Dalton Transactions

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PAPER

# Room Temperature Carbon(CO)-Carbon(α) Bond Activation of Ketones by Rhodium(II) Porphyrins with Water

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The mild and selective aliphatic C(CO)-C(α) bond activation (CCA) of ketones was successfully achieved at room temperature using rhodium(II) porphyrins in the presence of $H_2O$. $Rh^{II}$(tmp) (tmp = tetrakismesitylporphyrinate dianion) disproportionates in $H_2O$ to generate the highly reactive intermediate $Rh^{III}$(tmp)(OH) for cleaving the C-C bond of ketone, giving up to 90 % of $Rh^{III}$(tmp)(COR) and the corresponding oxidized carbonyl product in up to 76 % yield within 10 min. Substrate scopes cover aliphatic as well as aromatic ketones. Both isopropyl and cyclic ketones worked well.

## Introduction

Carbon-carbon bond activation (CCA) represents one of the most important strategies in structural modification and synthesis of commodities.[1] Transition metal complexes can assist the activation and functionalization of inert aliphatic C-C bonds which are of vital importance in catalytic cracking of hydrocarbons[2] and degradation of non-biodegradable plastics.[3] However, they are too robust (> 83 kcal $mol^{-1}$)[4] to be cleaved under mild conditions, and the surrounding C-H bonds usually react preferentially for steric and statistical reasons. Various strategies such as chelation assistance,[5] ring strain release,[6] aromatization[7,8] and carbonyl group directing,[9,10] have been developed to accomplish the challenging task successfully. It remains a goal to achieve CC bond activation of organic substrates in mild reaction conditions.[11]

Group 9 metalloporphyrins exhibited rich bond activation chemistry on aliphatic organic compounds. We have reported that $Rh^{III}$(ttp)Cl and $Rh^{III}$(ttp)(Me) **1** (ttp = tetratolylporphyrinate dianion) can activate the C(CO)-C($sp^3$) bond of ketones at 200 °C in the presence of water.[12] $Rh^{III}$(ttp)(OH) formed from the hydrolysis of α-C-H bond activation product of ketone was proposed as the intermediate to cleave the C-C bond of ketone consistent with the stoichiometry. Later, our group has successfully developed the milder CCA of ketones using Rh(ttp)($CH_2CH_2OH$) **2** as the Rh(ttp)(OH) precursor.[13] Yet, the reaction takes a few days to complete in most of the ketone substrates examined. In order to achieve the facile C(CO)-C(α) bond cleavage under mild conditions, a more reactive and persistent metalloporphyrin radical $Rh^{II}$(tmp) **3** (tmp = tetramesitylporphyrinate dianion, Figure 1) was used together with $H_2O$. Indeed, the disproportionation of $Rh^{II}$(tmp) with $H_2O$ has been reported to generate $Rh^{III}$(tmp)(OH) to cleave the C(α)-C(β) bond of ether at room temperature in 10 min.[14]

In short, a mild and selective C(CO)-C(α) bond activation of ketones has evolved based on mechanistic understanding and strategically modifying the reaction conditions to aid the transformation. The key intermediate $Rh^{III}$(por)(OH) can be generated in three different methods: (1) hydrolysis of Rh(por)(R)[12] (2) β-hydroxyl elimination[13] and (3) disproportionation of $Rh^{II}$(por) (this work). Table 1 shows a summary on the three strategies to achieve the selective C(CO)-C(α) bond cleavage of ketones.

Herein, we report the development of a selective CCA of unstrained ketones under room temperature without assistance from strain energy or aromatization.

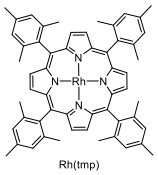
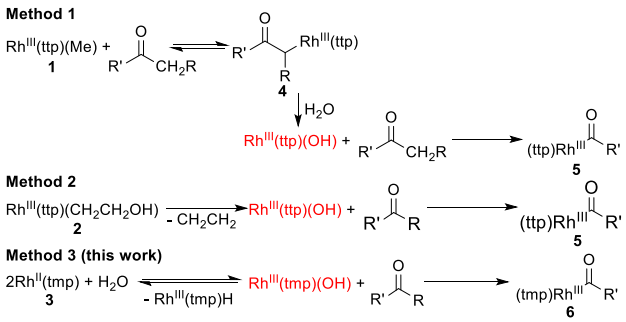



**Fig. 1** Structure of Rh(tmp).

**Table 1. Comparison on Reaction Conditions on CCA of Ketones using Different Strategies**




| Method | Temp/°C | Time | [Rh] yield/% | Ref |
|---|---|---|---|---|
| 1 | 200 | 30 min – 19 d | 20 - 97 | 12 |
| 2 | 25-50 | 15 min – 3 d | 17 - 80 | 13 |
| 3 | 25 | 1 min – 2 d | 15 - 90 | This work |

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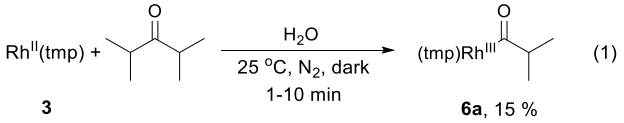
†Electronic Supplementary Information (ESI) available: Table, figure, $^1$H and $^{13}$C NMR spectra.

## Results and Discussions

Initially, $Rh^{II}$(tmp) activated the C(CO)-C(α) bond of diisopropyl ketone selectively to give 15 % Rh(tmp)($CO^{i}Pr$) **6a** at room temperature with residual water present (eq 1). Despite the low reaction yield, the reaction completed rapidly in 10 min that encouraged us to further optimize the conditions.




(1)

**3** **6a**, 15 %

**Conditions Optimization**

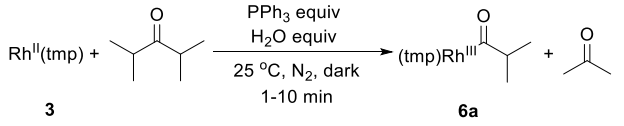
The $PPh_3$ ligand (1 equiv) significantly increased the yield from 15 to 52 % (Table 2, entries 1 and 2). A higher loading of $PPh_3$ (2 equiv) was not beneficial (Table 2, entry 3). Addition of $H_2O$ (50 equiv) promoted the reaction yield up to 90 % (Table 2, entry 4). Higher water loading is not necessary due to the limited solubility of $H_2O$ in diisopropyl ketone as evidenced by the similar product yields (Table 2, entries 4 and 5).

**Substrate Scope**

Rh(tmp) reacted selectively with various aryl and aliphatic ketones under room temperature (Table 3). Isopropyl ketones reacted almost instantaneously to give the corresponding rhodium porphyrin acyls in good yields (Table 3, entries 1-3). Other ketones such as acetophenone, propiophenone and *n*-butyrophenone reacted much slower to give lower yields of Rh(tmp)(COPh) **6b** (Table 3, entries 4-6). Probably, the proposed rhodium-catalyzed aldol addition or condensation of these ketones is a competitive process that consumes some concentrations of the Lewis acidic Rh(tmp)(OH), and ketones during the course of reaction.[12]

Acetone was observed as the organic co-product in the carbon-carbon bond activation of isopropyl ketones (Table 3, entries 1-3). To support that acetone is formed from the oxidation of C(CO)- C(α) bond, an "intramolecular trap" 2,6-dimethylcyclohexanone was then reacted with Rh(tmp) at 25 °C. To our delight, 83 % of Rh(tmp)[$COCHMe(CH_2)_3COMe$] 6d was yielded (eq 2). The two carbonyl groups in the product observed imply that an extra oxygen was inserted into the product. This suggests an oxygen-containing species as the key intermediate.

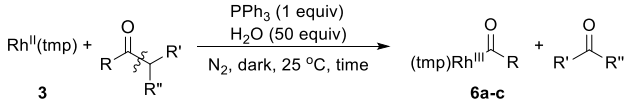
**Table 2. Conditions Optimization on CCA of Ketones by Rh(tmp)**



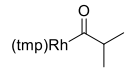
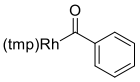
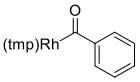
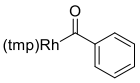
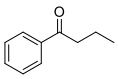
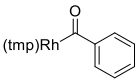

**3** **6a**

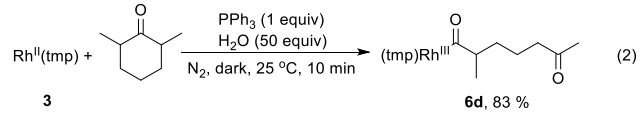
| Entry | $PPh_3$ equiv | $H_2O$ equiv | Yield (%) | |
|---|---|---|---|---|
| | | | **6a** | acetone |
| 1 | 0 | 0 | 15 | not determined |
| 2 | 1 | 0 | 52 | not determined |
| 3 | 2 | 0 | 46 | not determined |
| 4 | 1 | 50 | 90 | 76 |
| 5 | 1 | 200 | 89 | not determined |

**Table 3. Substrate Scopes on the CCA of Ketones**




**3** **6a-c**

| Entry | Ketones | C(CO)-C(α) BDE /kcalmol$^{-1}$ | Time | Yield (%) | |
|---|---|---|---|---|---|
| | | | | **6a-c** | Organics |
| 1 |  | ~81.3 | 10 min |  **(6a)** / 90 |  76 |
| 2 |  | - | 10 min |  **(6b)** / 72 |  48 |
| 3 |  | 81.3 | 10 min |  **(6c)** / 54 |  32 |
| 4 |  | 85.0 | 2 d |  **(6b)** / 25 | - |
| 5 |  | 82.2 | 1 d |  **(6b)** / 39 | - |
| 6 |  | - | 4 d |  **(6b)** / 13 | - |
| 7 |  | 80.8 | 10 min |  **(6c)** / 0 | - |
| 8 |  | - | 10 min |  **(6c)** / 0 | - |

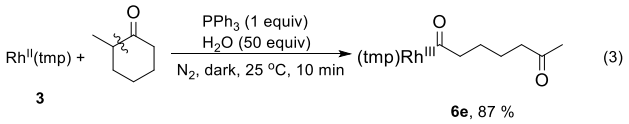



(2)

**3** **6d**, 83 %

When the asymmetric cyclic 2-methylcyclohexanone was used, the sterically more hindered but weaker C(CO)-C($^{i}Pr$) bond (~81.3 kcal mol$^{-1}$)[4] was cleaved selectively than the less

hindered but stronger C(CO)-C(methylene) bond (~83.0 kcal $mol^{-1}$)[4] to give 87 % yield of Rh(tmp)[$CO(CH_2)_4COMe$] **6e** (eq 3) similar to the Rh(ttp) complexes.[12, 13]




1,3-Diketones (Table 3, entres 7 and 8) did not work in solvent free conditions. α-Arylated ketones such as diphenyl acetone and benzyl phenyl ketone were investigated. Due to their high melting points, the reactions were carried out in acetone (10 equiv substrates). However, no desired C(CO)-C(α) cleavage product formed after 10 mins.

Generally, in solvent free conditions, the relative reactivity of ketones follows the order: isopropyl ketone >> ethyl ketone > methyl ketone > propyl ketone. The observation is explained by the much weaker C(CO)-C($^i$Pr) bond (81.3 kcal $mol^{-1}$)[4] than other C(CO)-C(α) bonds (> 82.2 kcalmol-1).[4] While the C(CO)-C(Et) bond (82.2 kcal $mol^{-1}$)[4] is at least 2 kcal $mol^{-1}$ weaker than the C(CO)-C(Me) bond (85 kcal $mol^{-1}$), it reacts faster than the former.[4] The cleavage of the C(CO)-C($n$Pr) bond in butyrophenone requires the longest reaction time presumably due to the higher viscosity in the reaction mixture.

**Water as Oxidizing Agent**

Water has been shown to be the extra oxygen source incorporated in the C-C bond oxidation product of ketones according to an $^{18}O$-labelling experiment and stoichiometry.[15] The anaerobic oxidation or oxygen incorporation by water may potentially reduce or eliminate undesirable over-oxidation in aerobic conditions. The promoting effect of water with $Ph_3P$ is significant (Table 1, entries 2 and 4) and supports that $Ph_3P/H_2O$ promotes the oxidative addition of Rh(tmp) to generate Rh(tmp)(OH) as the key intermediate.

**Rh(tmp)OH as the Key Intermediate**

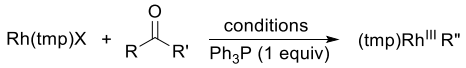
Direct synthesis of ($PPh_3$)Rh(tmp)OH **7** was employed to support that ($PPh_3$)Rh(tmp)OH **7** is the key intermediate for carbon(CO)-carbon(α) activation as the oxygen transfer species into C-C bonds. The distinct color change from dark orange to red when $PPh_3$ and $H_2O$ were added to Rh(tmp) in benzene-$d_6$ solvent, clearly demonstrated the change of metal oxidation state from $Rh^{II}$(tmp) to $Rh^{III}$(tmp)OH. Unfortunately, the proton signal of ($PPh_3$)Rh(tmp)O-H was not observed in $^1H$ NMR spectrum, likely due to the rapid exchange with water, but the characteristic peaks of Rh(tmp) disappeared. Furthermore, HRMS (ESI-MS) result also supports the formation of ($PPh_3$)Rh(tmp)OH.

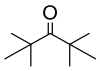
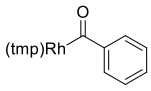
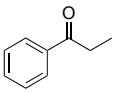
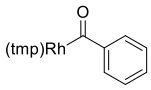
We have reported the proposed mechanism of the CC bond cleavage of carbonyls by analogous Rh(por)OH in a concerted four centered, sterically hindered transition state.[15] At this stage, we could not rule out other alternative such as radical chain mechanism.

**Reactivity and Selectivity Comparison of Rh(tmp) and Rh(tmp)(OH) in Bond Activation**

Table 4 lists the comparison of reactivity of Rh(tmp) and Rh(tmp)(OH) in bond activation of selected ketones. We have reported earlier that Rh(tmp)/$Ph_3P$ also cleaves the C(α)-C(β) bonds (BDE = 82-86 kcal $mol^{-1}$)[4] of non-enolizable alkyl ketone such as ditertbutyl ketone at 130 °C in 1 d to give Rh(tmp)(Me) in a low yield of 31% (Table 4**B**, entry 1).[17] Rh(tmp) reacts with acetophenone to produce complex mixture at 130 °C and with propiophenone to give Rh(tmp)(Me) in just 3% yield (Table 4**B**, entries 2 and 3). The C(α)-C(β) bond cleavage occurs in lower yields and in harsh conditions. In contrast, the CCA by Rh(tmp)(OH) occurs selectively at the C(CO)-C(α) bond of acetophenone and propiophenone at r.t. in 1-2 d to give higher yields of Rh(tmp)(COPh) (Table 4**A**, entries 2-3). For other isopropyl ketones (Table 3, entries 1-3), the reactions are also selective at the C(CO)-C(α) bond, higher yielding and much faster within 10 min at r.t.. Thus Rh(tmp)(OH) is much more reactive than Rh(tmp) and selectively cleaves the weaker C(CO)-C(α) bonds of ketones. The origins of their reactivity difference could in part due to the metalloradical attack on an aliphatic CC bond by Rh(tmp) requiring higher temperatures to form a Rh-C bond and break an aliphatic C-C bond. However, Rh(tmp) is the dominant species at high temperature in benzene as Rh(tmp)OH is thermally labile.[18] On the other hand, the concerted sigma bond metathesis cleavage of CC bond by Rh(tmp)(OH) lowers the activation barriers with the simultaneous formation of C-OH and Rh-C bonds.

**Table 4. Reactivity Comparison between Rh(tmp)OH and Rh(tmp) towards the CCA of Ketones**




| Entry | Ketones | **A** (X = OH) Rh(tmp)OH [Rh] products, conditions, % yield | **B** (X = e$^-$) Rh(tmp) [Rh] products, conditions, % yield |
|---|---|---|---|
| 1 |  | N/A | Rh(tmp)Me 130 °C, 1 d, 31% |
| 2 |  |  r.t, 2 d, 25% | complex mixture, 130 °C, 1 d |
| 3 |  |  r.t., 1 d, 39% | Rh(tmp)Me 130 °C, 1 d, 3% |

## Conclusions

In summary, we have discovered the mild, selective C(CO)-C(α) bond activation of ketones by $Rh^{II}$(tmp)/$Ph_3P$/$H_2O$ in good yields. The reactions worked well with various unstrained ketones, including straight chain, branched chain and cyclic ketones. Bulkier isopropyl ketones are more reactive towards CCA, followed by ethyl, methyl and *n*-propyl ketones. Through mechanistic investigation, Rh(tmp)(OH) has been proposed as the key intermediate generated from the $H_2O$-assisted disproportionation of $Rh^{II}$(tmp). Identification of the organic co-products further supports that Rh(tmp)(OH) is the intermediate.

## Experimental Section

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.[19-21] All solutions used were degassed thrice by freeze-thaw-pump cycle and stored in a Teflon screwhead stoppered flask, which was wrapped with aluminum foils to protect from light.

Thin-layer chromatography was performed on pre-coated silica gel 60 $F_{254}$ plates. Silica gel (Merck, 70-230 mesh) was used for column chromatography.

$^1$H NMR spectra were recorded on a 400 MHz or 700 MHz NMR instrument. Chemical shifts were referenced internally to the residual proton resonance in $C_6D_6$ ($\delta$ = 7.15 ppm), $CDCl_3$ ($\delta$ = 7.26 ppm) or with tetramethylsilane ($(TMS)_4Si$, $\delta$ = 0.00 ppm) as the internal standards. $^{13}C\{^1H\}$ NMR spectra were recorded on a 700 MHz NMR instrument at 175 MHz. Chemical shifts were referenced internally to the residual proton resonance in $CDCl_3$ ($\delta$ = 77.16 ppm) as the internal standard. Chemical shifts ($\delta$) were reported as part per million (ppm) in (δ) scale downfield from TMS. Coupling constants (*J*) were reported in Hertz (Hz).

GC-MS analysis was conducted using a Rtx-5MS column (30 m x 0.25 mm). Details of GC program are as follows: The column oven temperature and injection temperature were 50.0 and 250 $^o$C. Helium was used as carrier gas. Flow control mode was chosen as linear velocity (36.3 cm $s^{-1}$) with pressure 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 inject with split ratio 20.0 was applied. After injection, the column oven temperature was kept at 50 $^o$C for 5 min and was then elevated at a rate of 30 $^o$C $min^{-1}$ for 10 min until 250 $^o$C. The temperature of 250 $^o$C was kept for 5 min. The retention time and mass spectrum of organic products obtained were identical to that of commercially available authentic samples.

**Preparation of 5,10,15,20-Tetramesitylporphyrinato Rhodium(II) [Rh(tmp)] (3)**.[21] To a Teflon screw-head stoppered flask, Rh(tmp)$CH_3$ (10.0 mg, 0.011 mmol) was dissolved in $C_6H_6$ (4.0 mL) to form a clear orange solution. The reaction mixture was then degassed thrice by the freeze-pump-thaw cycle and refilled with nitrogen. The reaction mixture was irradiated under a 400 W Hg-lamp at 6 - 10 $^o$C until complete Rh(tmp)($CH_3$) consumption was confirmed by TLC analysis (> 4 h). Addition of excess iodine to the mixture yielded Rh(tmp)I in 80 % average yield after column chromatography. $^1$H NMR of Rh(tmp) ($C_6D_6$, 400 MHz) δ 3.55 (bs, 24 H), 3.50 (s, 12 H), 8.87 (bs, 8 H), 18.2 (bs, 8 H). If assuming the yield was 100 % in the reaction between Rh(tmp)[21] **3** and $I_2$, the yield of photolysis was estimated to be 80 %.

**Preparation of Rh(tmp)(CO$^i$Pr) (6a) from diisopropyl ketone**. In the benzene solution of $Rh^{II}$(tmp) **3** (0.0089 mmol), $PPh_3$ (2.3 mg, 0.0089 mmol) was added and the reaction mixture was stirred at 25 $^o$C. After 10 min, the benzene solvent was removed by vacuum evaporation and then degassed diisopropyl ketone (2.0 mL) and $H_2O$ (8 μL) were added. The mixture was then stirred under nitrogen at 25 $^o$C for 10 min. Excess diisopropyl ketone was removed and the dark red crude product was then purified by column chromatography on silica gel eluting with hexane/$CH_2Cl_2$ (1:1) to give the reddish purple solid of Rh(tmp)(CO$^i$Pr)[16] **6a** (7.6 mg, 0.0080 mmol, 90% yield). $R_f$ = 0.52 (Hexane:$CH_2Cl_2$ = 1:1). $^1$H NMR (700 MHz, $CDCl_3$) δ -3.33 (hept, 1 H, $^3J_{H\text{-}H}$ = 7.12 Hz), -2.04 (d, 6 H, $^3J_{H\text{-}H}$ = 7.91 Hz), 1.79 (s, 12 H), 1.97 (s, 12 H), 2.61 (s, 12 H), 7.24 (s, 4 H), 7.28 (s, 4 H), 8.53 (s, 8 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 175 MHz): 15.46, 43.54, 120.24, 127.83, 130.72, 137.63, 138.49, 139.30, 142.76, 207.05 (d, $^1J_{Rh\text{-}C}$ = 32.0 Hz). HRMS (ESI-MS): Calcd. for $[C_{60}H_{59}N_4ORh + Na]^+$: m/z 977.3636. Found: m/z 977.3628. Acetone (76 %) was observed in GC/MS using naphthalene as the internal standard. Acetone, $t_R$ = 2.153 min, EIMS: *m/z* (rel.%) 58 (3), 43 (10).

**Preparation of Rh(tmp)(COPh) (6b) from isopropyl phenyl ketone**. In the benzene solution of $Rh^{II}$(tmp) **3** (0.0089 mmol), $PPh_3$ (2.3 mg, 0.0089 mmol) was added and the reaction mixture was stirred at 25 $^o$C. After 10 min, the benzene solvent was removed by vacuum evaporation and then degassed isopropyl phenyl ketone (2.0 mL) and $H_2O$ (8 μL) were added. The mixture was then stirred under nitrogen at 25 $^o$C for 10 min. Excess isopropyl phenyl ketone was removed and the dark red crude product was then purified by column chromatography on silica gel eluting with hexane/$CH_2Cl_2$ (1:1) to give the reddish purple solid of Rh(tmp)(COPh) **6b** (6.3 mg, 0.0064 mmol, 72 % yield). $R_f$ = 0.45 (Hexane : $CH_2Cl_2$ = 1 : 1). $^1$H NMR (700 MHz, $CDCl_3$) δ 1.70 (s, 12 H), 1.94 (s, 12 H), 2.61 (s, 12 H), 2.84 (d, 2 H, $^3J_{H\text{-}H}$ = 7.8 Hz), 5.87 (m, 2 H), 6.26 (t, 1 H, $^3J_{H\text{-}H}$ = 7.4 Hz), 7.22 (s, 4 H), 7.28 (s, 4 H), 8.54 (s, 8 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 175 MHz): d 118.43, 120.45, 126.11, 126.66, 127.89, 130.89, 137.66, 138.40, 138.61, 139.34, 142.72, 200.17 (d, $^1J_{Rh\text{-}C}$ = 31.4 Hz). HRMS (FABMS): Calcd. for $[C_{63}H_{57}N_4ORh]^+$: m/z 988.3587. Found: m/z 988.3582. Acetone (48 %) was observed in GC/MS using naphthalene as the internal standard. Acetone, $t_R$ = 2.153 min, EIMS: *m/z* (rel.%) 58 (3), 43 (10).

**Preparation of Rh(tmp)(COMe) (6c) from isopropyl methyl ketone**. In the benzene solution of $Rh^{II}$(tmp) **3** (0.0089 mmol), $PPh_3$ (2.3 mg, 0.0089 mmol) was added and the reaction mixture was stirred at 25 $^o$C. After 10 min, the benzene solvent was removed by vacuum evaporation and then degassed isopropyl methyl ketone (2.0 mL) and $H_2O$ (8 μL) were added. The mixture was then stirred under nitrogen at 25 $^o$C for 10 min. Excess isopropyl methyl ketone was removed and the dark red crude product was then purified by column chromatography on silica gel eluting with hexane/$CH_2Cl_2$ (1:1) to give the reddish purple solid of Rh(tmp)(COMe) **6c** (4.5 mg, 0.0048 mmol, 54 % yield). $R_f$ = 0.61 (Hexane:$CH_2Cl_2$ = 1:1). $^1$H NMR (700 MHz, $CDCl_3$) δ -2.63 (s, 3 H), 1.86 (s, 12 H), 1.88 (s, 12 H), 2.61 (s, 12 H), 8.55 (s, 8 H). *m*-Phenyl hydrogens are obscured by solvent (7.26). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 175 MHz): d 30.04, 120.19, 127.82, 130.65, 137.67, 138.41, 139.04, 139.59, 142.61, 198.43 (d, $^1J_{Rh\text{-}C}$ = 30.3 Hz). HRMS (FABMS): Calcd. for $[C_{58}H_{55}N_4ORh]^+$: m/z 926.3431. Found: m/z 926.3425. Acetone (32 %) was observed in GC/MS using naphthalene as the internal standard. Acetone, $t_R$ = 2.153 min, EIMS: *m/z* (rel.%) 58 (3), 43 (10).

**Preparation of Rh(tmp)[COCHMe$(CH_2)_3$COMe] (6d)**. In the benzene solution of $Rh^{II}$(tmp) **3** (0.0089 mmol), $PPh_3$ (2.3 mg, 0.0089 mmol) was added and the reaction mixture was stirred at 25 $^o$C. After 10 min, the benzene solvent was removed by vacuum

evaporation and then degassed 2,6-dimethylcyclohexanone (2.0 mL) and $H_2O$ (8 μL) were added. The mixture was then stirred under nitrogen at 25 °C for 10 min. Excess 2,6-dimethylcyclohexanone was removed and the dark red crude product was then purified by column chromatography on silica gel eluting with hexane/$CH_2Cl_2$ (1:1) to give the reddish purple solid of Rh(tmp)[COCHMe$(CH_2)_3$COMe] **6d** (7.6 mg, 0.0074 mmol, 83 % yield). $R_f$ = 0.08 (Hexane:$CH_2Cl_2$ = 1:1). $^1$H NMR (700 MHz, $CDCl_3$) δ -3.29 (sext, 1 H, $^3J_{H-H}$ = 6.8), -2.23 (d, 3 H, $^3J_{H-H}$ = 6.7), -1.72 (m, 1 H), -1.40 (m, 1 H), -0.89 (m, 1 H), -0.46 (m, 1 H), 1.20 (m, 2H), 1.63 (s, 3 H), 1.71 (s, 12 H), 2.05 (s, 12 H), 2.61 (s, 12 H), 7.23 (s, 4 H), 7.30 (s, 4 H), 8.54 (s, 8 H). $^{13}$C{$^1$H} NMR (175 MHz, $CDCl_3$) δ 12.29, 19.43, 29.37, 30.54, 42.82, 49.13, 120.36, 127.95, 130.82, 137.69, 138.43, 139.06, 139.49, 142.81, 206.67 (d, $^1J_{Rh-C}$ = 28.93 Hz), 208.04. HRMS (ESI-MS): Calcd. for $[C_{64}H_{65}N_4O_2Rh+H]^+$: m/z 1025.4235. Found: m/z 1025.4238.

**Preparation of Rh(tmp)[CO$(CH_2)_4$COMe] (6e)**. In the benzene solution of $Rh^{II}$(tmp) **3** (0.0089 mmol), $PPh_3$ (2.3 mg, 0.0089 mmol) was added and the reaction mixture was stirred at 25 °C. After 10 min, the benzene solvent was removed by vacuum evaporation and then degassed 2-methylcyclohexanone (2.0 mL) and $H_2O$ (8 μL) were added. The mixture was then stirred under nitrogen at 25 °C for 10 min. Excess 2-methylcyclohexanone was removed and the dark red crude product was then purified by column chromatography on silica gel eluting with hexane/$CH_2Cl_2$ (1:1) to give the reddish purple solid of Rh(tmp)[CO$(CH_2)_4$COMe] **6e** (7.8 mg, 0.0077 mmol, 87 % yield). $R_f$ = 0.08 (Hexane:$CH_2Cl_2$ = 1:1). $^1$H NMR (700 MHz, $CDCl_3$) δ -2.94 (t, 2 H, $^3J_{H-H}$ = 7.2), -1.21 (m, 2 H), -0.49 (m, 2 H), 1.13 (t, 2 H, $^3J_{H-H}$ = 7.4), 1.58 (s, 3 H), 1.86 (s, 12 H), 1.89 (s, 12 H), 2.61 (s, 12 H), 8.54 (s, 8 H). *m*-Phenyl hydrogens are obscured by solvent (7.26). $^{13}$C{$^1$H} NMR ($CDCl_3$, 175 MHz) δ 21.22, 22.64, 29.43, 42.28, 44.74, 120.14, 127.85, 130.82, 137.68, 138.39, 139.38, 142.60, 200.90 (d, $^1J_{Rh-C}$ = 30.52 Hz), 207.99. HRMS (FABMS): Calcd. for $[C_{63}H_{63}N_4O_2Rh]^+$: m/z 1010.4006. Found: m/z 1010.4079.

**Preparation of Rh(tmp)(COPh) (6b) from acetophenone**. In the benzene solution of $Rh^{II}$(tmp) **3** (0.0089 mmol), $PPh_3$ (2.3 mg, 0.0089 mmol) was added and the reaction mixture was stirred at 25 °C. After 10 min, the benzene solvent was removed by vacuum evaporation and then degassed acetophenone (2.0 mL) and $H_2O$ (8 μL) were added. The mixture was then stirred under nitrogen at 25 °C for 2 d. Excess acetophenone was removed and the dark red crude product was then purified by column chromatography on silica gel eluting with hexane/$CH_2Cl_2$ (1:1) to give the reddish purple solid of Rh(tmp)(COPh) **6b** (2.2 mg, 0.0022 mmol, 25 % yield).

**Preparation of Rh(tmp)(COPh) (6b) from propiophenone**. In the benzene solution of $Rh^{II}$(tmp) **3** (0.0089 mmol), $PPh_3$ (2.3 mg, 0.0089 mmol) was added and the reaction mixture was stirred at 25 °C. After 10 min, the benzene solvent was removed by vacuum evaporation and then degassed propiophenone (2.0 mL) and $H_2O$ (8 μL) were added. The mixture was then stirred under nitrogen at 25 °C for 1 d. Excess propiophenone was removed and the dark red crude product was then purified by column chromatography on silica gel eluting with hexane/$CH_2Cl_2$ (1:1) to give the reddish purple solid of Rh(tmp)(COPh) **6b** (3.4 mg, 0.0035 mmol, 39 % yield).

**Preparation of Rh(tmp)(COPh) (6b) from *n*-butyrophenone**. In the benzene solution of $Rh^{II}$(tmp) **3** (0.0089 mmol), $PPh_3$ (2.3 mg, 0.0089 mmol) was added and the reaction mixture was stirred at 25 °C. After 10 min, the benzene solvent was removed by vacuum evaporation and then degassed *n*-butyrophenone (2.0 mL) and $H_2O$ (8 μL) were added. The mixture was then stirred under nitrogen at 25 °C for 4 d. Excess *n*-butyrophenone was removed and the dark red crude product was then purified by column chromatography on silica gel eluting with hexane/$CH_2Cl_2$ (1:1) to give the reddish purple solid of Rh(tmp)(COPh) **6b** (1.2 mg, 0.0012 mmol, 13 % yield).

**Preparation of Rh(tmp)(COMe) (6c) from 2,4-pentanedione**. In the benzene solution of $Rh^{II}$(tmp) **3** (0.0045 mmol), $PPh_3$ (1.2 mg, 0.0050 mmol) was added and the reaction mixture was stirred at 25 °C. After 10 min, the benzene solvent was removed by vacuum evaporation and then degassed 2,4-pentanedione (1.0 mL) and $H_2O$ (4 μL) were added. The mixture was then stirred under nitrogen at 25 °C for 10 min. Excess 2,4-pentanedione was removed and there was no Rh(tmp)(COMe) in the dark red crude product.

**Preparation of Rh(tmp)(COMe) (6c) from 3-methyl-2,4-pentanedione**. In the benzene solution of $Rh^{II}$(tmp) **3** (0.0045 mmol), $PPh_3$ (1.2 mg, 0.0050 mmol) was added and the reaction mixture was stirred at 25 °C. After 10 min, the benzene solvent was removed by vacuum evaporation and then degassed 3-methyl-2,4-pentanedione (1.0 mL) and $H_2O$ (4 μL) were added. The mixture was then stirred under nitrogen at 25 °C for 10 min. Excess 3-methyl-2,4-pentanedione was removed and there was no Rh(tmp)(COMe) in the dark red crude product.

**Preparation of ($PPh_3$)Rh(tmp)OH (7).** In a benzene-$d_6$ solution (500 μL) of $Rh^{II}$(tmp) (0.00056 mmol) at r.t., the degassed benzene-$d_6$ solution (500 μL) of $H_2O$ (4 μL) and $PPh_3$ (0.1 mg, 0.00044 mmol) was added. The mixture was kept under nitrogen at 25 °C. Immediately, the color changed from dark orange to red. $^1$H NMR of ($PPh_3$)Rh(tmp) ($C_6D_6$, 400 MHz) δ 1.92 (s, 12 H), 2.14 (s, 12 H), 2.43 (s, 12 H), 8.83 (s, 8 H). The ($PPh_3$)Rh(tmp)O-H signal is not observed in $^1$H NMR spectrum, likely due to the rapid exchange with water. HRMS (ESI-MS) result: calcd for $C_{74}H_{68}N_4OPRh$ $[M]^+$ m/z 1162.4180, found m/z 1162.4194.

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## Notes and references

1 J. H. Sinfelt, *Catalysis-Science and Technology*; Anderson, J. R., Boudart, M**.** Eds.; Springer-Verlag: West Berlin, 1981; Vol. 1, Chapter 5, pp 257-300. (b) M. Murakam and Y. Ito In *Topics in Organometallic Chemistry, Vol. 3, Cleavage of Carbon-Carbon Single Bonds by Transition Metals*, Murai, S. Ed., Springer-Verlag: Berlin Heidelberg, 1999, 97-129. (c) M. Gozin, A. Weisman，Y. Ben-David and D. Milstein, *Nature*, 1993, **364**, 699-701. (d) B. Rybtchinski and D. Milstein, *Angew. Chem., Int. Ed.,* 1999, **38,** 870-883.

2 L. E. J. Brouwer, *The Petroleum Handbook*, 5th Ed; Shell Co. of Hong Kong: London, 1966.

3 B. S. Appel, T. N. Adams, M. J. Roberts, W. F. Lange, J. H. Freiss, C. T. Einfeldt and M. C. Carnesi, Process for Conversion of Organic, Waste, or Low-value Materials into Useful Products. U.S. Patent 8,003,833, Aug 23, 2011.

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

5 (a) B. Rybtchinski, A. Vigalok, Y. Ben-David and D. Milstein, *J. Am. Chem. Soc.* 1996, **118,** 12406-12415. (b) B. Rybtchinski and D. Milstein, *Angew. Chem. Int. Ed.,* 1999, **38**, 870-883.

6 (a) L. Cassar, Eaton, P. E. Eaton and J. Halpern, *J. Am. Chem. Soc.* 1970, **92**, 3515-3518. (b) H. Ogoshi, J. Setsume and Z. Yoshida,

*Chem. Commun.,* 1975, **14,** 572-573. (c) C. Perthuisot and D. A. Sweigart, *Organometallics,* 1999, **18**, 4887-4888.
7 P. Eilbracht and P. Dahler, *Chem. Ber.,* 1980, **113**, 542-554.
8 F. W. S. Benfield and M. L. H. Green *J. Chem. Soc., Dalton Trans.*, 1974, 1324-1331.
9 (a) J. W. Suggs and C. H. Jun, *J. Am. Chem. Soc.,* 1984, **106**, 3054-3056. (b) J. W. Suggs and C. H. Jun, *J. Am. Chem. Soc.,* 1986, **108**, 4679-4681. (c) J. W. Suggs, M. J. Wovkulich and S. D. Cox ,*Organometallics,* 1985, **4**, 1101-1107.
10 (a) M. Murakami, H. Amii and Y. Ito, *Nature*, 1994, **370**, 541-542. (b) M. Murakami, T. Tsuruta and Y. Ito, *Angew. Chem. Int. Ed.* 2000, **39**, 2484-2486.
11 A. Sachio and U. Kazuak,i *Preparation of Lower Fatty Acids From Lower Aliphatic Ketones*; Jpn. Kokai Tokkyo Koho 06-329577, Nov 29, 1994.
12 H. S. Fung, B. Z. Li and K. S. Chan, *Organometallics,* 2010**, 29**, 4421-4423.
13 C. S. Chan, S. Y. Lee and K. S. Chan, *Organometallics,* 2013, **32**, 151-156.
14 S. Y. Lee, T. H. Lai, K. S. Choi and K. S. Chan, *Organometallics*, 2011, **30**, 3691-3693.
15 S. Y. Lee and K. S. Chan, *Organometallics,* 2013, **32**, 5391-5401.
16 H. S. Fung, B. Z. Li and K. S. Chan, *Organometallics,* 2010, **29**, 4421-4423. (b) H. S. Fung, B. Z. Li and K. S. Chan, *Organometallics,* 2012, **31**, 570-579.
17 L. Zhang and K. S. Chan, *J. Organomet. Chem.,* 2006, **691**, 3785-3787.
18 K. S. Choi, T. H. Lai, S. Y. Lee, K. S. Chan, *Organometallics,* **2011**, *30*, 2633-2635.
19 (a) R. W. Wagner, D. S. Lawrence and J. S. Lindsey, *Tetrahedron Lett*., 1987, **28**, 3069-3070. (b) K. S. Chan, X. M. Chen and T. C. W. Mak, *Polyhedron,* 1992, **11**, 2703-2716.
20 (a) X. Zhou, Q. Li, T. C. W. Mak and K. S. Chan, *Inorg. Chim. Acta.,* 1998, **270,** 551-554. (b) X. Zhou, R.-J. Wang, F. Xue, T. C. W. Mak and K. S. Chan, *J. Organomet. Chem.,* 1999, **580**, 22-25.
21 B. B. Wayland, A. E. Sherry, G. Poszmik and A. G. Bunn, *J. Am. Chem. Soc.,* 1992, **114**, 1673-1681.