

at  $\delta -14.33$  whereas that of **6** displays a complex AA'BB' pattern with superimposed P-H coupling (Table VII). Accordingly, the spectroscopic evidence supports the green isomer **7** as most likely possessing an all-cis disposition of the three  $\pi$ -acceptor ligands (as is also the case for complexes **2a** and **2b**) while **6** may well have a structure closely akin to that of **1a** and **1b**. If this is the case, we would expect **6** to be converted to **7** upon heating, in a fashion similar to the conversion of **1** to **2** (vide supra). This has been confirmed upon heating yellow **6** in 1,2-dichloroethane for 12 h (see Experimental Section). The solution slowly changed from yellow to green, and upon workup the green isomer **7** was identified on the basis of its electrochemical and infrared spectral properties.

(d) **Concluding Remarks.** The present work clearly establishes that isomerism can occur in edge-shared bioctahedral complexes that contain  $\pi$ -acceptor RNC and CO ligands and that are derived from multiply bonded dimetal precursor complexes. In the case of complexes that contain three such ligands, an all-cis configuration appears to be the thermodynamically favored one. Apparently, the considerable kinetic stability of the isomers  $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CO})_2(\text{CNR})]\text{PF}_6$  (**1**, R = *t*-Bu or xylyl) and

$[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CO})(\text{CNR})_2]\text{PF}_6$  (**6**, R = xylyl) may reflect the high activation energy barriers associated with the bond-breaking-bond-making processes that must accompany their conversion to  $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CO})_2(\text{CNR})]\text{PF}_6$  (**2**, R = *t*-Bu or xylyl) and  $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CO})(\text{CNR})_2]\text{PF}_6$  (**7**, R = xylyl), respectively. The crystal structure of the reduced complex  $\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CO})_2(\text{CN-}i\text{-Pr})$ , which is derived from the all-cis isomer  $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CO})_2(\text{CN-}i\text{-Pr})]\text{PF}_6$ , shows that it retains the basic structure of its parent, a conclusion that had previously been inferred from IR spectroscopic and electrochemical measurements.<sup>8</sup>

**Acknowledgment.** Support from the National Science Foundation (Grant No. CHE85-14588 to F.A.C. and Grant Nos. 82-06117 and 85-06702 to R.A.W.) is gratefully acknowledged.

**Supplementary Material Available:** For the crystal structures of **1a** and **4**, full tables of bond distances and bond angles and tables of anisotropic displacement parameters and, for **4**, figures showing 19 contoured sections of the final difference Fourier map (33 pages); for both crystal structures, listings of observed and calculated structure factors (37 pages). Ordering information is given on any current masthead page.

## Notes

Contribution from the Department of Chemistry,  
University of Houston, Houston, Texas 77004

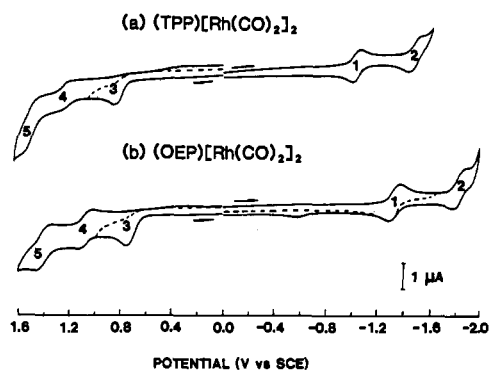
### Electrochemistry of ( $\mu$ -Porphinato)bis(dicarbonylrhodium(I)) Complexes. Oxidative Conversion of $(\text{P})[\text{Rh}(\text{CO})_2]_2$ to $(\text{P})\text{Rh}^+$ , Where P = Octaethyl- or Tetraphenylporphyrin

C.-L. Yao, J. E. Anderson, and K. M. Kadish\*

Received February 5, 1987

Rhodium(I) porphyrins of the form  $(\text{TPP})[\text{Rh}(\text{CO})_2]_2$  and  $(\text{OEP})[\text{Rh}(\text{CO})_2]_2$ , where TPP and OEP are the dianions of tetraphenylporphyrin and octaethylporphyrin, respectively, have two rhodium atoms bonded to two of the four nitrogen atoms on the porphyrin ring.<sup>1-5</sup> Two carbonyl ligands complete the approximate square-planar arrangement around each rhodium atom. The Rh(I) ions are on opposite sides of the porphyrin plane, and a metal-metal separation of 3.09 Å is reported for  $(\text{OEP})[\text{Rh}(\text{CO})_2]_2$ .<sup>6,7</sup> This distance is too long to suggest a direct rhodium-rhodium bond.

The photochemistry<sup>8,9</sup> and chemical reactivity<sup>1-5,10</sup> of bimetallic Rh(I) porphyrins have been reported, but their electrochemical properties have never been investigated. The combination of the two rhodium atoms with the porphyrin ring presents an interesting system. An electrochemical oxidation of these species may lead to formation of reactive intermediates such as are observed in the chemistry of monomeric or dimeric rhodium porphyrins.<sup>11-17</sup>



**Figure 1.** Cyclic voltammograms of (a)  $8.1 \times 10^{-4}$  M  $(\text{TPP})[\text{Rh}(\text{CO})_2]_2$  and (b)  $5.9 \times 10^{-4}$  M  $(\text{OEP})[\text{Rh}(\text{CO})_2]_2$  in PhCN containing 0.1 M TBAP. Scan rate = 100 mV/s.

This work presents the electrochemistry of  $(\text{TPP})[\text{Rh}(\text{CO})_2]_2$  and  $(\text{OEP})[\text{Rh}(\text{CO})_2]_2$  in benzonitrile (PhCN) and methylene chloride ( $\text{CH}_2\text{Cl}_2$ ). Either one or two reversible one-electron reductions and up to three one-electron oxidations are observed depending upon the solvent media. The first oxidation involves a  $\text{Rh}(\text{I}) \rightleftharpoons \text{Rh}(\text{II})$  transition for one of the two rhodium atoms and is followed by a chemical reaction resulting in  $(\text{P})\text{Rh}^+$  formation. This is the first example of direct metal insertion in porphyrin chemistry that is triggered by an electrochemical oxidation. The electrochemistry was monitored by electronic absorption spectroscopy and FTIR, and on the basis of these data an overall reaction mechanism is formulated.

### Experimental Section

( $\mu$ -Tetraphenylporphinato)bis(dicarbonylrhodium(I)),  $(\text{TPP})[\text{Rh}(\text{CO})_2]_2$ , and ( $\mu$ -octaethylporphinato)bis(dicarbonylrhodium(I)),  $(\text{OEP})$ -

- (1) Yoshida, Z.; Ogoshi, H.; Omura, T.; Watanabe, E.; Kurosaki, T. *Tetrahedron Lett.* **1972**, 1077.
- (2) Ogoshi, H.; Setsune, J.; Omura, T.; Yoshida, Z. *J. Am. Chem. Soc.* **1975**, *97*, 6461.
- (3) Grigg, R.; Trocha-Grimshaw, J.; Viswanatha, V. *Tetrahedron Lett.* **1976**, 289.
- (4) Abeyskera, A. M.; Grigg, R.; Trocha-Grimshaw, J.; Viswanatha, V. *J. Chem. Soc., Perkin Trans. 1* **1977**, 36.
- (5) Fleischer, E. B.; Dixon, F. *Bioinorg. Chem.* **1977**, *7*, 129.
- (6) Takenaka, A.; Sasada, Y.; Ogoshi, H.; Omura, T.; Yoshida, Z.-I. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 1.
- (7) Takenaka, A.; Sasada, Y.; Omura, T.; Ogoshi, H.; Yoshida, Z.-I. *J. Chem. Soc., Chem. Commun.* **1973**, 792.
- (8) Yamamoto, S.; Hoshino, M.; Yasufuku, K.; Imamura, M. *Inorg. Chem.* **1984**, *23*, 195.
- (9) Hoshino, M.; Yasufuku, K. *Inorg. Chem.* **1985**, *24*, 4408.
- (10) Ogoshi, H.; Setsune, J.; Yoshida, Z. *J. Organomet. Chem.* **1978**, *159*, 317.
- (11) Wayland, B. B.; Newman, A. R. *Inorg. Chem.* **1981**, *20*, 3093.

- (12) Farnos, M. D.; Woods, K. A.; Wayland, B. B. *J. Am. Chem. Soc.* **1986**, *108*, 3659.
- (13) Anderson, J. E.; Yao, C.-L.; Kadish, K. M. *Inorg. Chem.* **1986**, *25*, 718.
- (14) Anderson, J. E.; Yao, C.-L.; Kadish, K. M. *J. Am. Chem. Soc.* **1987**, *109*, 1106.
- (15) Anderson, J. E.; Yao, C.-L.; Kadish, K. M. *Organometallics* **1987**, *6*, 706.
- (16) Kadish, K. M.; Anderson, J. E.; Yao, C.-L.; Guillard, R. *Inorg. Chem.* **1986**, *25*, 1277.
- (17) Paonessa, R. S.; Thomas, N. C.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *107*, 4333.

**Table I.** Spectral Data of (P)[Rh(CO)<sub>2</sub>]<sub>2</sub> in PhCN and CH<sub>2</sub>Cl<sub>2</sub> Containing 0.2 M TBAP

compd	solvent	electrode reacn	$\lambda_{\max}$ , nm ( $10^{-3}\epsilon$ )		
(TPP)[Rh(CO) <sub>2</sub> ] <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	none	370 (66.4)	459 (73.6)	708 (6.6)
		1st redn	404 (39.5)	535 (19.8)	
		1st oxidn <sup>a</sup>	419 (239)	531 (23.4)	565 (4.9)
(TPP)[Rh(CO) <sub>2</sub> ] <sub>2</sub>	PhCN	none	373 (63.0)	460 (72.9)	707 (6.7)
		1st redn	405 (54.6)	537 (25.8)	
		1st oxidn <sup>a</sup>	423 (263)	536 (27.5)	570 (9.6)
(OEP)[Rh(CO) <sub>2</sub> ] <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	none	367 (81.2)	445 (51.5)	518 (12.5)
		1st redn	379 (42.5)	441 (31.8)	510 (14.7)
		1st oxidn <sup>a</sup>	398 (132)	515 (17.2)	550 (29.5)
(OEP)[Rh(CO) <sub>2</sub> ] <sub>2</sub>	PhCN	none	369 (70.7)	445 (43.6)	512 (14.1)
		1st redn	387 (69.0)	518 (23.7)	667 (4.7)
		1st oxidn <sup>a</sup>	403 (209)	518 (24.1)	551 (42.4)

<sup>a</sup>Spectra correspond to electrogenerated [(P)Rh]<sup>+</sup>.

[Rh(CO)<sub>2</sub>]<sub>2</sub>, were prepared according to methods described in the literature.<sup>1,2</sup> Reagent grade benzonitrile (PhCN) was vacuum-distilled from P<sub>2</sub>O<sub>5</sub> while spectroscopic grade dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) was distilled from CaH<sub>2</sub>. Tetra-*n*-butylammonium perchlorate (TBAP) (Fluka Co.) was twice recrystallized from ethyl alcohol and stored in a vacuum oven at 40 °C.

A three-electrode system was used in the electrochemical studies. This consisted of two platinum electrodes and a saturated calomel reference electrode (SCE). The working electrode was a Pt disk with a measured area of  $8.8 \times 10^{-3}$  cm<sup>2</sup>. Cyclic voltammetric and polarographic measurements were obtained on a Princeton Applied Research Model 174A polarographic analyzer and a PAR Model 175 signal generator or an IBM 225/2A voltammetric analyzer coupled with a Houston Instruments Model 2000 X-Y recorder. A Tracor Northern 1710 spectrometer/multichannel analyzer was used for spectroelectrochemical experiments. ESR spectra were recorded on an IBM Model ED-100 electron spin resonance system. The spectroelectrochemical cell has been previously described.<sup>18</sup>

## Results and Discussion

**Reduction of (TPP)[Rh(CO)<sub>2</sub>]<sub>2</sub> and (OEP)[Rh(CO)<sub>2</sub>]<sub>2</sub>.** Cyclic voltammograms of (TPP)[Rh(CO)<sub>2</sub>]<sub>2</sub> and (OEP)[Rh(CO)<sub>2</sub>]<sub>2</sub> in PhCN containing 0.2 M TBAP are shown in Figure 1. Reversible reductions occur at  $E_{1/2} = -1.04$  and  $-1.51$  V for (TPP)[Rh(CO)<sub>2</sub>]<sub>2</sub> (Figure 1a, peaks 1 and 2) and at  $E_{1/2} = -1.34$  and  $-1.84$  V for (OEP)[Rh(CO)<sub>2</sub>]<sub>2</sub> (Figure 1b, peaks 1 and 2). The separation of  $E_{1/2}$  between the two reductions of (TPP)[Rh(CO)<sub>2</sub>]<sub>2</sub> is 0.47 V in PhCN, while for (OEP)[Rh(CO)<sub>2</sub>]<sub>2</sub> this separation is 0.50 V. An average  $\Delta E_{1/2} = 0.44 \pm 0.04$  V has been experimentally observed for the first and second ring reductions of a series of metalloporphyrins,<sup>19</sup> and this suggests that the two reductions of (P)[Rh(CO)<sub>2</sub>]<sub>2</sub> occur at the porphyrin  $\pi$  ring system.

Spectroelectrochemical results confirm that the reductions of (P)[Rh(CO)<sub>2</sub>]<sub>2</sub> are porphyrin ring centered. The Soret bands of (TPP)[Rh(CO)<sub>2</sub>]<sub>2</sub> at 373 and 460 nm and the visible band at 707 nm decrease in intensity, and new absorption bands appear at 405 and 537 nm as this compound is reduced at  $-1.25$  V in PhCN containing 0.2 M TBAP. The final spectrum is indicative of a porphyrin anion radical.<sup>19</sup> This reduction is spectrally reversible, and the original spectrum can be recovered if the potential is set at 0.0 V after the first reduction of (TPP)[Rh(CO)<sub>2</sub>]<sub>2</sub>. This is consistent with the reversible reduction observed in the cyclic voltammogram. (OEP)[Rh(CO)<sub>2</sub>]<sub>2</sub> gave similar spectral changes after the first reduction, and spectral data for reduced (TPP)-[Rh(CO)<sub>2</sub>]<sub>2</sub> and (OEP)[Rh(CO)<sub>2</sub>]<sub>2</sub> are presented in Table I.

Application of potentials more negative than the second reduction resulted in almost featureless UV-visible spectra for both compounds. This implies a chemical reaction following the second reduction. In addition, a reoxidation peak is observed for (OEP)[Rh(CO)<sub>2</sub>]<sub>2</sub> at  $-0.6$  V if the potential is scanned negatively past the second reduction. This peak is not observed if the potential is terminated after the first reduction of the compound (see Figure 1b, dashed line), also implying that a chemical reaction involving the doubly reduced porphyrin species has taken place.

**Table II.** Half-Wave Potentials and Peak Potentials (V vs. SCE) of (P)[Rh(CO)<sub>2</sub>]<sub>2</sub> in PhCN and CH<sub>2</sub>Cl<sub>2</sub> Containing 0.2 M TBAP<sup>a</sup>

porphyrin, P	solvent	oxidn			redn	
		reacn 5	reacn 4	reacn 3	reacn 1	reacn 2
TPP	CH <sub>2</sub> Cl <sub>2</sub>	1.28 <sup>b,c</sup>	0.98	0.78	-1.17	-1.57
	PhCN	1.52 <sup>b,c</sup>	1.23 <sup>c</sup>	0.84 <sup>b</sup>	-1.04	-1.51
OEP	CH <sub>2</sub> Cl <sub>2</sub>	1.16 <sup>b,c</sup>	0.94	0.66	-1.43	
	PhCN	1.39 <sup>c</sup>	1.06 <sup>c</sup>	0.74 <sup>b</sup>	-1.34	-1.84

<sup>a</sup> Values listed are half-wave potentials unless otherwise noted. Reactions 1-5 are noted in Figure 1. <sup>b</sup>  $E_{\text{red}}$  at a scan rate of 0.10 V/s. <sup>c</sup> Oxidations of electrogenerated [(P)Rh]<sup>+</sup>.

Bulk electrolyses of both complexes show that the total number of electrons transferred in the first reduction is  $1.0 \pm 0.1$ . Frozen-solution ESR spectra were recorded in PhCN for singly reduced (TPP)[Rh(CO)<sub>2</sub>]<sub>2</sub> and (OEP)[Rh(CO)<sub>2</sub>]<sub>2</sub>. The distorted porphyrin ring structure reduces the symmetry of the molecule, and an anisotropic ESR signal results. The signal for reduced (TPP)[Rh(CO)<sub>2</sub>]<sub>2</sub> is characterized by  $g_{\perp} = 2.00$  and  $g_{\parallel} = 1.97$  while the signal for reduced (OEP)[Rh(CO)<sub>2</sub>]<sub>2</sub> has  $g_{\perp} = 2.00$  and  $g_{\parallel} = 1.96$ .

(TPP)[Rh(CO)<sub>2</sub>]<sub>2</sub> and (OEP)[Rh(CO)<sub>2</sub>]<sub>2</sub> show similar reductive behavior in CH<sub>2</sub>Cl<sub>2</sub>, but a second reduction of (OEP)-[Rh(CO)<sub>2</sub>]<sub>2</sub> is not observed in the potential range of this solvent. Potentials for the reduction of both complexes in CH<sub>2</sub>Cl<sub>2</sub> are listed in Table II.

**Oxidation of (TPP)[Rh(CO)<sub>2</sub>]<sub>2</sub> and (OEP)[Rh(CO)<sub>2</sub>]<sub>2</sub>.** Three oxidations of (P)[Rh(CO)<sub>2</sub>]<sub>2</sub> occur in PhCN. The first oxidation (peak 3, Figure 1) is irreversible, but the second and third oxidations (peaks 4 and 5, Figure 1) are reversible to quasi-reversible. Also, the second oxidation of both complexes has a relatively low peak current compared to that of the other redox reactions.

The first oxidation peak has  $|E_p - E_{p/2}| = 60 \pm 5$  mV and a constant  $i_p/v^{1/2}$  value. This is characteristic of a diffusion-controlled, one-electron process. In addition, bulk oxidation of (TPP)[Rh(CO)<sub>2</sub>]<sub>2</sub> and (OEP)[Rh(CO)<sub>2</sub>]<sub>2</sub> after process 3 gives coulometric values of  $1.0 \pm 0.2$  electrons in either PhCN or CH<sub>2</sub>Cl<sub>2</sub>. The lack of a corresponding coupled cathodic wave thus implies a chemical reaction following an initial reversible one-electron transfer (an electrochemical EC mechanism). The first and second oxidations of both complexes are quasi-reversible to reversible in CH<sub>2</sub>Cl<sub>2</sub>, indicating that the chemical reaction after initial electrooxidation is slower in CH<sub>2</sub>Cl<sub>2</sub> than in PhCN. A summation of oxidation potentials in these two solvents is presented in Table II.

Figure 2a shows the spectral changes that occur upon oxidation of (TPP)[Rh(CO)<sub>2</sub>]<sub>2</sub> at  $+0.90$  V in PhCN containing 0.2 M TBAP. The original absorption peaks at 373, 460, and 707 nm decrease in intensity as a compound with a Soret band at 423 nm and visible bands at 536 and 570 nm is formed. The final spectrum is identical<sup>16</sup> with that of [(TPP)Rh]<sup>+</sup>, demonstrating formation of this species.

Similar spectral changes and formation of [(TPP)Rh]<sup>+</sup> were found during oxidation of (TPP)[Rh(CO)<sub>2</sub>]<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>. In addition, the UV-visible spectrum of singly oxidized (OEP)[Rh-

(18) Lin, X.-Q.; Kadish, K. M. *Anal. Chem.* **1985**, *57*, 1498.

(19) Kadish, K. M. *Prog. Inorg. Chem.* **1986**, *34*, 435.

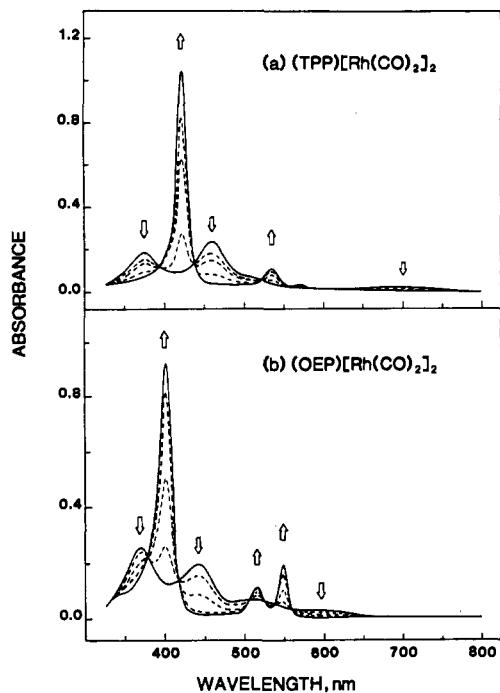


Figure 2. Electronic absorption spectra for the oxidation of (a)  $1.2 \times 10^{-5}$  M (TPP)[Rh(CO)<sub>2</sub>]<sub>2</sub> at 0.95 V and (b)  $1.4 \times 10^{-5}$  M (OEP)[Rh(CO)<sub>2</sub>]<sub>2</sub> at 0.90 V in PhCN containing 0.2 M TBAP.

(CO)<sub>2</sub>]<sub>2</sub> indicates formation of [(OEP)Rh]<sup>+</sup> (Figure 2b). These spectral details are summarized in Table I. It should also be noted that negligible photochemical reactivity of (P)[Rh(CO)<sub>2</sub>]<sub>2</sub> occurred on the spectroelectrochemical time scale (about 2–4 min). This was verified by independent photolysis experiments under the same experimental conditions.

Oxidation of (P)[Rh(CO)<sub>2</sub>]<sub>2</sub> was monitored in the CO region of the infrared spectrum by spectroelectrochemical techniques. (OEP)[Rh(CO)<sub>2</sub>]<sub>2</sub> is characterized<sup>1-5</sup> by two M–CO absorption bands at 2053 and 1990 cm<sup>-1</sup>. Upon oxidation, an intermediate is observed with absorption bands at 2094 and 2035 cm<sup>-1</sup>. The intensities of the new bands are substantially less than those of the original spectrum and may indicate that a large concentration of the intermediate cannot be generated. The large shift in the CO absorption bands reflects an oxidation of the metal and a decrease in the metal  $\pi$  back-bonding ability. After bulk electrolysis of (OEP)[Rh(CO)<sub>2</sub>]<sub>2</sub> no absorptions associated with a M–CO band are observed. In addition, frozen solutions of electrooxidized compound do not have an ESR signal, consistent with formation of [(P)Rh]<sup>+</sup>.

Oxidation of (TPP)[Rh(CO)<sub>2</sub>]<sub>2</sub> produces similar results. The initial spectrum of (TPP)[Rh(CO)<sub>2</sub>]<sub>2</sub> has two M–CO bands at 2050 and 1994 cm<sup>-1</sup>, and the oxidized intermediate has two M–CO absorption bands at 2070 and 2031 cm<sup>-1</sup>. No M–CO absorption bands are observed in the infrared region after bulk electrolysis of (TPP)[Rh(CO)<sub>2</sub>]<sub>2</sub>.

**Reaction Scheme.** The overall oxidation/reduction scheme of (P)[Rh(CO)<sub>2</sub>]<sub>2</sub> is given in Figure 3. The two successive reductions result in formation of a porphyrin  $\pi$  anion radical and dianion. These electron additions are given by reactions 1 and 2.

The first oxidation of (P)[Rh(CO)<sub>2</sub>]<sub>2</sub> is a one-electron process (reaction 3) and ultimately results in formation of a Rh(III) species. This may occur via an intramolecular electron-transfer reaction, i.e., a reaction between Rh(I) and Rh(II) in the same porphyrin molecule. After formation of Rh(III), this metal ion is inserted into the porphyrin plane with loss of Rh<sup>0</sup>, which is observed as an insoluble black precipitate after bulk oxidation of the complexes. An intermolecular electron-transfer reaction may also occur with the generation of [(P)Rh]<sup>+</sup> and Rh<sup>0</sup>. In both schemes, [(P)Rh]<sup>+</sup> is generated as the only porphyrin species in solution. The second and third oxidation waves observed in the cyclic voltammograms in PhCN (reactions 4 and 5) correspond

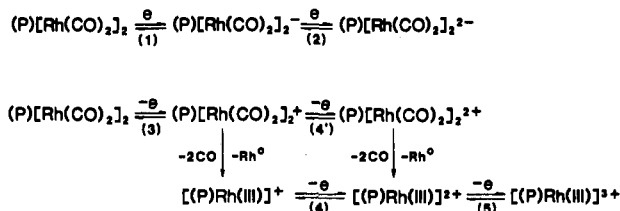


Figure 3. Reaction scheme of (P)[Rh(CO)<sub>2</sub>]<sub>2</sub> for reduction and oxidation.

to reactions of this species. The oxidation properties of [(TPP)Rh]<sup>+</sup> have been previously discussed.<sup>16</sup>

**Acknowledgment.** The support of the National Science Foundation (Grant No. CHE-8515411) and the Robert A. Welch Foundation (Grant No. E-680) is gratefully acknowledged.

**Registry No.** (TPP)[Rh(CO)<sub>2</sub>]<sub>2</sub>, 88083-36-7; (TPP)[Rh(CO)<sub>2</sub>]<sub>2</sub><sup>-</sup>, 109152-56-9; (TPP)[Rh(CO)<sub>2</sub>]<sub>2</sub><sup>2-</sup>, 109152-57-0; (TPP)[Rh(CO)<sub>2</sub>]<sub>2</sub><sup>+</sup>, 109152-59-2; (TPP)[Rh(CO)<sub>2</sub>]<sub>2</sub><sup>2+</sup>, 109152-60-5; (OEP)[Rh(CO)<sub>2</sub>]<sub>2</sub>, 51320-70-8; (OEP)[Rh(CO)<sub>2</sub>]<sub>2</sub><sup>-</sup>, 109182-00-5; (OEP)[Rh(CO)<sub>2</sub>]<sub>2</sub><sup>2-</sup>, 109152-58-1; (OEP)[Rh(CO)<sub>2</sub>]<sub>2</sub><sup>+</sup>, 109182-01-6; (OEP)[Rh(CO)<sub>2</sub>]<sub>2</sub><sup>2+</sup>, 109152-61-6; [(TPP)Rh]<sup>+</sup>, 98756-66-2; [(TPP)Rh]<sup>3+</sup>, 109152-62-7; [(OEP)Rh]<sup>+</sup>, 99327-15-8; [(OEP)Rh]<sup>3+</sup>, 109152-63-8; Rh, 7440-16-6.

Contribution from the Department of Chemistry,  
University of Georgia, Athens, Georgia 30602

#### (Dialkylamido)selenium Derivatives

R. B. King\* and S. A. Sangokoya

Received February 18, 1987

The extensive applications of SeO<sub>2</sub> as an oxidant in organic chemistry<sup>1</sup> suggests that (dialkylamido)selenium(IV) derivatives might be useful in organic synthesis as sources of dialkylamino groups under potentially oxidizing conditions. However, relatively little is known about the preparation and properties of (dialkylamido)selenium derivatives. Furthermore, such derivatives have received essentially no attention since the report by Paetzold and Rönisch in 1965<sup>2</sup> on the preparation and properties of (Me<sub>2</sub>N)<sub>2</sub>SeO. Since that time selenium-77 NMR spectroscopy (<sup>77</sup>Se:  $I = 1/2$ , natural abundance 7.6%, receptivity  $5.26 \times 10^{-4}$  that of the proton) has been shown to be a useful method for the characterization of organoselenium compounds.<sup>3-6</sup> Accordingly, we have reinvestigated and extended these original results by Paetzold and Rönisch<sup>2</sup> using selenium-77 NMR as a method for the analysis of reaction mixtures and products isolated therefrom. This paper summarizes our results in this area.

#### Experimental Section

Selenium-77 NMR spectra were taken on a multinuclear JEOL FX-90Q spectrometer operating at a nominal frequency of 17.04 MHz in the pulsed Fourier-transform mode. For chemical shift determinations the spectrum was calibrated against an external sample of dimethyl selenide

- (1) Rabjohn, N. *Org. React. (N.Y.)* **1976**, *24*, 261.
- (2) Paetzold, R.; Rönisch, E. *Z. Anorg. Allg. Chem.* **1965**, *338*, 22.
- (3) Rodger, R.; Sheppard, N.; McFarlane, H. C. E.; McFarlane, W. In *NMR and the Periodic Table*; Harris, R. K.; Mann, B. E., Eds.; Academic: London, 1978; pp 402–419.
- (4) Luthra, N. P.; Odom, J. D. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, England, 1986; Vol. 1, pp 189–241.
- (5) Denney, D. B.; Denney, D. Z.; Hammond, P. J.; Hsu, Y. F. *J. Am. Chem. Soc.* **1981**, *103*, 2340.
- (6) Eggert, H.; Nielsen, O.; Henriksen, L. *J. Am. Chem. Soc.* **1986**, *108*, 1725.