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Electrochemistry of Coordination Compounds.
VIII. Polarographic Behaviour of Iridium Hydride Complexes

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The electrochemical reduction of an isostructural series of D^6 complexes where the halide ligands are, step by step, substituted by a hydride one has been studied. The obtained half-wave potentials seem to constitute a relative measure of the increased orbital interaction or increased covalency of the metal–hydrogen bond in comparison with the metal–halogen one. Furthermore a linear relationship between the half-wave potential and ν_{CO} has been found, indicating that both these parameters reflect the polarity of the molecular orbitals.

Introduction

The structural data of transition metal hydride complexes show that the internuclear distances allow an extensive overlap of the metal–hydrogen orbitals, *i.e.*, extensive covalent bonding[1]. As a consequence, in considering an isostructural series of complexes with identical neutral ligands and metal but with the "charged ligand" substituted by the "hydridic" one, we must expect a change in the polarographic behaviour which reflects the changes in the electronegativity related to the substitution in the coordination sphere. Having this in mind and with the aim to contribute to a further broader basis for a quali–quantitative understanding of metal–hydrogen bonds, we studied the polarographic reduction of the isostructural complexes $IrCl_3(Ph_3P)_2(CO)$, $IrHCl_2(Ph_3P)_2(CO)$ and $IrH_2Cl(Ph_3P)_2(CO)$.

Experimental

Materials

Iridium complexes were prepared as described in the literature[2–4]. Their identity and purity were checked by IR spectra and elemental analyses. Purification of acetonitrile and tetraethylammonium perchlorate (TEAP) has been described previously[5]. Triphenylphosphine (Fluka *puriss.*) was recrystallized from n-hexane and dried at 65° C/<1 torr over P_2O_5. Dry benzene was obtained by doubly distilling high purity benzene from Na–K alloy. The other chemicals were reagent grade (C. Erba and Schuchardt) and used without further purification. Stock solutions of anhydrous hydrogen chloride in acetonitrile were prepared by oxidizing on platinum electrode hydrogen gas dissolved in Bu_4NCl–acetonitrile solutions[6].

Apparatus and Procedure

All experiments were carried out at 25 ± 0.1° C under nitrogen or argon athmosphere, in an H-shaped cell with cathodic and anodic compartments separated by a sintered glass disk. All potentials are referred to a silver/0.1*M* silver nitrate electrode in acetonitrile medium. In the voltammetric measurements the working electrodes were either a spherical platinum microelectrode with renewal of the diffusion layer[7] or a dropping mercury electrode with mechanical control of the drop time. The voltammetric tests were performed by employing a three electrode system made up with operational amplifiers assembly MP-System 1000 connected to a Hewlett–Packard 7004B recorder.

In the controlled potential electrolyses an Amel Model 557/SU potentiostat was used and the associated coulometer was an Amel integrator Model 558. The working electrode was a mercury pool. Owing to the poor solubility of the complexes in acetonitrile, all measurements have been carried out in CH_3CN–Benzene (75–25 V/V) with 0.1*M* TEAP as supporting electrolyte and in the presence of free Ph_3P to supply the ligand needed by the stoichiometry of the processes.

In this medium significant concentrations of the complexes $IrCl_3(Ph_3P)_2(CO)$ and $IrH_2Cl(Ph_3P)_2(CO)$ can be achieved. Only the solubility of the complex

$IrHCl_2(Ph_3P)_2(CO)$ is too low to give meaningful results. However this difficulty was avoided since it was found that when prepared *in situ* by treating, as reported in the literature[2], $IrCl(Ph_3P)_2(CO)$ with the stoichiometric amount of HCl, a sufficient concentration of complex ($5 \times 10^{-3} M$), $IrHCl_2(Ph_3P)_2(CO)$, remained in solution as long as the experiments were performed.

The IR spectra were recorded with a Perkin–Elmer 457 spectrometer on KBr disk.

Results

$IrCl_3(Ph_3P)_2(CO)$

The polarographic reduction of $IrCl_3(Ph_3P)_2(CO)$ shows two irreversible and diffusion controlled waves with the half-wave potentials at –1.08 V and about –2.2 V*.

Exhaustive controlled potential electrolysis in the potential range of the plateau of the first wave requires two equivalents of electrons *per* mol of complex leading to the formation of two anodic waves ($E_{1/2}$ = –0.65 V and –0.50 V). The solution changes from colourless to yellow. The electrolysis does not influence the wave at –2.2 V. The anodic waves are attributed to free chlorid ion by comparison with the behaviour of this ion under our experimental conditions. Furthermore, by addition to the reduced solution of known amounts of Cl^-, it was proved that two mol of chloride *per* mol of complex were released in the electrochemical process. The evaporation under reduced pressure of the solvent and the subsequent extraction with benzene followed by addition of petroleum ether afforded the recovery of a yellow crystalline precipitate, identified by IR spectrum and elemental analysis as $IrCl(Ph_3P)_2(CO)$. The polarogram of an authentic sample of $IrCl(Ph_3P)_2(CO)$ in CH_3CN–benzene solution shows a single irreversible wave at the same potential of the second reduction wave of $IrCl_3(Ph_3P)_2(CO)$.

To account for the above experimental results the following scheme is proposed for the electrochemical reduction of $IrCl_3(Ph_3P)_2(CO)$:

$$IrCl_3Ph_3P)_2(CO) + 2\,e \rightarrow IrCl(Ph_3P)_2(CO) + 2\,Cl^-$$

$IrHCl_2(Ph_3P)_2(CO)$

The polarogram of $IrHCl_2(Ph_3P)_2(CO)$ exhibits a single well defined two-electron irreversible wave ($E_{1/2}$ = –2.05 V). The two-electron reduction was confirmed by controlled potential coulometric experiments. In particular, the exhaustive electrolysis on the plateau of the wave yields a yellow solution whose polarogram shows only two anodic waves attributed to free chloride ion. From the height of these waves it was inferred that two mol of halide *per* mol of depolarizer were released in the reduction process, showing that the reduction product, by analogy with the reduction pattern of $IrCl_3(Ph_3P)_2(CO)$, was $IrH(Ph_3P)_3(CO)$. Since the anodic behaviour of this complex had been previously characterized[8] some voltammetric tests in the anodic region were performed on the reduced solution using a platinum electrode. Thus, the identity of the product was confirmed.

These findings can be summarized as follows:

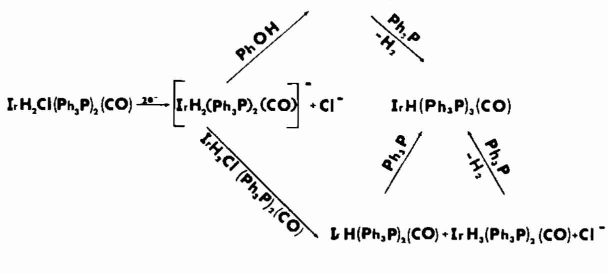
$$IrHCl_2(Ph_3P)_2(CO) + 2\,e + Ph_3P \rightarrow IrH(Ph_3P)_3(CO) + 2Cl^-$$

$IrH_2Cl(Ph_3P)_2(CO)$

The electrochemical behaviour of the $IrH_2Cl(Ph_3P)_2(CO)$ complex has been investigated under hydrogen atmosphere since it is known that in solution loss of the coordinated hydrogen can take place in some extent[9]. Under these conditions the polarographic pattern consists of a single two-electron irreversible wave ($E_{1/2}$ = –2.45 V). The exhaustive controlled potential electrolysis required, in every experiment, a number of electrons less than two (≃1.5) indicating a chemical reaction between the reduction product and the parent compound. During the electrolysis the colourless solution became dark yellow and at the end the polarographic pattern exhibited only one anodic wave ($E_{1/2}$ = –1.20 V) in addition to those of the released chloride. Furthermore, voltammetric measurements with Pt electrode[8] confirmed the presence of $IrH(Ph_3P)_3(CO)$. The anodic wave disappeared with time while the concentration of $IrH(Ph_3P)_3(CO)$ increased and the solution changed to a lemon yellow colour.

In order to identify the primary reduction products coulometric experiments in the presence of proton donors such as C_6H_5OH were carried out. In these cases exactly two equivalents of electrons *per* mol of complex were required and the only products were $IrH(Ph_3P)_3(CO)$ and $C_6H_5O^-$.

The following scheme can account for our observations:



This is strongly supported by the recovery of $IrH_3(Ph_3P)_2(CO)$ as the only product in the reduction of $IrH_2Cl(Ph_3P)_2(CO)$ in the absence of free phosphine[4] and in the presence of C_6H_5OH. This complex,

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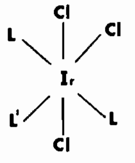
* This wave is affected by the presence of a maximum.

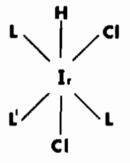
$IrH_3(Ph_3P)_2(CO)$, under hydrogen atmosphere and in the absence of free phosphine to prevent the loss of the coordinated hydrogen[4], exhibits a single two-electron irreversible wave at −2.95 V giving as final product $IrH(Ph_3P)_3(CO)$ in concentration half that of the starting compound[10].

Discussion

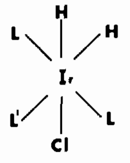
The octahedral complexes,



(A)



(B)



(C)

(L = Ph_3P, L′ = CO) differ only by the stepwise substitution of one ligand (chloride) by another one (hydride). This and the experimental results, *i.e.* identical number of electrons accepted, nature of the products, solid state structure and ligands unchanged when these complexes are transferred to solution, similar charge transfer coefficients α (about 0.5) allow us to put forward a common reduction mechanism at the electrode and consequently to correlate the behaviour of the different species. In considering the behaviour of (A) as typical of an iridium(III) complex it appears that also (B) and (C) behave identically but at more negative potentials. Furthermore, since the electrode processes are totally irreversible, the half-wave reduction potentials are dependent only on the starting compounds and consequently must be related, at least as a first approximation, to the presence of the "changed" ligand which dictates the different ease of reduction in the order (A) > (B) > (C).

The ease of reduction is known to be a function of the energy of the lowest unoccupied orbital in the depolarizer[11, 12], *i.e.* in our case, the antibonding e_g orbital*. Its electron affinity seems to be very low so that a very negative potential would be needed for the acceptance of electrons. As indicated by the irreversible electrode process, a rearrangement of the depolarizer has to take place to give a structure capable of direct reaction with the electrode. Following Chatt's suggestion on the stability toward dissociation of metal–carbon σ-bonds[13, 14] it is likely that the formation of this new state, not necessarily a spectroscopic one, will also depend on contribution from the occupied (particularly the highest t_{2g}) and the lowest unoccupied e_g levels while the energy required will depend on the energy separation between these orbitals. We find that the change of the chloride ligand by the hybride one makes the electrode field more negative. This suggests a bigger requirement of energy for the rearrangement of the molecule which must originate from the bigger splitting of the e_g and t_{2g} orbitals because of the increased interaction of the *s* hydrogen orbital in the molecular orbital. Therefore the $E_{1/2}$ values, which in our case reflect the energy for the rearrangement, constitute a relative measure of the increased orbital interaction or increased covalency of the metal–hydrogen in comparison with the metal–halogen bonds.

This increased covalency should influence also such parameters as the stretching frequencies of the ligands, which are sensitive to the variation of electron density on the metal[15]. In fact, in the complexes studied, the half-wave potentials show (Figure 1) a linear relationship with ν_{CO} indicating that both these parameters reflect the polarity of the molecular orbital. It is noteworthy that also $E_{1/2}$ and ν_{CO} of $IrH_3(Ph_3P)_2(CO)$, which we considered only for analytical pourposes (see experimental), fit very well in the previous diagram (Figure 1). This result, if not fortuitous, suggests that either the structure of this complex (which is unknown) is identical to that of complexes (A), (B) and (C) or the correlation we found is not influenced by structural differences, implying that the

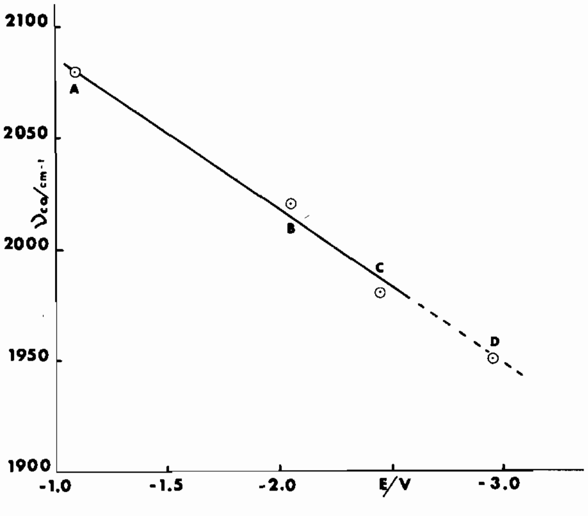


Figure 1. Plot of $E_{1/2}$ *vs.* ν_{CO}: A = $IrCl_3(Ph_3P)_2(CO)$, ν_{CO} = 2080[a], 2079[b]; B = $IrHCl_2(Ph_3P)_2(CO)$, ν_{CO} = 2020[a], 2024[b]; C = $IrH_2Cl(Ph_3P)_2(CO)$, ν_{CO} = 1980[a], 1983[b]; D = $IrH_3(Ph_3P)_2(CO)$, ν_{CO} = 1950[a], 1955–1960–1965[c].

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[a] Present work. [b] R. Craig Taylor, J. F. Young and G. Wilkinson, *Inorg. Chem.*, 5, 20 (1966) and references therein. [c] See ref. 4.

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* Although the complexes discussed here do not have O_h symmetry the notation "e_g, t_{2g}" will be used to simplify the discussion.

reduction mechanism at the electrode is independent of the structure of the depolarizer.

To date we have no data to support either of these hypotheses. This problem, however, is under investigation.

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