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Preliminary communication

ACTIVATION OF C—H BONDS BY OCTAETHYLPORPHYRINRHODIUM DIMER

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Summary

Octaethylporphyrinrhodium dimer, $[\mathrm{RhOEP}]_2$, reacts thermally with arylmethyl C—H bonds to produce octaethylporphyrinbenzylrhodium compounds.

Reactions of C—H bonds with metallo species are emerging as a major focal point for organometallic-catalysis studies [1]. A major advance in this area came with the discovery of metallo complexes that give well characterized oxidative addition reactions of the C—H fragment of alkanes (reaction 1) [2].

$$\mathrm{M + H{-}C}\!\leqslant\ \rightleftarrows\ \mathrm{H{-}M{-}C}\!\leqslant \qquad (1)$$

Our efforts in this field have centered on the search for a system where a net oxidative addition of the C—H unit occurs across a M—M single bond (reaction 2).

$$\mathrm{M{-}M} + \geqslant\!\mathrm{C{-}H} \rightarrow \mathrm{M{-}H + M{-}C}\!\leqslant \qquad (2)$$

In this manner, the M—H and $\mathrm{M{-}C}\!\leqslant$ units can be separated and permitted to react independently. We wish to report that octaethylporphyrinrhodium dimer, $(\mathrm{RhOEP})_2$, accomplished this type of reactivity with methyl groups of arenes $(\mathrm{CH_3})\mathrm{C_6H_5}$, $(\mathrm{CH_3})_2\mathrm{C_6H_4}$, $((\mathrm{CH_3})_3\mathrm{C_6H_3})$ to produce rhodium hydride and benzylrhodium derivatives (reaction 3). RhOEP(H) subsequently eliminates H_2 to give the overall process depicted by reaction 4.

$$(\mathrm{RhOEP})_2 + \mathrm{CH_3C_6H_5} \rightarrow \mathrm{RhOEP(H)} + \mathrm{RhOEP(CH_2C_6H_5)} \qquad (3)$$

$$(\mathrm{RhOEP})_2 + 2\mathrm{CH_3C_6H_5} \rightarrow 2\ \mathrm{OEPRhCH_2C_6H_5} + \mathrm{H_2} \qquad (4)$$

In one typical experiment, 4 mg of $(\mathrm{RhOEP})_2$ was placed in an NMR tube adapted for vacuum manipulation. *m*-Xylene, distilled from benzophenone-sodium, was vacuum distilled into the NMR tube. The solution was heated at

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120°C for 3 h. Electronic absorption studies conducted on samples more dilute than those studied by NMR reveal the reaction to be complete after 3 h (Fig. 1). NMR spectra for the reaction products were obtained in tubes that were sealed after removal of excess *m*-xylene and replacement with C_6D_6 solvent. NMR spectra of samples that were prepared with minimal exposure to light demonstrate essentially quantitative formation of the organometallic, RhOEP-($CH_2C_6H_4CH_3$). The high field (δ −4.0) doublet ($J(^{103}\underline{Rh}\text{-}C\underline{H})$ 3.9 Hz) corresponding to the benzylic CH_2 group is most characteristic of the organometallic product (Table 1). Samples exposed to laboratory lighting invariably contain $(RhOEP)_2$ which results from the homolytic photodissociation of the Rh—C fragment. Proton NMR spectral data for the organometallic products appear in Table 1.

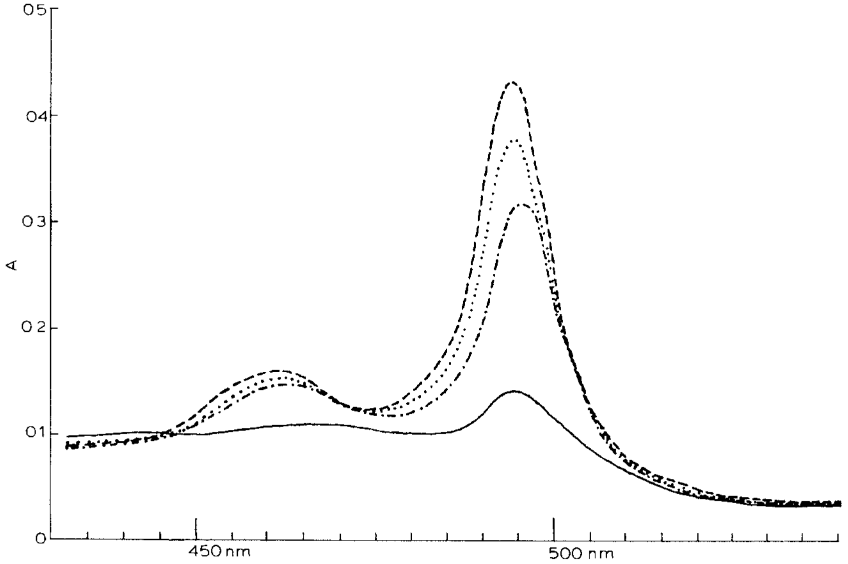

Fig. 1. Electronic absorption spectra for a 9.8×10^{-5} *M* solution of $(RhOEP)_2$ in *m*-xylene at 95°C. (——) *t* = 0, (—•—•) *t* 1 h, (···) *t* 2 h, (– – –) *t* 3 h. (Electronic absorption spectrum at *t* 18 his identical to that observed at *t* 3 h.)

TABLE 1

^{1}H NMR SPECTRA OF OCTAETHYLPORPHYRINBENZYLRHODIUM COMPOUNDS[a,b]

	Porphyrin			Benzyl group				
	C—H	CH_2	CH_3	CH_2	CH_3	*o*	*m*	*p*
Toluene	10.110(s)	3.961(q)	1.908(t)	−4.019(d)	—	2.820(d)	5.681(t)	6.162(t)
p-Xylene	10.102(s)	3.950(q)	1.905(t)	−4.013(d)	1.468(s)	2.767(d)	5.490(d)	—
m-Xylene	10.128(s)	3.965(q)	1.923(t)	−4.000(d)	[c]	2.709(d) 2.595(s)	5.628(t)	6.048(d)

[a] C_6D_6 solvent. [b] Values in δ relative to TMS. [c] Peak obscured by overlapping spectra.

The thermodynamic criteria for oxidative addition to the M—M bond (reaction 2) are more stringent than to a single metal center (reaction 1) by approximately the M—M bond energy, but this is partially compensated by a more favorable entropy change. The homolytic dissociation energy for $(\mathrm{RhOEP})_2$ has been estimated to be 17 kcal from NMR studies for the reaction $(\mathrm{RhOEP})_2 \rightleftarrows 2\mathrm{RhOEP}^{\bullet}$ [3]. A methyl C—H bond energy of 88 kcal in toluene requires that the average of the Rh—H and Rh—C bond energies must exceed 52 kcal in order for reaction 3 to be exothermic. Thermodynamic studies of RhOEP(H) and RhOEP(CHO) indicate that the Rh—H and Rh—C bond energies are comparable and approximately 55—60 kcal [3], which suggests that the organometallic chemistry depicted by reaction 2 may be obtained even when the C—H bond energy exceeds 100 kcal.

$(\mathrm{Rh^{III}OEP})^+$ has recently been shown to react by electrophilic substitution with aromatic molecules to produce arylrhodium compounds [4]. The reaction of $(\mathrm{RhOEP})^+$ with toluene is reported to yield p-$\mathrm{RhOEP(C_6H_4CH_3)}$ as the exclusive product. Absence of aromatic substitution in the reaction of $(\mathrm{RhOEP})_2$ with toluene suggests that an ionic mechanism involving heterolytic cleavage of the Rh—Rh bond is not important in this reaction. We believe that the reactions of $(\mathrm{RhOEP})_2$ with hydrocarbons proceed by a pathway involving the interaction of a metal centered radical with a C—H unit.

$$(\mathrm{RhOEP})_2 \rightleftarrows 2\mathrm{OEPRh^{II\bullet}}$$

$$\mathrm{OEPRh^{II\bullet}} + \mathrm{HC}{<}\!\!\!{-} \rightarrow ([\mathrm{OEPRh^{\bullet}HC}{<}\!\!\!{-}] \leftrightarrow [\mathrm{OEPRhH^{\bullet}C}{<}\!\!\!{-}])$$

$$\mathrm{OEPRh^{II\bullet}} + ([\mathrm{OEPRh^{\bullet}HC}{<}\!\!\!{-}] \leftrightarrow [\mathrm{OEPRhH^{\bullet}C}{<}\!\!\!{-}]) \rightarrow \mathrm{OEPRh\text{-}C}{<}\!\!\!{-} + \mathrm{RhOEP(H)}$$

$$\mathrm{OEPRh(H)} \rightleftarrows \tfrac{1}{2}(\mathrm{OEPRh})_2 + \tfrac{1}{2}\mathrm{H_2}$$

Absence of a β-hydrogen in the benzylic derivatives allows observation of the organometallic by promoting kinetic stability. Our primary goal is to demonstrate the feasibility of establishing catalytic reactions of C—H bonds. A photocatalytic cycle corresponding to homolytic cleavage of the C—H bond can be established for the specific systems reported in this study. Thermal catalytic cycles can be visualized for systems where the organometallic intermediate either has a weaker M—C bond or is capable of β-hydride elimination. Reactions of $(\mathrm{RhOEP})_2$ with hydrocarbons capable of manifesting these two types of behavior are presently being evaluated.

$$\mathrm{C_6H_5CH_3} + (\mathrm{RhOEP})_2 \rightarrow \mathrm{RhOEP(H)} + \mathrm{RhOEP(CH_2C_6H_5)}$$

$$\mathrm{RhOEP(H)} \rightleftarrows \tfrac{1}{2}(\mathrm{RhOEP})_2 + \tfrac{1}{2}\mathrm{H_2}$$

$$\mathrm{RhOEP(H)} \xrightarrow{h\nu} \tfrac{1}{2}(\mathrm{RhOEP})_2 + \mathrm{H^{\bullet}}$$

$$\mathrm{RhOEP(CH_2C_6H_5)} \xrightarrow{h\nu} \tfrac{1}{2}(\mathrm{RhOEP})_2 + \mathrm{C_6H_5CH_2}\cdot$$

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