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Electrochemistry of organometallic halide complexes III*. Oxidation of $[C_6Me_6RuCl_2]_2$

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Abstract

The oxidative electrochemistry of $[(HMB)RuCl_2]_2$ (**1**) (HMB = η^6-C_6Me_6) reveals the formation of an Ru^{III} arene complex $(HMB)RuCl_3$ (**2**). It is shown that the corresponding anion $[(HMB)RuCl_3]^-$ (**2**$^-$) is present in an equilibrium in CH_2Cl_2 solution of **1**. Complex **2** is prepared by chlorination of **1** as the first arene complex of Ru^{III}.

Key words: Electrochemistry; Ruthenium complexes; Hexamethylbenzene complexes; Halide complexes

Introduction

Organometallic halide complexes, composed of a transition metal bearing an aromatic π-cyclic ring and halide ligands, similar to some transition metal halide clusters [2], often change their coordinative environment when subjected to a change in oxidation state. Reactions encountered are loss of halide concurrent with reduction, in many cases accompanied by addition of a neutral ligand L. Conversely, uptake of halide ion on oxidation along with monomer oligomer interconversion by formation and cleavage of halide bridges is frequently observed [3]. Cyclic voltammetry has proven particularly valuable in elucidating the course of such reactions and in the case of $[Cp^*RhCl_2]_2$, for example, has led to identification of a novel, isolable Rh^{II} dimer [1, 4].

In view of the known ability of Ru to form organometallic complexes in higher oxidation states (+III [5] and +IV [6]) we considered it worthwhile to look at the oxidation chemistry of $(arene)RuX_2$ complexes, a class of compounds from which an extended and diverse substitution chemistry at the metal derives [7] similar to the isoelectronic $Cp^{(*)}RhX_2$ analogues. Reductive electrochemistry of $[(arene)RuCl_2]_2$ has been thoroughly investigated [8] but oxidation has not been explored. The hexamethylbenzene derivatives seemed most suited for this purpose since the methylated ligand restricts the range of possible oligomers to dimers. Moreover, the electron releasing effect of the methyl groups should be most effective in stabilizing higher oxidation states.

Results

Cyclic voltammetry

When a solution of $[(HMB)RuCl_2]_2$ (**1**) is scanned anodically in CH_2Cl_2 from 0 to 1.8 V versus SCE[†] (Fig. 1(a)), two oxidation peaks, P1 and P2, and two to three reduction peaks, P1′, P2′ and P3, are seen depending on scan rate and temperature. At ambient temperature and a scan rate <200 mV/s the first oxidation peak P1 at about 1.12 V is totally irreversible. The associated reduction P1′ gradually appears with increasing scan rate and when cooling the solution to −20 °C. Peak separation is 70 mV for $v = 1000$ mV/s at ambient temperature. This first oxidation/reduction couple is followed by a second one P2/P2′ of about equal height at 1.65 V, which is only partly reversible even at scan speeds of several V/s, Fig. 1(b). A reductive peak P3 with peak potential of 0.7 V appears all the more intense the more irreversible the oxidation at either P1 or P2 is found and is thus the competitive product

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*Part II is ref. 1.

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[†] Aqueous SCE separated from the solution by a frit. Ferrocene$^{+/0}$ is +0.39 V SCE.

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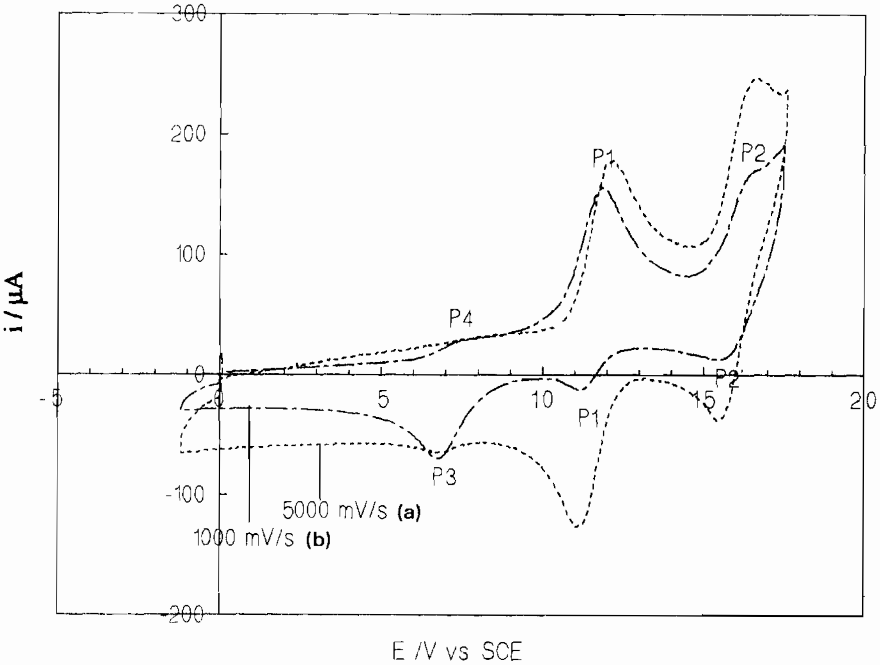


Fig. 1. Cyclic voltammogramm of $[(HMB)RuCl_2]_2$ (1), 10^{-3} M in CH_2Cl_2/Bu_4NPF_6.

from the cations formed in these processes. The reduction at P3 is irreversible as shown by scan reversal after passing through this peak.

In the cathodic region an irreversible reduction is seen with a peak potential of −1.16 V (100 mV/s) as observed previously [8] and which is assigned to the formation of a mixed valence Ru^{II}/Ru^{I} species.

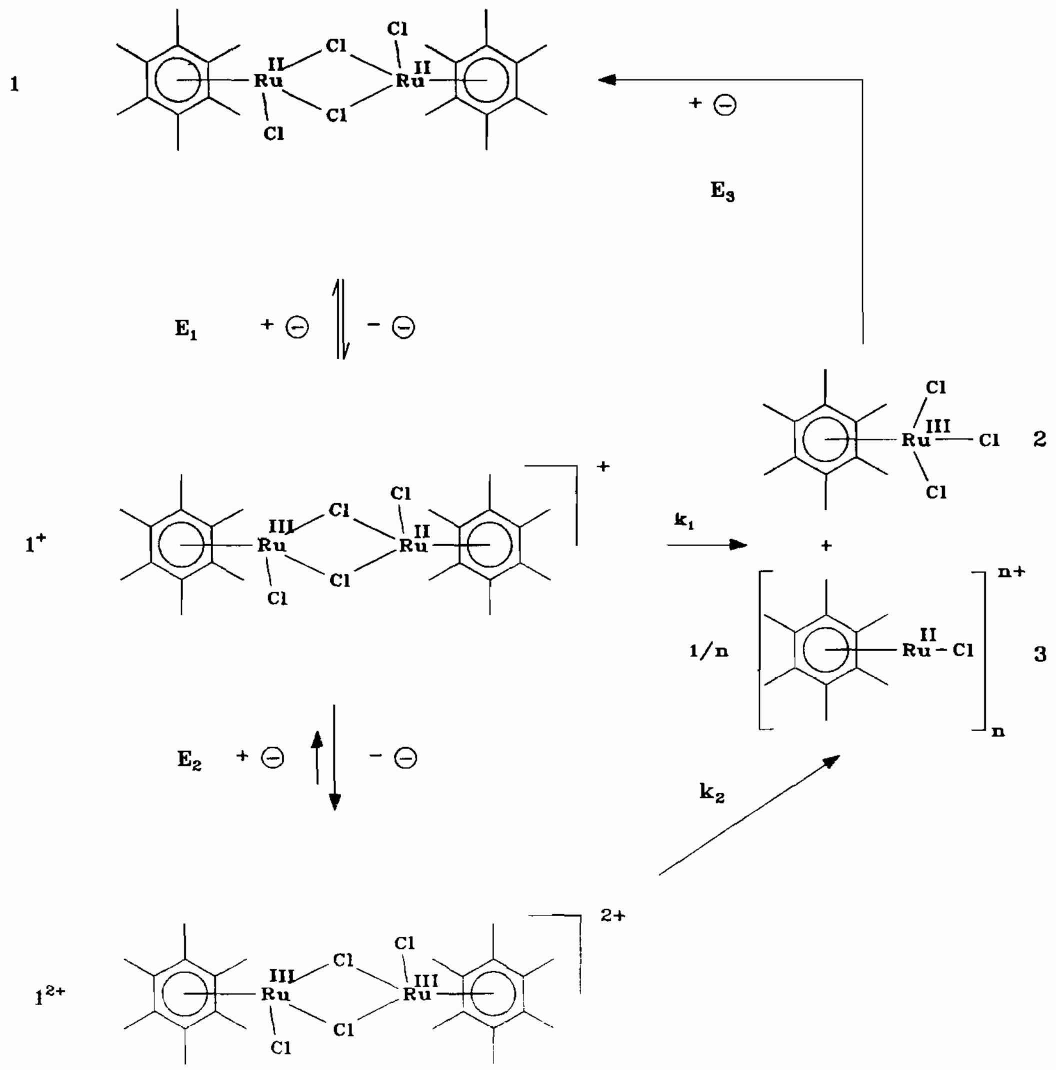
Reactions summarized in Scheme 1 are proposed to represent the oxidative pattern: the oxidation of **1** in two equal steps, where the first one at potential E_1 is more and the second one at E_2 is less reversible, can be understood as the formation of a dinuclear mixed valence cation $\mathbf{1}^+$ and a corresponding dication $\mathbf{1}^{2+}$. Both species are medium to short lived on the cyclovoltammetric time scale. The return peak P3 occurs at more negative potential than either oxidation and should thus belong to a structurally different species. A monomeric neutral complex **2** is proposed to be formed in a follow-up reaction of either $\mathbf{1}^+$ or $\mathbf{1}^{2+}$, which is further reduced at P3. The formation of **2** from $\mathbf{1}^{2+}$ is faster than from $\mathbf{1}^+$ ($k_2 > k_1$ in Scheme 1) as evidenced from the poorer reversibility of the pair P2/P2′.

If **2** is formed by disproportionation from $\mathbf{1}^+$, for example, the second component must have the composition $(HMB)RuCl^+$ and should stabilize as an oligomer. A tetramer $[HMBRuCl]_4^{4+}$, analogous to the known hydroxo complex $[(HMB)RuOH]_4^{4+}$[9] or the hydride $[(HMB)RuH]_4^{4+}$ [10] and closely related to the neutral tetramers $[Cp^*RuX]_4$, X = Cl [11], OH [12], appears as a plausible option.

The irreversibility of the reduction of **2**, P3, is traced back to rapid loss of Cl^- from the primary reduction product $\mathbf{2}^-$ and ensuing dimerization to reform **1**, as depicted in Scheme 2.

Cyclic voltammograms at slow scan speed exhibit in addition a small oxidation peak P4 at a potential that relates this peak to P3. In fact, slow scans with high amplification show the presence of a quasi reversible pair P3/P4. Note that the intensity of P3 under these conditions is much less than after a passage through P1 or P2. P4 then should be the oxidation of the trichloro Ru^{II} anion $\mathbf{2}^-$ which then must be present initially in the solution in small concentration. A pre-equilibrium with ionization of **1** into $\mathbf{4}^+\mathbf{2}^-$ as depicted in Schemes 2 and 3 can be envisaged to explain the occurrence of peak P4 in the cyclic voltammograms. At slow scan rate there is sufficient time for this equilibrium to shift towards the ion pair leading to relatively higher intensity of P4 than with more rapid scans. A similar equilibrium but with simple Cl^- as the anion was suggested by Mugnier and co-workers [8] in their study of the reduction of $[(arene)RuCl_2]_2$. Oxidative scans, however, establish $\mathbf{2}^-$ as the anionic component in the present case.

The above suggestions are substantiated by the following experiments. The CV pattern drastically changes if excess chloride, in the form of triethylbenzylammonium chloride (TEBACl), is added to the CH_2Cl_2 solution. The sweep under these conditions can only be extended to about 1 V, thus P1/P1′ as well as P2/



Scheme 1.

P2′ are masked by the onset of Cl^- oxidation to Cl_2. A chemically reversible pair, as shown in Fig. 2, is now seen at an apparent $E_{1/2}$ value of 0.56 V* corresponding to P3/P4 in the previous case. This means that the trichloro anion $\mathbf{2}^-$ must be formed to a larger extent under these conditions. Cleavage of **1** by excess Cl^- to give $\mathbf{2}^-$ (lower reaction in Scheme 3) accounts for this observation.

The irreversible cathodic peak with a peak potential of −1.16 V (100 mV/s) has completely disappeared in the presence of Cl^- ion. Since from absorption spectra (see below) it is clear that even in the presence of excess Cl^- an appreciable part of the complex should still be present as **1**, the reduction must be attributed to the cation $\mathbf{4}^+$. In the presence of excess Cl^- the upper equilibrium in Scheme 3 is shifted towards neutral **1**, thus $\mathbf{4}^+$ is no longer present in solution.

To obtain independent evidence for the equilibria of Scheme 3 we have measured concentration dependent conductivities and absorption spectra. The conductivities of two solutions (4×10^{-3} and 8×10^{-4} M in CH_2Cl_2) were only slightly above the level of the pure solvent, indicating a rather small extent of ionization in CH_2Cl_2. Also the absorption spectra show no concentration shifts and reasonably obey Beers law. However, band shifting and changes in absorption of a solution of **1** on addition of excess TEBACl as shown in Fig. 3 clearly indicate the formation of a new species, notably $\mathbf{2}^-$.

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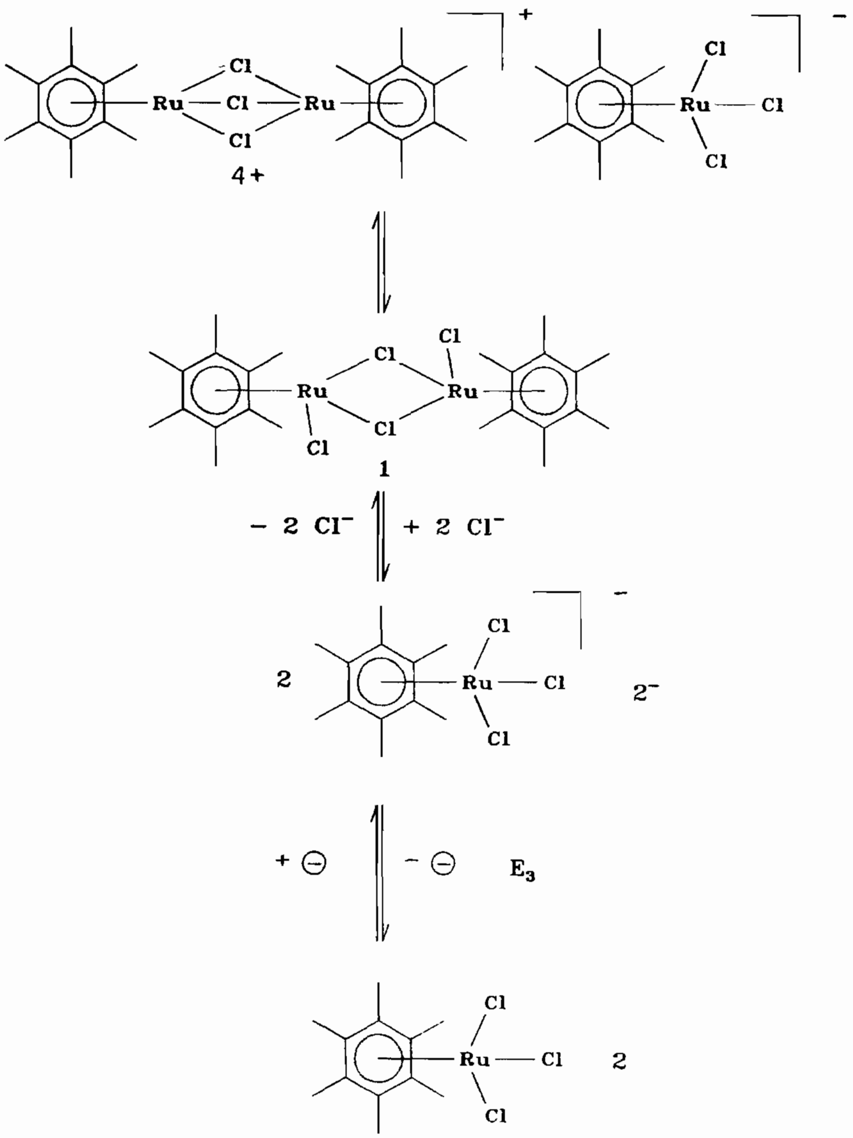
*The potential scale of an SCE shifts to more positive values on addition of excess chloride. From these potentials read in the presence of chloride about 150 mV has to be subtracted to convert them to those of the CH_2Cl_2/Bu_4NPF_6 solution.



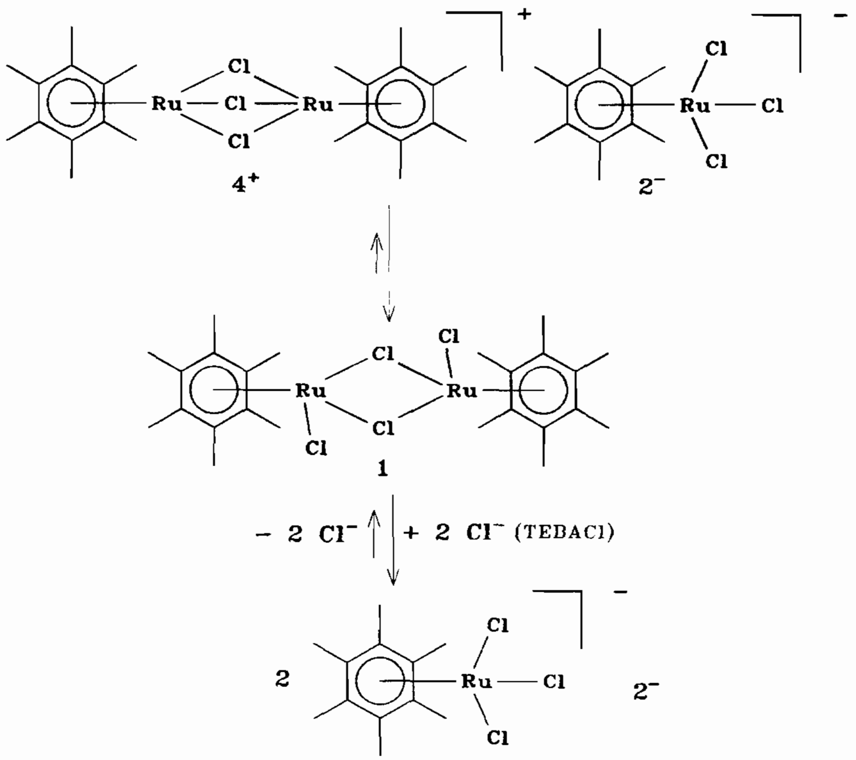
Scheme 2.

The cyclic voltammogram of isolated complex **2** (see below) in CH_2Cl_2 is depicted in Fig. 4. A scan started at 0.8 V in the anodic direction shows no oxidation up to 1.6 V where the decomposition of the electrolyte starts. In the cathodic direction peak P3 is now the only one present and on the return sweep the couple P1/P1′ appears as a follow-up product of the reduction of **2**, thus closing the cycle. Again a fully reversible pair with apparent $E_{1/2} = 0.805$ V and $\Delta E_p = 65$ mV develops in the presence of TEBACl.

These experiments fully confirm the assignments made for the peaks observed in the oxidation of **1**. It establishes the novel Ru^{III} complex as the oxidation product of **1**, which forms quantitatively on electrochemical oxidation in the presence of excess Cl^- ion.

Chemical oxidation of $[(HMB)RuCl_2]_2$ to $(HMB)RuCl_3$

Oxidation of **1** with Cl_2 gives access to the compound **2**. Treatment of a suspension of **1** in CH_2Cl_2 with chlorine gas at ambient temperature causes dissolution of the material to a dark red solution. The ^1H NMR spectrum of the red microcrystals isolated after precipitation with pentane shows a broad ($\Delta\nu$ 80 Hz) methyl resonance at about 20 ppm. We have observed similar chemical shifts for the methyl resonances of the C_5Me_5 ligand in monomeric $C_5Me_5Ru^{III}$ complexes [5]. An EPR spectrum was obtained in frozen CH_2Cl_2 and exhibited g values of 4.4, 2.78 and 2.17. The IR spectrum between 3000 and 600 cm^{-1} closely resembles that of the starting material showing bands of the HMB



Scheme 3.

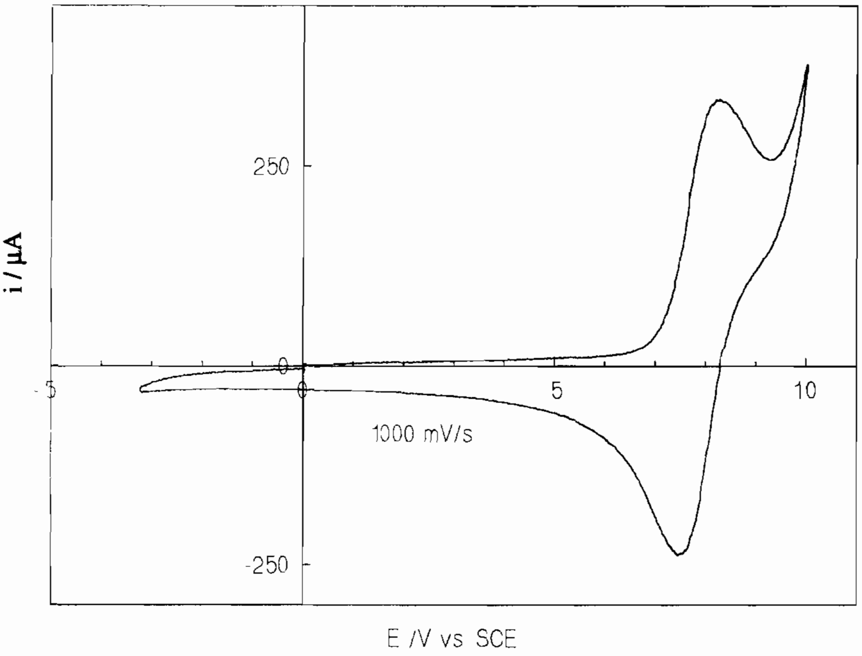


Fig. 2. Cyclic voltammogramm of $[(HMB)RuCl_2]_2$ (1), 10^{-3} M in CH_2Cl_2/Et_3BzNCl.

ligand in about equal intensity but shifted to variable amounts. At lower frequency in the CsI region two new bands at 326 and 301 cm^{-1} are seen which are attributed to Ru–Cl stretching modes of a $RuCl_3$ group.

Compound **2** is soluble in CH_2Cl_2 and $CHCl_3$ and reacts with base (pyridine) to give unknown products. It is reasonably stable as a solid but decomposes in solution at room temperature within some hours, obvious

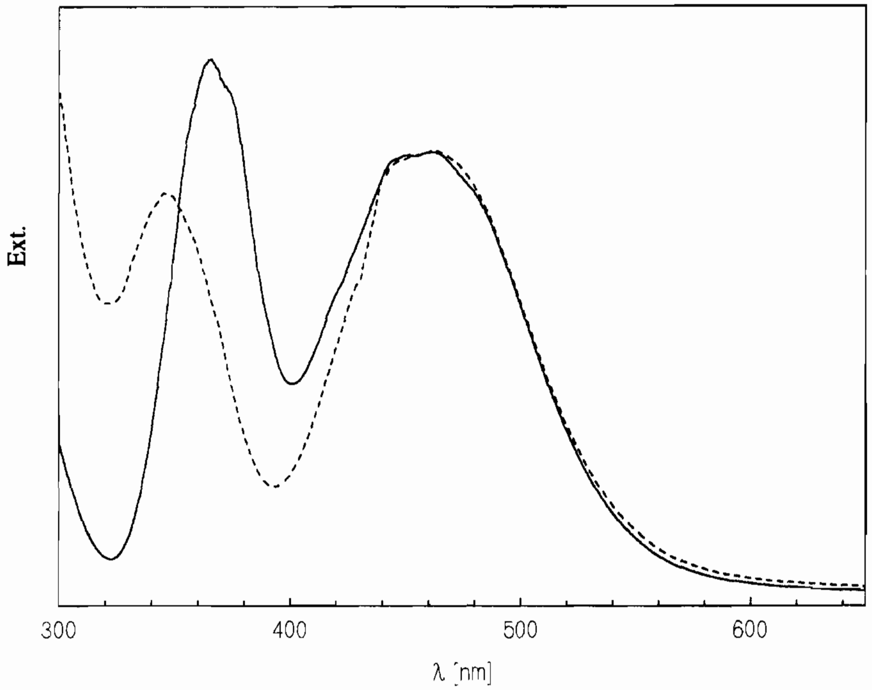


Fig. 3. Absorption spectrum of $[(HMB)RuCl_2]_2$ (**1**), 1.5×10^{-3} M (1 cm) in CH_2Cl_2. —— without, ---- with excess Et_3BzNCl (TEBACl).

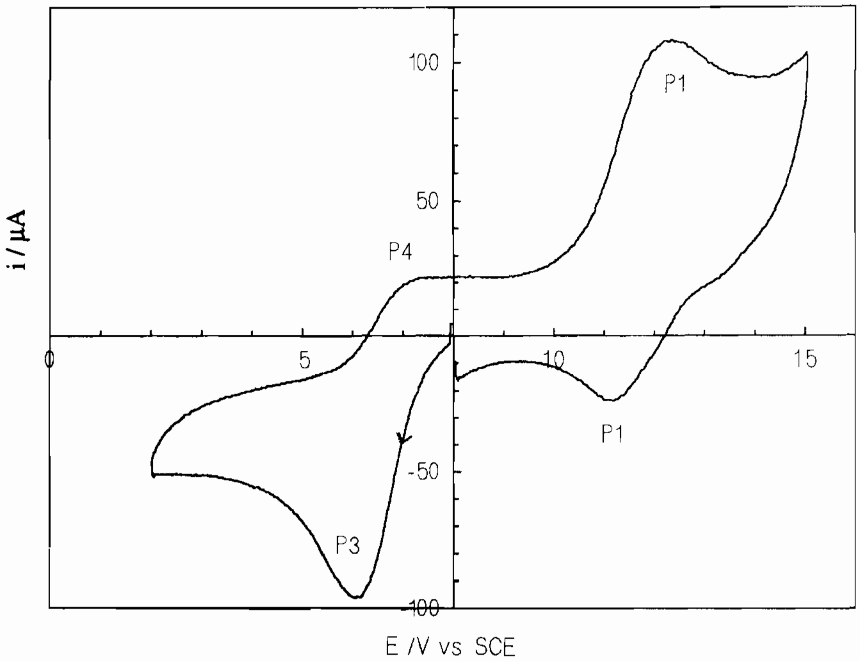


Fig. 4. Cyclic voltammogramm of $(HMB)RuCl_3$ (**2**), 10^{-3} M in CH_2Cl_2/Bu_4NPF_6, $\nu=1000$ mV/s

by a color change and changes in the cyclic voltammogram. After prolonged storing at ambient temperature the starting complex **1** was eventually recovered.

Experimental

300 mg (0.9 mmol Ru) $[(HMB)RuCl_2]_2$ were suspended in 10 ml of dichloromethane. On adding an excess of Cl_2, the material dissolved immediately with formation of a deep red solution. After 1 h at ambient temperature were added 30 ml of pentane. A dark red powder precipitated which was washed with pentane and dried *in vacuo*. Yield 320 mg (97%). MS (70 eV) *m/z* (%): 369 (20, M^+), 334 (25, $M-$Cl), 299 (35, $M-$2Cl), 263 (50, (HMB)Ru-H), 162 (100, HMB). *Anal.*

Calc. for $(HMB)RuCl_3CH_2Cl_2$ (454.6): C, 34.34; H, 4.43. Found: C, 34.80; H, 4.31%.

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