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Electrochemical generation of 19- and 20-electron rhodocenium complexes and their properties

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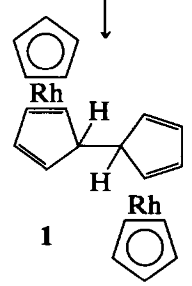
Abstract

The electrochemical reduction of the rhodocenium salts $[Rh(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}L)]^+PF_6^-$ ($\mathbf{2}^+$, $L = C_5H_5$; $\mathbf{3}^+$ $L = C_5Me_5$; $\mathbf{4}^+$ $L = C_9H_7$) has been studied by cyclic voltammetry. All three complexes ($\mathbf{2}^+$–$\mathbf{4}^+$) are reduced in two one-electron processes, first to the 19-electron radicals (**2**–**4**) and then to the 20-electron anions ($\mathbf{2}^-$–$\mathbf{4}^-$). When complex $\mathbf{2}^+$ was reduced in bulk (Na–Hg in THF) the dinuclear complex, $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}\eta^4:\eta^4\text{-}C_5Me_5\text{-}C_5H_5)Rh(\eta^5\text{-}C_5Me_5)]$ (**6a**), obtained by dimerization of **2**, was isolated as sole product. Analogous reduction of $\mathbf{3}^+$ gave the η^4-pentamethylcyclopentadiene complex, $[Rh(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5Me_5H)]$ (**7**). Reduction of $\mathbf{4}^+$ leads to formation of a stable radical **4**.

1. Introduction

Nineteen-electron complexes play an important role in a wide range of organometallic reactions [1,2]. However the factors that influence their reactivity and stability are only partly understood. One difficulty is that great differences in stability and reactivity are often observed even for structurally similar isoelectronic complexes, thus complicating the prediction of the properties and reactivities of such compounds. For example, cobaltocene, $[Co(\eta^5\text{-}C_5H_5)_2]$, is quite stable, while rhodocene, $[Rh(\eta^5\text{-}C_5H_5)_2]$, could only be characterized by ESR-spectroscopy and cyclic voltammetry at low temperature [3,4] since it dimerized to **1** on warming [5], eqn. (1).

$$[(C_5H_5)_2Rh]^+ \xrightarrow{+e} [(C_5H_5)_2Rh] \longrightarrow [(C_5H_5)_2Rh]^- \quad (1)$$



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Modification of the π-ligands, for example by the introduction of alkyl substituents at the ring, also substantially modifies the behavior of such complexes [6]. In this paper we report a study of the electrochemistry of the rhodocenium salts $[Rh(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}L)]^+ PF_6^-$ ($\mathbf{2}^+$ $L = C_5H_5$, $\mathbf{3}^+$ $L = C_5Me_5$, $\mathbf{4}^+$ $L = C_9H_7$) which differ only in the structure of one π-ligand, and which

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sheds new light on the behaviour of the 19-electron radicals **2**–**4**.

2. Results and discussion

Like rhodocenium itself, the complexes $\mathbf{2}^+$–$\mathbf{4}^+$ are reduced in two one-electron processes. This is shown by the similarity of the heights of the two cathodic peaks in the cyclic voltammograms to those of cobaltocenium (at the same concentration, as reference) and also by coulometry data. The cyclic voltametric peak potentials are very similar on both Hg and Pt electrodes, showing that the electrode material does not participate in the reduction process. As may be expected, the reduction potentials of the methyl-substituted complexes, $\mathbf{2}^+$ and $\mathbf{3}^+$ are more negative (by 30–60 mV for each methyl group) by comparison with rhodocenium, $[Rh(\eta^5\text{-}_5H_5)_2]^+$, $\mathbf{5}^+$. The differences in peak potentials of the first and the second reduction processes (0.8–1.0 V) are very similar for complexes $\mathbf{2}^+$–$\mathbf{4}^+$.

These data show that complexes $\mathbf{2}^+$–$\mathbf{4}^+$, like $\mathbf{5}^+$, are able to add two electrons sequentially to give, first, the 19-electron radicals and then the 20-electron anions. The stability of the radicals and of the anions was evaluated by a comparison of the ratio i_{pa}/i_{pc} (ratio of anodic to cathodic current for the redox couple; Table 1), which showed that the stability of the radicals increases in the order **2** < **3** < **4**.

2.1. The electrochemical reduction of pentamethylrhodocenium, $\mathbf{2}^+$, to give $[Rh(\eta^5\text{-}C_5H_5)(\mu\text{-}\eta^4:\eta^4\text{-}C_5Me_5\text{-}\eta^4\text{-}C_5H_5)Rh(\eta^5\text{-}C_5Me_5)]$, 6a

We find that, i_{pa} and i_{pc} become equal, and the reduction is reversible only at −35°C for pentamethylrhodocenium $\mathbf{2}^+$ at a Pt-electrode; similar results have been reported for rhodocenium $\mathbf{5}^+$ itself [5]. By contrast, the anodic oxidation peak of $\mathbf{2}^-$ could not be observed, even at −70°C, showing $\mathbf{2}^-$ to be less stable than $[Rh(\eta^5\text{-}C_5H_5)_2]^-$. The height of the anodic oxidation peak of the 19-electron **2** (Fig. 1) decreases with increasing temperature, and a new peak appears, the height of which increases with increase in temperature. This anodic peak may be attributed to the oxidation of the product of the chemical transformation undergone by **2**.

TABLE 1. Cyclic voltammetry data for rhodim compounds (200 mV s^{-1}, $c = 2 \cdot 10^{-3}$ M L^{-1}, THF, 0.2 M Bu_4NBF_4, SCE reference)

Complex	Mercury electrode		Platinum electrode	
	$-E_{red}$(V)	i_{pa}/i_{pc}	$-E_{red}$(V)	i_{pa}/i_{pc}
$\mathbf{2}^+$	1.51(1)	0.40	1.47	0.35
	2.50(2)	0		
$\mathbf{3}^+$	1.82(1)	0.63	1.82	0.60
	2.78(2)	0		
$\mathbf{4}^+$	1.14(1)	0.85	1.18(1)	1.0
	1.96(2)	0.55	1.88(2)	1.0

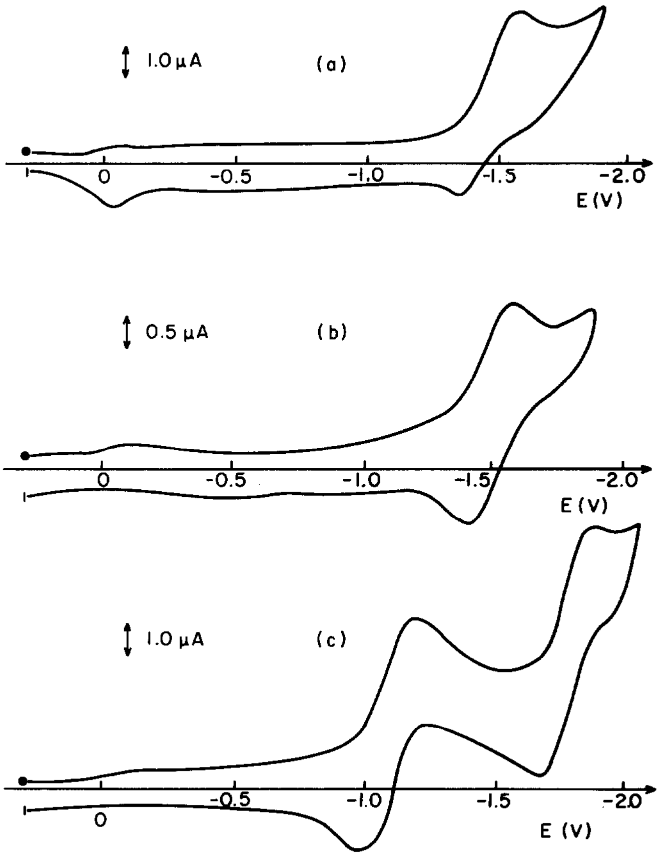
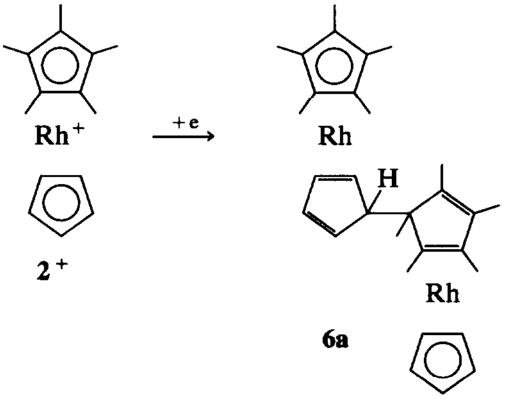


Fig. 1. Cyclic voltammetry scan for complexes $\mathbf{2}^+$ and $\mathbf{4}^+$ (Pt-electrode, THF, 0.2 M Bu_4NBF_4): (a) $\mathbf{2}^+$, $t = 20°C$; (b) $\mathbf{2}^+$, $t = -35°C$; (c) $\mathbf{4}^+$, $T = 30°C$.

To elucidate the structure of this product, bulk electrolysis of a solution of $\mathbf{2}^+$ in THF was carried out at the first plateau potential (−1.9 V). One electron was consumed and dimer **6a** was obtained in high yield, eqn. 2). The same result was obtained when $\mathbf{2}^+$ was reduced in THF solution by an excess of 1% Na–Hg.

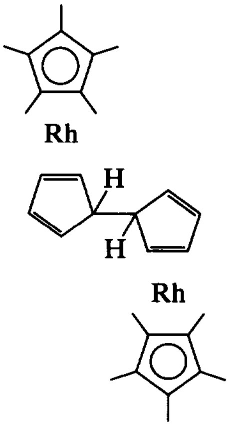


(2)

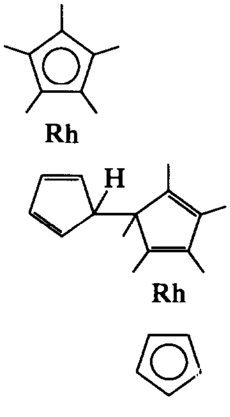
The dimer complex **6a** was characterized as [Rh(η^5-C_5H_5)(μ-$\eta^4:\eta^4$-C_5Me_5-C_5H_5)Rh(η^5-C_5Me_5)] by elemental analysis and by ^1H and ^{13}C NMR spectroscopy, which showed the presence of one η^5-C_5H_5(δ 5.04, J(Rh–H) 1 Hz; 83.8, J(Rh–C) 5 Hz) and one η^5-C_5Me_5 (d 2.02; 11.2 and 94.0, J(Rh–C) 6 Hz) ring. The μ-$\eta^4:\eta^4$-C_5H_5-C_5Me_5 ligand was indicated by the methyl signals at δ 1.34 (2) 1.52 (1) and 2.16 (2) in the ^1H NMR spectrum and the C-Me's at δ 12.9, 14.8, 22.8 (2:2:1, Me's) and 60.8 (CMe, d, J(Rh–C) 13 Hz); 67.0 s, CMe, 90.0 (d, CMe, J(Rh–C) 10 Hz), in the ^{13}C spectrum.

Electrochemical oxidation of **6a**, at either Hg- or Pt-electrodes, resulted in the regeneration of $\mathbf{2}^+$ by scission of the C–C bond. There was however, a difference in the peak potentials on the two electrodes (Hg −0.4, V, Pt −0.06 V) for this process.

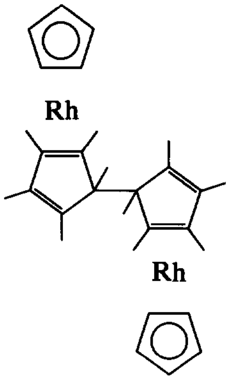
Thus the main features of the reduction of $\mathbf{2}^+$, *i.e.* the two one-electron reduction waves, the values of the reduction potentials, the dependence of the height of the oxidation peak of **2** on the temperature, and the formation of ligand-bridged dimer **6a**, are the same as for the reduction of $[Rh(\eta^5\text{-}C_5H_5)_2]^+$ [5]. However, only the dimer with structure **6a** was formed; the dimers **6b**, and **6c**, which could have been expected, were not observed. We have noted elsewhere that pentamethyliridocenium also undergoes reduction to give dimer [7]. However, in that case two isomers were found, that corresponding to **6a** in 66% yield, and also that corresponding to **6c**, in 33% yield. The third isomer, corresponding to **6b**, was again absent. These results suggest that the dimerization of **2** and its iridium analogue, is dominated by spin density and electron localisation energy effects and that steric considerations are of lesser importance. Were steric effects significant, then one would expect the formation of at least some of isomer **6c**, where C–C bond formation has occurred between the η^5-C_5H_5 rings. Further work to probe this point is in progress.



6b



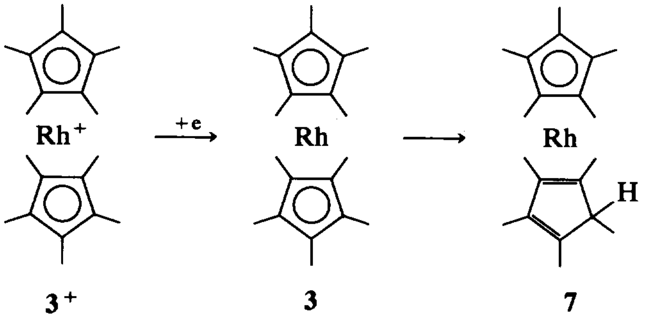
6a



6c

2.2. Reduction of decamethylrhodocenium 3^+ to the η^4-pentamethylcyclopentadiene complex, [Rh(η^5-C_5Me_5)(η^4-C_5Me_5H)], 7

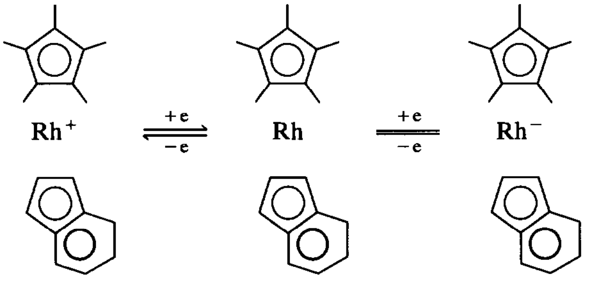
The ratio of anodic to cathodic current, i_{pa}/i_{pc} for the decamethyl radical **3** (0.63) is greater than for the pentamethyl radical **2** (0.40), showing that the decamethyl radical is more stable than the pentamethyl radical. No coupling product analogous to **6**, was found, indicating that coupling of two pentamethylcyclopentadienyl ligands is unfavorable, probably for steric reasons. Instead, reduction of decamethylrhodocenium $\mathbf{3}^+$ resulted in the formation of the η^4-pentamethylcyclopentadiene complex, [Rh(η^5-C_5Me_5)(η^4-C_5Me_5H)], **7**, rather than of the dimer, [(η^5-C_5Me_5)Rh(μ-$\eta^4:\eta^4$-C_5Me_5-C_5Me_5)Rh(η^5-C_5Me_5)]. However, the yield of **7** was low (14%), and its formation was accompanied by considerable decomposition. Thus other reactions (abstraction of a hydrogen atom, presumably from the solvent, and decomposition) take place instead of dimerization.



(3)

2.3. The reduction of $[Rh(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_5H_5)]^+$, 4^+, to $[Rh(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_5H_5)]$, 4

The behaviour of the indenyl cation $\mathbf{4}^+$ on reduction is substantially different from that of $\mathbf{2}^+$ or $\mathbf{3}^+$; the reduction potentials are less negative (Table 1), and both the first and second stages are electrochemically and chemically reversible even at room temperature. This indicates a high stability for both the radical **4** and the anion **4**$^-$, which is comparable with the stability of $[Co(\eta^5\text{-}C_5H_5)_2]$ and $[Co(\eta^5\text{-}C_5H_5)_2]^-$. Electrolysis of **4**$^+$ in THF on an Hg-electrode results in the formation of a dark-blue solution of radical **4** eqn. (4), the ESR-spectrum of which shows $g_\perp = 2.0118$, $g_\| = 1.8463$, $g_{iso} = 1.96$.



(4)

4$^+$ **4** **4**$^-$

Complex **4** is the first example of a stable rhodium sandwich radical. The enhanced stability of **4** and **4**$^-$ is probably caused by the electron-withdrawing character of the indenyl ligand; we also note the similarity to cobalt in that the positive shift of the reduction potential of **4**$^+$ relative to **2**$^+$ is similar to that found between $[Co(\eta^5\text{-}C_9H_7)_2]^+$ and $[Co(\eta^5\text{-}C_5H_5)_2]$ [8]. The increased stability of **4**$^-$ may also be associated with the ability of the idenyl ligand to ring-slip and bind η^3 rather than η^5 [9]; this would make it an 18-electron, rather than a 20-electron complex, with a substantial enhancement of the stability. Following arguments propounded by Astruc [1], this may also be true for the radical **4**, which would be a 17- rather than a 19-electron species if the indenyl ring were bound η^3 as a consequence of this slippage.

3. Experimental details

All experiments were performed under argon in solvents purified by standard methods. Complexes $[(C_5H_5)Rh(C_5Me_5)]^+PF_6^-$ and $[(C_5Me_5)Rh(C_9H_7)]^+PF_6^-$ were prepared by the methods described in references [10] and [11] respectively. Decamethylrhodocenium, $[Rh(C_5Me_5)_2]^+PF_6^-$, was obtained by reaction of $[(C_5Me_5)RhCl_2]_2$ with C_5Me_5Li [12]. Polarographic measurements were made with a potentiostat PI-50-1, and peak potentials were recorded with reference to SCE. The supporting electrolyte was Bu_4NBF_4 0.2 M in each case. Coulometric measurements were made with a OH-404 Radelkis coulometer. ^1H and ^{13}C NMR spectra were obtained with a Bruker-WP200-SY spectrometer in C_6D_6 solution. All chemical shifts are reported in p.p.m. (δ) with reference to TMS. ESR spectra were recorded on a Varian 112 spectrometer.

3.1. *Bulk electrolysis of* $[Rh(C_5H_5)(C_5Me_5)]^+PF_6^-$

Electrolysis of **2**$^+$ (0.09 g, 0.2 mmol) was carried out at a stirred Hg-electrode −1.9 V in THF (50 cm^3; 0.2 M Bu_4NBF_4); after the consumption of 19.8 Q ($Q_{theor} = 19.6$, $n = 1$) the current decreased from 20 mA to 2 mA and electrolysis was stopped. The solution was decanted and the THF removed *in vacuo*, to leave a residue that was crystallized from hexane, yield of **6a** 0.05 g (86%).

3.2. *Reduction of* $[Rh(C_5H_5)(C_5Me_5)]^+PF_6^-$ *and* $[Rh(C_5Me_5)_2]^+PF_6^-$ *by Na–Hg*

A suspension of **2**$^+$ (0.22 g, 0.5 mmol) in THF (30 cm^3) was stirred with an excess of 1% Na–Hg (2 h at 25°C). The solution was decanted, filtered and the solvent removed *in vacuo*, to leave a residue that was crystallized from hexane. Yield of **6a** 0.12 g (80%). Anal. Found: C, 59.62; H, 6.88. $C_{30}H_{40}Rh_2$ calc.: C, 59.41; H, 6.65. ^1H NMR (C_6D_6): δ 1.34 (s, 6H, $2CH_3$); 1.52 (s, 3H, CH_3); 2.02 (s, 15H, C_5Me_5); 2.16 (s, 6H, $2CH_3$); 2.61 (m, 3H); 4.52 (m, 2H); 5.04 (d, 5H, C_5H_5, J(Rh-H) 1.0 Hz). ^{13}C NMR (C_6D_6): δ 11.2 (C_5Me_5); 12.85 (2Me); 14.8 (2Me); 22.75 (1Me); 47.8 (d, CH, $J(\text{Rh-C}) = 12$ Hz); 60.8 (d, CMe, $J(\text{Rh-C}) = 13$ Hz); 64.0 (CH); 67.0 (CMe); 73.4 (d, 2CH, $J(\text{Rh-C}) = 9$ Hz); 83.8 (d, C_5H_5, $J(\text{Rh-C}) = 5$ Hz); 89.6 (d, 2CMe, $J(\text{Rh-C}) = 10$ Hz); 94.0 (d, C_5Me_5, J(Rh-C) 6 Hz).

Under similar conditions $[Rh(C_5Me_5)_2]^+PF_6^-$ (0.26 g, 0.5 mmol) gave $[(C_5Me_5)Rh(C_5Me_5H)]$, **7**, (0.03 g; 14%). ^1H NMR (C_6D_6); δ 1.05 (s, 6H, $2CH_3$); 1.74 (d, 3H, CH_3, $J(\text{H-H}) = 6.6$ Hz); 1.32 (s, 15H, C_5Me_5); 3.25 (q, 1H, $J(\text{H-H}) = 6.6$ Hz).

Acknowledgment

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