Reaction of Electrochemically Generated Monomeric (Tetraphenylporphinato)rhodium(II) with Alkenes and Alkynes. Formation of Rhodium(III) σ-Bonded Complexes

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The reaction of electrochemically generated (tetraphenylporphinato)rhodium(II) with $HC{\equiv}CR$ and $H_2C{=}CHR$, where R is n-C_3H_7, n-C_4H_9, n-C_5H_{11}, or n-C_6H_{13}, was investigated by electrochemical and spectroscopic techniques. The ultimate rhodium porphyrin product was identified as (TPP)Rh(R), where TPP is the dianion of tetraphenylporphyrin and R is n-C_3H_7, n-C_4H_9, n-C_5H_{11}, or n-C_6H_{13}. An intermediate is observed in this reaction, and UV–visible, ESR, and electrochemical data are presented for this species. In addition, a complete reaction scheme consistent with all of the electrochemical, spectroelectrochemical, and spectroscopic data is presented. The unusual reactivity reported in this paper has not previously been observed in the reactions of rhodium porphyrins with alkenes or alkynes.

Introduction

Monomeric (tetraphenylporphinato)rhodium(II), (TPP)Rh, can be generated by the one-electron reduction of $[(TPP)Rh(L)_2]^+$, where TPP is the dianion of tetraphenylporphyrin and L is dimethylamine.[1] This species will react with alkyl halides (RX) to form complexes of the type (TPP)Rh(R).[2,3] The formation of (TPP)Rh(R) from (TPP)Rh was evaluated with 24 different alkyl halides, and from this data a general reaction mechanism has been proposed.[3] This method has also been utilized to synthesize 15 new (TPP)Rh(R) complexes.[2,3]

The reactivity of electrogenerated (TPP)Rh toward RX is similar to but not identical with that observed for $[(OEP)Rh]_2$ (OEP = octaethylporphyrin).[4,5] For example, the reaction of $[(OEP)Rh]_2$ with RX results in formation of both (OEP)Rh(R) and (OEP)RhX. In contrast, (TPP)RhX is not formed during electrochemical generation of (TPP)Rh(R) from (TPP)Rh and RX. The difference in reaction products for Rh porphyrins with OEP and TPP macrocycles may be due to the different methods of generating the monomeric rhodium(II) porphyrins (monomeric (OEP)Rh is formed upon dissociation of dimeric $[(OEP)Rh]_2$[4-8]), or it may reflect the different types of alkyl halides used in the separate studies.[2-5]

Rh(II) porphyrins react with alkenes and alkynes to generate (P)Rh(R) complexes.[9] The reaction of $[(OEP)Rh]_2$ with $HC{\equiv}CR$, where R is H or C_6H_5, results in formation of $(OEP)RhCH{=}CRRh(OEP)$.[4,5] A bridged Rh(III) dimer is also reported to be generated from $[(OEP)Rh]_2$ and $CH_2{=}CHC_6H_5$. In this case the final product is $(OEP)RhCH_2CH(C_6H_5)Rh(OEP)$.[8] In contrast, the reaction of $[(OEP)Rh]_2$ with $CH_2{=}CHCH_2R$, where R is C_6H_5, CN, or n-C_3H_7, produces $(OEP)RhCH_2CH{=}CHR$.[4,5]

In this paper we present a study of electrogenerated (TPP)Rh with $HC{\equiv}CR$ and $H_2C{=}CHR$, where R is n-C_3H_7, n-C_4H_9, n-C_5H_{11}, or n-C_6H_{13}. These reactions were monitored by electrochemical, spectroelectrochemical, ESR, and NMR techniques. The primary rhodium product is (TPP)Rh(R), where R is n-C_3H_7, n-C_4H_9, n-C_5H_{11}, or n-C_6H_{13}. This implies cleavage of the carbon–carbon bond adjacent to the double- or triple-bond functionality. Cyclic voltammetric, spectroelectrochemical, and ESR studies of an intermediate formed in the reaction of (TPP)Rh with $HC{\equiv}CR$ and $H_2C{=}CHR$ are also presented, and the intermediate is suggested to be a π complex. Finally, a complete reaction scheme for the reduction of $[(TPP)Rh(L)_2]^+Cl^-$ in the presence of alkynes and alkenes is proposed.

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. Cells modified for Schlenk techniques were used for all electrochemical measurements and bulk electrolysis experiments, with the exception of the thin-layer spectrochemistry. Platinum-disk electrodes were used for cyclic voltammetric measurements. Platinum-minigrid electrodes were used in the thin-layer spectroelectrochemical cell and the bulk electrolysis cell. The thin-layer spectroelectrochemical cell has been previously described.[10] 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. 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, tetra-n-butylammonium perchlorate (TBAP), 0.2 M, was the supporting electrolyte for cyclic voltammetric, bulk solution electrolysis, and spectroelectrochemical measurements.

UV–visible spectra were measured either on the Tracor Northern 1710 spectrometer/multichannel analyzer or with an IBM 9430 spectrophotometer with 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. The carrier gas was

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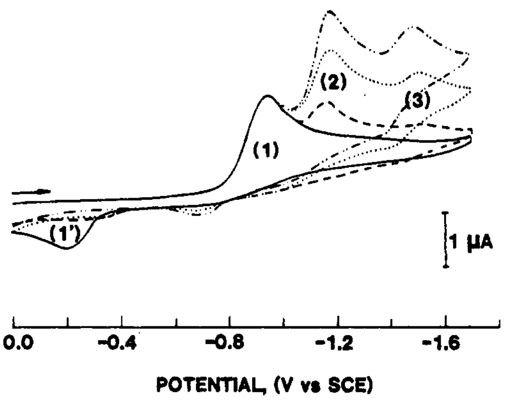

Figure 1. Cyclic voltammogram of 7.9 × 10^{-4} M [(TPP)Rh$(L)_2]^+Cl^-$ in the presence of 0 equiv of 1-pentyne (——), 280 equiv of 1-pentyne (- - -), 540 equiv of 1-pentyne (···), and 1400 equiv of 1-pentyne (−··−··−). The solvent was THF, 0.2 M TBAP. Scan rate = 100 mV/s.

nitrogen. One of two packed columns, a 6 ft, 3% OV-1 on 100/120 Chromosorb or a 10 ft, 10% TCEP on 100/120 Chromosorb, was used with an FID detector. In addition, a 15 m × 0.32 mm bonded FSOT (Alltech RSL-160 5 µm) was used with a TCD detector. Various flow rates and temperature profiles were optimized for the particular column and sample used.

Generation of (TPP)Rh by bulk electrolysis and reaction of (TPP)Rh with either the alkenes or alkynes was performed by the following general method: All steps were done by Schlenk techniques, unless otherwise noted. (TPP)Rh was generated by the controlled potential electrolysis at −1.20 V vs. SCE in a THF solution (0.2 M TBAP) containing 10–20 mg of $[(TPP)Rh(L)_2]^+Cl^-$ and 100–500 equiv of the alkene or alkyne. Current–time curves were monitored during the bulk electrolysis experiments. After the current reached background levels both ESR and UV–visible measurements were taken. From the current–time curve, the number of electrons was calculated. The remainder of the solution was then transferred to another flask and was kept at room temperature until the UV–visible spectra indicated no further change. (This took up to 40 min.) At that point, the solution was evaporated to dryness and extracted with benzene at 10 °C to remove the majority of supporting electrolyte. Pure (TPP)Rh(R) was then obtained from a silica gel column, either on the Schlenk line or in a dri-box, with benzene as the solvent. Finally, the product was dried and was then suitable for NMR, UV–visible, or electrochemical experiments. NMR measurements were made by dissolving the sample in deuteriated benzene (C_6D_6) before the NMR tube was flame-sealed.

Materials. Spectroscopic grade tetrahydrofuran (THF) was purchased from Aldrich and purified by distillation under nitrogen first from CaH_2 and then from Na/benzophenone just prior to use. Spectroscopic grade benzene (C_6H_6) was purchased from Aldrich and purified by distillation under nitrogen from sodium. 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 procedures[11] where necessary, and checked for impurities by gas chromatographic analysis prior to use. Deuteriated benzene-d_6 (C_6D_6) was purchased from Aldrich and used without further purification. The rhodium porphyrin complex $[(TPP)Rh(L)_2]^+Cl^-$, where L is dimethylamine $[NH(CH_3)_2]$, was synthesized by literature methods.[1,12]

Results and Discussion

Electrochemical Monitoring of the Reaction between (TPP)Rh and HC≡CR or H_2C=CHR. Reactions of (TPP)Rh with HC≡CR or H_2C=CHR, where R is *n*-C_3H_7, *n*-C_4H_9, *n*-C_5H_{11}, or *n*-C_6H_{13}, were monitored by both routine cyclic voltammetry and thin-layer cyclic voltammetry. The cyclic voltammetric method is shown in Figure 1. This figure illustrates cyclic voltammograms of $[(TPP)Rh(L)_2]^+Cl^-$ in THF containing various amounts of 1-pentyne. In the absence of 1-pentyne two major electrode processes occur in THF between 0.00 and −1.6 V vs. SCE. These are an irreversible reduction process at E_p = −0.92 V (peak 1, Figure 1) and an irreversible oxidation process at E_p = −0.22 V (peak 1′, Figure 1).[13] The first process is due to the irreversible, one-electron reduction of $[(TPP)Rh(L)_2]^+Cl^-$ and results in the electrochemical generation of (TPP)Rh. This electrode reaction is followed by a dimerization of (TPP)Rh to give $[(TPP)Rh]_2$. The process at E_p = −0.22 V (peak 1′) is due to the oxidation of this dimeric species.[1]

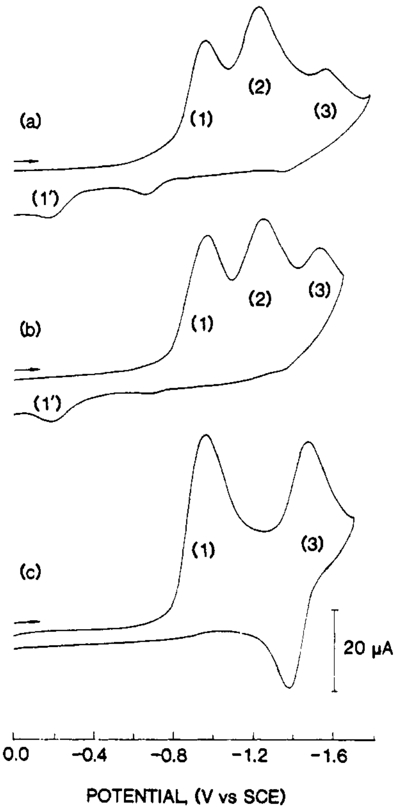

Figure 2. Thin-layer cyclic voltammograms of (a) 2.8 × 10^{-4} M $[(TPP)Rh(L)_2]^+Cl^-$ in the presence of 1400 equiv of 1-pentyne, (b) 3.0 × 10^{-4} M $[(TPP)Rh(L)_2]^+Cl^-$ in the presence of 2000 equiv of 1-hexyne, and (c) 2.7 × 10^{-4} M $[(TPP)Rh(L)_2]^+Cl^-$ in the presence of 6300 equiv of 1-heptyne. The solvent was THF, 0.2 M TBAP. Scan rate = 10 mV/s.

Figure 1 also shows the changes that occur in cyclic voltammograms of $[(TPP)Rh(L)_2]^+Cl^-$ as 1-pentyne is added to the solution. The first reduction is invariant with increases in the 1-pentyne concentration, but new processes at E_p = −1.20 V (process 2, Figure 1) and $E_{1/2}$ = −1.42 V (process 3, Figure 1) progressively increase in current as the 1-pentyne concentration increases. At the same time the oxidation at E_p = −0.22 V, which is associated with $[(TPP)Rh]_2$, decreases in current. The currents for processes 2 and 3 continue to increase up to the addition of 1400 equiv of 1-pentyne, after which no further changes in the voltammogram are observed. The voltammogram under these conditions is given in Figure 1 and is characterized by three reductions at E_p = −0.92 V (peak 1), E_p

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Table I. Electrochemical Data for the Second and Third Reductions of $[(TPP)Rh(L)_2]^+Cl^-$ in THF Containing 0.2 M TBAP and HC≡CR or H_2C=CHR

reactant	peak 2 E_p, V vs. SCE[a]	peak 3 $E_{1/2}$, V vs. SCE[a]	C_R/C_{Rh}[b]
$HC≡CC_3H_7$	−1.22 (−1.20)	−1.45 (−1.43)	1400
$HC≡CC_4H_9$	−1.24 (−1.19)	−1.46 (−1.44)	2000
$HC≡CC_5H_{11}$		−1.43	6300
$HC≡CC_6H_{13}$		−1.46	3100
$H_2C=CHC_3H_7$	(−1.19)	(−1.45)	2800
$H_2C=CHC_4H_9$	−1.22	−1.45	1700
$H_2C=CHC_6H_{13}$	−1.29	−1.46	3000

[a] Potentials obtained by thin-layer voltammetry at a scan rate of 0.01 V/s or by conventional cyclic voltammetry at a scan rate of 0.10 V/s (values in parentheses). [b] C_R/C_{Rh} = alkene or alkyne to $[(TPP)Rh(L)_2]^+Cl^-$ concentration ratio at which no further changes are observed in the thin-layer cyclic voltammogram.

= −1.20 V (peak 2), and $E_{1/2}$ = −1.42 V (peak 3). All three of these processes involve the porphyrin and are not associated with the excess 1-pentyne, which shows no reduction processes up to −1.80 V vs. SCE.

Figure 2 illustrates thin-layer cyclic voltammograms of $[(TPP)Rh(L)_2]^+Cl^-$ in THF containing 1400 equiv of 1-pentyne (Figure 2a), 2000 equiv of 1-hexyne (Figure 2b), and 6300 equiv of 1-heptyne (Figure 2c). The same basic type of reactivity is observed with the three different alkynes. However, as the chain length of the alkyne is increased, its concentration must be increased for waves 2 and 3 to be observed. This implies that alkynes with longer chain lengths have a slower reactivity with (TPP)Rh. A similar dependence of reactivity on chain length was obtained with alkyl halides.[3]

Figure 2 demonstrates that the relative currents of peaks 2 and 3 are also dependent upon the chain length of the alkyne. The current for peak 2 is much larger than that of peak 3 for the reaction of (TPP)Rh with 1-pentyne (Figure 2a). However, the current for peak 2 is decreased relative to peak 3 on going to 1-hexyne (Figure 2b) and then to 1-heptyne (Figure 2c). In the case of 1-heptyne, peak 2 is not observed and peak 3 is the major process. This is also the case for 1-octyne.

The reaction between (TPP)Rh and H_2C=CHR, where R is n-C_3H_7, n-C_4H_9, n-C_5H_{11} or n-C_6H_{13}, was also investigated, and in general, a similar reaction sequence was observed for all of these compounds. Table I lists the second and third reduction potentials (processes 2 and 3) of $[(TPP)Rh(L)_2]^+Cl^-$ in THF containing excess HC≡CR or H_2C=CHR. The reversible reduction at $E_{1/2}$ = 1.44 ± 0.02 V (peak 3) indicates formation of a σ-bonded (TPP)Rh(R) species.[2,3,14] The irreversible process at −1.22 ± 0.02 V (peak 2) implies formation of a new type of rhodium porphyrin species that has not previously been observed. This process was investigated by spectroelectrochemical experiments and, as will be shown in latter sections of this paper, is due to reduction of an intermediate (TPP)Rh–alkene or –alkyne complex.

Several differences may be noted in the reactions of (TPP)Rh with alkyl halides and alkenes or alkynes. With alkenes and alkynes two distinct products are observed as discussed above. However, two distinct rhodium species are not formed during the reaction of (TPP)Rh with alkyl halides, and the only detectable rhodium product is (TPP)Rh(R).[2,3] In addition, excess alkene or alkyne is necessary in order to monitor the reaction by cyclic voltammetry. For example, a similar titration with CH_3I requires only 1 equiv of CH_3I to obtain a final cyclic voltammogram similar to that shown in Figure 1.[3] This implies that (TPP)Rh reacts with alkynes or alkenes much slower than with alkyl halides.

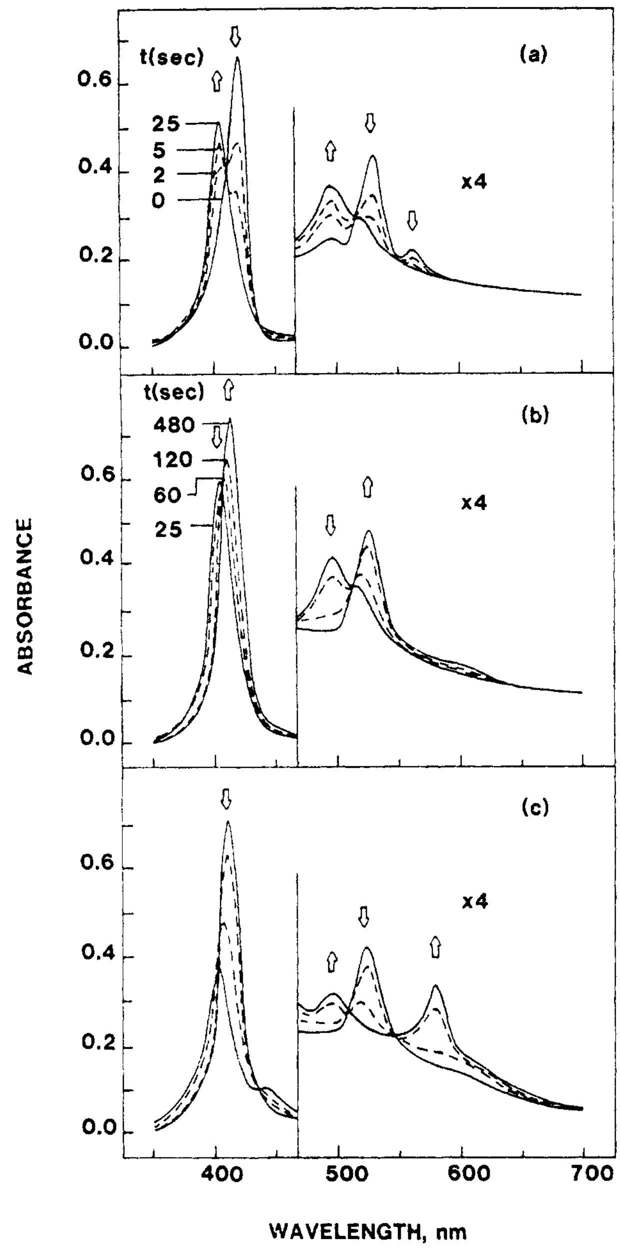

Figure 3. Electronic absorption spectra taken during reduction of 9.7 × 10^{-5} M $[(TPP)Rh(L)_2]^+Cl^-$ in THF, 0.2 M TBAP containing 5100 equiv of 1-octyne. Reduction at −1.10 V: (a) up to 25 s, (b) from 25 to 480 s, and (c) after complete reduction at −1.60 V.

Spectroscopic Monitoring of the Reaction between (TPP)Rh and HC≡CR or H_2C=CHR. Table II presents the electronic absorption spectra for all of the electroreduced species examined in this study. The data indicate that on the spectroelectrochemical time scale the reaction products are dependent upon the alkene or alkyne chain length. This can be seen by comparing the spectroelectrochemical data taken during reduction of $[(TPP)Rh(L)_2]^+Cl^-$ in THF containing 1-octyne or 1-pentyne. Parts a and b of Figure 3 show the changes that occur in the electronic absorption spectra upon reduction of $[(TPP)Rh(L)_2]^+Cl^-$ in THF containing 5100 equiv of 1-octyne. Only process 1, process 1′, and process 3 are observed in the thin-layer cyclic voltammograms. This indicates the formation of only $[(TPP)Rh]_2$ and a rhodi-

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Table II. Spectral Data for Products Formed after Reduction of $[(TPP)Rh(L)_2]^+Cl^-$ at Various Potentials in THF Containing 0.2 M TBAP and Excess $HC{\equiv}CR$ or $H_2C{=}CHR$

alkene or alkyne	applied potential, V	absorbing species	λ_{max}, nm ($\epsilon \times 10^{-3}$)		
none		$[(TPP)Rh(L)_2]^+$	418 (253)	529 (23.7)	562 (5.0)
	-1.10	$[(TPP)Rh]_2$	404 (177)	496 (14.8)	
$HC{\equiv}CC_3H_7$	-1.10	(TPP)Rh π complex[a]	423 (233)	536 (15.3)	
	-1.30	$[(TPP)Rh]_2$	404 (165)	496 (17.0)	
$HC{\equiv}CC_4H_9$	-1.10	$(TPP)Rh(C_4H_9)$	411 (211)	525 (21.0)	
	-1.60	$[(TPP)Rh(C_4H_9)]^-$	406 (146)	494 (16.5)	600 (5.7)
$HC{\equiv}CC_5H_{11}$	-1.10	$(TPP)Rh(C_5H_{11})$	413 (205)	525 (20.4)	
	-1.60	$[(TPP)Rh(C_5H_{11})]^-$	408 (167)	527 (16.7)	600 (5.6)
$HC{\equiv}CC_6H_{13}$	-1.10	$(TPP)Rh(C_6H_{13})$	412 (224)	525 (19.0)	
	-1.60	$[(TPP)Rh(C_6H_{13})]^-$	404 (128)	496 (9.0)	580 (21.4)
$H_2C{=}CHC_4H_9$	-1.10	(TPP)Rh π complex[a]	424 (228)	535 (18.0)	
	-1.30	$[(TPP)Rh]_2$	404 (180)	496 (14.6)	
$H_2C{=}CHC_6H_{13}$	-1.10	$[(TPP)Rh]_2$	404 (174)	496 (16.4)	

[a] Transient complex. See text.

um–carbon σ-bonded species as reaction products in the presence of 1-octyne. This is also the conclusion from spectroscopic data.

The original $[(TPP)Rh(L)_2]^+Cl^-$ species is characterized by a Soret band at 418 nm and two Q bands at 529 and 562 nm. Upon reduction, two different species are observed. The initial product has spectral absorption bands at 404 and 496 nm (Figure 3a), but on longer time scales of electrolysis a new species is formed that has absorption bands at 412 and 525 nm. This spectrum is shown in Figure 3b.

The spectra in Figure 3a are well-known and correspond to $[(TPP)Rh]_2$.[1] The spectra in Figure 3b are also well-known and are due to $(TPP)Rh(C_6H_{13})$.[3] Dimeric $[(TPP)Rh]_2$ is formed (reaction 1) because the reaction of

$$2(TPP)Rh \rightleftharpoons [(TPP)Rh]_2 \qquad (1)$$

(TPP)Rh with 1-octyne is slow. This is also the case for 1-octene. Reaction 1 is reversible, and a dissociation of the dimer will occur as (TPP)Rh slowly reacts with 1-octyne to give $(TPP)Rh(C_6H_{13})$. The formation of this Rh(III) σ-bonded complex is irreversible, and hence the final spectrum shown in Figure 3b is indicative of complete $(TPP)Rh(C_6H_{13})$ formation.

Formation of (TPP)Rh(R) was observed as a product in the reaction with all of the investigated alkynes and alkenes, but the length of time required was dependent upon the chain length of the alkene or alkyne. The R group of each (TPP)Rh(R) product was identified by NMR spectroscopy.

The spectral changes shown in Figure 3c are observed when the potential for reduction of $[(TPP)Rh(L)_2]^+Cl^-$ in THF containing 1-octyne is set to -1.60 V. The generated spectrum is characteristic of a reduction at the porphyrin π-ring system.[15] Process 3 thus results in formation of $[(TPP)Rh(C_6H_{13})]^-$. The Soret band of the reduction product is decreased in intensity and the final spectrum has absorption bands at 404, 496, and 580 nm. Formation of an anion radical at -1.60 V is in agreement with formation of rhodium–carbon bonded species.[14]

The thin-layer cyclic voltammogram of $[(TPP)Rh(L)_2]^+Cl^-$ in the presence of 1-pentyne (Figure 2a) indicates the presence of two distinct (TPP)Rh alkyne compounds since both process 2 and process 3 are observed. This is also spectrally observed. Figure 4a shows the changes that occur in the electronic absorption spectrum during reduction of $[(TPP)Rh(L)_2]^+Cl^-$ in THF containing 1500 equiv of 1-pentyne. Reduction at -1.10 V results in formation of a new species characterized by bands at 423 and 536 nm. The electronic absorption spectra of this complex is shown in Figure 4a and illustrates that the absorption bands are all shifted to longer wavelengths compared to those of $[(TPP)Rh]_2$, $[(TPP)Rh(L)_2]^+$, or (TPP)Rh(R). In addition, the UV–visible data clearly demonstrate that the new species is not a anion radical where the charge is localized at the porphyrin π-ring system. No other species is observed by spectroelectrochemistry for up to 10–15 min. However, if the potential is switched from -1.10 to -1.30 V after formation of the new species, then $[(TPP)Rh]_2$ is generated. Hence, process 2 results in loss of the alkyne

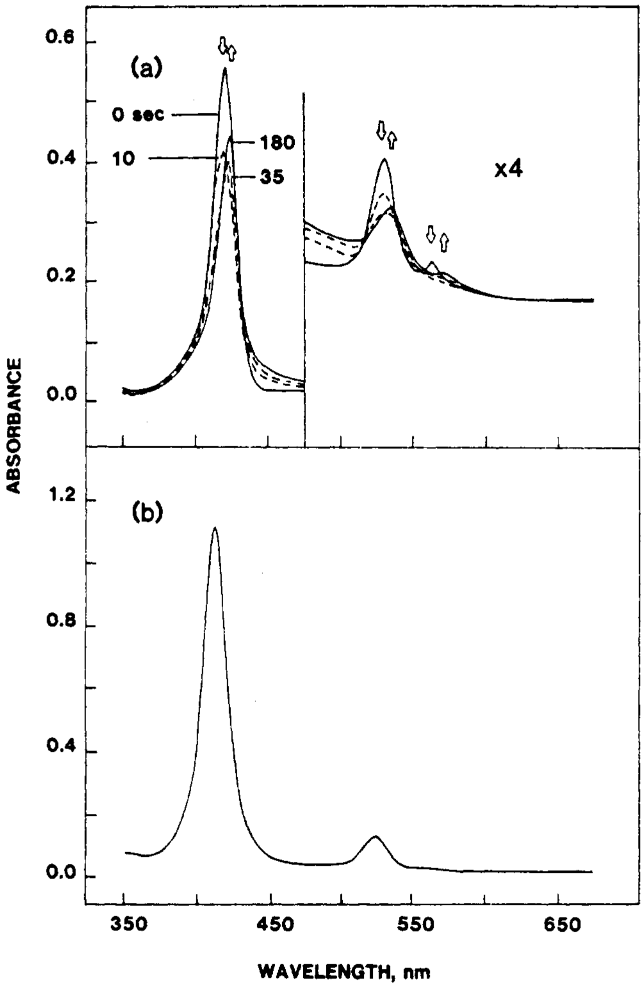

Figure 4. Electronic absorption spectra taken during reduction of a 7.3×10^{-5} M $[(TPP)Rh(L)_2]^+Cl^-$ in THF, 0.2 M TBAP containing 1500 equiv of 1-pentyne. Reduction at -1.10 V: (a) initial spectra up to 180 s and (b) final spectrum from bulk electrolysis solution.

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Table III. Bulk Electrolysis Data and Characteristics of Electrochemically Generated (TPP)Rh(R) Complexes

reactant	product	n^a	$E_{1/2}$,^{b} V	spectral data solv	λ_{max}, nm	
$HC{\equiv}CC_3H_7$	$(TPP)Rh(C_3H_7)$	1.1	-1.42	C_6H_6	414	522
				THF	412	524
$HC{\equiv}CC_4H_9$	$(TPP)Rh(C_4H_9)$	1.3	-1.41	C_6H_6	414	526
				THF	410	524
$HC{\equiv}CC_5H_{11}$	$(TPP)Rh(C_5H_{11})$	1.2	-1.42	C_6H_6	412	524
$HC{\equiv}CC_6H_{13}$	$(TPP)Rh(C_6H_{13})$	1.2	-1.43	C_6H_6	413	526
$H_2C{=}CHC_3H_7$	$(TPP)Rh(C_3H_7)$	1.2	-1.42	C_6H_6	413	521
$H_2C{=}CHC_4H_9$	$(TPP)Rh(C_4H_9)$	1.3	-1.42	C_6H_6	417	531
				THF	412	527
$H_2C{=}CHC_5H_{11}$	$(TPP)Rh(C_5H_{11})$	1.3	-1.42	C_6H_6	415	522

^{a} Coulometric values (±0.20) for controlled potential reduction of $[(TPP)Rh(L)_2]^+Cl^-$ in the presence of excess reactant. ^{b} In THF, 0.2 M TBAP.

and production of the dimer. This behavior is totally different from that of other known σ-bonded (TPP)Rh(C_nH_{2n+1}) complexes. For these complexes electroreduction results in formation of a relatively stable π-anion radical.[2,3,14]

The species whose spectrum is shown in Figure 4a is not stable and the product isolated from bulk electrolysis gives the spectrum shown in Figure 4b. Conversion from the intermediate species to the final species is complete after approximately 40 min. The final spectrum has absorption bands at 412 and 524 nm and indicates formation of $(TPP)Rh(C_3H_7)$.

ESR spectra were taken in frozen THF, 0.2 M TBAP, solutions at −150 °C immediately after reduction of $[(TPP)Rh(L)_2]^+Cl^-$ and 1-pentyne at −1.10 V and show an asymmetric signal with $g = 2.00$ and a signal width of 17 G. In addition, there is no indication of rhodium hyperfine splitting in the ESR spectrum. After the new species reacts to form $(TPP)Rh(C_3H_7)$, no ESR signal is observed under similar conditions. In contrast, no ESR signal is observed upon reduction of $[(TPP)Rh(L)_2]^+Cl^-$ at −1.10 V in THF containing 3000 equiv of 1-octyne.

Spectroscopic monitoring of $[(TPP)Rh(L)_2]^+Cl^-$ reductions in the presence of $H_2C{=}CHR$, where R is C_4H_9 or C_6H_{13}, indicates a similar reaction as with the alkynes. The intermediate is the main product on the spectroelectrochemical time scale with 1-pentyne and 1-hexene. In addition, thin-layer cyclic voltammograms indicate some formation of the intermediate with most of the alkenes or alkynes. However, in all cases the final stable product is invariably a (TPP)Rh(R) species.

The exact nature of the intermediate is not known. However, one possibility consistent with the electrochemistry, ESR, and UV–visible data is a (TPP)Rh–alkyne or –alkene π complex. This Rh π complex should have one unpaired electron that is consistent with data from ESR measurements. The reduction of this species (at −1.3 V) is postulated to occur at the Rh–alkyne or –alkene center and would lead to cleavage of the π bond with the subsequent formation of $[(TPP)Rh]_2$. Another possibility for the intermediate would be the radical resulting from Rh–carbon σ bond formation with the alkene or alkyne. The reductive properties of this intermediate suggests π-complex formation. However, the data do not eliminate either possibility.

Rhodium porphyrin π complexes have been proposed in the literature[4,5,9] but have never been directly observed. Similar π complexes have also been assigned in the reactions of $[(P)Ru]_2$.[16] The UV–visible spectrum of $[(TPP)Ru]_2$ has bands at 412, 422, and 505 nm in C_6H_6, while the porphyrin π complex $(TPP)Ru(CH_2{=}CH_2)$ is reported to have a UV–visible spectrum with bands at 408, 504, and 524 nm in THF.[16,17] Thus, the Soret band of the π complex is shifted to shorter wavelengths while the Q bands are shifted to longer wavelengths. In our case, the spectral bands of the intermediate are all shifted to longer wavelengths relative to those for $[(TPP)Rh]_2$.

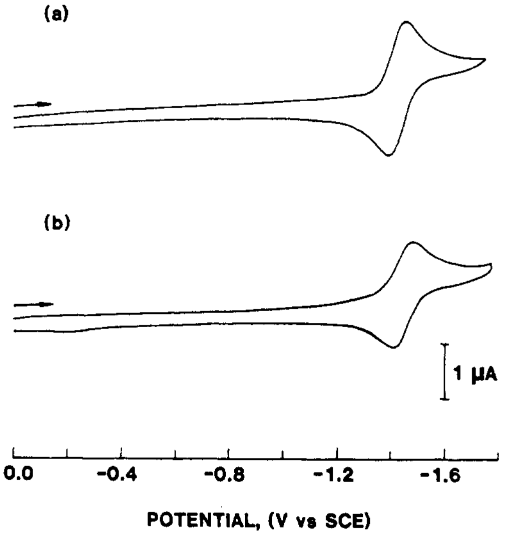

Figure 5. Cyclic voltammogram of the product isolated after bulk electrolysis of $[(TPP)Rh(L)_2]^+Cl^-$ −1.05 V in THF, 0.2 M TBAP containing (a) 1-pentyne and (b) 1-octyne. Scan rate = 100 mV/s.

Identification of Final Bulk Electrolysis Products from the Reaction between (TPP)Rh and $HC{\equiv}CR$ or $H_2C{=}CHR$. Both cyclic voltammetric and the spectroelectrochemical data suggest that (TPP)Rh(R) species are the final products formed in reactions between (TPP)Rh and $HC{\equiv}CR$ or $H_2C{=}CHR$. This was verified by isolation and identification of bulk electrolysis products formed during reduction at −1.10 V. Table III gives coulometric values for the reduction of $[(TPP)Rh(L)_2]^+Cl^-$ in THF solutions containing alkene or alkyne as well as cyclic voltammetric and UV–visible data of the isolated product. In all cases, reduction at −1.10 V results in the addition of 1.0 ± 0.2 electron/Rh atom, consistent with the initial generation of (TPP)Rh. Cyclic voltammograms of the isolated product show only one reduction process. This process is at the same potential as that of process 3 in the titration experiments (see Figure 1). This is illustrated in Figure 5a for the product isolated after reaction of (TPP)Rh and 1-pentyne and in Figure 5b for the product of (TPP)Rh and 1-octyne.

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(16) Collman, J. P.; Brothers, P. J.; McElwee-White, L.; Rose, E.; Wright, L. J. *J. Am. Chem. Soc.* **1985**, *107*, 4570.

(17) Collman, J. P.; Barnes, C. E.; Swepston, P. N.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 3500.

Table IV. ^{1}H NMR Data of (TPP)Rh(R) Recovered after Bulk Electrolysis of $[(TPP)Rh(L)_2]^+Cl^-$ at -1.10 V in THF Containing HC≡CR or H_2C=CHR or RX

reactant	product	J_{Rh-H}, Hz	resonances of σ-bonded ligands (R groups),[a] ppm					
$HC{\equiv}CC_3H_7$	$(TPP)Rh(C_3H_7)$	2.68	-4.62 (m, 2 H)	-4.12 (m, 2 H)	-1.77 (t, 3 H)			
$H_2C{=}CHC_3H_7$	$(TPP)Rh(C_3H_7)$	2.37	-4.65 (m, 2 H)	-4.12 (m, 2 H)	-1.77 (t, 3 H)			
C_3H_7Br	$(TPP)Rh(C_3H_7)$	2.40	-4.65 (m, 2 H)	-4.11 (m, 2 H)	-1.78 (t, 3 H)			
$HC{\equiv}CC_4H_9$	$(TPP)Rh(C_4H_9)$	2.90	-4.62 (m, 2 H)	-4.17 (m, 2 H)	-1.57 (m, 2 H)	-0.81 (t, 3 H)		
$H_2C{=}CHC_4H_9$	$(TPP)Rh(C_4H_9)$	2.75	-4.61 (m, 2 H)	-4.17 (m, 2 H)	-1.57 (m, 2 H)	-0.81 (t, 3 H)		
$HC{\equiv}CC_5H_{11}$	$(TPP)Rh(C_5H_{11})$	2.54	-4.63 (m, 2 H)	-4.18 (m, 2 H)	-1.59 (m, 2 H)	-0.51 (m, 2 H)	-0.27 (t, 3 H)	
$C_5H_{11}Br$	$(TPP)Rh(C_5H_{11})$	2.44	-4.62 (m, 2 H)	-4.18 (m, 2 H)	-1.61 (m, 2 H)	-0.50 (m, 2 H)	-0.27 (t, 3 H)	
$HC{\equiv}CC_6H_{13}$	$(TPP)Rh(C_6H_{13})$	2.36	-4.62 (m, 2 H)	-4.18 (m, 2 H)	-1.58 (m, 2 H)	-0.55 (m, 2 H)	-0.14 (m, 2 H)	+0.11 (t, 3 H)

[a] (TPP)Rh resonances: Py–H, 8.89 ± 0.05 (s, 8 H); Ph–H, 8.20 ± 0.05 (m, 8 H); Ph–H, 7.50 ± 0.05 (m, 12 H). Solvent: C_6D_6.

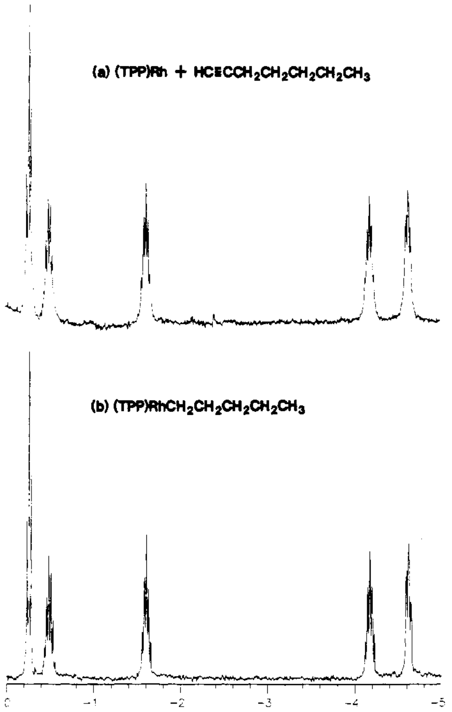

Figure 6. ^{1}H NMR spectra from 0 to -5 ppm of (a) the isolated product after reaction of 1-heptyne and (TPP)Rh and (b) $(TPP)Rh(C_5H_{11})$ prepared by reaction of electrogenerated (TPP)Rh with n-$C_5H_{11}Br$.

Figure 6a shows the ^{1}H NMR spectrum of the product isolated from bulk electrolysis of $[(TPP)Rh(L)_2]^+Cl^-$ in the presence of 1-heptyne. The ^{1}H NMR spectra from 0 to -5 ppm of $(TPP)Rh(C_5H_{11})$ synthesized by reaction with n-$C_5H_{11}Br$ is also shown (Figure 6b). Clearly, (TPP)Rh-(C_5H_{11}) is formed in both reactions.

The ^{1}H NMR data of other isolated products is presented in Table IV. ^{1}H NMR data of (TPP)Rh(R) complexes prepared from the reaction with RX[3] are also presented in Table IV and show that the reaction of (TPP)Rh with HC≡CR produces (TPP)Rh(R), where R is n-C_3H_7, n-C_4H_9, n-C_5H_{11}, or n-C_6H_{13}. The data in this table demonstrate that the above reaction is general for all of the alkynes studied. Tables III and IV give cyclic voltammetric data, electronic absorption spectra, and ^{1}H NMR spectra of products isolated from the reaction of (TPP)Rh with H_2C=CHR, where R is C_3H_7, C_4H_9, or C_5H_{11}, and the same conclusion is reached. This conclusion is that the final product is invariably (TPP)Rh(R). The percent yield for formation of the (TPP)Rh(R) complexes after isolation based on $[(TPP)Rh(L)_2]^+Cl^-$ ranged from 40% to 60%. Finally, a (TPP)Rh(R′) side product was found in all of the reactions. The identity of this species has not been conclusively determined.[18] This species could be related to the C_2 fragment lost from the alkene and alkyne, or it could be from a side reaction of the (P)Rh intermediate.

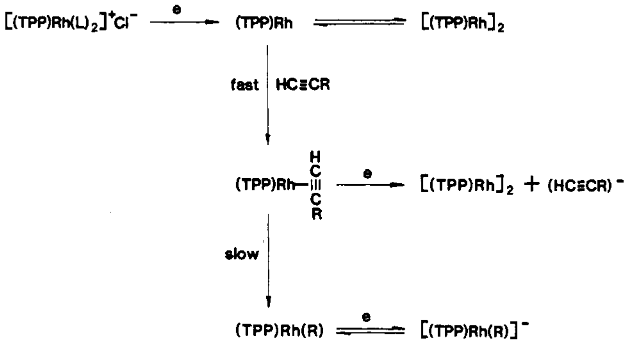

Figure 7. Overall scheme for reduction of $[(TPP)Rh(L)_2]^+Cl^-$ in the presence of HC≡CR, where R is n-C_3H_7, n-C_4H_9, n-C_5H_{11} or n-C_6H_{13}.

Mechanism for the Reaction between (TPP)Rh and Alkynes or Alkenes. Figure 7 presents a scheme for the reactions of electrogenerated (TPP)Rh with HC≡CR. This scheme was formulated on the basis of electrochemical, spectroelectrochemical, and spectroscopic data. Both formation of the intermediate suggested to be a π complex and the eventual formation of (TPP)Rh(R) are indicated in Figure 7. The reduction of these species is also presented. The mechanism presented in Figure 7 can also be applied to reactions with the alkenes.

The final formation of (TPP)Rh(R) from the alkenes and alkynes is very interesting and highlights the radical nature of (P)Rh reactivity.[6-8] The location of the alkyne or alkene carbon–carbon bond cleavage is unusual. However, formation of (TPP)Rh(R) products is not surprising if one considers the relative stability of these species in rhodium porphyrin chemistry.[19]

Acknowledgment. The support of the National Science Foundation (Grant CHE-8515411) is gratefully acknowledged.

Registry No. $[(TPP)Rh(Me_2NH)_2]Cl$, 51669-90-0; $HC{\equiv}CC_3H_7$, 627-19-0; $HC{\equiv}CC_4H_9$, 693-02-7; $HC{\equiv}CC_5H_{11}$, 628-71-7; $HC{\equiv}CC_6H_{13}$, 629-05-0; $H_2C{=}CHC_3H_7$, 109-67-1; $H_2C{=}CHC_4H_9$, 592-41-6; $H_2C{=}CHC_5H_{11}$, 592-76-7; $(TPP)Rh(C_3H_7)$, 106161-22-2; $(TPP)Rh(C_4H_9)$, 106161-23-3; $(TPP)Rh(C_5H_{11})$, 106161-24-4; $(TPP)Rh(C_6H_{13})$, 106799-98-8.

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[18] The complex is characterized by a ^{1}H NMR spectrum in C_6D_6: Py–H, 8.89 (s, 8 H); Ph–H, 8.17 (m, 8 H); Ph–H, 7.52 (m, 12 H) and a resonance at -2.53 ppm (d, 2 H). The UV–visible spectra of this complex showed absorptions at 413 and 526 nm in THF, and the complex has a reversible one-electron reduction at -1.41 V vs. SCE in THF, 0.2 M TBAP.

[19] Farnor, M. D.; Woods, B. A.; Wayland, B. B. *J. Am. Chem. Soc.* **1986**, *108*, 3659.