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**Reaction between  $[(\text{TPP})\text{Ru}(\text{CO})]^-$  and Methyl Iodide.  
Evidence for Formation of a Ruthenium(II) Carbonyl  
Methylated Tetraphenylchlorin Derivative**

Y. J. Deng, X. H. Mu, P. Tagliatesta, and K. M. Kadish\*

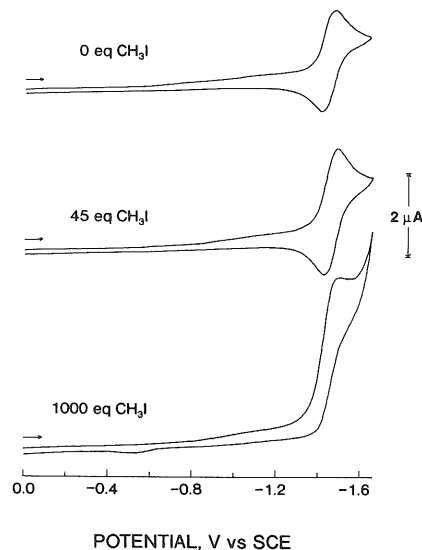
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**Introduction**

The electroreduction of  $(\text{P})\text{Ru}(\text{CO})$ , where P = the dianion of a given porphyrin ring, has been extensively investigated in nonaqueous media.<sup>1-7</sup> Two well-defined one-electron reductions are generally observed, and stable electroreduction products are obtained in virtually all nonaqueous solvents except for dichloromethane and dichloroethane, which rapidly react with the singly reduced species to give an overall irreversible electroreduction.<sup>2,3,6</sup>

The first electroreduction of cobalt(II),<sup>8</sup> nickel(II)<sup>9</sup> and rhodium(III)<sup>10,11</sup> porphyrins is also irreversible in  $\text{CH}_2\text{Cl}_2$  and, in the case of the cobalt and rhodium derivatives, is due to the formation of  $\sigma$ -bonded porphyrin complexes, as demonstrated by the isolation and characterization of  $(\text{TPP})\text{Co}(\text{CH}_2\text{Cl})^8$  and  $(\text{TPP})\text{Rh}(\text{CH}_2\text{Cl})^{10}$  where TPP = the dianion of tetraphenylporphyrin. The formation of a  $\text{CH}_2\text{Cl}$  adduct occurs via an oxidative addition reaction that is similar to those involving alkyl or aryl halides (RX) and  $[(\text{TPP})\text{Co}]^-$  or  $[(\text{TPP})\text{Fe}]^-$  to give free  $\text{X}^-$  and a  $\sigma$ -bonded porphyrin complex of the type  $(\text{TPP})\text{M}(\text{R})$ .<sup>12</sup>

$\sigma$ -Bonded  $(\text{TPP})\text{Ru}(\text{C}_2\text{H}_5)$  and  $(\text{TPP})\text{Ru}(\text{C}_2\text{H}_5)_2$  complexes have also been synthesized from chemically reduced  $[(\text{TPP})\text{Ru}]_2$  and  $\text{C}_2\text{H}_5\text{X}$ ,<sup>13,14</sup> but a reaction between chemically or electrochemically reduced  $(\text{P})\text{Ru}(\text{CO})$  and alkyl halides has never been reported. This was investigated in the present study for electrogenerated  $[(\text{TPP})\text{Ru}(\text{CO})]^-$  and  $\text{CH}_3\text{I}$ . The resulting porphyrin product was not a  $\sigma$ -bonded methyl complex but rather was a methylated ruthenium(II) carbonyl chlorin. The formation



**Figure 1.** Cyclic voltammograms of  $1.1 \times 10^{-3}$  M  $(\text{TPP})\text{Ru}(\text{CO})$  in THF, containing 0.2 M TBAP and 0, 45, and 1000 equiv of  $\text{CH}_3\text{I}$ .

of this species was monitored by in situ UV-visible and FTIR spectroelectrochemistry and the resulting final product identified by fast atom bombardment (FAB) mass spectrometry and electrochemistry.

**Experimental Section**

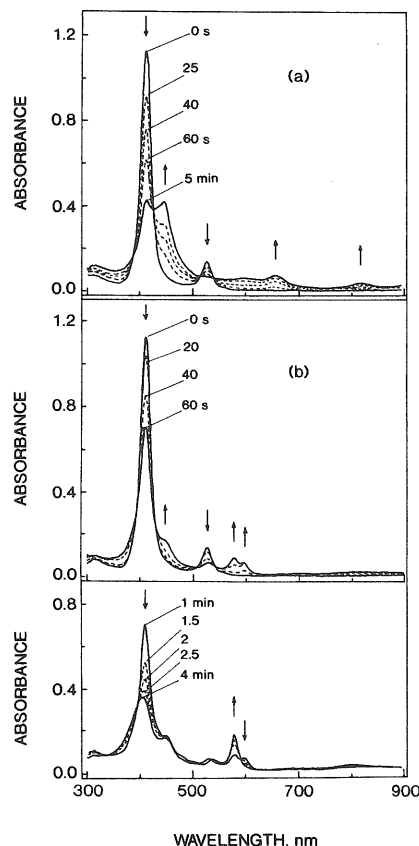
**Instrumentation.** Cyclic voltammetric measurements were obtained with an IBM EC 225 voltammetric analyzer. A platinum button served as the working electrode, and a platinum wire, as the counter electrode. A saturated calomel electrode (SCE) was separated from the bulk solution by a fritted-glass disk and was used as the reference electrode. Bulk controlled-potential coulometry was performed on an EG&G Princeton Applied Research Model 173 potentiostat which contained a Model 179 coulometer system that was coupled with a Princeton Applied Research Model RE0074 time base X-Y recorder. Thin-layer spectroelectrochemical measurements were made with an EG&G Princeton Applied Research Model 173 potentiostat coupled with a Tracor Northern 6500 rapid scan spectrometer. Construction of the thin-layer cell is described in the literature.<sup>15</sup>

Infrared measurements were carried out by using an IBM 32 FTIR spectrometer and an FTIR spectroelectrochemical cell whose construction and application have been described in the literature.<sup>2,16</sup> Mass spectra were recorded on a VG-70 SEQ mass spectrometer and 3-nitrobenzyl alcohol (NBA) was used as the matrix.

**Materials.** Reagent grade tetrahydrofuran (THF) was distilled first from  $\text{CaH}_2$  and then from Na-benzophenone. Dimethylformamide (DMF) and benzonitrile (PhCN) were vacuum distilled from activated

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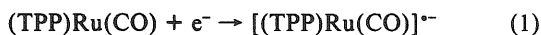
**Figure 2.** UV-visible spectral changes obtained during controlled-potential reduction of (TPP)Ru(CO) at  $-1.60$  V (a) from 0 to 5 min in THF containing 0.2 M TBAP and (b) from 0 to 4 min in THF containing 0.2 M TBAP and 700 equiv  $\text{CH}_3\text{I}$ .

4-Å molecular sieves and  $\text{P}_2\text{O}_5$ , respectively. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Fluka Chemical Co., purified by two recrystallizations from ethyl alcohol, and stored in a vacuum oven at  $40^\circ\text{C}$ . Methyl iodide was purchased from Aldrich Chemical Co. and used without further purification. (TPP)Ru(CO) was synthesized according to the procedure of Rillema et al.<sup>6</sup>

## Results

**Electrochemistry and Spectroelectrochemistry.** (TPP)Ru(CO) in THF undergoes a reversible room-temperature one-electron reduction at  $E_{1/2} = -1.46$  V.<sup>2,3</sup> This reduction remains reversible in THF containing up to 400 equiv of  $\text{CH}_3\text{I}$  but becomes irreversible in solutions with higher  $\text{CH}_3\text{I}$  concentrations. There is also an increase in the maximum cathodic peak current, and this is illustrated in Figure 1 by cyclic voltammograms obtained in THF containing 0, 45, and 1000 equiv of  $\text{CH}_3\text{I}$ . Under the latter solution conditions, the reduction is totally irreversible in that no reoxidation peak is coupled to the initial reduction, which occurs at  $E_p = -1.51$  V for a scan rate of 0.1 V/s. The peak current is approximately double the value obtained in the absence of  $\text{CH}_3\text{I}$ , but the electrode reaction is not catalytic as is the case for reduction of cobalt<sup>8</sup> or nickel<sup>9</sup> porphyrins in THF solutions containing  $\text{CH}_3\text{I}$ .

Time-resolved UV-visible spectra were obtained during controlled-potential reduction of (TPP)Ru(CO) in THF with and without added  $\text{CH}_3\text{I}$ , and examples of these spectra are given in Figure 2. Isosbestic points are located at 387, 426, 515, and 540 nm in the absence of  $\text{CH}_3\text{I}$  (Figure 2a), indicating the presence of only two spectrally detectable species in equilibrium. The final spectrum after reduction by one electron is that of the anion radical and the overall reaction corresponds to the formation of [(TPP)Ru(CO)]<sup>•−</sup> as shown in eq 1.<sup>2,3</sup>



The spectral changes that occur in THF solutions containing  $\text{CH}_3\text{I}$  pass through two separate stages as shown in Figure 2b. At the early stage of reduction (0–60 s), the Soret and Q bands

**Table I.** UV-Visible Data for Neutral and Singly Reduced (TPP)Ru(CO)

solvent <sup>a</sup>	UV-vis data, nm		
	before redn	after redn in $\text{CH}_3\text{I}$ soln <sup>b</sup>	after redn in neat solvent
THF	411, 527	407, 578	412, 446, 654, 813
DMF	413, 531	413, 581	413, 449, 665, 828
PhCN	415, 534	420, 584	421, 450, 678, 847

<sup>a</sup> All solvents contained 0.2 M TBAP. <sup>b</sup> Solutions contained 700 equiv of  $\text{CH}_3\text{I}$ .

decrease in intensity with a concomitant appearance of new bands at 578 and 598 nm. Isosbestic points are located at 393, 430, 509, and 542 nm. The Soret band continues to decrease in intensity from 1 to 4 min as the peak maximum shifts from 411 to 407 nm. At the same time, the absorbance at 578 nm continues to increase while the 598-nm band decreases and finally disappears. A new isosbestic point is observed at 590 nm during this latter stage of reduction while the other isosbestic points either shift in wavelength or disappear.

Metallophlorins are formed in reactions between reduced metalloporphyrins and methanol,<sup>17,18</sup> and a similar product might be expected in solutions containing [(TPP)Ru(CO)]<sup>•−</sup> and  $\text{CH}_3\text{I}$ . However, this appears not to be the case since phlorin absorption bands, which are typically located above 700 nm,<sup>17,19</sup> are not observed in the UV-visible spectrum of Figure 2b. On the other hand, the final UV-visible spectrum in Figure 2b has a strong absorption band at 578 nm and is characteristic of a chlorin.<sup>20,21</sup>

Metallochlorins are generally easier to oxidize than metalloporphyrins by 200 to 300 mV,<sup>20,22,23</sup> and a cyclic voltammogram of the isolated product further supports the conclusion of chlorin formation. The electrosynthesized ruthenium(II) carbonyl methylated chlorin undergoes a reversible room temperature oxidation at  $E_{1/2} = 0.87$  V in THF, 0.2 M TBAP, and this value is 260 mV more cathodic than the  $E_{1/2}$  of 1.13 V for oxidation of (TPP)Ru(CO) under the same experimental conditions.

Metallochlorin-type UV-visible spectra are also obtained when the reduction of (TPP)Ru(CO) is carried out in DMF or PhCN containing  $\text{CH}_3\text{I}$ . These UV-visible data are summarized in Table I. The spectra for the resulting products are similar to each other, but there is a shift of all peak maxima in DMF or PhCN with respect to values obtained in THF. This shift is consistent with an axial coordination of one or more solvent molecules to the electrogenerated product and has been previously reported for neutral (TPP)Ru(CO) under the same experimental conditions.<sup>3</sup>

The fate of the bound CO ligand after electroreduction of (TPP)Ru(CO) was ascertained by analysis of in situ FTIR spectra that were recorded before and after controlled-potential electrolysis of the complex in THF, PhCN, or DMF solutions containing  $\text{CH}_3\text{I}$ . Examples of the resulting spectra in THF are depicted in Figure 3. The initial porphyrin has a CO stretching vibration at  $1941\text{ cm}^{-1}$  in THF (Figure 3a) and this peak shifts to  $1894\text{ cm}^{-1}$  upon formation of [(TPP)Ru(CO)]<sup>•−</sup>, consistent with the increased negative charge on the complex. In contrast, the  $1941\text{-cm}^{-1}$  band of (TPP)Ru(CO) remains unchanged after reduction in THF solutions containing  $\text{CH}_3\text{I}$  (Figure 3b).

**Mass Spectrometry.** Twenty milligrams of (TPP)Ru(CO) was bulk electroreduced at  $-1.70$  V in THF containing 0.1 M TBAP, after which the solution was transferred to a flask containing 20–50 equiv of  $\text{CH}_3\text{I}$  and the mixture stirred overnight. The solvent was

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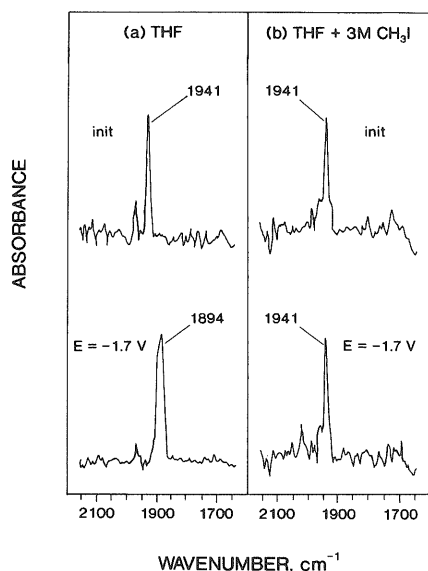


Figure 3. In situ FTIR spectra of  $1.0 \times 10^{-3}$  M (TPP)Ru(CO) before (top) and after (bottom) reduction at  $-1.70$  V in THF containing  $0.2$  M TBAP (a) in the absence and (b) in the presence of  $\text{CH}_3\text{I}$ .

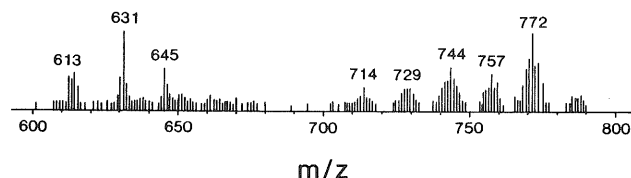


Figure 4. Mass spectrum of ruthenium(II) carbonyl tetraphenyldimethylchlorin.

Table II. FAB Mass Spectral Data<sup>a</sup>

positive ion	$m/z$	rel abund
[TPP] <sup>+</sup>	613	18
[(TPP)H <sub>2</sub> + CH <sub>3</sub> + H] <sup>+</sup>	631	100
[(TPP)H <sub>2</sub> + 2CH <sub>3</sub> ] <sup>+</sup>	645	55
[(TPP)Ru] <sup>+</sup>	714	30
[(TPP)Ru + CH <sub>3</sub> ] <sup>+</sup>	729	30
[(TPP)Ru + 2CH <sub>3</sub> ] <sup>+</sup>	744 <sup>b</sup>	58
[(TPP)Ru(CO) + CH <sub>3</sub> ] <sup>+</sup>	757	48
[(TPP)Ru(CO) + 2CH <sub>3</sub> ] <sup>+</sup>	772	100

<sup>a</sup>Listed values with a ruthenium central metal are consistent with the  $^{102}\text{Ru}$  isotope. <sup>b</sup>Another possible fragment is [(TPP)Ru(CO)]<sup>+</sup>.

evaporated under reduced pressure, the residue dissolved in  $\text{C}_6\text{H}_6$ , and the supporting electrolyte removed by filtration. The filtrate was then chromatographed on a silica gel column. The first eluent with  $\text{C}_6\text{H}_6$  had a red color and was characterized as unreacted (TPP)Ru(CO). The second portion eluted with  $\text{C}_6\text{H}_6/(\text{CH}_3)_2\text{CO}$  (1:1) and exhibited a green color. This band could not be further separated, and the isolated green porphyrin product was characterized by fast-atom-bombardment mass spectrometry.

The resulting mass spectrum is shown in Figure 4, and an assignment of each main fragment is listed in Table II. The highest relative abundances of the porphyrin fragments are found at mass units of 772 and 631 but the base peak (not shown) corresponds to the protonated NBA matrix and is located at  $m/z = 154$ . The fragment at  $m/z = 772$  corresponds to the molecular ion of ruthenium(II) carbonyl tetraphenyldimethylchlorin and the  $m/z = 631$  peak to a free base tetraphenylmethylchlorin with one additional hydrogen atom.

## Discussion

All of the data are self-consistent and indicate  $\text{CH}_3$  addition to the porphyrin ring of reduced [(TPP)Ru(CO)]<sup>-</sup>. The resulting product is a chlorin, and this is best indicated by the electrochemical data. As earlier mentioned, one major difference between metallochlorins and metalloporphyrins is that the former species

are easier to oxidize by 200–300 mV.<sup>20,22,23</sup> This is also the case for the product produced in the reaction between [(TPP)Ru(CO)]<sup>-</sup> and  $\text{CH}_3\text{I}$ . The initial porphyrin is oxidized at  $E_{1/2} = 1.13$  V in THF while the product of the chemical reaction is oxidized at  $E_{1/2} = 0.87$  V under the same solution conditions. This magnitude of potential shift is too large to be accounted for by a simple substituent effect of the added  $\text{CH}_3$  group, but fits well with the expected difference in  $E_{1/2}$  between oxidation of a metalloporphyrin and oxidation of a metallochlorin containing the same central metal.

The similar CO frequencies of neutral and reduced (TPP)Ru(CO) in the presence of  $\text{CH}_3\text{I}$  indicate that the CO ligand remains axially coordinated after electroreduction and that there is no significant difference between the electron density at the central metal of the initial complex and that of the final product. This result is also consistent with formation of a ruthenium(II) carbonyl chlorin and rules out formation of a Ru(III)  $\sigma$ -bonded methyl derivative. Published data on iron(II) carbonyl complexes of octaethylporphyrin (OEP) and octaethylchlorin (OEC) indicate that these two derivatives have virtually identical CO stretching frequencies,<sup>24</sup> and this also appears to be the case for the presently investigated porphyrin and electrogenerated chlorin.

The FAB mass spectrum in Figure 4 is well-defined, and the resulting  $m/z$  ratios indicate fragments for both metallated and demetallated  $\text{CH}_3$  adducts. Each fragment with a Ru central metal ion appears as a cluster in the mass spectrum, and this behavior is consistent with the complex isotope pattern of the metal.<sup>25</sup> The most abundant isotope is  $^{102}\text{Ru}$  and the listed  $m/z$  ratios in Table II are for fragments having this isotope.

The highest relative abundances of the porphyrin fragments are observed at  $m/z = 631$  and 772 (see Table II and Figure 4) and these correspond to [(TPP)H<sub>2</sub> + CH<sub>3</sub> + H]<sup>+</sup> and [(TPP)Ru(CO) + 2CH<sub>3</sub>]<sup>+</sup>, respectively. Demetallated fragments of TPP are also observed at  $m/z = 613$  and 645, and this is consistent with the known demetallation of metalloporphyrins in a FAB mass spectral matrix.<sup>26</sup>

The addition of  $\text{CH}_3$  to reduced (TPP)Ru(CO) might also occur at one of the porphyrin nitrogens to give an N-substituted porphyrin.<sup>27</sup> Three strong absorption bands of N-substituted metalloporphyrins are generally located in the region 500–700 nm.<sup>27</sup> These are not observed in the UV-visible spectrum of the resulting product (see Figure 2b), and this gives additional evidence that the two methyl groups from  $\text{CH}_3\text{I}$  can only be attached to the pyrrole carbons of the porphyrin.

The addition of two methyl groups to the macrocycle of reduced (TPP)Ru(CO) can result in a mixture of cis and trans isomers, as in the case for octaethylchlorins,<sup>28</sup> or the isolated species may be a mixture of different chlorin derivatives (i.e. those with one or more methyl groups attached to the porphyrin ring). Alternatively, the isolated species might also be mixtures of different structural isomers as was discussed for the case of the  $\alpha,\delta$ -dimethyl- $\alpha,\delta$ -dihydroporphyrin produced as a product in the reaction.<sup>29</sup> Unfortunately, the exact stereochemical orientation is not known in the present case.

In summary, this study has provided the first example for electrogeneration of a methylated chlorin. The reaction between [(TPP)Ru(CO)]<sup>-</sup> and  $\text{CH}_3\text{I}$  differs from that of reduced cobalt, iron, and rhodium porphyrins in that a stable  $\sigma$ -bonded  $\text{CH}_3$  derivative is not formed as a final reaction product. The first electroreduction of (TPP)Ru(CO) is clearly ring-centered,<sup>2</sup> and the electron density located at the porphyrin  $\pi$ -ring system favors

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an electrophilic attack to give the final chlorin product. Attempts are now underway to see if this is a general phenomenon for TPP complexes or is limited only to the case of reduced (TPP)Ru(CO).

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