

Formation and Thermal Reactions of Rh-C Bonds Derived from the Reactions of (RhOEP)₂ with Alkyl C-H Bonds in Alkylaromatics

Kenneth J. Del Rossi and Bradford B. Wayland*

Contribution from the Department of Chemistry and the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104.

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Abstract: (Octaethylporphyrin)rhodium(II) dimer, (RhOEP)₂, reacts with toluene and related methyl-substituted aromatics at the methyl C-H bonds to form organometallic benzyl derivatives. Longer chain alkyl substituents react initially at the benzylic C-H bond but subsequently rearrange to place the RhOEP unit at a less hindered alkyl carbon position. Isopropylbenzene reacts with (RhOEP)₂ to form RhOEP(CH₂CH(CH₃)C₆H₅) as the only observed organometallic compound. Thermal decompositions of the alkylaromatic complexes of RhOEP result in equal amounts of alkane and alkene in the absence of O₂ and aldehydes and ketones in the presence of O₂.

Carbon-hydrogen bond reactivity by alkylaromatics with metallo species can potentially occur at the arene and alkyl C-H fragments.¹⁻³ Numerous examples exist where arene C-H bond reactivity is manifested by formation of metalloaryl species and arene H-D exchange.⁴⁻¹¹ Reactions at the alkyl side chain are unusual, but several examples have been reported.¹²⁻¹⁴ The species resulting from photoactivation of (η⁵-C₅Me₅)(PPh₃)IrH₂¹² and (η⁵-C₅Me₅)(PMe₃)RhH₂¹³ are known to react with alkylaromatics to produce metalloaryl compounds as the main product, but small quantities of benzyl derivatives (η⁵-C₅Me₅)(PPh₃)Ir(H)(CH₂-(C₆H₄)CH₃) and (η⁵-C₅Me₅)(PMe₃)Rh(H)(CH₂C₆H₅) are observed. Photolysis of (η⁵-C₅H₅)₂W(H)(C₆H₄CH₃), but the corresponding reactions in *p*-xylene and mesitylene occur at the alkyl C-H bond to produce (η⁵-C₅H₅)₂W(R)₂ (R = CH₂C₆H₄CH₃, CH₂C₆H₃(CH₃)₂).¹⁴

We wish to report that (octaethylporphyrin)rhodium(II) dimer, (RhOEP)₂, thermally reacts with alkylaromatic molecules exclusively at the alkyl C-H unit to produce organometallic products, Rh^{III}OEP(R) (R = alkylaromatic) and Rh^{III}OEP(H).

Experimental Section

(a) **General Comments:** Proton NMR spectra were obtained on Bruker WH-250 and IBMWP200SY Fourier transform spectrometers. Spectra were internally referenced to the residual proton resonance in C₆D₆ or CD₃C₆D₅. Low-resolution mass spectra were obtained on a VG Analytical 7070 mass spectrometer interfaced to a Kratos DS50S data system. GC analyses were performed on a Perkin Elmer 154-D vapor fractometer with columns purchased from Alltech Associates.

All reagents were commercially obtained and purified by standard procedures. All manipulations, unless otherwise specified, were carried out with standard vacuum and Schlenk techniques or in a Vacuum Atmospheres Co. inert atmosphere box.¹⁵

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(Octaethylporphyrin)rhodium (II) dimer, (RhOEP)₂ (I), (octaethylporphyrin)rhodium(III) hydride, RhOEP(H) (II), and (octaethylporphyrin)rhodium(III) deuteride, RhOEP(D), were prepared according to the methods reported by Ogoshi.¹⁶

(b) **Reactions of (RhOEP)₂ with Alkylaromatics.** Thermal reactions were carried out on solutions of (RhOEP)₂ (2 mg) in neat reaction solvent or in solutions of (RhOEP)₂ and C₆D₆ with approximately 1%, by volume, reaction reagent. The solutions were sealed under vacuum in amber NMR tubes and heated by immersion in a silicon oil bath encased in a black box to exclude light. NMR spectra for the reaction products from neat solutions were obtained in tubes that were sealed after removal of excess solvent and replacement with C₆D₆. Yields are based on total (RhOEP).

(c) **RhOEP Anion Reactions.** (Octaethylporphyrin)rhodium(I) anion, RhOEP⁻ (III),¹⁷ was generated by adding approximately 2 mL of alcoholic-hydroxide solution (0.5 N OH⁻/MeOH) to 10 mg of RhOEP(H) in 20 mL of benzene under argon. The solution was stirred until the pink-red color changed to a deep brown (15 min), indicating the presence of RhOEP⁻. A slight excess of alkyl halide was added, the mixture was stirred for 10 min, and the solvent was removed under vacuum. The crude product was loaded on a column of silica gel (ICN 100-200 mesh) and eluted with benzene. The first orange fraction which consists of the RhOEP(R) complex was collected and dried in vacuum.

(d) **Reactions of RhOEP(R).** Thermal reactions were carried out on solutions of RhOEP(R) (2-4 mg) in C₆D₆ (99.5%) distilled from benzophenone-sodium. For reactions performed under anaerobic conditions, the solutions were sealed under high vacuum in amber NMR tubes and heated by immersion in a silicon oil bath encased in a black box to exclude light. For reactions performed under aerobic conditions the solutions were sealed in amber NMR tubes with 200 torr of air and heated as previously stated.

(e) **Photochemical Reactions.** Photochemical reactions were performed in an adaptable Rayonet photoreactor.¹⁸ Samples were sealed in 507-PP NMR tubes purchased from Wilmad Glass Co. Typical samples were composed of approximately 2 mg of (RhOEP)₂ and approximately 0.3 mL of reaction reagent.

(f) **Reactions of RhOEP(H) and RhOEP(D) with Olefins.** Reactions were carried out on solutions of RhOEP(H) (2-3 mg) in C₆D₆ (99.5%) (0.3 mL) distilled from benzophenone-sodium. The solutions were sealed in amber NMR tubes with a slight excess of olefin and approximately 200 torr of H₂ gas.

OEPRh(CH₂C₆H₅) (IV). With use of procedure b, reaction of I with toluene for 24 h at 125 °C produced IV in approximately 50% yield. IV was also prepared in 70% yield by procedure c, the reaction of III with benzyl chloride. ¹H NMR (δ): porphyrin -CH=, s, 4 H, 10.11; -CH₂-, q, 16 H, 3.96; -CH₃-, t, 24 H, 1.91; axial ligand -CH₂-, d, 2 H, -4.02; J_{Rh-CH} = 3.9 Hz, ortho d, 2 H, 2.82, meta t, 2 H, 5.68, para t, 1 H 6.16. Mass measurement calculated for IV, RhN₄C₄₃H₅₁, 726.80, found 726 (major fragments at m/e 636, 318, 91).

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(18) Wavelengths of 357 nm, >445 nm, and >500 nm were used in various photoreactions.

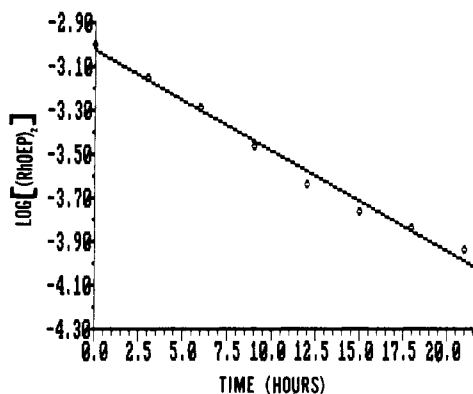


Figure 1. $\log[(\text{RhOEP})_2]$ vs. time (h) for a 9.96×10^{-4} M solution of $(\text{RhOEP})_2$ in C_7D_8 at 125°C .

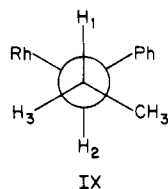
OEPRh(*p*-CH₂C₆H₄CH₃) (V). With use of procedure b, reaction of I with *p*-xylene for 24 h at 125°C produced V in approximately 50% yield. ^1H NMR (δ): porphyrin-CH=, s, 4 H, 10.10; -CH₂-, q, 16 H, 3.95; -CH₃, t, 24 H, 1.91; axial ligand -CH₂-, d, 2 H, -4.01; $J_{\text{Rh-CH}} = 3.9$ Hz, ortho d, 2 H, 2.77, meta d, 2 H, 5.49, *p*-CH₃, s, 3 H, 1.47.

OEPRh(*m*-CH₂C₆H₄CH₃) (VI). With use of procedure b, reaction of I with *m*-xylene for 24 h at 125°C produced VI in approximately 50% yield. ^1H NMR (δ): porphyrin-CH=, s, 4 H, 10.13; -CH₂-, q, 16 H, 3.96; -CH₃, t, 24 H, 1.92; axial ligand -CH₂-, d, 2 H, -4.00; $J_{\text{Rh-CH}} = 3.9$ Hz, ortho d, 1 H, 2.709, s, 1 H, 2.60, meta t, 1 H, 5.628, para d, 1 H, 6.05, *m*-CH₃ (not found).

OEPRh(CH(C₆H₅)CH₃) (VII). With use of procedure b, reaction of I with ethylbenzene for 24 h at 109°C produced VII in 45% yield. VII was alternatively prepared in 80% yield by procedure c, the reaction of III with 1-bromo-1-phenylethane. ^1H NMR (δ): porphyrin-CH=, s, 4 H, 10.07; -CH₂-, q, 16 H, 3.95; -CH₃, t, 24 H, 1.90; axial ligand -CH₃, dd, 3 H, -4.30; $J_{\text{Rh-CH}_3} = 1.5$ Hz, $J_{\text{CH-CH}_3} = 6.6$ Hz, -H, m, 1 H, -3.60; $J_{\text{Rh-CH}} = 4.0$ Hz, ortho br s, 2 H, 2.94, meta t, 2 H, 5.85, para t, 1 H, 6.32. Mass measurement calculated for VII, $\text{RhN}_4\text{C}_{44}\text{H}_{53}$, 740.83, found 740 (major fragments at m/e 636, 318, 104).

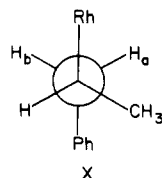
OEPRh(CH₂CH₂C₆H₅) (VIII). With use of procedure b, reaction of I with ethylbenzene for 3 h at 160°C produced VIII in 20% yield. VIII was independently prepared in 45% yield by procedure c, the reaction of III with 2-bromo-1-phenylethane. ^1H NMR (δ): porphyrin-CH=, s, 4 H, 10.23; -CH₂-, m, 16 H, 3.96; -CH₃, t, 24 H, 1.92; axial ligand -C_(α)H₂-, td, 2 H, -5.03; $J_{\text{Rh-CH}} = 2.9$ Hz, $J_{\text{CH}_2\text{-CH}_2} = 8.1$ Hz, -C_(β)H₂-, t 2 H, -3.43, ortho d, 2 H, 4.51, meta t, 2 H, 5.88, para t, 1 H, 6.11. Mass measurement calculated for VIII, $\text{RhN}_4\text{C}_{44}\text{H}_{53}$, 740.83, found 740 (major fragments at m/e 635, 317, 104).

OEPRh(CH(C₆H₅)CH₂CH₃) (IX). With use of procedure b, reaction of I with *n*-propylbenzene for 24 h at 109°C yielded IX in 36% yield.



IX was also prepared in 70% yield by procedure c, the reaction of III with 1-bromo-1-phenylpropane. ^1H NMR (δ): porphyrin-CH=, s, 4 H, 10.04; -CH₂-, q, 16 H, 3.93; -CH₃, t, 24 H, 1.90; axial ligand -H₁, m, 1 H, -3.63; $J_{\text{trans}} = 11.7$ Hz, $J_{\text{gem}} = 12.7$ Hz, $J_{\text{CH-CH}_3} = 7.2$ Hz, -H₃, m, 1 H, -4.72; $J_{\text{cis}} = 3.1$ Hz, -H₂, dt, -3.77; $J_{\text{Rh-CH}} = 3.4$ Hz, -CH₃, t, 3 H, 1.85, ortho dd, 2 H, 3.01, meta t, 2 H, 5.83, para t, 1 H 6.30. Mass measurement calculated for IX, $\text{RhN}_4\text{C}_{45}\text{H}_{55}$, 754.83, found 754 (major fragments at m/e 636, 318, 119).

OEPRh(CH(CH₃)CH₂C₆H₅) (X). With use of procedure b, reaction of I with *n*-propylbenzene for 24 h at 145°C produced X in 5% yield.



X was independently prepared in 95% yield by procedure f, the addition of II to β -methylstyrene. X was also prepared in 40% yield by reaction of III with 2-bromo-1-phenylpropane according to the method reported

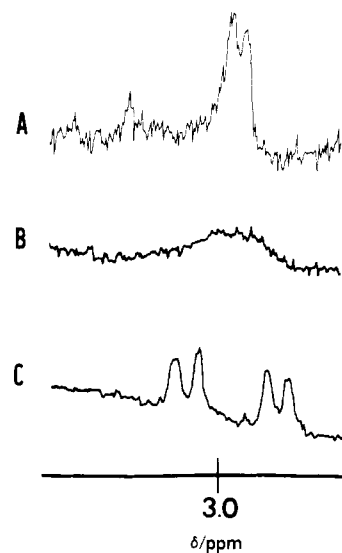


Figure 2. Variable-temperature 200-MHz ^1H NMR spectra for the ortho protons in compound VII, $\text{RhOEP}(\text{CH}(\text{C}_6\text{H}_5)\text{CH}_3)$, in C_7D_8 solvent: (A) at 333 K, (B) at 295 K, and (C) at 233 K.

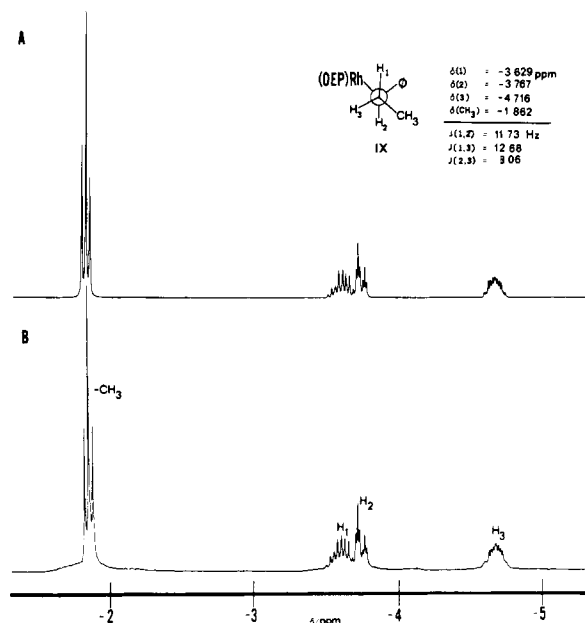
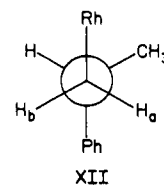


Figure 3. Calculated (A) and experimental (B) 250-MHz ^1H NMR spectra for compound IX, $\text{RhOEP}(\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_3)$, in C_6D_6 .

by Ogoshi.¹⁷ ^1H NMR (δ): porphyrin-CH=, s, 4 H, 10.23; -CH₂-, m, 16 H, 3.97; -CH₃, t, 24 H, 1.88; axial ligand -H_a, dd, 1 H, -2.91; $J_{\text{gem}} = 11$ Hz, $J_{\text{trans}} = 13$ Hz, -H_b, d, 1 H, -4.07; -CH₃, br s, 3 H, -4.61; -H overlapped, ortho d, 2 H, 4.66, meta t, 2 H, 6.05, para t, 1 H, 6.16.

OEPRh(CH₂CH₂CH₂C₆H₅) (XI). With use of procedure b, reaction of I with *n*-propylbenzene for 24 h at 145°C produced XI in 3% yield. XI was independently prepared in 60% yield by procedure c, the reaction of III with 3-bromo-1-phenylpropane. ^1H NMR (δ): porphyrin-CH=, s, 4 H, 10.18; -CH₂-, m, 16 H, 3.95; -CH₃, t, 24 H, 1.90; axial ligand -C_(α)H₂-, td, 2 H, -5.17; $J_{\text{Rh-CH}_2} = 3.3$ Hz, $J_{\text{CH}_2\text{-CH}_2} = 7.7$ Hz, -C_(β)H₂-, p, 2 H, -4.37; -C_(γ)H₂-, t, 2 H, -0.85, ortho d, 2 H, 5.26, meta, para m, 3 H, 6.53. Mass measurement calculated for XI, $\text{RhN}_4\text{C}_{45}\text{H}_{55}$, 754.83, found 754 (major fragments at m/e 636, 318, 117, 91, 28).

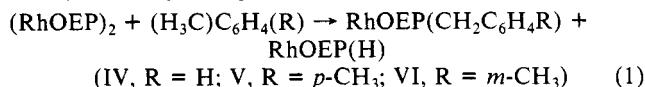
OEPRh(CH₂CH(C₆H₅)CH₃) (XII). With use of procedure b, reaction of I with isopropylbenzene for 24 h at 109°C produced XII in 40% yield. XII was independently prepared in 90% yield by procedure f, the addition



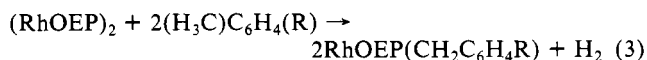
of II to α -methylstyrene. ^1H NMR (δ): porphyrin $-\text{CH}=\text{}$, s, 4 H, 10.13; $-\text{CH}_2-$, q, 16 H, 3.96; $-\text{CH}_3$, t, 24 H, 1.91; axial ligand $-\text{H}_{\text{a,b}}$, m, 2 H, -4.97; $-\text{H}$, m, 1 H, -4.06; $-\text{CH}_3$, d, 3 H, -2.14, ortho d, 2 H, 4.40, meta t, 2 H, 6.28, para t, 1 H, 6.46.

Results

Reactions of $(\text{RhOEP})_2$ and Alkylaromatics. Toluene, *m*-Xylene, *p*-Xylene. Arylmethyl species thermally react with $(\text{RhOEP})_2$ (125 °C; 24 h) to produce (octaethylporphyrin)rhodium(III) benzyl compounds and $\text{RhOEP}(\text{H})$ (reaction 1).¹⁹



$\text{RhOEP}(\text{H})$ slowly eliminates hydrogen according to reaction 2, to give the overall process depicted in reaction 3. Trace amounts of rhodium metal remaining from $(\text{RhOEP})_2$ synthesis were found



to catalyze reaction 2. Reaction 1 produces approximately equal amounts of $\text{RhOEP}(\text{CH}_2\text{C}_6\text{H}_4\text{R})$ and $\text{RhOEP}(\text{H})$ when no rhodium metal is present. Mass spectral and GC analyses of the solvent taken from reaction 1 (R = H) indicated no detectable bibenzyl was produced. Photolytic generation of IV from $(\text{RhOEP})_2$ and toluene was unsuccessful.

Kinetic measurements for reaction 1 (R = H) were performed at 125 °C on 9.96×10^{-4} M solutions of $(\text{RhOEP})_2$ in neat toluene-*d*₈. The change in the molar concentration of $(\text{RhOEP})_2$ as a function of time was determined by integration of the porphyrin methine hydrogens and followed until 95% complete (4 half-lives). The rate of disappearance of $(\text{RhOEP})_2$ best conforms to first-order dependence on $[(\text{RhOEP})_2]$, $-\text{d}[(\text{RhOEP})_2]/\text{d}t = k[(\text{RhOEP})_2]$, with a rate constant of $4.606 \times 10^{-2} \pm 2.148 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$ (Figure 1).

Ethylbenzene. Reaction of $(\text{RhOEP})_2$ with ethylbenzene for 1 h at 109 °C produced $\text{RhOEP}(\text{CH}(\text{C}_6\text{H}_5)\text{CH}_3)$ (VII) in 12.5% yield and 12.5% $\text{RhOEP}(\text{H})$ (reaction 4). A longer reaction

$(\text{RhOEP})_2 + \text{CH}_3\text{CH}_2\text{C}_6\text{H}_5 \rightarrow \text{RhOEP}(\text{CH}(\text{C}_6\text{H}_5)\text{CH}_3) + \text{RhOEP}(\text{H})$ (4)

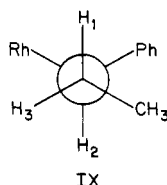
period (24 h) produced VII in 45% yield, 4% of the terminal product, $\text{RhOEP}(\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5)$ (VIII) and 45% of $\text{RhOEP}(\text{H})$. The yield of VIII is increased by reaction at higher temperature, for example, VIII is produced in 20% yield after 3 h at 160 °C.

Variable-temperature ^1H NMR spectra for the ortho hydrogens of compound VII are shown in Figure 2. The broad resonance associated with the ortho hydrogens (δ 2.94) at 295 K resolves into two doublets at 235 K (δ 2.85 and 3.02), which is indicative of hindered rotation of the phenyl group in the (α -phenyl)ethyl ligand.

***n*-Propylbenzene.** Thermal reaction between $(\text{RhOEP})_2$ and *n*-propylbenzene at 109 °C for 1 h produced $\text{RhOEP}(\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_3)$ (IX) in 4% yield and 4% of $\text{RhOEP}(\text{H})$ (reaction 5). A longer reaction period (24 h) produced IX in 36%

$(\text{RhOEP})_2 + \text{CH}_3\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5 \rightarrow \text{RhOEP}(\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_3) + \text{RhOEP}(\text{H})$ (5)

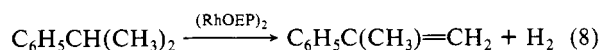
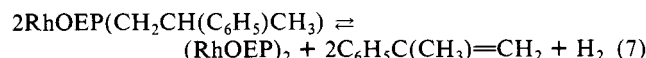
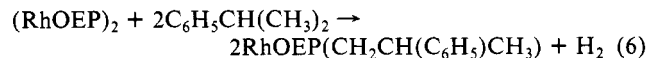
yield, with 4% of $\text{RhOEP}(\text{CH}(\text{CH}_3)\text{CH}_2\text{C}_6\text{H}_5)$ (X), 1% of $\text{RhOEP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5)$ (XI), and 34% of $\text{RhOEP}(\text{H})$. Compound IX contains diastereotopic hydrogen atoms H₁ and



H₃, which produce a characteristic splitting pattern in the ^1H NMR (Figure 3). The geminal ($J_{\text{gem}} = 12.7 \text{ Hz}$), trans (J_{trans}

$= 11.7 \text{ Hz}$), and cis ($J_{\text{cis}} = 3.0 \text{ Hz}$) coupling constants were obtained by spectral simulation and are in agreement with values reported for similar systems.^{20,21}

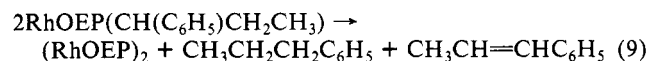
Isopropylbenzene and *tert*-Butylbenzene. The thermal reaction of $(\text{RhOEP})_2$ and isopropylbenzene at 109 °C for 24 h produced $\text{RhOEP}(\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{CH}_3)$ (XII) in 40% yield (reaction 6). $\text{RhOEP}(\text{H})$ was not observed in reaction 6. After 30 days at room temperature, 40% of the organometallic product, XII, had converted to $(\text{RhOEP})_2$ and α -methylstyrene (reaction 7). The overall process, depicted in reaction 8, is the dehydrogenation of isopropylbenzene by $(\text{RhOEP})_2$. When isopropylbenzene-*d*₁, $(\text{C}_6\text{H}_5)_2\text{CDC}_6\text{H}_5$, was reacted with $(\text{RhOEP})_2$ under identical conditions, deuterium was not observed in the organometallic product.



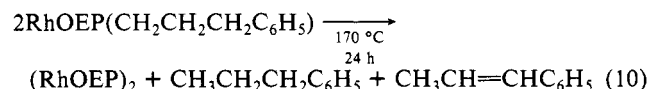
tert-Butylbenzene yielded no detectable organometallic products when reacted at 125 °C for 24 h with $(\text{RhOEP})_2$.

Thermolysis of $\text{RhOEP}(\text{R})$. Anaerobic Conditions. The thermal reactions of compounds IX and XI were performed in scrupulously dried and degassed C_6D_6 and were monitored by ^1H NMR spectroscopy and gas chromatography. Product ratios were determined by integration of NMR spectra and mass measurement of GC peaks.

Thermolysis of compound IX, $\text{RhOEP}(\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_3)$, was complete, according to reaction 9, after 120 h at 100 °C. Final analysis indicated that equal amounts of *n*-propylbenzene and β -methylstyrene were produced by reaction 9.

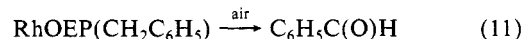


Thermolysis of compound XI, $\text{RhOEP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5)$, yielded a 1:1 mixture of *n*-propylbenzene and β -methylstyrene (reaction 10). Allylbenzene was not detected in the GC analysis.

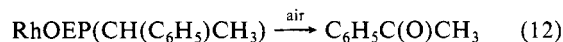


Thermolysis of $\text{RhOEP}(\text{R})$. Aerobic Conditions. Thermal reactions of compounds IV, VII, and IX in the presence of air were followed by ^1H NMR spectroscopy. Yields were based upon integration of selected ^1H resonances.

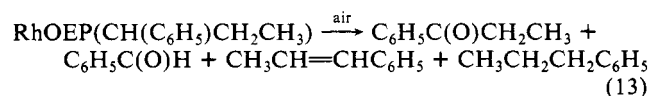
Compound IV, $\text{RhOEP}(\text{CH}_2\text{C}_6\text{H}_5)$, when heated at 130 °C for 20 h in the presence of air (200 torr) is 40% converted to benzaldehyde (reaction 11).



Thermal reaction of compound VII, $\text{RhOEP}(\text{CH}(\text{C}_6\text{H}_5)\text{CH}_3)$, at 110 °C for 24 h in the presence of air (200 torr) results in quantitative conversion to acetophenone (reaction 12).



Thermolysis of compound IX, $\text{RhOEP}(\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_3)$, at 110 °C for 20 h in the presence of air (200 torr) yields 75% of propiophenone, 5% of benzaldehyde, and 5% each of β -methylstyrene and *n*-propylbenzene (reaction 13).



Discussion

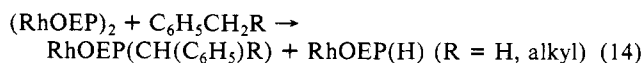
C-H Bond Activation by $(\text{RhOEP})_2$. $(\text{RhOEP})_2$ reacts with alkylaromatics to produce benzylic derivatives as the initial

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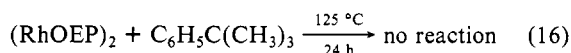
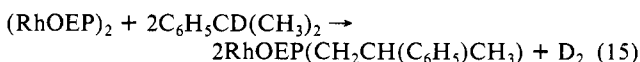
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products (reaction 14). Hindered rotation of the phenyl group and adoption of conformations that minimize steric effects are



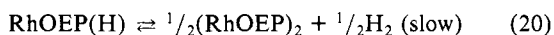
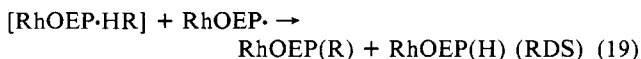
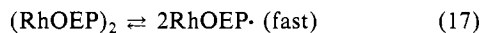
both indicative of the crowding that occurs when OEPRh bonds at the benzylic carbon site (Figures 2 and 3). Continued thermolysis produces isomerizations that result in transferring the Rh-C bond from the benzylic carbon to a less sterically hindered alkyl carbon. For example, thermal reaction between $(\text{RhOEP})_2$ and ethylbenzene at 109 °C for 1 h produces compound VII, $\text{RhOEP}(\text{CH}(\text{C}_6\text{H}_5)\text{CH}_3)$, as the only organometallic, but a longer reaction period (24 h) yields VII and the terminal organometallic, $\text{RhOEP}(\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5)$ (VIII). The thermal isomerizations observed for the (octaethylporphyrin)rhodium(III) alkyls studied resemble the behavior found in the hydrozirconation of alkenes.²²

When the benzylic carbon has two alkyl groups, as in isopropylbenzene, the only observed organometallic product has OEPRh bonded to a terminal alkyl carbon (reaction 6). Labeling studies support a mechanism involving initial attack at the benzylic carbon and fast rearrangement to the terminal site (reaction 15). The importance of having an activated benzylic hydrogen site for initial reaction is illustrated by the absence of reaction by *tert*-butylbenzene (reaction 16).



Benzylic C-H bond energies (85 kcal) are about 15–20 kcal weaker than aryl or unactivated alkyl C-H bonds.²³ Reaction 14 is expected to be highly exothermic (25 kcal), based on estimates of Rh-C (55–60 kcal)²⁴ and Rh-Rh (20 kcal)²⁵ bond energies. These thermochemical estimates suggest that hydrocarbon C-H bonds approaching 100 kcal should react as in eq 14. Isomerization of the Rh-C bond from the partially activated benzylic position to the terminal site illustrates the thermodynamic feasibility of reaction 14 for unactivated C-H bonds (95–100 kcal).

Previously recognized patterns of $(\text{RhOEP})_2$ reactivity²⁶ and initial attack at the benzylic position are compatible with a metalloradical mechanism.¹ Absence of bibenzyl and related organic coupling products argues against the formation of authentic organic free radicals in reaction 1. The rate of disappearance of $(\text{RhOEP})_2$ in reaction 1, using deuteriotoluene (C_7D_8), is found to be first order in $[(\text{RhOEP})_2]$. One possible mechanism consistent with these observations is given by 17–20. The observed

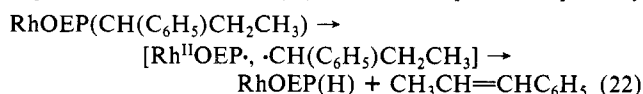


C-H bond reactivity is proposed to occur by initial dissociation of $(\text{RhOEP})_2$ into the metalloradical $\text{Rh}^{\text{II}}\text{OEP}\cdot$ (eq 17) and the subsequent coordination assisted hydrogen abstraction compatible with first-order rate dependence on $[(\text{RhOEP})_2]$ (eq 19).

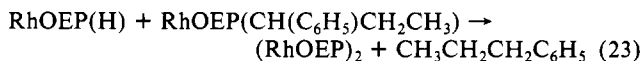
Thermal Reactions of $\text{RhOEP}(\text{R})$ Compounds in C_6D_6 . A prominent feature in the thermolysis of $\text{RhOEP}(\text{R})$ compounds is the production of equal amounts of alkane and alkene without any evidence for the coupling products (R_2). For example, $\text{RhOEP}(\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_3)$ reacts to form equal quantities of β -methylstyrene and *n*-propylbenzene (reaction 9). A probable reaction pathway involves formation of a geminate radical pair that is trapped in a benzene solvent cage.²⁷ When β -hydrogens



are available OEPRh^{II} can abstract a hydrogen atom from R, and the resulting stable molecules can diffuse out of the solvent cage. Addition of $\text{RhOEP}(\text{H})$ to the alkene provides a pathway



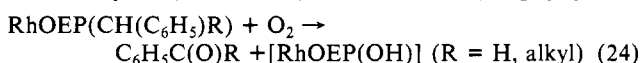
for rhodium-alkyl rearrangement or intermolecular reductive elimination by reaction 23 produces the alkane. Reaction 23 has been independently studied and shown to occur at the conditions required for the overall reaction (reaction 9). Geminate radical



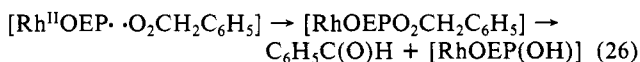
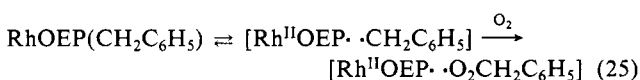
pair mechanisms have been previously implicated in the thermal homolysis of cobalt-alkyl bonds^{28–30} and may be a general reaction pathway for many metal-alkyl species.^{31,32}

Evidence for a geminate radical pair intermediate comes from rearrangements observed for the alkene products. Thermolysis of $\text{RhOEP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5)$ produces $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$ and $\text{CH}_3\text{CH}=\text{CHC}_6\text{H}_5$ rather than $\text{CH}_2=\text{CHCH}_2\text{C}_6\text{H}_5$ (reaction 10), which suggests rearrangement to the more stable benzylic radical ($\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HC}_6\text{H}_5$) may be occurring in the solvent cage. Migration of organic radicals from the geminate radical pair is apparently an inefficient process because no radical coupling products have been observed.

Further chemical evidence for a radical pair intermediate has been obtained from reactions of dioxygen that produce ketones and aldehydes (reaction 24).^{31–34} $\text{RhOEP}(\text{CH}_2\text{C}_6\text{H}_5)$ and



$\text{RhOEP}(\text{CH}(\text{C}_6\text{H}_5)\text{CH}_3)$ react quantitatively by eq 24 to produce benzaldehyde, $\text{C}_6\text{H}_5\text{C}(\text{O})\text{H}$, and acetophenone, $\text{C}_6\text{H}_5\text{C}(\text{O})\text{CH}_3$, respectively. Dioxygen presumably intercepts the radical pair by the usual mechanism³⁴ to produce peroxy species that subsequently form carbonyl compounds (reactions 25 and 26).



Our continuing studies in this area are focused on direct observation of the geminate radical pair, the insertion of small molecules like CO and CO_2 into Rh-C bonds, and examination of C-H bond reactivity for a wider range of organic molecules.

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Registry No. I, 63439-10-1; II, 63372-77-0; IV, 57650-51-8; V, 95297-24-8; VI, 95297-25-9; VII, 99248-50-7; VIII, 96502-53-3; IX, 99248-51-8; X, 99248-52-9; XI, 99248-53-0; XII, 99248-54-1; $\text{RhOEP}(\text{D})$, 99248-49-4; $(\text{H}_3\text{C})\text{C}_6\text{H}_5$, 108-88-3; *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_3$, 106-42-3; *m*- $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_3$, 108-38-3; $\text{CH}_3\text{CH}_2\text{C}_6\text{H}_5$, 100-41-4; $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$, 103-65-1; $\text{CH}_3\text{CH}=\text{CHC}_6\text{H}_5$, 637-50-3; $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2$, 98-82-8; $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)=\text{CH}_2$, 98-83-9; $\text{C}_6\text{H}_5\text{C}(\text{O})\text{H}$, 100-52-7; $\text{C}_6\text{H}_5\text{C}(\text{O})\text{CH}_3$, 98-86-2; $\text{C}_6\text{H}_5\text{C}(\text{O})\text{CH}_2\text{CH}_3$, 93-55-0; $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$, 100-44-7; 1-bromo-1-phenylethane, 585-71-7; 1-bromo-1-phenylpropane, 2114-36-5; 2-bromo-1-phenylpropane, 2114-39-8; 3-bromo-1-phenylpropane, 637-59-2; 2-bromo-1-phenylethane, 103-63-9.

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