Paramagnetic Rh(III) Complexes from Reactions of Phosphines with Hydride-Bridged and Nonbridged Rhodium Phthalocyanine Dimers: Metal-to-Ligand Charge Transfer Induced by Phosphines

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The paramagnetic rhodium phthalocyanine complex (RPc)$(PMe_3)_2$Rh (**4**) (RPc = dianion of 1,4,8,11,15,18,22,25-octa-*n*-pentylphthalocyanine) has been prepared by the reaction of trimethylphosphine (PMe_3) with hydride-bridged and nonbridged rhodium phthalocyanine dimers. The reaction of the μ-hydrido complex (RPcH)Rh(μ-H)Rh(RPc) (**5**) (RPcH = RPc with one of its meso nitrogens protonated) with PMe_3 at −10 °C produces (RPc)(PMe_3)RhH (**6**), which further reacts with PMe_3 to produce **4** and H_2 at higher temperatures. If the solution of **6** is allowed to warm in the absence of free PMe_3, H_2 is also liberated and **6** is converted to an equal number of moles of **4** and $[(RPc)Rh]_2(PMe_3)$ (**7**). In contrast, the reaction of **5** with pyridine (py) produces (RPc)(py)RhH (**11**), which does not react with additional pyridine. Alternatively, **4** is generated by the reaction of the Rh−Rh bonded dimer $[(RPc)Rh]_2$ (**1**) with PMe_3. In this reaction, the formation of **7** as an intermediate may be shown by the titration of **1** with PMe_3. Complex **1** reacts with **4** to produce $(RPc)Rh^-$ (**10**) and $(RPc)(PMe_3)_2Rh^+$ (**9**). A redox exchange between **4** and **9** ensues. The cobalt analogue of **4**, i.e., $(RPc)(PMe_3)_2Co$ (**12**), was generated reversibly by the reaction of (RPc)Co (**13**) with PMe_3 at low temperatures. The ^1H NMR and the ESR spectra of **4**, **12**, and **13** indicate that while **13** is a metal-centered radical, **4** and **12** are best described as ligand-centered radicals. Therefore, **4** and **12** are formulated as Rh(III) and Co(III) complexes of the singly reduced π-radical anion $RPc^{\bullet -}$, generated by metal-to-ligand charge-transfer reactions induced by phosphines. Consistent with formulation of **4** as a Rh(III) complex, it is only slowly oxidized in air and its PMe_3 ligand is slow to exchange with the free phosphine.

Introduction

The coordination chemistry of rhodium is dominated by mononuclear Rh(I) and Rh(III) complexes. Only a few monomeric Rh(II) complexes have been prepared and isolated. The scarcity of mononuclear Rh(II) complexes, in contrast to the abundance of mononuclear Co(II) complexes, is the result of the more favorable energetics for their dimerization. As a result, most of the reported mononuclear Rh(II) complexes have been characterized by their ESR spectra at low temperature or inferred from electrochemical studies only. In recent years, more mononuclear Rh(II) complexes have been isolated and characterized. Dimerization of these complexes is prevented by the presence of sterically demanding ligands or electron-withdrawing ligands that can effectively reduce the unpaired electron density on rhodium. Steric constraint is definitely the most important factor for the stability of the following Rh(II) complexes: (TMP)Rh,[1] (TTEPP)Rh,[2] $(C_5HPh_4)_2$Rh,[3] $[P(i\text{-}Pr)_3]_2Cl_2$Rh,[4] and $[(TMPP)Rh](BF_4)_2$.[5] On the other hand, the stability of the planar $[(MNT)_2Rh]^{2-}$[6] and $(R_2NCS_2)_2$Rh[7] has to be attributed to electronic factors only, since protective bulky ligands are not present in these complexes. Apparently, the presence of the soft sulfur atom and the conjugated π-bonds in these ligands so effectively stabilizes these Rh(II) complexes that dimerization does not occur. With the exception of $(C_5HPh_4)_2$Rh, all of the isolated Rh(II) complexes are either 15-electron or 17-electron complexes. To our knowledge, $(C_5HPh_4)_2$Rh is the only 19-electron Rh(II) complex that has been isolated. Another class of "Rh(II)" complexes, as exemplified by (OETAP)$(py)_2$Rh,[8] $(PPh_3)_2(NO)Cl_3$Rh,[9] and (Pc)$(CN)_2Rh^{2-}$,[10] is the six-coordinate 19-electron or 18 + δ complexes[11] that have the odd electrons residing primarily on a ligand-centered orbital. The δ indicates the residual odd electron density on the metal center. This class of compounds is best described as Rh(III) complexes of singly reduced radical anions of the ligands. A comprehensive review on mononuclear Rh(II) complexes has recently been published by DeWit.[12]

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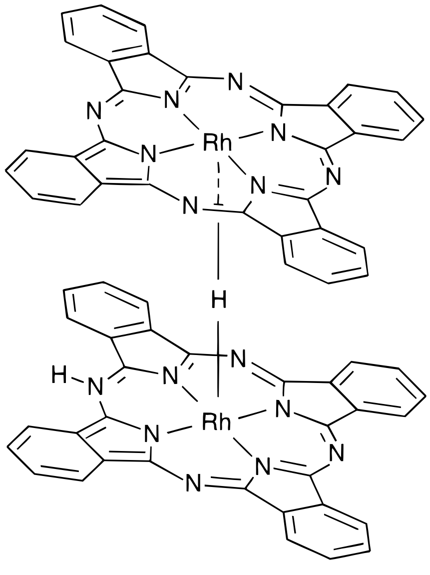

Figure 1. Molecular structure of (RPcH)Rh(μ-H)Rh(RPc) (**5**). The pentyl groups are omitted for clarity.

Our interest in mononuclear Rh(II) complexes began with our study of using the Rh–Rh bonded dimer $[(RPc)Rh]_2$ (**1**) (RPc = dianion of 1,4,8,11,15,18,22,25-octa-*n*-pentylphthalocyanine) as a catalyst for hydrocarbon activation.[13] We found that the results of **1**-catalyzed hydrocarbon activation are consistent with a radical mechanism, in which the reaction is initiated by homolysis of **1** to generate the (RPc)Rh (**2**) radical. This highly reactive radical then abstracts a hydrogen atom from a C–H bond of the substrate. In this report, we describe our study of the reactions of phosphines with hydride-bridged and nonbridged rhodium phthalocyanine dimers to generate monomeric Rh(III) complexes of phthalocyanine radical anions. We have succeeded in breaking the Rh–Rh bond of **1**, which is estimated to be about 22 kcal/mol from the kinetics of its reaction with toluene,[13b] with phosphine ligands at ambient temperature. However, instead of generating the five-coordinate $(RPc)(PMe_3)Rh$ (**3**), the reaction of **1** with PMe_3 leads to formation of six-coordinate $18 + \delta$ $(RPc)(PMe_3)_2Rh$ (**4**), even in solutions in which the mole ratio of PMe_3/Rh is 1. The ^1H NMR and ESR spectra of **4**, along with its chemical reactivities, indicate that it is best described as a Rh(III) complex of the singly reduced π-radical anion $RPc^{\bullet-}$. The cobalt analogue of **4**, i.e., $(RPc)(PMe_3)_2Co$, has also been prepared. The preparation and characterization of these paramagnetic complexes, together with some related Rh(III)–hydride and Rh(I) complexes, are described.

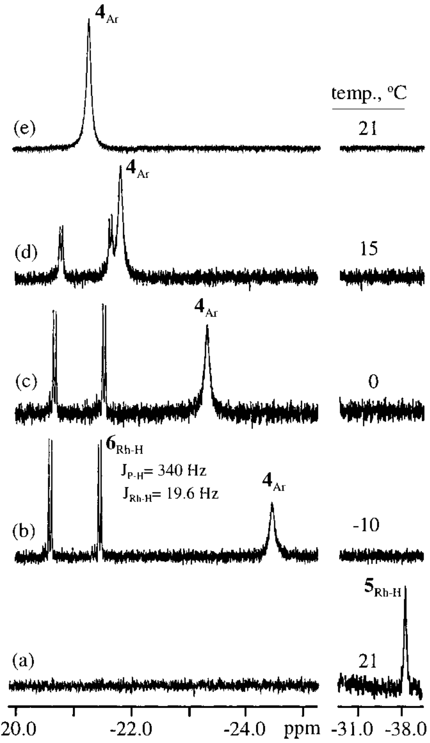

Figure 2. ^1H NMR spectra for the reaction of (RPcH)Rh(μ-H)Rh(RPc) (**5**) with PMe_3 to generate $(RPc)(PMe_3)_2Rh$ (**4**), with $(RPc)(PMe_3)RhH$ (**6**) as an intermediate: (a) 0.91 μmol of (RPcH)Rh(μ-H)Rh(RPc) in 0.50 mL of toluene-d_8; (b) PMe_3 from 1.6 μmol of $Ag(PMe_3)_4I$ added to the frozen solution, and the solution warmed to −10 °C; (c−e) recorded over 2-h period at different temperatures.

Results

$(RPc)(PMe_3)RhH$ (6) and $(RPc)(PMe_3)_2Rh$ (4) from the Reaction of (RPcH)Rh(μ-H)Rh(RPc) (5) with PMe_3. The change in the high-field region of the ^1H NMR spectrum that accompanies the reaction of (RPcH)Rh(μ-H)Rh(RPc) (**5**, Figure 1) (RPcH = RPc with one of its meso nitrogens protonated)[13] with trimethylphosphine is shown in Figure 2. Figure 2a shows the hydride resonance of **5** in toluene-d_8 at δ −38.1 ppm, which appears as a broad resonance because of the dynamic exchange among its four isomers at room temperatures. Addition of excess PMe_3 at low temperatures led to immediate formation of six-coordinate $(RPc)(PMe_3)RhH$ (**6**) in 91% yield, as revealed by its hydride resonance at δ −21.03 ppm (Figure 2b) (dd, $J_{P-H} = 340.0$ Hz and $J_{Rh-H} = 19.6$ Hz) and the methyl resonance of PMe_3 at δ −2.71 ppm (dd, $J_{P-H} = 6.8$ Hz and $J_{Rh-H} = 1.6$ Hz). The only other product observed was the six-coordinate paramagnetic $(RPc)(PMe_3)_2Rh$ (**4**) (9%; H_{Ar} at δ −24.4 ppm), which was isolated from the reaction of $[(RPc)Rh]_2$ with PMe_3 in a separate experiment. The complete ^1H NMR resonances of **4** are presented in Table 1. Compound **6** was found to be quite stable in the presence of PMe_3 at low temperatures. However, it reacted with PMe_3 to produce **4** and H_2 as the solution was allowed to warm to room temperature over a 2-h period, as shown in Figure 2b−e. These reactions are depicted by eqs 1 and 2.

$$(RPcH)Rh(\mu\text{-}H)Rh(RPc) + 2PMe_3 \rightarrow 2(RPc)(PMe_3)RhH \quad (1)$$

$$2(RPc)(PMe_3)RhH + 2PMe_3 \rightarrow 2(RPc)(PMe_3)_2Rh + H_2 \quad (2)$$

All the ^1H NMR resonances of **4** are broad and temperature dependent, as expected of a paramagnetic complex. The resonance for the aromatic H's is shifted upfield by ~29 ppm, while the α H's of the pentyl group are shifted downfield by ~8 ppm from those of diamagnetic Rh(III) complexes. Unlike typical Rh(II) complexes,[12] this paramagnetic rhodium complex is inert toward ligand substitution reactions. Its exchange with free trimethylphosphine is slow on the NMR scale even at 80 °C, and it is only slowly oxidized in air to give a complicated product mixture. These results suggest that **4** is more appropriately formulated as a Rh(III) complex of the π-radical

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Table 1. ^{1}H NMR Spectra of Rhodium and Cobalt Complexes of 1,4,8,11,15,18,22,25-Octa-*n*-pentylphthalocyanine

compound	temp, °C	solvent	H_{Ar}, ppm	other resonances, ppm
(RPc)(PMe$_3$)RhH	−40	$C_6D_5CD_3$	7.78 (s, 8H)	−20.81 (H_{Rh-H}, dd, 1H, $J_{P-H} = 347$ Hz, $J_{Rh-H} = 19.6$ Hz); −2.79 (H_{PMe_3}, d, 9H, $J_{P-H} = 6.8$ Hz, $J_{Rh-H} = 1.6$ Hz); 4.78 (H_α, mult, 16H); 2.38 (H_β, *q*, 16H); 1.73 (H_γ , mult, 16H); 1.41 (H_δ, mult, 16H); 0.93 (H_{Me}, t, 24H, $J_{H-H} = 7.4$ Hz)
(RPc)(PMe$_3$)$_2$Rh	room	C_6D_6	−20.98 (br s, 8H)	0.250 (H_{PMe_3}, br s, 18H); 13.19 (H_α, br s, 16H); 7.21 (H_β, br s, 16H); 1.35 (H_γ, mult, 16H); 1.08 (H_δ, mult, 16H); 0.99 (H_{Me}, t, 24H, $J_{H-H} = 7.4$ Hz)
[(RPc)Rh]$_2$(PMe$_3$)	room	C_6D_6	8.03 (s, 8H) 8.14 (s, 8H)	−4.68 (H_{PMe_3}, d, 9H, $J_{P-H} = 13.2$ Hz); 4.83 ($H_{\alpha 1} + H_{\alpha 1'}$, mult, 16H); 3.93 ($H_{\alpha 2}$, mult, 8H); 3.74 ($H_{\alpha 2'}$, mult, 8H); 2.40 ($H_{\beta 1}$, mult, 16H); 2.33 ($H_{\beta 2}$, mult, 16H); 1.80 ($H_\gamma + H_{\gamma'}$, mult, 32H); 1.57 ($H_\delta + H_{\delta'}$, mult, 32H); 1.03 (H_{Me}, t, $J_{H-H} = 7.4$ Hz, 24H); 0.99 (H_{Me}, t, $J_{H-H} = 7.2$ Hz, 24H)
[(RPc)(PMe$_3$)Rh]$_2$	room	C_6D_6	8.09 (s, 16H)	4.84 ($H_{\alpha 1}$, mult, 16H); 3.84 ($H_{\alpha 2}$, mult, 16H); 2.41 ($H_{\beta 1}$, mult, 16H); 2.33 ($H_{\beta 2}$, mult, 16H); 1.78 (H_γ, mult, 32H); 1.56 (H_δ, mult, 32H); 1.00 (H_{Me}, t, $J_{H-H} = 7.2$ Hz, 48H)
(RPc)Rh$^-$	room	C_6D_6	7.67 (s, 8H)	4.59 (H_α, t, $J_{H-H} = 7.2$ Hz, 16H)
(RPc)(py)RhH	−75	$C_6D_5CD_3$	7.80 (s, 8H)	−28.73 (H_{Rh-H}, d, 1H, $J_{Rh-H} = 24.8$ Hz); 2.82 (H_{py}, br s, 2H); 4.06 (H_{py}, br s, 2H); 4.72 ($H_{\alpha 1}$, br s, 8H); 4.84 ($H_{\alpha 2}$, br s, 8H); 2.40 (H_β, br s, 16H); 1.72 (H_γ, br s, 16H); 1.39 (H_δ, br s, 16H); 0.98 (H_{Me}, t, 24H, $J_{H-H} = 6.4$ Hz)
(RPc)Co	room	$C_6D_5CD_3$	10.17 (br s, 8H)	8.04 (H_α, br s, 16H); 4.54 (H_β, br s, 16H); 3.06 (H_γ, br s, 16H); 1.89 (H_δ, br s, 16H); 0.99 (H_{Me}, br s, 24H)
(RPc)(PMe$_3$)$_2$Co	−80	$C_6D_5CD_3$	−36.76 (br s, 8H)	0.724 (H_{PMe_3}, br s, 18H); 18.47 (H_α, br s, 16H); 9.94 (H_β, br s, 16H); 2.09 (H_γ, br s, 16H); 1.29 (H_δ, br s); 1.19 (H_{Me}, br s)

anion $RPc^{\bullet -}$. Results from ESR studies, which are presented later, are also consistent with **4** as a ligand-centered radical complex.

The hydride resonance of **6** in Figure 2b−d shifted upfield and became broader as the temperature was raised. Since the methyl resonances of free PMe$_3$ and the PMe$_3$ ligand of **6** in these spectra also exhibited line broadening and shifting, it is concluded that the PMe$_3$ ligand of **6** is labile and that eq 3 is responsible for the line-shape change of the hydride resonance in Figure 2b−d.

$$(RPc)(PMe_3)RhH \rightleftharpoons (RPc)RhH + PMe_3 \qquad (3)$$

Reductive Elimination of H$_2$ from (RPc)(PMe$_3$)RhH (6). We have shown that **6** reacts with excess PMe$_3$ to give (RPc)(PMe$_3$)$_2$Rh (**4**) and H$_2$ according to eq 2. To test the stability of **6** in the absence of free phosphine, a solution was similarly prepared from 0.85 μmol of (RPcH)Rh(μ-H)Rh(RPc) (**5**) and 2.0 μmol of PMe$_3$. The ^{1}H NMR spectrum of the solution at 0 °C showed that it contained 1.45 μmol of **6** and 0.25 μmol of **4**. After the solution was allowed to stand overnight at room temperature, H$_2$ was produced and the solution contained 0.65 μmol of **4** and 0.53 μmol of [(RPc)-Rh]$_2$(PMe$_3$) (**7**). The characterization of **7** is described in the following section. This composition is in reasonable agreement with the calculated composition of 0.73 μmol of **4** and 0.48 μmol of **7**, if we assume that **6** decomposes to produce H$_2$ and an equal number of moles of **4** and **7** according to eq 4, possibly with formation of (RPc)(PMe$_3$)Rh (**3**) as an intermediate.

$$6(RPc)(PMe_3)RhH \rightarrow 2(RPc)(PMe_3)_2Rh + 2[(RPc)Rh]_2(PMe_3) + 3H_2 \quad (4)$$

[(RPc)Rh]$_2$(PMe$_3$), [(RPc)(PMe$_3$)Rh]$_2$, (RPc)(PMe$_3$)$_2$Rh$^+$, and (RPc)Rh$^-$. As mentioned earlier, (RPc)(PMe$_3$)$_2$Rh (**4**) is also prepared by the reaction of [(RPc)Rh]$_2$ (**1**) with PMe$_3$ as shown in eq 5.

$$[(RPc)Rh]_2 + 4PMe_3 \rightarrow 2(RPc)(PMe_3)_2Rh \qquad (5)$$

If **1** is titrated with PMe$_3$, the monophosphine adduct [(RPc)-Rh]$_2$(PMe$_3$) (**7**) is obtained in the addition of the first equivalent of PMe$_3$, as depicted in eq 6.

$$[(RPc)Rh]_2 + PMe_3 \rightarrow [(RPc)Rh]_2(PMe_3) \qquad (6)$$

Figure 3 shows the ^{1}H and the $^{31}P\{^1H\}$ spectra of a solution prepared by the reaction of nearly equimolar amounts of PMe$_3$ and **1** in C$_6$D$_6$, with **1** in a slight excess. All of the ^{1}H resonances of the aromatic and the pentyl H's can be easily assigned to the two nonequivalent (RPc)Rh macrocycles of **7**. However, the two doublets at δ −4.66 ppm ($J_{P-H} = 13.2$ Hz) and −4.80 ppm ($J_{P-H} = 12.8$ Hz) in the ratio of 90:10 in the region of coordinated PMe$_3$ suggest the presence of two isomers of **7**, which are designated as **7a** and **7b**. Our deduction of having two isomers of **7** in the product solution is also supported by the $^{31}P\{^1H\}$ spectrum in inset A of Figure 3, which shows two sets of doublets of doublets at δ −54.28 ppm (δ 0.00 for H$_3$PO$_4$; $J_{Rh1-P} = 89.0$ Hz; $J_{Rh2-P} = 75.0$ Hz) and δ −50.01 ppm ($J_{Rh1-P} = 82.0$ Hz; $J_{Rh2-P} = 71.2$ Hz) in the ratio of 93:7. This ratio of 90:10 (determined by ^{1}H NMR) was always obtained when **7a** and **7b** were generated from eq 6. However, the ratio varied with reaction conditions when **7a** and **7b** were obtained from the reaction of **4** and **6** (described later), and as much as 25% of **7b** was obtained.

The expanded spectrum for the aromatic H's in inset B of Figure 3 reveals a shoulder for the higher field resonance of the two singlets for **7a**. We assign the shoulder to an aromatic resonance of the minor isomer **7b**, since its relative intensity to **7a** changes with the relative intensities of the two PMe$_3$ resonances of **7a** and **7b**. The other aromatic resonance of **7b** is assumed to be buried under the other aromatic resonance of **7a**. The ratio of **7a** to **7b** remained unchanged, and there was no dynamic exchange between these two isomers even at 105 °C, indicating a considerable barrier for their interconversion.

The fact that only one aromatic resonance was observed for each of the two RPc ligands of **7a** suggests that the two (RPc)-Rh macrocycles are either exactly eclipsed or are 45°-staggered. Such a conclusion is also supported by the three multiplets in the ratio of 2:1:1 (or partially resolved 1:1:1:1 multiplets) for the α-methylene protons of the 16 pentyl groups. Twice as many resonances for the α H's would have been observed if the two pentyl groups on each (RPc)Rh macrocycle were not equivalent.

Addition of PMe$_3$ beyond the 1:1 ratio led to broadening and shifting of the resonances of **7a** and **7b**, and this effect is attributed to reversible formation of [(RPc)(PMe$_3$)Rh]$_2$ (**8**). In

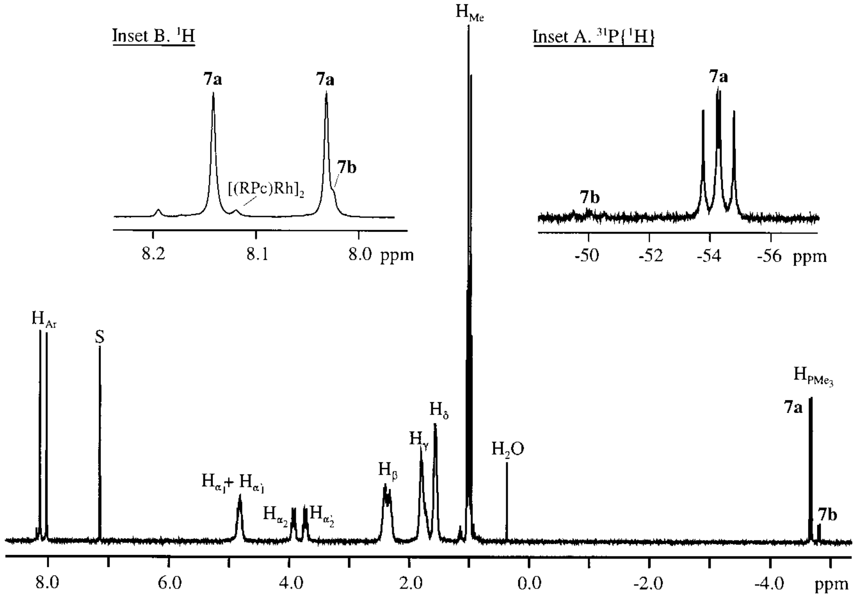

Figure 3. ^{1}H and ^{31}P{^{1}H} NMR spectra of [(RPc)Rh]$_2$(PMe$_3$) (**7**) in toluene-*d*$_8$. The solution was prepared by the reaction of nearly equimolar amounts of [(RPc)Rh]$_2$ and PMe$_3$, with a very slight excess of [(RPc)Rh]$_2$.

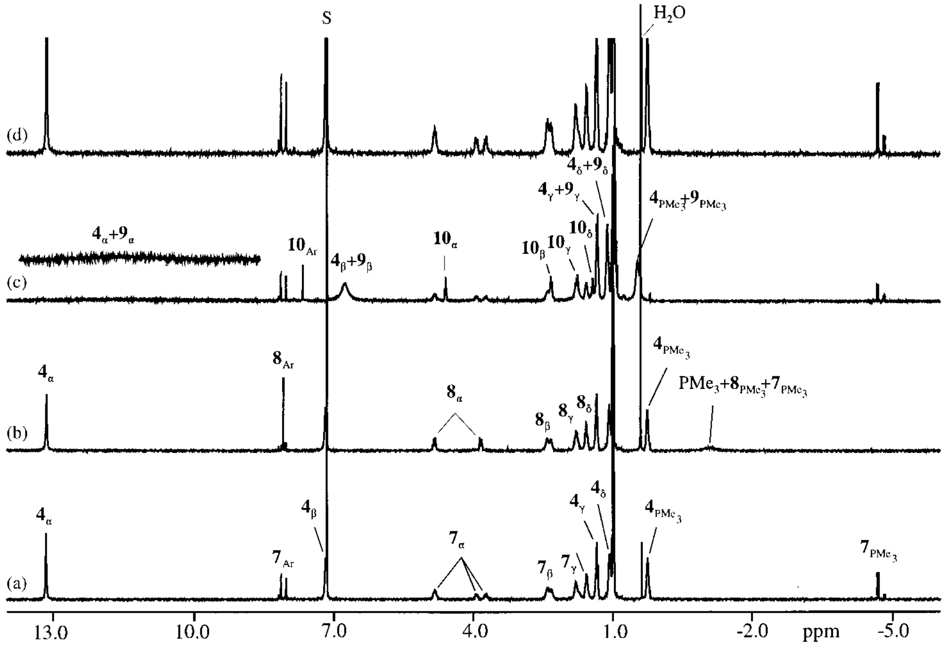

Figure 4. Reaction of (RPc)(PMe$_3$)$_2$Rh (**4**) with [(RPc)Rh]$_2$ (**1**) in benzene-*d*$_6$, producing (RPc)(PMe$_3$)$_2$Rh$^+$ (**9**) and (RPc)Rh$^-$ (**10**) as reaction intermediates: (a) ^{1}H NMR of **4** and [(RPc)Rh]$_2$(PMe$_3$) (**7**) generated from 0.74 μmol of **1** and 1.93 μmol of PMe$_3$; (b) 0.64 μmol of PMe$_3$ added; (c) solution at 50 °C for 6 h, and 0.18 μmol of **1** added; (d) 4 days later.

a much slower process, **8** is converted to **4**, presumably by the homolysis of **8** to generate **3**, which then takes up the second PMe$_3$ ligand. These results are depicted in eqs 7 and 8.

$$[(\mathrm{RPc})\mathrm{Rh}]_2(\mathrm{PMe}_3) + \mathrm{PMe}_3 \rightleftharpoons [(\mathrm{RPc})(\mathrm{PMe}_3)\mathrm{Rh}]_2 \quad (7)$$

$$[(\mathrm{RPc})(\mathrm{PMe}_3)\mathrm{Rh}]_2 + 2\mathrm{PMe}_3 \rightarrow 2(\mathrm{RPc})(\mathrm{PMe}_3)_2\mathrm{Rh} \quad (8)$$

Figure 4a shows the ^{1}H NMR spectrum of a solution containing **4**, **7a**, and **7b**, which were produced by the reaction of 0.74 μmol of [(RPc)Rh]$_2$ (**1**) and 1.93 μmol of PMe$_3$ for 4 days at room temperature. The sharpness of these resonances indicates that exchange reactions among these three compounds are slow. Subsequent addition of 0.64 μmol of PMe$_3$ to the solution yielded Figure 4b, which shows no change in the resonances of **4**; however, the resonances of **7a** and **7b** were replaced by a set of resonances that are consistent with a dimer having two equivalent (RPc)Rh macrocycles and are assigned to **8**. The methyl resonance of PMe$_3$ at δ -1.20 ppm is broad because of the dynamic exchange in eq 7 and is, therefore, assigned to the weighted average of **7**, **8**, and free PMe$_3$. The solution was then heated to drive reaction 8 to completion, resulting in a spectrum (not shown) similar to that in Figure 4a. The product solution, which contained **4** and **7** in a mole ratio of 8:1, was then reacted with 0.18 μmol of **1** to give the spectrum in Figure 4c. The spectrum indicates that **4** has reacted but **7a** and **7b** remained unchanged. The broadened and shifted resonances of **4** are assigned to the weighted average of **4** and (RPc)(PMe$_3$)$_2$Rh$^+$ (**9**). There is also a new set of sharp resonances, some of which sit on top of the resonances of **7**.

This set of resonances does not have a corresponding resonance for a coordinated PMe_3 and is assigned to $(RPc)Rh^-$ (**10**). These spectral assignments may be explained in terms of the following two reactions, the reduction of **1** by **4** to produce **10** and **9** (eq 9) and the ensuing redox exchange between **4** and **9** (eq 10):

$$[(RPc)Rh]_2 + 2(RPc)(PMe_3)_2Rh \rightarrow 2(RPc)Rh^- + 2(RPc)(PMe_3)_2Rh^+ \quad (9)$$

$$(RPc)(PMe_3)_2Rh^* + (RPc)(PMe_3)_2Rh^+ \rightleftharpoons [(RPc)(PMe_3)_2Rh^*]^+ + (RPc)(PMe_3)_2Rh \quad (10)$$

In support of these conclusions, it was observed that all the resonances assigned to the weighted average of **4** and **9**, including the omitted aromatic resonance, gradually evolved into those of **4** as the resonances for **10** continued to decrease over the course of 4 days.

In another experiment, a solution of 0.76 μmol of $[(RPc)Rh]_2$ and 1.66 μmol of $(RPc)(PMe_3)_2Rh$ in 0.60 mL of C_6D_6 was prepared under vacuum. Immediate formation of a spectrum similar to that of Figure 4c was observed. The solution was then heated at 80 °C for 5 h to achieve complete reaction. The product solution contained 52% of $(RPc)(PMe_3)_2Rh$ and 48% of $[(RPc)Rh]_2(PMe_3)$. The overall results are consistent with the reaction of $[(RPc)Rh]_2$ with an excess of $(RPc)(PMe_3)_2Rh$ according to eq 11.

$$3[(RPc)Rh]_2 + 2(RPc)(PMe_3)_2Rh \rightarrow 4[(RPc)Rh]_2(PMe_3) \quad (11)$$

(RPc)(py)RhH. In contrast to PMe_3, pyridine reacts with $(RPcH)Rh(\mu\text{-}H)Rh(RPc)$ (**5**) in toluene-d_8 to give (RPc)(py)RhH (**11**), which does not react with excess pyridine. Complex **5** is regenerated if the solution is pumped to dryness. Therefore, the formation of **11** is reversible, as depicted in eq 12.

$$(RPcH)Rh(\mu\text{-}H)Rh(RPc) + 2py \rightleftharpoons 2(RPc)(py)RhH \quad (12)$$

(RPc)(py)RhH gave a broad hydride resonance at δ −29.33 ppm (HHW = 62 Hz) at 21 °C. The Rh−H splitting became discernible at −30 °C, and the well-resolved hydride resonance appeared at δ −28.73 ppm (J_{Rh-H} = 24.8 Hz) at −75 °C. These results are consistent with reversible dissociation of pyridine from (RPc)(py)RhH shown in eq 13.

$$(RPc)(py)RhH \rightleftharpoons (RPc)RhH + py \quad (13)$$

There were also two resonances at δ 2.82 and δ 4.06 ppm, which started to appear at −30 °C and grew sharper as the temperature was lowered. Both of these resonances have twice the intensity of the hydride resonance and are assigned to the ortho and the meta hydrogens of the coordinated pyridine. We have not been able to locate the resonance for the para hydrogen of pyridine, which is presumably obscured by a resonance of the pentyl group.

ESR of $(RPc)(PMe_3)_2Rh$ (4). The ESR spectrum of $(RPc)(PMe_3)_2Rh$ was recorded at −263 °C. Because of the fast relaxation of the electron spin, low temperature was required to record the spectrum. It was barely observed at −195 °C. Simulation of the spectrum gives $g_1 = 1.9993$, $g_2 = 1.9925$, and $g_3 = 1.9880$, respectively. The fact that these g values, in contrast to those of metal-centered Rh(II) complexes,[1−7] are very close to the free-electron value of 2.0023 supports our conclusion that the unpaired electron is located primarily in an antibonding π-orbital of the RPc ligand. Similar assignments of the odd electron to a ligand orbital have also been made for $(OETAP)(py)_2Rh$[8] and $(PPh_3)_2(NO)Cl_3Rh$.[9] As described in the following section, the ESR spectrum of the cobalt analogue of **4**, i.e., $(RPc)(PMe_3)_2Co$, also has g values close to 2.0023, in great contrast to that of the four-coordinate metal-centered radical (RPc)Co.

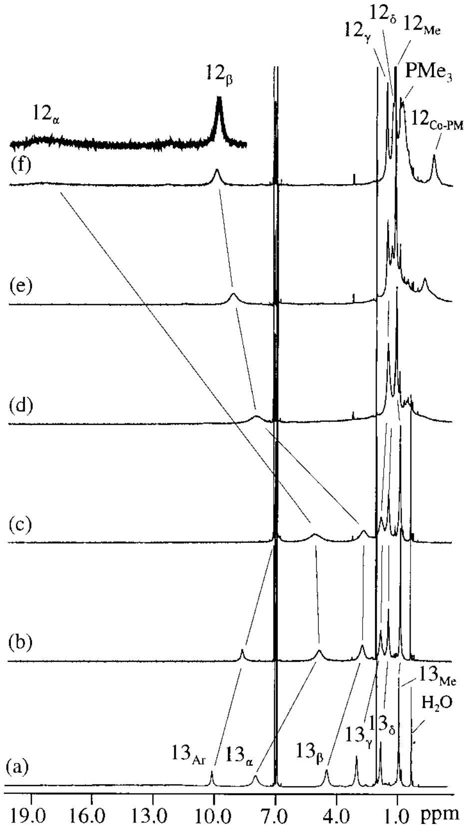

Figure 5. Low-temperature ^1H NMR spectra for the reaction of (RPc)Co (**13**) with excess PMe_3 to generate $(RPc)(PMe_3)_2Rh$ (**11**) in toluene-d_8: (a) 0.66 μmol of (RPc)Co in 0.60 mL of toluene-d_8, 20 °C; (b) 6.3 μmol of PMe_3 added, 20 °C; (c) −40 °C; (d) −60 °C; (e) −70 °C; (f) −80 °C.

^1H and ESR Studies of $(RPc)(PMe_3)_2Co$ (12). The ^1H NMR spectrum of the paramagnetic (RPc)Co (**13**) in toluene-d_8 in Figure 5a shows that all of the resonances of the RPc ligand are broad at room temperature. These resonances appear not more than 2 ppm downfield of the corresponding resonances of diamagnetic (RPc)Rh(III) complexes, indicating that the contact shifts are small for these protons. Addition of PMe_3 causes all the resonances of **13** to shift upfield, as is shown in Figure 5b. These shifts may be attributed to coordination of PMe_3 to **13**. As the temperature of the solution was lowered, the spectrum went through complicated changes, leading to the spectrum in Figure 5f, which is very similar to that of $(RPc)(PMe_3)_2Rh$ (**4**) and is, therefore, assigned to **12**. Not shown in Figure 5 is the resonance for the aromatic H's of **12**, which appeared at δ −21.5, −31.6, and −36.8 ppm in parts d, e, and f of Figure 5, respectively. Consistent with the assignment, the integration also shows that two PMe_3 ligands were added to each (RPc)Co macrocycle. Therefore, it is concluded that two PMe_3 ligands were added to **13** as the temperature was lowered to −60 °C, presumably through formation of the five-coordinate $(RPc)(PMe_3)Co$, as depicted in eq 14.

$$(RPc)Co + 2PMe_3 \rightleftharpoons [(RPc)(PMe_3)Co + PMe_3] \rightleftharpoons (RPc)(PMe_3)_2Co \quad (14)$$

The distinctive difference in the spectra of parts c and d of Figure 5 and in the shift patterns of Figure 5a−c and Figure 5d−f suggests that the first PMe_3 ligand was added until the temperature reached about −50 °C, below which the second PMe_3 ligand was added.

By extension of the similarity of the ^1H NMR spectrum of **12** to that of **4**, the ESR resonance of **12** in the frozen toluene glass at −258 °C is also close to 2.0023. Simulation of the spectrum gives $g_{\parallel} = 1.983$ ($A_{\parallel} = 19.5$ G) and $g_{\perp} = 1.994$. The hyperfine coupling constant for ^{59}Co in the perpendicular direction ($A_{\perp}$) was not observed but is estimated to be ≤7 G. Both the *g* values and the small hyperfine coupling constants indicate that the odd electron of **12** resides primarily on a ligand orbital and that **12**, like **4**, is best formulated as a Co(III) complex of the π-radical anion $RPc^{\bullet-}$.

ESR Study of (RPc)Co (13). For comparison with **12**, the ESR spectrum of (RPc)Co in a toluene glass at −258 °C was also recorded. The spectrum, which is very similar to previously reported spectra of Co(II) complexes of phthalocyanines and porphyrins,[14−16] exhibits higher *g* values and much larger hyperfine couplings to ^{59}Co nuclei. Simulation of the spectrum gives $g_{\parallel} = 1.982$ ($A_{\parallel} = 175$ G) and $g_{\perp} = 2.627$ ($A_{\perp} = 148$ G).

Discussion

The six-coordinate $(RPc)(PMe_3)_2Rh$ has been shown to be an $18 + \delta$ ligand-centered Rh(III) complex of the π-radical anion $RPc^{\bullet-}$, i.e., $(RPc^{\bullet-})(PMe_3)_2Rh$. In the analogous cobalt system, we have observed that PMe_3 converts the planar 15-electron metal-centered (RPc)Co radical to the $18 + \delta$ ligand-centered $(RPc)(PMe_3)_2Co$ radical via 17-electron $(RPc)(PMe_3)Co$, presumably also a metal-centered radical. Similar metal-to-ligand charge-transfer chemistry induced by a base has also been observed in the reactions of pyridine with (OETAP)Rh(II) to form $(OETAP^{\bullet-})(py)_2Rh(III)$[8] (OETAP = dianion of octaethyltetraazaporphyrin) and with $[(oebOx)Co(II)]^+$ (oeb = trianion of octaethylbilindione and oebOX = doubly oxidized oeb) to form $[(oebOx^{\bullet-})(py)_2Co(III)]^+$.[17] On the other hand, such charge-transfer reactions were not observed in the studies of various amines with some Co(II) complexes of porphyrins,[18] phthalocyanines,[19] and dimethylglyoximes.[20] In these systems, five-coordinate 17-electron and six-coordinate 19-electron Co(II) complexes were formed and high unpaired-electron spin densities for cobalt were demonstrated by the high *g* values and large hyperfine couplings of the unpaired electron spins to ^{59}Co nuclei. These results indicate that the distribution of the odd electron-spin density between Co and the ligand can be easily manipulated by the axial ligands. The square planar (RPc)Rh, which has been postulated as an intermediate in the activation of hydrocarbons by $[(RPc)Rh]_2$,[13] is very likely a metal-centered radical like (RPc)Co but is much more reactive. As we have shown that PMe_3 reduces the Rh−Rh bond energy in $[(RPc)Rh]_2$, it is conceivable that addition of a base (L) may enhance the catalytic activity of $[(RPc)Rh]_2$ for the activation of hydrocarbons, even though the five-coordinate (RPc)LRh may be less reactive than (RPc)Rh.

We have postulated the bimolecular elimination of H_2 from two molecules of $(RPc)(PMe_3)RhH$ to generate $(RPc)(PMe_3)Rh$ followed by coordination of PMe_3 as the mechanism for the formation of $(RPc)(PMe_3)_2Rh$ from $(RPc)(PMe_3)RhH$. This mechanism is attractive, since H_2 has been shown to react reversibly with two (TMP)Rh (TMP = dianion of tetramesitylporphyrin) radicals to form (TMP)RhH in a termolecular reaction.[21] A variation of this process is the migration of a proton from Rh to one of the meso nitrogens to form $(RPcH)(PMe_3)Rh$, which then reacts with $(RPc)(PMe_3)RhH$ to produce H_2. This alternative is possible, since we have previously observed the reversible proton migration between Rh and the meso nitrogen atoms in (RPcH)Rh(μ-H)Rh(RPc).[13c]

The reductive elimination of H_2 from $(RPc)(PMe_3)RhH$ is unusual among mononuclear *trans*-phosphine−Rh(III)−H complexes. The failure of (RPc)(py)RhH to eliminate H_2 may be taken as an indication that pyridine is less effective in reducing the Rh−H bond energy in these complexes. The higher stability of the pyridine hydride complex is in keeping with the lower trans-labilizing effect of pyridine.

The ^1H and $^{31}P\{^1H\}$ NMR spectra in Figure 3 strongly support our conclusion of the existence of two isomers of the monophosphine adduct $[(RPc)Rh]_2(PMe_3)$. We assume that **7a** and **7b** are rotational isomers and are formed because of the barrier created by the 16 pentyl groups for rotation around the Rh−Rh bond. Rotational isomerisms have also been suggested for the Rh−Rh bonded (RPcH)RhRh(RPc)H,[13c] the hydride-bridged (RPcH)Rh(μ-H)Rh(RPc),[13c] and the oxo-bridged (phthalocyaninato)Si dimers.[22] The barrier between **7a** and **7b** appears to be substantial, since equilibration between the two isomers does not occur even at 105 °C. As mentioned earlier, the ^1H NMR spectrum in Figure 3 indicates that all 16 pentyl groups of **7a** are equivalent. Therefore, the two (RPc)Rh macrocycles of **7a** are either exactly eclipsed or exactly 45°-staggered. However, the exactly eclipsed isomer can be ruled out if we assume that the Rh−Rh bond length of **7** is close to that of $[(Pc)(py)Rh]_2$, i.e., 2.74 Å.[23] Such a short distance between the two (RPc)Rh macrocycles results in repulsion between the π-electrons of the two (RPc)Rh macrocycles and precludes the formation of the exactly eclipsed isomer. We, therefore, propose that **7a** and **7b** are a 45°-staggered isomer and an isomer that has a torsion angle deviating from 45°. With such a torsion angle, the two aromatic H's of each RPc ligand of **7b** are not equivalent and four resonances are expected for the aromatic H's. It appear that there are only two aromatic resonances (only one observed) for **7b**, and we assume that the chemical shifts of the two kinds of aromatic H's on each (RPc)Rh macrocycle of **7b** are too close to be resolved.

In contrast to **7**, which gives good evidence for rotational isomerism in Figure 3, no evidence for rotational isomerism was obtained for $[(RPc)Rh]_2$. No change in the NMR spectrum of $[(RPc)Rh]_2$ was observed in the temperature range of −75−110 °C.[24] On the basis of the facts that the less rigid hydride-bridged (RPcH)Rh(μ-H)Rh(RPc) forms rotational isomers at −35 °C and that $[(RPc)Rh]_2(PMe_3)$ forms rotational isomers that do not interconvert even at 105 °C, it is very unlikely that

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$[(RPc)Rh]_2$ rotates freely in the temperature range of −75 to 110 °C. We, therefore, propose that $[(RPc)Rh]_2$ is a 45°-staggered isomer with rotational freedom within an angle smaller than 90° and that coordination of one PMe_3 molecule creates a new barrier within this rotational coordinate, resulting in the formation of **7a** and **7b**.

Experimental Section

General. All the chemicals were reagent grade and were used without further purification. The preparation of $[(RPc)Rh]_2$ (**1**) and (RPcH)Rh(μ-H)Rh(RPc) (**5**) has been described previously.[13b] A Varian Unity 400 NMR spectrometer and a Bruker ESP300E ESR spectrometer were used for spectral measurements. Most of the NMR experiments were carried out in an NMR tube that was fitted with a J-Young valve for transferring volatiles under vacuum. Simulation of the ESR spectra was performed with the WIN-EPR SimFonia, version 1.0, of Bruker Instruments, Inc.

$(RPc)(PMe_3)_2Rh$. (RPcH)Rh(μ-H)Rh(RPc) (126 mg) in 10 mL of toluene was freeze-pumped, and excess PMe_3, obtained by thermal decomposition of 75 mg of $[Ag(PMe_3)I]_4$, was transferred under vacuum. The solution was then thawed. The solvent and the excess PMe_3 were removed by vacuum transfer, and the product residue was recrystallized from 3.0 mL of toluene at 5 °C. The crystals were collected by filtration, washed with cold isooctane, and dried in a vacuum to give 54 mg of the product. Anal. Found: C, 69.37; H, 8.93; N, 8.27; P, 4.56; Rh, 7.22. Calcd for $C_{78}H_{114}N_8P_2Rh$: C, 70.51; H, 8.65; N, 8.43; P, 4.66; Rh, 7.74.

$(RPc)(PMe_3)RhH$ from Reaction of (RPcH)Rh(μ-H)Rh(RPc) with PMe_3. A solution of 2.15 mg (0.91 μmol) of (RPcH)Rh(μ-H)Rh(RPc) in 0.50 mL of toluene-d_8 was prepared in an NMR tube with a J-Young valve under N_2. The solution was frozen with liquid N_2, and PMe_3, obtained by thermal decomposition of 2.0 mg (1.6 μmol) of $(AgI{\cdot}PMe_3)_4$, was vacuum-transferred. The solution was then put into the NMR probe at −10 °C. The ^1H NMR spectrum shows that $(RPc)(PMe_3)RhH$ (**6**) (91%) and $(RPc)(PMe_3)_2Rh$ (**4**) (9%), as well as H_2, were produced. The reaction was followed by recording the spectra at various temperatures as the solution was warmed to room temperature over a 2-h period.

Reductive Elimination of H_2 from $(RPc)(PMe_3)RhH$. A solution of (RPcH)Rh(μ-H)Rh(RPc) (0.85 μmol) in toluene-d_8 (0.50 mL) was prepared under vacuum, and trimethylphosphine from thermal decomposition of 0.50 μmol of $(AgI{\cdot}PMe_3)_4$ was transferred under vacuum. The solution was then thawed. Care was taken to keep the solution at low temperatures. The first spectrum, recorded at 0 °C, showed that the solution contained 84% of $(RPc)(PMe_3)RhH$ and 16% of $(RPc)(PMe_3)_2Rh$. After being allowed to stand overnight, the solution contained 55% of $(RPc)(PMe_3)_2Rh$ and 45% of $[(RPc)Rh]_2(PMe_3)$. Production of H_2 was also revealed by its resonance at δ 4.601 ppm.

$[(RPc)Rh]_2(PMe_3)$ (7) from Reaction of $[(RPc)Rh]_2$ with PMe_3. A solution of 30.0 mg (12.8 μmol) of $[(RPc)Rh]_2$ and PMe_3 from 3.75 mg (3.02 μmol) of $(AgI{\cdot}PMe_3)_4$ in 2.50 mL of C_6D_6 was prepared in a 10-mm NMR tube for recording the $^{31}P\{^1H\}$ spectrum of **7**, with external H_3PO_4 at δ 0.00 ppm as the reference. A sample of the same composition, but at lower concentrations, was prepared in a 5-mm NMR tube for recording its ^1H NMR spectrum. These spectra are shown in Figure 3.

Reaction of $[(RPc)Rh]_2(PMe_3)$ (7) with PMe_3. A solution containing 0.74 μmol of $[(RPc)Rh]_2$ and 1.93 μmol of PMe_3 in 0.50 mL of C_6D_6 under vacuum was allowed to react at the ambient temperature. Figure 4a, recorded 4 days later, shows that the reaction was complete and the solution contained $[(RPc)Rh]_2(PMe_3)$ and $(RPc)(PMe_3)_2Rh$. PMe_3 from 0.20 mg (0.64 μmol) of $(AgI{\cdot}PMe_3)_4$ was added, and the spectrum in Figure 4b recorded.

Reaction of $[(RPc)Rh]_2$ with $(RPc)(PMe_3)_2Rh$. The solution characterized in Figure 4b was heated at 50 °C for 6 h for reaction 8 to go to completion, as indicated by the ^1H NMR spectra. The solution was then frozen in a liquid N_2 bath, and 0.42 mg (0.18 μmol) of $[(RPc)Rh]_2$ was added. The frozen sample was put on the vacuum line and was subjected to three freeze−pump−thaw processes. Figure 4c was recorded after the solution was thawed.

In a separate experiment, a solution of 1.8 mg (0.76 μmol) of $[(RPc)Rh]_2$ and 2.2 mg (1.66 μmol) of $(RPc)(PMe_3)_2Rh$ in 0.60 mL of C_6D_6 was prepared under vacuum in an NMR tube fitted with a J-Young valve. Immediate appearance of a spectrum similar to that shown in Figure 4c was observed. The solution was then heated at 80 °C for 2 h for the reaction to proceed to completion. The product solution contained 52% of $(RPc)(PMe_3)_2Rh$ and 48% of $[(RPc)Rh]_2(PMe_3)$.

Reaction of (RPcH)Rh(μ-H)Rh(RPc) with Pyridine. (RPcH)Rh(μ-H)Rh(RPc) (1.0 mg) in an NMR tube with a J-Young valve was pumped, and 1.0 μL of pyridine in 0.50 mL of toluene-d_8 was then transferred under vacuum. Hydrogen at 1 atm was then introduced, and the solution was heated in an oil bath at 110 °C to convert the small amount of $[(RPc)Rh]_2$ in the sample to (RPcH)Rh(μ-H)Rh(RPc). The ^1H NMR spectra of the sample at low temperatures were recorded.

Preparation of (RPc)Co. A solution of 300 mg of $RPcH_2$ and 75 mg of anhydrous $CoCl_2$ in 10 mL of 1-pentanol was refluxed for 80 min. The solvent was removed. The dark-blue residue was washed with water and methanol and dried under vacuum. The crude product (300 mg) in 8.0 mL of toluene and 20 mL of 2,2,4-trimethylpentane was heated to boiling, and more 2,2,4-trimethylpentane (∼10 mL) was added until the solution turned turbid. The solution was then allowed to cool in the oil bath. The dark-blue needle crystals were collected on a fritted glass filter, washed with 2,2,4-trimethylpentane, and dried. Yield: 180 mg. Anal. Found: C, 75.84; H, 8.63; N, 9.82; Co, 6.07. Calcd for $C_{72}H_{96}N_8Co$: C, 76.36; H, 8.54; N, 9.89; Co, 5.20.

Reaction of (RPc)Co with PMe_3. A solution of 0.75 mg of (RPc)Co in 0.60 mL of toluene-d_8 was prepared in an NMR tube fitted with a J-Young valve, and the ^1H NMR spectrum was recorded. Trimethylphosphine from thermal decomposition of 1.95 mg of $(AgI{\cdot}PMe_3)_4$ was then added, and the reversible reaction between (RPc)Co and PMe_3 was studied by recording the NMR spectra at low temperatures (Figure 5).

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Supporting Information Available: The ^1H NMR spectrum of $(RPc)(PMe_3)_2Rh$ (**4**) and the recorded and the calculated ESR spectra of $(RPc)(PMe_3)_2Co$ (**12**) and (RPc)Co (**13**) (1 page). Ordering information is given on any current masthead page.

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