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ELECTROCHEMISTRY OF COORDINATION COMPOUNDS

XV *. PARAMAGNETIC HYDRIDO COMPLEXES OF COBALT(II), RHODIUM(II) AND IRIDIUM(II)

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Summary

The electrochemical behaviour of a series of d^8-hydrido complexes of cobalt, rhodium and iridium containing phosphorus ligands has been studied. The oxidation proceeds in two one-electron steps involving a rare hydrido complex in the II state, which, in the case of rhodium and iridium, is unstable and decays through a disproportionation pathway. An oxidation—reduction mechanism accounting for the chemical and electrochemical results is proposed.

Introduction

Attention has been recently focused on the preparation of paramagnetic transition metal hydrides [1,2]. In this field electrochemical studies would provide particularly useful data. As part of our study on unusual oxidation states obtained by electrochemical methods, we previously described the first example of an unstable rhodium(II) and iridium(II) hydrido derivative [3]. These results prompted us to reexamine the anodic behaviour of a series of d^8-hydrido complexes of cobalt, rhodium and iridium and to investigate the factors which determine the relative stabilities of the oxidation products, with particular reference to the role of the ligands and of the metal.

Results and discussion

Oxidation—reduction mechanisms

$CoH(Ph_2PCH_2CH_2PPh_2)_2$. At 25°C the electrochemical oxidation at the platinum microelectrode of $CoH(DPE)_2$ (DPE = $Ph_2PCH_2CH_2PPh_2$) in acetonitrile/

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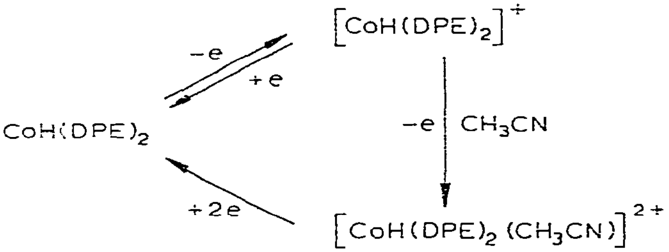
[*] For part XIV see ref. 24.

toluene (50% v/v) (owing to the poor solubility of the complex in acetonitrile) occurs in two one-electron diffusion controlled waves. The first wave ($E_{1/2} = -1.08$ V) corresponds to an uncomplicated reversible one-electron transfer, as supported by the logarithmic analysis of the wave and by the cyclic voltammetric profile, i.e. $E_p - E_{p/2} = 60$ mV, E_p being independent of the scan rate. Furthermore, a constant ratio of cathodic to anodic peak current is observed. The second wave ($E_{1/2} = 0.20$ V) is irreversible and cyclic voltammetry displays a cathodic peak at $E_p \simeq -1.1$ V (scan rate 100 mV s^{-1}) on the reverse sweep.

Exhaustive controlled potential electrolysis on the plateau of the first wave requires one equivalent of electrons per mol of complex, leading to the formation of a cathodic wave having the same $E_{1/2}$ and the same limiting current as the starting wave. The electrolysis does not influence the wave at $E_{1/2} = 0.20$ V. The orange solution turns golden-yellow. The golden-yellow solid isolated from the solution (see below) is paramagnetic, behaves as a 1/1 electrolyte and shows in the IR spectrum an hydridic band at 1885 cm^{-1} (br). Elemental analysis confirms the presence of the cation $[CoH(DPE)_2]^+$.

Controlled potential electrolysis on the plateau of the second wave, while requiring two equivalents of electrons per mol of depolarizer, produces a stable lemon-yellow solution whose voltammogram shows a single two-electron irreversible cathodic wave ($E_{1/2} = -1.02$ V). Electrochemical reduction on the plateau of this wave results in the formation of the d^8 starting compound. From the oxidized solution a bright yellow, crystalline salt, identified by elemental analysis and IR spectrum as $[CoH(DPE)_2(CH_3CN)](ClO_4)_2$, has been isolated (see below).

These results can be summarized as follows:



CoH[P(OMe)$_3$]$_4$ and CoH[P(OEt)$_3$]$_4$. At 25°C the anodic voltammetric pattern of $CoHL_4$ in acetonitrile is quite similar to that previously reported: a reversible one-electron wave ($E_{1/2} = -0.58$ V and -0.74 V for L = $P(OMe)_3$ and $P(OEt)_3$, respectively) and a further irreversible one-electron diffusion controlled wave ($E_{1/2} = 0.46$ V and 0.50 V) are displayed. Exhaustive controlled potential electrolysis on the plateau of the first wave requires one equivalent of electrons per mol of depolarizer and gives a stable green solution whose voltammogram shows a reversible cathodic wave and an irreversible anodic wave having the same $E_{1/2}$ and the same limiting currents as the starting compound. Emerald green, crystalline salts have been isolated from the solution (see below), which have magnetic moments with values corresponding to the presence of one unpaired electron. Furthermore, conductivity measurements suggest they are 1/1 electrolytes and therefore contain monomeric cations. Elemental analyses and IR spectra lead to the formulation $[CoHL_4](BPh_4)$.

If a further equivalent of electrons is passed on the plateau of the anodic wave, the green solution turns dark-yellow. The final products in 1/1 ratio are H^+ and $[CoL_4]^+$ [4] as supported by polarographic measurements. Identical final results are obtained at —35°C. At this temperature, however, the appearance during the electrolysis of a cathodic wave changing in time into those of the final products strongly suggests the formation of a fugitive cobalt(III) hydride.

$IrH(Ph_2PCH_2CH_2PPh_2)_2$. At 25°C in acetonitrile/toluene (50% v/v) the voltammogram of $IrH(DPE)_2$ shows a first anodic wave corresponding to a reversible one-electron process with $E_{1/2} = -1.03$ V. A second irreversible wave is exhibited at more positive potentials, but the height is lower than that expected for a one-electron transfer. On cooling to —35°C, two fully developed one-electron waves appear with $E_{1/2}(I) = -1.05$ V and $E_{1/2}(II) = -0.82$ V. Cyclic voltammetric tests are in line with the voltammetric ones displaying a reversible oxidation peak at $E_{pa} = -1.02$ V and $E_{pc} = -1.08$ V and a further irreversible oxidation peak which, compared with the first, increases either as the scan rate increases or the temperature decreases.

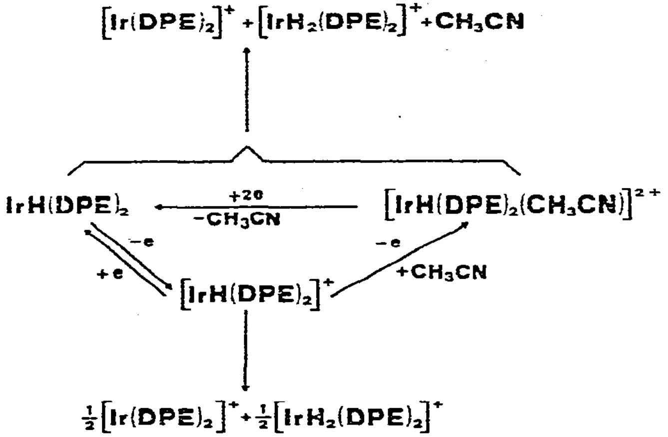
Electrolysis on the plateau of the second wave at 25°C requires one equivalent of electrons per mol of complex indicating, by analogy with the voltammetric behaviour, a fast chemical reaction between the oxidation product and the parent compound. The products in 1/1 ratio are $[Ir(DPE)_2]^+$ [5] and $[IrH_2(DPE)_2]^+$ [6] as supported by polarographic tests. At —35°C the electrolysis requires a number of electrons intermediate between one and two; at the end the polarographic pattern exhibits, in addition to those of $[Ir(DPE)_2]^+$ and $[IrH_2(DPE)_2]^+$, a new cathodic wave at $E_{1/2} = -2.08$ V.

As far as the electrolysis on the plateau of the first wave is concerned, at 25°C the final result is identical to that of the oxidation on the second wave. During the electrolysis the anodic wave is transformed into a cathanodic one, and at the same time there is a fall in the sum of the limiting currents due to the fast disappearance of the cathodic component. At —35°C the anodic wave is transformed into a cathanodic and finally into a cathodic one having the same half-wave potential and about the same limiting current as the starting wave. The electrolysis does not influence the wave at $E_{1/2} = -0.82$ V. If a further equivalent of electrons is passed on the plateau of this wave, the orange solution becomes colourless and a two-electron irreversible cathodic wave ($E_{1/2} = -2.08$ V) is generated. The diamagnetic white solid recovered from the solution (see below), behaves as a 1/2 electrolyte and its IR spectrum shows a sharp peak at 2220 cm^{-1} attributable to the stretching mode $\nu(Ir—H)$. The elemental analysis corresponds well to the formula $[IrH(DPE)_2(CH_3CN)](ClO_4)_2$. Its electrochemical reduction at —35°C requires less than two equivalents of electrons leading to a mixture of $[Ir(DPE)_2]^+$, $[IrH_2(DPE)_2]^+$ and $IrH(DPE)_2$. At 25°C the one-electron reduction products are $[Ir(DPE)_2]^+$ and $[IrH_2(DPE)_2]^+$.

Reaction Scheme 1 is proposed to account for the above observations.

$RhH(Ph_2PCH_2CH_2PPh_2)_2$. The electrochemical pattern of $RhH(DPE)_2$ in an acetonitrile/toluene mixture is virtually identical with that found in the oxidation of the related iridium complex. Voltammetric and cyclic voltammetric measurements infer that $RhH(DPE)_2$ undergoes a reversible one-electron step ($E_{1/2} = -0.94$ V) and a further irreversible, one-electron transfer ($E_{1/2} = -0.75$ V). The noteworthy differences are (a) a lower stability of the one-electron oxidation product (i_{pc}/i_{pa} increases toward unity as the scan rate increases or the tem-

SCHEME 1. Oxidation—reduction mechanism of IrH(DPE)$_2$ in 50% acetonitrile/toluene.



perature decreases) and (b) a higher rate of the chemical reaction between the two-electron oxidation product and the parent compound (the ratio of the height of the second wave to the height of the first one does not reach a value of unity even at —35°C).

Controlled potential coulometric experiments on the plateau of the second wave at both 25°C and —35°C require one equivalent of electrons per mol of complex leading to the formation of [Rh(DPE)$_2$]$^+$ [5] and H$_2$ (mass spectrum) in a 2/1 molar ratio. The electrolysis on the plateau of the first wave shows a one-electron oxidation with a pattern at —35°C similar to that observed for the iridium complex at 25°C. The final result is identical with that of the oxidation on the second wave.

These results can be accounted for by a reaction scheme similar to that for the iridium complex, the one exception being the recovery of hydrogen in accordance with the well-known lack of oxidative-addition of the H$_2$ molecule to the square-planar rhodium(I) complex [7].

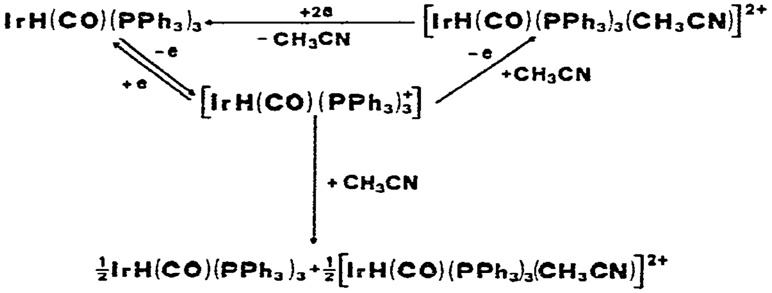
IrH(CO)(PPh$_3$)$_3$. In a previous paper [3] we mentioned the formation of the hydrido complex of iridium(II), [IrH(CO)(PPh$_3$)$_3$]$^+$, by electrochemical oxidation of IrH(CO)(PPh$_3$)$_3$. Since no mechanistic details were obtained, we have reinvestigated the electrochemical behaviour of this complex.

At 25°C in acetonitrile/toluene (50% v/v) the voltammogram of IrH(CO)-(PPh$_3$)$_3$ shows a first reversible, one-electron wave ($E_{1/2}$ = —0.30 V) and a second well-developed, irreversible, diffusion controlled, one-electron wave at more positive potentials ($E_{1/2}$ = —0.05 V). Upon addition of free PPh$_3$ the half-wave potentials, the limiting currents, and the slope of the single waves are not affected. The uncomplicated reversibility of the first process and the irreversibility of the second is confirmed by the cyclic voltammetric profile.

Electrolysis on the plateau of the second wave requires two equivalents of electrons per mol of depolarizer and affords a colourless solution whose voltammogram shows a single two-electron irreversible cathodic wave at $E_{1/2}$ = —1.08 V. The white crystalline salt isolated (see below) from the solution is diamagnetic; it dissolves easily in acetonitrile and other polar solvents in which it behaves as a 1/2 electrolyte, and has bands in the IR spectrum at 2170 (ν(Ir—H)) and 2070 cm^{-1} (ν(CO)). The formulation [IrH(CO)(PPh$_3$)$_3$(CH$_3$CN)](ClO$_4$)$_2$ has been confirmed by elemental analysis and by electrochemical reduction, which reforms IrH(CO)(PPh$_3$)$_3$.

Exhaustive controlled potential electrolysis on the plateau of the first wave, while producing a greenish colour vanishing with time, requires a number of electrons per mol of depolarizer approaching two. If only one equivalent of electrons is quickly passed the voltammogram shows an anodic wave ($E_{1/2}$ = —0.05 V) and a cathodic wave ($E_{1/2}$ = —0.30 V). The latter wave is transformed into a cathanodic and finally into an anodic one having the same $E_{1/2}$ but a limiting current half of that of the IrH(CO)(PPh$_3$)$_3$ wave, while the total anodic limiting current remains unchanged and the cathodic wave of [IrH(CO)(PPh$_3$)$_3$(CH$_3$CN)]$^{2+}$ appears. If a further equivalent of electrons is allowed to pass, the final voltammetric profile and the colour of the solution are identical with those of direct oxidation on the second wave. At —35°C the electrolysis shows a one-electron oxidation and the greenish solution remains stable for several hours. As the temperature is allowed to rise, a discharge of the colour is noted and IrH(CO)(PPh$_3$)$_3$ and [IrH(CO)(PPh$_3$)$_3$(CH$_3$CN)]$^{2+}$ in a 1/1 ratio are formed. These findings are consistent with Scheme 2.

SCHEME 2. Oxidation—reduction mechanism of IrH(CO)(PPh$_3$)$_3$ in 50% acetonitrile/toluene.



In view of the coordinating ability of CH$_3$CN, the electrochemical behaviour of IrH(CO)(PPh$_3$)$_3$ has also been studied in 1,2-dichloroethane. In this medium the noteworthy differences that can be observed are a shift of the second anodic wave of 100 mV towards more positive potentials ($E_{1/2}$ = 0.05 V) and a modification from irreversible shape to a reversible one. At 25°C the electrolysis on the plateau of the first wave, both in the presence and in the absence of free PPh$_3$, requires one equivalent of electrons per mol of complex leading to the formation of a greenish solution whose voltammogram shows a one-electron reversible cathodic wave having the same $E_{1/2}$ and the same limiting current as that of IrH(CO)(PPh$_3$)$_3$. The electrolysis does not influence the wave at $E_{1/2}$ = 0.05 V. This solution is stable in time but exceedingly air-sensitive. Its IR spectrum shows two bands at 2100 and 1985 cm^{-1} attributable to the ν(Ir—H) and ν(CO), respectively. NMR spectroscopic determination of the paramagnetic susceptibility gives a magnetic moment of 1.6 B.M. Owing to the high solubility of the complex in dichloroethane, to its high reactivity towards oxygen and to the presence of the supporting electrolyte, attempts to isolate it have not been successful.

With electrolysis on the second wave, the final result differs depending to whether the depolarizer is $IrH(CO)(PPh_3)_3$ or $[IrH(CO)(PPh_3)_3]^+$. In the first case the electrolysis requires one equivalent of electrons and the final products are in 1/1 ratio $[IrH_2(CO)(PPh_3)_3]^+$ and $[Ir(CO)(PPh_3)_3]^+$, in the second the stepwise one-electron oxidation products are H^+ and $[Ir(CO)(PPh_3)_3]^+$, as supported by polarographic [6], voltammetric [3] and IR [8,9] measurements on the oxidized solution. These results indicate that in dichloroethane the coordinatively unsaturated $[IrH(CO)(PPh_3)_3]^{2+}$ * is unstable, and dissociates into H^+ and $[Ir(CO)(PPh_3)_3]^+$. The release of H^+ accounts also for the recovery of $[IrH_2(CO)(PPh_3)_3]^+$ via the oxidative-addition reaction:

$$IrH(CO)(PPh_3)_3 + H^+ \xrightarrow[25^\circ C]{} [IrH_2(CO)(PPh_3)_3]^+$$

$RhH(CO)(PPh_3)_3$. From voltammograms and cyclic voltammetric measurements it was established that $RhH(CO)(PPh_3)_3$ underwent a reversible one-electron oxidation step, and evidence for the fugitive $[RhH(CO)(PPh_3)_3]^+$ had been obtained [3]. In the light of the results described above a more detailed study of $RhH(CO)(PPh_3)_3$ and species formed from it by electrochemical oxidation was clearly needed.

In acetonitrile/toluene (50% v/v) at −35°C and in the presence of a tenfold molar excess of PPh_3 to prevent dissociation of the complex [10], the electrochemical oxidation of $RhH(CO)(PPh_3)_3$ occurs in two one-electron, diffusion controlled steps: $E_{1/2}$ (I) = −0.30 V, $E_{1/2}$ (II) = 0.02 V. The first anodic response is that of an uncomplicated reversible charge transfer, the second one being consistent with an irreversible process and displaying in cyclic voltammetry a cathodic peak current at $E_p = -0.89$ V on the reverse sweep. Almost identical voltammetric behaviour is observed at 0°C, the only difference being the occurrence of the cathodic peak on the reverse sweep at more negative potentials ($E_p \simeq -1.08$ V). On further raising the temperature to 25°C, the decrease both of the ratio of cathodic to anodic peak currents and of the height of the second wave compared with the first is observed.

Controlled potential electrolysis on the plateau of the second wave at −35°C requires two equivalents of electrons per mol of complex, leading to the formation of a two-electron cathodic wave ($E_{1/2} = -1.10$ V). The solution meanwhile turns from yellow to colourless. Mass spectral examination of the gases evolved during the electrolysis shows that carbon monoxide is produced. On heating to 25°C the colourless solution becomes dark-yellow and the change is not reversed upon cooling to −35°C. The final products are identified as $[HPPh_3]^+$ and $[Rh(PPh_3)_4]^+$ by their polarographic behaviour [11,12]. The electrochemical reduction at low temperature of the colourless solution produces a dark-yellow solution whose oxidation pattern resembles that of d^8-hydrido complexes. Addition of a large volume of acetonitrile to the reduced solution causes precipitation of a yellow crystalline product identified as $RhH(PPh_3)_4$ by comparison with an authentic sample [13].

As far as the electrolysis on the plateau of the first wave at −35°C is concerned, a two-electron oxidation still occurs, with a pattern quite similar to that

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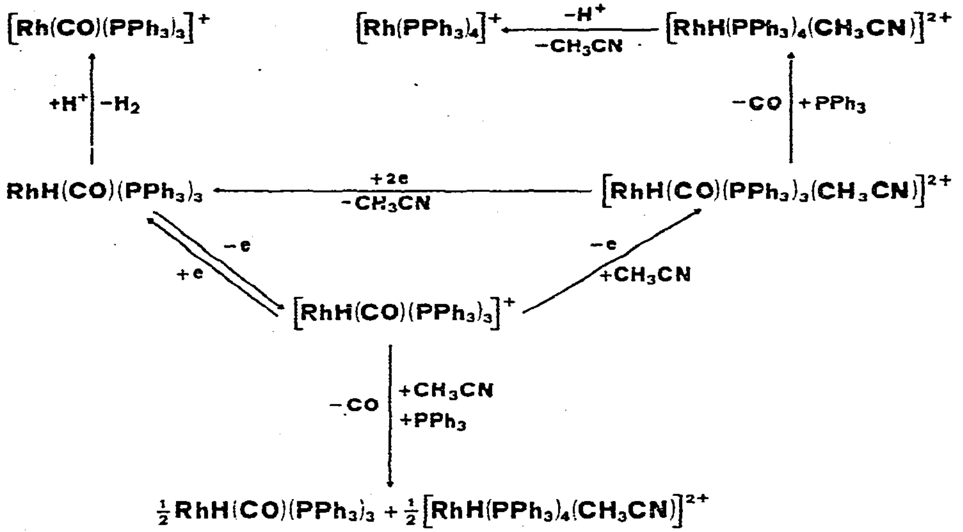
* Experiments performed in the presence of large amounts of PPh_3 suggest that there is no tendency for PPh_3 to occupy the free position on the d^6 complex.

observed for the iridium complex at 25°C. At the end of the electrolysis the voltammetric profile of the colourless solution is identical to that of the direct oxidation on the second wave. At 25°C electrolyses, whatever the voltage, require one equivalent of electrons per mol of $RhH(CO)(PPh_3)_3$ to give the stoichiometric amount of products identified as $[Rh(PPh_3)_4]^+$ and $[Rh(CO)(PPh_3)_3]^+$ [12]. Mass spectral examination reveals that H_2 and CO are evolved. These results lead to Scheme 3.

SCHEME 3. Oxidation/reduction mechanism of $RhH(CO)(PPh_3)_3$ in 50% acetonitrile/toluene.



Although the identity of the primary two-electron oxidation product has not been definitely established, the formulation $[RhH(CO)(PPh_3)_3(CH_3CN)]^{2+}$ can be inferred by analogy with the corresponding iridium compound. Furthermore, the shift of the cathodic peak in cyclic voltammetry from −0.89 V at −35°C to −1.08 V at 0°C (see above) strongly suggests the release of the CO ligand is very fast.

Changing from acetonitrile to dichloroethane as solvent produces a change in the voltammetric pattern of $RhH(CO)(PPh_3)_3$ quite similar to that observed in the oxidation of the related iridium compound, a shift of the second wave toward more positive potentials ($E_{1/2} = 0.08$ V) and a modification from irreversible shape to a reversible one again occurring. Exhaustive controlled potential electrolysis on the plateau of the first wave at −35°C requires one equivalent of electrons per mol of complex yielding a stable orange solution whose voltammogram shows, in addition to the anodic wave at $E_{1/2} = 0.08$ V, a one-electron cathodic wave having the same $E_{1/2}$ and the same limiting current as the starting wave. On heating up to 25°C the solution becomes slowly (≃1 hour) yellow with the contemporary disappearance of both the cathodic and anodic waves. The final products are the same as in CH_3CN, i.e. $[Rh(CO)(PPh_3)_3]^+$, $[Rh(PPh_3)_4]^+$, carbon monoxide and hydrogen.

The IR spectrum of the orange solution at low temperature shows two bands at 2100 (ν(Rh—H)) and 2060 (ν(CO) cm^{-1}). NMR spectroscopic determination of the paramagnetic susceptibility at −35°C gives a magnetic moment value corresponding to the presence of one unpaired electron (μ 1.65 BM). Attempts to isolate a solid from such a solution have given only mixtures of $[Rh(CO)(PPh_3)_3]^+$ and $[Rh(PPh_3)_4]^+$.

The one-electron oxidation of $[RhH(CO)(PPh_3)_3]^+$ results in formation of $[Rh(PPh_3)_4]^+$ and $[HPPh_3]^+$. The occurrence of the reaction between $[Rh(PPh_3)_4]^+$ and the released carbon monoxide accounts for the recovery of small amounts of $[Rh(CO)(PPh_3)_3]^+$.

Kinetics of decay of metal(II) hydride complexes

From our results it appears that the rhodium(II) and iridium(II) hydrido complexes, unlike those of cobalt, are unstable and decay by a disproportionation pathway. In order to obtain some information on the mechanism of this reaction, kinetic investigations have been necessary. The electrochemical techniques of controlled potential coulometry and amperometry were found to be the most convenient methods of producing known quantities of d^7 metal complex and monitoring its disappearance as a function of time. It has been found that $[IrH(Ph_2PCH_2CH_2PPh_2)_2]^+$, $[RhH(Ph_2PCH_2CH_2PPh_2)_2]^+$ and $[IrH(CO)(PPh_3)_3]^+$ disproportionate in acetonitrile/toluene (50% v/v) with a rate law which is second order in the complex. The results of the studies are recorded in Table 1. Each value, reproducible to within the standard deviations, is the result of approximately six determinations. The activation energies, determined by applying the method of the least squares to standard Arrhenius plots, are 12.5 ± 1, 10.0 ± 1 and 11.5 ± 1 kcal mol^{-1} for the complexes $[IrH(Ph_2PCH_2CH_2PPh_2)_2]^+$, $[RhH(Ph_2PCH_2CH_2PPh_2)_2]^+$ and $[IrH(CO)(PPh_3)_3]^+$, respectively.

From the thermodynamic point of view the instability of these d^7 species towards disproportionation in acetonitrile is predicted by their oxidation—reduction pattern in such a medium. In considering the behaviour of $[IrH(CO)(PPh_3)_3]^+$ as typical of these complexes *, it appears that in the poorly coordinating solvent dichloroethane, it can both be reduced and oxidized in reversible steps ($\Delta E_{1/2}$ = 350 mV), so that the disproportionation equilibrium 1 must be con-

$$2[IrH(CO)(PPh_3)_3]^+ \rightleftharpoons IrH(CO)(PPh_3)_3 + [IrH(CO)(PPh_3)_3]^{2+} \qquad (1)$$

sidered ($pK_{eq} = \Delta E_{1/2}/59.15 \simeq 5.9$). This result accounts for the stability of the d^7 complex in dichloroethane. On the other hand, in acetonitrile $[IrH(CO)(PPh_3)_3]^+$ is still reduced in a reversible step, but is oxidized in an irreversible, diffusion controlled one at a less positive potential than in dichloroethane. This implies that CH_3CN plays an important role in favouring the electron transfer reaction 2.

$$[IrH(CO)(PPh_3)_3]^+ + CH_3CN \rightarrow [IrH(CO)(PPh_3)_3(CH_3CN)]^{2+} + e \qquad (2)$$

The formal potential, $E°(II)$, of this system can still be evaluated, provided the half-wave potentials of both, irreversible oxidation of $[IrH(CO)(PPh_3)_3]^+$ and irreversible reduction of $[IrH(CO)(PPh_3)_3(CH_3CN)]^{2+}$, are known. Now, since the calculated value is more negative than the half-wave potential of the reversible

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* Electrochemical study of $RhH(DPE)_2$ and $IrH(DPE)_2$ in dichloroethane was omitted because of their instability in this solvent.

TABLE 1

THE DISPROPORTIONATION RATE CONSTANTS, k_{obs}, IN ACETONITRILE/TOLUENE (50% v/v), 0.1 M TBAP, AT VARIOUS TEMPERATURES

Complex	Temperature (°C)	k_{obs} (l mol^{-1} s^{-1})
$[RhH(DPE)_2]^+$	−44.0 ± 0.5	5.6 ± 0.5
	−34.0 ± 0.5	13.0 ± 1.0
	−25.0 ± 0.2	29.0 ± 2.0
$[IrH(DPE)_2]^+$	−27.0 ± 0.2	0.57 ± 0.05
	−18.0 ± 0.2	1.40 ± 0.10
	−9.5 ± 0.1	3.20 ± 0.20
	0.0 ± 0.1	7.20 ± 0.50
$[IrH(CO)(PPh_3)_3]^+$	0.0 ± 0.1	0.44 ± 0.05
	8.0 ± 0.1	0.79 ± 0.10
	16.0 ± 0.1	1.36 ± 0.10
	25.0 ± 0.1	2.60 ± 0.20

reduction of $[IrH(CO)(PPh_3)_3]^+$, the occurrence of the disproportionation reaction can be argued.

Thus, the promotion of disproportionation by acetonitrile could be accounted for by assuming that in CH_3CN the equilibrium 3 is rapidly established, while the

$$[IrH(CO)(PPh_3)_3]^+ + CH_3CN \overset{K_{eq}}{\rightleftharpoons} [IrH(CO)(PPh_3)_3(CH_3CN)]^+ \quad (3)$$

species $[IrH(CO)(PPh_3)_3(CH_3CN)]^+$ is responsible for the disproportionation via cross-reaction 4.

$$[IrH(CO)(PPh_3)_3(CH_3CN)]^+ + [IrH(CO)(PPh_3)_3]^+ \xrightarrow{k_3}$$
$$IrH(CO)(PPh_3)_3 + [IrH(CO)(PPh_3)_3(CH_3CN)]^{2+} \quad (4)$$

Thus, the rate law is:

$$-d[Ir(II)]/dt = 2k_3\, K_{eq}[Ir(II)]^2[CH_3CN]/(1 + K_{eq}[CH_3CN])^2 \quad (5)$$

where [Ir(II)] represents the total analytical concentration of the d^7-iridium complex. To confirm the proposed mechanism some kinetic measurements have been carried out in dichloroethane/acetonitrile mixtures. The value of the observed rate constant, k_{obs}, is linearly related to the concentration of CH_3CN, as shown in Fig. 1. This implies that K_{eq} $[CH_3CN] \ll 1$, and thus that equilibrium 3, lies far to the left, i.e. the equilibrium favours the unsolvated species.

An examination of the data in Table 2 shows that the overall activation free energy for disproportionation, ΔF_{obs}, is proportional to the separation of the anodic, $E_{1/2}$ (II), and cathodic, $E_{1/2}$ (I) waves, $\Delta E_{1/2}$, of the three complexes. Since $\Delta E_{1/2}$ includes both the overvoltage of the electrode process (eq. 2), $E_{1/2}$ (II) − $E°$ (II), and the "driving force" of the cross-process (eq. 4), $E_{1/2}$ (I) − $E°$ (II), if the correlation is not fortuitous, it seems that the same parameters govern both the chemical and the electrochemical processes, perhaps suggesting a new guide for predicting the relative energetics of analogous disproportionation reactions.

As far as $[RhH(CO)(PPh_3)_3]^+$ is concerned, this complex, unlike the previous

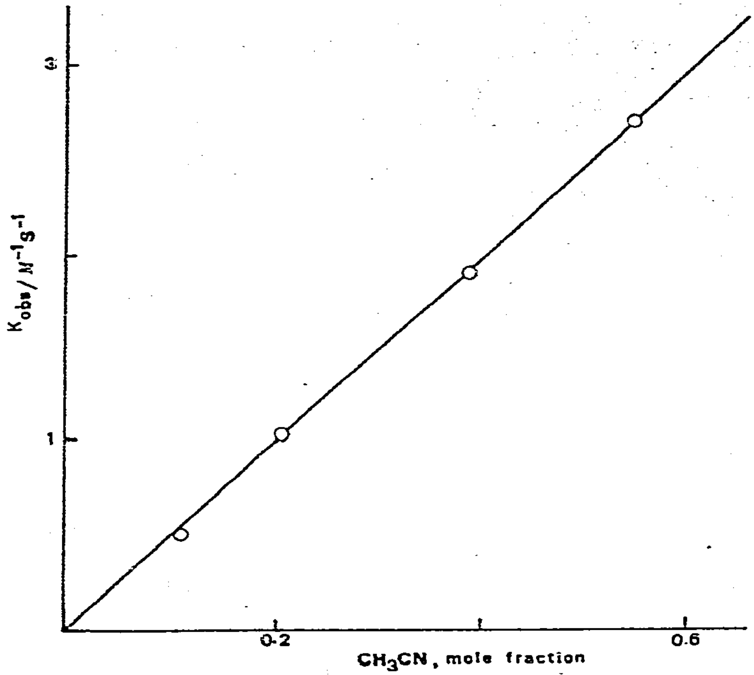

Fig. 1. Dependence of k_{obs} for the disproportionation reaction of $[IrH(CO)(PPh_3)_3]^+$ in dichloroethane at 25°C on CH_3CN concentration.

ones, decays via a first order reaction. Dissociation of the CO ligand from the "intermediate" (eq. 6) in the rate-determining step is strongly suggested by the

$$[RhH(CO)(PPh_3)_3(CH_3CN)]^+ \xrightarrow{k_3} [RhH(PPh_3)_3(CH_3CN)]^+ + CO \qquad (6)$$

following facts: (i) the oxidation—reduction pattern both in acetonitrile and dichloroethane resembles that of the related iridium compound; (ii) the observed rate constant is independent of the concentration of added PPh_3 in the range 5×10^{-4} to 0.2 M; (iii) no loss of the hydride ligand takes place, as revealed by the nature of the products; (iv) the value of k_{obs} in dichloroethane is linearly related to the concentration of added acetonitrile (see Fig. 2); (v) the d^6 comcomplex, $[RhH(CO)(PPh_3)_3(CH_3CN)]^{2+}$, loses carbon monoxide very quickly. Consequently the species $[RhH(PPh_3)_3(CH_3CN)]^+$ must be responsible for the

TABLE 2

COMPARISON BETWEEN k_{obs} AND $\Delta E_{1/2}$, IN ACETONITRILE/TOLUENE (50% v/v), 0.1 M TBAP, at —34°C

Complex	k_{obs} (l mol^{-1} s^{-1})	ΔF_{obs} (kcal mol^{-1})	$E_{1/2}$ (II) (V)	$E_{1/2}$ (I) (V)	$\Delta E_{1/2}$ (V)
$[RhH(DPE)_2]^+$	13.0	13.0	—0.75	—0.94	0.19
$[IrH(DPE)_2]^+$	0.27 ^{a}	14.8	—0.82	—1.05	0.23
$[IrH(CO)(PPh_3)_3]^+$	0.024 ^{a}	16.0	—0.04	—0.30	0.26

^{a} Value extrapolated from data in Table 1.

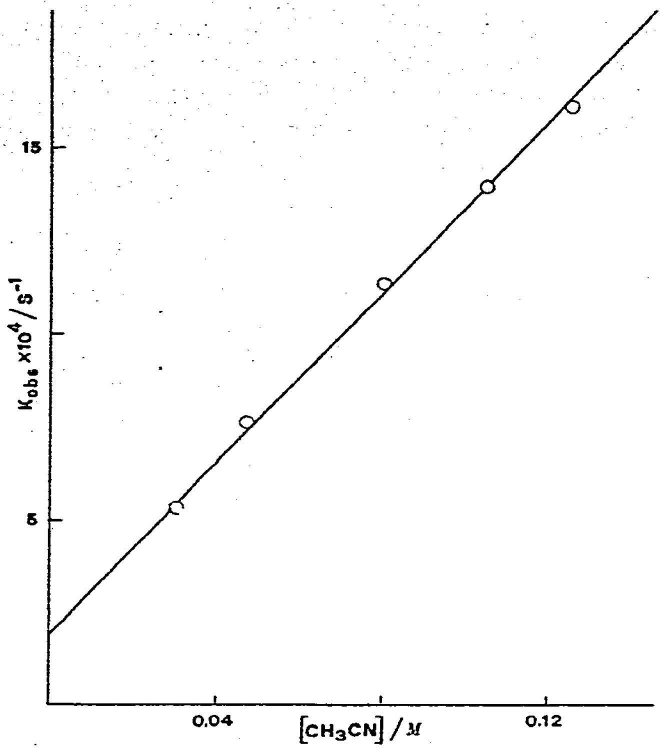

Fig. 2. Dependence of k_{obs} for the disproportionation reaction of $[RhH(CO)(PPh_3)_3]^+$ in dichloroethane at 25°C on CH_3CN concentration.

disproportionation via the fast redox reaction (eq. 7).

$$[RhH(PPh_3)_3(CH_3CN)]^+ + [RhH(CO)(PPh_3)_3]^+ \xrightarrow{PPh_3} RhH(CO)(PPh_3)_3 + [RhH(PPh_3)_4(CH_3CN)]^{2+} \quad (7)$$

Since $[RhH(PPh_3)_4]^+$ is oxidizable at a potential ($E_{1/2} = -0.44$ V) more negative than the reduction potential ($E_{1/2} = -0.30$ V) of $[RhH(CO)(PPh_3)_3]^+$, the proposed mechanism is further supported. The observed rate constant derived from the mechanism in the form:

$$k_{obs} = 2k_3K_{eq}[CH_3CN]/(1 + K_{eq}[CH_3CN]) \quad (8)$$

does indeed reduce (see Fig. 2) to:

$$k_{obs} = 2k_s + 2k_3K_{eq}[CH_3CN] \quad (9)$$

where $2k_s$ is the rate constant in dichloroethane, i.e. k_s is the rate constant for dissociation of the unsolvated complex. From the slopes of the plot k_{obs} vs. $[CH_3CN]$ in dichloroethane at different temperatures the overall enthalpy change is found to be 13.5 ± 1 kcal mol^{-1}. This value, too low to be consistent with a dissociation mechanism, agrees with the previous assumption that an intermediate involving an increase in the coordination number is formed by an equilibrium prior to the transition state.

Finally it is remarkable that the value of the second order rate constant extrapolated from the half-wave potentials difference, $\Delta E_{1/2}$ (see above), is about 1×10^{-4} l mol^{-1} s^{-1} in 50% acetonitrile/toluene at −34°C. Since under these conditions $k_{obs} = 1.2 \times 10^{-3}$ s^{-1}, it is clear that the second-order pathway is strongly disfavoured compared with the first-order route.

Conclusions

The rhodium and iridium complexes obtained by the electrochemical method belong to the group of rare monomeric transition metal compounds of the second and third row in d^7-electronic configurations. Furthermore, while most of the paramagnetic transition-metal hydrido complexes so far known are cobalt derivatives [1], the preparation of $[RhH(CO)(PPh_3)_3]^+$ and $[IrH(CO)(PPh_3)_3]^+$, although only in solution, provides the first example of well-characterized paramagnetic hydrido complexes of these metals. The complexes are five-coordinate and their geometry, as inferred from the reversible electron transfer, must be almost identical with that of the starting d^8 compounds. The assumption of a relationship between the structure and the possibility of obtaining d^7-monomeric species has previously been put forward [14], but the reduction of the octahedral hydrides occurs in a single two-electron step leading to the final d^8 species with no intermediate stable state [15].

Among the d^6-hydrido complexes now described, the qualitative sequence of "acidity" in the complexes with the same ligand environment is in the order Rh > Ir > Co, which agrees with that observed for the reactivity of planar d^8-metal(I) complexes towards the oxidative-addition reactions [16]. Thus the unexpected high acid strength of the hydride complexes of cobalt with phosphite ligands could arise from a different structure [16] of the corresponding four-coordinate d^8 complex [4], since the strong σ-donation by phosphite ligands to metals are well known. Similarly the tendency to lose carbon monoxide in going from $[IrH(CO)(PPh_3)_3(CH_3CN)]^{2+}$ to $[RhH(CO)(PPh_3)_3(CH_3CN)]^{2+}$ as well as from $[IrH(CO)(PPh_3)_3]^+$ to $[RhH(CO)(PPh_3)_3]^+$ can easily be rationalized in terms of "metal basicity" [17]. As the electron density on the central metal atom decreases, the CO stretching frequency increases from iridium to rhodium. The unusual, very high stretching frequency of the CO group in $[RhH(CO)(PPh_3)_3]^+$ reflects the weakness of the metal—carbon bond, and the lability of the complexes.

Experimental

Chemicals and reagents

The following hydrido complexes were prepared and purified by published procedures: $[CoH(Ph_2PCH_2CH_2PPh_2)_2]$ [18], $[CoH\{P(OMe)_3\}_4]$ [19], $[CoH\{P(OEt)_3\}_4]$ [19], $[RhH(Ph_2PCH_2CH_2PPh_2)_2]$ [18], $[RhH(CO)(PPh_3)_3]$ [10], $[IrH(PPh_2CH_2CH_2PPh_2)_2]$ [20] and $[IrH(CO)(PPh_3)_3]$ [21]. 1,2-Dichloroethane was purified by shaking with concentrated H_2SO_4, washing with water, then diluted KOH, and again with water. After an initial drying over $CaCl_2$, it was refluxed with CaH_2 and fractionally distilled. The purifications of acetonitrile, tetrabuthylammonium perchlorate (TBAP) and toluene have been described previously [12]. All the chemicals employed were of reagent grade quality (C. Erba and Schuchardt). All solutions contained 0.1 *M* TBAP as supporting electrolyte.

99.999% argon, rendered oxygen-free by passage over reduced copper at 450°C, was used.

Apparatus and procedure

All experiments were carried out in a H-shaped cell with cathodic and anodic compartments separated by a sintered glass disc. All potentials are referred to a silver/0.1 *M* silver perchlorate electrode in acetonitrile. In the voltammetric measurements the working electrode was a spherical platinum microelectrode with renewal of the diffusion layer [22]. Unless otherwise stated the renewal time was fixed at 2.0 s. An Amel (Milan, Italy) model 471 multipolarograph was employed for voltammetric and low scan-rate (up to 200 mV s^{-1}) cyclic voltammetric measurements. Fast scan-rate cyclic voltammograms were recorded with an Amel model 448 oscillographic polarograph provided with a Polaroid camera attachment.

In the controlled potential electrolyses a Tacussel model PRT 200-lX potentiostat was used and the associated coulometer was an Amel integrator model 558. The working electrode was a platinum gauze. The counter electrode was external, the connection being made through an appropriate salt bridge.

Infrared spectra were recorded on a Perkin—Elmer model 457 grating spectrometer. IR spectra of solids were measured with KBr discs. Solution spectra were measured, with compensation, in 0.5 or 1 mm liquid cells. NMR-spectroscopic determinations of the paramagnetic susceptibility [23] were obtained using a Varian T60 spectrometer. Mass spectra were obtained using a Hitachi Perkin—Elmer RMU-6 spectrometer. Molar conductivities were determined in mmolar acetonitrile solutions at 25°C.

Electrochemical preparations

Bis[1,2-bis(diphenylphosphino)ethane]hydridocobalt(II) tetraphenylborate, [CoH(DPE)$_2$](BPh$_4$). A suspension of COH(DPE)$_2$ (0.5 mmol) in 50 ml of acetonitrile/toluene (50% v/v) containing 0.1 *M* $NaClO_4$ is electrolyzed under carefully deoxygenated argon atmosphere at —0.5 V vs. Ag/0.1 *M* Ag^+ acetonitrile electrode in a two-compartment cell. With a platinum working electrode (approximate area 100 cm^2) the electrolysis time is about 1 h. After completion of the electrolysis the yellow solution is evaporated under reduced pressure almost to dryness and the residue dissolved in 20 ml of methanol. Addition of an equivalent amount of sodium tetraphenylborate dissolved in the smallest volume of methanol causes precipitation of golden-yellow crystals, which are filtered off, washed with methanol, and dried in vacuum. Anal. Found: C, 78.0; H, 6.0; P, 10.4. $C_{74}H_{69}B\,CoP_4$ calcd.: C, 77.6; H, 5.9; P, 10.5%. ν(MH) 1885 cm^{-1}. μ 2.2 BM. Molar conductance: 76 Ω^{-1} cm^2 mol^{-1}.

Tetrakis(trimethylphosphite)hydridocobalt(II)tetraphenylborate, [CoH{P(OMe)$_3$}$_4$](BPh$_4$). This is similarly prepared by oxidation at —0.5 V of CoH[P(OMe)$_3$]$_4$ (0.5 mmol) in 50 ml of 0.1 *M* $NaClO_4$ acetonitrile solution, and isolated as emerald-green crystals. Anal. Found.: C, 49.0; H, 6.6; P, 14.2.

$C_{36}H_{57}BCoO_{12}P_4$ calcd.: C, 49.4; H, 6.5; P, 14.2%. ν(MH) 1930 cm^{-1}. μ 1.9 BM. Molar conductance: 95 Ω^{-1} cm^2 mol^{-1}.

Tetrakis(triethylphosphite)hydridocobalt(II) tetraphenylborate, [CoH{P(OEt)₃}₄](BPh₄). Similarly prepared by oxidation at −0.5 V of $CoH[P(OEt)_3]_4$. Anal. Found: C, 55.5; H, 7.7; P, 11.7. $C_{48}H_{81}BCoO_{12}P_4$ calcd.: C, 55.2; H, 7.7; P, 11.9%. ν(M—H) 1930 cm^{-1}. μ 2.0 BM. Molar conductance: 86 Ω^{-1} cm^2 mol^{-1}.

Bis[1,2-(bisdiphenylphosphino)ethane]acetonitrilehydridocobalt(III) perchlorate, $[CoH(DPE)_2(CH_3CN)](ClO_4)_2$. A suspension of $CoH(DPE)_2$ (0.5 mmol) in 50 ml of acetonitrile/toluene (50% v/v) containing 0.1 *M* $NaClO_4$ is electrolyzed at +0.5 V vs. Ag/0.1 *M* Ag^+ acetonitrile electrode. At the end of the electrolysis the lemon-yellow solution is evaporated under reduced pressure to small volume and 20 ml of dichloromethane are added to the residue. After filtering off of sodium perchlorate, addition of light petroleum affords a yellow precipitate, which is washed with light petroleum and dried under vacuum. Anal. Found: C, 59.4; H, 4.7; N, 1.2; P, 11.2. $C_{54}H_{52}Cl_2CoNO_8P_4$ calcd.: C, 59.1; H, 4.7; N, 1.3; P, 11.3% ν(M—H) 2000, ν(CN) 2280 cm^{-1}. Molar conductance: 278 Ω^{-1} cm^2 mol^{-1}.

Tris(triphenylphosphine)carbonylacetonitrilehydridoiridium(III) perchlorate, $[IrH(CO)(PPh_3)_3(CH_3CN)](ClO_4)_2$. This is obtained as white crystals similarly by oxidation at +0.40 V of $IrH(CO)(PPh_3)_3$. Anal. Found: C, 54.6; H, 4.0; N, 1.1; P, 10.0 $C_{57}H_{49}Cl_2IrNO_9P_3$ calcd.: C, 54.8; H, 3.9; N, 1.1; P, 9.9%. ν(M—H) 2170, ν(CO) 2070, ν(CN) 2290 cm^{-1}. Molar conductance: 285 Ω^{-1} cm^2 mol^{-1}.

Bis[1,2-bis(diphenylphosphino)ethane]acetonitrilehydridoiridium(III)perchlorate, $[IrH(DPE)_2(CH_3CN)](ClO_4)_2$. Similarly obtained as white crystals by oxidation of $IrH(DPE)_2$ at −30°C in two successive steps, first at −0.95 V and subsequently at −0.60 V. Anal. Found: C, 52.3; H, 4.2; N, 1.0; P, 10.1. $C_{54}H_{52}Cl_2IrNO_8P_4$ calcd.: C, 52.7; H, 4.2; N, 1.1; P, 10.0%. ν(M—H) 2220, ν(CN) 2290 cm^{-1}. Molar conductance: 273 Ω^{-1} cm^2 mol^{-1}.

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