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J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/ja3047415 • Publication Date (Web): 28 Jun 2012

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Catalytic Carbon-Carbon σ-Bond Hydrogenation with Water Catalyzed by Rhodium Porphyrins

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Supporting Information Placeholder

ABSTRACT: The catalytic carbon-carbon σ-bond activation and hydrogenation of [2.2]paracyclophane with water in neutral reaction medium is demonstrated. The hydrogen from water is transferred to the hydrocarbon to furnish hydrogen enrichment in good yields.

Selective intermolecular, catalytic carbon-carbon activation[1] (CCA) with transition metal complexes is challenging. Despite the generally weaker carbon-carbon bond than the carbon-hydrogen bond, carbon-hydrogen activation[2] (CHA) occurs predominantly due to the statistically more abundant and sterically more accessible natures of C-H bonds in organic compounds.[3] Examples of successful stoichiometric CCA in homogenous solutions take advantages of ring strain relief,[4a,b] chelation assistance[1b] or photochemical activation.[4c] Similar strategies are also employed to the catalytic CCA of strained carbonyls[5] or simple carbonyls assisted with chelation.[6] Hydrogenolysis of C-C bond catalyzed by transition metals has also been reported.[7] However, these examples are limited to functionalized substrates.

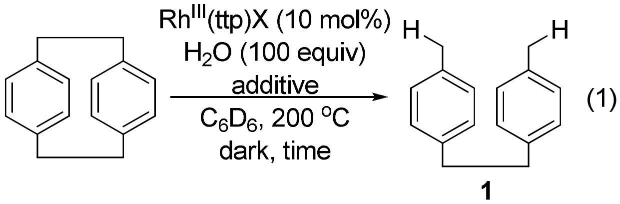
Replacing the hydrogen gas with water as the hydrogen donor in hydrogenation process is benefited from the reduced cost and the safety issue. When coupled with the CCA of hydrocarbon, catalytic hydrogenation of carbon-carbon σ-bond in neutral medium can be achieved (Scheme 1).

Recently, we have reported the stoichiometric CCA of cyclooctane,[8] and water splitting by Rh^{II} porphyrin.[9] We like to couple these two reactions for the catalytic carbon-carbon σ-bond hydrogenation with water to provide hydrogen enriched fuels. Herein, we report our initial success using [2.2]paracyclophane (PCP) as the organic substrate.

Scheme 1. Catalytic Hydrogenation of Carbon-Carbon σ-Bond using Water

$$\text{R-R'} + H_2O \xrightarrow{\text{catalyst}} \text{R-H} + \text{R'-H} + 1/2O_2$$

Table 1. Catalytic Carbon-Carbon Bond Hydrogenation of PCP with Water



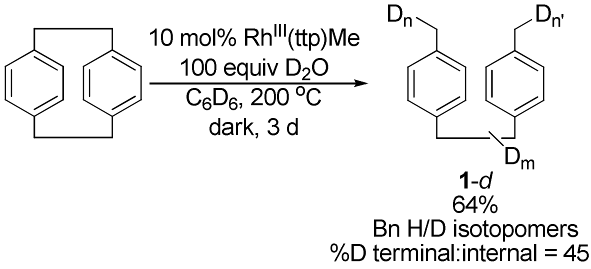
1

Entry	X	Additive	Time / h	Yield **1** / %
1	I	KOH (1 equiv)	25	83
2[a]	Me	--	54	78

[a] 79% CH_4 was formed w.r.t. Rh^{III}(ttp)Me.

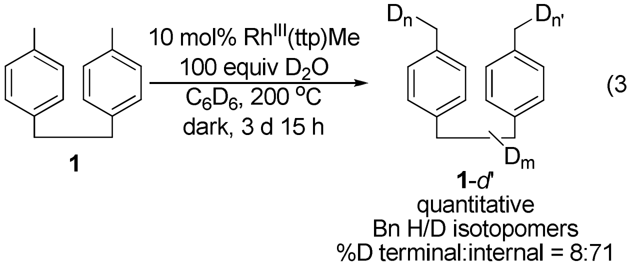
Initially, a benzene-d_6 solution of PCP, in the presence of H_2O, was reacted in the dark[10] with Rh^{III}(ttp)I and KOH as a convenient source of Rh^{II}(ttp) via the Rh^{III}(ttp)OH intermediate, which undergoes rapid elimination to give H_2O_2 as well.[9] Surprisingly, no benzylic CHA product of PCP was obtained.[11] Instead, PCP was catalytically converted to 4,4'-dimethylbibenzyl **1** in 83% yield (Table 1, eq 1, entry 1). The benzylic carbon-carbon σ-bond of PCP was catalytically hydrogenated. As Rh^{III}(ttp)Me can undergo hydrolysis in neutral conditions to give Rh^{III}(ttp)OH, which rapidly gives Rh^{II}_2(ttp)$_2$,[12] we tested its catalytic ability as well. To our delight, PCP was catalytically hydrogenated to give 78% yield of **1** in 54 h in neutral conditions when 10 mol% of Rh^{III}(ttp)Me was used (Table 1, eq 1, entry 2).[13] 79% yield of CH_4 was also detected by ^1H NMR spectroscopy. The hydrolysis of Rh^{III}(ttp)Me to Rh^{III}(ttp)OH was further ascertained.

To test whether water is the hydrogen source, labeling experiments using D_2O were carried out. In a benzene-d_6 solution with excess D_2O and 10 mol% of Rh^{III}(ttp)Me, PCP was catalytically converted to deuterium enriched **1**-*d* in 64% yield in 3 d (eq 2). ^1H NMR analysis of **1**-*d* confirmed the deuterio percentage at the terminal and internal benzylic positions were 45% and 47%, respectively.



(2)

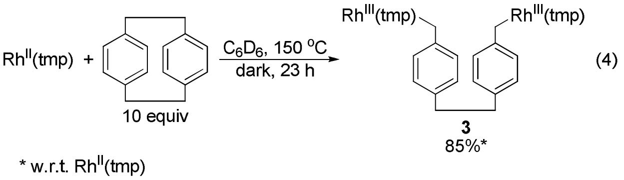
The deuterium incorporation via exchange of D_2O with terminal benzylic hydrogens of **1** was very minor. As a control experiment, when **1** was heated with 10 mol% of Rh^{III}(ttp)Me and excess D_2O to produce a deuterium enriched **1**-*d*', only 8% of the terminal benzylic hydrogens underwent deuterium exchange in a long reaction time over 3 d (eq 3). The extensive benzylic H/D exchanges at the internal positions were much faster as reported in the more rapid benzylic CHA in $PhCH_2CH_3$ by Wayland.[14] Therefore, water was confirmed to be the hydrogen source for the catalytic hydrogenolysis of PCP to **1**.



(3)

To investigate whether benzylic CHA is an intermediate for benzylic CCA of PCP,[15] the reaction of PCP with Rh^{III}(ttp)Cl, KOH and D_2O in benzene-d_6 at lower reaction temperatures were closely monitored by ^1H NMR spectroscopy (SI, Table S1, eq S1, Figure S1). Initially, Rh^{III}(ttp)Cl was completely consumed to give 71% yield of $Rh^{II}_2(ttp)_2$ only after heating at 60 °C for 4 d and 120 °C for 8 d. When the temperature was further raised to 130 °C, benzylic CCA of PCP began to occur slowly to afford 6% of the di-rhodium benzyl **2** (Scheme 2) in 1 d, which was confirmed structurally by an independent synthesis of **2** (SI, eq S2). No benzylic CHA products were observed even with ~0.4 mM $Rh^{II}_2(ttp)_2$ existing in the reaction mixture, which should be very reactive towards benzylic hydrogens. Moreover, the ratio of the benzylic protons to the aromatic protons of PCP remained unchanged. These observations suggested that benzylic CCA of PCP occurred directly without passing through any CHA intermediate.

To gain further knowledge on the benzylic CCA step of PCP with rhodium porphyrins by kinetic studies, the monomeric Rh^{II}(tmp) was chosen to react with PCP, without the complication due to the thermal equilibrium of $Rh^{II}_2(ttp)_2$ with Rh^{II}(ttp).[16] Rh^{II}(tmp) reacted smoothly with PCP at 150 °C for 23 h to yield 85% of **3** (eq 4), establishing the high yielding stoichiometric reaction.



(4)

The kinetic studies of reaction 4 were conducted at $[Rh^{II}(tmp)]$ = 0.24–0.48 mM, [PCP] = 4.8–14.4 mM, temperatures of 140–170 °C and monitored by ^1H NMR spectroscopy. With at least 20-fold excess of PCP, the disappearance of Rh^{II}(tmp) exhibited pseudo second order kinetics over at least 4 half-lives (Figure 1). The rate of disappearance of Rh^{II}(tmp) increased with increasing [PCP] from 4.8 mM to 14.4 mM, giving a linear pseudo first order kinetic plot (Figure 2). The kinetic measurements indicated an overall third order reaction, with second order in Rh^{II}(tmp) and first order in PCP. Therefore, the rate of reaction can be expressed as rate = $k_{obs}[Rh^{II}(tmp)]^2[PCP]$.

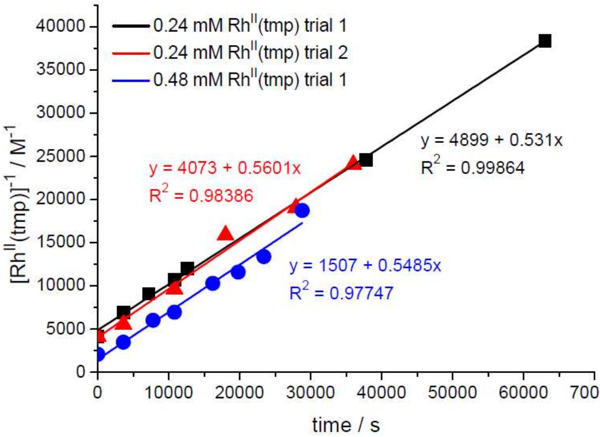


Figure 1. Second order kinetic plots for the reactions of Rh^{II}(tmp) with 9.6 mM PCP in C_6D_6 at 150 °C.

Analysis of the temperature dependent rate constants (140-170 °C) yielded the activation parameters $\Delta H^{\ddagger}$ = 37.9±4.7 kcal mol^{-1}, $\Delta S^{\ddagger}$ = 38.4±11.1 cal mol^{-1} K^{-1} and $\Delta G^{\ddagger}$ = 21.7±4.7 kcal mol^{-1} (Figure 3). The $\Delta H^{\ddagger}$ agrees very well with that of the thermal ring-opening of PCP at 188 °C measured by Roth et al ($\Delta H^{\ddagger}$ = 37.7±0.5 kcal mol^{-1}).[17] Hence, the benzylic CCA of PCP occurs via the carbon-carbon bond homolysis. The positive and large magnitude of $\Delta S^{\ddagger}$ suggests a dissociative nature of the transition state. The second order dependence of Rh^{II}(tmp) indicates a possible formation of a compact encounter complex between two Rh^{II}(tmp) and a PCP molecules prior to the carbon- carbon bond cleavage.[18,19]

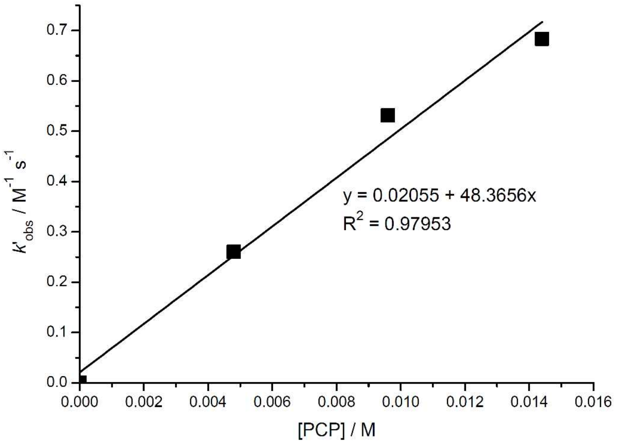


Figure 2. Plot of k'_{obs} against [PCP]. [Rh^{II}(tmp)] = 0.24 mM, [PCP] = 4.8-14.4 mM.

Based on the above findings, scheme 2 illustrates the proposed catalytic cycle. Rh^{III}(ttp)OH is first generated by ligand substitution of Rh^{III}(ttp)I with KOH,[9] or hydrolysis of Rh^{III}(ttp)Me with H_2O.[12] At 200 °C, Rh^{III}(ttp)OH is unstable and rapidly decomposes to produce Rh^{II}(ttp) and H_2O_2. H_2O_2 rapidly disproportionates to give H_2O and O_2.[20] Two Rh^{II}(ttp) combine to form $Rh^{II}_2(ttp)_2$ as a non-productive equilibrium. PCP reacts productively with Rh^{II}(ttp) to furnish benzylic CCA with the formation of **2**. Subsequently, hydrolysis of **2** with H_2O completes the hydrogenation process to give **1** and Rh^{III}(ttp)OH is thus recycled for the catalysis. This process is supported by the hydrolysis of Rh^{III}(ttp)Bn to give toluene in 66% yield as a model study (eq 5).

$$\begin{array}{ccccccc} \mathrm{Rh^{III}(ttp)Bn} & \xrightarrow[\text{200 °C, dark, 3.5 d}]{\text{1000 equiv H}_2\text{O, benzene-}d_6} & \mathrm{PhCH_3} & + & \mathrm{Rh^{III}(ttp)H} & + & \text{Rh porphyrin unknowns} \\ 2\% & & 66\% & & 15\% & & 41\% \end{array} \quad (5)$$

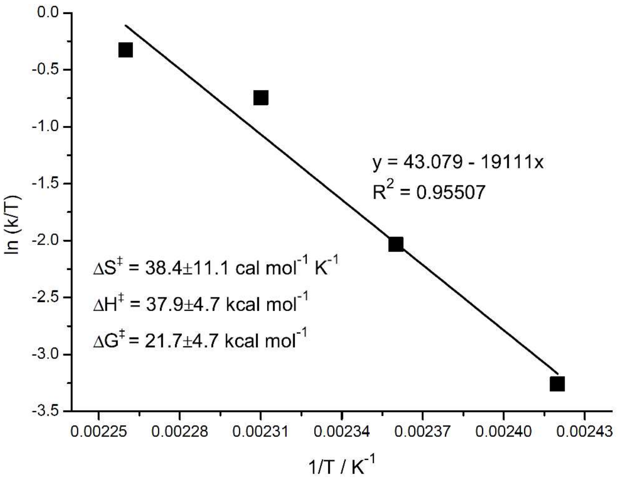
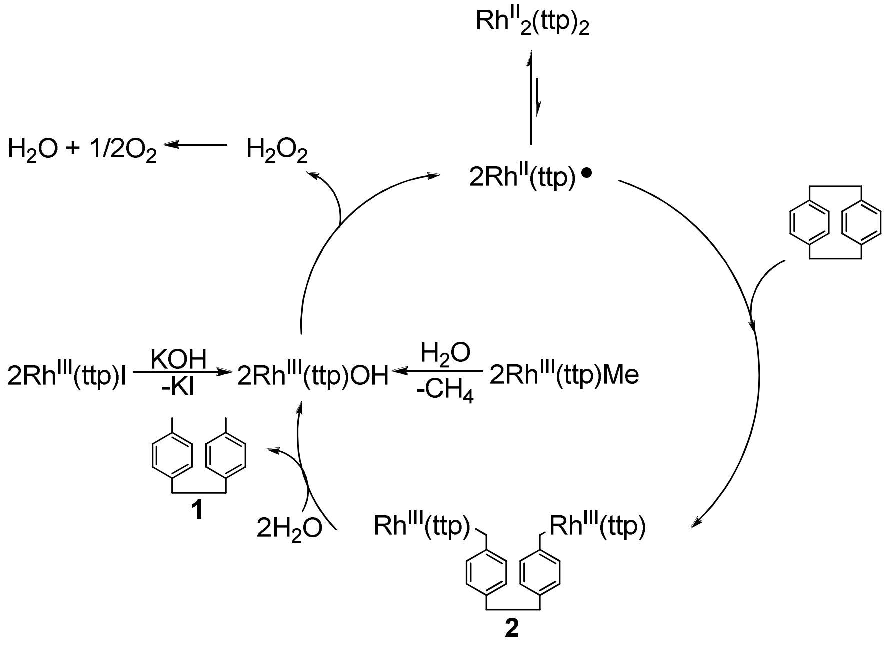


Figure 3. Determination of activation parameters for the reactions of Rh^{II}(tmp) with PCP in C_6D_6 at 140-170 °C. [Rh^{II}(tmp)] = 0.24 mM, [PCP] = 9.6 mM.

In summary, the catalytic carbon-carbon σ-bond activation and hydrogenation of PCP with water is demonstrated. The hydrogen from water is transferred to the hydrocarbon. Further studies are ongoing.

Scheme 2. Proposed Catalytic Cycle.



ASSOCIATED CONTENT

Supporting Information.
Experimental procedures, kinetic data, ^{1}H NMR and mass spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

We thank the Direct Grant of Chinese University of Hong Kong for financial support.

ABBREVIATIONS

PCP, [2.2]paracyclophane; ttp, tetratolylporphyrinato dianion; tmp, tetramesitylporphyrinato dianion.

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Graphical Abstract: