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REDOX BEHAVIOUR OF COMPLEXES OF RHODIUM(I) AND IRIDIUM(I) WITH SCHIFF BASES DERIVED FROM PYRIDINE-2-ALDEHYDE AND SOME PRIMARY AMINES INCLUDING THE OPTICALLY ACTIVE α-PHENYLETHYLAMINE

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Summary

The polarographic and voltammetric behaviour of complexes of the type [M(Chel)cod]PF_6 (M = Rh, Ir; Chel = pyridinalmethyliminde, pyridinal-isopropylimine, pyridinal-α-phenylethylimine; cod = cyclooctadiene) have been studied in acetonitrile and dichloroethane with 0.1 *M* tetrabutylammonium perchlorate as supporting electrolyte. The reduction proceeds in two reversible one-electron steps, followed by one or two irreversible waves, complicated by adsorption phenomena and chemical side reactions. The electrooxidation shows only a single one-electron step, associated to catalytic phenomena at the electrode. The electrochemical data suggest that the pyridinalphenylethylimine derivative must be the most active reduction catalyst among the above complexes.

Introduction

The electrochemical behaviour of some bipyridine and phenanthroline complexes of rhodium(I) and iridium(I) containing π-bonding ligands was previously investigated [1] as part of a systematic study of relations between structure and redox properties of complexes active as homogeneous catalysts. In this paper we report on the non-aqueous electrochemistry of another series of [M(Chel)cod]PF_6 complexes of these metals, where cod = *cis,cis*-cycloocta-1,5-diene and the chelates are structural analogues of bipyridine, that is Schiff bases derived from pyridin-2-aldehyde and primary amines (PMI = pyridinal-

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TABLE 1

ELECTROCHEMICAL DATA FOR THE COMPOUNDS

Complex	$M^I \overset{e^-}{\rightleftharpoons} M^0$				$M^0 \overset{e^-}{\rightleftharpoons} M^{-I}$				Next reduction steps	$M^I \overset{-e^-}{\rightleftharpoons} M^{II}$	
	E_p^c (V)	E_p^a (V)	$E_{1/2}^{(1)}$ (V)	i_d/c (A/mmol)	E_p^c (V)	E_p^a (V)	$E_{1/2}^{(2)}$ (V)	i_d/c (A/mmol)	E_p^c (V)	$E_{1/2}$ (V)	slope (mV)
[Rh(PIPI)cod]$^+$	−0.965	−0.903	−0.934	1.20	−1.620	−1.560	−1.590	0.90	−2.10 −2.50	+0.680	37
[Rh(PMI)cod]$^+$	−0.947	−0.887	−0.917	1.20	−1.602	−1.558	−1.580	0.82	−2.020 −2.440	+0.660	43
[Rh(R)(PPEI)cod]$^+$	−0.914	−0.854	−0.884	0.90	−1.566	−1.506	−1.536	0.52	−2.01	+0.689	39
[Ir(PMI)cod]$^+$	−0.750	−0.692	−0.721	1.10	−1.364	−1.304	−1.334	1.08	−2.18	+0.521	40
[Ir(R)(PPEI)cod]$^+$	−0.702	−0.642	−0.672	0.96	−1.352	—	−1.322	3.5	−2.0	+0.491	47

methylimine; PiPI = pyridinal-iso-propylimine; PPEI = pyridinal-α-phenylethylimine) [2]. These complexes have been found to be efficient homogeneous catalysts for the reduction of ketones by hydrogen transfer from alcohols. By using the optically active PPEI derivatives as catalysts and prochiral substrates as acceptors, it is also possible to obtain enantioselective reductions [3].

Results and discussion

The redox behaviour of the above complexes has been studied at the mercury electrode using conventional polarography, cyclic voltammetry and some related techniques. All the complexes exhibit similar patterns for their reduction and oxidation steps, which implies that the redox processes are closely related *. The observed electrochemical data are given in Table 1.

Electroreduction

The reduction process was studied in acetonitrile (AN) in the presence of 0.1 *M* tetrabutylammonium perchlorate (TBAP). A typical pattern for the process at the mercury electrode is shown in Fig. 1A. Analogous results are given by voltammetry at a stationary hanging mercury drop electrode (Fig. 2). The

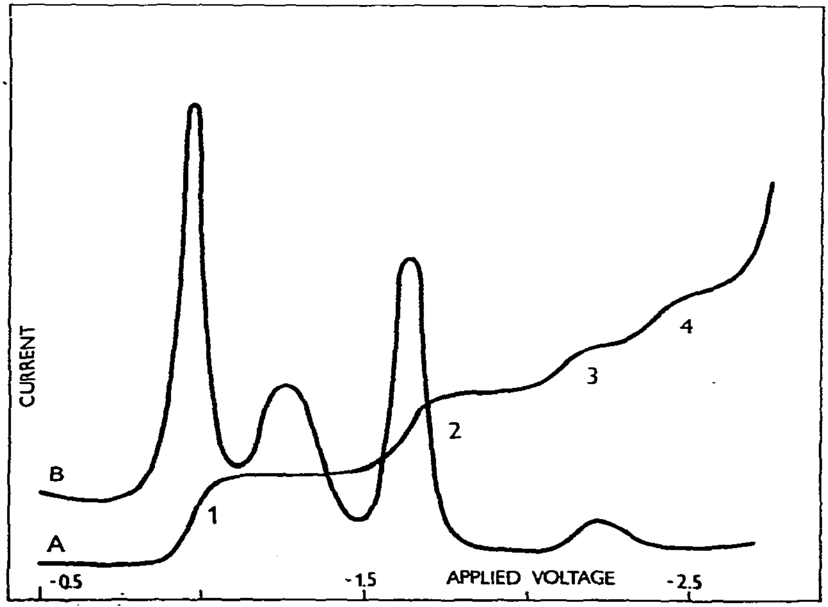

Fig. 1. Polarograms of $[Rh(PMI)cod]PF_6$ in acetonitrile (0.1 *M* TBAP). Curve A: DC-polarogram; Curve B: Phase-sensitive AC-polarogram. Out-of-phase component (frequency 80 Hz, peak-to-peak amplitude 15 mV).

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* Strictly anhydrous conditions have to be maintained during the experiments owing to the extremely high reactivity of the species in low oxidation states towards proton donors. Traces of the latters are sufficient to change dramatically the electrochemical picture. On the other hand, the water content also plays an important role in homogeneous catalytic processes (see for example refs. 3 and 4).

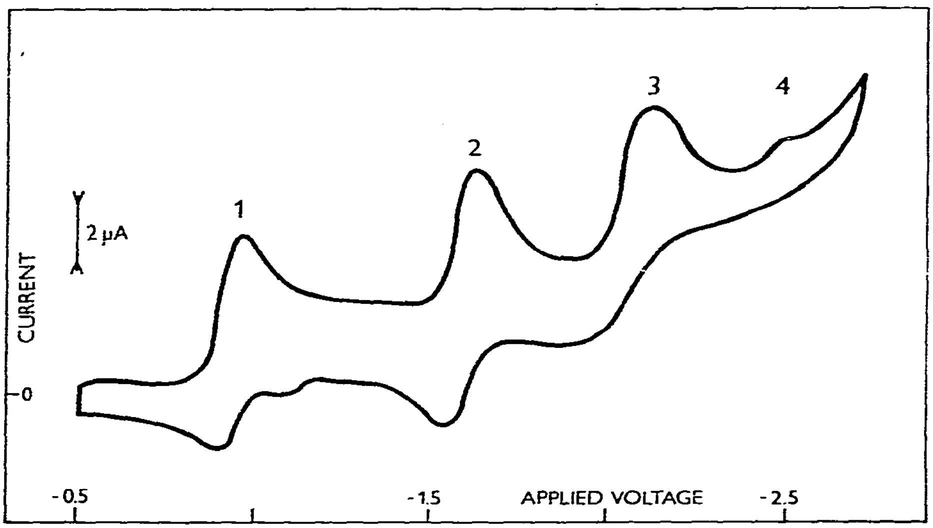

Fig. 2. Cyclic voltammogram (single-mode) of [Rh(PiPI)cod]PF$_6$ in acetonitrile (0.1 M TBAP) at stationary mercury electrode. Scan rate v = 0.0988 V/s.

reduction proceeds via two reversible one-electron steps, followed by one or two wholly irreversible steps (eq. 1)

$$[\mathrm{M(Chel)cod}]^{+} \overset{e^-}{\rightleftharpoons} [\mathrm{M(Chel)cod}] \overset{e^-}{\rightleftharpoons} \underset{\substack{\downarrow \\ \text{reductive side-reactions}}}{[\mathrm{M(Chel)cod}]^{-}} \qquad (1)$$

The first two waves are due to simple redox processes, without chemical side-reactions. Also the adsorption phenomena, evidenced by AC-polarograms (Fig. 1B) do not interfere with the behaviour at the mercury dropping electrode.

The reversibility of the first two steps was proved by logarithmic analysis of the polarographic waves. The slopes of nearly 60 mV (in agreement with the value for a reference compound under the same conditions) correspond well to polarographic reversible processes. Using rectangular polarography (Kalousek commutator [5]), commuted anodic polarographic waves with heights corresponding to a simple one-electron transfer reaction (in agreement again with the behaviour of the reference compound) were found for the above steps. Furthermore, when a constant potential, preceding the polarographic wave, was applied to the electrode during an electrolysis half-period, the increase of the limiting current for the commutated wave was equal to that of the limiting current of the anodic one. These results confirm the chemical stability of the new species with the metal atom in formal oxidation states 0 and —1, formed during the fast reversible multiple one-electron redox change at the electrode.

The reversible half-wave potentials depend mainly on the metal of the central atom, the iridium complexes being reduced at less negative potentials than the corresponding rhodium complexes.

At the stationary mercury electrode the processes are influenced by adsorption phenomena and chemical side-reactions. AC-polarography (Fig. 1B) shows

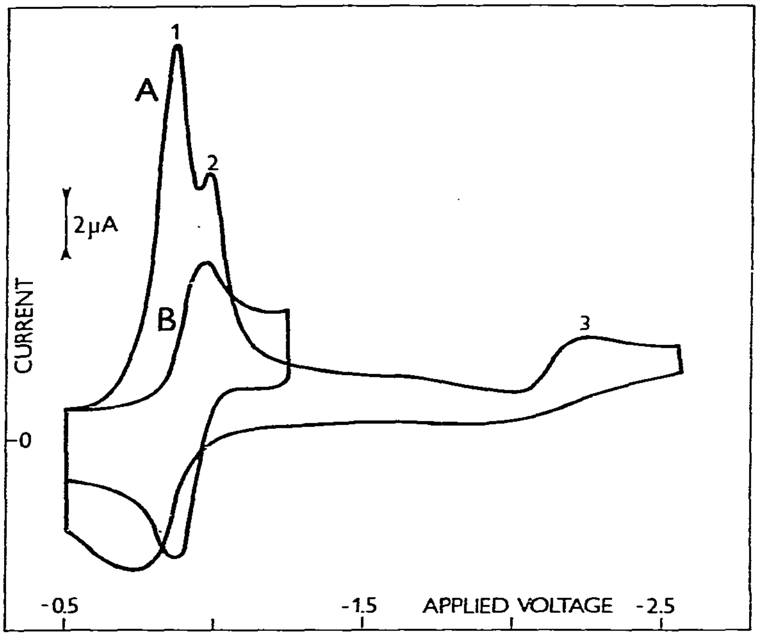

Fig. 3. Cyclic voltammogram (multi-mode) of [Rh(PMI)cod]PF_6 in acetonitrile (0.1 *M* TBAP), after one minute of cycling. Dependence of voltammetric picture on reverse potential: A: reverse potential E_λ = —2.6 V; B: reverse potential E_λ = —1.3 V. In A a new redox couple (1) is formed before the original (2).

an adsorption peak following the polarographic wave 1 (Fig. 1A), suggesting that an interaction between the electrode reaction product and the material of the electrode itself must be taken into account. This is reflected also in the different patterns of single- and multi-mode cyclic voltammograms. When the potential range is limited to the two former redox steps, the results agree (Fig. 3B) with those already described for the single-mode voltammetry (Fig. 2), but on extending the potential range to the next reduction step(s) the pattern changes dramatically (Fig. 3A). The redox process following the first two reversible waves is thus electrochemically wholly irreversible. Assuming that the third electron goes into a π-ligand centered orbital, the resulting species is unstable and tries to change to a more stable state through further chemical reactions. This mechanism of reduction was previously observed for similar complexes [1,6].

Electrooxidation

The oxidation of the complexes was studied in 0.1 *M* TBAP in dichloromethane (DCM) *. All the above complexes show only a single step with formation of the corresponding Rh^{II} and Ir^{II} complexes, which can be advantageously prepared by this electrochemical route. The reaction is reversible. The low slope values (Table 1) calculated from the logarithmic analysis of these polarographic oxidation waves, suggest the presence of catalytic processes at the electrode surface.

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* Oxidation does not occur in AN.

The electrochemical data of Table 1 call for some further comments.

The influence of the substituent R in the chelating ligand is evident. The reduction proceeds at more negative potential in the order PFEI < PMI < PiPI and exhibits a parallel trend for rhodium and iridium complexes. The substituent R also influences the electrooxidation process, but in this case the half-wave potentials of rhodium complexes are shifted towards more negative values and those of iridium derivatives in the opposite direction.

The difference between the half-wave potential for the oxidation process and the first reduction wave of the above complexes is nearly constant for the rhodium compounds, while for the iridium derivatives it increases with the donor power of R. Probably in the rhodium complexes the redox orbital has a more metal-centered character, while in iridium complexes, the redox orbital is more ligand-centered.

In general the electrochemical characteristic of bipyridine and pyridinal-R-imine complexes are similar, as expected in the light of the analogy in their chemical structure. For the new series, however, the differences between the reversible half-wave reduction potentials $E_{1/2}$ (1) — $E_{1/2}$ (2), is approximately 0.6 V, which is much higher than that for the analogous [M(bipy)cod]PF_6 complexes [1]. The lower value has been found for the PPEI derivative, which should thus be the strongest Lewis acid and the most active towards reducible substrates. Preliminary experimental results of homogeneous catalysis confirm this conclusion.

Experimental

The [M(Chel)cod]PF_6 complexes were synthesized as already described [2]. They were studied in AN (reduction process) and in DCM (oxidation process) in the presence of 0.1 *M* TBAP as supporting electrolyte. Reagent grade AN (Uvasol Merck), containing less than 0.1% water (K. Fischer), and DCM were further dried and purified by distillation from phosphorus pentoxide immediately before use. TBAP was prepared from tetrabutylammonium hydroxide and perchloric acid, recrystallized three times from water, dried under vacuum for five days at 60° C and stored over phosphorus pentoxide.

The instrumentation has been described previously [7]. The reference electrode was a calomel one (CE, Radelkis, Hungary) filled with aqueous 1 M lithium chloride. It was connected to the solution by a salt bridge, with a porous ceramic tip. The bridge was filled with 0.1 M TBAP in AN or DCM. Bis-(diphenyl)chromium iodide was used as a reference compound.

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