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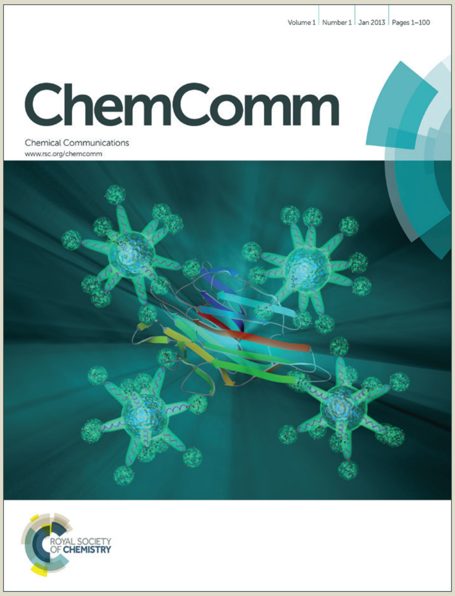

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Visible Light Promoted Hydration of Alkynes Catalyzed by Rhodium(III) Porphyrins

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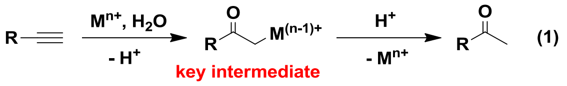
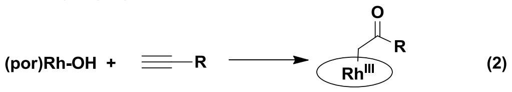
Visible light promoted hydration of a wide scope of alkynes to ketones catalyzed by rhodium(III) porphyrin complexes was described. The key intermediate β-carbonyl alkyl was observed and independently synthesized. The rate of the photolysis is over two orders of magnitude faster than that of the thermal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

Hydration of alkynes provides a perfect approach for synthesis of carbonyl compounds with 100% atom efficiency. [1]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.[2] Recently, replacement of mercury by more efficient metal catalysts has been developed, such as Ag,[3] Au,[4] Co,[5] Fe,[6] In,[7] Ir,[8] Pd,[9] Pt,[10] Rh,[11] Ru,[12] and Sn-W.[13] The metal ketonyl complexes were generally suggested as the key intermediates[14] and the cleavage of the metal-carbon bonds might be the rate determining step (eq 1).



Our group has accomplished aerobic oxidation of alkenes to ketones in water catalyzed by porphyrin rhodium(III).[16] 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 alkenes (eq 2) but without forming β-hydroxy alkyl rhodium porphyrins.[16a].

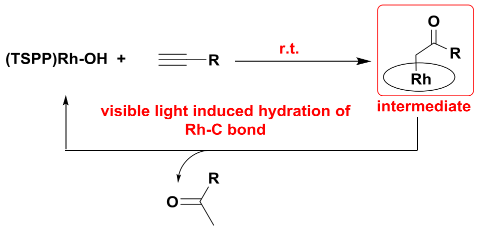


More importantly, if the β-carbonyl alkyl rhodium porphyrins could be converted to porphyrin rhodium (III) and ketone, catalytic hydration of alkynes with 100% atom efficiency will be obtained. Thus, the most challenging step is the hydration of the Rh-C bond in (por)Rh-$CH_2C(O)R$ complex to form $CH_3C(O)R$ 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 N4 ligand, our recent study in catalytic hydroxylation of a Si-C(sp^3) 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 (eq3).[17]

$$\text{(por)Rh-R} + \text{H-OH} \xrightarrow{\text{visible light, r.t.}} \text{(por)Rh-OH} + \text{R-H} \qquad (3)$$

Photo-chemical processes attracted increasing attentions which provide promising pathways to obtain both thermodynamic and kinetic challenging reactions.[18] We turned our attention to photo induced organometallic transformations by taking advantage of porphyrin ligand as a dye through incorporation of valuable organometallic intermediates of organo-metal porphyrin complexes into novel photo catalysis. Herein we report on visible light promoted hydration of alkynes using tetra(p-sulfonatophenyl)porphyrin rhodium(III) ((TSPP)Rh^{III}) as the catalyst where the porphyrin rhodium ketonyl complex (TSPP)Rh-CH_2COPh was observed as the reactive intermediate (Scheme 1).



Scheme 1. (TSPP)Rh^{III} catalyzed hydration of alkynes

The catalytic hydration of phenylacetylene 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)Rh^{III} in acidic conditions ([HCl] = 0.01 mol/L). The yield increased to 38% with addition of one equivalent of H_2SO_4

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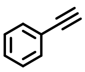
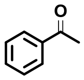
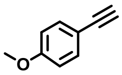
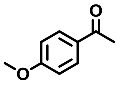
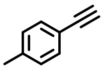
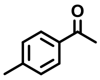
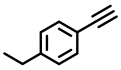
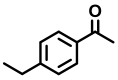
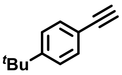
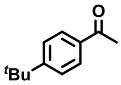
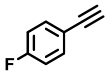
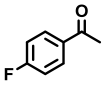
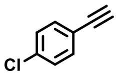
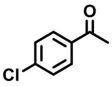
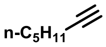
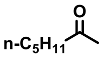
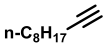
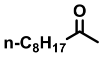
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x instead of HCl (Table 1, entry 2). Various organic acids including benzene sulfonic acid, trifluoromethane sulfonic acid, methanesulfonic acid and trifluoromethane sulfonimide were tested, and trifluoromethane sulfonimide showed the highest selectivity (Table 1, entry 3-6). Control experiments indicated that acid, (TSPP)Rh^{III} and light were all necessary (Table 1, entry 1, 7-8).

Table 1. Visible Light Promoted Hydration of Phenylacetylene Catalyzed by (TSPP)Rh^{III} at Room Temperature[a]

entry	Acid	conversion[b]	yield[b]
1	1eq HCl	39%	10%
2	1eq H_2SO_4	76%	38%
3	30 mol% $PhSO_3H$	96%	57%
4	10 mol% CF_3SO_3H	100%	69%
5	30 mol% CH_3SO_3H	100%	70%
6	30 mol% $(CF_3SO_2)_2NH$	99%	77%
7[c]	30 mol% $(CF_3SO_2)_2NH$	21%	2%
8[d]	30 mol% $(CF_3SO_2)_2NH$	7%	0%

[a]Reaction conditions: phenylacetylene 0.20 mmol and (TSPP)Rh^{III} 2.0 μmol mixing in 1.0 ml methanol, 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. [b]GC results. [c]In the dark. [d]No (TSPP)Rh^{III} was added

Table 2. Scope of the Alkyne Substrates[a]

entry	substrate	product	conversion[b]	yield[b]
1			99%	77%
2			100%	73%
3			100%	83%
4			100%	80%
5			100%	91%
6			95%	80%
7[c]			100%	83%
8[c]			100%	69%
9[c]			100%	64%

[a]Reaction conditions: alkyne 0.20 mmol, (TSPP)Rh^{III} 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. [b]GC results. [c]50°C

Under the optimized reaction conditions, the scope of the alkyne substrates was examined. Phenylacetylene derivatives containing electron rich and electron withdrawing groups on the phenyl ring were all converted to the corresponding methyl ketones (Table 2, entry 1-7). The methoxy, methyl, ethyl and *tert*-butyl group remained stable during the photo reaction (Table 2, entry 2-5). The reactivity of aliphatic alkynes was relatively low so the hydration reaction of 1-heptyne and 1-decyne were performed at 50 °C (Table 2, entry 8-9)

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 alkyl rhodium porphyrins through the same pathway in analogous to the reaction of (TSPP)Rh^{III} complex with olefins to produce β-methoxyalkyl complexes.[16a]

Heating the methanol solution containing 0.2 mmol of phenylacetylene and 2 μmol of (TSPP)Rh^{III} in acidic conditions ([HCl] = 0.01 mol/L) at 60 °C for 48 hours resulted in the formation of (TSPP)Rh-CH_2COPh with a yield of 50%. When performed in methanol-d^4 solution, (TSPP)Rh-CD_2COPh was obtained and confirmed by ESI-MS(Figure 2S). The (TSPP)Rh-CH_2COPh was also independently prepared by reaction of (TSPP)Rh^{I} with $PhCOCH_2Br$ (eq5 and Figure 3S).

$$\mathbf{(TSPP)Rh^{I} + PhCOCH_2Br \xrightarrow[< 5\ min]{RT} (TSPP)Rh\text{-}CH_2COPh + Br^{-} \quad (5)}$$

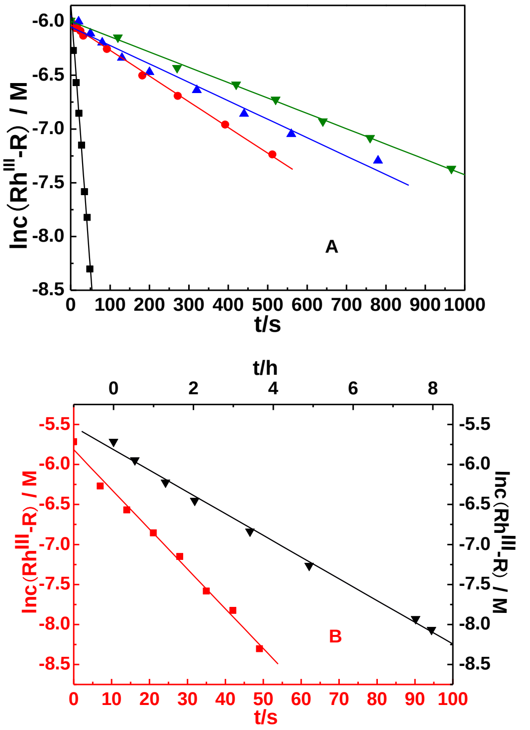
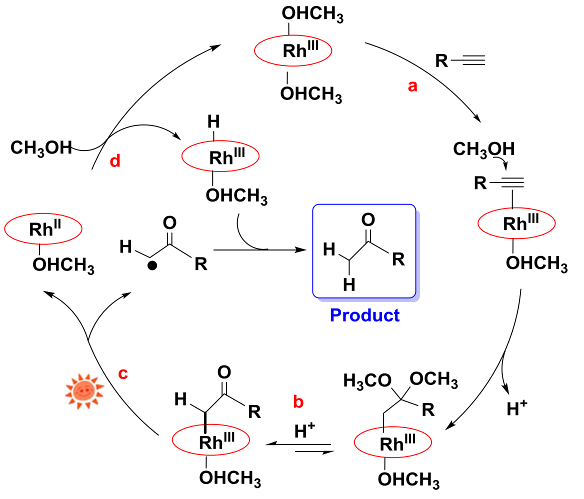


Figure 1. A: Photo production of ketonyl from (TSPP)Rh-CH_2COPh complex at various pH value; ▼: pH ~ 6.5, $k_{obs.}$ = 0.00143 s^{-1}, ▲: pH ~ 4.5, 298 K, $k_{obs.}$ = 0.00172 s^{-1}, ●: pH ~ 3.5, $k_{obs.}$ = 0.00239 s^{-1}, ■: pH ~ 1.2, $k_{obs.}$ = 0.0497 s^{-1}; B: Thermal and photo production of ketonyl from(TSPP)Rh-CH_2COPh complex; ▼: pH ~ 1.2, dark, $k_{obs.}$ =7.94 x 10^{-5} s^{-1}(0.286 h^{-1}),■: pH ~ 1.2, visible light, $k_{obs.}$ = 0.0497 s^{-1}



Scheme 2. Photo induced hydration of alkynes catalyzed by rhodium porphyrin

In acidic methanol-d^4 solution (pH=6.5), (TSPP)Rh-CH_2COPh was completely converted to acetophenone and (TSPP)Rh^{III} at 298 K within 20 min under visible light irradiation (500 W Hg lamp, 420-780 nm filter, 25 cm distance, 27mW/cm^2) (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)Rh-CH_2COPh and the rate constants were listed in Figure 1.

The hydration of alkynes catalyzed by (TSPP)Rh^{III} was envisioned to proceed through a four-step cycle involving: a) coordination of alkynes to (TSPP)Rh^{III}(MeOH)$_2$ which was the dominant species at pH<3,[19] 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)Rh-CH_2COPh; c) photolysis of the (TSPP)Rh-CH_2COPh complex yielded $PhCOCH_2$ 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 $PhCOCH_2$ 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 underwentfast 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.

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