ORGANOMETALLICS
Article
pubs.acs.org/Organometallics

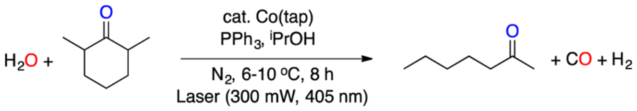
Visible Light Photocatalysis of Carbon−Carbon σ-Bond Anaerobic Oxidation of Ketones with Water by Cobalt(II) Porphyrins

Siu Yin Lee, Hong Sang Fung, Shiyu Feng, and Kin Shing Chan*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, People's Republic of China

S *Supporting Information*

ABSTRACT: Co^{II}(por) (por = porphyrinato dianion) reacted selectively with isopropyl ketones at the carbon (CO)−carbon (α) bond at room temperature to give high yields of Co^{III}(por) acyls and the corresponding oxidized carbonyl compounds in up to 89% yields. Co^{III}(por)OH is proposed to be the C−C bond activation (CCA) intermediate. The stoichiometric reaction is further developed into the photocatalytic CCA using both UV and visible light sources (λ 405 nm). Under ambient conditions, the photocatalytic C−C oxidation of 2,6-dimethylcyclohexanone gives 2-heptanone in up to 24 turnovers in the presence of isopropyl alcohol as the H atom donor and H_2O as the oxidant. Various isopropyl ketones successfully undergo photocatalysis.

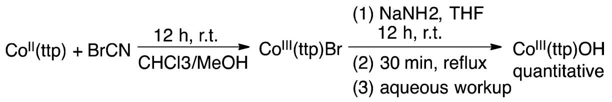


INTRODUCTION

While C−C bond activation (CCA) chemistry using group 9 precious metals such as rhodium and iridium has been widely investigated,[1−5] examples of the economically attractive cobalt are rare. Rhodium(II) and iridium(II) porphyrins are more reactive in forming stronger M−X bond species as either intermediates or products[6−8] and have been much more investigated. Cobalt(II) porphyrins, however, are much less reactive and more challenging in the cleavage of carbon−carbon bonds.[9] Thus, the exploration of cobalt(II) porphyrins to achieve the CCA of ketone is not known and is highly desirable for both fundamental reasons and economical attractiveness.

From the proposed mechanisms for the CCA of ketones by rhodium(II) porphyrins reported recently,[10] it is anticipated that the generation of M^{III}(por)OH is the key to achieve the reaction. Though the preparation of Co^{III}(ttp)OH (ttp = 5,10,15,20-tetratolylporphyrinato dianion) by a two-step synthesis from Co^{II}(ttp) has been reported (Scheme 1),[11] this method is too tedious and could not be reproduced by us. Therefore, the readily available Co^{II}(ttp) was tactically reacted with water in order to generate Co^{III}(ttp)OH and Co^{III}(ttp)H in situ through a formal oxidative addition or activation (eq 1) on the basis of analogous literature examples shown below.[12]

Scheme 1. Preparation of Co^{III}(ttp)OH from Co^{II}(ttp)



$$2Co^{II}(ttp) + H_2O \rightleftharpoons Co^{III}(ttp)OH + Co^{III}(ttp)H \qquad (1)$$

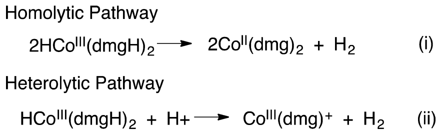
The activation of water with cobalt(II) porphyrin is less developed than that with the rhodium analogue. A few examples include the comparative studies among group 9 metalloporphyrins in aqueous solution reported by Wayland et al.[13] Furthermore, the activation of water by pentacyanocobaltate(II) ($[Co^{II}(CN)_5]^{3-}$) to give an unfavorable equilibrium of $[Co^{III}(CN)_5OH]^{3-}$ and $[Co^{III}(CN)_5H]^{3-}$ is precedented but has been less explored (eq 2).[14] The macrocyclic Co^{II}(pc) (pc = tetrakis(neopentoxy)-phthalocyanine) also reacts with the hydroxide ion to give $[Co^{III}(pc)(OH)_2]^-$ and $[Co^{I}(pc)]^-$ instantly (eq 3). The coproduct, the cobalt(III) hydride, can be recycled back to Co(II) porphyrin via dehydrogenation analogous to the known reaction of cobalt(III) dimethylglyoxime hydride ($HCo(dmgH)_2$) by either a homolytic or heterolytic pathway to give $Co(dmgH)_2$, as reported by the groups of Espenson,[15] Gray[16a] and Peters[16b] (Scheme 2).

$$\begin{aligned} &2Co^{II}(CN)5^{3-} + H_2O \\ &\quad \rightleftharpoons Co^{III}(CN)_5OH^{3-} + Co^{III}(CN)_5H^{3-} \end{aligned} \qquad (2)$$

$$\begin{aligned} &2Co^{II}(pc) + 2OH^- \\ &\quad \xrightarrow[C_6H_4Cl_2, N_2]{\text{instant}} \underset{1}{[Co^{III}(pc)(OH)_2]^-} \underset{:}{+} \underset{1}{[Co^{I}(pc)]^-} \end{aligned} \qquad (3)$$

Cobalt(III) porphyrin hydroxide can exhibit rich chemistry due to the weak metal−oxygen bond that originates from the p_π−d_π repulsion between filled p orbitals of oxygen and d

Scheme 2. Proposed Pathways for H_2 Evolution from Cobalt(III) Glyoxime Hydride



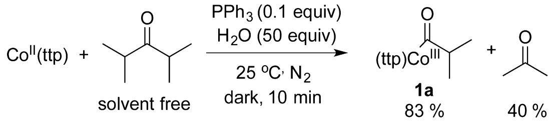
Received: May 9, 2016

DOI: 10.1021/acs.organomet.6b00352

orbitals of cobalt.[17] Herein, we report the novel cobalt(II) porphyrin catalyzed carbon (CO)−carbon (α) bond oxidation of ketones by H_2O assisted by light in either UV or visible light.

■ RESULTS AND DISCUSSION

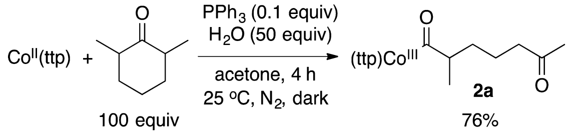
Initially, Co^{II}(ttp), like its Rh analogues,[10] successfully cleaved the C(CO)−C(α) bond of diisopropyl ketone under solvent-free conditions in the presence of PPh_3 at room temperature over 10 min to give Co^{III}(ttp)CO^{i}Pr (**1a**) and acetone in 83% and 40% yields, respectively (eq 4). The observation of acetone



(4)

in the reactions supports the notion that the isobutyryl group is transferred to the cobalt center and the isopropyl fragment is oxidized into a carbonyl moiety. Co^{III}(ttp)OH with or without Ph_3P is likely an intermediate for the stoichiometric CCA process.

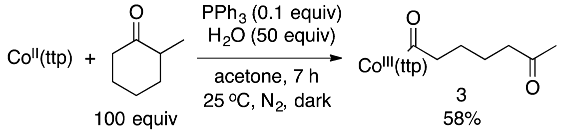
The mild CCA conditions were then applied to other isopropyl ketones. 2,6-Dimethylcyclohexanone reacted with Co^{II}(ttp) at room temperature over 4 h to give a 76% yield of Co^{III}(ttp)COCHMe(CH_2)$_3$COMe (**2a**) (eq 5). The ^{1}H NMR



(5)

signal of Co^{III}(ttp)COCHMe(CH_2)$_3$COMe at 1.72 ppm with three protons suggests the presence of an acetyl group. However, there is only one acyl carbon signal in its ^{13}C NMR spectrum at 208.05 ppm (COMe; see the Supporting Information). The absence of the acyl carbon in the ^{13}C NMR is ascribed to the coupling by the quadrupolar ^{59}Co nucleus (I = 7/2; 100% abundance).[18] Two absorption peaks from the IR spectrum at the carbonyl region (1717 and 1756 cm^{-1}) suggest the presence of two kinds of carbonyl groups (see the Supporting Information). The diastereotopic protons at the γ and δ positions give four distinct proton signals in the ^{1}H NMR spectrum. Peak assignments were done with the help of COSY NMR (see the Supporting Information): Hc (m, −1.59 ppm), Hc′ (m, −1.34 ppm), Hd (m, −1.15 ppm), and Hd′ (m, −0.66 ppm). The structures of Co^{III}(ttp)CO^{i}Pr and Co^{III}(ttp)COCHMe(CH2)$_3$COMe have been firmly established.

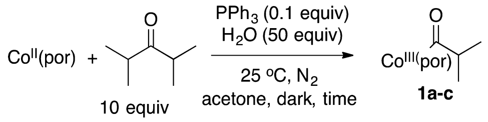
Regioselective CCA occurred at the bulky CO−^{i}Pr bond when 2-methylcyclohexanone was reacted with Co^{II}(ttp) at room temperature for 7 h to give a 58% yield of Co^{III}(ttp)-CO(CH_2)$_4$COMe (**3**) (eq 6). No other CCA product was observed by ^{1}H NMR and GC/MS analysis of the crude reaction mixture.



(6)

We then investigated the porphyrin ligand effect briefly (Table 1). In acetone solvent, both Co(ttp) and Co(tap) (tap = tetrakis(4-anisyl)porphyrin) completely reacted with diisopropyl ketone (10 equiv) within 2 h, while Co(tpclp) (tpclp = tetrakis(4-chlorophenyl)porphyrin) only reacted partially over 3 h to give **1c** in 32% yield (Table 1, entry 3). The more electron rich Co(tap) gave a slightly higher yield of CCA product **1b** in comparison to that of **1a** from Co(ttp) (Table 1, entries 1 and 2). Co(tap) also reacted more quickly than Co(ttp) with a shorter reaction time of 1.5 h. Likely the more electron rich Co^{II}(por) favors the formation of Co^{III}(por)OH (eq 1). Therefore, we chose to carry out the photocatalytic chemistry of Co(tap).

Table 1. Porphyrin Ligand Effect on CCA of Isopropyl Ketone

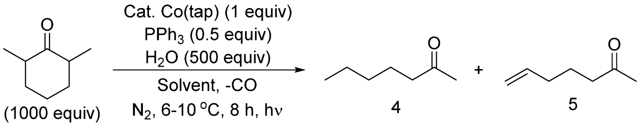


entry	Co(por)	time/h	product, yield of Co(por)CO^{i}Pr/%
1	ttp	2	**1a**, 78
2	tap	1.5	**1b**, 89
3	tpclp	3	**1c**, 32[a]

[a] Co(tpclp) recovered in 40% yield.

Taking advantage of the weak Co(por)−acyl bond,[19] we envisioned that the homolytic bond cleavage could turn the stoichiometric carbon−carbon bond oxidation into catalysis. To our delight, the C(CO)−C(α) bond of 2,6-dimethylcyclohexanone was catalytically cleaved by Co(tap) under photolysis conditions to give 2-heptanone (**4**) and the terminal unsaturated alkyl 2-hept-6-enone **5** in 106% and 40% yields, respectively, on the basis of Co(tap) loading (Table 2, entry 1).

Table 2. Photocatalytic CCA of 2,6-Dimethylcyclohexanone in Different Solvents



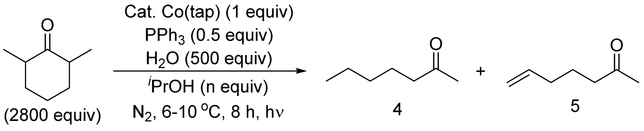
			yield/%		
entry[a]	solvent	dielectric constant[20]	**4**[b]	**5**[b]	Co(tap) recovery/%
1	THF	7.52	106	40	58
2	^{i}PrOH	20.18	26	5	63
3	acetone	21.01	129	29	67
4	MeCN	36.64	17	10	41
5	DMF	38.25	17	15	56
6	none		573	357	72

[a] A 400 W quartz mercury halide lamp was used, with a B+W 67 mm MRC UV filter for cutting off light rays below 350 nm. [b] Based on Co(tap) loading.

On the basis of the findings from the stoichiometric CCA of ketone, Co^{III}(tap)OH was proposed as the key intermediate to cleave the C(CO)−C(α) bond of ketone. To favor the formation and stabilization of Co^{III}(tap)OH, more polar solvents with higher dielectric constants were examined;[20] however, none of them showed very good catalytic efficiency (Table 2). The highest yield of 129% (based on Co(tap) loading) of 2-heptanone was obtained in acetone solvent, but the efficiency was still very low (Table 2, entry 3). Instead, the reaction carried out under solvent-free conditions gave 2-heptanone (**4**) and 2-hept-6-enone (**5**) in much improved yields of 573% and 357%, respectively (Table 2, entry 6). We reason that the higher concentration effect on ketone dominates the catalysis. Therefore, the addition of polar solvent was not beneficial.

To tune the reaction to be more chemoselective toward the more saturated product **4**, a strong hydrogen atom donor was introduced to facilitate the hydrogenation via a likely HAA (HAA = hydrogen atom abstraction) step (see the mechanistic discussion below). To our delight, addition of 20 equiv of isopropyl alcohol successfully improved the selectivity from 62% to 92% (Table 3, entries 1 and 2). Further addition of 50 equiv of ^{i}PrOH resulted in a totally chemoselective photocatalysis. Catalytic CCA on 2,6-dimethylcyclohexanone by $\mathrm{Co^{II}}$(tap) yielded 2-heptanone selectively in 13.2 turnovers (Table 3, entry 3). We do not know the reason for the low selectivity of **4** and **5** when the reaction was conducted in ^{i}PrOH solvent. In view of the lower product yield of **4** and **5**, other side reaction may have occurred such as oxidation of isopropyl alcohol. However, a small amount of isopropyl alcohol (50 equiv) added to the ketone substrate under solvent-free conditions likely did not undergo Co(por) catalyzed photo-oxidation but the higher concentration of ketone substrate underwent more facile carbon−carbon bond cleavage for the yield of the product.

Table 3. Effect of Isopropyl Alcohol on Chemoselectivity



entry[a]	^{i}PrOH/ equiv	TON 4	TON 5	4 selectivity/%[b]	Co(tap) recovery/%
1	0	5.7	3.6	62	72
2	20	10.2	0.9	92	70
3	50	13.2	0	100	71

[a]A 400 W quartz mercury halide lamp was used, with a B+W 67 mm MRC UV filter for cutting off light rays below 350 nm. [b]The percentage of **4** in total conversion of **4** and **5**.

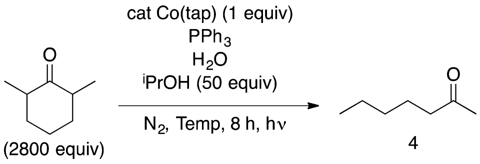
To increase the electron density on Co(tap), a donor ligand PPh_3 was added.[10c,d] While the photocatalysis still proceeded in the absence of PPh_3, a low turnover number of 6.5 was obtained (Table 4, entry 1). Addition of 0.5 equiv of PPh_3 increased the turnover number to 13.2 (Table 4, entry 2). With 1 equiv of PPh_3, only slight improvement in TON was achieved (Table 4, entry 3). Presumably, the competitive though probably slow photo-oxidation of Ph_3P to Ph_3PO becomes more significant with H_2O_2 generated from Co(tap)OH. Indeed, we observed the formation of Ph_3PO after the photocatalysis (Table 4, entry 3).

To shift the equilibrium from $\mathrm{Co^{II}}$(tap) to the proposed intermediate $\mathrm{Co^{III}}$(tap)OH or (Ph_3P)Co(tap)OH (eq 7), the

$$\mathrm{Co^{II}(tap)} + \mathrm{H_2O} \overset{2\mathrm{PPh_3}}{\rightleftharpoons} \mathrm{(Ph_3P)Co^{III}(tap)OH} + \mathrm{(Ph_3P)Co^{III}(tap)H} \qquad (7)$$

water concentrations were varied. Without added water, Co(tap) only slightly catalyzed the photocatalytic CCA of 2,6-dimethylcyclohexanone in 2.8 turnovers (Table 4, entry 4), likely due to the presence of small amounts of residual water in reagents and solvents. The TON increased with higher H_2O loadings and leveled off when 1000 equiv of H_2O was added (Table 4, entries 3, 5, and 6). Further improvement was limited by the poor solubility of water in the ketone substrate.

Table 4. Conditions Optimization on Photocatalytic CCA of 2,6-Dimethylcyclohexanone



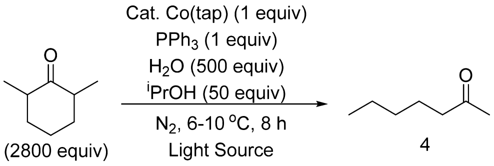
entry[a]	PPh_3/equiv	H_2O/equiv	temp/°C	TON of 4
1	0	500	6−10	6.5
2	0.5	500	6−10	13.2
3	1	500	6−10	15.9
4	1	0	6−10	2.8
5	1	100	6−10	9.1
6	1	1000	6−10	14.8
7	1	500	20−25	11.1
8	1	500	35−40	10.2

[a]A 400 W quartz mercury halide lamp was used, with a B+W 67 mm MRC UV filter for cutting off light rays below 350 nm.

To our surprise, a lower rather than a higher reaction temperature enhanced the TONs. A reaction temperature above 20 °C slightly retarded the photocatalysis to give a lower turnover number of 10 (Table 3, entries 7 and 8). The reaction temperature was optimized at 6−10 °C to give 15.9 turnovers (Table 4, entry 3). Probably, a lower temperature stabilizes the thermally labile reactive intermediate (Ph_3P)Co(tap)OH without extensive reductive elimination to give H_2O_2, which is detrimental to the photocatalyst. The reverse reaction, the known oxidative addition of H_2O_2 by the analogous $[\mathrm{Co^{II}(CN)_5}]^{3-}$ to give $[\mathrm{(HO)Co^{II}(CN)_5}]^{3-}$, has been reported,[14] thus supporting the rationale. The reductive dimerization of $\mathrm{Rh^{III}}$(ttp)OH to generate $\mathrm{Rh^{II}_2(ttp)_2}$ and H_2O_2 also requires a temperature of more than 60 °C.[21] A much lower thermal stability is expected for $\mathrm{Co^{III}}$(tap)OH, and a higher temperature thus reduces the catalytic efficiency.

Under the optimized photocatalytic conditions, a visible light laser source (405 nm, 300 mW) that matches well with the porphyrin Soret band (~400 nm) was used in place of the 400 W broad-band mercury halide lamp (16 TON; Table 5, entry

Table 5. Light Source Effect on Co(tap)-Catalyzed CCA of 2,6-Dimethylcyclohexanone



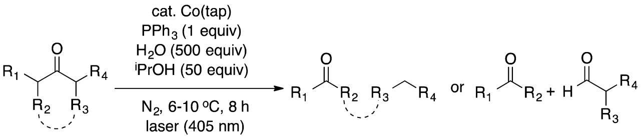
entry	light source	TON of 4	Co(tap) recovery/%
1[a]	Hg lamp (>350 nm, 400 W)	15.9	73
2	laser (405 nm, 300 mW)	23.8	78

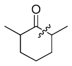
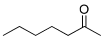
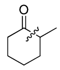
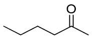
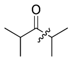
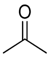
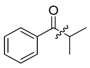
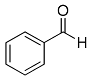
[a]B+W 67 mm MRC UV filter for cutting off light rays below 350 nm.

1). A much more efficient photocatalysis to give 2-heptanone in a higher 24 turnovers (Table 5, entry 2) then resulted. Though the mercury halide lamp used has a higher power output than the laser source, it is a broad-band emitter and mostly nonabsorbing by Co(tap).[10c] Thus, the laser light source works better.

Various ketones also underwent successful visible light photocatalysis under the optimized reaction conditions. Isopropyl ketones worked well to give the corresponding carbonyl compounds (Table 6, entries 1−4). Photocatalytic CCA of unsymmetrical 2-methylcyclohexanone yielded 2-hexanone in 9.2 turnovers (Table 6, entry 2). The more hindered but weaker (C═O)−CH(Me)R bond (∼81.3 kcal mol^{-1})[8,22] in comparison to the (C═O)−CH$_2$R bond (∼84.1 kcal mol^{-1})[8,22] was cleaved selectively. Acetone was produced from the photocatalytic cleavage of diisopropyl ketone in 11.1 turnovers (Table 6, entry 3). The unsymmetrical isobutyrophenone was also catalytically cleaved on the more hindered but weaker (C═O)−^{i}Pr bond (∼81.3 kcal mol^{-1})[8,22] rather than the (C═O)−Ph bond (∼97.2 kcal mol^{-1}).[8,22] The decarbonylation of the proposed benzoyl radical intermediate did not occur, due to its very low rate constant of decarbonylation (1.5 × 10^{-7} s^{-1} at 296 K), though we do not understand the lower TON of isobutyrophenone.[23]

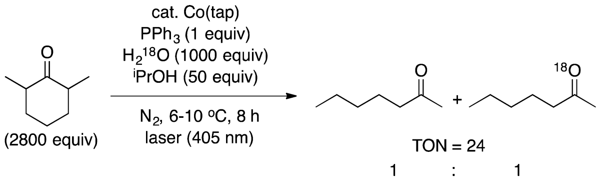
Table 6. Substrate Scope of the Photocatalytic CCA of Ketones by Co(tap)



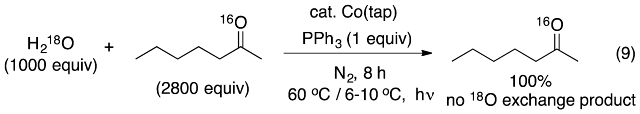
Entry	Substrate	Product[a]	TON
1			23.8
2			9.2
3			11.1
4			1.8

[a]No olefinic products were observed.

Since an extra oxygen atom has been incorporated into the carbonyl products obtained, an $H_2{}^{18}O$ labeling experiment was conducted to identify the source of oxygen. The photocatalytic C(CO)−-C(α) bond oxidation of 2,6-dimethylcyclohexanone by $H_2{}^{18}O$ and Co(tap) yielded 2-heptanone and ^{18}O-labeled 2-heptanone in a 1:1 ratio with a turnover number of 24 (eq 8). From the control experiments of the $H_2{}^{18}O$ exchange reaction with 2-heptanone, no ^{18}O-enriched 2-heptanone was found (eq 9). We can thus rule out direct $^{16}O/^{18}O$ exchange on the 2-heptanone product under both photolytic and thermal conditions to give ^{18}O-enriched 2-heptanone. This establishes that the oxygen source in 2-heptanone is from H_2O and H_2O serves as an anaerobic oxidant similarly to the Rh porphyrin analogues.[10c]



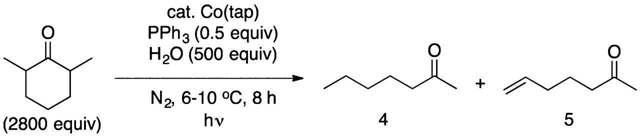
(8)



(9)

The wavelength effect on chemoselectivity on the photocatalysis was further investigated. The high-power broad-band Hg halide lamp irradiation (>350 nm, 400 W) gave 60% selectivity to 2-heptanone (**4**), while laser irradiation at 405 nm promoted the selectivity to 89% to 2-heptanone (**4**) (Table 7, entries 1 and 2). Likely, the coupling of the alkyl radical **6** and Co(tap) is a reversible step (Scheme 3). The laser irradiation promotes a faster homolysis of Co^{III}(tap)alkyl **7** to give Co^{II}(tap) and the alkyl radical **6** rather than the thermal Co-mediated β-H elimination to give the unsaturated ketone **5**.

Table 7. Chemoselectivity with Different Light Sources



4 **5**

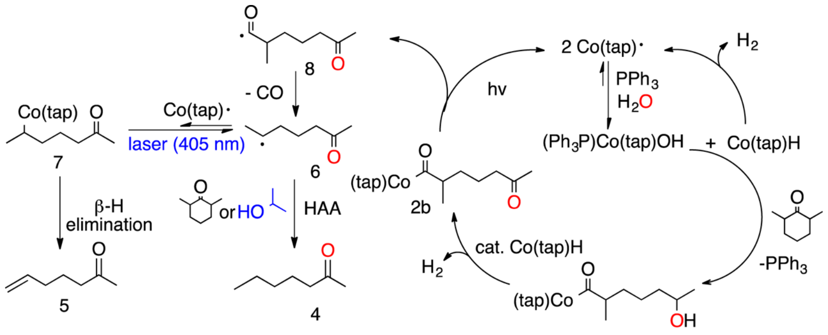
		TON			
entry	light source	**4**	**5**	**4** selectivity/%[a]	Co(tap) recovery/%
1	Hg halide lamp (>350 nm, 400 W)	6	4	60	72
2	laser (405 nm, 300 mW)	8	1	89	70

[a]The percentage of **4** in total conversion of **4** and **5**.

On the basis of the results obtained above, we propose the mechanism given in Scheme 3. Co^{II}(tap) rapidly undergoes a formal oxidative addition with H_2O in the presence of PPh_3 to generate $(Ph_3P)Co^{III}(tap)OH$ and $(Ph_3P)Co^{III}(tap)H$. While we are not sure about the detailed mechanism, a disproportionation mechanism of $(Ph_3P)Co^{II}(tap)(H_2O)$ to give (Ph_3P)-$Co^{III}(tap)$ (OH), $Co^{I}(tap)^{-}$, and H^{+} occurs. Reprotonation of $Co^{I}(tap)^{-}$ gives the thermally labile $Co^{III}(tap)H$. Co(tap)OH with or without Ph_3P ligated then cleaves the C(CO)−C(α) bond of 2,6-dimethylcyclohexanone followed by $Co^{III}(tap)H$-catalyzed dehydrogenation to generate the stoichiometric product $Co^{III}(tap)COCHCH_3(CH_2)_3COCH_3$. The observed cobalt acyl **2b** then undergoes photolytic homolysis to generate the acyl radical **8** and Co^{II}(tap). Decarbonylation of the acyl radical, especially for less stable species, gives the secondary alkyl radical **6**. The alkyl radical **6** either undergoes HAA from isopropyl alcohol or the α-C−H bond of 2,6-dimethylcyclohexanone to give 2-heptanone (**4**) or alternatively couples with Co(tap) to form Co(tap) alkyl **7**. Subsequent β-H elimination produces the 2-hept-6-enone **5**.

Indeed, the reverse of homolysis, the coupling of cobalt(II) and alkyl radical, has been reported in reversible alkyl group transfer reactions.[24−26] The subsequent β-hydride elimination pathway on cobalt alkyl to generate an alkene has also been proposed by Wayland et al. in the reaction of Co^{II}(tap) with 2,2-dimethylcyanoethyl radicals (eq 10).[26] The dehydrogen-

Scheme 3. Proposed Mechanism of Photocatalytic CCA of 2,6-Dimethylcyclohexanone by Co(tap)



ation of related Co macrocycle hydrides has been well reported (Scheme 2).[15,16]

$$(\text{tap})\text{Co}^{\text{II}\bullet} + {}^{\bullet}\text{CC}(\text{CH}_3)_2\text{CN} \xrightarrow{\text{DMF}} \text{Co(tap)H} + \text{CH}_2{=}\text{C}(\text{CH}_3)\text{CN} \tag{10}$$

In conclusion, we have successfully prepared reactive cobalt porphyrin acyls in stoichiometric amounts from the selective, anaerobic oxidation of isopropyl ketones with water and unreactive Co(II) porphyrin. The monochromatic visible-light, selective photocatlytic CCA of isopropyl ketones with water by Co^{II}(tap) under mild conditions was achieved. Through mechanistic investigations, (Ph_3P)Co(tap)OH has been proposed as the intermediate to cleave the carbon−carbon bond of ketones and H_2O is the oxidizing agent. Lower chemoselectivity was observed in the photocatalytic C(CO)−C(α) bond oxidation of 2,6-dimethylcyclohexanone to give both 2-heptanone and 2-hept-6-enone. The selectivity can be tuned by adjusting the concentration of the hydrogen atom source as well as using a strong light source that emits at the Soret band of porphyrins.

■ EXPERIMENTAL SECTION

General Procedures. All materials were obtained from commercial suppliers and used without further purification unless otherwise specified. Benzene was distilled from sodium under nitrogen. Porphyrins and metalloporphyrins were prepared according to the literature procedures, and they had been characterized.[27−31] All solutions used were degassed three times by freeze−thaw−pump cycles and stored in a Teflon screwhead stoppered flask.

Thin-layer chromatography was performed on Merck precoated silica gel 60 F254 plates. Silica gel (Merck, 70−230 mesh) or alumina (90 active neutral, 70−230 mesh) was used for column chromatography.

Physical and Analytical Measurements. ^{1}H NMR spectra were recorded on a Bruker AvanceIII 400 instrument at 400 MHz. Chemical shifts were referenced internally to the residual proton resonance in C_6D_6 (δ 7.15 ppm) or $CDCl_3$ (δ 7.26 ppm) as the internal standard. Chemical shifts (δ) are reported as parts per million (ppm) on the δ scale downfield from TMS. Coupling constants (J) are reported in hertz (Hz).

GC-MS analysis was conducted on a GCMS-QP2010 Plus system using an Rtx-5MS column (30 m × 0.25 mm). Details of the GC program are as follows. The column oven temperature and injection temperature were 50.0 and 250 °C, respectively. Helium was used as the carrier gas. The flow control mode was chosen as linear velocity (36.3 cm s^{-1}) with a pressure of 53.5 kPa. The total flow, column flow, and purge flow were 24.0, 1.0, and 3.0 mL min^{-1}, respectively. Split mode injection with a split ratio of 20.0 was applied. After injection, the column oven temperature was kept at 50 °C for 5 min and was then elevated at a rate of 30 °C min^{-1} for 10 min until 250 °C. The temperature of 250 °C was kept for 5 min. Commercially available authentic samples of 2-heptanone, 2-hexanone, acetone, benzaldehyde, and toluene were analyzed independently by GC/MS to obtain the respective retention times and mass spectra, which were identical with those of the corresponding organic products obtained.

The photolysis was carried out using a 400 W Philips halide lamp with a water circulation system to control the reaction temperature or a 300 mW laser emitting at 405 nm. The light source and the reaction flask were kept at a distance of 5 cm from each other.

Reaction of Co(ttp) and Diisopropyl Ketone with 0.1 equiv of PPh_3 and 50 equiv of H_2O at 25 °C (Solvent Free). Co(ttp) (0.0137 mmol), PPh_3 (0.36 mg, 1.37×10^{-3} mmol), and H_2O (12 μL) were added to diisopropyl ketone (1 mL). The reaction mixture was degassed with three freeze−thaw−pump cycles and was then stirred at 25 °C in the dark under nitrogen for 10 min. Excess diisopropyl ketone was removed, and the dark red crude product was then purified by column chromatography to give a reddish purple solid of Co(ttp)CO^{i}Pr (**1a**; 9.1 mg, 0.0114 mmol, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ −2.77 (sept, 1 H, J = 6.5 Hz), −1.93 (d, 6 H, J = 6.2 Hz), 2.69 (s, 12 H), 7.52 (d, 8 H, J = 6.6 Hz), 7.99 (br. s, 8 H), 8.86 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 16.7, 21.7, 41.8, 121.2, 127.6, 132.7, 133.7, 137.4, 139.1, 145.5. HRMS (FABMS): calcd for $[C_{52}H_{43}N_4OCo+H]^+$, m/z 799.2842; found, m/z 799.2834. IR (KBr, cm^{-1}): ν(C═O) 1751 (s). Acetone was obtained in 40% yield by GC/MS using naphthalene as the internal standard.

Reaction between Co(ttp) and 2,6-Dimethylcyclohexanone (100 equiv) with 0.1 equiv of PPh_3 and 50 equiv of H_2O in Acetone at 25 °C for 4 h. Co(ttp) (10.8 mg, 0.015 mmol), 2,6-dimethylcyclohexanone (100 equiv, 205 μL), water (50 equiv, 13 μL), PPh_3 (0.1 equiv, 0.38 mg), and acetone (795 μL) were stirred at 25 °C under N_2 for 4 h. The excess solvent was removed by vacuum. The red product Co(ttp)COCHMe$(CH_2)_3$COMe (**2a**; 9.9 mg, 0.011 mmol, 76%) with R_f = 0.01 (hexane/CH_2Cl_2 5/1) was purified and collected by column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ −2.72 (sext, 1 H, J = 6.8 Hz), −2.15 (d, 3 H, J = 6.8 Hz), −1.59 (m, 1 H), −1.34 (m, 1 H), −1.15 (m, 1 H), −1.66 (m, 1 H), 1.16 (m, 2 H), 1.72 (s, 3 H), 2.69 (s, 12 H), 7.52 (d, 8 H, J = 7.8 Hz), 7.99 (br. s, 8 H), 8.87 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.8, 19.4, 21.7, 29.5, 31.9, 42.7, 46.6, 121.6, 127.7, 132.7, 132.8, 133.8, 137.5, 139.1, 145.7, 208.0. HRMS (FABMS): calcd for $[C_{56}H_{49}N_4O_2Co+H]^+$, m/z 869.3260; found, m/z 869.3255. IR (KBr, cm^{-1}): ν(C═O) 1756 (s), 1717 (s).

Reaction between Co(ttp) and 2-Methylcyclohexanone (100 equiv) with 0.1 equiv of PPh_3 and 50 equiv of H_2O in Acetone at 25 °C for 7 h. Co(ttp) (10.8 mg, 0.015 mmol), 2-methylcyclohexanone (100 equiv, 205 μL), water (50 equiv, 13 μL), PPh_3 (0.1 equiv, 0.38 mg), and acetone (795 μL) were stirred at 25 °C under N_2 for 7 h. The excess solvent was removed by vacuum. No hexanoic acid was observed by GC/MS analysis with the solvent. The red product Co(ttp)CO$(CH_2)_4$COMe (**3**; 7.4 mg, 0.009 mmol, 58%) with R_f = 0.01 (hexane/CH_2Cl_2 5/1) was purified and collected by column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ −2.33 (t, 2 H, J = 6.9 Hz), −1.10 (quin, 2 H, J = 7.2 Hz), −0.48 (quin, 2 H, J = 7.5 Hz), 1.05 (t, 2 H, J = 7.5 Hz), 1.66 (s, 3 H), 2.69 (s, 12 H), 7.53 (d, 8 H, J = 7.9 Hz), 8.00 (d, 8 H, J = 6.9 Hz), 8.87 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.0, 21.7, 23.1, 29.6, 39.9, 41.8, 121.4, 127.7, 132.8, 133.7, 137.5, 138.9, 145.4, 208.1. HRMS (FABMS): calcd for $[C_{55}H_{47}N_4O_2Co+H]^+$, m/z 855.3104; found, m/z 855.3091. IR (KBr, cm^{-1}): ν(C═O) 1733 (s), 1717 (s).

Reaction of Co(ttp) and Diisopropyl Ketone (10 equiv) with 0.1 equiv of PPh_3 and 50 equiv of H_2O at 25 °C (Acetone). Co(ttp) (0.0137 mmol), PPh_3 (0.36 mg, 1.37×10^{-3} mmol), diisopropyl ketone (19.5 μL), and H_2O (12 μL) were added to acetone. The reaction mixture was degassed with three freeze−thaw−pump cycles and was then stirred at 25 °C in the dark under nitrogen for 2 h. Excess solvent was removed, and the dark red crude product was then purified by column chromatography to give a reddish purple solid of Co(ttp)CO^{i}Pr (**1a**; 8.6 mg, 0.0107 mmol, 78% yield).

Reaction of Co(tap) and Diisopropyl Ketone (10 equiv) with 0.1 equiv of PPh_3 and 50 equiv of H_2O at 25 °C (Acetone). Co(tap) (0.0126 mmol), PPh_3 (0.33 mg, 1.26×10^{-3} mmol), diisopropyl ketone (17.9 μL), and H_2O (11 μL) were added to acetone. The reaction mixture was degassed with three freeze−thaw−pump cycles and was then stirred at 25 °C in the dark under nitrogen for 1.5 h. Excess solvent was removed, and the dark red crude product was then purified by column chromatography to give the reddish purple solid Co(tap)CO^{i}Pr (**1b**; 9.7 mg, 0.0112 mmol, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ −2.80 (sept, 1 H, J = 6.8 Hz), −1.96 (d, 6 H, J = 6.8 Hz), 4.07 (s, 12 H), 7.22 (br. s, 8 H), 8.00 (br. s, 8 H), 8.85 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 16.7, 41.9, 55.7, 112.4, 120.9, 132.7, 134.3, 134.8, 145.8, 159.4. HRMS (FABMS): calcd for $[C_{52}H_{43}N_4O_5Co + H]^+$, m/z 863.2638; found, m/z 863.2654. IR (KBr, cm^{-1}): ν(C═O) 1750 (s).

Reaction of Co(tpclp) and Diisopropyl Ketone (10 equiv) with 0.1 equiv of PPh_3 and 50 equiv of H_2O at 25 °C (Acetone). Co(tpclp) (0.0124 mmol), PPh_3 (0.32 mg, 1.22×10^{-3} mmol), diisopropyl ketone (17.5 μL), and H_2O (11 μL) were added to acetone. The reaction mixture was degassed with three freeze−thaw−pump cycles and was then stirred at 25 °C in the dark under nitrogen for 3 h. Excess solvent was removed, and the dark red crude product was then purified by column chromatography to give the reddish purple solid Co(tpclp)CO^{i}Pr (**1c**; 3.5 mg, 0.0040 mmol, 32% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ −2.85 (sept, 1 H, J = 6.8 Hz), −1.97 (d, 6 H, J = 6.8 Hz), 7.71 (d, 8 H, J = 8.0 Hz), 8.03 (br. s, 8 H), 8.82 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 16.7, 41.9, 120.1, 127.3, 132.9, 134.4, 134.8, 140.1, 145.3. HRMS (FABMS): calcd for $[C_{48}H_{31}N_4Cl_4OCo + H]^+$, m/z 881.0627; found, m/z 881.0598. IR (KBr, cm^{-1}): ν(C═O) 1754 (s).

Photolysis of 2,6-Dimethylcyclohexanone with Co(tap), PPh_3 (0.5 equiv), and H_2O (500 equiv) in THF for 8 h. Co(tap) (1.0 mg, 0.0013 mmol), PPh_3 (0.15 mg, 5.7×10^{-4} mmol), H_2O (11 μL, 0.611 mmol), and 2,6-dimethylcyclohexanone (182 μL) were dissolved in THF (308 μL). The reaction mixture was degassed three times by freeze−thaw−pump cycles, purged with N_2, and photolyzed at 6−10 °C under nitrogen for 8 h. The crude solution was collected by vacuum distillation and was analyzed by GC/MS. 2-Heptanone and 2-hept-6-enone were obtained in 106% and 40% yields, respectively, using naphthalene as the internal standard. Data for 2-heptanone: t_R = 7.203 min; EIMS m/z (rel %) 114 (1), 99 (1), 85 (1), 71 (2), 59 (1), 58 (6), 43 (10), 41 (1). Data for 2-hept-6-enone: t_R = 7.065 min; EIMS m/z (rel %) 112 (1), 97 (1), 71 (1), 58 (3), 55 (2), 43 (10), 41 (2).

Photolysis of 2,6-Dimethylcyclohexanone with Co(tap), PPh_3 (0.5 equiv), and H_2O (500 equiv) in ^{i}PrOH for 8 h. Co(tap) (1.0 mg, 0.0013 mmol), PPh_3 (0.15 mg, 5.7×10^{-4} mmol), and H_2O (11 μL, 0.611 mmol) were dissolved in 2,6-dimethylcyclohexanone (182 μL) and ^{i}PrOH (318 μL). The reaction mixture was degassed three times by freeze−thaw−pump cycles, purged with N_2, and photolyzed at 6−10 °C under nitrogen for 8 h. The crude solution was collected by vacuum distillation and was analyzed by GC/MS. 2-Heptanone and 2-hept-6-enone were obtained in 26% and 5% yields, respectively, using naphthalene as the internal standard.

Photolysis of 2,6-Dimethylcyclohexanone with Co(tap), PPh_3 (0.5 equiv), and H_2O (500 equiv) in Acetone for 8 h. Co(tap) (1.0 mg, 0.0013 mmol), PPh_3 (0.15 mg, 5.7×10^{-4} mmol), and H_2O (11 μL, 0.611 mmol) were dissolved in 2,6-dimethylcyclohexanone (182 μL) and acetone (318 μL). The reaction mixture was degassed three times by freeze−thaw−pump cycles, purged with N_2, and photolyzed at 6−10 °C under nitrogen for 8 h. The crude solution was collected by vacuum distillation and was analyzed by GC/MS. 2-Heptanone and 2-hept-6-enone were obtained in 129% and 29% yields, respectively, using naphthalene as the internal standard.

Photolysis of 2,6-Dimethylcyclohexanone with Co(tap), PPh_3 (0.5 equiv), and H_2O (500 equiv) in MeCN for 8 h. Co(tap) (1.0 mg, 0.0013 mmol), PPh_3 (0.15 mg, 5.7×10^{-4} mmol), and H_2O (11 μL, 0.611 mmol) were dissolved in 2,6-dimethylcyclohexanone (182 μL) and MeCN (318 μL). The reaction mixture was degassed three times by freeze−thaw−pump cycles, purged with N_2, and photolyzed at 6−10 °C under nitrogen for 8 h. The crude solution was collected by vacuum distillation and was analyzed by GC/MS. 2-Heptanone and 2-hept-6-enone were obtained in 17% and 10% yields, respectively, using naphthalene as the internal standard.

Photolysis of 2,6-Dimethylcyclohexanone with Co(tap), PPh_3 (0.5 equiv), and H_2O (500 equiv) in DMF for 8 h. Co(tap) (1.0 mg, 0.0013 mmol), PPh_3 (0.15 mg, 5.7×10^{-4} mmol), and H_2O (11 μL, 0.611 mmol) were dissolved in 2,6-dimethylcyclohexanone (182 μL) and DMF (318 μL). The reaction mixture was degassed three times by freeze−thaw−pump cycles, purged with N_2, and photolyzed at 6−10 °C under nitrogen for 8 h. The crude solution was collected by vacuum distillation and was analyzed by GC/MS. 2-Heptanone and 2-hept-6-enone were obtained in 17% and 15% yields, respectively, using naphthalene as the internal standard.

Photolysis of 2,6-Dimethylcyclohexanone with Co(tap), H_2O (500 equiv), and PPh_3 (0.5 equiv) at 6−10 °C for 8 h. Co(tap) (1.0 mg, 0.0013 mmol), H_2O (11 μL, 0.611 mmol), and PPh_3 (0.15 mg, 5.7×10^{-4} mmol) were dissolved in 2,6-dimethylcyclohexanone (500 μL). The reaction mixture was degassed three times by freeze−thaw−pump cycles, purged with N_2, and photolyzed at 6−10 °C under nitrogen for 8 h. The crude solution was collected by vacuum distillation and was analyzed by GC/MS. 2-Heptanone and 2-hept-6-enone were obtained in 5.7 and 3.6 turnovers, respectively, using naphthalene as the internal standard.

Photolysis of 2,6-Dimethylcyclohexanone with Co(tap), H_2O (500 equiv), PPh_3 (0.5 equiv), and ^{i}PrOH (20 equiv) at 6−10 °C for 8 h. Co(tap) (1.0 mg, 0.0013 mmol), H_2O (11 μL, 0.611 mmol), PPh_3 (0.15 mg, 5.7×10^{-4} mmol), and ^{i}PrOH (2.0 μL, 0.026 mmol) were dissolved in 2,6-dimethylcyclohexanone (500 μL). The reaction mixture was degassed three times by freeze−thaw−pump cycles, purged with N_2, and photolyzed at 6−10 °C under nitrogen for 8 h. The crude solution was collected by vacuum distillation and was analyzed by GC/MS. 2-Heptanone and 2-hept-6-enone were obtained in 10 and 0.9 turnovers, respectively, using naphthalene as the internal standard.

Photolysis of 2,6-Dimethylcyclohexanone with Co(tap), H_2O (500 equiv), PPh_3 (0.5 equiv), and ^{i}PrOH (50 equiv) at 6−10 °C for 8 h. Co(tap) (1.0 mg, 0.0013 mmol), H_2O (11 μL, 0.611 mmol), PPh_3 (0.15 mg, 5.7×10^{-4} mmol), and ^{i}PrOH (5.0 μL, 0.065 mmol) were dissolved in 2,6-dimethylcyclohexanone (500 μL). The reaction mixture was degassed three times by freeze−thaw−pump cycles, purged with N_2, and photolyzed at 6−10 °C under nitrogen for 8 h. The crude solution was collected by vacuum distillation and was analyzed by GC/MS. 2-Heptanone was obtained in 13.2 turnovers using naphthalene as the internal standard.

Photolysis of 2,6-Dimethylcyclohexanone with Co(tap), H_2O (500 equiv), and ^{i}PrOH (50 equiv) at 6−10 °C for 8 h. Co(tap) (1.0 mg, 0.0013 mmol), H_2O (11 μL, 0.611 mmol), and ^{i}PrOH (5.0 μL, 0.065 mmol) were dissolved in 2,6-dimethylcyclohexanone (500 μL). The reaction mixture was degassed three times by freeze−thaw−pump cycles, purged with N_2, and photolyzed at 6−10 °C under nitrogen for 8 h. The crude solution was collected by vacuum distillation and was analyzed by GC/MS. 2-Heptanone was obtained in 6.5 turnovers using naphthalene as the internal standard.

Photolysis of 2,6-Dimethylcyclohexanone with Co(tap), H_2O (500 equiv), PPh_3 (1 equiv), and ^{i}PrOH (50 equiv) at 6−10 °C for 8 h. Co(tap) (1.0 mg, 0.0013 mmol), H_2O (11 μL, 0.611 mmol), PPh_3 (0.3 mg, 0.0011 mmol), and ^{i}PrOH (5.0 μL, 0.065 mmol) were dissolved in 2,6-dimethylcyclohexanone (500 μL). The reaction

DOI: 10.1021/acs.organomet.6b00352

mixture was degassed three times by freeze−thaw−pump cycles, purged with N_2, and photolyzed at 6−10 °C under nitrogen for 8 h. The crude solution was collected by vacuum distillation and was analyzed by GC/MS. 2-Heptanone was obtained in 15.9 turnovers using naphthalene as the internal standard.

Photolysis of 2,6-Dimethylcyclohexanone with Co(tap), PPh_3 (1 equiv), and ^{i}PrOH (50 equiv) at 6−10 °C for 8 h. Co(tap) (1.0 mg, 0.0013 mmol), PPh_3 (0.3 mg, 0.0011 mmol), and ^{i}PrOH (5.0 μL, 0.065 mmol) were dissolved in 2,6-dimethylcyclohexanone (500 μL). The reaction mixture was degassed three times by freeze−thaw−pump cycles, purged with N_2, and photolyzed at 6−10 °C under nitrogen for 8 h. The crude solution was collected by vacuum distillation and was analyzed by GC/MS. 2-Heptanone was obtained in 2.8 turnovers using naphthalene as the internal standard.

Photolysis of 2,6-Dimethylcyclohexanone with Co(tap), H_2O (100 equiv), PPh_3 (1 equiv), and ^{i}PrOH (50 equiv) at 6−10 °C for 8 h. Co(tap) (1.0 mg, 0.0013 mmol), H_2O (2 μL, 0.121 mmol), PPh_3 (0.3 mg, 0.0011 mmol), and ^{i}PrOH (5.0 μL, 0.065 mmol) were dissolved in 2,6-dimethylcyclohexanone (500 μL). The reaction mixture was degassed three times by freeze−thaw−pump cycles, purged with N_2, and photolyzed at 6−10 °C under nitrogen for 8 h. The crude solution was collected by vacuum distillation and was analyzed by GC/MS. 2-Heptanone was obtained in 9.1 turnovers using naphthalene as the internal standard.

Photolysis of 2,6-Dimethylcyclohexanone with Co(tap), H_2O (1000 equiv), PPh_3 (1 equiv), and ^{i}PrOH (50 equiv) at 6−10 °C for 8 h. Co(tap) (1.0 mg, 0.0013 mmol), H_2O (22 μL, 1.22 mmol), PPh_3 (0.3 mg, 0.0011 mmol), and ^{i}PrOH (5.0 μL, 0.065 mmol) were dissolved in 2,6-dimethylcyclohexanone (500 μL). The reaction mixture was degassed three times by freeze−thaw−pump cycles, purged with N_2, and photolyzed at 6−10 °C under nitrogen for 8 h. The crude solution was collected by vacuum distillation and was analyzed by GC/MS. 2-Heptanone was obtained in 14.8 turnovers using naphthalene as the internal standard.

Photolysis of 2,6-Dimethylcyclohexanone with Co(tap), H_2O (500 equiv), PPh_3 (1 equiv), and ^{i}PrOH (50 equiv) at 20−25 °C for 8 h. Co(tap) (1.0 mg, 0.0013 mmol), H_2O (11 μL, 0.611 mmol), PPh_3 (0.3 mg, 0.0011 mmol), and ^{i}PrOH (5.0 μL, 0.065 mmol) were dissolved in 2,6-dimethylcyclohexanone (500 μL). The reaction mixture was degassed three times by freeze−thaw−pump cycles, purged with N_2, and photolyzed at 20−25 °C under nitrogen for 8 h. The crude solution was collected by vacuum distillation and was analyzed by GC/MS. 2-Heptanone was obtained in 11.1 turnovers using naphthalene as the internal standard.

Photolysis of 2,6-Dimethylcyclohexanone with Co(tap), H_2O (500 equiv), PPh_3 (1 equiv), and ^{i}PrOH (50 equiv) at 35−40 °C for 8 h. Co(tap) (1.0 mg, 0.0013 mmol), H_2O (11 μL, 0.611 mmol), PPh_3 (0.3 mg, 0.0011 mmol), and ^{i}PrOH (5.0 μL, 0.065 mmol) were dissolved in 2,6-dimethylcyclohexanone (500 μL). The reaction mixture was degassed three times by freeze−thaw−pump cycles, purged with N_2, and photolyzed at 35−40 °C under nitrogen for 8 h. The crude solution was collected by vacuum distillation and was analyzed by GC/MS. 2-Heptanone was obtained in 10.2 turnovers using naphthalene as the internal standard.

Photolysis of 2,6-Dimethylcyclohexanone with Co(tap), H_2O (500 equiv), PPh_3 (1 equiv), and ^{i}PrOH (50 equiv) at 6−10 °C for 8 h using a 300 mW Laser at 405 nm. Co(tap) (1.0 mg, 0.0013 mmol), H_2O (11 μL, 0.611 mmol), PPh_3 (0.3 mg, 0.0011 mmol), and ^{i}PrOH (5.0 μL, 0.065 mmol) were dissolved in 2,6-dimethylcyclohexanone (500 μL). The reaction mixture was degassed three times by freeze−thaw−pump cycles, purged with N_2, and photolyzed at 6−10 °C under nitrogen for 8 h using a 300 mW laser at 405 nm. The crude solution was collected by vacuum distillation and was analyzed by GC/MS. 2-Heptanone was obtained in 23.8 turnovers using naphthalene as the internal standard.

Photolysis of 2-Methylcyclohexanone with Co(tap), H_2O (500 equiv), PPh_3 (1 equiv), and ^{i}PrOH (50 equiv) at 6−10 °C for 8 h using a 300 mW Laser at 405 nm. Co(tap) (1.0 mg, 0.0013 mmol), H_2O (11 μL, 0.611 mmol), PPh_3 (0.3 mg, 0.0011 mmol), and ^{i}PrOH (5.0 μL, 0.065 mmol) were dissolved in 2-methylcyclohexanone (500 μL). The reaction mixture was degassed three times by freeze−thaw−pump cycles, purged with N_2, and photolyzed at 6−10 °C under nitrogen for 8 h. The crude solution was collected by vacuum distillation and was analyzed by GC/MS. 2-Hexanone was obtained in 9.2 turnovers using naphthalene as the internal standard.

Photolysis of Diisopropyl Ketone with Co(tap), H_2O (500 equiv), PPh_3 (1 equiv), and ^{i}PrOH (50 equiv) at 6−10 °C for 8 h using a 300 mW Laser at 405 nm. Co(tap) (1.0 mg, 0.0013 mmol), H_2O (11 μL, 0.611 mmol), PPh_3 (0.3 mg, 0.0011 mmol), and ^{i}PrOH (5.0 μL, 0.065 mmol) were dissolved in diisopropyl ketone (500 μL). The reaction mixture was degassed three times by freeze−thaw−pump cycles, purged with N_2, and photolyzed at 6−10 °C under nitrogen for 8 h. The crude solution was collected by vacuum distillation and was analyzed by GC/MS. Acetone was obtained in 11.1 turnovers using naphthalene as the internal standard.

Photolysis of Isobutyrophenone with Co(tap), H_2O (500 equiv), PPh_3 (1 equiv), and ^{i}PrOH (50 equiv) at 6−10 °C for 8 h using a 300 mW Laser at 405 nm. Co(tap) (1.0 mg, 0.0013 mmol), H_2O (11 μL, 0.611 mmol), PPh_3 (0.3 mg, 0.0011 mmol), and ^{i}PrOH (5.0 μL, 0.065 mmol) were dissolved in isobutyrophenone (500 μL). The reaction mixture was degassed three times by freeze−thaw−pump cycles, purged with N_2, and photolyzed at 6−10 °C under nitrogen for 8 h. The crude solution was collected by vacuum distillation and was analyzed by GC/MS. Benzaldehyde was obtained in 1.8 turnovers using benzene as the internal standard.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00352.

^{1}H NMR and ^{13}C NMR spectra, IR spectra, X-ray data, comparison of output power of the light sources, ^{18}O labeling experiment, and experimental details (PDF)
Crystallographic data (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for K.S.C.: ksc@cuhk.edu.hk.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the GRF No. 400113 of Hong Kong for financial support.

■ ABBREVIATIONS

TON, turnover number; por, porphyrin

■ REFERENCES

(1) Chan, K. S.; Li, X. Z.; Dzik, W. I.; de Bruin, B. *J. Am. Chem. Soc.* **2008**, *130*, 2051−2061.

(2) Chan, K. S.; Li, X. Z.; Zhang, L.; Fung, C. W. *Organometallics* **2007**, *26*, 2679−2687.

(3) Zhang, L.; Chan, K. S. *J. Organomet. Chem.* **2007**, *692*, 2021−2027.

(4) Chan, Y. W.; Chan, K. S. *J. Am. Chem. Soc.* **2010**, *132*, 6920−6922.

(5) Li, B. Z.; Fung, H. S.; Song, X.; Chan, K. S. *Organometallics* **2011**, *30*, 1984−1990.

(6) Sarkar, S.; Li, S.; Wayland, B. B. *J. Am. Chem. Soc.* **2010**, *132*, 13569−13571.

(7) Wayland, B. B.; Ba, S.; Sherry, A. E. *J. Am. Chem. Soc.* **1991**, *113*, 5305−5311.

(8) Luo, Y. R. *Comprehensive Handbook of Chemical Bond Energies*; CRC Press: Boca Raton, FL, 2007.

(9) (a) Fukuzumi, S.; Miyamoto, K.; Suenobu, T.; Caemelbecke, E. V.; Kadish, K. M. *J. Am. Chem. Soc.* **1998**, *120*, 2880−2889. (b) Cui, W. H.; Li, S.; Wayland, B. B. *J. Organomet. Chem.* **2007**, *692*, 3198−3206.

(10) (a) Fung, H. S.; Li, B. Z.; Chan, K. S. *Organometallics* **2010**, *29*, 4421−4423. (b) Fung, H. S.; Li, B. Z.; Chan, K. S. *Organometallics* **2012**, *31*, 570−579. (c) Lee, S. Y.; Chan, K. S. *Organometallics* **2013**, *32*, 5391−5401. (d) Lee, S. Y.; Feng, S.; Chan, K. S. *Dalton* **2016**, *45*, 3522−3527.

(11) Datta-Gupta, N. *J. Inorg. Nucl. Chem.* **1971**, *33*, 4219−4225.

(12) Wayland, B. B.; Balkus, K. J., Jr.; Farnos, M. D. *Organometallics* **1989**, *8*, 950−955.

(13) Bhagan, S.; Sarkar, S.; Wayland, B. B. *Inorg. Chem.* **2010**, *49*, 6734−6739.

(14) Chock, P. B.; Dewar, R. B. K.; Halpern, J.; Wong, L. *J. Am. Chem. Soc.* **1969**, *91*, 82−84.

(15) (a) Connolly, P.; Espenson, J. H. *Inorg. Chem.* **1986**, *25*, 2684−2688. (b) Chao, T.; Espenson, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 129−133.

(16) (a) Dempsey, J. L.; Brunschwig, B. S.; Winkler, J. R.; Gray, H. B. *Acc. Chem. Res.* **2009**, *42*, 1995−2004. (b) Lacy, D. C.; Roberts, G. M.; Peters, J. C. *J. Am. Chem. Soc.* **2015**, *137*, 4860−4864.

(17) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25−41.

(18) Cao, Y.; Petersen, J. L.; Stolzenberg, A. M. *Inorg. Chim. Acta* **1997**, *263*, 139−148.

(19) (a) The (P)Co(oep)−R bond energy has been reported to be 30 kcal mol^{-1}: Simões, J. A. M.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629−688. (b) Estimation of the BDEs of Co(ttp)−R can also be made on the basis of the kinetic measurements of the BDEs of Fe(oep)R (17−33 kcal mol^{-1}), where the Fe(oep)−R bond dissociation energies have been reported to be 10−15 kcal mol^{-1} weaker than those for the Co derivatives; see: Riordan, C. G.; Halpern, J. *Inorg. Chim. Acta* **1996**, *243*, 19−24.

(20) Lide, D. R. *Handbook of Chemistry and Physics*, 84th ed.; CRC Press: Boca Raton, FL, 2004.

(21) Choi, K. S.; Lai, T. H.; Lee, S. Y.; Chan, K. S. *Organometallics* **2011**, *30*, 2633−2635.

(22) Speight, J. G. *Lange's Handbook of Chemistry*, 16th ed.; McGraw-Hill: New York, 2005.

(23) The decarbonylation rate constants of acyl radicals are at least 10^4 s^{-1}, except for the PhCO radical; see: Garcia-Garibay, M. A.; Campos, L. M. In *Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Lenci, F., Eds.; CRC Press: Boca Raton, FL, 2004; Vols. *1* and *2*, Chapter 48.

(24) Dodd, D.; Johnson, M. D. *J. Chem. Soc. D* **1971**, *21*, 1371−1372.

(25) Van Den Bergen, A.; West, B. O. *J. Chem. Soc. D* **1971**, *1*, 52−53.

(26) Gridnev, A. A.; Ittel, S. D.; Fryd, M.; Wayland, B. B. *Organometallics* **1993**, *12*, 4871−4880.

(27) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476−476.

(28) Plater, M. J.; Aiken, S.; Bourhill, G. *Tetrahedron* **2002**, *58*, 2415−2422.

(29) Sugamoto, K.; Matsushita, Y.; Matsui, T. *J. Chem. Soc., Perkin Trans. 1* **1998**, *23*, 3989−3998.

(30) Tse, A. K. S.; Mak, K. W.; Chan, K. S. *Organometallics* **1998**, *17*, 2651−2655.

(31) Yang, J. P.; Huang, P. C. *Chem. Mater.* **2000**, *12*, 2693−2697.

DOI: 10.1021/acs.organomet.6b00352
Organometallics XXXX, XXX, XXX−XXX