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Scope and Mechanism of Carbonyl Carbon and α-Carbon Bond Cleavage of Ketones by Iridium(III) Porphyrin Complexes

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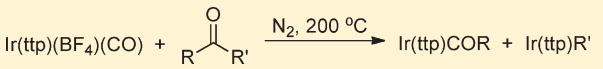
Supporting Information

ABSTRACT: Chemoselective carbonyl carbon and α-carbon bond activation (CCA) of ketones (RCOR′) was successfully achieved with various iridium(III) tetrakis-4-tolylporphyrinato complexes Ir(ttp)X (X = $(BF_4)(CO)$, Cl(CO), and Me) to give the corresponding Ir(ttp)COR (R = Ar, Me, or Et) and Ir(ttp)R′ (R′ = Me or Et) complexes. $Ir(ttp)(BF_4)(CO)$ exhibited the highest reactivity toward CCA, as it possesses a higher Lewis acidity in catalyzing the aldol condensation of ketones to give water, which hydrolyzes the kinetic products, C−H bond activation (CHA) complexes, into the proposed Ir(ttp)OH for a subsequent CCA process. The CCA step is nonregioselective in giving both Ir(ttp)R′ and Ir(ttp)COR. However, Ir(ttp)R′ was kinetically less stable toward hydrolysis to give Ir(ttp)OH. Thus, only Ir(ttp)COR was observed as the sole CCA product.



INTRODUCTION

Carbon−carbon bond activation (CCA) of carbonyl compounds at the C(=O)−C(α) bond with low-valent transition metal complexes has been applied in organic synthesis by utilizing ring-strained[1] and chelation-assisted systems.[2] These applications have furnished valuable organic intermediates, and mechanistic studies suggested that oxidative addition (OA) is the commonly accepted mechanism.[1,2]

For high-valent Rh(III) and Ir(III) complexes, OA is challenging due to the much less accessible M(V) intermediate.[3] OA is even more difficult for group 9 metalloporphyrins, as it involves the sterically demanding intermediate with three substituents located in a *cis*-manner to the porphyrin plane.

Recently, we have communicated that high-valent iridium(III) tetrakis-4-tolylporphyrinato carbonyl chloride (Ir(ttp)Cl(CO)) cleaved the carbonyl carbon and α-carbon bond of acetophenones (ArCOMe) to give the corresponding iridium porphyrin acyl complexes (Ir(ttp)COAr) (eq 1).[4] Mechanistic studies suggested that Ir(ttp)Cl(CO) reacted with acetophenones to give the α- and aromatic carbon−hydrogen bond activation (CHA) products as the kinetic products. Then the CHA products further underwent hydrolysis with water, formed from the iridium porphyrin-catalyzed aldol condensation of ketones, to give the proposed intermediates of Ir(ttp)OH and/or Ir(ttp)H. Finally, Ir(ttp)OH and/or Ir(ttp)H likely underwent σ-bond metathesis in the CCA process (Scheme 1). An intriguing reaction feature is the sole formation of Ir(ttp)COAr as the only CCA product, suggesting the apparent and surprisingly highly regioselective bond cleavage.

$$\underset{\mathbf{1a}}{Ir(ttp)Cl(CO)} + \underset{\mathbf{2a\text{-}d}}{ArCOMe} \xrightarrow[12-20\ d]{N_2,\ 200\ ^\circ C} \underset{\mathbf{3a\text{-}d}\ 71-79\%}{Ir(ttp)COAr} \quad (1)$$

$$Ar = p\text{-}F\text{-}C_6H_4, Ph, p\text{-}Me\text{-}C_6H_4, p\text{-}OMe\text{-}C_6H_4$$

Recently, we have reported the CCA of various unstrained ketones, with Rh(ttp)Me with the bulkier isopropyl ketones being more reactive.[5] Mechanistic studies revealed that Rh(ttp)OH was the intermediate in cleaving the C(=O)−C(α) bonds.

We have thus undertaken systematic studies of the CCA of various ketones (RCOR′) with iridium porphyrin complexes bearing different counteranions to define the scopes and the reactivties. Furthermore, mechanistic studies revealed that the CCA step is chemo- but not regioselective, giving both Ir(ttp)COR and Ir(ttp)R′. The formation of Ir(ttp)COR as the only or major product is due to its higher stability toward hydrolysis than Ir(ttp)R′. We have thus proposed that Ir(ttp)OH is the more likely intermediate for CCA. We now report our findings.

RESULTS AND DISCUSSION

Ir(ttp) X-Anion Effect on CCA. Initially, the chemoselective C(=O)−C(α) bond activation of ketone was studied by heating Ir(ttp)X (X = $(BF_4)(CO)$, **1b**, Cl(CO), **1a**, Me, **1c**) in acetophenone **2b** at 200 °C, respectively (Table 1 and eq 2). The most Lewis acidic, $Ir(ttp)(BF_4)(CO)$ **1b**, reacted with acetophenone **2b** to give the sole CCA product of Ir(ttp)COPh **3b** in 58% yield together with the aromatic carbon−hydrogen bond activation (ArCHA) products of Ir(ttp)(*para*- and *meta*-COMe-C_6H_4) **4b,c** in trace amount (<5%) in the shortest reaction time of 2 days (Table 1, entry 1). Similarly, the more electron-rich Ir(ttp)Cl(CO) **1a** and Ir(ttp)Me **1c** cleaved the C(=O)−C(α) bond of acetophenone **2b** to give Ir(ttp)COPh **3b** in 71% and 80% yields in longer reaction times of 20 days[4] and 26 days, respectively (Table 1, entries 2 and 3).

To identify the reaction intermediates, the reaction of acetophenone **2b** with $Ir(ttp)(BF_4)(CO)$ **1b** was then conducted in a shorter time. In 4 h, $Ir(ttp)(BF_4)(CO)$ **1b** reacted with acetophenone **2b** to give a mixture of CHA products of **4a**−**c** in <5% (**4a**), 13% (**4b**), and 26% (**4c**) yields, in addition to a 13% yield of

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Scheme 1. Previous Proposed Pathway for the CCA of Acetophenone with Ir(ttp)X (X = OH, H) via σ-Bond Metathesis[4]

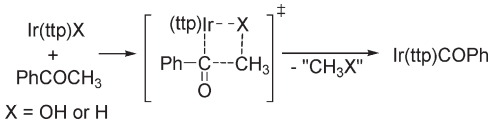


Table 1. CCA of Acetophenone by Ir(ttp)X

$$\underset{\textbf{1a-c}}{\text{Ir(ttp)X}} + \underset{\textbf{2b}}{\text{PhCOMe}} \xrightarrow[\text{time}]{\text{N}_2,\ 200\ ^\circ\text{C}} \underset{\textbf{3b}}{\text{Ir(ttp)COPh}} \qquad (2)$$

entry	X	time/d	yield **3b**/%
1[a]	$(BF_4)(CO)$, **1b**	2	58
2[b]	Cl(CO), **1a**	20	71
3	Me, **1c**	26	80

[a] **4b** and **4c** were observed by TLC analysis in trace amount (<5%). [b] **4b** and **4c** were isolated in 4% and 8% yield, respectively. See ref 4 for details.

Ir(ttp)COPh **3b**. Ir(ttp)Me **1c**, resulting from nonregioselective CCA, was also observed in trace amount (<5%) (eq 3). No Ir(ttp)Ph or Ir(ttp)COMe was observed from the C(=O)−C(Ph) cleavage probably due to the stronger C(=O)−C(Ph) bond (~94.7 kcal mol^{-1})[6] over the C(=O)−C(Me) bond (85.0 kcal mol^{-1})[6] and the sterically more hindered phenyl group. This result suggests that the α-carbon−hydrogen bond activation (α-CHA) product (Ir(ttp)CH_2COPh, **4a**), ArCHA products (Ir(ttp)(*para*- and *meta*-COMe-C_6H_4), **4b,c**), and Ir(ttp)Me **1c** are possible intermediates to afford Ir(ttp)COPh **3b**.

$$\underset{\textbf{1b}}{\text{Ir(ttp)(BF}_4\text{)(CO)}} + \underset{\textbf{2b}}{\text{PhCOMe}} \xrightarrow[4\text{ h}]{\text{N}_2,\ 200^\circ\text{C}} \underset{\textbf{3b}\ 13\%}{\text{Ir(ttp)COPh}} + \underset{\substack{\textbf{4b}\ \textit{para}\text{-}\ 13\% \\ \textbf{4c}\ \textit{meta}\text{-}\ 26\%}}{\text{Ir(ttp)(m,p-COMe-C}_6\text{H}_4\text{)}} + \underset{\textbf{4a}\ <5\%}{\text{Ir(ttp)CH}_2\text{COPh}} + \underset{\textbf{1c}\ <5\%}{\text{Ir(ttp)Me}} \qquad (3)$$

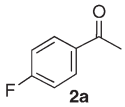
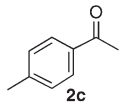
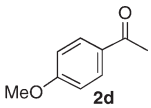
Therefore, Ir(ttp)CH_2COPh **4a**, Ir(ttp)Ph **4b′** (as an ArCHA complex analogue), and Ir(ttp)Me **1c** were independently heated in acetophenone **2b** at 200 °C. Ir(ttp)Ph **4b′** reacted poorly to give Ir(ttp)COPh **3b** in <5% yield with 88% recovery yield even upon prolonged heating for 28 days (eq 4).[4] Transformations of Ir(ttp)CH_2COPh **4a** to ArCHA complexes **4b,c** and Ir(ttp)Me **1c** to the α-CHA complex **4a** as the major products were observed in a shorter reaction time of 15 and 5 days (eqs 5[4] and 6), respectively. These results suggest none of Ir(ttp)CH_2COPh **4a**, Ir(ttp)(*para*- and *meta*-COMe-C_6H_4) **4b**, **c**, and Ir(ttp)Me **1c** directly reacted with acetophenone **2b** to give Ir(ttp)COPh **3b**, as these reaction are much too slow compared to that of Ir(ttp)(BF_4)(CO) (eq 2). It is believed that Ir(ttp)CH_2COPh **4a**, Ir(ttp)(*para*- and *meta*-COMe-C_6H_4) **4b**, **c**, and Ir(ttp)Me **1c** are first hydrolyzed by water, generated from the aldol condensation,[4] to give Ir(ttp)OH for the CCA process. Indeed, Ir(ttp)CH_2COPh **4a** was hydrolyzed by water (100 equiv) in a less polar solvent of benzene-d_6 to give acetophenone **2b** in 20% yield in 3 days (eq 7). The reaction stoichiometry suggests that the iridium porphyrin coproduct would be Ir(ttp)OH.[4] Thus, Ir(ttp)OH is proposed to be the intermediate

Table 2. *para*-Substituent Effect on the CCA of Acetophenones by Ir(ttp)X

$$\text{Ir(ttp)X} + \text{ArCOMe} \xrightarrow[\text{time}]{\text{N}_2,\ 200\ ^\circ\text{C}} \underset{\textbf{3a-d}}{\text{Ir(ttp)COAr}} \qquad (9)$$

X = (BF_4)(CO) **1b**, Cl(CO) **1a**, Me **1c**

Ar = *p*-F-C_6H_4 **2a**, *p*-Me-C_6H_4 **2c**, *p*-OMe-C_6H_4 **2d**

Entry	X	ArCOMe (p*K*a in DMSO)[11a]	Time / d	Product (% Yield)
1	(BF_4)(CO) **1b**	 **2a** (24.45)	2	**3a** (54)
2[a]	Cl(CO) **1a**		13	**3a** (74)
3	Me **1c**		6	**3a** (92)
4	(BF_4)(CO) **1b**	 **2c** (25.19)	2	**3c** (75)
5[a]	Cl(CO) **1a**		12	**3c** (78)
6	Me **1c**		21	**3c** (58)
7	(BF_4)(CO) **1b**	 **2d** (25.70)	2	**3d** (80)
8[a]	Cl(CO) **1a**		15	**3d** (79)
9	Me **1c**		24	**3d** (82)

[a] See ref 4 for details.

to cleave the C(=O)−C(α) bond of ketones, the same as in the rhodium porphyrin complex.[5] Further evidence for the intermediacy of Ir(ttp)OH is discussed in the reaction between Ir(ttp)(BF_4)(CO) **1b** and acetone **2e** (eq 12).

$$\underset{\substack{\textbf{4b'} \\ \text{recovery 88\%}}}{\text{Ir(ttp)Ph}} + \underset{\textbf{2b}}{\text{PhCOMe}} \xrightarrow[28\text{ d}]{\text{N}_2,\ 200\ ^\circ\text{C}} \underset{\textbf{3b}\ <5\%}{\text{Ir(ttp)COPh}} \qquad (4)$$

$$\underset{\textbf{4a}}{\text{Ir(ttp)CH}_2\text{COPh}} + \underset{\textbf{2b}}{\text{PhCOMe}} \xrightarrow[15\text{ d}]{\text{N}_2,\ 200\ ^\circ\text{C}} \underset{\textbf{3b}\ 21\%}{\text{Ir(ttp)COPh}} + \underset{\substack{\textbf{4b}\ \textit{para}\text{-}\ 21\% \\ \textbf{4c}\ \textit{meta}\text{-}\ 42\%}}{\text{Ir(ttp)(m,p-COMe-C}_6\text{H}_4\text{)}} \qquad (5)$$

$$\underset{\substack{\textbf{1c} \\ \text{recovery 74\%}}}{\text{Ir(ttp)Me}} + \underset{\textbf{2b}}{\text{PhCOMe}} \xrightarrow[5\text{ d}]{\text{N}_2,\ 200^\circ\text{C}} \underset{\textbf{3b}\ <5\%}{\text{Ir(ttp)COPh}} + \underset{\textbf{4a}\ 11\%}{\text{Ir(ttp)CH}_2\text{COPh}} \qquad (6)$$

$$\underset{\textbf{4a}}{\text{Ir(ttp)CH}_2\text{COPh}} + \underset{100\text{ equiv}}{\text{H}_2\text{O}} \xrightarrow[3\text{ d},\ \text{C}_6\text{D}_6]{200\ ^\circ\text{C}} \underset{20\%}{\text{Ir(ttp)H}} + \underset{\textbf{2b}\ 20\%}{\text{PhCOMe}} \qquad (7)$$

Ir(ttp) X-Effect on Aldol Condensation. To verify the importance of water formation, the rate of the aldol condensation catalyzed by Ir(ttp)X (X = (BF_4)(CO), **1b**, Cl(CO), **1a**, Me, **1c**) was examined. The most Lewis acidic, Ir(ttp)(BF_4)(CO) **1b**, gave higher yields of the aldol condensation products (**5a** and **5b**) in the shortest reaction time than Ir(ttp)Cl(CO) **1a**[4] and Ir(ttp)Me **1c** (eq 8).[7] These results rationalize the higher reactivity of Ir(ttp)(BF_4)(CO) **1b** toward ketone CCA in two ways: (1) It serves as a more efficient aldol condensation catalyst for the generation of water; and (2) HBF_4 (pK_a ca. 0.1 in MeCN, bp 130 °C (dec)),[8,9] formed from α-CHA, also catalyzes the aldol condensation more rapidly than HCl (pK_a ca. 8.6 in MeCN,

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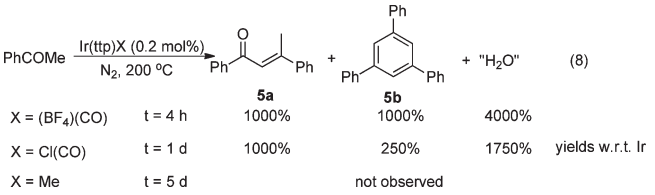
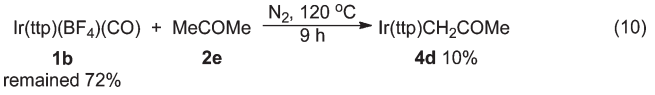
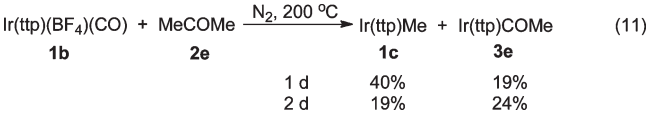
bp −85 °C).[8,10] The water formed from the aldol condensation facilitates the hydrolytic generation of Ir(ttp)OH for CCA.

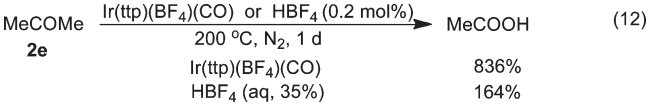


Acetophenones: *para*-Substituent Effect. *para*-Substituted acetophenones **2a,c,d** successfully reacted with Ir(ttp)X to give Ir(ttp)CO(*p*-FG-C_6H_4) **3a,c,d** in 54−92% yields at 200 °C (Table 2, eq 9). *para*-Substituted acetophenones **2a,c,d** underwent CCA with the most reactive iridium porphyrin, Ir(ttp)(BF_4)(CO) **1b**, at the same rate as acetophenone **2b**. *para*-Substituted acetophenones **2a,c,d**, however, reacted faster with the less reactive Ir(ttp)Cl(CO) **1a**[4] and Ir(ttp)Me **1c** than acetophenone **2b** likely due to the reduction or elimination of Ar−CHA by steric hindrance (Table 1 vs Table 2). The largest difference in reactivity order for *para*-substituted acetophenones was observed with Ir(ttp)Me **1c**, and the order is **2a** > **2c** ∼ **2d**, in the order of electron deficiency of ketones. We rationalize that the trend is due to the more facile aldol condensation of more acidic ketones (pK_a in DMSO: **2a** (24.45); **2b** (24.70); **2c** (25.19); **2d** (25.70)).[11]

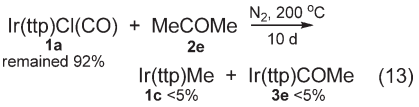
Aliphatic Ketone CCA. To extend the substrate scope of the CCA reaction with Ir(ttp)X, the prototypical aliphatic ketone, acetone **2e**, was examined first. Initially, Ir(ttp)(BF_4)(CO) **1b** was heated in acetone **2e** at 120 °C for 9 h. No CCA occurred, but only the α-CHA product of Ir(ttp)CH_2COMe **4d** in 10% yield was isolated with 72% yield of Ir(ttp)(BF_4)(CO) **1b** remaining unreacted (eq 10). When the reaction mixture of Ir(ttp)(BF_4)(CO) **1b** and acetone **2e** was heated at a higher temperature of 200 °C for 1 day, CCA was successfully achieved though nonregioselectively to give Ir(ttp)COMe **3e** in 19% yield and Ir(ttp)Me **1c** in 40% yield (eq 11). Upon further heating, Ir(ttp)Me **1c** was slowly converted to Ir(ttp)COMe **3e** (eq 11). On the other hand, MeCOOH in 836% yield (cf. Ir) was quantified from the reaction between acetone **2e** and Ir(ttp)(BF_4)(CO) **1b** at 200 °C for 1 day (eq 12). Although HBF_4, cogenerated from the α-CHA process, alone also assisted the formation of MeCOOH in 164% yield (cf. HBF_4) from acetone **2e** (eq 12), the significant yield enhancement with Ir(ttp)(BF_4)(CO) **1b** still suggests that the chemo- but not regioselective C(=O)−C(α) bond cleavage is via Ir(ttp)OH (Scheme 2).[12] The catalytic generation of MeCOOH is likely due to hydrolysis of Ir(ttp)COMe.[13] Thus, a catalytic CCA of acetone **2e** to acetic acid was achieved.

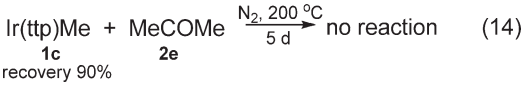






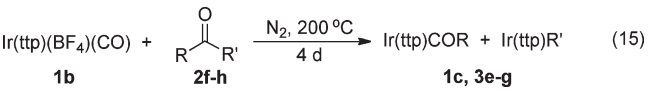
The less reactive iridium porphyrin complexes were then examined. Unfortunately, Ir(ttp)Cl(CO) **1a** dissolved poorly in acetone **2e**, and hence only trace amounts of CCA products Ir(ttp)Me **1c** and Ir(ttp)COMe **3e** were isolated, with most of the Ir(ttp)Cl(CO) **1a** unreacted upon prolonged heating at 200 °C for 10 days (eq 13). Besides, the lower acidity of acetone **2e** (pK_a in DMSO: **2b** (24.70);[11a] **2e** (26.5)[14]) may account for the lower reactivity. Unlike acetophenone, acetone **2e** did not react well with Ir(ttp)Me **1c** at 200 °C for 5 days (eq 14). Therefore, only the more Lewis acidic Ir(ttp)(BF_4)(CO) **1b** can activate the C(=O)−C(α) of acetone efficiently.





With the successful reaction with acetone **2e**, various aliphatic ketones **2f−h** were then reacted with Ir(ttp)(BF_4)(CO) **1b** at 200 °C (Table 3, eq 15). Generally, the CCA was chemoselective but not regionselective at the C(=O)−C(α) bond to give both Ir(ttp)COR and Ir(ttp)R′. The regioselectivity of CCA of ketones was dependent on the steric hindrance of the alkyl groups as well as the bond dissociation energy (BDE) of C(=O)−C(α) bonds (Table 3, entries 1 and 2).

Table 3. CCA of Aliphatic Ketones with Ir(ttp)(BF_4)(CO)

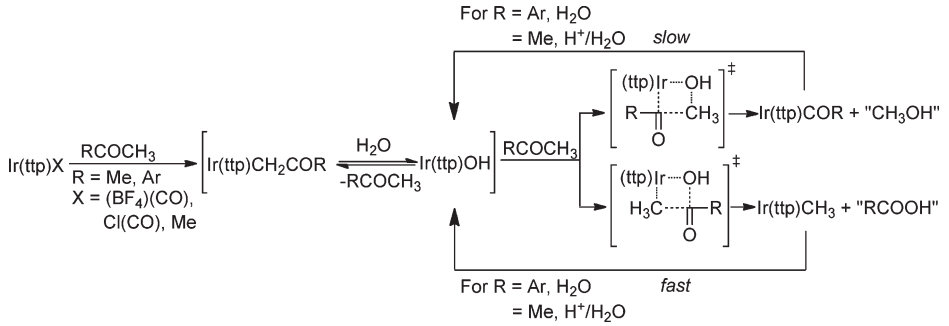


		yield/%	
entry	RCOR′	product (yield)	total
1	MeCOEt **2f**	Ir(ttp)Me **1c** (5); Ir(ttp)COMe **3e** (23); Ir(ttp)Et **3f** (<5); Ir(ttp)COEt **3g** (5)	33
2	MeCO^{i}Pr **2g**	Ir(ttp)Me **1c** (43); Ir(ttp)COMe **3e** (9)	52
3	EtCOEt **2h**	Ir(ttp)Et **3f** (19); Ir(ttp)COEt **3g** (11)	30[a]

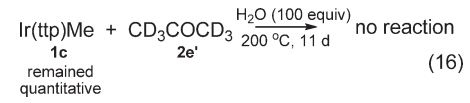
[a] **1c** and **3e** were observed in trace amounts (<5%). We proposed that **1c** was formed from the reduction of CO with Ir(ttp)H, and **3e** was generated from the CO insertion into **1c**. See ref 15 for details.

Four CCA products were obtained from methyl ethyl ketone **2f** as a result of nonregioselective CCA (Table 3, entry 1). The C(=O)−C(Et) bond was dominantly cleaved to give 23% yield of Ir(ttp)COMe **3e** and a trace amount of Ir(ttp)Et **3f** (<5%), while It(ttp)COEt **3g** and Ir(ttp)Me **1c** were both obtained in 5% yield from the C(=O)−C(Me) bond cleavage. The preferential cleavage of the C(=O)−C(Et) bond (83.0 kcal mol^{-1})[6] over the C(=O)−C(Me) bond (84.3 kcal mol^{-1})[6] is likely due to the weaker bond strength. However, steric effects play a significant role when the ketone possesses an isopropyl group. The C(=O)−C(Me) bond of methyl isopropyl ketone **2g** was cleaved mainly to give a 43% yield of Ir(ttp)Me **1c**. The C(=O)−C(^{i}Pr) bond cleavage also occurred but only gave a low yield of Ir(ttp)COMe **3e** of 9% (Table 3, entry 2). We reason that the isopropyl group is sterically large enough to inhibit cleavage of the weaker C(=O)−C(^{i}Pr) bond (81.3 kcal mol^{-1}).[6] For the symmetric diethyl ketones **2h**, chemoselective CCA occurred at the C(=O)−C(Et) bond to give Ir(ttp)COEt **3g** in 11% yield and Ir(ttp)Et **3f** in 19% yield, respectively (Table 3, entry 3).

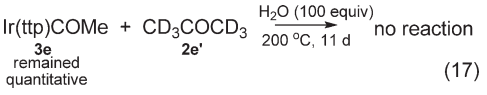
Scheme 2. Modified Proposed Mechanism[4] for the CCA of Ketones by Ir(ttp)X



Stability of Ir(ttp)COMe and Ir(ttp)Me. It is puzzling that the C(=O)−C(α) bond activation of ketone is nonregioselective, but Ir(ttp)COR is generally the final observed product. It is conceivable that Ir(ttp)R′ can further convert to Ir(ttp)COR upon prolonged heating (Table 1, entry 3, and eq 11). Therefore, the thermal and hydrolytic stabilities of Ir(ttp)Me **1c** and Ir(ttp)COMe **3e** in acetone **2e** were studied. Both Ir(ttp)Me **1c** and Ir(ttp)COMe **3e** were thermally and hydrolytically stable in acetone **2e′** at 200 °C in the presence of water (100 equiv) (eqs 16 and 17). Upon the addition of HBF_4 (1.0 equiv, 35% solution), Ir(ttp)CD_3 **1c′** reacted with acetone **2e** at 200 °C in 1 day to give both Ir(ttp)Me **1c** and Ir(ttp)COMe **3e** in 24% and 10% yield (eq 18), respectively. On the other hand, Ir(ttp)COMe **3e** was found to be stable under the same reaction conditions, and only a 7% yield of Ir(ttp)Me **1c** was isolated with the recovery of Ir(ttp)COMe **3e** in 91% yield (eq 19).[16] Therefore, Ir(ttp)Me **1c** undergoes more facile acid-catalyzed hydrolysis than Ir(ttp)COMe **3e**, likely to generate an unstable Ir(ttp)OH.



(16)



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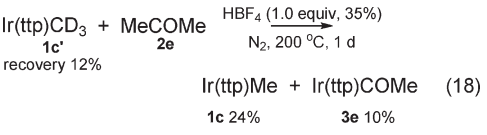

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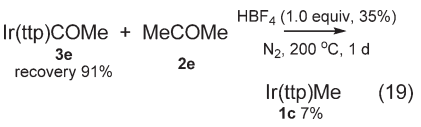

(19)

Mechanistic Studies. Based on the above experimental results and the mechanism reported in the ketone CCA with Rh(ttp)Me, we propose a more complete mechanism for the CCA of ketones with iridium(III) porphyrin complexes (Ir(ttp)X, X=$(BF_4)(CO)$, **1b**, Cl(CO), **1a**, Me, **1c**) (Scheme 2). First, Ir(ttp)X catalyzes the aldol condensation of ketone to give water (eq 8). Concurrently, Ir(ttp)X reacts in a stoichiometric manner with ketones to give the α-CHA complexes as the kinetic products. Then the α-CHA complexes are hydrolyzed by water (catalyzed by acid as well) to give Ir(ttp)OH (eq 7), which cleaves the C(=O)−C(α) bond of ketone in a nonregioselective manner to give both Ir(ttp)COR and Ir(ttp)R′ (eqs 3, 11, and 15). Since Ir(ttp)R′ is hydrolytically less stable than Ir(ttp)COR, Ir(ttp)R′ is hydrolyzed to Ir(ttp)OH, which yields Ir(ttp)COR as product (Table 1, entry 3, and eq 11). This mechanism accounts for the sole formation of Ir(ttp)COAr from the CCA of acetophenones, as Ir(ttp)Me hydrolyzes much more rapidly than Ir(ttp)COAr.

In conclusion, we have systematically studied the CCA of ketones with high-valent iridium(III) porphyrin complexes. We discovered that Ir(ttp)$(BF_4)(CO)$ **1b** exhibited a higher reactivity toward the CCA of ketones, which is likely due to its higher Lewis acidity, and the coformation of strong Brønsted acid HBF_4 to catalyze the aldol condensation of ketones. Ir(ttp)OH was proposed as the intermediate to cleave the C(=O)−C(α) bonds of ketones to give the corresponding iridium porphyrin acyl and alkyl complexes nonregioselectively. The final isolation of iridium porphyrin acyls in the reaction with acetophenones is due to its hydrolytic stability. For the unsymmetric aliphatic ketones, the selectivity was dependent on the bond dissociation energy as well as the steric hindrance of the alkyl group.

EXPERIMENTAL SECTION

Unless otherwise noted, all chemicals were obtained from commercial suppliers and used without further purification. Hexane for chromatography was distilled from anhydrous calcium chloride. Thin-layer chromatography analysis for the reaction was performed on precoated silica gel 60 F_{254} plates. All preparation reactions were carried out in a Teflon screw-head stoppered tube under N_2. For purification of iridium porphyrin complexes, fresh column chromatography was used and carried out in air using alumina (90 active neutral, 70−230 mesh). Ir(ttp)$(BF_4)(CO)$[17] **1a**, Ir(ttp)Cl(CO)[18] **1b**, Ir(ttp)Me[18] **1c**, and Ir(ttp)CD_3[19] **1c′** were prepared according to the literature.

^{1}H NMR spectra were recorded on a Bruker AV400 (400 MHz). Chemical shifts were reported with reference to the residual solvent protons in $CDCl_3$ (δ 7.26 ppm) or C_6D_6 (δ 7.15 ppm) as the internal standards. Chemical shifts (δ) were reported in parts per million (ppm) in δ scale downfield from TMS. Coupling constants (*J*) are reported in hertz (Hz). ^{13}C NMR spectra were recorded on a Bruker AV400 (100 MHz) spectrometer and referenced to $CDCl_3$ (δ 77.10 ppm). High-resolution mass spectra (HRMS) were performed on a Thermofinnign MAT 95 XL in FAB (using 3-nitrobenzyl alcohol (NBA) matrix and

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CH_2Cl_2 as the solvent) and ESI model ($MeOH/CH_2Cl_2$, 1:1, as the solvent).

Reactions of Ir(ttp)X 1b,c with Acetophenones. General Procedure. The reaction of Ir(ttp)(BF_4)(CO) **1b** with acetophenone **2b** for 2 days is described as a typical example. Acetophenone **2b** (0.8 mL, 500 equiv) was added to Ir(ttp)(BF_4)(CO) (12.5 mg, 0.013 mmol), and the mixture was degassed by the freeze−pump−thaw method (3 cycles). Then the mixture was heated at 200 °C for 2 days. The crude product was purified by column chromatography on alumina eluting with hexane/CH_2Cl_2 (3:1). A purple solid of Ir(ttp)COPh[4,17] **3b** (7.3 mg, 0.0075 mmol, 58%) was isolated. R_f = 0.28 (hexane/CH_2Cl_2, 1:1). ^{1}H NMR (C_6D_6, 400 MHz): δ 2.42 (s, 12 H), 2.90 (d, 2 H, J = 7.2 Hz), 5.87 (t, 2 H, J = 7.6 Hz), 6.21 (t, 1 H, J = 7.2 Hz), 7.27 (d, 4 H, J = 7.6 Hz), 7.34 (d, 4 H, J = 7.2 Hz), 7.99 (d, 4 H, J = 7.6 Hz), 8.16 (d, 4 H, J = 7.6 Hz), 8.86 (s, 8 H). Then the solvent was changed to hexane/CH_2Cl_2 (1:2), and a purple solid mixture of Ir(ttp)(*para*-COMe-C_6H_4)[4] **4b** and Ir(ttp)(*meta*-COMe-C_6H_4)[4] **4c** was isolated in trace amount (<5%). Ir(ttp)(*para*-COMe-C_6H_4) **4b**: R_f = 0.14 (hexane/CH_2Cl_2, 1:2). ^{1}H NMR (C_6D_6, 400 MHz): δ 0.95 (s, 3 H), 1.00 (d, 2 H, J = 8.8 Hz), 2.39 (s, 12 H), 5.24 (d, 2 H, J = 8.4 Hz), 7.20 (d, 4 H, J = 8.0 Hz), 7.34 (d, 4 H, J = 7.6 Hz), 7.93 (dd, 4 H, J = 1.6, 7.8 Hz), 8.12 (dd, 4 H, J = 1.2, 6.6 Hz), 8.82 (s, 8 H). Ir(ttp)(*meta*-COMe-C_6H_4) **4c**: R_f = 0.23 (hexane/CH_2Cl_2, 1:2). ^{1}H NMR (C_6D_6, 400 MHz): δ 1.12 (s, 3 H), 1.19 (d, 1 H, J = 8.0 Hz), 1.69 (s, 1 H), 2.39 (s, 12 H), 4.73 (t, 1 H, J = 8.0 Hz), 5.53 (d, 1 H, J = 7.6 Hz), 7.23 (d, 4 H, J = 7.6 Hz), 7.34 (d, 4 H, J = 7.6 Hz), 8.09 (d, 4 H, J = 7.6 Hz), 8.14 (d, 4 H, J = 7.6 Hz), 8.82 (s, 8 H).

Reaction between Ir(ttp)(BF_4)(CO) 1b and Acetophenone 2b for 4 Hours. Acetophenone **2b** (0.9 mL, 500 equiv) was added to Ir(ttp)(BF_4)(CO) **1b** (14.9 mg, 0.015 mmol). Then the mixture was heated at 200 °C for 4 h, and the crude product was purified by column chromatography on alumina eluting with hexane/CH_2Cl_2 (3:1). A purple solid mixture of Ir(ttp)COPh[4,17] **3b** (1.9 mg, 0.0020 mmol, 13%) and Ir(ttp)Me (<5%) was isolated. Then the solvent was changed to hexane/CH_2Cl_2 (1:2), and a purple solid mixture of Ir(ttp)-CH_2COPh[4] **4a** (<5%), Ir(ttp)(*para*-COMe-C_6H_4)[4] **4b** (2.0 mg, 0.0020 mmol, 13%), and Ir(ttp)(*meta*-COMe-C_6H_4)[4] **4c** (4.0 mg, 0.0040 mmol, 26%) was isolated. On the other hand, the aldol condensation products PhCOCH═CMePh **5a** and 1,3,5-triphenylbenzene **5b** were both observed in 1000% yields (cf. Ir), respectively, according to the ^{1}H NMR with Si($SiMe_3$)$_4$ used as the internal standard.

Reaction between Ir(ttp)Me 1c and Acetophenone 2b for 26 Days. Acetophenone **2b** (0.8 mL, 500 equiv) was added to Ir(ttp)Me **1c** (12.7 mg, 0.014 mmol). Then the mixture was heated at 200 °C for 26 days, and the crude product was purified by column chromatography on alumina eluting with hexane/CH_2Cl_2 (3:1). A purple solid of Ir(ttp)COPh[4,17] **3b** (10.8 mg, 0.0112 mmol, 80%) was isolated.

Reaction between Ir(ttp)Me 1c and Acetophenone 2b for 5 Days. Acetophenone **2b** (1.1 mL, 500 equiv) was added to Ir(ttp)Me **1c** (15.9 mg, 0.018 mmol). Then the mixture was heated at 200 °C for 5 days, and the crude product was purified by column chromatography on alumina eluting with hexane/CH_2Cl_2 (3:1). A purple solid of Ir(ttp)Me (11.7 mg, 0.0134 mmol, 74%) was recovered together with Ir(ttp)COPh **3b** (<5%). Then the solvent was changed to hexane/CH_2Cl_2 (1:2), and a purple solid of Ir(ttp)CH_2COPh[4] **4a** (1.9 mg, 0.0019 mmol, 11%) was isolated. R_f = 0.18 (hexane/CH_2Cl_2, 1:2). ^{1}H NMR (C_6D_6, 400 MHz): δ −3.53 (s, 2 H), 2.42 (s, 12 H), 5.13 (d, 2 H, J = 7.6 Hz), 6.48 (t, 2 H, J = 7.8 Hz), 6.81 (t, 1 H, J = 7.2 Hz), 7.30 (dd, 8 H, J = 8.0, 8.0 Hz), 8.04 (d, 4 H, J = 7.6 Hz), 8.14 (d, 4 H, J = 7.6 Hz), 8.75 (s, 8 H). No aldol condensation products of PhCOCH═CMePh **5a** and 1,3,5-triphenylbenzene **5b** were observed by both ^{1}H NMR and GC-MS analysis.

Reaction between Ir(ttp)(BF_4)(CO) 1b and 4-Fluoroacetophenone 2a. 4-Fluoroacetophenone **2a** (0.8 mL, 500 equiv) was added to Ir(ttp)(BF_4)(CO) **1b** (12.6 mg, 0.013 mmol). Then the mixture was heated at 200 °C for 2 days, and the crude product was purified by column chromatography on alumina eluting with hexane/CH_2Cl_2 (3:1). A purple solid of Ir(ttp)CO(4-F-C_6H_4)[4,17] **3a** (6.9 mg, 0.0070 mmol, 54%) was isolated. R_f = 0.28 (hexane/CH_2Cl_2, 1:1). ^{1}H NMR (C_6D_6, 400 MHz): δ 2.41 (s, 12 H), 2.73 (dd, 2 H, $^4J_{H-F}$ = 5.4 Hz, J = 8.6 Hz), 5.50 (dd, 2 H, $^3J_{H-F}$ = 8.8 Hz, J = 8.8 Hz), 7.28 (d, 4 H, J = 8.0 Hz), 7.34 (d, 4 H, J = 7.6 Hz),7.98 (dd, 4 H, J = 1.6, 7.6 Hz), 8.14 (dd, 4 H, J = 1.6, 8.4 Hz), 8.85 (s, 8 H).

Reaction between Ir(ttp)(BF_4)(CO) 1b and 4-Methylacetophenone 2c. 4-Methylacetophenone **2c** (0.8 mL, 500 equiv) was added to Ir(ttp)(BF_4)(CO) **1b** (12.5 mg, 0.013 mmol). Then the mixture was heated at 200 °C for 2 days, and the crude product was purified by column chromatography on alumina eluting with hexane/CH_2Cl_2 (3:1). A purple solid of Ir(ttp)CO(4-Me-C_6H_4)[4,17] **3b** (9.6 mg, 0.0098 mmol, 75%) was isolated. R_f = 0.28 (hexane/CH_2Cl_2, 1:1). ^{1}H NMR (C_6D_6, 400 MHz): δ 1.65 (s, 3 H), 2.42 (s, 12 H), 2.83 (d, 2 H, J = 8.0 Hz), 5.67 (d, 2 H, J = 8.0 Hz), 7.28 (d, 4 H, J = 7.6 Hz), 7.35 (d, 4 H, J = 7.6 Hz), 7.96 (dd, 4 H, J = 1.6, 7.6 Hz), 8.17 (dd, 4 H, J = 1.6, 7.6 Hz), 8.86 (s, 8 H).

Reaction between Ir(ttp)(BF_4)(CO) 1b and 4-Methoxylacetophenone 2d. 4-Methoxylacetophenone **2d** (0.8 mL, 500 equiv) was added to Ir(ttp)(BF_4)(CO) **1b** (12.4 mg, 0.013 mmol). Then the mixture was heated at 200 °C for 2 days, and the crude product was purified by column chromatography on alumina eluting with hexane/CH_2Cl_2 (3:1). A purple solid of Ir(ttp)CO(4-OMe-C_6H_4)[4,17] **3b** (10.4 mg, 0.0104 mmol, 80%) was isolated. R_f = 0.11 (hexane/CH_2Cl_2, 1:1). ^{1}H NMR (C_6D_6, 400 MHz): δ 2.42 (s, 12 H), 2.90 (d, 2 H, J = 6.8 Hz), 2.92 (s, 3H), 5.45 (d, 2H, J = 8.8 Hz), 7.27 (d, 4 H, J = 8.1 Hz), 7.35 (d, 4 H, J = 7.6 Hz), 8.01 (d, 4 H, J = 7.6 Hz), 8.17 (d, 4 H, J = 7.6 Hz), 8.87 (s, 8 H).

Reaction between Ir(ttp)Me 1c and 4-Fluoroacetophenone 2a. 4-Fluoroacetophenone **2a** (0.9 mL, 500 equiv) was added to Ir(ttp)Me **1c** (13.1 mg, 0.015 mmol). Then the mixture was heated at 200 °C for 6 days, and the crude product was purified by column chromatography on alumina eluting with hexane/CH_2Cl_2 (3:1). A purple solid of Ir(ttp)CO(4-F-C_6H_4)[4,17] **3a** (13.6 mg, 0.0138 mmol, 92%) was isolated.

Reaction between Ir(ttp)Me 1c and 4-Methylacetophenone 2c. 4-Methylacetophenone **2c** (0.9 mL, 500 equiv) was added to Ir(ttp)Me **1c** (11.5 mg, 0.013 mmol). Then the mixture was heated at 200 °C for 21 days, and the crude product was purified by column chromatography on alumina eluting with hexane/CH_2Cl_2 (3:1). A purple solid of Ir(ttp)CO(4-Me-C_6H_4)[4,17] **3a** (7.4 mg, 0.0075 mmol, 58%) was isolated.

Reaction between Ir(ttp)Me 1c and 4-Methoxylacetophenone 2d. 4-Methoxylacetophenone **2d** (0.9 mL, 500 equiv) was added to Ir(ttp)Me **1c** (12.6 mg, 0.014 mmol). Then the mixture was heated at 200 °C for 24 days, and the crude product was purified by column chromatography on alumina eluting with hexane/CH_2Cl_2 (3:1). A purple solid of Ir(ttp)CO(4-OMe-C_6H_4)[4,17] **3a** (11.4 mg, 0.0114 mmol, 82%) was isolated.

Reaction between Ir(ttp)(BF_4)(CO) 1b and Acetone 2e for 9 Hours at 120 °C. Acetone **2e** (0.7 mL, 500 equiv) was added to Ir(ttp)(BF_4)(CO) **1b** (18.1 mg, 0.018 mmol). Then the mixture was heated at 120 °C for 9 h, and the crude product was purified by column chromatography on alumina eluting with hexane/CH_2Cl_2 (1:2). A purple solid of Ir(ttp)CH_2COMe **4d** (1.8 mg, 0.0018 mmol, 10%) was isolated. R_f = 0.23 (hexane/CH_2Cl_2, 1:2). ^{1}H NMR (C_6D_6, 400 MHz): δ −4.03 (s, 2 H), −1.54 (s, 3 H), 2.41 (s, 12 H), 7.25 (d, 4 H, J = 7.6 Hz), 7.36 (d, 4 H, J = 7.6 Hz), 8.10 (dd, 4 H, J = 1.5, 7.6 Hz), 8.19 (dd, 4 H, J = 1.5, 7.6 Hz), 8.78 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ −13.0, 21.6, 25.4, 124.0, 127.5, 127.7, 131.6, 133.3, 134.2, 137.4, 138.6, 143.2, 207.2. HRMS (FAB): calcd for $(C_{51}H_{41}N_4O_1Ir_1)^+$ m/z 918.2904; found m/z 918.2899.

Reaction between Ir(ttp)(BF_4)(CO) 1b and Acetone 2e for 1 Day at 200 °C. Acetone **2e** (0.7 mL, 500 equiv) was added to Ir(ttp)(BF_4)(CO) **1b** (18.4 mg, 0.019 mmol). Then the mixture was heated at 200 °C for 1 day, and the crude product was purified by column chromatography on alumina eluting with hexane/CH_2Cl_2 (5:1). A purple solid of Ir(ttp)COMe **3e** (3.3 mg, 0.0037 mmol, 19%) was isolated. R_f = 0.35 (hexane/CH_2Cl_2, 1:2). ^{1}H NMR (C_6D_6, 400 MHz): δ −2.65 (s, 3 H), 2.41 (s, 12 H), 7.22 (d, 4 H, J = 7.7 Hz), 7.34 (d, 4 H, J = 7.1 Hz), 7.99 (dd, 4 H, J = 1.7, 7.7 Hz), 8.16 (dd, 4 H, J = 1.7, 7.6 Hz), 8.88 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.6, 28.9, 123.9, 127.5, 127.6, 131.4, 133.6, 134.0, 137.4, 138.8, 142.9, 164.3. HRMS (ESIMS): calcd for $[C_{50}H_{39}N_4OIr+H]^+$ m/z 905.2826; found m/z 905.2785. Then the solvent was changed to hexane/CH_2Cl_2 (3:1), and a purple solid of Ir(ttp)Me (6.6 mg, 0.0075 mmol, 40%) was isolated. In addition, CH_3COOK was observed in 1.67% yield based on acetone (836% yield based on Ir(ttp)(BF_4)(CO)) according to the ^{1}H NMR spectrum with ^{t}BuOH (10 μL) used as the internal standard when KOH (ex) was added to the reaction mixture.

Reaction between Ir(ttp)(BF_4)(CO) 1b and Acetone 2e for 2 Days at 200 °C. Acetone **2e** (0.8 mL, 500 equiv) was added to Ir(ttp)(BF_4)(CO) **1b** (22.4 mg, 0.023 mmol). Then the mixture was heated at 200 °C for 2 days, and the crude product was purified by column chromatography on alumina eluting with hexane/CH_2Cl_2 (5:1). A purple solid of Ir(ttp)COMe **3e** (4.9 mg, 0.0054 mmol, 24%) was isolated. Then the solvent was changed to hexane/CH_2Cl_2 (3:1), and a purple solid of Ir(ttp)Me **1c** (3.8 mg, 0.0043 mmol, 19%) was isolated.

Reaction between Ir(ttp)Cl(CO) 1a and Acetone 2e. Acetone **2e** (0.9 mL, 500 equiv) was added to Ir(ttp)Cl(CO) **1a** (23.1 mg, 0.025 mmol). Then the mixture was heated at 200 °C for 10 days, and the crude product was purified by column chromatography on alumina eluting with hexane/CH_2Cl_2 (5:1). A purple solid mixture of Ir(ttp)COMe **3e** and Ir(ttp)Me **1c** was isolated in trace amount (<5%). Ir(ttp)Cl(CO) **1a** (~92%) remained according to the ^{1}H NMR spectrum of the crude reaction mixture.

Reaction between Ir(ttp)Me 1c and Acetone 2e. Acetone **2e** (0.9 mL, 500 equiv) was added to Ir(ttp)Me **1c** (22.1 mg, 0.025 mmol). Then the mixture was heated at 200 °C for 5 days, and the crude product was purified by column chromatography on alumina eluting with hexane/CH_2Cl_2 (3:1). A purple solid of Ir(ttp)Me **1c** (19.7 mg, 0.0225 mmol, 90%) was recovered. No CH_3COOK was observed when KOH (ex) was added according to the ^{1}H NMR spectrum.

Reaction between Ir(ttp)(BF_4)(CO) 1b and Methyl Ethyl Ketone 2f. Methyl ethyl ketone **2f** (1.0 mL, 500 equiv) was added to Ir(ttp)(BF_4)(CO) **1b** (21.1 mg, 0.022 mmol). Then the mixture was heated at 200 °C for 4 days, and the crude product was purified by column chromatography on alumina eluting with hexane/CH_2Cl_2 (5:1). A purple solid mixture of Ir(ttp)COEt[17] **3g** (1.0 mg, 0.0011 mmol, 5%) was isolated. R_f = 0.66 (hexane/CH_2Cl_2, 1:2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ −3.20 (q, 2 H, J = 7.2 Hz), −1.71 (t, 3 H, J = 7.2 Hz), 2.69 (s, 12 H), 7.52 (d, 8 H, J = 8.1 Hz), 8.02 (d, 8 H, J = 7.8 Hz), 8.67 (s, 8 H). Then the solvent was changed to hexane/CH_2Cl_2 (3:1), and a purple solid mixture of Ir(ttp)COMe **3e** (4.5 mg, 0.0050 mmol, 23%) was isolated. When the solvent was changed to hexane/CH_2Cl_2 (1:1), a purple solid mixture of Ir(ttp)Me **1c** (1.0 mg, 0.0011 mmol, 5%) and Ir(ttp)Et[18] **3f** (<5%) was isolated. R_f = 0.25 (hexane/CH_2Cl_2, 2:1). ^{1}H NMR (C_6D_6, 400 MHz): δ −5.20 (q, 2 H, J = 7.2 Hz), −4.27 (t, 3 H, J = 7.2 Hz), 2.41 (s, 12 H), 7.22 (d, 4 H, J = 7.6 Hz), 7.35 (d, 4 H, J = 7.6 Hz), 7.99 (dd, 4 H, J = 2.0, 7.6 Hz), 8.19 (dd, 4 H, J = 1.6, 7.8 Hz), 8.76 (s, 8 H).

Reaction between Ir(ttp)(BF_4)(CO) 1b and Methyl Isopropyl Ketone 2g. Methyl isopropyl ketone **2g** (0.8 mL, 500 equiv) was added to Ir(ttp)(BF_4)(CO) **1b** (19.8 mg, 0.020 mmol). Then the mixture was heated at 200 °C for 4 days, and the crude product was purified by column chromatography on alumina eluting with hexane/CH_2Cl_2 (3:1). A purple solid of Ir(ttp)COMe **3e** (1.6 mg, 0.0018 mmol, 9%) was isolated. Then the solvent was changed to hexane/CH_2Cl_2 (2:1), and a purple solid of Ir(ttp)Me **1c** (7.6 mg, 0.0087 mmol, 43%) was isolated.

Reaction between Ir(ttp)(BF_4)(CO) 1b and Diethyl Ketone 2h. Diethyl ketone **2h** (0.7 mL, 500 equiv) was added to Ir(ttp)(BF_4)(CO) **1b** (13.0 mg, 0.013 mmol). Then the mixture was heated at 200 °C for 4 days, and the crude product was purified by column chromatography on alumina eluting with hexane/CH_2Cl_2 (5:1). A purple solid mixture of Ir(ttp)COMe **3e** (<5%), Ir(ttp)COEt[17] **3g** (1.3 mg, 0.0014 mmol, 11%), Ir(ttp)Me **1c** (<5%), and Ir(ttp)Et[18] **3f** (2.2 mg, 0.0025 mmol, 19%) was isolated.

Reaction between Ir(ttp)Me 1c and Acetone-d_6 2e′ with 100 Equivalents of Water. Acetone-d_6 **2e′** (0.5 mL, 1000 equiv) and H_2O (9 μL, 100 equiv) were added to Ir(ttp)Me **1c** (4.5 mg, 0.0052 mmol) in a NMR tube with a Rotaflo stopper, and the mixture was degassed by the freeze−pump−thaw method (3 cycles). Then the NMR tube was flamed-sealed under vacuum. The mixture was heated at 200 °C and was monitored with ^{1}H NMR spectroscopy. After 11 days, Ir(ttp)Me remained in quantitative yield, and no Ir(ttp)COMe was observed.

Reaction between Ir(ttp)COMe 3e and Acetone-d_6 2e′ with 100 Equivalents of Water. Acetone-d_6 **2e′** (0.5 mL, 1000 equiv) and H_2O (11 μL, 100 equiv) were added to Ir(ttp)COMe **3e** (5.2 mg, 0.0058 mmol) in a NMR tube with a Rotaflo stopper, and the mixture was degassed by the freeze−pump−thaw method (3 cycles). Then the NMR tube was flamed-sealed under vacuum. The mixture was heated at 200 °C and was monitored with ^{1}H NMR spectroscopy. After 12 days, Ir(ttp)COMe remained in quantitative yield, and no Ir(ttp)Me was observed.

Reaction between Ir(ttp)CD_3 1c′ and Acetone 2e with HBF_4. Acetone **2e** (0.9 mL, 500 equiv) and HBF_4 (4.8 μL, 1.0 equiv, 35%) were added to Ir(ttp)CD_3 **1c′** (20.8 mg, 0.024 mmol). Then the mixture was heated at 200 °C for 1 day, and the crude product was purified by column chromatography on alumina eluting with hexane/CH_2Cl_2 (5:1). A purple solid mixture of Ir(ttp)COMe **3e** (2.1 mg, 0.0023 mmol, 10%) was isolated. Then the solvent was changed to hexane/CH_2Cl_2 (3:1), and a purple solid mixture of Ir(ttp)Me **1c** (5.0 mg, 0.0057 mmol, 24%) and Ir(ttp)CD_3 **1c′** (2.5 mg, 0.0028 mmol, 12%) was isolated. In addition, CH_3COOK was observed in 2.05% yield based on acetone (1023% yield based on Ir(ttp)CD_3) according to the ^{1}H NMR spectrum with ^{t}BuOH (10 μL) used as the internal standard when KOH (ex) was added to the reaction mixture.

Reaction between Ir(ttp)COMe 3e and Acetone 2e with HBF_4. Acetone **2e** (0.8 mL, 500 equiv) and HBF_4 (4.2 μL, 1.0 equiv, 35%) were added to Ir(ttp)COMe **3e** (18.7 mg, 0.021 mmol). Then the mixture was heated at 200 °C for 1 day, and the crude product was purified by column chromatography on alumina eluting with hexane/CH_2Cl_2 (3:1). A purple solid mixture of Ir(ttp)COMe **3e** (17.3 mg, 0.0191 mmol, 91%) and Ir(ttp)Me **1c** (1.3 mg, 0.0015 mmol, 7%) was isolated.

Reaction of Acetone 2e with HBF_4. Acetone **2e** (0.8 mL, 500 equiv) and HBF_4 (4.6 μL, 1.0 equiv, 35%) were heated at 200 °C for 1 day. CH_3COOK was observed in 0.33% yield based on acetone (164% yield based on HBF_4) according to the ^{1}H NMR spectrum with ^{t}BuOH (10 μL) used as the internal standard when KOH (ex) was added to the reaction mixture.

■ ASSOCIATED CONTENT

Supporting Information. ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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