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Electrochemical Reduction of Chlorodi-(1,3-Bisdiphenylphosphinopropane)osmium(II) Hexafluorophosphate

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The d^7 configuration is rather rare among monomeric transition metal complexes, the known examples being most exclusively complexes of cobalt(II) which dictate the solution chemistry of these species. In particular the low-spin cobalt(II) complexes are labile to substitution in one or more axial positions and, in these positions, exhibit little affinity for binding of ligands [1]. In line with these results there has been found the chemistry of $[Rh(NH_3)_5Cl]^+$ generated by pulse radiolysis [1] and the chemistry of $RuCl(DPP)_2$ (DPP = 1,3-bisdiphenylphosphinopropane) electrochemically generated, suggesting that the axial lability could be a common feature to d^7 species.

With the aim to check this conclusion inside the iron triad it seemed to us appropriate to study the electrochemical reduction of $[OsCl(DPP)_2]^+$ and here we report the results.

Experimental

The osmium complex, $[OsCl(DPP)_2](PF_6)$, was prepared and purified according to the literature [3]. The other chemicals, 1,2-dimethoxyethane, tetrabutylammonium perchlorate (TBAP), tetrabutylammonium chloride (TBAC), were as previously described [2].

The apparatus and the technique which were involved in the use of the polarographic apparatus, controlled potential coulometry and cyclic voltammetry have also been described previously [2].

Results and Discussion

The electrochemical pattern of $[OsCl(DPP)_2]^+$ in 1,2-dimethoxyethane containing TBAP (0.1 *M*) is virtually identical with that found in the reduction of the related ruthenium complex [2]. Polarographic and cyclic voltammetric measurements indicate that $[OsCl(DPP)_2]^+$ undergoes an uncomplicated, reversible, one-electron step ($E_{1/2} = -0.84$ V *vs.* SCE) and a further reversible, one-electron transfer ($E_{1/2} = -1.45$ V) followed by a fast, irreversible, chemical reaction:

$$\begin{tikzcd}
{[OsCl(DPP)_2]^+} \arrow[r, shift left] \arrow[r, leftarrow, shift right, "1e"'] & OsCl(DPP)_2 \arrow[r, shift left] \arrow[r, leftarrow, shift right, "1e"'] & {[OsCl(DPP)_2]^-} \arrow[d] \\
 & & \text{products}
\end{tikzcd} \quad (1)$$

Controlled potential electrolysis on the plateau of the second wave requires two equivalents of electrons per mol of depolarizer and affords a pale yellow solution whose polarogram shows an anodic wave at -0.25 V attributed to free Cl^-. By evaporation of the solvent and subsequent extraction with toluene followed by addition of light petroleum a crystalline yellow product is obtained. Its IR spectrum (KBr disc) shows a hydride band at 2040 cm^{-1} and a further band at 730 cm^{-1} characteristic of an *ortho*-substituted benzene [4]. These results suggest that the chemical reaction following the electron transfer is:

$$[OsCl(DPP)_2]^- \longrightarrow Cl^- + HOs(C_6H_4PPh\cdot CH_2CH_2CH_2\cdot PPh_2)(DPP) \quad (2)$$

Elemental analysis and the known reaction of hydride complexes with CCl_4 confirm the proposed formulation.

Controlled potential electrolysis on the plateau of the first wave, while requiring one mol of electrons per mol of depolarizer, affords a blue, exceedingly air sensitive, solution which shows an absorption band at 485 nm with a shoulder at 710 nm and gives a strong ESR signal (frozen sample) pointing to the presence of one unpaired electron. With time a discharge of the colour is noted and the one-electron reduction product, *viz.* $OsCl(DPP)_2$, by analogy with the behaviour of the corresponding ruthenium complex [2], slowly undergoes a disproportionation reaction to yield $[OsCl(DPP)_2]^+$, $HOs(C_6H_4PPh\cdot CH_2CH_2CH_2\cdot PPh_2)(DPP)$ and Cl^-. However, the disproportionation rate of $OsCl(DPP)_2$, unlike that of $RuCl(DPP)_2$ [2], is not drepressed by the presence of an excess of TBAC and obeys a first order kinetic law ($k_{obs} = 1 \times 10^{-4}$ s^{-1} at 25 °C), meaning that in this case the loss of the chloride ligand is the rate determining step [2].

Once more it appears that the d^7 pentacoordinated species is characterized by the lability in the ligands. In this context the lability of Cl^- is in the order Os < Ru, suggesting that the five-coordinate d^7 complex is kinetically more stable in the third series in comparison with the second one. Similar results have already been reported for rhodium(II) and iridium(II) hydrido complexes [5].

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