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Generation of the 15-Electron Rhodium(II) Complex $[RhCl(PPh_3)_3]^+$ by 1-Electron Oxidation of Wilkinson's Catalyst

Frédéric Barrière and William E. Geiger*

Department of Chemistry, University of Vermont, Burlington, Vermont 05405

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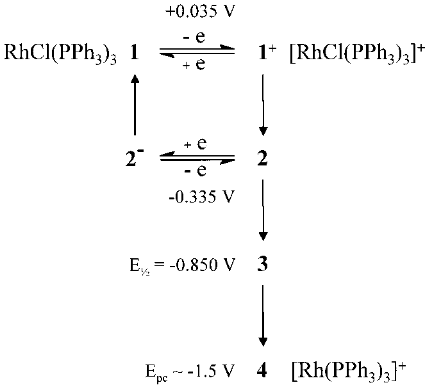
*Summary: Wilkinson's catalyst, $RhCl(PPh_3)_3$ (**1**), undergoes a one-electron oxidation at a sufficiently low potential ($E_{1/2}$ = +0.035 V vs Fc) to allow a facile electron-transfer reaction with mild oxidants such as the ferrocenium ion. The Rh(II) cation $\mathbf{1}^+$ decomposes rapidly to the very reactive intermediate **2**, which over longer reaction times gives rise to the three-coordinate complex $[Rh(PPh_3)_3]^+$ (**4**).*

Although the very important complex[1] $RhCl(PPh_3)_3$ (Wilkinson's catalyst **1**) has been the subject of intense catalytic, mechanistic, and physical studies,[2] the prospect of its 1-electron oxidation and the chemical fate of the putative 15-electron Rh(II) cation $\mathbf{1}^+$ does not seem to have been addressed. One-electron processes are certainly expected to affect the dissociative reactions crucial[3] to the activity of Rh catalysts and may be involved when Rh(I) compounds are combined with latent oxidants (e.g., silver salts) for catalysis of cycloadditions[4] and other organic reactions. There is precedent for the oxidation of phosphine-substituted Rh(I) (and even Rh(III)) complexes being thermodynamically quite facile.[5] Given these facts and the known high reactivity[6] of mononuclear Rh(II) complexes, we are investigating the oxidative redox chemistry of $RhCl(PPh_3)_3$ and the possible catalytic properties of its oxidation products. Although the reduction of **1** has been described in several papers,[7] its oxidation by electrochemistry or by one-electron-transfer agents does not appear to have been previously reported.

$RhCl(PPh_3)_3$ undergoes a one-electron oxidation process in CH_2Cl_2−$[NBu_4][PF_6]$[8] at an $E_{1/2}$ value of +0.035 V vs ferrocene (Fc) ($\mathbf{1} \rightleftharpoons \mathbf{1}^+$; Scheme 1). The 15-electron complex $\mathbf{1}^+$ has a limited lifetime at room temperature, so that cyclic voltammetry (CV) at scan rates higher than about 1 V/s is necessary to significantly outrun the implied follow-up reaction ($\mathbf{1}^+ \rightarrow \mathbf{2}$; Scheme 1). The stability of $\mathbf{1}^+$ increases at subambient temperatures, its half-life being about 2 s at 273 K (Figure 1a).[9] Full chemical reversibility at slow scan rates is observed at temperatures below 240 K (Figure 1b). A variety of voltammetric and electrolytic methods, including bulk coulometry, firmly establish a stoichiometry of one electron for the oxidation. The separation between the anodic and cathodic peak potentials (ΔE_p) was found to be only qualitatively reproducible on gold or glassy-carbon electrodes, but occasionally ΔE_p values were obtained that were quantitatively reproducible and close to those of the decamethylferrocene/decamethylferrocenium couple (Fc^*/Fc^{*+}) under the same conditions (Figure 1b). The observed electrode dependence of the couple will be fully described at another time, but we can state that the heterogeneous electron-transfer process of the couple $\mathbf{1}/\mathbf{1}^+$ is reasonably rapid, with a k_s value of ca. 10^{-2} cm s^{-1} at a gold electrode (T = 250 K).[10a] The voltammetric behavior was independent of concentration over the range 0.1−3 mM.

Scheme 1



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(8) Analogous CV behavior was also observed when the supporting electrolyte employed a poorly coordinating anion: viz., $[B(C_6F_5)_4]^-$.

(9) A first-order reaction rate (k_c) for the follow-up reaction $\mathbf{1}^+ \rightarrow \mathbf{2}$ was measured from the values of i_c/i_a at different scan rates (Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706. Nicholson, R. S. *Anal. Chem.* **1966**, *38*, 1406): k_c = 0.4 s^{-1} at T = 273 K.

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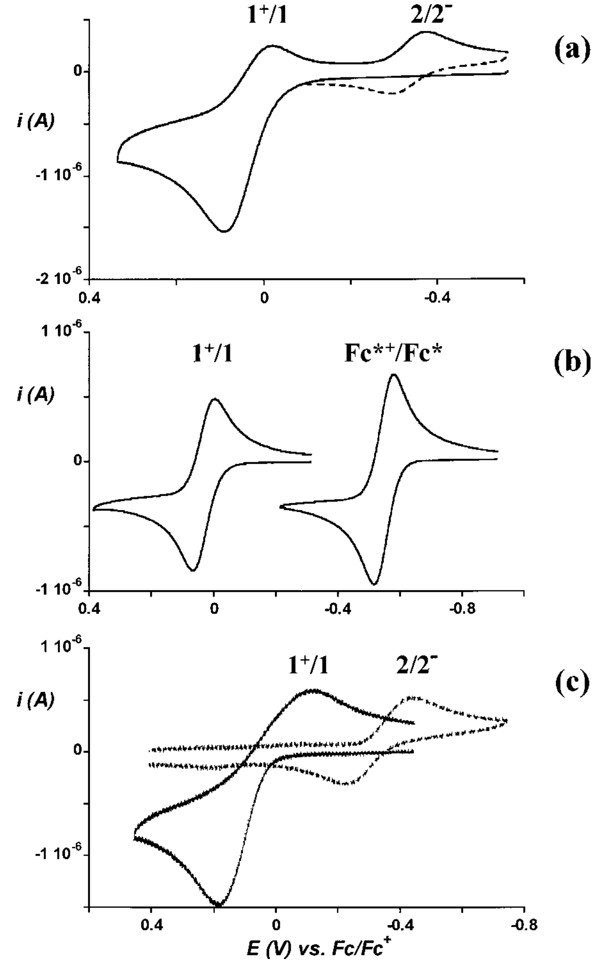

Figure 1. CVs recorded under uncompensated solution resistance conditions in $CH_2Cl_2-[NBu_4][PF_6]$ 0.1 M under N_2. Potentials are referenced against the Fc/Fc^+ couple. (a) $T = 273$ K, [**1**] = 1.1 mM, $\nu = 200$ mV/s. The dotted line is the second cycle, showing the reversible reduction of product **2**. The working electrode is a 1 mm diameter glassy-carbon disk. (b) $T = 230$ K, [**1**] = 1.0 mM ($\Delta E_p = 69$ mV), [Fc*] = 0.5 mM ($\Delta E_p = 64$ mV), $\nu = 100$ mV/s. The working electrode is a 1 mm diameter gold disk.[10a] (c) $T = 215$ K, [**1**] = 1.8 mM, $\nu = 200$ mV/s. The solid line is before electrolysis at +0.3 V; the dotted line is after electrolysis. The working electrode is a 1 mm diameter glassy-carbon disk.

The initial product from the decomposition of $\mathbf{1}^+$ is also electroactive, as shown in Figure 1a. The redox couple of product **2** is reversible with $E_{1/2} = -0.335$ V. After this product is formed in about 40% yield[10b] by bulk oxidation of **1** at 215 K (Figure 1c), it can be reduced by electrolysis at −0.6 V. When the solution containing the *reduced form* of **2** is warmed to room temperature, **1** is recovered in ca. 40% yield, as estimated by CV peak current comparisons. Complex **2** has, to date, resisted identification (vide infra). Low-temperature oxidative electrolysis of **1** also gives other products having reduction waves at $E_{1/2} = -0.850$ V (**3**, 20% yield, reversible CV) and $E_{pc} \approx -1.5$ V (somewhat broad, irreversible, 40% yield). Raising the temperature of the solution containing the *oxidized forms* of **2** and **3** increases the yield of the apparent single wave at about −1.5 V by an additional 60%. This wave is ascribed to the major long-term oxidation product of **1**, the three-coordinate cation $[Rh(PPh_3)_3]^+$ (**4**) (**2** → **4**; Scheme 1).[11−13] This process was complete in about 1 h at room temperature. The complexity of the follow-up reactions of $\mathbf{1}^+$ is consistent with the fact that Rh(II) complexes are prone to competitive reactions, including dimerization, disproportionation, and reductive elimination processes.[5d,e,6]

The identity of the 14-electron complex **4** was established by NMR spectroscopy and by the close agreement between literature values and the presently observed experimental value of its reduction potential.[14] To facilitate the NMR experiments, it was first established by CV scans that treatment of **1** with an innocent one-electron oxidant such as the ferrocenium ion results in the same products and relative yields as those obtained by bulk electrolysis. Then, in a separate experiment **1** was oxidized by an equimolar amount of $[Cp_2Fe][PF_6]$ in cold (ca. 220 K) d_2-dichloromethane in an NMR tube. Just after mixing, the solution showed low-temperature spectra with several independent features, consistent with the complexity of the electrochemical oxidation. Two $^{31}P\{^1H\}$ NMR resonances, tentatively assigned to **2** and **3**, were detected at 26.7 and 74.2 ppm, respectively. Both of these features were very broad, more likely owing to fast exchange processes than to the presence of paramagnetic species, since frozen solutions of these samples at 140 K are ESR silent. As expected from bulk electrolysis data, these signals disappear upon raising the temperature, after which the spectrum of complex **4** becomes dominant. This approximately T-shaped complex[11−13] shows temperature-dependent $^{31}P\{^1H\}$ spectra, exhibiting coalescence at 300 K, well-resolved peaks at reduced temperatures, and detection of the four-coordinate $[Rh(PPh_3)_4]^+$ cation at lower temperatures in the presence of trace PPh_3.[12b,14] An-

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[10] (a) On one occasion, examination of the gold electrode with the naked eye or the optical microscope revealed that the metal surface had lost its shiny aspect and that it was covered with a fine layer of black material. That electrode gave reproducible small ΔE_p's for the oxidation of **1** and could be reused in several experiments after being simply rinsed with acetone and let dry. (b) The "% yields" of electrolysis experiments are based on the assumption that diffusion coefficients are equal.

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[13] Besides the coordination of the metal to three phosphine ligands, complex **4** appears to also interact with one solvent molecule in solution or (weakly) to two carbons of one of the phenyl rings in the solid state.[11,12]

[14] $^{31}P\{^1H\}$ NMR data for **4** in CD_2Cl_2 (in agreement with data reported in ref 12b) are as follows. (i) At 300 K: coalescence, 36 ppm, broad peak. (ii) Below 250 K: doublet of triplets, 49.3 ppm, $^1J_{Rh,P} = 244$ Hz, $^2J_{P,P} = 30.5$ Hz, doublet of doublet, 31.0 ppm, $^1J_{Rh,P} = 133.5$ Hz, $^2J_{P,P} = 30.5$ Hz, well-resolved peaks. (iii) Below 230 K: additional doublet at 32.1 ppm, $^1J_{Rh,P} = 133.5$ Hz, assigned to the entropically controlled formation of the four-coordinate $[Rh(PPh_3)_4]^+$ cation by reaction of **4** with free phosphine. Unassigned broad peaks (44−48 ppm) were also detected. All chemical shifts are externally referenced to 80% H_3PO_4. The hexafluorophosphate heptet was centered at −144.2 and −141.0 ppm in CD_2Cl_2 and CD_3CN, respectively. The irreversible reduction of $[Rh(PPh_3)_3]^+$ in $CH_2Cl_2-[NBu_4][PF_6]$ (0.1 M) was found to be dependent on both temperature and free PPh_3 concentration (cf. ref 12a for the electrochemical study of $[Rh(PPh_3)_3(DME)]^+$ in dimethoxyethane (DME)$-[NBu_4][ClO_4]$ (0.2 M)). $[Rh(PPh_3)_3]^+$ was also prepared as its hexafluorophosphate salt by chloride abstraction from **1** with $TlPF_6$ in dichloromethane, adapting the procedure described in ref 11. This allowed independent NMR and electrochemical studies and the characterization of **4**.

other short-term product which has been identified is the chlorotriphenylphosphonium ion, $[ClPPh_3]^+$, from its resonance at 66 ppm. The origin of the chlorine atom in the phosphonium product is not the chlorinated solvent, since it is detected as well when the solvent is d_3-acetonitrile.[15]

Although Ag^+ is a strong oxidant in low-polarity solvents[16] (e.g., $E_{1/2}$ ca. $+0.65$ V in CH_2Cl_2),[17] treatment of **1** with $Ag[CF_3SO_2]$ was shown by NMR monitoring to rapidly yield **4** by simple chloride abstraction rather than to follow the complex oxidative path.

The present work shows that Wilkinson's catalyst is subject to a 1-electron oxidation, giving the detectable 15-electron Rh(II) monocation $\mathbf{1}^+$. The potential of the Rh(I)/Rh(II) couple ($+0.035$ V vs Fc) is sufficiently low that the possibility of one-electron oxidation must be considered whenever **1** may interact with even mild oxidizing agents.[18] On an electrolytic time scale, very reactive intermediates are formed which, in part, eventually yield the formally 14-electron cation **4**. Summarizing the rough stoichiometries of the electrochemical processes, anodic electrolysis of **1** at low temperature gives **2** (40%), **3** (20%), and **4** (40%). After intermediate **2** is reduced, warming the solution to room temperature yields **1** (40%) and **4** (60%). That is, reduced **2** gives back Wilkinson's catalyst, whereas **3** yields the three-coordinate complex **4**. The electron-transfer route is not followed when **1** reacts with Ag(I) triflate. Given the fact that mononuclear Rh(II) complexes may be active catalysts or catalyst precursors,[19] it seems worthwhile to explore the possibility that oxidative treatment of $RhCl(PPh_3)_3$ and its analogues may give rise to useful low-temperature catalytic processes.

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[18] It should be noted that the oxidation of **1** by ferrocenium is complete in a short time period, even though its $E_{1/2}$ potential ($+0.035$ V) is slightly positive of that of Fc/Fc^+. The follow-up reaction $\mathbf{1}^+ \rightarrow \mathbf{2}$ provides the driving force for completeness of the homogeneous oxidation process.

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