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

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Supporting Information

ABSTRACT: The catalytic carbon−carbon σ-bond activation and hydrogenation of [2.2]paracyclophane with water in a 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 fact that carbon−carbon bonds are generally weaker than carbon−hydrogen bonds, carbon−hydrogen activation[2] (CHA) occurs predominantly because of the statistically more abundant and sterically more accessible natures of C−H bonds in organic compounds.[3] Examples of successful stoichiometric CCA in homogeneous solutions take advantage of ring strain relief,[4a,b] chelation assistance,[1b] or photochemical activation.[4c] Similar strategies have also been employed to achieve catalytic CCA of strained carbonyls[5] or simple carbonyls assisted by chelation.[6] Hydrogenolysis of C−C bonds catalyzed by transition metals has also been reported.[7] However, these examples are limited to functionalized substrates.

Replacing hydrogen gas with water as the hydrogen donor in hydrogenation processes would be beneficial because of the reduced cost and increased safety. When coupled with the CCA of hydrocarbons, catalytic hydrogenation of carbon−carbon σ-bonds in neutral media can be achieved (Scheme 1).

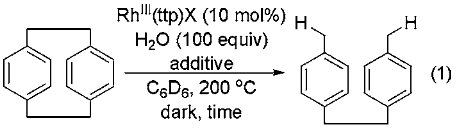
Scheme 1. Catalytic Hydrogenation of Carbon−Carbon σ-Bonds Using Water

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

We recently reported the stoichiometric CCA of cyclooctane[8] and water splitting by rhodium(II) porphyrin.[9] We envisioned that these two reactions could be coupled to achieve 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.

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 (ttp = tetratolylporphyrinato dianion) 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 (eq 1 and Table 1, entry 1). The benzylic carbon−carbon σ-bond of PCP was catalytically hydrogenated. As Rh^{III}(ttp)Me can undergo hydrolysis under 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 a 78% yield of **1** in 54 h under neutral conditions when 10 mol % Rh^{III}(ttp)Me was used (eq 1 and Table 1, entry 2).[13] A 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.

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



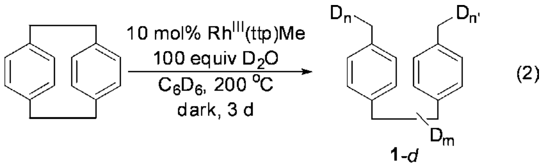
(1)

1

entry	X	additive	time/h	yield of **1** (%)
1	I	KOH (1 equiv)	25	83
2[a]	Me	−	54	78

[a] A 79% yield of CH_4 with respect to Rh^{III}(ttp)Me was formed.

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



(2)

1-*d*
64%
Bn H/D isotopomers
%D terminal:internal = 45:47

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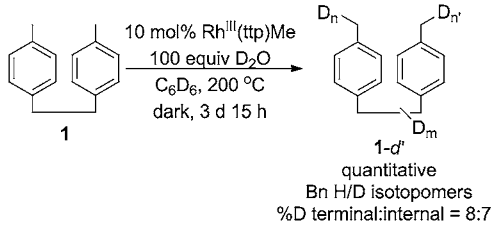
Deuterium incorporation via exchange of D_2O with the terminal benzylic hydrogens of **1** was very minor. As a control experiment, when **1** was heated with 10 mol % Rh^{III}(ttp)Me and excess D_2O to produce deuterium enriched **1**-*d*′, only 8% of the terminal benzylic hydrogens underwent deuterium exchange during a long reaction time of over 3 days (eq 3).

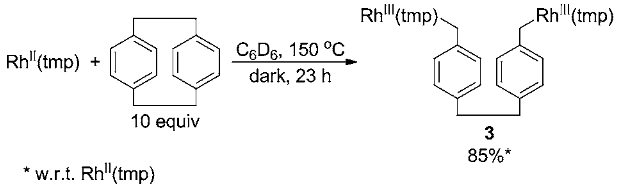


(3)

The extensive benzylic H/D exchanges at the internal positions were much faster, as in the more rapid benzylic CHA in $PhCH_2CH_3$ reported by Wayland.[14] Therefore, water was confirmed to be the hydrogen source for the catalytic hydrogenolysis of PCP to **1**.

To investigate whether benzylic CHA is an intermediate for benzylic CCA of PCP,[15] the reactions 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 [Table S1, eq S1, and Figure S1 in the Supporting Information (SI)]. Initially, Rh^{III}(ttp)Cl was completely consumed to give a 71% yield of $Rh^{II}_2(ttp)_2$ only after heating at 60 °C for 4 days and 120 °C for 8 days. When the temperature was further raised to 130 °C, benzylic CCA of PCP began to occur slowly, after 1 day affording a 6% yield of dirhodium benzyl **2** (Scheme 2), whose structure was confirmed by an independent synthesis (eq S2). No benzylic CHA products were observed even when the reaction mixture included ~0.4 mM $Rh^{II}_2(ttp)_2$, which should be very reactive toward 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 about the benzylic CCA step of PCP with rhodium porphyrins by kinetic studies, monomeric Rh^{II}(tmp) (tmp = tetramesitylporphyrinato dianion) was chosen to react with PCP, avoiding 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 give an 85% yield 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, and T = 140−170 °C and monitored by ^1H NMR spectroscopy. With at least a 20-fold excess of PCP, the disappearance of Rh^{II}(tmp) exhibited pseudo-second-order kinetics over at least four half-lives (Figure 1). The rate of disappearance of Rh^{II}(tmp) increased with increasing [PCP] from 4.8 to 14.4 mM, giving a linear pseudo-first-order kinetic plot (Figure 2).

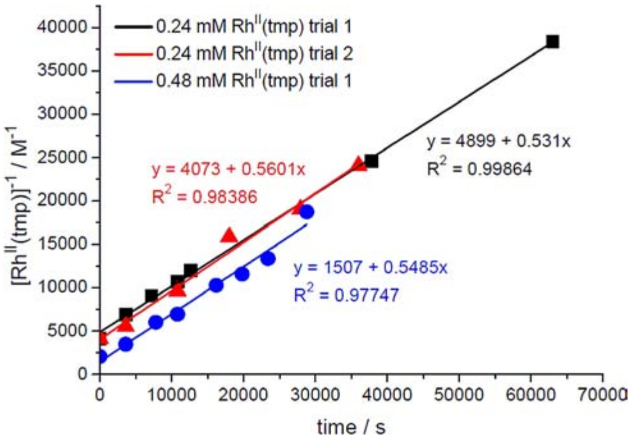


Figure 1. Second-order kinetic plots for the reactions of Rh^{II}(tmp) at various concentrations with 9.6 mM PCP in C_6D_6 at 150 °C.

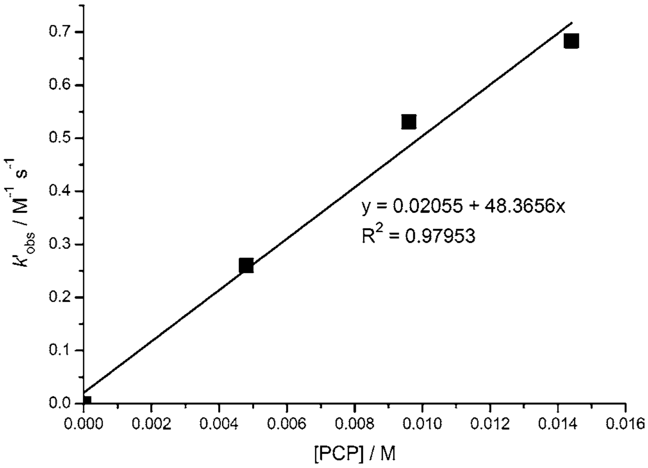


Figure 2. Plot of k'_{obs} against [PCP] for reactions with [Rh^{II}(tmp)] = 0.24 mM and [PCP] = 4.8−14.4 mM.

The kinetic measurements indicated an overall third-order reaction, second-order in Rh^{II}(tmp) and first-order in PCP. Therefore, the rate of reaction can be expressed as rate = $k_{obs}[Rh^{II}(tmp)]^2[PCP]$.

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

On the basis of the above findings, the catalytic cycle shown in Scheme 2 is proposed. 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 molecules of Rh^{II}(ttp) combine to form $Rh^{II}_2(ttp)_2$ as a nonproductive equilibrium. PCP reacts productively with

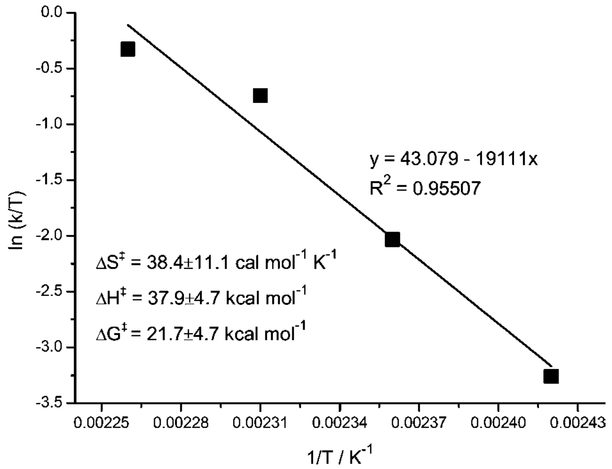
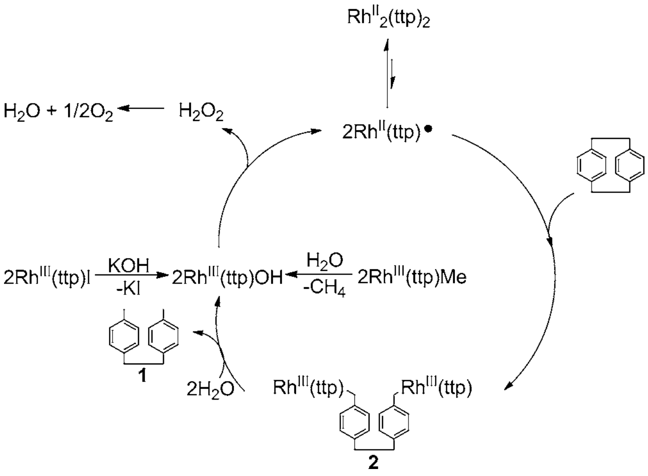
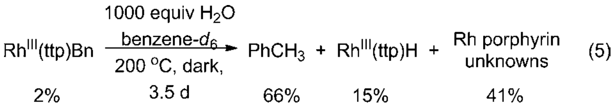


Figure 3. Determination of the activation parameters for the reactions of Rh^{II}(tmp) with PCP in C_6D_6 at 140–170 °C with [Rh^{II}(tmp)] = 0.24 mM and [PCP] = 9.6 mM.

Scheme 2. Proposed Catalytic Cycle



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 regenerates the Rh^{III}(ttp)-OH catalyst. This process is supported by the hydrolysis of Rh^{III}(ttp)Bn to give toluene in 66% yield in a model study (eq 5).



$$\underset{2\%}{Rh^{III}(ttp)Bn} \xrightarrow[\text{200 °C, dark, 3.5 d}]{\text{1000 equiv } H_2O,\ \text{benzene-}d_6} \underset{66\%}{PhCH_3} + \underset{15\%}{Rh^{III}(ttp)H} + \underset{41\%}{\begin{matrix}\text{Rh porphyrin}\\ \text{unknowns}\end{matrix}} \qquad (5)$$

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

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, kinetic data, and ^{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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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(10) The catalytic hydrogenation was retarded in a control experiment performed under light conditions. Therefore, photochemical carbon–carbon bond cleavage does not occur. For details, see the SI.

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(18) Alternatively, the thermolysis of the benzylic C–C bond of PCP generates the bisbenzylic radical.

(19) For examples of four-centered transition states, see: (a) Sherry, A. E.; Wayland, B. B. *J. Am. Chem. Soc.* **1990**, *112*, 1259–1261. (b) Wayland, B. B.; Ba, S.; Sherry, A. E. *J. Am. Chem. Soc.* **1991**, *113*, 5305–5311. (c) Wayland, B. B.; Ba, S.; Sherry, A. E. *Inorg. Chem.*

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