

Electrochemistry of (Tetraphenylporphinato)rhodium(III) Alkyl and Alkyl Halide Complexes. Effect of the σ -Bonded Ligand on Porphyrin Reactivity

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The electrochemistry of 17 different (tetraphenylporphinato)rhodium(III) complexes of the form (TPP)Rh(R) and (TPP)Rh(RX) are reported, where TPP is the dianion of tetraphenylporphyrin, R = C₆H₅ or C_nH_{2n+1} (n = 1-6), and RX = C_nH_{2n}Cl (n = 3-5), C_nH_{2n}Br (n = 3-5), or C_nH_{2n}I (n = 3-6). The nature of the R or RX group determines the overall electrochemical behavior for the reduction of (P)Rh(R) or (P)Rh(RX). For some complexes the bound alkyl halide can be reduced without cleavage of the metal-carbon bond, and this results in the electrochemically initiated conversion of (TPP)Rh(RX) to a (TPP)Rh(R) complex. A general reduction scheme is presented that summarizes the electrochemistry of these compounds.

Introduction

Electrochemical properties of monomeric and dimeric rhodium porphyrins of the type [(TPP)Rh(L)₂]⁺Cl⁻, (TPP)Rh(L)(Cl), and [(TPP)Rh]₂ have been reported,¹ where TPP is the dianion of tetraphenylporphyrin and L is dimethylamine. Oxidation of the monomeric Rh(III) complex occurs at the porphyrin π ring system while reduction of the complex occurs at the metal center. This Rh(III)/Rh(II) reaction is followed by one of two types of chemical reactions. One involves formation of a σ -bonded Rh(III) complex while the other involves dimerization of (TPP)Rh to give [(TPP)Rh]₂. These competing reaction pathways of (TPP)Rh are summarized in Scheme I. The electrochemical properties of [(TPP)Rh]₂ and (TPP)Rh(R) synthesized via these pathways have been reported^{1,2} and compared to properties of (TPP)Rh(COCH₃).³

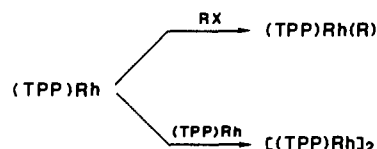
In this paper we report the synthesis and electrochemical properties of different rhodium(III) porphyrins containing σ -bonded alkyl halides. The synthesis of these rhodium porphyrins σ -bonded to alkyl halides has not been previously reported and provides a series of compounds where the electrochemical reduction may occur at the porphyrin π ring system, at the central Rh(III) ion, or at the complexed alkyl halide. Seventeen different complexes are investigated in this study. These include (TPP)Rh(R), where R = C_nH_{2n+1} (n = 1-6) or C₆H₅, and (TPP)Rh(RX), where RX = C_nH_{2n}Cl (n = 3-5), C_nH_{2n}Br (n = 3-5), or C_nH_{2n}I (n = 3-6). In all cases the R or RX group is the straight-chain isomer and for RX, the halide is on the CH₂ group farthest from the Rh center.

A generally accepted mechanism for reduction of free RX in nonaqueous media is shown by eq 1-3.^{4,5} This study demonstrates



that a similar reduction of the bound alkyl halide on (TPP)Rh(RX) is possible without cleavage of the Rh-carbon bond and that this reduction occurs at potentials significantly positive of those for reduction of free RX. Also, the results of this study clearly demonstrate that the nature of the R or RX group of (TPP)Rh(R) and (TPP)Rh(RX) can determine the overall electrochemical behavior for reduction.

Scheme I



Experimental Section

Instrumentation and Methods. An IBM 225/2A voltammetric analyzer and a Houston Instruments Model 2000 X-Y recorder were used for cyclic voltammetric measurements. Thin-layer spectroelectrochemical measurements were performed with an IBM 225/2A voltammetric analyzer coupled with a Tracor Northern 1710 spectrometer/multichannel analyzer. Bulk controlled-potential coulometry was performed on an EG&G Princeton Applied Research Model 174 potentiostat/179 coulometer system, coupled with an EG&G Princeton Applied Research Model RE-0074 time base X-Y recorder. Cells used for bulk electrolysis experiments were modified for Schlenk techniques. Platinum-disk electrodes were used for cyclic voltammetric measurements, and platinum-mercuric iodide electrodes were used in both the thin-layer spectroelectrochemical cell and the bulk electrolysis cell. The thin-layer spectroelectrochemical cell has been previously described.⁶ Potentials were measured vs a saturated calomel electrode (SCE) separated from the bulk of the solution by a fritted-glass disk junction. The ferrocene/ferrocenium couple was used as an internal standard against which potentials were also measured. Unless otherwise noted, 0.2 M tetrabutylammonium (TBAP) was used as supporting electrolyte in all electrochemical and spectroelectrochemical experiments.

UV-visible spectra were measured either on a Tracor Northern 1710 spectrometer/multichannel analyzer or with an IBM 9430 spectrophotometer using cells adapted for inert-atmosphere measurements. NMR spectra were measured on a Nicolet FT 300 spectrometer. Gas chromatographic analysis was performed with a Hewlett Packard 5890 gas chromatograph coupled with a Hewlett Packard 3392A integrator.

Materials. Reagent grade benzonitrile (PhCN) was predried with Na₂CO₃ and then vacuum distilled over P₂O₅ prior to use. Spectroscopic grade tetrahydrofuran (THF) was purchased from Aldrich and purified by distillation under nitrogen first from CaH₂ and then from Na/benzophenone just prior to use. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Fluka Chemical Co., twice recrystallized from ethyl alcohol, and dried in a vacuum oven at 40 °C. All organic reagents (Aldrich) were purchased at the highest level of purity available, purified by standard procedures⁷ where necessary, and checked for impurities by gas chromatographic analysis. Deuteriated benzene-*d*₆ (C₆D₆) was purchased from Aldrich and used without further purification.

Synthesis of (TPP)Rh(R). (TPP)Rh(C₆H₅), (TPP)Rh(CH₃), and [(TPP)Rh(L)₂]⁺Cl⁻, where L is dimethylamine, were synthesized by literature methods.^{1,8-10} The other (TPP)Rh(R) and (TPP)Rh(RX)

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Table I. ¹H NMR Data for the σ -Bonded Alkyl Group of (P)Rh(R)^a

compd	n	δ , splitting, ^b no. of H					
		-5.54, d, 3 H ^c		-4.19, t, 3 H		-1.77, t, 3 H	
(TPP)Rh(C _n H _{2n+1})	2	-4.61, m, 2 H	-4.10, h, 2 H	-1.57, h, 2 H	-0.81, t, 3 H		
	3	-4.65, m, 2 H	-4.18, p, 2 H	-1.62, p, 2 H	-0.51, h, 2 H	-0.27, t, 3 H	
	4	-4.60, m, 2 H	-4.16, p, 2 H	-1.56, p, 2 H	-0.53, p, 2 H	0.08, h, 2 H	0.13, t, 3 H
	5	-4.63, m, 2 H	-4.16, p, 2 H	-1.56, p, 2 H	-0.53, p, 2 H	0.08, 2, 2 H	
	6	-4.61, m, 2 H	-4.16, p, 2 H	-1.56, p, 2 H	-0.53, p, 2 H	0.08, 2, 2 H	
	(TPP)Rh(C _n H _{2n} Cl)	3	-4.87, m, 2 H	-4.21, p, 2 H	-1.52, p, 2 H	1.31, t, 2 H	
(TPP)Rh(C _n H _{2n} Br)	4	-4.83, m, 2 H	-4.32, p, 2 H	-1.70, p, 2 H	-0.36, p, 2 H	1.91, t, 2 H	
	5	-4.77, m, 2 H	-4.32, p, 2 H	-1.70, p, 2 H	-0.36, p, 2 H	1.91, t, 2 H	
	6	-4.89, m, 2 H	-3.80, p, 2 H	-0.07, t, 2 H			
(TPP)Rh(C _n H _{2n} I)	4	-4.84, m, 2 H	-4.21, p, 2 H	-1.45, p, 2 H	1.17, t, 2 H		
	5	-4.78, m, 2 H	-4.33, p, 2 H	-1.72, p, 2 H	-0.31, p, 2 H	1.74, t, 2 H	
	6	-4.96, m, 2 H	-3.85, p, 2 H	-0.30, t, 2 H			
	4	-4.86, m, 2 H	-4.27, p, 2 H	-1.51, p, 2 H	0.89, t, 2 H		
	5	-4.79, m, 2 H	-4.35, p, 2 H	-1.76, p, 2 H	-0.35, p, 2 H	1.49, t, 2 H	
	6	-4.73, m, 2 H	-4.30, p, 2 H	-1.82, p, 2 H	-0.73, p, 2 H	0.26, p, 2 H	1.92, t, 2 H

^aSolvent C₆D₆. ^bm = multiplet due to J_{Rh-H}; t = triplet; p = pentet; h = hextet. ^cReference 2.

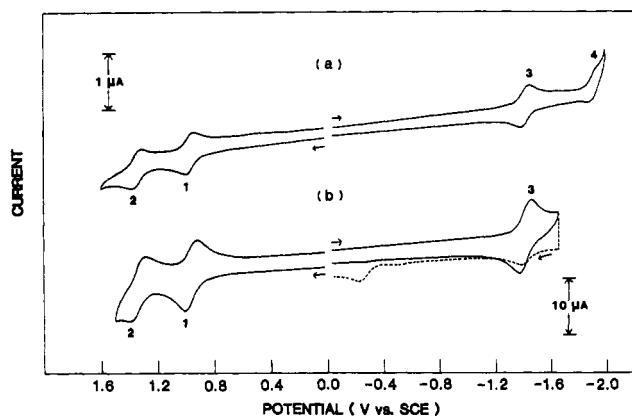


Figure 1. (a) Cyclic voltammogram of a 1.1×10^{-3} M (TPP)Rh(C₂H₅) in PhCN containing 0.2 M TBAP (scan rate = 0.1 V/s). (b) Thin-layer cyclic voltammogram of (TPP)Rh(C₂H₅) in PhCN containing 0.2 M TBAP (scan rate = 0.01 V/s): (—) first scan; (---) reverse scan after holding for 5 min at -1.6 V.

complexes were synthesized by an electrochemical procedure similar to the one that has been previously described.² The identification and purity of the resulting (TPP)Rh(C_nH_{2n+1}) or (TPP)Rh(C_nH_{2n}X) complexes were determined from NMR data.

¹H NMR Data. ¹H NMR spectra for the tetraphenylporphyrin ring of (TPP)Rh(R) and (TPP)Rh(RX) can be summarized as follows: pyr-H, 8.86 ± 0.05 ppm, s, 8 H; o-H, 8.20 ± 0.5 ppm, m, 8 H; m,p-H, 7.49 ± 0.05 ppm, m, 12 H. Resonances of the σ -bonded R and RX ligand for each individual compound are summarized in Table I.

Results and Discussion

Oxidation of (TPP)Rh(R) and (TPP)Rh(RX). Each (TPP)Rh(R) and (TPP)Rh(RX) complex undergoes two reversible, diffusion-controlled one-electron oxidations by cyclic voltammetry. Both processes are characterized by $\Delta E_p = 60 \pm 5$ mV, a constant $i_p/v^{1/2}$ and $|E_p - E_{p/2}| = 60 \pm 5$ mV. This is illustrated by the voltammogram of (TPP)Rh(C₂H₅) in PhCN containing 0.1 M TBAP (Figure 1).

Similar reversible oxidative behavior was observed for all 17 investigated (TPP)Rh(R) and (TPP)Rh(RX) complexes whose oxidation potentials are listed in Table II. As seen in this table, the values of $E_{1/2}$ vary little with the nature of the σ -bonded alkyl ligand and occur at 0.98 ± 0.01 V (wave 1, Figure 1a) and 1.35 ± 0.01 V (wave 2, Figure 1a) in PhCN. The insensitivity of $E_{1/2}$ to the specific R or RX group suggests that the electron abstractions occur at the porphyrin π ring system. This site of electron abstraction is also suggested by the 0.37 ± 0.02 V difference in $E_{1/2}$ between the two oxidations in PhCN, which is close to the experimentally observed $\Delta E_{1/2}$ of 0.29 ± 0.05 V for consecutive ring oxidations of a number of metalloporphyrins.¹¹

Thin-layer cyclic voltammograms of (TPP)Rh(R) and (TPP)Rh(RX), where R = C₆H₅, CH₃, C₂H₅, or C₅H₁₁ and RX

Table II. Oxidation and Reduction Potentials (V vs SCE) for (TPP)Rh(R)

R group	solvent	temp, °C	oxidn		redn	
			$E_{1/2}$	$E_{1/2}$	$E_{1/2}$	$E_{1/2}$
CH ₃	THF	23			-1.45	-1.90
C ₂ H ₅	THF	23	1.12		-1.41	-1.90
	PhCN	23	0.97	1.35	-1.41	-1.90
C ₃ H ₇	THF	23			-1.42	-1.91
	PhCN	23	0.97	1.33	-1.40	-1.89
C ₄ H ₉	THF	23			-1.42	-1.92
	PhCN	23	0.97	1.34	-1.41	-1.90
C ₅ H ₁₁	THF	23			-1.42	-1.91
	PhCN	23	0.98	1.34	-1.40	-1.89
C ₆ H ₁₃	THF	23			-1.42	-1.91
	PhCN	23	0.97	1.34	-1.41	-1.90
C ₆ H ₅	THF	23			-1.40	-1.81
	PhCN	23	0.99	1.38	-1.39	-1.84
C ₃ H ₆ Cl	THF	23	1.17		-1.41	-1.86
	PhCN	23	1.14		-1.41	-1.88
C ₄ H ₈ Cl	THF	23	1.14		-1.42	-1.90
	PhCN	23	1.14		-1.42	-1.90
C ₅ H ₁₀ Cl	THF	23			-1.39	-1.83 ^b
	PhCN	23	0.98	1.34	-1.41	-1.89 ^a
C ₃ H ₆ Br	THF	-75	1.11	1.32	-1.42	-1.88
	PhCN	23	1.14		-1.40	-1.85 ^a
C ₄ H ₈ Br	THF	-70	1.10	1.33	-1.44	-1.87
	PhCN	23	1.14		-1.40	-1.89 ^a
C ₅ H ₁₀ Br	THF	-74	1.10	1.34	-1.44	-1.88
	PhCN	23	1.15		-1.38 ^a	-1.83 ^b
C ₃ H ₆ I	THF	-70	1.13	1.34	-1.43	-1.88 ^a
	PhCN	23	0.98	1.35	-1.37 ^a	-1.84
C ₄ H ₈ I	THF	23	1.15		-1.39	-1.78 ^a
	PhCN	23	0.97	1.34	-1.41	-1.92 ^a
C ₅ H ₁₀ I	THF	-75	1.09	1.33	-1.42	-1.86 ^a
	PhCN	23	1.15		-1.40	-1.88
C ₆ H ₁₂ I	THF	-76	1.10	1.33	-1.43	-1.90 ^a
	PhCN	23	0.98	1.35	-1.41	-1.86 ^a
C ₆ H ₁₂ I	THF	23	1.14		-1.41	-1.82 ^a
	PhCN	23	0.99	1.35	-1.40	-1.89

^a E_p , scan rate = 100 mV/s, process 5; see text. ^bDue to reduction of [(TPP)Rh]₂; see ref 1.

= C_nH_{2n}I (n = 3–6), also show two reversible, one-electron oxidations on the cyclic voltammetric time scale. This is illustrated in Figure 1b for (TPP)Rh(C₂H₅) in PhCN. Thin-layer coulometric oxidation of (TPP)Rh(C₂H₅) at 1.20 V gives a calculated value of $n = 1.2 \pm 0.1$ electrons abstracted per rhodium atom. However, bulk electrolysis of (TPP)Rh(C₂H₅) as well as other compounds in the (TPP)Rh(R) or (TPP)Rh(RX) series indicates that a chemical reaction follows the initial oxidation and n values greater than 1.0 are obtained. For example, bulk electrolysis of (TPP)Rh(C₃H₇) at 1.20 V in PhCN shows the abstraction of 2.1 ± 0.1 electrons. This suggests a cleavage of the Rh–carbon bond and further oxidation of the generated [(TPP)Rh]⁺ species.

Changes in the electronic absorption spectrum of (TPP)Rh(C₂H₅) as the compound is oxidized at 1.20 V vs SCE in PhCN

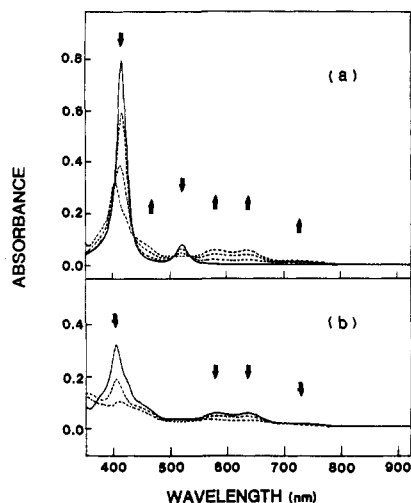


Figure 2. Electronic absorption spectra of (a) neutral and singly oxidized (TPP)Rh(C₂H₅) and (b) singly and doubly oxidized (TPP)Rh(C₂H₅) in PhCN containing 0.2 M TBAP.

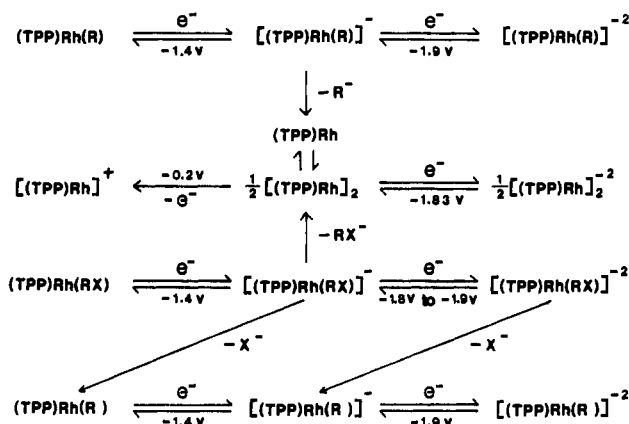


Figure 3. Reaction scheme for the electroreduction of (TPP)Rh(R) and (TPP)Rh(RX) in THF.

are shown in Figure 2a. As the oxidation proceeds, the Soret band, which is initially at 416 nm, decreases in intensity and shifts to 403 nm. The absorption band at 522 nm also decreases in intensity as new bands are observed at 585 and 640 nm. These changes in the UV-visible spectrum indicate electron abstraction from a porphyrin ring based orbital with formation of a cation radical.¹¹

The electrooxidation of (TPP)Rh(C₂H₅) is not reversible, and the original spectrum is not regenerated when the potential is reset to 0.70 V. This type of irreversibility upon electrooxidation was observed for the other (TPP)Rh(R) and (TPP)Rh(RX) compounds. In all cases, a chemical reaction followed the initial oxidation, but for most complexes the rate of this reaction was relatively slow and reversible cyclic voltammetric behavior was obtained.

Figure 2b shows representative changes that occur in the UV-visible spectrum of (TPP)Rh(C₂H₅) upon switching the potential from 1.20 to 1.50 V. The Soret band continues to decrease in intensity during the second oxidation. There is also a general decrease in intensity of the Q bands, typical of dication formation.¹¹ This oxidation is also not reversible, and the original spectrum is not regenerated if the potential is set back to 0.70 V. Similar UV-visible spectral changes are obtained during the second oxidation of each (TPP)Rh(R) and (TPP)Rh(RX) complex investigated. Thus spectroelectrochemical results confirm that the initial oxidations of (TPP)Rh(R) and (TPP)Rh(RX) occur at the porphyrin π ring system but also indicate that the singly and doubly oxidized species are involved in a chemical

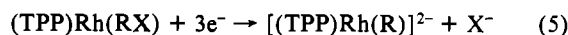
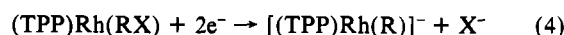
Table III. UV-Visible Spectra of Complexes in PhCN Containing 0.2 M TBAP

complex	R group	solvent	λ_{max} , nm ($\epsilon \times 10^{-4}$)		
(TPP)Rh(R)	CH ₃	PhCN	418 (22.9)	525 (2.3)	
		THF	411 (21.6)	524 (1.9)	
	C ₂ H ₅	PhCN	416 (21.3)	522 (2.2)	
		THF	411 (17.7)	524 (1.5)	
	C ₃ H ₇	THF	411 (21.5)	524 (1.7)	
		THF	411 (25.2)	524 (2.3)	
	C ₅ H ₁₁	PhCN	416 (20.1)	522 (2.3)	
		THF	411 (27.9)	524 (2.8)	
	C ₆ H ₅	THF	413 (20.8)	525 (2.2)	
		THF	411 (27.2)	524 (2.5)	
(TPP)Rh(RX)	C ₃ H ₆ Cl	THF	411 (27.2)	524 (2.5)	
		THF	411 (27.9)	524 (2.7)	
	C ₅ H ₁₀ Cl	THF	411 (24.9)	524 (2.0)	
		THF	411 (24.7)	524 (2.4)	
	C ₃ H ₆ Br	THF	411 (29.2)	524 (3.2)	
		THF	411 (23.7)	524 (1.9)	
	C ₅ H ₁₀ Br	THF	411 (26.9)	524 (2.2)	
		PhCN	417 (21.9)	524 (2.2)	
	C ₄ H ₈ I	THF	411 (30.9)	524 (2.6)	
		THF	411 (27.7)	524 (2.2)	
C ₆ H ₁₂ I	THF	411 (27.2)	524 (2.2)		
	PhCN	404 (8.8)	583 (1.6)	645 (1.4)	
[(TPP)Rh(R)] ⁺	C ₂ H ₅	PhCN	403 (8.7)	585 (1.5)	640 (1.4)
	C ₅ H ₁₁	PhCN	403 (8.6)	579 (1.5)	639 (1.4)
	C ₃ H ₆ I	PhCN	405 (9.7)	583 (1.7)	539 (1.5)
[(TPP)Rh(RX)] ⁺	CH ₃	PhCN	413 (3.4)	564 (0.8)	645 (0.7)
		PhCN	411 (2.6)	566 (0.8)	640 (0.6)
	C ₅ H ₁₁	PhCN	408 (3.9)	566 (1.1)	651 (0.7)
[(TPP)Rh(RX)] ²⁺	C ₃ H ₆ I	PhCN	408 (4.8)	562 (1.0)	654 (0.6)

reaction. A complete summary of the spectroelectrochemical data for the oxidation of each (TPP)Rh(R) and (TPP)Rh(RX) complex before the chemical reaction occurs is presented in Table III.

Reduction Pathways of (TPP)Rh(R) and (TPP)Rh(RX). Figure 3 summarizes the overall electrochemical and chemical reaction pathways that can occur upon reduction of different (TPP)Rh(R) and (TPP)Rh(RX) complexes. The specific group of compounds that follow a given reduction pathway can be divided into two sets. The first set of compounds is comprised of (TPP)Rh(R), where R = C_nH_{2n+1} (n = 1–6) or C₆H₅, and (TPP)Rh(RX), where RX = C_nH_{2n}Cl (n = 3–5). These metalloporphyrins can undergo two reversible ring reductions (at -1.4 and -1.9 V), but the singly reduced species undergo a cleavage of the Rh-carbon bond on longer time scales.

The second set of compounds is comprised of (TPP)Rh(RX), where RX = C_nH_{2n}Br (n = 3–5) or C_nH_{2n}I (n = 3–6). For these compounds an important intermediate in the electrochemistry is the [(TPP)Rh(RX)]⁻ monoanion. This species can lose X⁻, lose RX⁻, or be further reduced at the axial ligand. The particular pathway for reaction of (TPP)Rh(RX) depends upon the individual RX species and the given reaction conditions such as temperature or scan rate. These pathways are given by the overall reactions 4 and 5 and are discussed in the following sections.



Reversible Reductions of (TPP)Rh(R) and (TPP)Rh(RX), Where RX = C_nH_{2n}Cl (n = 3–5). (TPP)Rh(R) and (TPP)Rh(RX), where RX = C_nH_{2n}Cl (n = 3–5), undergo two reversible reductions at the porphyrin π ring system. The electrochemical behavior of these complexes is typified by (TPP)Rh(C₂H₅) in which two reversible, one-electron, diffusion-controlled reductions are observed on the cyclic voltammetric time scale. These reductions occur at $E_{1/2} = -1.41$ and $E_{1/2} = -1.90$ V and are labeled as waves 3 and 4 in Figure 1a. For both processes, $\Delta E_p = 60 \pm 5$ mV, $|E_p - E_{p/2}| = 60 \pm 5$ mV and $i_p/v^{1/2}$ is a constant. Similar diffusion-controlled reductions are obtained in THF.

Thin-layer cyclic voltammograms of (TPP)Rh(C₂H₅) (Figure 1b) also suggest reversible electrochemical processes, and thin-layer coulometric values for the reduction of (TPP)Rh(C₂H₅) at -1.62 V give values of $n = 1.2 \pm 0.1$. However, decomposition of reduced (TPP)Rh(C₂H₅) and formation of [(TPP)Rh]₂ occurs when the potential is held at potentials negative of the first reduction for

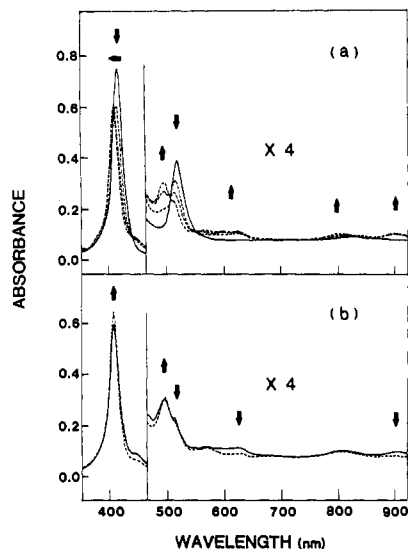


Figure 4. Electronic absorption spectra (a) during the initial reduction of (TPP)Rh(C₂H₅) at -1.6 V in PhCN containing 0.2 M TBAP and (b) after holding the reduction potential at -1.6 V for 5 min.

5 min. Dimer formation is indicated by the presence of an oxidation peak at $E_p = -0.2$ V (see dotted line, Figure 1b).¹

Figure 4a shows changes that occur in the UV-visible spectra of (TPP)Rh(C₂H₅) upon reduction at -1.65 V in PhCN. As the reduction proceeds, the Soret band is reduced in intensity and shifts to 407 nm. The Q bands also show a decrease in intensity and shift to 497 and 516 nm. New absorption bands are observed at 814 and 908 nm and are indicative of anion radical formation.¹¹ The original spectrum can be obtained if the potential is immediately reset to 0.0 V, but there is evidence of a chemical reaction involving the anion radical.

Spectral changes associated with porphyrin dianion formation are initially observed when the compound is reduced at -1.94 V. However, the final UV-visible spectrum has bands at 447 and 807 nm and is close to that of the product formed after decomposition of the dianion. In addition, when the potential is set back to 0.00 V, the original species is not regenerated, thus suggesting a more rapid chemical reaction of the dianion.

Figure 4b spectrally demonstrates the conversion of [(TPP)Rh(C₂H₅)]⁻ to [(TPP)Rh]₂. This was accomplished by reducing (TPP)Rh(C₂H₅) at -1.65 V and holding the potential for 5 min. The final electronic absorption spectra is characterized by bands at 407, 497, and 516 nm and is indicative of [(TPP)Rh]₂ in PhCN solution.

Similar reductive properties are observed for (TPP)Rh(R), where R = C_nH_{2n+1} ($n = 1-6$) or C₆H₅ and RX = C_nH_{2n}Cl ($n = 3-5$). Reduction potentials for this set of compounds are listed in Table II and suggest that the successive addition of one and two electrons occur at the porphyrin π ring system. The separation of 0.50 ± 0.05 V between $E_{1/2}$ values for the two reductions agrees with the $\Delta E_{1/2} = 0.44 \pm 0.04$ V generally observed for the two successive one-electron ring reductions of numerous metalloporphyrins.¹¹

Spectroelectrochemical data for the reduction of (TPP)Rh(C_nH_{2n+1}) and (TPP)Rh(C_nH_{2n}Cl) demonstrates that the initial reduction is ring centered. In most cases the anion radicals are not stable, and cleavage of the rhodium-carbon bond occurs with formation of [(TPP)Rh]₂. The rate of the following chemical reaction is dependent upon the R group. A relatively stable anion radical is observed for (TPP)Rh(C₆H₅) and (TPP)Rh(COCH₃)³ on the spectroelectrochemical time scale.

Reduction of (TPP)Rh(C₃H₆I). The reduction of (TPP)Rh(C₃H₆I) is irreversible by cyclic voltammetry in PhCN (see Figure 5a). The first reduction occurs at $E_p = -1.37$ V (peak 3, Figure 5a) and is shifted by +40 mV relative to $E_{1/2}$ for the first reduction of (TPP)Rh(C₂H₅). Normal pulse polarograms have twice the reduction current as the first one-electron oxidation. This is shown in Figure 5b and suggests an overall two-electron reduction of

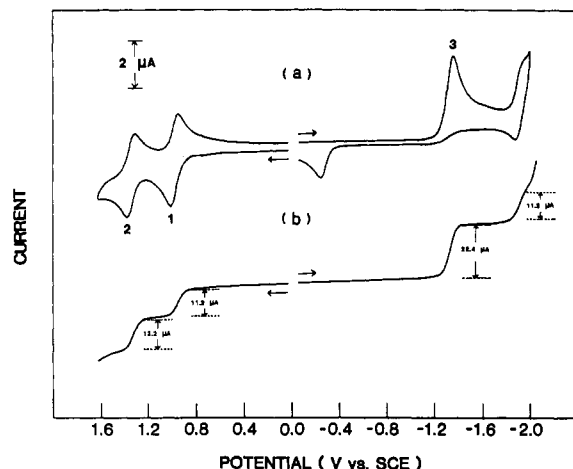


Figure 5. (a) Cyclic voltammogram and (b) normal-pulse voltammogram of (TPP)Rh(C₃H₆I) in PhCN containing 0.2 M TBAP.

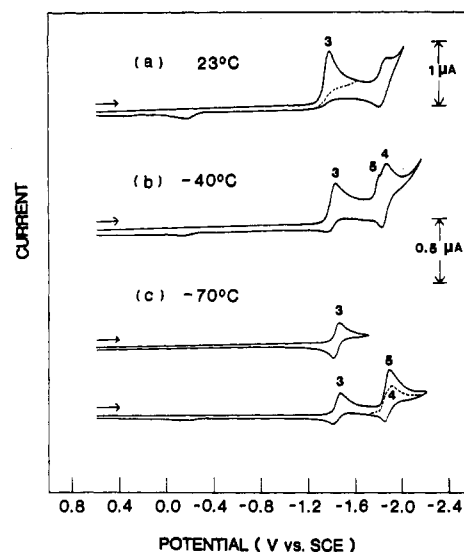


Figure 6. Cyclic voltammogram of 1.3×10^{-3} M (TPP)Rh(C₃H₆I) in THF containing 0.2 M TBAP at (a) 23, (b) -40, and (c) -70 °C: (—) single scan; (---) single scan with reversal of potential and second scan between -1.7 and -2.2 V (dashed line).

(TPP)Rh(C₃H₆I) in the first process. This was confirmed by thin-layer coulometry, which gave a value of $n = 2.2 \pm 0.2$ for controlled potential reduction at -1.62 V in THF.

An additional electroreduction is also observed at $E_{1/2} = -1.84$ V, and there is an irreversible oxidation at $E_p = -0.20$ V in the cyclic voltammogram. These two processes are due to [(TPP)Rh]₂, which is generated as a product of the chemical reaction following electroreduction.¹ The formation of [(TPP)Rh]₂ and I⁻ was detected by thin-layer voltammetric experiments on (TPP)Rh(C₃H₆I). An irreversible reduction of (TPP)Rh(C₃H₆I) occurs at $E_p = -1.37$ V. This process is coupled with a reversible wave at $E_{1/2} = -1.84$ V and an irreversible reoxidation wave at -0.20 V. There is also an additional oxidation wave at $E_p = 0.35$ V vs SCE. This process is due to the oxidation of I⁻. This was confirmed by independent experiments with TBA⁺I⁻ and a comparison with literature values for the oxidation of iodide in nonaqueous media.^{2,12}

The formation of [(TPP)Rh]₂ upon reduction of (TPP)Rh(C₃H₆I) demonstrates cleavage of the Rh-carbon bond, but low-temperature electrochemical data suggest that [(TPP)Rh(C₃H₆I)]⁻ can be stabilized and further reduced near -1.8 V. However, loss of (C₃H₆I)⁻ occurs at room temperature, and the

(12) Bard, A. J.; Merz, A. J. *Am. Chem. Soc.* **1979**, *101*, 2959 and references therein.

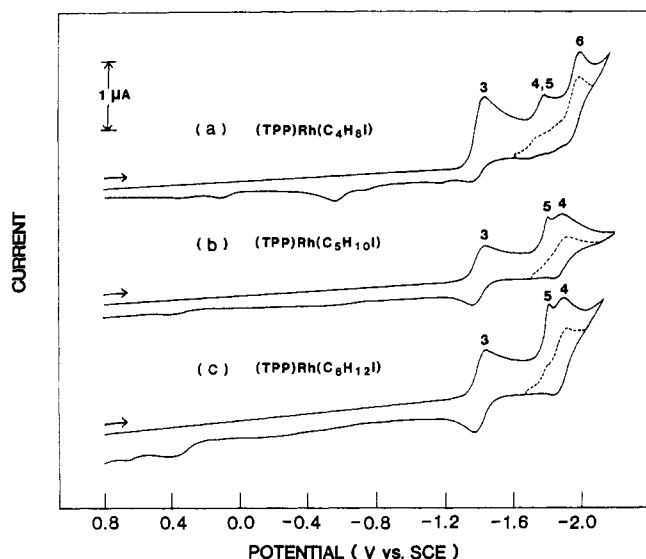


Figure 7. Cyclic voltammograms of (a) (TPP)Rh(C₄H₈I), (b) (TPP)Rh(C₅H₁₀I), and (c) (TPP)Rh(C₆H₁₂I) in THF containing 0.2 M TBAP at a scan rate of 0.1 V/s: (—) first scan; (---) second scan.

second electron in the overall two-electron reduction of (TPP)Rh(C₃H₆I) can be added to either (C₃H₆I)⁻ or its decomposition products.

The effect of temperature on the cyclic voltammogram of (TPP)Rh(C₃H₆I) is shown in Figure 6 and demonstrates that an ECE mechanism occurs for either the first or the second process depending upon temperature. The room-temperature cyclic voltammogram of (TPP)Rh(C₃H₆I) in THF (Figure 6a) suggests a similar room-temperature mechanism in THF and PhCN. However, as the temperature is reduced, the rate of the chemical reaction following the initial reduction is slowed down. At -70 °C the first reduction (wave 3, Figure 6c) becomes reversible and occurs at $E_{1/2} = -1.43$ V. No reduction or oxidation processes associated with [(TPP)Rh]₂ are observed at this temperature.

At -70 °C the second reduction process at -1.88 V (wave 5, Figure 6c) is then due to a further reduction of electrogenerated [(TPP)Rh(C₃H₆I)]⁻. This reduction is irreversible in that the ratio of the anodic to cathodic peak current is no longer equal to unity. The peak current of the cathodic process is approximately twice that of the initial one-electron transfer on the first potential sweep, and the values of E_{pc} and E_{pa} are -1.88 and -1.84 V, respectively, at 100 mV/s. However, if the potential is scanned a second time, a reversible process ($i_{pc} = i_{pa}$) occurs at $E_{1/2} = -1.86$ V. This process is labelled as wave 4 and is shown by the dashed line in Figure 6c. The maximum current of wave 4 is approximately the same height as the initial one-electron reduction at -70 °C (wave 3). This behavior suggests an ECE type mechanism at low temperature where the two electron transfers occur at or near -1.86 V.

The first reduction of (TPP)Rh(C₃H₆I) appears to be reversible at low temperatures, even after scanning past the second irreversible process. However, a chemical reaction follows the second reduction of (TPP)Rh(C₃H₆I) and results in a species that has reversible processes at $E_{1/2} = -1.43$ and -1.86 V. One species with this electrochemical behavior is (TPP)Rh(R), as indicated by the scheme in Figure 3. This implies a loss of I⁻ from [(TPP)Rh(C₃H₆I)]²⁻ in a reaction that is initiated by an electrochemical process. However, the exact nature of the R group of the electrogenerated species is unknown and the chemical reaction may involve more than loss of I⁻. Similar voltammetric behavior is observed for complexes in the (TPP)Rh(C_nH_{2n}I) and (TPP)Rh(C_nH_{2n}Br) series.

Irreversible first reductions are obtained for (TPP)Rh(RX), where RX = C_nH_{2n}I ($n = 3-6$). However, as the chain length of RX is increased from $n = 3$ to $n = 6$, the loss of RX⁻ following the initial one-electron reduction becomes kinetically very slow so that for $n = 5$ or 6 this reaction no longer has a significant

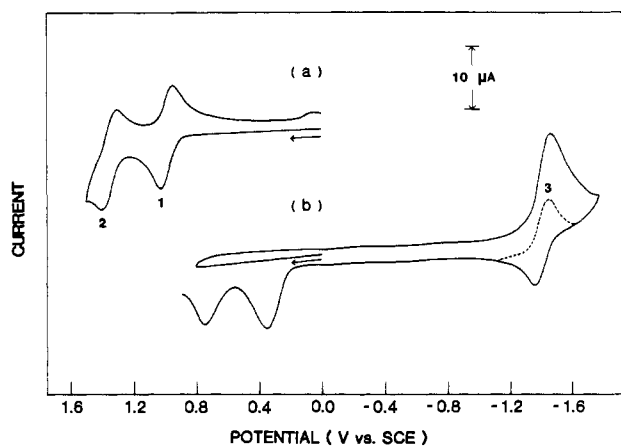


Figure 8. Thin-layer cyclic voltammogram for the (a) oxidation and (b) reduction of (TPP)Rh(C₆H₁₂I) in PhCN containing 0.2 M TBAP: (—) first scan; (---) second scan.

influence on the cyclic voltammetry. The effect of chain length is illustrated by the cyclic voltammograms in Figure 7. The cyclic voltammogram of (TPP)Rh(C₆H₁₂I) at room temperature (Figure 7c) is similar to that of (TPP)Rh(C₃H₆I) at -40 °C (Figure 6b). The loss of I⁻ from the doubly reduced (TPP)Rh(C₆H₁₂I) with generation of a [(TPP)Rh(R)]⁻ complex is proposed to be the primary reaction pathway on the cyclic voltammetry time scale. At -70 °C, each (TPP)Rh(C_nH_{2n}I) complex has the same reductive behavior.

Figure 8 shows a thin-layer cyclic voltammogram of (TPP)Rh(C₆H₁₂I) in PhCN. On this time scale, [(TPP)Rh(C₆H₁₂I)]⁻ reacts chemically and the loss of I⁻ is observed. Two reversible one-electron oxidations (waves 1 and 2, Figure 8a) are observed at $E_{1/2} = 0.99$ and 1.35 V when the potential is scanned in a positive direction. Figure 8b shows the reduction of this species on both the initial scan (solid line, Figure 8b) and the second scan (dashed line, Figure 8b). The data suggest an initial two-electron reduction of (TPP)Rh(C₆H₁₂I). The value of i_{pc} is approximately twice i_{pa} for reoxidation of this complex, but additional sweeps give a reversible wave (wave 3, Figure 8b) with $i_{pc} = i_{pa}$.

Formation of I⁻ upon reduction of (TPP)Rh(C₆H₁₂I) is indicated by the oxidation waves at $E_p = 0.35$ and 0.75 V. Thin-layer coulometric reduction of (TPP)Rh(C₆H₁₂I) at -1.70 V gives a value of $n = 2.1 \pm 0.2$, while reoxidation at 0.00 V gives $n = 1.0 \pm 0.2$. This coulometric data is consistent with a loss of I⁻ from [(TPP)Rh(C₆H₁₂I)]⁻. Hence, wave 3 in Figure 8b is assigned as the reversible reduction of the electrogenerated (TPP)Rh(R) complex. Similar behavior is observed on the thin-layer cyclic voltammetric time scale for (TPP)Rh(C₅H₁₀I) and hence demonstrates a similar chemical reaction following reduction.

The thin-layer cyclic voltammogram of (TPP)Rh(C₄H₈I) is substantially different from conventional cyclic voltammograms of this compound. The initial reduction is irreversible in the thin-layer experiment indicating a chemical reaction on this time scale. Two new reversible waves are observed at $E_{1/2} = +0.10$ and -0.59 V. The identity of the generated species is not known, but loss of I⁻ from (TPP)Rh(C₄H₈I) also occurs as indicated by the observation of an irreversible wave at $E_p = 0.35$ and 0.75 V.

The spectroelectrochemically monitored reduction of (TPP)Rh(C₃H₆I) demonstrates that formation of [(TPP)Rh(C₃H₆I)]⁻ (process 3) at -1.65 V is followed by cleavage of the rhodium-carbon bond and generation of [(TPP)Rh]₂. The initial species is characterized by bands at 411 and 524 nm. After reduction by two electrons, the Soret band is shifted to 403 nm while a new band is observed at 496 nm as [(TPP)Rh]₂ is formed.¹ The initial reduction of (TPP)Rh(C₅H₁₀I) and (TPP)Rh(C₆H₁₂I) appear to be ring centered, and in the case of (TPP)Rh(C₆H₁₂I) the spectrum is characterized by bands at 403, 497, 580, and 700 nm.

Reduction of (TPP)Rh(C_nH_{2n}Br). Cyclic voltammograms for (TPP)Rh(C_nH_{2n}Br) ($n = 3-5$) in THF are shown in Figure 9 and indicate that the chemical reactions following the initial one-electron transfer are slower than the chemical reactions observed

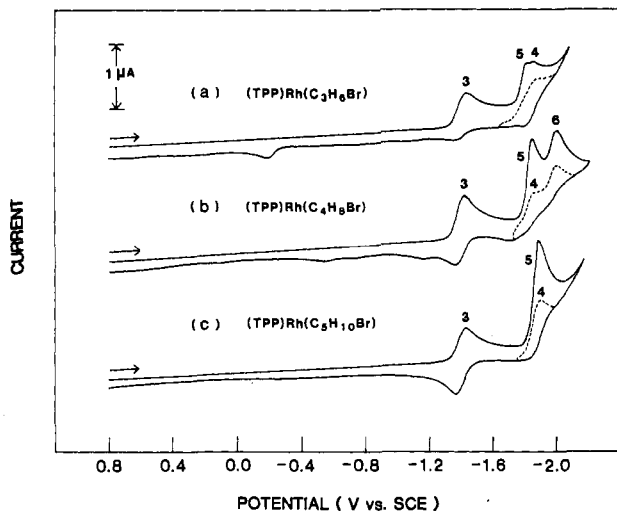


Figure 9. Cyclic voltammograms of (a) (TPP)Rh(C₃H₆Br), (b) (TPP)Rh(C₄H₈Br) and (c) (TPP)Rh(C₅H₁₀Br) in THF containing 0.2 M TBAP at a scan rate of 0.1 V/s: (—) first scan; (---) second scan.

for compounds in the (TPP)Rh(C_nH_{2n}I) series. The first reduction of (TPP)Rh(C₃H₆Br) (wave 3, Figure 9a) is not totally reversible on the cyclic voltammetric time scale, but a further reduction of [(TPP)Rh(C₃H₆Br)]⁻ (waves 4 and 5, Figure 9a) can be observed. Reduction of [(TPP)Rh(C₃H₆Br)] results in cleavage of the rhodium-carbon bond and formation of [(TPP)Rh]₂. The mechanism for dimer formation is similar to the one suggested for (TPP)Rh(C₃H₆I) and is supported by thin-layer cyclic voltammetric experiments that show an irreversible reduction at $E_p = -1.39$ V in THF containing 0.2 M TBAP. Thin-layer coulometric values of $n = 2.6 \pm 0.2$ are observed for reduction of (TPP)Rh(C₃H₆Br) at -1.62 V in THF.

The primary difference between (TPP)Rh(C₃H₆Br) and (TPP)Rh(C₃H₆I) is that the chemical reaction following the initial reduction is slower for (TPP)Rh(C₃H₆Br). Hence, room-temperature cyclic voltammograms of (TPP)Rh(C₃H₆Br) resemble those of (TPP)Rh(C₃H₆I) at reduced temperatures. In addition, the cyclic voltammogram of (TPP)Rh(C₃H₆Br) at -70 °C is characterized by two reversible reductions and is basically the same as that of (TPP)Rh(C₃H₆Cl) at room temperature. This indicates that the chemical reaction following reduction of (TPP)Rh(C₃H₆Br) is not significant at low temperature on the cyclic voltammetric time scale.

The first reduction of (TPP)Rh(C₄H₈Br) (wave 3, Figure 9b) is nearly reversible, and a second and third reduction are also observed. (waves 4 and 5, Figure 9b). An additional reduction (wave 6) is observed for this species at $E_p = -2.01$ V and is assigned as reduction of a decomposition product. This assignment is based on low-temperature cyclic voltammetric studies of (TPP)Rh(C₄H₈Br). At -70 °C, wave 6 is decreased in current relative to waves 3, 4, and 5, and the overall appearance of the cyclic

voltammogram is similar to that of (TPP)Rh(C₃H₆I) at -70 °C. Thin-layer cyclic voltammetric studies on (TPP)Rh(C₄H₈Br) suggest that reduction of this species results in loss of both Br⁻ and C₄H₉Br⁻ since [(TPP)Rh]₂ and a (TPP)Rh(R) species are observed.

The cyclic voltammogram of (TPP)Rh(C₅H₁₀Br) is shown in Figure 9c and is similar to the voltammogram of (TPP)Rh(C₆H₁₂I). Loss of Br⁻ and possible further reaction of [(TPP)Rh(C₅H₁₀Br)]²⁻ with generation of a [(TPP)Rh(R)]⁻ complex is observed on the cyclic voltammetric time scale. The thin-layer cyclic voltammogram of (TPP)Rh(C₅H₁₀Br) is very similar to that of (TPP)Rh(C₅H₁₀I) or (TPP)Rh(C₆H₁₂I), but differs in that Br⁻ rather than I⁻ oxidation is observed at anodic potentials. Hence, loss of Br⁻ from the singly reduced species is proposed to occur on this time scale.

Spectroelectrochemical experiments also demonstrate that the rhodium-carbon bond is cleaved following an initial ring-centered reduction of (TPP)Rh(C₃H₆Br). For example, the original UV-visible bands of (TPP)Rh(C₃H₆Br) decrease in intensity upon reduction at -1.62 V while new bands are observed at 403, 497, and 516 nm. Hence, formation of [(TPP)Rh]₂ is observed when the potential is held at -1.62 V.

In general, irreversible reductions at the bound RX ligand are observed for (TPP)Rh(RX), where RX = C_nH_{2n}I or C_nH_{2n}Br. The value of E_{pc} for this reduction is dependent upon the chain length and the halide of the R group and follows the trend predicted for reduction of alkyl halides.^{4,5} This provides further evidence for a reduction and chemical reaction of the R group. Reduction of the bound RX occurs at $E_{1/2}$ values significantly less negative than those for reduction of free RX or RX₂ under the same solution conditions.

In summary, we have demonstrated that the R group in (TPP)Rh(R) can direct the electrochemical behavior observed for these compounds. This is perhaps unexpected since the initial reduction of (TPP)Rh(R) occurs at the porphyrin π ring system and $E_{1/2}$ for (TPP)Rh(R) and (TPP)Rh(RX) reduction varies within a narrow potential range. Hence, any changes in reactivity are not due to an inductive effect of the R group.

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Registry No. (TPP)Rh(CH₃), 103562-25-0; [(TPP)Rh(CH₃)]⁺, 110316-76-2; [(TPP)Rh(CH₃)]²⁺, 110316-80-8; (TPP)Rh(C₂H₅), 103533-58-0; [(TPP)Rh(C₂H₅)]⁺, 110316-77-3; [(TPP)Rh(C₂H₅)]²⁺, 110316-81-9; (TPP)Rh(C₃H₇), 106161-22-2; (TPP)Rh(C₄H₉), 106161-23-3; (TPP)Rh(C₅H₁₁), 106161-24-4; [(TPP)Rh(C₃H₇)]⁺, 110316-78-4; [(TPP)Rh(C₅H₁₁)]²⁺, 110316-82-0; (TPP)Rh(C₆H₁₃), 106799-98-8; (TPP)Rh(C₆H₅), 110316-66-0; (TPP)Rh(C₃H₆Cl), 110316-67-1; (TPP)Rh(C₃H₆Br), 110316-69-3; [(TPP)Rh(C₃H₆I)]⁻, 110316-84-2; (TPP)Rh(C₃H₆I), 110316-72-8; [(TPP)Rh(C₃H₆I)]⁺, 110316-79-5; [(TPP)Rh(C₃H₆I)]²⁺, 110316-83-1; (TPP)Rh(C₄H₈Cl), 110330-24-0; (TPP)Rh(C₄H₈Br), 110316-70-6; (TPP)Rh(C₄H₈I), 110316-73-9; (TPP)Rh(C₅H₁₀Cl), 110316-68-2; (TPP)Rh(C₅H₁₀Br), 110316-71-7; (TPP)Rh(C₅H₁₀I), 110316-74-0; [(TPP)Rh(C₆H₁₂I)]⁻, 110316-85-3; (TPP)Rh(C₆H₁₂I), 110316-75-1; [(TPP)Rh]₂, 88083-37-8; Rh, 7440-16-6.