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Reversible Hydrocarbon Activation by Rhodium Phthalocyanine Dimer $[(R_8Pc)Rh]_2$ (R_8Pc^{2-} = Dianion of 1,4,8,11,15,18,22,25-Octa-*n*-pentylphthalocyanine)[†]

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We have synthesized four rhodium−phthalocyanine complexes: $(R_8Pc)(C_6H_5CN)ClRh$, $[(R_8Pc)(MeOH)_2Rh]Cl$, $[(R_8Pc)Rh]_2$ (**1**), and $(R_8PcH)RhRh(R_8Pc)H$ (**2**). In this notation R_8Pc^{2-} is the dianion of 1,4,8,11,15,18,22,25-octa-*n*-pentylphthalocyanine. The Rh−Rh bonded dimer **1** reacts with H_2 to give **2**, and it activates the C−H bonds of toluene and the R_8Pc^{2-} ligand at temperatures of 150 °C. It also catalyzes the H−D exchange between the R_8Pc^{2-} ligand and D_2O and between the ligand and toluene-d_8. Although all of the H's of the R_8Pc^{2-} ligand are activated, only the benzylic H's of toluene are activated. A radical mechanism, initiated by homolysis of **1**, is proposed for these reactions.

Introduction

Among the various approaches for the activation of hydrocarbons,[1−5] direct activation of carbon−hydrogen bonds by low-valent transition metal complexes was greatly promoted by the reports of Bergman[6] and Graham[7] that the C−H bonds of unactivated hydrocarbons oxidatively add to coordinately unsaturated 16-electron Ir(I) complexes under very mild conditions. A considerable volume of literature reporting such oxidative addition reactions has appeared in the past decade. Most of these reactions are stoichiometric, because the active metal centers are not easily regenerated. However, some progress has been made in the catalytic functionalization of hydrocarbons by low-valent metal complexes.[8−10] There are also reports of photocatalytic functionalization of hydrocarbons. In these systems, the active metal centers are regenerated by photolysis.[10−12]

We have been interested in metallophthalocyanine complexes for their applications in catalysis at high temperatures. Metallophthalocyanines may be expected to catalyze reactions that are known to be catalyzed by structurally related metalloporphyrins and may exhibit novel catalytic reactions at temperatures at which metalloporphyrins and most other homogeneous catalysts are not stable. We report here catalytic C−H bond activation by a Rh−Rh bonded Rh−phthalocyanine complex, $[(R_8Pc)Rh]_2$, at the temperatures of 170−180 °C, as shown by the production of hydrido−Rh and alkyl−Rh complexes and by the catalytic H−D exchange reactions between the R_8Pc^{2-} ligand and D_2O, as well as between the ligand and toluene-d_8. The results may be explained in terms of the radical chemistry of Rh(II)−porphyrins reported by Wayland[13] and by Halpern;[14] however, additional reactions have to be added to explain the catalytic H−D exchange reactions, which have not been reported for the Rh−porphyrin systems.

Results

Hydrogenation of $[(R_8Pc)Rh]_2$ (1). **1** reacts reversibly with H_2 in C_6D_6 to give $(R_8PcH)RhRh(R_8Pc)H$ (**2**). At 150 °C, a 95% conversion was achieved in 1 h and no further conversion was observed for additional 15 h. **2** has also been prepared from the reaction of H_2 with $[(R_8Pc)(MeOH)_2Rh]Cl$, and may be envisaged as a Rh−Rh bonded hydrido complex, formed by the heterolytic splitting of H_2 by **1**, with the H^- ion bonded to a Rh and the H^+ ion bonded to one of the four pyrrolic nitrogens coordinated to the other Rh (Figure 1). The characterization of **2** has been described in an earlier communication.[15]

Thermolysis of $[(R_8Pc)Rh]_2$. **2** is also produced when solutions of $[(R_8Pc)Rh]_2$ in C_6D_6 are heated to 150 °C under anaerobic conditions, as revealed by the ^1H NMR spectrum of the product solution. The reaction is reversible and the conversion increases from 30% to 60% as the temperature is increased from 150 to 207 °C.

The formation of **2** indicates that the C−H bonds of the R_8Pc^{2-} ligand, rather than the C−D bonds of C_6D_6 are activated; activation of the C−D bonds would have

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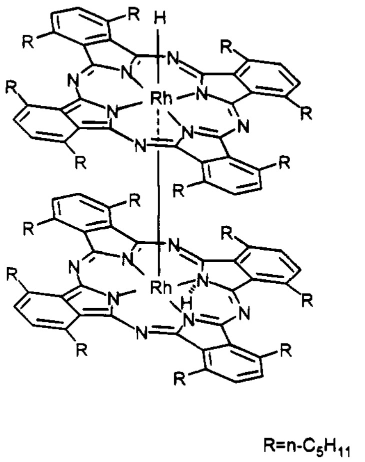

Figure 1. Proposed structure of $(R_8PcH)RhRh(R_8Pc)H$ (**2**).

resulted in the formation of $(R_8PcD)RhRh(R_8Pc)D$, or **2**-d_2. No high-field resonance other than that of the hydride at δ −38.1 ppm[16] was observed, indicating the absence of any Rh−alkyl complex as these resonances are known to be shifted upfield of TMS by the dimagnetic ring current.[17,18] After the solution was exposed to air, its ^1H NMR spectrum was not significantly different from the spectrum obtained before thermolysis, except for an increase in the H_2O resonance. Therefore, thermolysis of **1** in C_6D_6 results in the partial conversion of **1** to **2**, and when the resulting solution is exposed to air, **2** is converted back to **1**. These results may be described by eqs 1 and 2, where **3** is a derivative of **1**

$$\underset{\mathbf{1}}{2[(R_8Pc)Rh]_2} \rightleftharpoons \underset{\mathbf{2}}{(R_8PcH)RhRh(R_8Pc)H} + \underset{\mathbf{3}}{(R_8Pc)RhRh(R_7PcCH{=}CHC_3H_7)} \quad (1)$$

$$\mathbf{2} + {}^1/_2O_2 \rightarrow \mathbf{1} + H_2O \quad (2)$$

with two hydrogen atoms removed from a pentyl group to form a pentenyl group, presumably an α,β-unsaturated pentenyl group. Complex **3** is introduced to account for the formation of **2**. Equation 2 has been independently confirmed by the reaction of **2** with O_2 in dry C_6D_6;[19] the corresponding reaction for a hydrido−Rh(porphyrin) complex has also been reported.[20]

For simplicity, we have introduced **3** to explain the formation of **2** in eq 1. However, it is most likely that the H_γ's and H_δ's also contribute to the formation of **2**, since the H_α's and the H_β's are only a little more reactive than the H_γ's and the H_δ's, as shown by the H−D exchange reactions between the R_8Pc^{2-} ligand and D_2O (described in the following section). Therefore, the dehydrogenated product is most likely a mixture of the cis- and trans-isomer of **3** and the four possible isomers of the product that contains a α,β- and γ,δ-unsaturated diolefin side chain. The sum of the resonances of these olefinic H's should have twice the intensity of the N−H (or the Rh−H) resonance of **2** and is expected to be shifted into the aromatic region by the ring current. We have not been able to identify these olefinic H's, and we believe that the complexity of the product mixture and the couplings of these olefinic H's to their neighboring H's make it difficult to observe them.

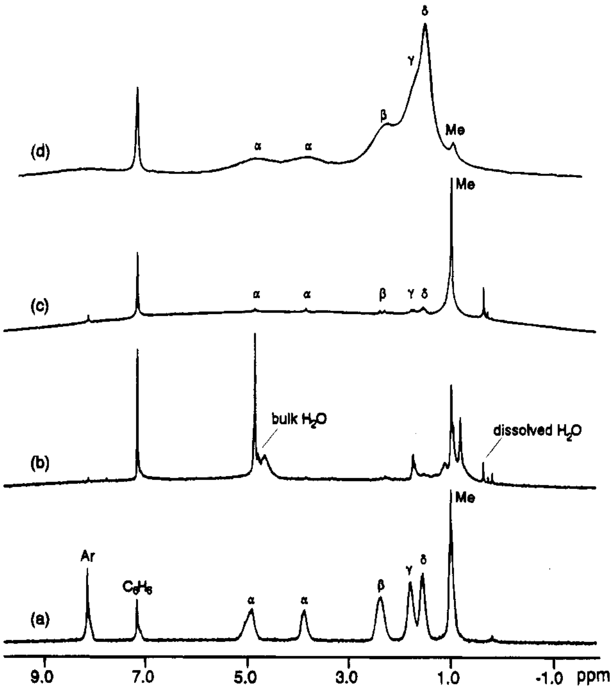

Figure 2. ^1H and ^2H NMR spectral changes accompanying the H−D exchange between $[(R_8Pc)Rh]_2$ and D_2O: (a) ^1H for solution of $[(R_8Pc)Rh]_2$ (1.4 μmol) and D_2O (1640 μmol) in 0.50 mL C_6D_6; (b) ^1H for solution after reaction at 180 °C for 260 h; (c) ^1H for air-oxidized product residue in C_6D_6; (d) ^2H for product residue of part c in C_6H_6. In parts a and b, there is a separate aqueous phase.

As both H_2 and the C−H bonds of the pentyl group of the R_8Pc^{2-} ligand are activated at 150 °C, it seems likely that both reactions are initiated by homolysis of **1** to generate $(R_8Pc)Rh^\bullet$ radical. We have, therefore, looked for evidence for the homolysis of **1** in C_6D_6 by variable temperature ^1H NMR spectroscopy. No line-broadening was observed at 140 °C. At higher temperatures, refluxing of the solvent and formation of **2** was observed. Use of higher boiling solvent has not been attempted because formation of **2**, which would exchange with $(R_8Pc)Rh^\bullet$, complicates the analysis of the data.

Catalytic H−D Exchange between $[(R_8Pc)Rh]_2$ and D_2O. The thermal activation of the C−H bonds of the R_8Pc^{2-} ligand depicted in eq 1 suggested that H−D exchange between $[(R_8Pc)Rh]_2$ and D_2O might also occur. This was indeed observed. A solution of 1.4 μmol of $[(R_8Pc)Rh]_2$ and 1640 μmol of D_2O in 0.50 mL of C_6D_6 was sealed in an NMR tube under vacuum and heated at 180 °C for 260 h. The ^1H NMR spectra of the solution before and after the reaction are shown in Figure 2, parts a and b. The fine structures of the resonances of the pentyl H's of **1**, as described in the Experimental Section, are lost in Figure 2a because of magnetic field inhomogeneity brought about by the phase separation, which was induced by the large excess of D_2O added. In Figure 2b, the resonances of the R_8Pc^{2-} ligand have been greatly attenuated, while a strong, broad reso-

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[16] The ^1H NMR spectra of **2** is concentration and temperature dependent. See ref 15 for variable temperature NMR study of **2**.

[17] Chen, M. J.; Rathke, J. W. *Organometallics* **1993**, 4673.

[18] Del Rossi, K. J.; Wayland, B. B. *J. Am. Chem. Soc.* **1985**, *107*, 7941.

[19] Formation of H_2O_2 as an intermediate is a possibility. We have no data that would allow us to conclude on this possibility.

[20] Setsune, J. I.; Yoshida, Z. I.; Ogoshi, H. *J. Chem. Soc., Perkin Trans.* **1982**, *1*, 893.

Table 1. H−D Exchange Reactions between $[(R_8Pc)Rh]_2$ and D_2O[a]

expt no.	Rh, μmol	D_2O, μmol	temp, °C	time, h	percent deuteration[b]					
					H_{Ar}	H_α	H_β	H_γ	H_δ	H_{Me}
1	1.4	1640	180	260	96	96	96	95	91	2[c]
2	1.3	550	170	7.0	30	78	56	25	25	0

[a] In 0.5 mL of benzene-d_6. [b] Calculated from residual ^{1}H resonances except for H_{Me}. [c] Estimated from Figure 2d.

nance for H_2O appears at 4.2−5.2 ppm.[21] After air-oxidation to regenerate **1**, the product residue was redissolved in C_6D_6 to give the spectrum in Figure 2c, which indicates that all the H's of the ligand, except that of the methyl, have been nearly completely deuterated. Integration of these various H's, which is summarized in Table 1 (experiment 1), indicates that the H_α's, the H_β's, the H_γ's, and the H_{Ar}'s were deuterated to the same extent, and the H_δ's somewhat less. The methyl H's were only slightly deuterated.

The ^{2}H NMR spectrum of the oxidized product in C_6H_6 is shown in Figure 2d. Consistent with the ^{1}H NMR spectrum in Figure 2c, Figure 2d shows all the broad, strong resonances expected for the perdeuterated **1**, except that of the methyl group, which is very weak. It is interesting to note that in Figure 2c, the ^{1}H NMR resonances for the two diastereotopic H's of each of the α-, the β-, and the γ-carbon appear as two singlets of equal intensity, broadened at the base. The extensive deuteration apparently has removed, almost completely, the couplings between geminal H's and between vicinal H's. As a result, the two diastereotopic H's on each of the α-, the β-, and the γ-carbon appear as two singlets of equal intensity. The resonances for the two H_δ's are not resolved because of their couplings to the methyl H's.

In another experiment, a solution of 1.3 μmol of **1** and 550 μmol of D_2O in 0.50 mL of C_6D_6 was sealed under vacuum and heated at 170 °C for 7 h. The deuterium incorporation into various H's of **1** is also summarized in Table 1. The result in experiment 1 (Table 1), which does not show any difference in the degree of deuteration of the H_α's and the H_β's because of their exhaustive deuteration, indicates that the H_γ's are slightly more deuterated than the H_δ's. On the other hand, the result in experiment 2, which shows no difference in the degree of deuteration of the H_γ's and the H_δ's because of their low conversion, clearly indicates that the H_α's are more reactive than the H_β's. Therefore, the rates of H−D exchange reactions for the various H's fall in the following order: $H_\alpha > H_\beta > H_{Ar} > H_\gamma > H_\delta \gg H_{Me}$.

Activation of Toluene by $[(R_8Pc)Rh]_2$. A solution of 1.19 μmol of **1** in 0.50 mL of toluene was heated at 180 °C for 66 h, then the solution was air-oxidized to give a product mixture of $(R_8Pc)RhCH_2C_6H_5$, **4** (60%), and **1** (40%, based on Rh). Analysis of the gas phase by gas chromatography indicated production of 0.11 μmol of H_2.

We also carried out parallel study of the reaction of **1** with neat toluene-d_8 at 180 °C. In this case, we followed the progress of the reaction by monitoring the ^{1}H NMR spectra of the solution without any workup. The results (Figure 3) show that **2** (i.e., sum of **2**-d_0, **2**-d_1, and **2**-d_2) was produced faster than **4**-d_7 at the beginning, but ultimately the solution reached a constant composition with a higher concentration of **4**-d_7 than **2**. After 5 h, the solution has the composition of 8% of **1**, 37% of **2**, and 55% of **4**-d_7 (based on Rh), and the composition did not change thereafter. Apparently, equilibria involving **1**, **2**, and **4**-d_7 were established. Although the partition of Rh among **1**, **2**, and **4**-d_7 remained unchanged as the reaction continued, the ^{1}H NMR spectra of the solution showed that the methyl resonance of toluene at δ 2.09 ppm continued to increase at the expense of the resonances of the R_8Pc^{2-} ligand. This result clearly indicates that H−D exchange occurred between the R_8Pc^{2-} ligand and toluene-d_8. The enrichment of the methyl H's of the solvent corresponds to 58 turnovers in 66 h. No enrichment of the aromatic H's of the solvent was observed. However, as much as 40% of the aromatic H's of the R_8Pc^{2-} ligand were deuterated. As expected, a 45:55 product mixture of **1** and **4**-d_7 was obtained after the solution was exposed to air.

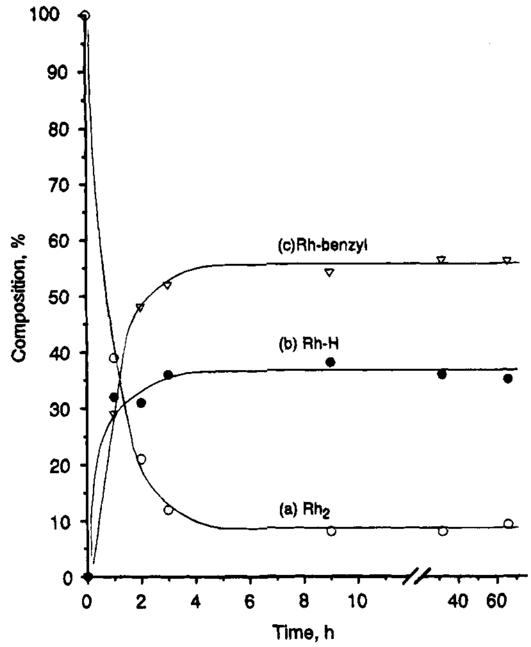

Figure 3. Rate plots for the reaction of $[(R_8Pc)Rh]_2$ with toluene-d_8 at 180 °C: Initial solution, 1.19 μmol of $[(R_8Pc)Rh]_2$ in 0.50 mL of toluene-d_8; curve a, $[(R_8Pc)Rh]_2$ (○); curve b, $(R_8Pc)Rh$−hydride (**2** + **2**-d_1 + **2**-d_2) (●); curve c, $(R_8Pc)Rh$−(benzyl-d_7) (▽).

These results can be explained in terms of eqs 1, 3, and 4. Apparently, both eqs 1 and 3 contribute to the

$$\underset{\mathbf{1}}{[(R_8Pc)Rh]_2} + C_6H_5CH_3 \overset{K_3}{\rightleftharpoons} \underset{\mathbf{4}}{(R_8Pc)RhCH_2C_6H_5} + {}^1/_2\,\underset{\mathbf{2}}{(R_8PcH)RhRh(R_8Pc)H} \tag{3}$$

$$\mathbf{2} \overset{K_4}{\rightleftharpoons} \mathbf{1} + H_2 \tag{4}$$

formation of **2** at the beginning of the reaction, but eq 1 is suppressed by eq 3 after further reaction. This would explain why **2** is initially formed at a higher rate than **4**. The net effect of eq 1 is that it, in conjunction with eq 3, provides a path for the catalytic H−D exchange between the R_8Pc^{2-} ligand and toluene-d_8 in cases where toluene-d_8 was the solvent. Reaction 3 alone should yield a 1:1 product mixture of **2** and **4**

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(21) The complicated resonance for H_2O has been reproduced with a two-phase $H_2O-C_6D_6$ solution.

(based on Rh). However, since the liberation of H_2 from **2** in eq 4 regenerates **1**, eqs 3 and 4 provide a path for **4** to accumulate at the expense of **2**. Liberation of H_2 from hydrido(octaethylporphyrinato)rhodium(III) complex has also been reported.[18]

As mentioned earlier, H_2 was produced in the reaction of **1** with toluene. The amount of H_2 measured accounts for 30% of the expected yield, based on the yield of **4** and **2**.[22]

Activation of Ethylbenzene by $[(R_8Pc)Rh]_2$. Ethylbenzene also reacts with **1** to give $(R_8Pc)RhCH(Ph)CH_3$, **5**, with a 40% yield after 17 h at 175 °C. At longer reaction times, additional high-field resonances were observed, at the expense of **5**. These new high-field resonances have not been assigned. It is assumed that the isomerization of **5** to the sterically less demanding $(R_8Pc)RhCH_2CH_2Ph$, together with reactions to other products, has occurred.

Discussion

The results of the H−D exchange experiments shown in Figure 2 and in Table 1 indicate that both the aliphatic and the aromatic H's of the R_8Pc^{2-} ligand are activated by **1**. The high turnovers observed in these H−D exchange experiments further indicate that the reactions are catalytic. The reactivities of the various H's of the R_8Pc^{2-} ligand fall in the following order: $H_\alpha > H_\beta > H_{Ar} > H_\gamma > H_\delta \gg H_{me}$. The activation of the pentyl H's of the R_8Pc^{2-} ligand may be rationalized in terms of the reactions shown in Scheme 1.

Scheme 1

$$\underset{\mathbf{1}}{[(R_8Pc)Rh]_2} \overset{K_5}{\rightleftharpoons} \underset{\mathbf{6}}{2(R_8Pc)Rh^\bullet} \qquad (5)$$

$$\mathbf{6} + \mathbf{1} \overset{K_6}{\rightleftharpoons} \underset{\mathbf{7}}{(R_8Pc)RhRh(R_7PcC^\bullet HC_4H_9)} + \underset{\mathbf{8}}{(R_8Pc)RhH} \qquad (6)$$

$$\mathbf{8} \overset{K_7}{\rightleftharpoons} {}^1/_2\underset{\mathbf{2}}{(R_8PcH)RhRh(R_8Pc)H} \qquad (7)$$

$$\mathbf{7} + \mathbf{6} \overset{K_8}{\rightleftharpoons} \underset{\mathbf{9}}{(R_8Pc)RhRh(R_7PcCH{=}CHC_3H_7)} + \mathbf{8} \qquad (8)$$

$$\mathbf{9} + \mathbf{6} \overset{K_9}{\rightleftharpoons} \underset{\mathbf{10}}{(R_8Pc)RhRh(R_7PcCH{=}CHC^\bullet HC_2H_5)} + \mathbf{8} \qquad (9)$$

$$\mathbf{10} + \mathbf{6} \overset{K_{10}}{\rightleftharpoons} \underset{\mathbf{11}}{(R_8Pc)RhRh(R_7PcCH{=}CHCH{=}CHCH_3)} + \mathbf{8} \qquad (10)$$

$$\mathbf{2} + D_2O \overset{K_{11}}{\rightleftharpoons} \mathbf{2}\text{-}d_2 + H_2O \qquad (11)$$

In this scheme, the reactions are initiated by the homolysis of the Rh−Rh bonded dimer **1** to generate the $(R_8Pc)Rh^\bullet$ radical, **6** (eq 5). Deuterium is introduced into the system by eq 11. To account for the catalytic H−D exchange, all the reactions in Scheme 1 are made reversible. Therefore, an H−D exchange occurs whenever $(R_8Pc)RhD$, or **8**-d_1, is substituted for $(R_8Pc)RhH$, **8**, in eqs 6 and 8−10. The difference in the degree of deuteration among different H's of the pentyl group reflects the relative rates of activation of these C−H bonds.

We have shown in an earlier study that the dimeric $(R_8PcH)RhRh(R_8Pc)H$, **2**,[15] which exists in the solid state and in benzene solutions, dissolves in tetrahydrofuran to give the monomeric **8**. Therefore, there is a low barrier for this interconversion, and it can be assumed that **2** and **8** are in equilibrium (eq 7) under the reaction conditions. Although **2** is thermodynamically more stable in benzene solutions, we assume that **8** is the active Rh−hydride complex in eqs 6 and 8−10. However, in eq 11, the reaction most likely proceeds through the reaction of **2** and D_2O, presumably through the H−D exchange between the N−H proton of **2** and D_2O.

The propagation of the deuterium incorporation along the pentyl chain is proposed to proceed by eqs 6 and 8−10. Nonconcerted abstractions of two hydrogen atoms from **1** by two radicals of **6** are depicted in eqs 6 and 8 to account for the activation of the H_α's and the H_β's. Both the reverse of eq 6 and the forward of eq 8 are thermodynamically favorable[23] and their reaction rates should be nearly diffusion-controlled. The fact that the H_α's are only a little more reactive than the H_β's suggests that most of **7**, generated in eq 6, proceeds to form **9**. For the same reasoning, most of **10**, generated in eq 9, proceeds to form **11**. The nonconcerted pathway is proposed because the alternative concerted termolecular reaction of **1** with two radicals of **6** requires that the α-H's and the β-H's have the same reactivity, likewise for the γ-H's and the δ-H's. This is not supported by the experimental results.

The reactions in Scheme 1 rationalize the C−H bond activations of the pentyl chains. However, these reactions do not provide a path for deuterium incorporation into the aromatic H's, which exchange with D_2O at a rate comparable to the rates for H_γ's and H_δ's. A very likely mechanism is the reversible H-atom transfer between **8** and **1** to generate the dienyl radical intermediate **12**, as shown in eq 12. On the basis of the estimated enthalpy of reaction of 36 kcal/mol for eq 13,[24] eq 12 could be accessible at 180 °C, since it should have a lower enthalpy of reaction than eq 13 because of the more extensive π-system in **1**. Such reversible H-atom transfer reactions have been proposed to account for the catalytic hydrogenation of polycyclic aromatic hydrocarbons by $(CO)_4CoH$.[25] An alternative mechanism for this H−D exchange reaction is the reversible H^+ ion transfers between **8** and **1**.[26]

It should be noted that the aromatic H's of **1** are activated with a turnover frequency of 0.3 h^{-1} at 180

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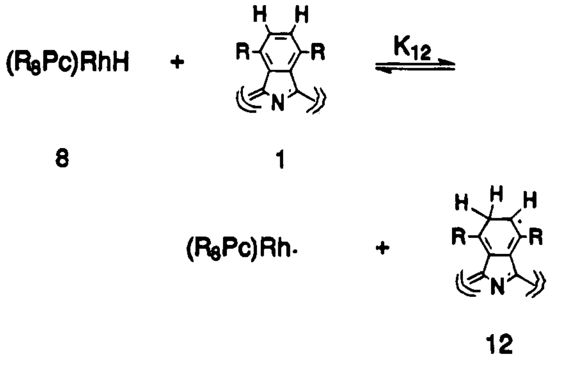
[22] Based on the assumption that the product solution before air oxidation contains 10% of **1** and 30% of **2**.

[23] Based on the bond dissociation energy of 60 kcal/mol for Rh−H for the corresponding Rh(OEP) complexes reported by Wayland, B. B.; Coffin, V. L.; Farnos, M. D. *J. Am. Chem. Soc.* **1988**, *27*, 2745. The ΔH's for the reverse of eq 6 and the forward of eq 8 are −25 and −15 kcal/mol, respectively, if it is assumed that the bond dissociation energy for the C_α−H bond of **1** is 85 kcal/mol (an upper limit) and that for the C_β-H bond of **7** is 45 kcal/mol.

[24] Based on the value of $\Delta H = -24$ kcal for the addition of $H^\bullet$ to benzene (Benson, S. W. *J. Chem. Ed.* **1967**, *42*, 502.) and on an estimated bond energy of 60 kcal/mol for the Rh-H bond in **8**.

[25] Feder, H. M.; Halpern, J. *J. Am. Chem. Soc.* **1975**, *97*, 7186.

[26] We thank one of the reviewers for suggesting this alternative mechanism.



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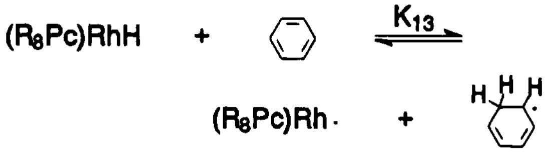

(13)

°C, while those of toluene are not activated. Since the concentrations of Rh−Pc used are about 0.1 mM, the aromatic H's of **1** are at least 5 orders of magnitude more reactive than those of toluene.

We have shown that the benzylic H's of toluene and the α-H's of the R_8Pc^{2-} ligand are activated at comparable rates in a solution of **1** in toluene. The reaction of toluene with **1** gives Rh−benzyl and Rh−hydride complexes, as depicted in eq 3. In contrast, the activation of the C−H bonds of the pentyl group by **1** produces no organo−Rh(R_8Pc) species. The absence of any organo−Rh species derived from the pentyl group undoubtedly arises from the large stearic constraint for their formation.

It seems possible that the activation of toluene proceeds by a termolecular reaction between two radicals of **6** and toluene, with a transition state similar to the linear transition state proposed by Wayland for the activation of methane by porphyrinato−Rh(II) radicals.[13] Alternatively, the reaction may proceed by H-atom transfer from toluene to radical **6** to generate **8** and the benzyl radical (eq 14), which displaces radical **6** from **1** to form **4**, as depicted by eq 15.

$$(R_8Pc)Rh^{\bullet} + C_6H_5CH_3 \overset{K_{14}}{\rightleftharpoons} (R_8Pc)RhH + C_6H_5CH_2^{\bullet} \tag{14}$$

$$C_6H_5CH_2^{\bullet} + [(R_8Pc)Rh]_2 \overset{K_{15}}{\rightleftharpoons} (R_8Pc)RhCH_2C_6H_5 + (R_8Pc)Rh^{\bullet} \tag{15}$$

Experimental Section

General Methods. All the chemicals were reagent grade and were used without further purification. 1,4,8,11,15,18,22,25-Octapentylphthalocyanine, R_8PcH_2, was synthesized according to the method of Cook.[27] A General Electric GN300/89 NMR spectrometer, a Varian Unity 400 NMR spectrometer, and a Perkin-Elmer 660 FT IR spectrometer were used for spectral measurements. A Hewlett-Packard 5890 Series II gas chromatograph was used for the GC analysis.

(R_8Pc)(PhCN)ClRh. A solution of 1.14 g (1.06 mmol) of R_8PcH_2 and 1.64 g (4.21 mmol) of $[Rh(CO)_2Cl]_2$ in 30 mL of benzonitrile was heated at 145 °C under N_2 for 3.5 h. The temperature was then lowered to 60 °C and benzonitrile was removed in vacuo until the mixture became a thick paste. Methanol (30 mL) was then added to digest the residue. The gummy product gradually solidified. The precipitate was collected, washed with MeOH, and dried to give 1.37 g of the product at 95% purity. The crude product was dissolved in $CHCl_3$ and the solution was filtered to remove the undissolved solid. The solvent was removed and the residue recrystallized from isooctane. Anal. Found: C, 69.23; H, 7.33; N, 9.48; Rh, 8.97; Cl, 3.38. Calcd for $C_{79}H_{101}N_9RhCl$: C, 72.15; H, 7.74; N, 9.58; Rh, 7.83; Cl, 2.70. ^1H NMR ($CDCl_3$, ppm) for PhCN: H_o, δ 5.557, dd, $J_{H_m\text{-}H}$ 8.4 Hz, $J_{H_p\text{-}H}$ 1.2 Hz, 2H; H_m, δ 6.587, dd, $J_{H_o\text{-}H}$, 8.4 Hz, $J_{H_p\text{-}H}$ 7.8 Hz, 2H; H_p, δ 6.969, tt, 1H. IR: ν_{CN} 2010 cm^{-1} for PhCN. The high carbon analysis is attributed to residual C_6H_6CN in the sample. We have some difficulty in removing C_6H_5CN completely from the sample. Attempts to dry the sample by pumping at 60 °C led to decomposition of the compound. The progress of the reaction was followed by ^1H NMR spectroscopy. Two other PhCN−(R_8Pc)Rh intermediate complexes formed early in the reaction and then disappeared. These products were not identified.

[(R_8Pc)(MeOH)$_2$Rh]Cl. To a solution of 833 mg of (R_8Pc)(PhCN)ClRh in 12 mL of $CHCl_3$ was slowly added 60 mL of MeOH. Crystals were deposited with cooling to 5 °C overnight and with additional cooling to −15 °C for 5 h. The crystals were collected, washed with cold MeOH and dried to give a yield of 700 mg. Anal. Found: C, 68.83; H, 8.23; N, 8.56; Rh, 8.20; O, 2.79; Cl, 3.12. Calcd for $C_{74}H_{104}N_8RhO_2Cl$: C, 69.67; H, 8.22; N, 8.78; Rh, 8.04; O, 2.51; Cl, 2.78. The compound reacts in benzene solution to produce (R_8Pc)(MeOH)ClRh in a few minutes. ^1H NMR for (R_8Pc)(MeOH)ClRh (C_6H_6, ppm): $H_{\textit{Me}OH}$, δ −2.113, d, $J_{H\text{-}H}$ 4.5 Hz, 3H; $H_{MeO\textit{H}}$, δ −6.518, q, 1H. The corresponding resonances for (R_8Pc)(MeOH)$_2$Rh$^+$ appear at δ −2.2 and −6.6 ppm, but quickly disappear as the compound decomposes.

[(R_8Pc)Rh]$_2$ (1). A sample of 220 mg of (R_8PcH)RhRh(R_8Pc)H, **2**, was dissolved in 15 mL of benzene. Oxidation of **2** by the dissolved O_2 occurred immediately, as shown by the dark blue color of the solution. The solution was filtered and the filtrate was rotary-evaporated. The fine, dark bluish-purple crystals were washed with benzene and dried in vacuum at room temperature to give 210 mg of **1**. The product was further purified by chromatography through a silica gel column with toluene/cyclohexane (1:1) as eluent. Anal. Found: C, 72.87; H, 8.17; N, 9.27; Rh, 8.74. Calcd for $C_{144}H_{192}N_{16}Rh_2$: C, 73.51; H, 8.23; N, 9.52; Rh, 8.75. ^1H NMR (C_6D_6, ppm): CH_3, δ 1.017, t, J_{H-H} 7.2 Hz; H_δ, δ 1.575, m; H_γ, δ 1.814, m; H_β, δ 2.407, m; $H_{\alpha1}$, δ 3.893, dt, $J_{H_{\alpha2}\text{-}H}$ 16.8 Hz, $J_{H_\beta\text{-}H}$ 7.8 Hz; $H_{\alpha2}$, δ 4.924, dt, $J_{H_\beta\text{-}H}$ 7.8 Hz; H_{ar}, δ 8.119, s.

(R_8PcH)RhRh(R_8Pc)H (2). A solution of 580 mg of [(R_8Pc)(MeOH)$_2$Rh]Cl in 40 mL of 1-pentanol was heated to 110 °C under a slow stream of H_2. Dark purplish fine-needle crystals were deposited during the course of 1 h. After the solution was cooled, the crystals were collected, washed with deaerated 1-pentanol and methanol, and dried at room temperature, for a yield of 520 mg. Anal. Found (sample 1): C, 72.89; H, 8.34; N, 9.42; Rh, 6.86. Found (sample 2): C, 73.34; H, 8.18; N, 9.28; Rh, 9.74. Calcd for $C_{144}H_{194}N_{16}Rh_2$: C, 73.34; H, 8.30; N, 9.52; Rh, 8.74. The spectral data are available in ref 15.

Reaction of 1 with H_2. A solution of 5.0 mg **1** in 0.50 mL C_6D_6 in an medium-walled NMR tube was sealed with 600 mmHg of H_2. The tube was put in an oven at 150 °C and the reaction was monitored by its ^1H NMR spectra. The reaction is slow at 120 °C. A parallel reaction with D_2 has also been carried out. In this case, the formation of HD and H_2 was observed. The later experiment was carried out to show that H_2 does react with **1** to give **2**. In the course of this study, we found that trace of impurity (presumably colloidal Rh) very effectively catalyzes the hydrogenation of benzene. This

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[27] Cook, M. J.; Daniel, M. F.; Harrison, K. J.; Mckeon, N. B.; Thomson, A. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1086.

impurity, which is a potential catalyst for the hydrogenation of **1**, was removed by chromatography through a silica gel column.

Reaction of 2 with O_2. A sample of 4.0 mg (1.7 μmol) of **2** was loaded into an NMR tube fitted with a PTFE valve (Aldrich) and 0.50 mL of C_6D_6, which has been dried with $LiAlH_4$, was vacuum distilled. The ^{1}H NMR of the solution was recorded, and O_2 at 150 mmHg was admitted to convert **2** to **1**. The ^{1}H NMR of the solution was again recorded. Using the aromatic resonances of the R_8Pc^{2-} ligand as the reference, the H_2O contents in these two samples are calculated to be 0.2 and 2.3 μmol, respectively. Subsequent exposure of the solution to 1 atm of O_2 did not increase the concentration of H_2O. Therefore, H_2O was produced from the reaction of **2** with O_2 rather than introduced from moist O_2.

H-D Exchange between $[(R_8Pc)Rh]_2$ and D_2O in Benzene-d_6. A solution of $[(R_8Pc)Rh]_2$ (1.43 μmol) and D_2O (1640 μmol) in C_6D_6 (0.50 mL) in a medium-walled NMR tube was sealed under vacuum after two freeze–pump–thaw cycles. The solution was heated in a furnace at 180 °C for 260 h. The ^{1}H NMR spectrum was recorded. After exposure to air, the solvent was removed, the residue redissolved in C_6D_6, and the spectrum recorded. The solvent was again removed, the residue dissolved in C_6H_6, and the ^{2}H NMR spectrum recorded.

Variable ^{1}H NMR Study of $[(R_8Pc)Rh]_2$. A solution of 2.0 mg of $[(R_8Pc)Rh]_2$ in 0.50 mL of C_6D_6 was sealed with a flame under 600 mmHg of N_2. The ^{1}H NMR spectra of the solution were recorded after time was allowed for the solution to reach the temperatures.

Reaction of $[(R_8Pc)Rh]_2$ with Toluene. A solution of 1.19 μmol of $[(R_8Pc)Rh]_2$ in toluene (0.50 mL) in an NMR tube was sealed under vacuum after two freeze–pump–thaw cycles. The solution was heated at 180 °C for 66 h. A rubber tubing was slipped over the NMR tube, which was then opened, and air was admitted via a syringe needle to bring the tube to atmospheric pressure. The head gas was then analyzed for H_2 on a 6-ft 5A molecular sieve column with a thermal conductivity detector. The solution was then exposed to air and the solvent removed. The ^{1}H NMR spectrum of the residue was recorded. ^{1}H NMR (C_6D_6, ppm) for CH_2Ph: CH_2, δ −3.050, d, $J_{Rh\text{-}H}$ 3.6 Hz, 2 H; H_o, δ 3.468, d, $J_{H\text{-}H}$ 7.5 Hz, 2 H; H_m, δ 5.660, t, 2 H, $J_{H\text{-}H}$ 7.5 Hz; H_p, δ 6.090, t, $J_{H\text{-}H}$ 7.5 Hz, 1 H.

Reaction of $[(R_8Pc)Rh]_2$ with Toluene-d_8. A solution $[(R_8Pc)Rh]_2$ (2.8 mg) in toluene-d_8 (0.5 mL) in a medium-walled NMR tube was sealed under vacuum after two freeze–pump–thaw cycles. The solution was then allowed to react at 180 °C. The tube was removed at various times to record its ^{1}H NMR spectra.

Reaction of $[(R_8Pc)Rh]_2$ with Ethylbenzene. The reaction of $[(R_8Pc)Rh]_2$ with ethylbenzene was carried out in similar procedures as for toluene. After 17 h at 175 °C, the product residue gave a 40% yield of $(R_8Pc)RhCHPhCH_3$. ^{1}H NMR (C_6D_6, ppm) for $CHPhCH_3$: CH_3, δ −3.45, dd, 3H, J_{HH} 6.8 Hz, J_{RhH} 1.7 Hz; CH, δ-2.184, m, 1H; H_m, δ 5.79, t (unresolved dd), 2H; H_p, δ 6.21, t, 1H, J_{HH} 7.2 Hz; H_o, δ 7.05, d, 2H, J_{HH} 8.4 Hz.

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