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Preliminary communication

Electrochemistry of "piano-stool"-type pentamethylcyclopentadienyl-ruthenium complexes

I. Electrochemical generation of higher oxidation state ruthenium complexes in $(\eta^5\text{-}C_5Me_5)Ru(L)Cl_2$ (L = tertiary phosphines)

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Abstract

The electrochemistry of 17-electron $(\eta^5\text{-}C_5Me_5)Ru(L)Cl_2$ (L = tertiary phosphines) in CH_2Cl_2 shows an electrochemically reversible one-electron $Ru^{III/IV}$ oxidation and an irreversible one-electron $Ru^{III/II}$ reduction. The electrochemical behavior of $(\eta^5\text{-}C_5Me_5)Ru(L)Cl_2$ is strongly dependent on the nature of the solvent. The electrochemical oxidation of $(\eta^5\text{-}C_5Me_5)Ru(L)Cl_2$ in the presence of Cl^- first gives Ru^{IV} and then probably Ru^{V} complexes, viz. $(\eta^5\text{-}C_5Me_5)Ru(L)Cl_3$ and $[(\eta^5\text{-}C_5Me_5)Ru(L)Cl_3]^+$, respectively, which can be detected electrochemically.

Recently, dichloro(pentamethylcyclopentadienyl)ruthenium, $[(\eta^5\text{-}C_5Me_5)RuCl_2]_n$, was synthesized and soon became recognized as a useful starting complex in the preparation of a number of new Ru^{III} and Ru^{II} complexes [1]. In addition, the chemical oxidation of $[(\eta^5\text{-}C_5Me_5)RuCl_2]_n$ by halogen has been shown to give the Ru^{IV} organometallics, $[(\eta^5\text{-}C_5Me_5)RuX_3]_n$ (X = Cl, Br, and I) [2]. The bridge-splitting reaction of the halogeno-bridged Ru^{III} or Ru^{IV} complexes with a tertiary phosphine or carbon monoxide takes place to give a series of monomeric Ru^{III} and Ru^{IV} complexes such as $(\eta^5\text{-}C_5Me_5)Ru(PPh_3)Cl_2$ and $(\eta^5\text{-}C_5Me_5)Ru(PPh_3)Cl_3$. Since a variety of coordination environments around ruthenium are now available, we have embarked on a systematic electrochemical study of the $(\eta^5\text{-}C_5Me_5)Ru$ complexes. Up to now, electrochemical studies of $(\eta^5\text{-}C_5Me_5)Ru$ complexes have

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Table 1

Electrochemical data for oxidation and reduction of $(\eta^5\text{-}C_5Me_5)Ru(L)Cl_2$ in either the absence of or the presence of Cl^- at a platinum electrode at a scan rate of 100 mV s^{-1} [a]

L	Solvent	In the absence of Cl^- ion		In the presence of Cl^- ion [b]	
		Oxidation Process I [c]	Reduction	Oxidation Process II [c]	Oxidation Process III [c]
		$E_{1/2}$ (ΔE_p) (V (mV))	E_{pc} or $E_{1/2}$ (ΔE_p) (V (mV))	E_{pa} (V)	$E_{1/2}$ (ΔE_p) (V (mV))
PPh_3	CH_2Cl_2	+0.377(132)	−0.890(irr)	+0.360(irr)	+0.961(130)
	acetone	+0.347(100)	−0.807(206)		
	THF	+0.278(350)	−0.960(285)		
	CH_3CN	+0.141(125)	−0.750(irr)		
	DMF	+0.192(253)	−0.788(irr)		
P(*p*-tolyl)$_3$	CH_2Cl_2	+0.356(131)	−0.928(irr)	+0.319(irr)	+0.870(135)
PPh_2Me	CH_2Cl_2	+0.292(138)	−0.928(irr)	+0.288(irr)	+0.898(130)
PMe_3	CH_2Cl_2	+0.143(135)	−1.071(irr)	+0.139(irr)	+0.843(140)

[a] All potentials relative to the ferrocene/ferrocenium (Fc/Fc^+) couple. $E_{1/2}$ = calulated reversible half-wave potential, ΔE_p = peak-to-peak separation of the anodic and cathodic waves. E_{pc} or E_{pa} = peak potential for cathodic or anodic wave. irr = irreversible process. Supporting electrolyte. 0.1 mol dm^{-3} Bu_4NBF_4. [b] The addition of Cl^- to a solution of $(\eta^5\text{-}C_5Me_5)Ru(L)Cl_2$ in CH_2Cl_2 leaves the reduction process essentially unaltered. [c] See Fig. 1.

been scarce [3]. Here we report the electrochemistry of formally 17-electron $(\eta^5\text{-}C_5Me_5)Ru(L)Cl_2$ complexes (L = tertiary phosphines) in either the absence or presence of Cl^- ion.

The cyclic voltammogram for $(\eta^5\text{-}C_5Me_5)Ru(PPh_3)Cl_2$ (**1a**) in a CH_2Cl_2 solution containing 0.1 mol dm^{-3} Bu_4NBF_4 exhibits a reversible one-electron oxidation wave at $E_{1/2}$ +0.377 V vs. Fc/Fc^+ at the platinum electrode. The controlled-potential electrolysis of (**1a**) in CH_2Cl_2 leads to the formation of the cationic $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)Cl_2]^+$ in a clean one-electron process, which was monitored by rotating disk voltammetry. On the other hand, the irreversible reduction process is observed at E_{pc} −0.890 V vs. Fc/Fc^+ in CH_2Cl_2. The value of cathodic limiting current of the rotating disk voltammogram is the same as that of the anodic limiting current under the same conditions, which confirms that this reduction process is one of a diffusion-controlled one-electron transfer. The oxidation potential is strongly dependent on solvent; the potential is shifted towards more positive potentials in the order CH_2Cl_2 > acetone > THF > DMF > CH_3CN (Table 1). The degree of potential shift reflects the donor ability of solvents, suggesting that the solvent may weakly interact with the ruthenium ion. When the phosphine ligand L in $(\eta^5\text{-}C_5Me_5)Ru(L)Cl_2$ is changed, the oxidation potential is shifted more towards negative potentials in the order L = PPh_3 < P(*p*-tolyl)$_3$ < PPh_2Me < PMe_3, as expected for increasing the electron donating properties of L (Table 1).

The addition of substoichiometric amounts of Cl^- to a CH_2Cl_2 solution of $(\eta^5\text{-}C_5Me_5)Ru(P(p\text{-tolyl})_3)Cl_2$ (**1b**) causes the wave at $E_{1/2}$ = +0.356 V (process I) to disappear, and a new oxidation wave appears at E_{pa} +0.319 V (process II) and $E_{1/2}$ +0.870 V vs. Fc/Fc^+ (process III) as shown in Fig. 1. An irreversible and a quasireversible one-electron oxidation (II and III in Fig. 1) are observed when roughly one equivalent of Cl^- is added to the solution.

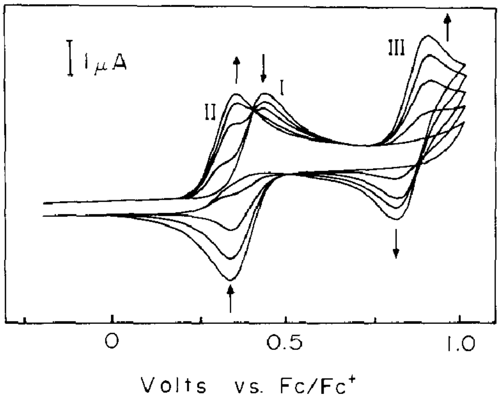

Fig. 1. Cyclic voltammograms of 0.48 mmol dm^{-3} complex (**1b**) in CH_2Cl_2/0.1 mol dm^{-3} Bu_4NBF_4 with varying concentrations of Et_4NCl. [Et_4NCl] 0, 0.13, 0.26, 0.39 and 0.52 mmol dm^{-3}. Scan rate 100 mV s^{-1}.

Bulk electrolysis of **1b** in CH_2Cl_2 at +0.5 V in the presence of Cl^- generates a brown solution, in which only the wave at +0.870 V is observed. This oxidation potential coincides with that of the Ru^{IV} complex, $(\eta^5\text{-}C_5Me_5)Ru(P(p\text{-tolyl})_3)Cl_3$ (**2b**), which can be separately prepared by the oxidation of **1b** by chlorine [2]. Thus, a formally Ru^V complex, $[(\eta^5\text{-}C_5Me_5)Ru(P(p\text{-tolyl})_3)Cl_3]^+$, can be electrochemically generated by the second oxidation, process **III**. Similar electrochemical behavior brought on by the addition of Cl^- is observed for the other $(\eta^5\text{-}C_5Me_5)Ru(L)Cl_2$ type complexes in CH_2Cl_2. Up to now attempts to isolate this Ru^V complex by oxidative electrolysis at +1.0 V have failed.

There are two mechanisms possible for interpreting the electrochemical oxidation behavior viz. (a) an ECE mechanism, or (b) an E-C_e-EC_{irr}E mechanism (Scheme 1). Digital simulations of the voltammograms in Fig. 1 have been carried out for both mechanisms [4]. Only the E-C_e-EC_{irr}E mechanism reproduces the observed cyclic voltammetric pattern, and in particular the isopotential point. Furthermore, the UV spectrum of **1a** in CH_2Cl_2 shows a small increase in absorbance at 415 nm upon addition of Cl^-. Similar changes in the absorption spectra are observed for complexes (**1b**–**1d**), which reveals the existence of the chemical equilibrium between **1** and Cl^-. Thus, equilibrium of the 17e complex (**1**) with the 19e complex $[(\eta^5\text{-}C_5Me_5)Ru(L)Cl_3]^-$ (Complex **A** in Scheme 1) is probably involved. Recently, rapid 17e/19e interconversion was reported for several systems such as the equilibration between the η^1-dppe(17e) and η^2-dppe(19e) complex in $(\eta^5\text{-}C_5Me_5)Fe(dppe)(CO)CH_3]^+$ (dppe = 1,2-bis(diphenylphosphino)ethane) [5]. The strong solvent effect on the oxidation potential of complex **1** described above can be also rationalized by this 17e/19e interconversion. In order to explain the electrochemical irreversibility for process II, the chemical step (**B** → **2**) in Scheme (1b) in the E-C_e-EC_{irr}E mechanism is probably accompanied by a structural rearrangement although little information about the structures of complexes **A** and **B** has been available at present *.

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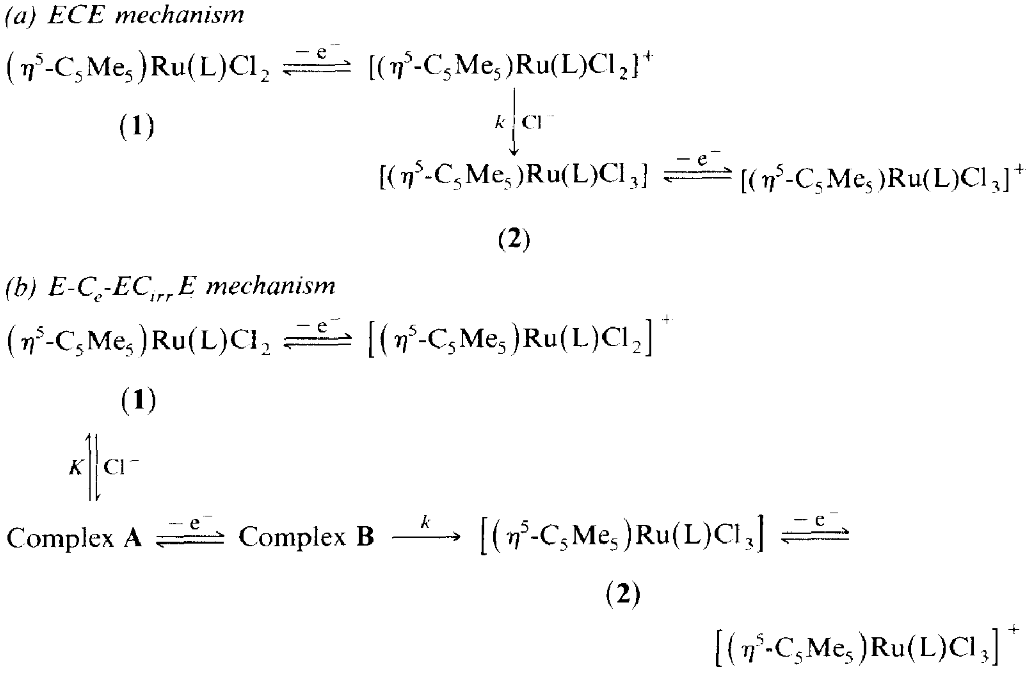
* It seems most plausible that the conversion from the "trigonal bipyramid" to the "four-legged piano stool"structure is involved.



(a) ECE mechanism

$$\begin{tikzcd}
(\eta^5\text{-}C_5Me_5)Ru(L)Cl_2 \ \mathbf{(1)} \arrow[r, shift left, "-e^-"] & {[(\eta^5\text{-}C_5Me_5)Ru(L)Cl_2]^+} \arrow[l, shift left] \arrow[d, "k"', "Cl^-"] & \\
& {[(\eta^5\text{-}C_5Me_5)Ru(L)Cl_3]} \ \mathbf{(2)} \arrow[r, shift left, "-e^-"] & {[(\eta^5\text{-}C_5Me_5)Ru(L)Cl_3]^+} \arrow[l, shift left]
\end{tikzcd}$$

(b) E-C_e-EC_{irr}E mechanism

$$\begin{tikzcd}
(\eta^5\text{-}C_5Me_5)Ru(L)Cl_2 \ \mathbf{(1)} \arrow[r, shift left, "-e^-"] \arrow[d, shift left, "Cl^-"] & {[(\eta^5\text{-}C_5Me_5)Ru(L)Cl_2]^+} \arrow[l, shift left] & & \\
\text{Complex } \mathbf{A} \arrow[u, shift left, "K"] \arrow[r, shift left, "-e^-"] & \text{Complex } \mathbf{B} \arrow[l, shift left] \arrow[r, "k"] & {[(\eta^5\text{-}C_5Me_5)Ru(L)Cl_3]} \ \mathbf{(2)} \arrow[r, shift left, "-e^-"] & {[(\eta^5\text{-}C_5Me_5)Ru(L)Cl_3]^+} \arrow[l, shift left]
\end{tikzcd}$$

Scheme 1.

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