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Visible Light Promoted Hydration of Alkynes Catalyzed by Rhodium(III) Porphyrins

Xu Liu, Lianghui Liu, Zikuan Wang and Xuefeng Fu*

Visible light promoted hydration of a wide scope of alkynes to ketones catalyzed by rhodium(III) porphyrin complexes was described. The key intermediate β-carbonyl alkyl was observed and independently synthesized. The rate of the photolysis is over two orders of magnitude faster than that of the thermal process.

Hydration of alkynes provides a perfect approach for synthesis of carbonyl compounds with 100% atom efficiency. Mercury(II) salt catalyzed hydration of acetylene was used to produce acetaldehyde and acetic acid before 1970s which gradually became obsolete due to the toxicity of mercurial waste. Recently, replacement of mercury by more efficient metal catalysts has been developed, such as Ag, Au, Cu, Co, Fe, In, Ir, Pd, Pt, Rh, Ru, and Sn-W. The metal ketonyl complexes were generally suggested as the key intermediates and the cleavage of the metal-carbon bonds might be the rate determining step (eq 1).

\[
\begin{align*}
R & \xrightarrow{M^{III}, H_2O} R \xrightarrow{H^+} \text{key intermediate} & \xrightarrow{M^{III}} R \xrightarrow{O} (1)
\end{align*}
\]

Our group has accomplished aerobic oxidation of alkynes to ketones in water catalyzed by porphyrin rhodium(III). Mechanistic studies indicated that β-hydroxy alkyl rhodium porphyrins were the key intermediate and the β-carbonyl alkyl rhodium porphyrins were side products which interrupted the catalytic cycle. However, it is worth noting that reactions of porphyrin rhodium(III) with alkynes might produce the β-carbonyl alkyl rhodium porphyrins, the key intermediate for hydration of alkynes, through the same pathway as the reaction with alkynes (eq 2) but without forming β-hydroxy alkyl rhodium porphyrins.

\[
\begin{align*}
R & \xrightarrow{(\text{por})Rh^{III}} R & \xrightarrow{\text{por}OH} R \xrightarrow{\text{H}_2O} R (2)
\end{align*}
\]

More importantly, if the β-carbonyl alkyl rhodium porphyrins could be converted to porphyrin rhodium (III) and ketone, catalytic hydration of alkynes with 100% atom efficiency will be obtained. Thus, the most challenging step is the hydration of the Rh-C bond in (por)Rh-CH₂C(O)R complex to form CH₃C(O)R and (por)Rh-OH.

Although migration-insertion reaction or reductive elimination reaction, typical product formation pathway for organometallic catalytic systems, is usually unfavourable for the planar aromatic metal ligand, our recent study in catalytic hydroxylation of a Si-C(sp³) bond by porphyrin rhodium(III) in water indicated that irradiation with visible light triggered the hydration of Rh-C bonds to form Rh-OH and alkanes, which afforded a novel strategy to accomplish unusual catalytic processes. The hydrogenation of alkynes was achieved at room temperature under visible light irradiation. And 10% yield of acetophenone was observed (Table 1, entry 1) after 12h irradiation of the methanol solution containing 0.2 mmol of phenylacetylene and 2 μmol of (TSPP)Rh³⁺ in acidic conditions ([HCl] = 0.01 mol/L). The yield increased to 38% with addition of one equivalent of H₂SO₄.
instead of HCl (Table 1, entry 2). Various organic acids including benzene sulfonic acid, trifluoromethane sulfonic acid, methanesulfonic acid and trifluoromethane sulfonimide were tested, and trifluoromethane sulfonimide showed the highest selectivity (Table 1, entry 3-6). Control experiments indicated that acid, (TSPP)Rh\(^{3+}\) and light were all necessary (Table 1, entry 1, 7-8).

Table 1. Visible Light Promoted Hydration of Phenylacetylene Catalyzed by (TSPP)Rh\(^{3+}\) at Room Temperature

<table>
<thead>
<tr>
<th>entry</th>
<th>Acid</th>
<th>conversion(^b)</th>
<th>yield(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1eq H(_2)SO(_4)</td>
<td>39%</td>
<td>10%</td>
</tr>
<tr>
<td>2</td>
<td>30 mol% PhH(_2)SO(_3)</td>
<td>76%</td>
<td>38%</td>
</tr>
<tr>
<td>3</td>
<td>10 mol% CF(_3)SO(_3)H</td>
<td>96%</td>
<td>57%</td>
</tr>
<tr>
<td>4</td>
<td>30 mol% CH(_2)(_2)(_2)SO(_3)H</td>
<td>100%</td>
<td>69%</td>
</tr>
<tr>
<td>5</td>
<td>30 mol% CF(_3)(_2)SO(_3)H</td>
<td>100%</td>
<td>70%</td>
</tr>
<tr>
<td>6</td>
<td>30 mol% CF(_3)(_2)(_2)SO(_3)H</td>
<td>100%</td>
<td>77%</td>
</tr>
<tr>
<td>7</td>
<td>30 mol% (CF(_3)(_2)SO(_3)H</td>
<td>21%</td>
<td>2%</td>
</tr>
<tr>
<td>8</td>
<td>30 mol% (CF(_3)(_2)(_2)SO(_3)H</td>
<td>7%</td>
<td>0%</td>
</tr>
</tbody>
</table>

\(^b\)Reaction conditions: phenylacetylene 0.20 mmol, (TSPP)Rh\(^{3+}\) 0.01 mol/L at 60 °C for 48 hours resul

Subsequently, the reaction mechanism was investigated. According to previous observations, the first step in catalytic hydration of alkynes could be the reactions of porphyrin rhodium(III) with alkynes producing the β-carbonyl alkyld rhodium porphyrins through the same pathway in analogous to the reaction of (TSPP)Rh\(^{3+}\) complex with olefins to produce β-methoxalkyl complexes.\(^{16a}\)

Heating the methanol solution containing 0.2 mmol of phenylacetylene and 2 μmol of (TSPP)Rh\(^{3+}\) in acidic conditions ([HCl] = 0.01 mol/L) at 60 °C for 48 hours resulted in the formation of (TSPP)Rh-CH\(_2\)COPh with a yield of 50%. When performed in methanol-\(^d\) solution, (TSPP)Rh-CD\(_2\)COPh was obtained and confirmed by ESI-MS (Figure 1S). The (TSPP)Rh-CH\(_2\)COPh was also independently prepared by reaction of (TSPP)Rh\(^{3+}\) with PhCOCH\(_2\)Br (eq 5 and Figure 3S).

Table 2. Scope of the Alkyne Substrates

<table>
<thead>
<tr>
<th>entry</th>
<th>substrate</th>
<th>product</th>
<th>conversion(^b)</th>
<th>yield(^b)</th>
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<tbody>
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<td>1</td>
<td></td>
<td>[O]</td>
<td>99%</td>
<td>77%</td>
</tr>
<tr>
<td>2</td>
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<td>[O]</td>
<td>100%</td>
<td>73%</td>
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<tr>
<td>3</td>
<td></td>
<td>[O]</td>
<td>100%</td>
<td>80%</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>[O]</td>
<td>100%</td>
<td>80%</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>[O]</td>
<td>100%</td>
<td>81%</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>[O]</td>
<td>95%</td>
<td>80%</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>[O]</td>
<td>100%</td>
<td>83%</td>
</tr>
<tr>
<td>8</td>
<td>n-C(_4)H(_9)</td>
<td>[O]</td>
<td>100%</td>
<td>69%</td>
</tr>
<tr>
<td>9</td>
<td>n-C(_5)H(_11)</td>
<td>[O]</td>
<td>100%</td>
<td>64%</td>
</tr>
</tbody>
</table>

\(^b\)Reaction conditions: alkyne 0.20 mmol, (TSPP)Rh\(^{3+}\) 2 mmol and methanol 1 ml, stirred at room temperature under visible light irradiation (500 W Hg lamp, 420-780 nm filter, 25 cm distance, 27 mW/cm\(^2\)) for 12 hours. \(^c\)GC results.

Figure 1. A: Photo production of ketonyl from (TSPP)Rh-CH\(_2\)COPh complex at various pH value; ▼: pH ~ 6.5, \(k_{\text{obs.}} = 0.00143 \text{ s}^{-1}\); ▲: pH ~ 4.5, 298 K, \(k_{\text{obs.}} = 0.00172 \text{ s}^{-1}\); △: pH ~ 3.5, \(k_{\text{obs.}} = 0.00239 \text{ s}^{-1}\); ◇: pH ~ 1.2, \(k_{\text{obs.}} = 0.0497 \text{ s}^{-1}\); B: Thermal and photo production of ketonyl from (TSPP)Rh-CH\(_2\)COPh complex; ▼: pH ~ 1.2, dark, \(k_{\text{obs.}} = 7.94 \times 10^{-12} \text{ s}^{-1}(0.286 \text{ h})\); ▲: pH ~ 1.2, visible light, \(k_{\text{obs.}} = 0.0497 \text{ s}^{-1}\).
In acidic methanol-d₈ solution (pH=6.5), (TSPP)Rh₂CH₂COPh was completely converted to acetophenone and (TSPP)Rh³⁺ at 298 K within 20 min under visible light irradiation (500 W Hg lamp, 420-780 nm filter, 25 cm distance, 27mW/cm²) (Figure 1A). The rate enhancement was observed with the increase of proton concentration, 50 seconds to reach completion at pH= 1.2 under visible light irradiation in comparison to without the irradiation of visible light which took 8 hours to reach completion at pH= 1.2 (Figure 1B). The photo irradiation largely enhanced the rate of Rh-C bond cleavage, and the photo irradiation process was much more efficient than that of thermal process for the hydration of Rh-C bonds. All of these reactions showed first-order kinetics on the (TSPP)Rh₂CH₂COPh and the rate constants were listed in Figure 1.

The hydration of alkynes catalyzed by (TSPP)Rh³⁺ was envisioned to proceed through a four-step process: a) coordination of alkynes to (TSPP)Rh³⁺(MeOH)₂ which was the dominant species at pH<3,²⁰ and then methanol functioned as the nucleophile to attack the alkynes to form β-acetal alkyl rhodium porphyrins; b) the interconversion between ketone and ketal to give the intermediate (TSPP)Rh₂CH₂COPh; c) photolysis of the (TSPP)Rh₂CH₂COPh complex yielded PhCOCH₃ radical and (TSPP)Rh(II); d) subsequently, (TSPP)Rh(II) reacted with methanol rapidly to produce (TSPP)Rh-H and (TSPP)Rh-OMe to complete the catalytic cycle,²⁰ and meanwhile, hydrogen atom transfer occurred from (TSPP)Rh-H to PhCOCH₃ radical to yield the final product (Scheme 2), completing the catalytic cycle.

Conclusions

In summary, we have, to the best of our knowledge, developed the first catalytic visible light promoted hydration of alkynes. The rhodium ketonyl intermediates were observed and independently prepared which underwent fast photo cleavage of Rh-C bonds in acidic solution to produce ketone products. Combination of alkyne hydration with visible light irradiation provides a green and novel protocol for organometallic catalysis.

Notes and references

16 (a) J. Zhang, S. Li, X. Fu and B. B. Wayland, Dalton Trans., 2009, 3661; (b) J. Zhang, B. B. Wayland, L. Yun, S. Li and X. Fu, Dalton Trans., 2010, 39, 477.