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Metal Alkylation of Electrochemically Generated Low-Valent Metalloporphyrins. Is There Something Special with Rhodium?

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Summary: Rhodium(III) porphyrins are converted into the corresponding σ-alkyl complexes by electrochemical reduction in the presence of an alkyl halide. The mechanism of this reaction is investigated by means of cyclic voltammetry and spectroelectrochemistry. On the basis of the kinetic data and on the recent finding that the rhodium(II) intermediates disproportionate rather than dimerize as believed earlier, it is shown that the σ-alkyl complex results from an S_N2 substitution by the rhodium(I) porphyrin rather than from a radical reaction involving the rhodium(II) intermediate. Rhodium(I) porphyrins, thus, exhibit an S_N2 reactivity similar to that of their cobalt and iron analogues.

The most common route to metal-alkylated metalloporphyrins consists of reacting a metal(III) complex with a Grignard or an alkyllithium reagent.[2] Another possibility is to react a low-valent metalloporphyrin with an alkyl halide. This reaction is well-documented in the case of electrochemically generated iron(I) and iron(0) porphyrins.[3] Kinetic studies have shown that unless the porphyrin and/or the reacting carbon are sterically hindered, the low-valent iron porphyrin reacts as a nucleophile rather than as a single electron donor, eq 1.[3,4] σ-Alkylcobalt porphyrins may likewise be obtained

$$\mathrm{M(I)^- + R \rightarrow M(III)R + X^-} \qquad (1)$$

from the reaction of alkyl halides with cobalt(I) porphyrins generated electrochemically[3a,5] or by chemical means.[6]

It has, however, been shown that cobalt(II)[7] and iron(II)[8] porphyrins or similar complexes may also react with alkyl halides according to a free radical mechanism, eqs 2 and 3. In the case of rhodium, the reaction

$$\mathrm{M(II) + R \rightarrow M(III)X + R^{\bullet}} \qquad (2)$$

$$\mathrm{M(II) + R^{\bullet} \rightarrow M(III)R} \qquad (3)$$

of Rh(I), generated from Rh(III) by sodium borohydride reduction, with alkyl halides affords the σ-alkyl complexes.[9] There also seems to be a possibility that Rh(II) porphyrins may react with alkyl halides according to the same radical mechanism as with cobalt and iron. However, the evidence for this reaction is indirect since, with simple porphyrins in apolar solvents, the Rh(II) oxidation state exists a Rh−Rh dimer. Among the large number of reactions of these Rh(II)−Rh(II) dimers that have been described,[10] one concerns the reaction of the rhodium octaethylporphyrin dimer with a halide, benzyl bromide, in which the carbon−halogen bond is particularly weak.[10a] Rh(III)Br and Rh(III)CH_2Ph are produced in moderate yields. The reaction mechanism is assumed to involve the homolytic dissociation of the dimer

$$\mathrm{Rh(II)-Rh(II) \rightleftharpoons 2Rh(II)}$$

followed by reactions 2 and 3.

σ-Alkylrhodium porphyrins may also be obtained by electrochemical reduction of the corresponding Rh(III)

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porphyrins in the presence of alkyl halides.[11] The formation and the electrochemical characteristics of the σ-alkyl complexes may be conveniently followed by cyclic voltammetry. Since the main reduction wave was ascribed to the reduction of the Rh(III) porphyrin into Rh(II) followed by the dimerization of the latter species,[12] the formation of the alkyl complex was quite naturally assumed to result from reactions 2 and 3 in competition with the dimerization reaction 4.

$$\mathrm{Rh(III)} + e^- \rightarrow \mathrm{Rh(II)}$$

$$2\mathrm{Rh(II)} \rightarrow \mathrm{Rh(II)}{-}\mathrm{Rh(II)} \qquad (4)$$

We now know that the electrochemical reduction of Rh(III) porphyrins does not lead to the Rh(II)−Rh(II) dimer but rather to the Rh(I) complex according to a mechanism which involves the disproportionation of the initially formed Rh(II) complex (in the polar solvents required by electrochemical experiments), eqs 5−7.[13] It

$$^{+}\mathrm{Rh(III)L_2} + e^- \rightleftharpoons \mathrm{Rh(II)L_2} \qquad (5)$$

$$\mathrm{Rh(II)L_2} \rightarrow \mathrm{Rh(II)L} + \mathrm{L} \qquad (6)$$

$$\mathrm{Rh(II)L_2} + \mathrm{Rh(II)L} \rightarrow {}^{+}\mathrm{Rh(III)L_2} + {}^{-}\mathrm{Rh(I)L} \qquad (7)$$

$$\overline{}$$

$$^{+}\mathrm{Rh(III)L_2} + 2\,e^- \rightarrow {}^{-}\mathrm{Rh(I)L} + \mathrm{L}$$

thus appeared necessary to reinvestigate the mechanism by which the electrochemical reduction of Rh(III) porphyrins in the presence of alkyl halides produces the corresponding σ-alkyl complexes.

Results and Discussion

The reaction of alkyl halides with reduced rhodium(III) porphyrins may be observed in cyclic voltammetry as illustrated in Figure 1 with the example of TPPRhI and EtBr in dimethyl sulfoxide (DMSO). In the absence of alkylating agent, the voltammogram exhibits two wave systems. The first involves an irreversible two-electron cathodic wave where Rh(III) is reduced into Rh(I) and an irreversible two-electron anodic wave where Rh(I) is reoxidized into Rh(III). The second is a reversible one-electron wave corresponding to the Rh(I)/Rh(I) anion radical couple (Figure 1a).[13] Upon addition of EtBr, the irreversible two-electron cathodic wave remains unchanged while the irreversible two-electron anodic wave disappears, indicating the consumption of the Rh(I) complex formed at the cathodic wave (Figure 1b). The two new waves that appear in the voltammogram are those of the product resulting from the reaction of Rh(I) with EtBr. The first is a one-electron reversible wave. The second, which is located close to the second reversible wave observed in the absence of EtBr, exhibits a catalytic character. These observations suggest that the rhodium(I) complex resulting from the two-electron reduction of Rh(III) reacts with the alkyl halide, similarly to what has been previously found with cobalt(I) and iron(I) porphyrins, eq 8. The waves of the

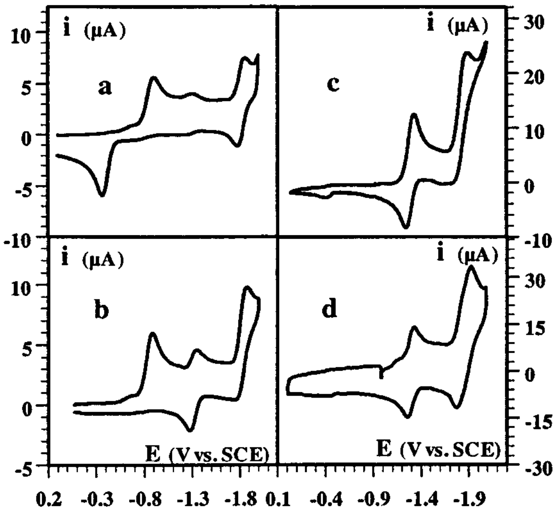


Figure 1. Cyclic voltammetry of TPPRhI (0.75 mM) at 0.1 V/s in the (a) absence and (b) presence of EtBr (1 mM) and (c and d) after electrolysis at −1.1 V vs SCE in the presence of 2 mM EtBr at (c) 0.1 and (d) 1 V/s.

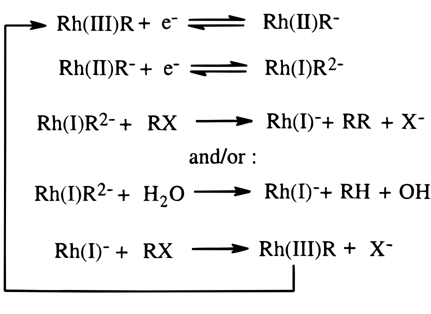
$$\mathrm{Rh(I)}^- + \mathrm{R} \rightarrow \mathrm{Rh(III)R} + \mathrm{X}^- \qquad (8)$$

alkyl complex are seen more clearly after electrolysis of the solution at a potential located just beyond the Rh(III) reduction wave (Figures 1c, d) when the starting Rh(III) has been entirely converted into products. It is then observed that the second wave tends to become reversible and its relative height decreases upon raising the scan rate (Figure 1d). Thus, at short times, the alkyl complex undergoes two successive reversible one-electron reductions:

$$\mathrm{Rh(III)R} + e^- \rightleftharpoons \mathrm{Rh(II)R}^-$$
$$\mathrm{Rh(II)R}^- + e^- \rightleftharpoons \mathrm{Rh(I)R}^{2-}$$

The catalytic current observed at low scan rates (which slightly persists at 1 V/s) can be explained by the set of reactions depicted in Scheme 1.

Scheme 1



The Rh(III) σ-alkyl complex was further characterized by thin-layer spectroelectrochemistry as depicted in Figure 2 , where the alkylating agent was methyl iodide

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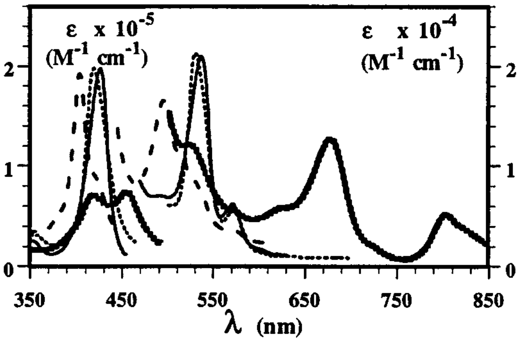

Figure 2. Thin-layer spectroelectrochemistry of TPPRhI (0.25 mM) in DMSO and 0.1 M Et_4NClO_4 upon addition of MeI: (—) initial complex (Rh(III)); (- - -) after electrolysis at −1.1 V vs SCE in the absence of MeI (Rh(I)); (···) after electrolysis at −1.1 V vs SCE in the presence of 0.5 mM MeI (Rh(III)R); (—) after further electrolysis at −1.4 V vs SCE.

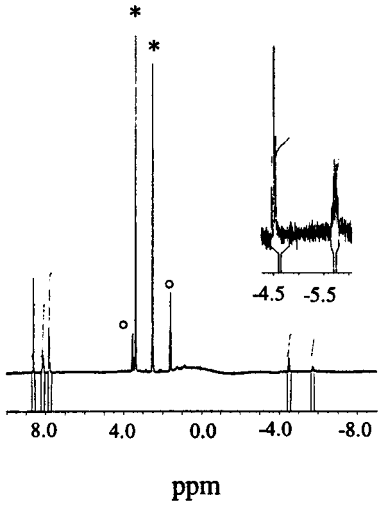

Figure 3. ^{1}HNMR spectrum of TPP−Rh(III)CH_2CH_3 (1 mM) in D_6 DMSO: (*) solvent peaks; (○) peaks of excess CH_3CH_2Br.

this time. Electrolysis in the presence of the alkyl halide produced a spectrum which is only slightly different from the initial spectrum, as expected from the fact that the two spectra are those of two Rh(III) complexes differing only by the nature of their axial ligands. In this connection, it is also interesting to note that the cyclic voltammetric behavior of Rh(III)R, showing two successive one-electron reversible waves (Figure 1d), is similar to the behavior observed when the rhodium bears strong and soft axial ligands such as PEt_3 and PMe_2Ph.[13]

Electrolysis in the presence of EtBr has also been carried out in DMSO-d_6 to characterize the Rh(III)CH_2CH_3 complex by ^{1}HNMR. The resulting spectrum (Figure 3) exhibits a doubled triplet at −4.5 ppm and a doubled quadruplet at −5.7 ppm, as expected for the methyl and methylene protons of the ethyl ligand, in agreement with literature.[3c] Indeed, such chemical shifts fall in line with a strong shielding by the porphyrin ring current which strongly influences the axially coordinated ethyl group to the rhodium atom, while the doubling of the bands results from the coupling with the $S = {}^1/_2$ nuclear spin of rhodium.

It might, thus, be concluded that the Rh(III) σ-alkyl complex simply results from an S_N2 substitution of the halide ion by the electrogenerated Rh(I) porphyrin as in the case of cobalt and iron. Another possibility should, however, be considered, namely that the reaction would involve X-atom abstraction by the initially formed Rh(II) complex generating the $R^•$ radical, which would combine with a second Rh(II) molecule. In other words, reactions 2 and 3 would compete with and possibly be more efficient than the disproportionation reaction 7 (Scheme 2).

The answer is given by the experiments summarized in Figure 4. Upon raising the scan rate from 0.1 (Figure 4a) to 5 (Figure 4b) V/s, the one-electron reversible wave of Rh(III)R (formed at the first two-electron wave) disappears while the reoxidation wave of Rh(I) reappears. The voltammogram at 5 V/s is then the same as the voltammogram of the initial Rh(III) complex in the absence of alkylating agent, where the disproportionation process is fast enough to make the cathodic wave a two-electron irreversible wave. These observations prove that the reaction of the rhodium(II) complex with the alkyl halide cannot compete with the disproportionation reaction.

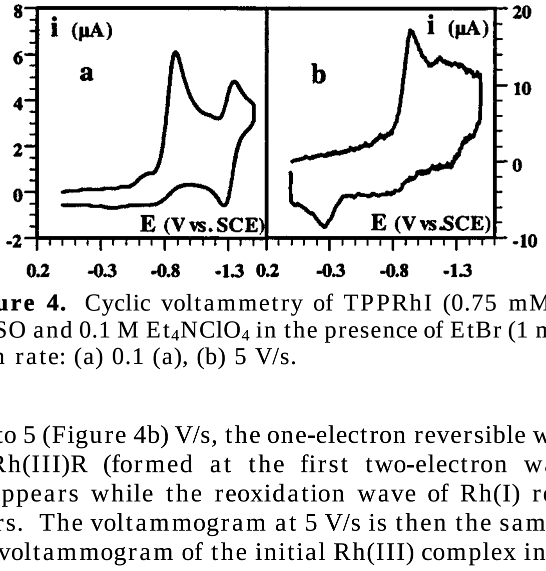

Figure 4. Cyclic voltammetry of TPPRhI (0.75 mM) in DMSO and 0.1 M Et_4NClO_4 in the presence of EtBr (1 mM). Scan rate: (a) 0.1 (a), (b) 5 V/s.

We may, thus, conclude that the mechanism of the electrochemical alkylation involves the formation of rhodium(I) by a two-electron disproportionation process and its S_N2 alkylation as with cobalt and iron porphyrins. It is also similar to the mechanism by which

Scheme 2

$$^{+}Rh(III)L_2 + e^- \rightleftharpoons Rh(II)L_2$$

$$Rh(II)L_2 \longrightarrow Rh(II)L + L$$

Rh(II) radical alkylation

(2) $Rh(II)L + RX \longrightarrow Rh(III)LX + R^•$

(3) $R^• + Rh(II)L \longrightarrow Rh(III)LR$

Rh(I) S_N2 alkylation

$Rh(II)L_2 + Rh(II)L \longrightarrow Rh(III)L_2 + {}^-Rh(I)L$ (7)

${}^-Rh(I) + RX \longrightarrow Rh(III)R + X^-$

rhodium(III) porphyrins hydrides are formed upon electrochemical reduction of rhodium(III) porphyrins in the presence of a Brönsted acid.[14]

Experimental Section

All cyclic voltammetric experiments were carried out with a 3-mm-diameter glassy carbon disk. Chemicals, instrumentation, and procedures were the same as described in refs 13 and 14.

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