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# ELECTROCHEMISTRY OF COORDINATION COMPOUNDS

# XXIII *. RHODIUM(0): ELECTROGENERATION AND CHARACTERIZATION OF TETRAKIS(TRIISOPROPYL-PHOSPHITE)RHODIUM

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## Summary

Cyclic voltammetry on $[RhL_4]^+$ (L = triisopropylphosphite) in 1,2-dimethoxyethane has shown that the complex undergoes a two-electron reduction to $[RhL_4]^-$, which is reoxidized to $[RhL_4]^+$ in two separate one-electron steps. The intermediate $d^9$ species $[RhL_4]$ is a long-lived species to which a square-planar geometry has been assigned on the basis of the electronic and ESR spectra.

## Introduction

We have previously reported the production of zerovalent rhodium and iridium complexes with mixed carbonyl and triphenylphosphine ligands [1] and rhodium complexes with triphenylphosphine ligands only [2], by electroreduction of the relevant cationic precursors. The species are true monomeric $d^9$ complexes, a study on which had never previously been encountered with $\pi$-acceptor phosphorus ligands; some authors have claimed the formation of relatively long-lived $[(M(DPE)_2]$ (M = Rh, Ir; DPE = 1,2-bis(diphenylphosphino)ethane) [3,4], but we had previously found [5] and subsequently confirmed [6] that the product was the $d^{10}$ anion $[(M(DPE)_2]^-$, the $d^9$ intermediate being obtained only as a transient species (with a life of milliseconds) by pulse-radiolysis techniques [7]. Surprisingly, some workers in

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* For part XXII see ref. 24.

this field do not appear to have taken much notice of our results (see for instance ref. 8), in spite of the amount of evidence given. Thus, in order to widen the electrochemistry of this class of compounds and to provide knowledge of the factors that determine the relative stability of the rare and intriguing $d^9$ intermediates, we have extended our previous investigations to rhodium complexes with phosphites as ligands. We describe here the electroreduction of $[\mathrm{RhL_4}]^+$ (L = triisopropylphosphite) and the spectroscopic characterization of the long-lived species, $[\mathrm{RhL_4}]$, produced.

## Experimental

### *Chemicals and reagents*

The complex $[\mathrm{RhL_4}](\mathrm{BPh_4})$ (L = triisopropylphosphite) was prepared as previously described [9]. The purification of 1,2-dimethoxyethane (DME) and tetrabutylammonium perchlorate (TBAP) was as described previously [10]. All other chemicals were of reagent-grade quality and used as received.

### *Apparatus and procedure*

Experiments were performed under argon in DME containing the supporting electrolyte, TBAP, in 0.2 *M* concentration. The reference electrode was a silver/0.1 *M* silver perchlorate in acetonitrile ($-0.05$ V vs. $\mathrm{Fc/Fc^+}$ in DME 0.2 *M* TBAP), and the working electrode was a platinum disk (ca. 0.03 $\mathrm{mm^2}$) in voltammetry or a platinum gauze (ca. 100 $\mathrm{cm^2}$) in coulometry. Voltammograms with renewal of the diffusion layer (RDL) [11] were run at a renewal time of 2.0 s.

The instrumentation used has been described [1,2].

## Results and discussion

The cyclic voltammogram of $[\mathrm{RhL_4}]^+$ at 25 °C (Fig. 1a) shows a single reduction process at $E_{\mathrm{p,c}}$ $-1.75$ V (scan rate 200 mV/s) followed in the reverse scan by two peaks, at $-1.6$ ($E_{\mathrm{p,a(2)}}$) and $-1.35$ V ($E_{\mathrm{p,a(1)}}$), respectively. The reduction process involves two electrons per mol, as shown by a comparison of the limiting current value in RDL voltammograms with those for other complexes of known electrochemical stoichiometry [1,2]. The $E_{3/4} - E_{1/4}$ value for the RDL voltammogram and the $E_{\mathrm{p}} - E_{\mathrm{p/2}}$ value for the cyclic voltammogram indicate that the electron transfer is slow ($\alpha n_\alpha = 0.5$).

In controlled potential electrolysis, the colour of the solution initially turns from orange to deep blue, then, after the passage of about one electron per mol, the colour begins to fade, and a colourless catholyte is finally obtained (2e per mol). At this stage the complete cyclic voltammogram (full line in Fig. 1b) is exactly the opposite of the starting one, which points to the chemical reversibility of the electrochemical reduction (some losses take place when electrolysis is lengthy, mainly due to the presence of a little water in the medium, so that better results are obtained by performing the electrolysis at $-20$ °C and then raising the temperature). If, however, the scan is reversed before the second oxidation peak (dashed line in Fig. 1b), the observed response is that for a one-electron reversible oxidation ($E_2^0$ $-1.64$ V). As far as the subsequent oxidation is concerned, the RDL voltammo-

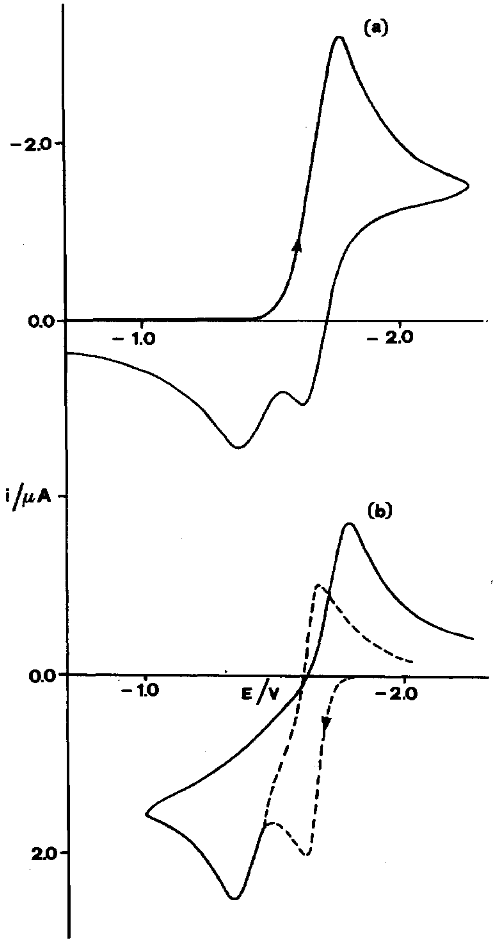


Fig. 1. Cyclic voltammogram on a platinum electrode of a $3\times10^{-3}$ *M* solution of $[RhL_4]^+$ in 0.2 *M* TBAP 1,2-dimethoxyethane before (a) and after (b) exhaustive reduction at −2.0 V. Temperature: 25° C. Scan rate: 0.2 V/s.

gram, consisting of two waves of the same height, shows that one electron is again involved, but the rate of the electron-transfer process is slow ($\alpha n_\alpha = 0.5$).

In order to establish whether the species produced in the two-electron reduction was the anion $[RhL_4]^-$, the spent catholyte was treated with proton donors. The fast reaction changes the voltammetric pattern into one similar to that displayed by hydrido complexes of formula $HML_4$(M = Co, Rh and Ir; L = phosphorus ligand) [12], consisting of a reversible one-electron oxidation ($E^0$ −0.5 V) and a further one-electron irreversible oxidation ($E_p$ ca. 0.1 V), which causes the appearance of the $[RhL_4]^+$ wave on the reverse scan. The product, isolated from the solution by evaporation of the solvent, extraction with toluene and reprecipitation with cold pentane, was identified as the known $HRhL_4$ [13].

From these results it appears that $[RhL_4]^+$ is reduced directly to $[RhL_4]^-$ (eq. 1), whereas $[RhL_4]^-$ is reoxidized to $[RhL_4]^+$ in two steps (eq. 2). The blue colour observed during electrolysis may be assigned to the intermediate zerovalent species, produced in a redox reaction between the anion diffusing from the electrode and the depolarizer (eq. 3).

$$[RhL_4]^+ \xrightarrow{2e} [RhL_4]^- \qquad (1)$$

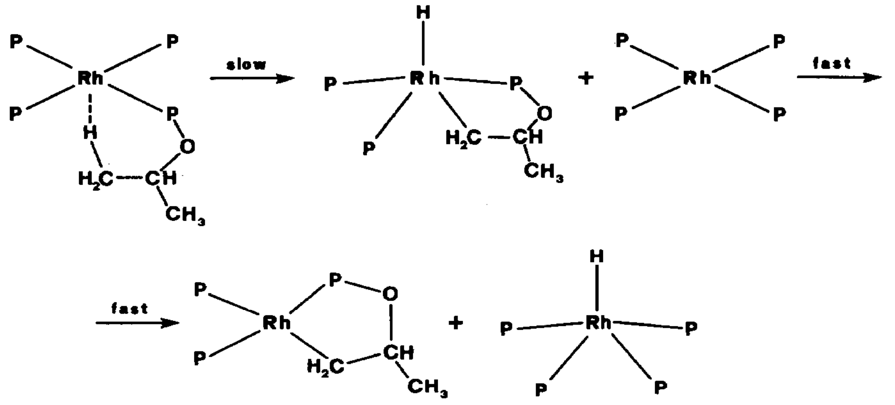
$$[RhL_4]^- \xrightarrow{1e} [RhL_4] \xrightarrow{1e} [RhL_4]^+ \qquad (2)$$

$$[RhL_4]^+ + [RhL_4]^- \rightarrow 2[RhL_4] \qquad (3)$$

According to this hypothesis $[RhL_4]$ must have a discrete existence. This implies that the formal redox potential for the $[RhL_4]^+/[RhL_4]$ couple is less negative than that for the $[RhL_4]/[RhL_4]^-$ couple. By use of the theoretical treatment developed by Ryan for two subsequent one-electron transfers, the first slow and merging with the second [14], it was possible to evaluate the standard potential for the first reduction of $[RhL_4]^+$ ($E_1^0$). This was accomplished using the experimental parameters $\alpha n_\alpha$, $E_{p,c}$, $E_{p,a(1)}$ and $E_2^0$ in eq. 4 and 20–25 of ref. 14.

The value of $E_1^0$ ($-1.49$ V) thus demonstrates as expected, and leads to an equilibrium constant of ca. 350 for the comproportionation reaction (eq. 3), which means that the neutral species must represent 90% of the species present in the equilibrium with its anionic and cationic counterparts.

The $d^9$ species was obtained by stopping the reductive electrolysis of $[RhL_4]^+$ after the passage of 1e per mol. However, the deep blue solution, which is quite stable at low temperatures ($-20\,^\circ$C), decays slowly at $25\,^\circ$C, following a first-order rate law ($k_{obs} = 8.5(\pm 0.5) \times 10^{-4}$ s$^{-1}$), from both amperometric and spectrophotometric techniques). Furthermore, the rate constant is independent of added phosphite up to a 0.5 $M$ concentration. The yellow solution ($\lambda_{max}$ 377 nm) obtained at the end of the decay shows the anodic pattern of the colourless $HRhL_4$, with current values corresponding to 50% of the starting rhodium content, and an ill-defined cathodic wave close to the solvent discharge ($E_{1/2}$ ca. $-2.8$ V). Although the rhodium compound responsible for both the reduction wave (the hydride is not reduced) and the yellow colour of the solution could not be isolated from the reaction mixture, it was identified as an organometallic species analogous to that



SCHEME 1

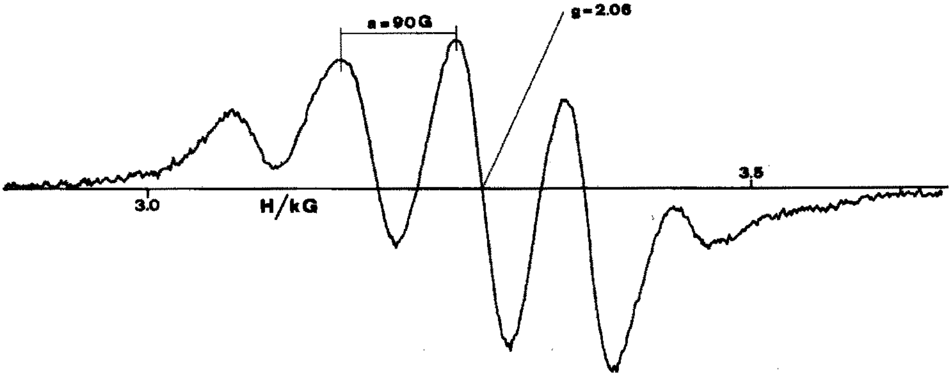


Fig. 2. ESR spectrum of [RhL$_4$] in 1,2-dimethoxyethane at 0 ° C.

obtained by elimination of $H_2$ from HRh[P(OPh)$_3$]$_4$, i.e. $(C_6H_5O)_2\dot{P}OC_6H_4\dot{R}h$-[P(OPh)$_3$]$_2$ [15], since bubbling of $H_2$ through the solution transformed it quickly into HRhL$_4$.

On the basis of these results the pathway of decay of [RhL$_4$] can be tentatively described as an intramolecular oxidative addition of C–H from a methyl group followed by a comparatively fast H-atom transfer to another [RhL$_4$] molecule (Scheme 1).

The spectral characteristics of the $d^9$ species are quite different from those of the analogous complexes Rh(CO)(PPh$_3$)$_3$ [1] and Rh(PPh$_3$)$_4$ [2]. [RhL$_4$] is blue, due to absorption at $\lambda_{max}$ 600 nm ($\epsilon$ 700 $M^{-1}$ cm$^{-1}$), in contrast with the phosphine containing analogues which are dark brown due to tailing of the UV-absorption into the visible region. Furthermore there is no $d \rightarrow d$ band in the near-infrared region 900–1100 nm, whereas such a band is observed for Rh(CO)(PPh$_3$)$_3$ [1], for zerovalent-cobalt phosphite complexes [16–18] and generally for $d^9$ compounds with tetrahedral geometry. The ESR spectrum (Fig. 2) shows a quintet ($g = 2.06$) consistent with coupling of the unpaired electron with four equivalent phosphorus nuclei ($a$ 90 G), which indicates that the ligands in [RhL$_4$] are in a square-planar geometry with the unpaired electron occupying the $d_{x^2-y^2}$ orbital [19]. In contrast, the tetrahedral analogues show a single signal with ill-resolved structure [1,2].

This structural difference may be rationalized on the basis of the steric requirements of the ligands. If we compare [RhL$_4$] with the triphenylphosphine analogue, we note that the cone angle of PPh$_3$ (145 °) is considerably higher than that of triisopropylphosphite (130 °) [20]. Thus the square-planar geometry, which would be seriously crowded for triphenylphosphine ligands, is available for the less bulky phosphite ligands. The angular overlap model predicts that for the four-coordinate $d^9$ electron configuration the geometry in which there is maximum ligand-hole overlap is not the tetrahedral but the square-planar arrangement [21]. Furthermore, $\pi$-back donation also favours square-planar over tetrahedral geometry, although to a lesser extent [22].

## Conclusions

The zerovalent adduct [RhL$_4$] reported here is a relatively long-lived species, and is one of the small number of members of the family of $d^9$ monomeric tetracoordinated complexes of rhodium containing phosphorus ligands; it is unusual having square-planar geometry.

In view of statements in refs. 3, 4 and 8, we must emphasize that the present electrochemical investigation confirms previous results [1,2,5,6,23] indicating that $d^8$ cationic complexes of rhodium whith phosphorus ligands are without exception reduced to the $d^{10}$ electron configuration, either directly or by steps, reversibly or irreversibly, in the large potential window offered by commonly used solvents (nitriles or ethers).

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