CO)_3(PPh_3)]_2$ [21] in a short time.

Reactivity of $M(CO)(PPh_3)_3$ towards water

Since water commonly acts as a proton rather than a H atom source [26], reaction 5 must be of the acid–base type and, thus proceed by the following sequence:

$$M(CO)(PPh_3)_3 + H_2O \rightleftarrows [HM(CO)(PPh_3)_3]^+ + OH^- \quad (7)$$

$$[HM(CO)(PPh_3)_3]^+ + M(CO)(PPh_3)_3 \rightarrow HM(CO)(PPh_3)_3 + [M(CO)(PPh_3)_3]^+ \quad (8)$$

$$[M(CO)(PPh_3)_3]^+ + OH^- \rightarrow M(OH)(CO)(PPh_3)_2 + PPh_3 \quad (9)$$

In fact the redox reaction 8 must proceed readily since the hydrido cation, $[HM(CO)(PPh_3)_3]^+$, is reversibly reduced at a potential far more anodic [22] than the oxidation potential of $M(CO)(PPh_3)_3$. Reaction 9 does, indeed, occur readily and irreversibly [20]. The proposed acid–base mechanism is also supported by the reaction of $M(CO)(PPh_3)_3$ with more acidic molecules such as thiophenol and triphenylphosphonium perchlorate. The reactions with the stoichiometrical amount of acid proceed instantaneously as follows:

$$2M(CO)(PPh_3)_3 + PhSH \rightarrow HM(CO)(PPh_3)_3 + M(SPh)(CO)(PPh_3)_2 + PPh_3 \quad (10)$$

$$2M(CO)(PPh_3)_3 + [HPPh_3]^+ \rightarrow HM(CO)(PPh_3)_3 + [M(CO)(PPh_3)_3]^+ + PPh_3 \quad (11)$$

In this context it is of interest to consider the reaction we observed with $Ir(CO)(PPh_3)_3$ in an attempt to promote dimer formation by CH_3CN, as observed for $Rh(CO)(PPh_3)_3$ (see above). Instead, acetonitrile quickly produces $HIr(CO)(PPh_3)_3$ and $Ir(CH_2CN)(CO)(PPh_3)_2$ [27] in equimolar amounts according to reaction 12. In spite of the radical nature of $Ir(CO)(PPh_3)_3$, hydride formation,

$$2Ir(CO)(PPh_3)_3 + CH_3CN \rightarrow$$
$$HIr(CO)(PPh_3)_3 + PPh_3 + Ir(CH_2CN)(CO)(PPh_3)_2 \quad (12)$$

claimed by some authors [9,10] to occur via H-atom abstraction from acetonitrile by the proposed $M(DPE)_2$ species, may again be reasonably accomodated on the acid–base reasoning, particularly when the proton donor capability of acetonitrile, well established towards highly basic anions [28,29], is taken into consideration.

TABLE 4

CYCLIC VOLTAMMETRIC DATA FOR THE TWO-ELECTRON REDUCTION OF $[M(CO)(PPh_3)_3]^+$ (M = Rh, Ir) IN CH_3CN 0.1 *M* TBAP AT 25°C

M	$[PPh_3]$ (*M*)	$E_{1/2}$(V)	ΔE_p(mV)
Rh	0.01	− 1.515	35
Rh	0.10	− 1.485	40
Ir	0.01	− 1.490	40
Ir	0.10	− 1.490	40

Acetonitrile as solvent

The reductive voltammetric profiles for $[Rh(CO)(PPh_3)_3]^+$ and $[Ir(CO)(PPh_3)_3]^+$ in acetonitrile are complex, as the waves are neither well defined nor diffusion controlled, and have limiting current values corresponding to a number of transferred electrons between one and two. In the presence of excess triphenylphosphine ($\geqslant 10^{-2}$ *M*), however, the responses, shifted anodically by about 300 mV, correspond to single two-electron diffusion controlled electron transfers. Cyclic voltammograms show the reversible character of the processes as the ratio of anodic to cathodic peak currents (i_a/i_c) is equal to unity and the peak potential separation (ΔE_p) is independent from the scan rate in the explored range (20–200 mV s^{-1}). A tenfold increase of phosphine concentration (from 10^{-2} to 10^{-1} *M*) does not influence either the $E_{1/2}$ or ΔE_p values for iridium, while shifting the $E_{1/2}$ of rhodium anodically by 30 mV and slightly increasing its ΔE_p value. Table 4 summarizes the voltammetric data.

Controlled potential electrolysis in the presence of excess PPh_3 requires two electrons/mol when performed at low temperature (−30°C) and $[M(CO)(PPh_3)_3]^-$ is produced. At room temperature and/or low current densities one electron/mol is consumed and, depending on the metal, the products are $[Rh(CO)(PPh_3)_2(CH_3CN)]_2$ or an equimolar mixture of $HIr(CO)(PPh_3)_3$ and $Ir(CH_2CN)(CO)(PPh_3)_2$. The change from two subsequent one-electron reductions to a single two-electron step in going from the ethereal to the nitrilic solvent could be ascribed to the existence in acetonitrile of coordinative equilibria involving the depolarizer. As a matter of fact, $[M(CO)(PPh_3)_3]^+$ loses one phosphorus ligand in CH_3CN to give the known $[M(CO)(PPh_3)_2(CH_3CN)]^+$ adduct [14,15] as inferred from an UV-VIS spectral comparison with authentic samples. Added triphenylphosphine does not appreciably change the spectrum of the rhodium species up to decimolar concentrations of ligand, so that the prevailing species in solution is $[Rh(CO)(PPh_3)_2(CH_3CN)]^+$. For iridium also, addition of phosphine does not regenerate the electronic spectrum of $[Ir(CO)(PPh_3)_3]^+$, but in this case the three bands of the d^8 square-planar complex, $[Ir(CO)(PPh_3)_2(CH_3CN)]^+$, [30] merge into a single absorption at λ_{max} 330 nm, suggesting the formation of the pentacoordinated adduct, $[Ir(CO)(PPh_3)_3(CH_3CN)]^+$; such five-coordination is not uncommon in iridium(I) complexes [20,31]. Spectrophotometric measurements gave an equilibrium constant value of 2.0(±0.1) $\times 10^3$ M^{-1} for reaction 13 at 25°C, so that in the explored concentration range of

$$[Ir(CO)(PPh_3)_2(CH_3CN)]^+ + PPh_3 \rightleftarrows [Ir(CO)(PPh_3)_3(CH_3CN)]^+ \qquad (13)$$

PPh_3 the predominant species in solution is $[Ir(CO)(PPh_3)_3(CH_3CN)]^+$.

Thus the electrochemical reduction processes in the presence of excess PPh_3 can be summarized as follows:

$$[Rh(CO)(PPh_3)_3]^+ + CH_3CN \rightleftarrows [Rh(CO)(PPh_3)_2(CH_3CN)]^+ + PPh_3 \qquad (14)$$

$$[Ir(CO)(PPh_3)_3]^+ + CH_3CN \rightleftarrows [Ir(CO)(PPh_3)_3(CH_3CN)]^+ \qquad (15)$$

$$[M(CO)(PPh_3)_3]^+ \overset{e}{\rightleftarrows} M(CO)(PPh_3)_3 \qquad (E_1^\circ) \qquad (16)$$

$$M(CO)(PPh_3)_3 \overset{e}{\rightleftarrows} [M(CO)(PPh_3)_3]^- \qquad (E_2^\circ) \qquad (17)$$

As two electrons are transferred under pure diffusion control and a response typical of a reversible charge transfer is observed over the whole range of sweep rates, the situation corresponds to complete mobility of the chemical equilibria 14 and 15, i.e. the chemical reactions are rapid relative to the time scale of the experiments. Under these conditions the nature of the overall response will depend on the equilibrium constant value, since the potential for the redox couple, $[M(CO)(PPh_3)_3]^+/M(CO)(PPh_3)_3$, is shifted cathodically by the reversible chemical reaction. As indicated by the observed peak potential separation, ΔE_p (see Table 4), the magnitude of the shift is such as to make the half-wave potentials of the first reduction close (within some millivolts) to that of the second [32]. Furthermore, the dependence of the voltammetric parameters on the phosphorus ligand concentration in the case of rhodium clearly results from eq.14.

Although the existence of the preceding chemical steps could not be unambiguously ascertained by means of voltammetric measurements under kinetic control (passivation phenomena, particularly easy at ligand concentrations lower than 10^{-2} *M*, were encountered) support was obtained in the ease of rhodium complexes from experiments in DME/CH_3CN mixtures under equilibrium conditions. When increasing amounts of excess acetonitrile are added to solutions of $[Rh(CO)(PPh_3)_3]^+$ in DME containing PPh_3 in at least a tenfold excess, the half-wave potential of the first reduction wave shifts becomes more negative, while all the other voltammetric parameters i.e. slopes, half-wave potential of the second wave and limiting currents, are almost unaffected. UV-VIS spectrophotometric measurements paralleling the voltammetric experiments enabled the evaluation of the equilibrium constant value for the formation of the nitrile adduct ($K_{eq} = 6.7 \pm 0.3$ at 25°C). The cathodic shift of the first wave was found to be equal to $RT\ln(1 + K^{\star}_{eq})$ where $K^{\star}_{eq} = K_{eq}[CH_3CN]/[PPh_3]$ up to a 10% molar fraction of acetonitrile.

Finally, a consequence of the preceding chemical equilibria in acetonitrile is the reduction in the stability range of the d^9 species, as revealed by their nearly identical oxidation and reduction potentials. However the coexistence of the d^9 intermediates with the d^8 and d^{10} species is still thermodynamically permitted in a percentage high enough to account for the recovery of the rhodium dimer and a mixture of the cyanomethyliridium complex and hydride in preparative electrolyses.

Conclusions

From the different voltammetric profiles of $[M(CO)(PPh_3)_3]^+$ in DME and CH_3CN one could expect the two-electron reversible reduction step of the analogous $[M(DPE)_2]^+$ cation in acetonitrile [2] to be resolved into two separate one-electron processes in DME. We have, however, not observed this to happen, nor have we noticed that ΔE_p deviates from the theoretical 30 mV value; thus it seems that these chelated complexes are not involved in equilibria with coordinating solvents and that $E^{\circ}_1 \ll E^{\circ}_2$. Obviously, geometrical requirements play a key role in determining the sequence of the redox potentials. In particular, the bidentate DPE ligand is likely to confine the change from the square-planar (d^8) to the tetrahedral (d^{10}) geometry to the second electron transfer process.

It is noteworthy that although the difference between the two subsequent half-wave potentials for rhodium is roughly twice that for iridium, their average values are almost identical (see Tables 1 and 4), reflecting once again [2,9–11] the similarity between elements of the second and third row.

Experimental

Chemicals and Reagents

The complexes $[Rh(CO)(PPh_3)_3](ClO_4)$ and $[Ir(CO)(PPh_3)_3](ClO_4)$ were prepared and purified by published procedures [14,15]. The purification of 1,2-dimethoxyethane (DME), acetonitrile and tetrabutylammonium perclorate (TBAP) has been described previously [19,33]. TBAP concentrations were 0.2 *M* in DME and 0.1 *M* in acetonitrile solutions. Reagent grade triphenylphosphine was used after crystallization from ethanol. Triphenylphosphonium perchlorate was made by treating the phosphine with an equivalent amount of concentrated perchloric acid in DME; the crystalline precipitate was filtered off and carefully dried under vacuum. All other chemicals (C. Erba and Fluka) were used as received. Argon (99.999%) rendered oxygen free by passage over reduced copper at 450°C was used.

Apparatus and procedure

The apparatus and technique employed in the voltammetric measurements have been described previously [34]. A silver/0.1 *M* silver perchlorate electrode in acetonitrile was used as the reference electrode. In the voltammetric measurements the working electrode was a planar platinum microelectrode (approx. area 0.3 mm^2); in the controlled potential electrolyses the working electrode was a platinum gauze (approx. area 100 cm^2).

Infrared (IR) spectra were recorded on a Perkin–Elmer model 682 spectrometer. Solution spectra were measured with compensation in 0.05 cm CaF_2 liquid cells. Electronic spectra were recorded on a Cary model 17D spectrometer. ESR spectra were recorded on a Brucker model ER 100D spectrometer with frozen samples (*T* 100 K).

Acknowledgement

The authors thank Mr. S. Sitran of CNR for experimental assistance.

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