ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

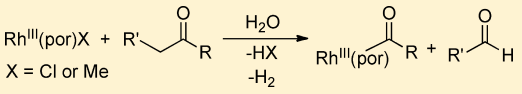
Mild and Selective C(CO)−C(α) Bond Cleavage of Ketones by Rhodium(III) Porphyrins: Scope and Mechanism

Hong Sang Fung, Bao Zhu Li, and Kin Shing Chan*

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

Supporting Information

ABSTRACT: Rhodium(III) porphyrins were found to undergo selective C(CO)−C(α) bond activation (CCA) of ketones promoted by water at temperatures as low as 50 °C. The acyl group of the ketone was transferred to the rhodium center, and the alkyl fragment was oxidized to a carbonyl moiety accordingly. The hydroxyl group of water is transferred to the rhodium porphyrin through hydrolysis of the kinetic α-carbon−hydrogen bond activation (α-CHA) product to give Rh^{III}(ttp)OH (ttp = 5,10,15,20-tetratolylporphyrinato dianion), which subsequently cleaves the C(CO)−C(α) bond of ketone.



INTRODUCTION

Carbon−carbon bond activation (CCA) by a transition-metal complex is fundamentally very important. However, many of the examples are limited to low valent transition-metal complexes through oxidative addition.[1] High valent transition-metal complexes are much less known to cleave a C−C bond through oxidative addition as an uncommon, high valent transition-metal intermediate would be involved. Therefore, CCA with a high valent transition-metal complex is mechanistically intriguing. In the past decade, examples of CCA with high valent group 9 transition-metal complexes have been reported. Brookhart and Bergman et al. reported the cleavage of the R−CN bond by the cationic rhodium(III) complex through migration of the alkyl group to the rhodium center without involving an oxidative addition.[2]

We have reported several CCA examples by group 9 metal(III) porphyrins.[3,4] Oxidative addition with a trivalent group 9 transition-metal complex to a carbon−carbon bond is even more challenging, as an M(V) (M = Co, Rh, or Ir) and sterically hindered intermediate with three ligands on the same side of the porphyrin plane in a cis manner would be involved. The proposed Rh^{II}(ttp)-catalyzed Rh^{III}(ttp)-H (ttp = 5,10,15,20-tetratolylporphyrinato dianion) insertion into the C−C bond of cyclooctane[3] and the direct insertion of Rh^{III}(tmp)-OH (tmp = 5,10,15,20-tetramesitylporphyrinato dianion) into the C(α)−C(β) bond of ethers[4] accounts for the CCA without the involvement of the high valent Rh^{V}(por) species.

Recently, iridium(III) porphyrins were reported to assist the cleavage of the carbon(CO)−carbon(α) bond of ketones with water at 200 °C.[5] Mechanistically, the water, formed from the iridium(III) porphyrin-catalyzed Aldol condensation of ketone, serves as the key oxygen source and hydrolyzes the α-carbon−hydrogen activation (α-CHA) complex to give Ir^{III}(ttp)OH. The C(CO)−C(α) bonds of the RCOR′ were then cleaved in a nonregioselective manner to give a mixture of Ir^{III}(ttp)COR′, Ir^{III}(ttp)R, Ir^{III}(ttp)COR, and Ir^{III}(ttp)R′. The reaction, however, suffers from a narrow substrate scope. Only acetophenone, acetone, methyl ethyl ketone, methyl isopropyl ketone, and diethyl ketone can undergo CCA successfully.

We have communicated that Rh^{III}(ttp)Me (Figure 1) can react with a wider range of ketones.[6] Specifically, the more

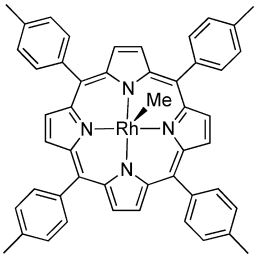
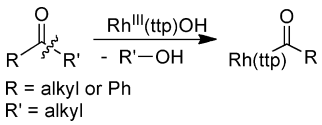


Figure 1. Structure of Rh^{III}(ttp)Me.

hindered isopropyl ketones can react and even react much faster than methyl and ethyl ketones. In this article, the full scope and mechanism of the selective C(CO)−C(α) bond activation of ketones by rhodium(III) porphyrins are reported (Scheme 1).

Scheme 1. Selective C(CO)−C(α) Activation of Ketones and Acyl Transfer by Rh^{III}(ttp)OH



RESULTS AND DISCUSSION

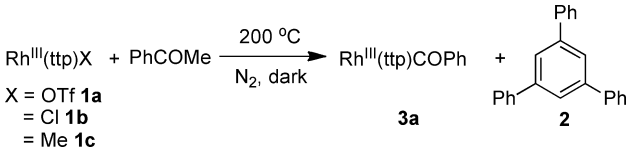
CCA with Rh^{III}(ttp)X (X = OTf, Cl, and Me). Initially, Rh^{III}(ttp)OTf **1a**, prepared in situ from Rh^{III}(ttp)Cl **1b** and AgOTf, catalyzed the Aldol condensation of acetophenone to

Received: August 25, 2011
Published: January 5, 2012

   dx.doi.org/10.1021/om200788p | *Organometallics* 2012, 31, 570−579

form a 58 800% yield of 1,3,5-triphenylbenzene **2** (with respect to rhodium) (Table 1, entry 1) without any carbon−carbon

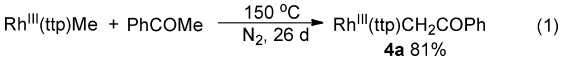
Table 1. CCA of Acetophenone with Various Rhodium Porphyrins



entry	Rh^{III}(ttp)X	time (d)	**3a** (% yield)	**2** (% yield)
1	Rh^{III}(ttp)OTf **1a**[a]	1	0	58 800
2	Rh^{III}(ttp)Cl **1b**	22	89	3600 (12 d)
3	Rh^{III}(ttp)Me **1c**	15	93	700 (12 d)

bond activation (CCA) product observed in solvent-free conditions. Only a solidified reaction mixture resulted. However, the CCA of acetophenone occurred successfully at the PhCO−Me bond with the less Lewis acidic Rh^{III}(ttp)Cl **1b** and Rh^{III}(ttp)Me **1c**. The benzoyl group was transferred to the rhodium center to give Rh^{III}(ttp)COPh **3a** in 89% and 93% yields, respectively, in addition to 3600% and 700%[7] yields of 1,3,5-triphenylbenzene (Table 1, entries 2 and 3). The benzoyl transfer over the acetyl transfer is attributed to the selective cleavage of the weaker CO−Me bond (85.0 kcal mol^{-1})[8] rather than the stronger CO−Ph bond (97.2 kcal mol^{-1}).[8]

CCA of Acetophenone at 150 °C. When Rh^{III}(ttp)Me and acetophenone were heated at 150 °C for 26 days, only an 81% yield of Rh^{III}(ttp)CH_2COPh **4a** was obtained (eq 1) as a



result of carbon−hydrogen bond activation. Figure 2 shows an X-ray structure of Rh^{III}(ttp)CH_2COPh. The cleavage of the

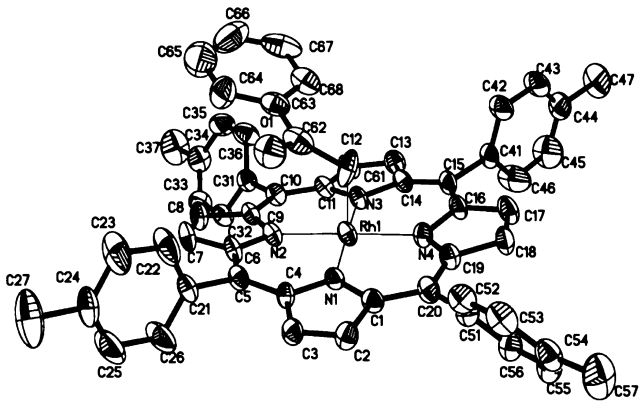
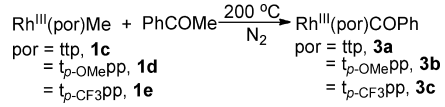


Figure 2. ORTEP presentation of the molecular structure with numbering scheme for Rh^{III}(ttp)CH_2COPh **4a** (30% probability displacement ellipsoids).

kinetically less accessible C(CO)−C(α) bond thus requires a higher temperature.

CCA with Various Porphyrin Ligands. The electronic effect of the porphyrin ligand was then examined in order to improve the CCA rate (Table 2). Both para-substituted methoxy and trifluoromethyl phenyl on the porphyrin ligand slightly increased the rate of the CCA of acetophenone as Rh^{III}($t_{p\text{-}OMe}$pp)Me **1d** and Rh^{III}($t_{p\text{-}CF_3}$pp)Me **1e** reacted with

Table 2. Reaction of Acetophenones with Rh^{III}(por)Me

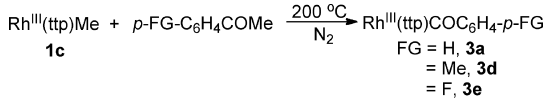


entry	Rh^{III}(por)Me	time (d)	**3a**−**3c** (% yield)
1	Rh^{III}($t_{p\text{-}OMe}$pp)Me **1d**	7	**3b** 95
2	Rh^{III}(ttp)Me **1c**	15	**3a** 93
3	Rh^{III}($t_{p\text{-}CF_3}$pp)Me **1e**	6	**3c** 94

acetophenone at 200 °C to give 95% yield of Rh^{III}($t_{p\text{-}OMe}$pp)-COPh **3b** and 94% yield of Rh^{III}($t_{p\text{-}CF_3}$pp)COPh **3c** in 7 and 6 days, respectively (Table 2). Although the methoxyl and trifluoromethyl substitutents promoted the reaction rate slightly, Rh^{III}(ttp)Me was used for further studies due to its synthetic availability and the reactivity comparison with other group 9 metallotetraarylporphyrins.

CCA with para-Substituted Acetophenones. We then examined the α-C−H acidity effect of the acetophenones as analogous CCA was promoted by the more acidic para-substituted acetophenones with the iridium(III) porphyrin.[5] However, para-substituted acetophenones, despite their differences in acidities, reacted in similar yields with Rh^{III}(ttp)Me (Table 3). *para*-Methylacetophenone and *para*-fluoroacetophenone

Table 3. Reaction of para-Substituted Acetophenones with Rh^{III}(ttp)Me



entry	FG	time (d)	**3a**, **3d**, **3e** (% yield)
1	Me	6	**3d** 72
2	H	15	**3a** 93

reacted with Rh^{III}(ttp)Me to give 72% yield of Rh^{III}(ttp)-COC_6H_4-*p*-Me **3d** and 80% yield of Rh^{III}(ttp)COC_6H_4-*p*-F **3e** in 6 and 12 days, respectively. The reaction rate was the fastest for *para*-methylacetophenone.

Scope of the Reaction. Besides acetophenone (Table 4, entry 1), various aromatic and aliphatic ketones also reacted successfully with Rh^{III}(ttp)Me and Rh^{III}(ttp)Cl to give the corresponding rhodium acyl complexes at 200 °C (Table 4). Rh^{III}(ttp)Me, in general, reacted more efficiently than Rh^{III}(ttp)Cl.

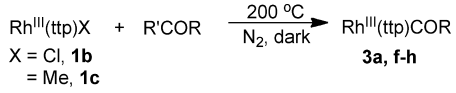
For the phenyl alkyl ketones, propiophenone and *n*-butyrophenone reacted with Rh^{III}(ttp)Me at 200 °C to give 44% and 43% yield of Rh^{III}(ttp)COPh in 15 and 19 days, respectively (Table 4, entries 2 and 3). Unexpectedly, the more sterically hindered isobutyrophenone reacted much faster to give 97% yield of Rh^{III}(ttp)COPh in only 1 day (Table 4, entry 4).

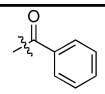
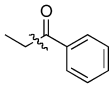
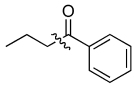
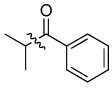
For aliphatic ketones, acetone and diethyl ketone poorly dissolved Rh^{III}(ttp)Me and thus reacted inefficiently to give 20% yield of Rh^{III}(ttp)COMe **3f** and 45% yield of Rh^{III}(ttp)COEt **3g** in 17 and 16 days, respectively (Table 4, entries 5 and 6). Diisopropyl ketone was the most reactive and required only 30 min to give 86% yield of Rh^{III}(ttp)CO^{i}Pr **3h** (Table 4, entry 7).

The regioselective CCA at the more sterically hindered CO−^{i}Pr bond was achieved when Rh^{III}(ttp)Me was reacted with methyl isopropyl ketone to give 95% yield of Rh^{III}(ttp)COMe in 1 day (Table 4, entry 8). The higher reactivity of the CO−^{i}Pr bond

dx.doi.org/10.1021/om200788p | *Organometallics* 2012, 31, 570−579

Table 4. Rh^{III}(ttp)Me vs Rh^{III}(ttp)Cl toward Aromatic and Aliphatic Ketones[a]



Entry	Ketones	Rh^{III}(ttp)Cl Time	Rh^{III}(ttp)Cl 3a,f-h/ % Yield	Rh^{III}(ttp)Me Time	Rh^{III}(ttp)Me 3a,f-h/ % Yield
1		22d	**3a** 89	15d	**3a** 93
2		21d	**3a** 61	15d	**3a** 44
3		20d	**3a** 21	19d	**3a** 43
4		1d	**3a** 12	1d	**3a** 97
5		26d	**3f** 34	17d	**3f** 20
6		20d	**3g** 23	16d	**3g** 45
7		1d	**3h** 24	30 min	**3h** 86[a]
8		8d	**3f** 14	1d	**3f** 95

[a]Acetone was obtained in quantitative yield by ^{1}H NMR.

(81.3 kcal mol^{-1})[8] than the CO–Me (84.1 kcal mol^{-1})[8] or CO–Et (83.0 kcal mol^{-1})[8] bond is probably due to the weaker CO–^{i}Pr bond strength (Figure 3).

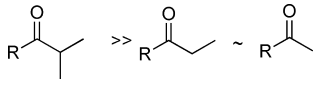


Figure 3. Relative reactivity of methyl, ethyl, and isopropyl ketones.

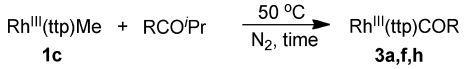
The more Lewis acidic Rh^{III}(ttp)Cl underwent the competitive Aldol condensation more extensively and thus is less productive in giving the CCA product. Propiophenone, *n*-butyrophenone, and isobutyrophenone reacted with Rh^{III}(ttp)Cl at 200 °C to give 61, 21, and 12% yield of Rh^{III}(ttp)COPh in 21, 20, and 1 days, respectively (Table 4, entries 2–4).

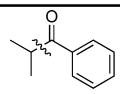
Rh^{III}(ttp)Cl also poorly dissolved in aliphatic ketones, and the CCA yields were low. Only 34% yield of Rh^{III}(ttp)COMe, 23% yield of Rh^{III}(ttp)COEt, and 24% yield of Rh^{III}(ttp)CO^{i}Pr were obtained from the reaction with acetone, diethyl ketone, and diisopropyl ketone with Rh^{III}(ttp)Cl at 200 °C for 26, 20, and 1 days, respectively (Table 4, entries 5–7).

Regioselective CCA also occurred at the CO–^{i}Pr bond when Rh^{III}(ttp)Cl was reacted with the methyl isopropyl ketone as 14% yield of Rh^{III}(ttp)COMe was obtained in 8 days (Table 4, entry 8).

CCA of Isopropyl Ketones at 50 °C. The higher reactivities of the bulky isopropyl ketones led us to examine the reaction at milder reaction conditions (Table 5). To our

Table 5. Reaction of Isopropyl Ketones with Rh^{III}(ttp)Me at 50 °C[a,b]



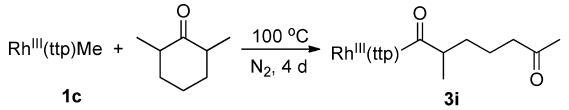
Entry	Ketones	Time/ d	3a,f,h/ % Yield
1		3	**3a** 41[a]
2		3	**3f** 57[b]
3		1	**3h** 94

[a]32% yield of **1c** recovered. [b]39% yield of **1c** recovered.

delight, isobutyrophenone and methyl isopropyl ketone reacted with Rh^{III}(ttp)Me at 50 °C to give 41% yield of Rh^{III}(ttp)COPh and 57% yield of Rh^{III}(ttp)COMe in 3 days, respectively (Table 5, entries 1 and 2). Diisopropyl ketone, being the most reactive substrate, required only 1 day to give 94% yield of Rh^{III}(ttp)CO^{i}Pr (Table 5, entry 3).

Fate of the Alkyl Fragment. While the acyl group of ketone is transferred to the rhodium center, the alkyl fragment is oxidized to a carbonyl compound. A quantitative amount of acetone (δ = 1.55 ppm in C_6D_6) was observed in the reaction of neat diisopropyl ketone with Rh^{III}(ttp)Me by ^{1}H NMR (Table 4, entry 7).

To further identify the organic coproduct structure, an "intramolecular trap", the cyclic 2,6-dimethylcyclohexanone, was then reacted with Rh^{III}(ttp)Me at 100 °C. Delightfully, 85% yield of Rh^{III}(ttp)COCHMe$(CH_2)_3$COMe **3i** was obtained in 4 days (eq 2). The ^{1}H NMR spectrum of Rh^{III}(ttp)COCHMe-$(CH_2)_3$COMe shows a singlet at 1.72 ppm with three protons, suggesting the presence of an acetyl group. The two types of acyl carbon signals were clearly identified in its ^{13}C NMR spectrum with peaks at 208.12 ppm (**CO**Me; singlet) and 207.42 ppm (Rh**CO**; doublet, $^1J_{Rh-C}$ = 29.8 Hz). The CCA product from the 2,6-dimethylcyclohexanone, therefore, clearly shows that the carbonyl group is transferred to the rhodium center and the alkyl fragment is oxidized to a carbonyl moiety. Figure 4 shows an X-ray structure of Rh^{III}(ttp)COCHMe$(CH_2)_3$COMe.



Source of Oxygen. As the Aldol condensation occurred before the CCA of acetophenone, water, therefore, is a possible oxygen source for the CCA. To examine the possible accelerating effect of water, the reaction of Rh^{III}(ttp)Me and the nonenolizable diisopropyl ketone with the addition of water was examined (Table 6). Without any water added, the reaction proceeded to give 95% yield of Rh^{III}(ttp)CO^{i}Pr in 1 day (Table 6, entry 1). The trace amount of water residue (max 0.2% in acetone

dx.doi.org/10.1021/om200788p | *Organometallics* 2012, 31, 570–579

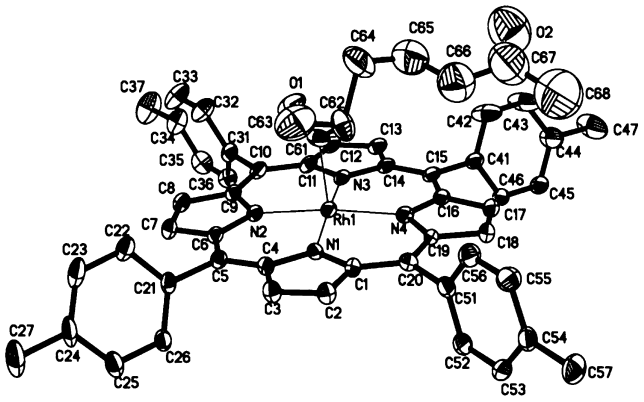


Figure 4. ORTEP presentation of the molecular structure with numbering scheme for $Rh^{III}(ttp)COCHMe(CH_2)_3COMe$ **3i** (30% probability displacement ellipsoids).

Table 6. Water Effect on CCA of Diisopropyl Ketone

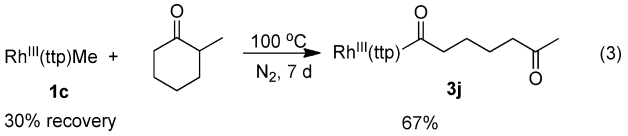
$Rh^{III}(ttp)Me$ (**1c**) + $^{i}PrCO^{i}Pr$ (200 equiv) $\xrightarrow[\text{acetone, } N_2,\ H_2O \text{ (equiv)}]{50\ ^{o}C}$ $Rh^{III}(ttp)CO^{i}Pr$ (**3h**)

entry	H_2O (equiv)	time	**3h** (% yield)
1	0	1 d	95
2	50	3 h	92
3	100	3 h	95
4	200	3 h	93

solvent) in the reaction mixture is likely the water source. When 50 equiv of water was added, the reaction time was shortened from 1 day to 3 h (Table 6, entry 1 vs 2). Further additions of 100 and 200 equiv of water did not improve the rate (Table 6, entries 3 and 4). The rate-accelerating effect of water and the reaction stoichiometry suggest that the CCA occurs through the Rh(ttp)−OH insertion across the C(CO)−C(α) bond, which has been reported in the iridium analogue.[5]

Regioselectivity of CCA. There are two regioselectivity issues associated with the ketone CCA: (i) selective cleavage of unsymmetric ketone and (ii) selective formation of rhodium porphyrin acyl.

Selective Cleavage of Unsymmetric Ketone. The sole formation of $Rh^{III}(ttp)COMe$ with methyl isopropyl ketone reveals that the C(CO)−C(α) bond cleavage is selective at the more-hindered CO−^{i}Pr bond (Table 4, entry 8). Likewise, regioselective CCA at the CO−^{i}Pr bond occurred in the unsymmetric 2-methylcyclohexanone to give $Rh^{III}(ttp)CO(CH_2)_4COMe$ **3j** only (carbonyl signal in ^{13}C NMR: 208.11 ppm (**CO**Me; singlet) and 202.01 ppm (Rh**CO**; doublet, $^{1}J_{Rh-C}$ = 30.0 Hz)) in 67% yield (eq 3). Figure 5 shows an X-ray structure of $Rh^{III}(ttp)CO(CH_2)_4COMe$.



Selective Formation of Rhodium Porphyrin Acyl. Previously, the C(CO)−C(α) bond of acetone was cleaved by $Ir^{III}(ttp)(CO)BF_4$ in a nonregioselective manner at 200 °C to give $Ir^{III}(ttp)Me$ and $Ir^{III}(ttp)COMe$ in 40% and 19% yields,

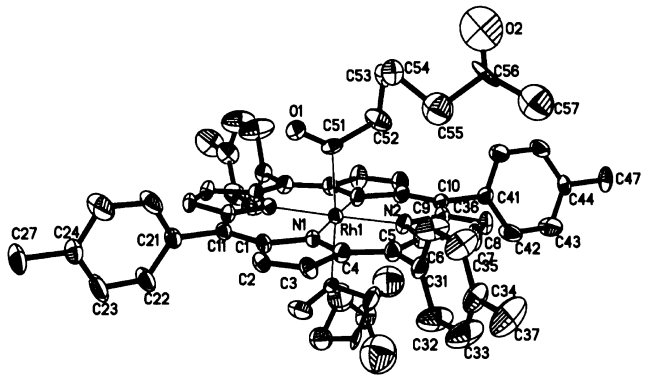


Figure 5. ORTEP presentation of the molecular structure with numbering scheme for $Rh^{III}(ttp)CO(CH_2)_4COMe$ **3j** (30% probability displacement ellipsoids).

respectively.[5] To find out the selectivity of bond cleavage in the rhodium analogues, the reaction of 2-methylcyclohexanone with $Rh^{III}(ttp)Me$ at 100 °C was conducted (eq 9; Scheme 2). Only the expected product $Rh^{III}(ttp)CO(CH_2)_4COMe$ was observed. The other possible CCA product, $Rh^{III}(ttp)CHMe(CH_2)_4COOH$, and its hydrolysis product, heptanoic acid[9] (see the section, Hydrolysis of the α-CHA Product, below), were not detected. The ketone CCA by rhodium porphyrin, therefore, is regioselective.

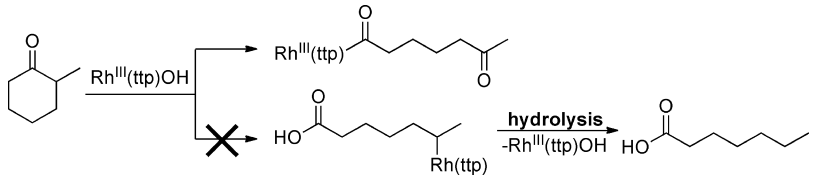
Reaction Mechanism. On the basis of the stoichiometry of the reaction, Aldol condensation, and the α-CHA product, Scheme 3 shows a proposed mechanism for the ketone CCA by $Rh^{III}(ttp)X$ (X = Me or Cl). $Rh^{III}(ttp)X$ first catalyzes the Aldol condensation of ketone to generate the corresponding product (1,3,5-triphenylbenzene in acetophenone case) and water (Scheme 3, eq i). Concurrently, $Rh^{III}(ttp)X$ can react with the α-carbon−hydrogen bond of an alkyl ketone to give an α-carbon−hydrogen bond activation (α-CHA) complex and methane (or HCl) (Scheme 3, eq iia). $Rh^{III}(ttp)OH$ is formed upon hydrolysis of the α-CHA complex (Scheme 3, eq iib). The C(CO)−C(α) bond is then cleaved by $Rh^{III}(ttp)OH$, presumably by σ-bond metathesis, to give a rhodium porphyrin acyl and an alcohol (Scheme 3, eq iii). Further dehydrogenation of the alcohol by $Rh^{III}(ttp)OH$ affords the carbonyl compound and $Rh^{III}(ttp)H$ (Scheme 3, eqs iva and ivb). The α-CHA complex is regenerated when $Rh^{III}(ttp)H$ or $Rh^{II}_2(ttp)_2$ further reacts with ketones (Scheme 3, eq iia). Experiments were then carried out to validate the proposed mechanism.

(Scheme 3, eq i) Aldol Condensation Catalyzed by Rh(ttp)X (X = Me or Cl). At a high temperature of 200 °C, a series of Aldol condensations of acetophenone occurred to give 1,3,5-triphenylbenzene and water (Table 1, Scheme 3), and two layers of immiscible liquids (water and acetophenone) were observed. This type of Lewis acidic rhodium(III) porphyrin catalyzed Aldol condensation is precedented. Ogoshi et al. have reported that the Lewis acidic $Rh^{III}(oep)ClO_4$ catalyzes the Aldol condensation of cyclohexanone at 50 °C.[10] Furthermore, the formation of 1,3,5-triphenylbenzene from the Aldol condensation of acetophenone in the presence of an electrophilic catalyst $Bi^{III}(OTf)_3$ has been reported.[11]

(Scheme 3, eq iia) Carbon−Hydrogen Bond Activation with Rh(ttp)X (X = Me or Cl). $Rh^{III}(ttp)X$ (X = Me or Cl) undergoes a kinetically more facile CHA than CCA with acetophenone. $Rh^{III}(ttp)Me$ reacted with neat acetophenone to give $Rh^{III}(ttp)CH_2COPh$ in quantitative yield in a short reaction time of 3 days at 200 °C (eq 10). After 15 days,

dx.doi.org/10.1021/om200788p | *Organometallics* 2012, 31, 570−579

Scheme 2. Possible CCA Products with 2-Methylcyclohexanone



Scheme 3. Proposed Mechanism of the Rhodium(III) Porphyrin-Assisted C(CO)−C(α) Bond Activation of Ketone

Aldol Condensation	$RCOCH_2R'$	$\xrightarrow{Rh^{III}(ttp)X}$ Aldol condesaton pdt + H_2O	(i)
CHA	$Rh^{III}(ttp)X + RCOCH_2R'$ (X = Me, H or Rh(ttp))	$\longrightarrow$ $Rh^{III}(ttp)CHR'COR + H\text{-}X$	(iia)
Hydrolysis	$Rh^{III}(ttp)CHR'COR + H_2O$	$\rightleftharpoons$ $Rh^{III}(ttp)OH + RCOCH_2R'$	(iib)
CCA	$Rh^{III}(ttp)OH + RCOCH_2R'$	$\longrightarrow$ $Rh^{III}(ttp)COR + R'CH_2\text{-}OH$	(iii)
Dehydrogenation	$R'CH_2\text{-}OH + Rh^{III}(ttp)OH$	$\longrightarrow$ $Rh^{III}(ttp)OCH_2R' + H_2O$	(iva)
	$Rh^{III}(ttp)OCH_2R'$	$\longrightarrow$ $Rh^{III}(ttp)H + R'CHO$	(ivb)

Rh^{III}(ttp)COPh was formed in 93% yield (eq 4). Therefore, the α-CHA is kinetically more facile than CCA.

$$\underset{\textbf{1c}}{Rh^{III}(ttp)Me} + PhCOMe \xrightarrow[N_2]{200\ ^\circ C} \underset{\textbf{4a}}{Rh^{III}(ttp)CH_2COPh} + \underset{\textbf{3a}}{Rh^{III}(ttp)COPh} \quad (4)$$

	3 d	15 d
4a	100%	0%
3a	0%	93%

For propiophenone, the CHA is also more facile but takes place at the β-C−H bond. $Rh^{III}(ttp)CH_2CH_2COPh$ **4b** in 68% yield was obtained in 3 days when Rh^{III}(ttp)Me was reacted with propiophenone at 200 °C (eq 5). Figure 6 shows an X-ray

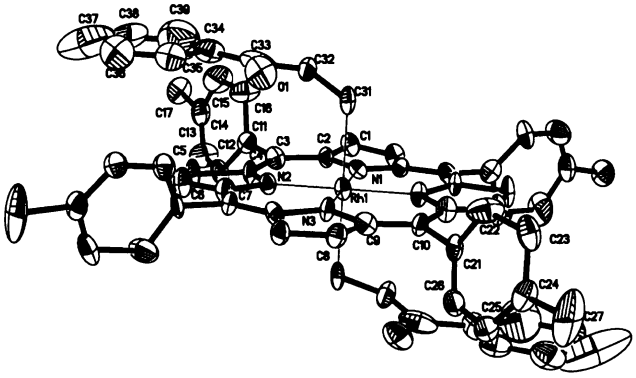


Figure 6. ORTEP presentation of the molecular structure with numbering scheme for $Rh^{III}(ttp)CH_2CH_2COPh$ **4b** (30% probability displacement ellipsoids).

structure of $Rh^{III}(ttp)CH_2CH_2COPh$. While the direct β-CHA is reasonable, a rapid consecutive α-CHA/1,2-isomerization to give $Rh^{III}(ttp)CH_2CH_2COPh$ is also possible. The 1,2-isomerization of rhodium porphyrin alkyl through β-hydride elimination/reinsertion is precedented.[12]

$$\underset{\textbf{1c}}{Rh^{III}(ttp)Me} + PhCOEt \xrightarrow[N_2]{200\ ^\circ C} \underset{\textbf{4b}}{Rh^{III}(ttp)CH_2CH_2COPh} + \underset{\textbf{3a}}{Rh^{III}(ttp)COPh} \quad (5)$$

	3 d	15 d
4b	68%	0%
3a	0%	44%

When Rh^{III}(ttp)Me was reacted with isobutyrophenone at 200 °C in a short reaction time of 1 h, the β-CHA product, $Rh^{III}(ttp)CH_2CHMeCOPh$ **4c**, was only observed in a trace amount in the crude reaction mixture by ^1H NMR: δ −5.14 (ddt, 1H, $^1J_{Rh-H}$ = 3.0 Hz, $^3J_{Ha-Hb}$ = 7.5 Hz, $^2J_{Ha-Ha'}$ = 15.1 Hz, Ha), −4.53 (ddt, 1H, $^1J_{Rh-H}$ = 3.5 Hz, $^3J_{Ha'-Hb}$ = 7.9 Hz, $^2J_{Ha'-Ha}$ = 12.4 Hz, Ha′), −2.99 (m, 1H, Hb), −2.24 (d, 3H, Hc)) and HRMS (Calcd: m/z 918.2796. Found: m/z 918.2799.). Presumably, the low yielding of $Rh^{III}(ttp)CH_2CHMeCOPh$ is due to its high reactivity toward hydrolysis (see the section, Hydrolysis of the α-CHA Product, below).

The more Lewis acidic Rh^{III}(ttp)Cl presumably activates the α-C−H bond through a heterolysis of the Rh^{III}(ttp)−Cl, followed by cationic activation as reported by Ogoshi et al.[10] For the less Lewis acidic Rh^{III}(ttp)Me, heterolysis of the Rh−Me bond is less likely. Probably, in the presence of water, hydrolysis of Rh^{III}(ttp)Me with water to give Rh^{III}(ttp)OH[13] and subsequent α-CHA with Rh^{III}(ttp)OH account for the α-CHA product.

Indeed, Rh^{III}(ttp)Me underwent hydrolysis with water in benzene-d_6 in 30 min to give 34% yield of $Rh^{II}_2(ttp)_2$ **1f** and a trace amount of Rh^{III}(ttp)H **1g** (eq 6). The formation of 11% yield of methane suggests that Rh^{III}(ttp)OH is likely formed. Presumably, the oxygen atom of water attacks the rhodium center to give Rh^{III}(ttp)OH and the methyl ligand leaves as methane upon protonation. The highly reactive Rh^{III}(ttp)OH once formed quickly yields $Rh^{II}_2(ttp)_2$ and H_2O_2. The independent reductive dimerization of Rh^{III}(ttp)OH to give $Rh^{II}_2(ttp)_2$ and H_2O_2 at 120 °C has been reported.[14] The trace amount of Rh^{III}(ttp)H is due to the disproportionation of $Rh^{II}_2(ttp)_2$ with H_2O to give Rh^{III}(ttp)OH and Rh^{III}(ttp)H.[4,15] The analogous equilibria between Rh^{I}(tspp), Rh^{II}(tspp), and Rh^{III}(tspp) in an aqueous medium have been published by Wayland et al. recently.[16]

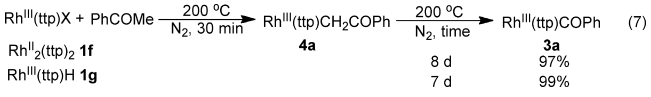
$$\underset{\textbf{1c}\ 60\%\ \text{remain}}{Rh^{III}(ttp)Me} + \underset{100\ \text{equiv}}{H_2O} \xrightarrow[C_6D_6,\ 30\ \text{min}]{200\ ^\circ C} \underset{\textbf{1f}\ 34\%}{Rh^{II}_2(ttp)_2} + \underset{\textbf{1g}\ \text{trace}}{Rh^{III}(ttp)H} + \underset{11\%}{CH_4} \quad (6)$$

NMR yield w.r.t. Rh

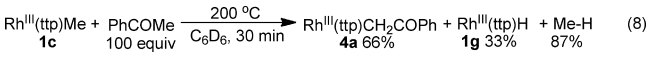
The Rh^{III}(ttp)H and $Rh^{II}_2(ttp)_2$ formed are then kinetically trapped by the α-C−H bond to give the CHA product. Indeed, Rh^{III}(ttp)H and $Rh^{II}_2(ttp)_2$ activated the α-C−H bond of

dx.doi.org/10.1021/om200788p | *Organometallics* 2012, 31, 570−579

acetophenone to give $Rh^{III}(ttp)CH_2COPh$ at 200 °C in a short period of 30 min (eq 7).

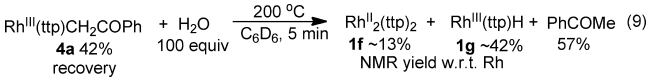


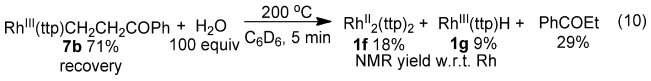
Alternatively, direct α-C−H bond activation with $Rh^{III}(ttp)$-Me by σ-bond metathesis is viable. Indeed, $Rh^{III}(ttp)Me$ reacted with acetophenone in benzene-d_6 in 30 min to give methane and $Rh^{III}(ttp)CH_2COPh$ in 87% yield and 66% yield, respectively (eq 8). This type of σ-bond metathesis has been shown to occur in the benzylic C−H bond activation of toluene by $Rh^{III}(ttp)Me$.[17] The direct CHA is faster than the hydrolysis, and both pathways can operate in parallel.



(Scheme 3, eq iib) Hydrolysis of the α-CHA Product. Direct transformation of the CHA product to the CCA product by a formal σ-bond metathesis[18] is ruled out by the reaction stoichiometry. Only the C−O bond formation at the alkyl fragment was observed, without any C−C bond formation product. Therefore, the Rh−O insertion into the C(CO)−C(α) bond suggests that the CHA product hydrolyzes to give $Rh^{III}(ttp)OH$ first.

Indeed, $Rh^{III}(ttp)CH_2COPh$ and $Rh^{III}(ttp)CH_2CH_2COPh$ were found to undergo hydrolysis more rapidly than $Rh^{III}(ttp)$-Me in the presence of 100 equiv of water in benzene-d_6 in 5 min at 200 °C (eqs 9 and 10 vs eq 6). The formation of acetophenone (57%) and propiophenone (29%) supports the hydrolytic cleavage of $Rh^{III}(ttp)R$ into $Rh^{III}(ttp)OH$ and RH rather than $Rh^{III}(ttp)H$ and R−OH.





Relative Rate of Hydrolysis. The faster hydrolysis rate of the CHA product to generate $Rh^{III}(ttp)OH$ promotes the rate of CCA. The low yield of $Rh^{III}(ttp)CH_2CHMeCOPh$ is attributed to its rapid hydrolysis rate relative to that of $Rh^{III}(ttp)CH_2COPh$ and $Rh^{III}(ttp)CH_2CH_2COPh$ (Figure 7).

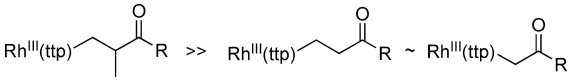


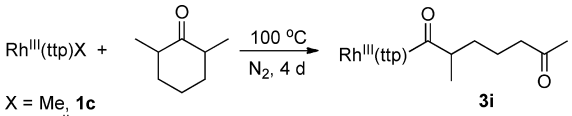
Figure 7. Relative reactivities of the CHA products toward hydrolysis.

The more basic α-carbon in $Rh^{III}(ttp)CH_2CHMeCOPh$ favors the faster hydrolysis. This is a key factor for the high CCA reactivity of isopropyl ketones over methy and ethyl ketones.

(Scheme 3, eq iii) Carbon(CO)−Carbon(α) Bond Oxidation with $Rh^{III}(ttp)OH$. The $Rh^{III}(ttp)R$ hydrolysis product, $Rh^{III}(ttp)OH$, is the only intermediate that cleaves the C(CO)−C(α) bond, as supported by the reaction stoichiometry. Other rhodium porphyrin species, such as $Rh^{III}(ttp)H$ and $Rh^{II}_2(ttp)_2$, though, exist in the reaction medium through equilibrium and react with ketone rapidly to give the CHA product, which would be eventually hydrolyzed into $Rh^{III}(ttp)$-OH for CCA (eq 7).

When $Rh^{III}(ttp)H$ or $Rh^{II}_2(ttp)_2$ were used to react with 2,6-dimethylcyclohexanone, the Rh−O insertion into the C(CO)−C(α) bond still occurred to give $Rh^{III}(ttp)COCHMe$-$(CH_2)_3COMe$ in moderate yield (Table 7). It implies that

Table 7. Reaction of 2,6-Dimethylcyclohexanone with Rh(I), Rh(II), and Rh(III)



X = Me, **1c**
= $Rh^{II}(ttp)$, **1f**
= H, **1g**
= Na, **1h**

entry	Rh(ttp)X	time (d)	**3i** (% yield)
1	$Rh^{III}(ttp)Me$ **1c**	4	85
2	$Rh^{II}_2(ttp)_2$ **1f**	5	46
3	$Rh^{III}(ttp)H$ **1g**	5	40

$Rh^{III}(ttp)H$ and $Rh^{II}_2(ttp)_2$ are transformed to $Rh^{III}(ttp)OH$, likely through equilibrium, in a polar environment before the CCA occurs. However, $Rh^{I}(ttp)^-$ did not give any observable product, probably due to rapid decomposition at high temperature.

The chemoselective C(CO)−C(α) bond activation of ketone by $Rh^{III}(ttp)OH$ can be rationalized in the following two points: (i) favorable $Rh^{III}(ttp)OH$ formation in polar solvent and (ii) weak Rh−OH bond.

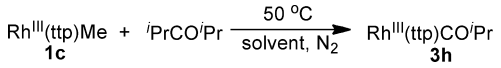
Favorable Rh(ttp)OH Formation in Polar Solvent. The reaction of $Rh^{III}(ttp)Me$ and diisopropyl ketone in benzene, THF, and acetone at 50 °C (Table 8) showed that the rate and yield of the CCA were enhanced in a polar solvent. The reaction with diisopropyl ketone in acetone (100 equiv, Table 8, entry 5) gave a high yield of 90% of $Rh^{III}(ttp)CO^iPr$ with only 6% of $Rh^{III}(ttp)Me$ remained unreacted. The reaction in benzene solvent only gave a lower yield of 77% of $Rh^{III}(ttp)CO^iPr$ (Table 8, entry 1) and recovered $Rh^{III}(ttp)Me$ in 18% yield. These results are consistent with the proposed $Rh^{III}(ttp)OH$ intermediate. A higher concentration of $Rh^{III}(ttp)OH$ can be generated in a polar medium and thus a faster rate of the reaction.

Weak Rh−OH Bond. The $Rh^{III}(ttp)$−OH bond (46 kcal mol^{-1})[21] is around 14 kcal mol^{-1} weaker than the $Rh^{III}(ttp)$−H bond (60 kcal mol^{-1}).[8] $Rh^{III}(ttp)$−H can cleave the C−C bond of cyclooctane in a nonpolar medium,[3] whereas the more reactive $Rh^{III}(ttp)$−OH cleaves the C(CO)−C(α) bond of ketone in a polar medium.

$Rh^{III}(ttp)OH$ cleaves the C(CO)−C(α) bond directly through σ-bond metathesis. The activation barrier for the cleavage of the strong C(CO)−C(α) bond (85.0 kcal mol^{-1})[8] is lower due to the synchronous and simultaneous formation of the Rh−C and C−O bonds. Indeed, benzylic C−H bond activation of toluene by $Rh^{III}(ttp)H$ and $Rh^{III}(ttp)Me$ through σ-bond metathesis is precedented.[17] The four centered metallocycle transition state is possible even though one of the corners is a sterically hindered metalloporphyrin. For the ketone CCA, although one of the corners is replaced by a more bulky sp^3 carbon (the C(α) of ketone), the less hindered sp^2 carbon of the ketone renders the four centered metallocycle

dx.doi.org/10.1021/om200788p | *Organometallics* 2012, 31, 570−579

Table 8. Solvent Effects toward Isobutyryl Transfer of Diisopropyl Ketone

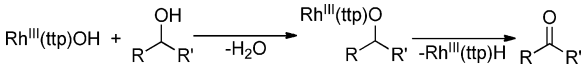


entry	solvent	donor number[19] (kcal mol^{-1})	dielectric constant[20]	^{i}PrCO^{i}Pr (equiv)	time (d)	**1c** (% recovery yield)	**3h** (% yield)
1	benzene	0.1	2.28	100	2	18	77
2	benzene			200	1	0	87
3	THF	20	7.52	100	2	24	75
4	THF			200	1	0	89
5	acetone	17	21.01	100	2	6	90
6	acetone			200	1	0	95

transition state feasible. Furthermore, the hydroxyl group of Rh^{III}(ttp)OH is relatively small, which makes the four centered metallocycle transition state less sterically sensitive. While the covalent radius of oxygen (0.66 Å)[22] doubles that of hydrogen (0.31 Å)[22] and is only slightly smaller than that of sp^3 carbon (0.76 Å),[22] the divalent hydroxyl oxygen is much less hindered than the tetravalent sp^3 carbon.

(Scheme 3, eqs iva and ivb) Dehydrogenation of Alcohol. The alcohol generated from the Rh−OH insertion to the C(CO)−C(α) bond is further oxidized to a carbonyl moiety in the presence of a catalytic amount of Rh^{III}(ttp)OH (Scheme 4). Such a mechanism has been proposed by Collman[23] and Fu.[24]

Scheme 4. Dehydrogenation of Alcohol by Rh^{III}(ttp)OH



In summary, Rh^{III}(ttp)Cl and Rh^{III}(ttp)Me were found to oxidatively cleave the C(CO)−C(α) bond of ketone with water at a temperature as low as 50 °C. The acyl group was transferred to the rhodium center while the alkyl fragment was oxidized to a carbonyl moiety.

EXPERIMENTAL SECTION

Unless otherwise noted, all reagents were purchased from commercial suppliers and directly used without further purification. Hexane was distilled from anhydrous calcium chloride. Thin-layer chromatography was performed on precoated silica gel 60 F_{254} plates. Silica gel (Merck, 70−230 mesh) was used for column chromatography. All reactions were carried out in a Telfon screw-capped tube under N_2 with the mixture degassed for three freeze−thaw-pump cycles and wrapped with aluminum foil to prevent undesired photochemical reactions. The crude mixture was dried under high vacuum. The products were further purified by silica gel column chromatography eluting with a solvent mixture of hexane/CH_2Cl_2.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-400 at 400 and 100 MHz or a Bruker AV-700 at 700 and 175 MHz, respectively. Chemical shifts were referenced with the residual solvent protons in chloroform-d (δ = 7.26 ppm) or tetramethylsilane (δ = 0.00 ppm) and benzene-d_6 (δ = 7.15 ppm) in ^{1}H NMR spectra, and $CDCl_3$ (δ = 77.16 ppm) in ^{13}C NMR spectra as the internal standards. Chemical shifts (δ) were reported as parts per million (ppm) in (δ) scale downfield from TMS. Coupling constants (J) were reported in hertz (Hz). High-resolution mass spectra (HRMS) were recorded on a ThermoFinnigan MAT 95 XL mass spectrometer. Fast atom bombardment spectra were performed with 3-nitrobenzyl alcohol (NBA) as the matrix. All single crystals were immersed in Paraton-N oil and sealed under N_2 in thin-walled glass capillaries. Data were collected at 123, 293, or 296 K on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation. An empirical absorption correction was applied using the SADABS program. All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations on F_2 using the SHELXTL program package. All hydrogen atoms were geometrically fixed using the riding model. Rh(ttp)Cl **1b**,[25] Rh(ttp)Me **1c**,[26] Rh($t_{p\text{-OMe}}$pp)Me **1d**:[26] ^{1}H NMR ($CDCl_3$, 400 MHz): δ −5.82 (d, 3H, $^2J_{Rh-H}$ = 2.8 Hz), 4.09 (s, 12H), 7.26 (m, 8H, overlapped with solvent residue), 8.04 (dd, 4H, J = 2.8, 7.9 Hz), 8.10 (dd, 4H, J = 2.7, 7.9 Hz), 8.75 (s, 8H). ^{13}C NMR ($CDCl_3$, 175 MHz): δ −11.7 (d, $^1J_{Rh-C}$ = 27.4 Hz), 55.7, 112.2, 112.3, 122.0, 131.5, 134.7, 135.0, 135.1, 143.5, 159.3. HRMS (FABMS): Calcd for $[C_{49}H_{39}N_4O_4Rh]^+$: m/z 850.2021. Found: m/z 850.2010. Rh($t_{p\text{-}CF_3}$pp)Me **1e**:[26] ^{1}H NMR ($CDCl_3$, 400 MHz): δ −5.81 (d, 3H, $^2J_{Rh-H}$ = 2.1 Hz), 8.03 (t, 8H, J = 5.6 MHz), 8.27 (d, 4H, J = 7.8 Hz), 8.32 (d, 4H, J = 7.6 Hz), 8.67 (s, 8H). ^{13}C NMR ($CDCl_3$, 175 MHz): δ −10.7 (d, $^1J_{Rh-C}$ = 25.7 Hz), 121.3, 122.3, 123.9, 124.0, 127.0, 130.4 (q, $^1J_{F-C}$ = 32.4 Hz), 131.9, 134.1, 134.2, 159.3, 143.0, 145.6. HRMS (FABMS): Calcd for $[C_{49}H_{27}N_4F_{12}Rh]^+$: m/z 1002.1094. Found: m/z 1002.1086.). $Rh_2(ttp)_2$ **1f**,[27] Rh(ttp)H **1g**,[27] and Rh(ttp)$^-$Na$^+$ **1h**[28] were synthesized according to the literature methods.

Reaction Between Rh(ttp)OTf and Acetophenone at 200 °C for 1 Day. Rh(ttp)OTf **1a**, freshly prepared from Rh(ttp)Cl **1b** (3.1 mg, 0.004 mmol) and AgOTf (2.0 mg, 0.008 mmol), and acetophenone (1.5 mL) were heated at 200 °C under N_2 for 1 day. A pale yellow solid of 1,3,5-triphenylbenzene **2** (58 800% wrt Rh, 720.1 mg, 2.4 mmol) was isolated by crystallization from ethanol. 1,3,5-Triphenylbenzene **2**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (t, 3H, J = 7.6 Hz), 7.49 (t, 6H, J = 7.6 Hz), 7.71 (d, 6H, J = 8.4 Hz), 7.79(s, 3H).

Reaction between Rh(ttp)Cl and Acetophenone at 200 °C for 22 Days. Rh(ttp)Cl **1b** (17.5 mg, 0.022 mmol) and acetophenone (1.5 mL) were heated at 200 °C under N_2 for 22 days. A red product Rh(ttp)COPh **3a**[29a] (17.2 mg, 0.020 mmol, 89%) with R_f = 0.43 (hexane/CH_2Cl_2 = 1:1) was purified and collected by column chromatography. Rh(ttp)COPh **3a**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.43 (dd, 2H, J = 8.1 Hz), 2.70 (s, 12H), 5.95−6.00 (m, 2H), 6.40 (t, 1H, J = 7.8 Hz), 7.52−7.56 (m, 8H), 7.95−8.01 (m, 8H), 8.76 (s, 8H). A 3600% yield of 1,3,5-triphenylbenzene **2** (wrt Rh) was observed when an aliquot of the reaction mixture at 12 days was analyzed by ^{1}H NMR spectroscopy.

Reaction between Rh(ttp)Me and Acetophenone at 200 °C for 3 Days. Rh(ttp)Me **1c** (17.3 mg, 0.022 mmol) and acetophenone (1.5 mL) were heated at 200 °C under N_2 for 3 days. A red product Rh(ttp)CH_2COPh **4a** (19.6 mg, 0.022 mmol, 100%) with R_f = 0.09 (hexane/CH_2Cl_2 = 1:1) was purified and collected by column chromatography. Rh(ttp)CH_2COPh **4a**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ −4.14 (d, 2H, J = 3.6 Hz), 2.70 (s, 12H), 4.59 (d, 2H, J = 7.6 Hz), 6.61 (t, 2H, J = 7.7 Hz), 7.06 (t, 1H, J = 7.3 Hz), 7.53 (t, 8H, J = 8.4 Hz), 7.91 (dd, 4H, J = 1.3, 7.4 Hz), 8.01 (dd, 4H, J = 1.5, 7.5 Hz), 8.70 (s, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 1.0 (d, $^1J_{Rh-C}$ = 29.7 Hz), 21.7, 123.1, 125.1, 126.9, 127.5, 127.6, 130.8, 131.9, 133.8, 134.2, 137.3, 139.1, 143.2, 196.8. HRMS (FABMS): Calcd for $C_{50}H_{41}N_4ORh^+$: m/z 890.2486. Found: m/z 890.2472.

Reaction between Rh(ttp)Me and Acetophenone at 200 °C for 15 Days. Rh(ttp)Me **1c** (17.4 mg, 0.022 mmol) and acetophenone (1.5 mL) were heated at 200 °C under N_2 for 15 days. A red product Rh(ttp)COPh **3a** (17.9 mg, 0.021 mmol, 93%)

dx.doi.org/10.1021/om200788p | Organometallics 2012, 31, 570−579

was purified and collected by column chromatography. A 700% yield of 1,3,5-triphenylbenzene **2** (wrt Rh) was observed when an aliquot of the reaction mixture at 12 days was analyzed by ^{1}H NMR spectroscopy.

Reaction between Rh(ttp)Me and Acetophenone at 150 °C for 26 days. Rh(ttp)Me **1c** (17.4 mg, 0.022 mmol) and acetophenone (1.5 mL) were heated at 150 °C under N_2 for 26 days. A red product Rh(ttp)CH_2COPh **4a** (15.9 mg, 0.018 mmol, 81%) was purified and collected by column chromatography.

Reaction between Rh$_2$(ttp)$_2$ and Acetophenone at 200 °C for 8 Days. Rh$_2$(ttp)$_2$ **1f**, freshly prepared from Rh(ttp)Cl **1b** (17.8 mg, 0.022 mmol), and acetophenone (1.5 mL) were heated at 200 °C under N_2. Rh(ttp)CH_2COPh **4a** formed quantitatively according to TLC analysis in 30 min. After 7 days, a red product Rh(ttp)COPh **3a** (18.7 mg, 0.021 mmol, 97%) was purified and collected by column chromatography.

Reaction between Rh(ttp)H and Acetophenone at 200 °C for 7 Days. Rh(ttp)H **1g**, freshly prepared from Rh(ttp)Cl **1b** (17.8 mg, 0.022 mmol), and acetophenone (1.5 mL) were heated at 200 °C under N_2. Rh(ttp)CH_2COPh **4a** formed quantitatively according to TLC analysis in 30 min. After 7 days, a red product Rh(ttp)COPh **3a** (19.1 mg, 0.022 mmol, 99%) was purified and collected by column chromatography.

Reaction between Rh(t$_{p\text{-OMe}}$pp)Me and Acetophenone at 200 °C for 7 Days. Rh(t$_{p\text{-OMe}}$pp)Me **1d** (18.7 mg, 0.022 mmol) and acetophenone (1.5 mL) were heated at 200 °C under N_2 for 7 days. A red product Rh(t$_{p\text{-OMe}}$pp)COPh **3b** (19.7 mg, 0.021 mmol, 95%) with R_f = 0.19 (hexane/CH_2Cl_2 = 1:1) was purified and collected by column chromatography. Rh(t$_{p\text{-OMe}}$pp)COPh **3b**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.44 (d, 2H, J = 7.3 Hz), 4.08 (s, 12H), 5.98 (t, 2H, J = 7.7 Hz), 6.43 (t, 1H, J = 7.4 Hz), 7.24 (d, 4H, J = 3.3 Hz), 7.28 (d, 4H, J = 2.5 Hz), 7.99 (dd, 4H, J = 1.5, 8.3 Hz), 8.07 (dd, 4H, J = 1.7, 8.2 Hz), 8.77 (s, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 55.7, 112.3, 112.3, 116.7, 122.5, 125.5, 125.8, 131.7, 134.6, 135.0, 135.2, 143.4, 159.4, 200.9 (d, $^1J_{Rh-C}$ = 30.8 Hz). HRMS (FABMS): Calcd for $C_{55}H_{41}N_4O_5Rh^+$: m/z 940.2127. Found: m/z 940.2152.

Reaction between Rh(t$_{p\text{-CF}_3}$pp)Me and Acetophenone at 200 °C for 6 Days. Rh(t$_{p\text{-CF}_3}$pp)Me **1e** (22.1 mg, 0.022 mmol) and acetophenone (1.5 mL) were heated at 200 °C under N_2 for 6 days. A red product Rh(t$_{p\text{-CF}_3}$pp)COPh **3c** (22.6 mg, 0.021 mmol, 94%) with R_f = 0.49 (hexane/CH_2Cl_2 = 1:1) was purified and collected by column chromatography. Rh(t$_{p\text{-CF}_3}$pp)COPh **3c**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.47 (d, 2H, J = 7.6 Hz), 6.03 (t, 2H, J = 7.6 Hz), 6.50 (t, 1H, J = 7.4 Hz), 8.06 (t, 8H, J = 6.24 Hz), 8.23 (d, 4H, J = 7.6 Hz), 8.32 (d, 4H, J = 8.0 Hz), 8.73 (s, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 116.6, 121.7, 124.0, 125.8, 126.0, 126.2, 130.5 (q, $^1J_{F-C}$ = 32.4 Hz), 132.0, 134.1, 134.3, 142.9, 145.5, 199.3 (d, $^1J_{Rh-C}$ = 30.82 Hz). HRMS (FABMS): Calcd for $[C_{55}H_{29}N_4F_{12}ORh + H]^+$: m/z 1093.1278. Found: m/z 1093.1270.

Reaction between Rh(ttp)Me and *p*-Methylacetophenone at 200 °C for 6 Days. Rh(ttp)Me **1c** (17.4 mg, 0.022 mmol) and *p*-methylacetophenone (1.5 mL) were heated at 200 °C under N_2 for 6 days. A red product Rh(ttp)COC_6H_4-*p*-Me **3d** (14.1 mg, 0.016 mmol, 72%) was purified and collected by column chromatography.

Reaction between Rh(ttp)Me and *p*-Fluoroacetophenone at 200 °C for 12 Days. Rh(ttp)Me **1c** (17.3 mg, 0.022 mmol) and *p*-fluoroacetophenone (1.5 mL) were heated at 200 °C under N_2 for 12 days. A red product Rh(ttp)COC_6H_4-*p*-F **3e** (15.7 mg, 0.018 mmol, 80%) was purified and collected by column chromatography.

Reaction between Rh(ttp)Cl and Propiophenone at 200 °C for 21 Days. Rh(ttp)Cl **1b** (17.4 mg, 0.022 mmol) and propiophenone (1.5 mL) were heated at 200 °C under N_2 for 21 days. A red product Rh(ttp)COPh **3a** (11.8 mg, 0.013 mmol, 61%) was purified and collected by column chromatography.

Reaction between Rh(ttp)Me and Propiophenone at 200 °C for 3 Days. Rh(ttp)Me **1c** (17.3 mg, 0.022 mmol) and propiophenone (1.5 mL) were heated at 200 °C under N_2 for 3 days. A red product Rh(ttp)CH_2CH_2COPh **4b** (13.5 mg, 0.015 mmol, 68%) with R_f = 0.12 (hexane/CH_2Cl_2 = 1:1) was purified and collected by column chromatography. Rh(ttp)CH_2CH_2COPh **4b**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ −4.76 (dt, 2H, J = 3.0, 8.4 Hz), −3.08 (t, 2H, J = 8.3 Hz), 2.70 (s, 12H), 5.86 (d, 2H, J = 7.6 Hz), 6.89 (t, 2H, J = 7.7 Hz), 7.15 (t, 1H, J = 7.4 Hz), 7.52 (d, 4H, J = 8.0 Hz), 7.55 (d, 4H, J = 8.2 Hz), 7.97 (d, 4H, J = 7.6 Hz), 8.10 (d, 4H, J = 7.7 Hz), 8.77 (s, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 5.5 (d, $^1J_{Rh-C}$ = 29.6 Hz), 21.7, 36.2, 122.7, 127.1, 127.6, 127.8, 131.8, 132.2, 133.8, 134.1, 137.4, 139.2, 143.4, 195.5. HRMS (FABMS): Calcd for $C_{57}H_{45}N_4ORh^+$: m/z 904.2643. Found: m/z 904.2627.

Reaction between Rh(ttp)Me and Propiophenone at 200 °C for 15 Days. Rh(ttp)Me **1c** (17.5 mg, 0.022 mmol) and propiophenone (1.5 mL) were heated at 200 °C under N_2 for 15 days. A red product Rh(ttp)COPh **3a** (8.5 mg, 0.010 mmol, 44%) was purified and collected by column chromatography.

Reaction between Rh(ttp)Cl and *n*-Butyrophenone at 200 °C for 20 Days. Rh(ttp)Cl **1b** (17.5 mg, 0.022 mmol) and *n*-butyrophenone (1.5 mL) were heated at 200 °C under N_2 for 20 days. A red product Rh(ttp)COPh **3a** (4.1 mg, 0.005 mmol, 21%) was purified and collected by column chromatography.

Reaction between Rh(ttp)Me and *n*-Butyrophenone at 200 °C for 19 Days. Rh(ttp)Me **1c** (17.6 mg, 0.022 mmol) and *n*-butyrophenone (1.5 mL) were heated at 200 °C under N_2 for 19 days. A red product Rh(ttp)COPh **3a** (8.3 mg, 0.009 mmol, 43%) was purified and collected by column chromatography.

Reaction between Rh(ttp)Cl and Isobutyrophenone at 200 °C for 1 Day. Rh(ttp)Cl **1b** (17.5 mg, 0.022 mmol) and isobutyrophenone (1.5 mL) were heated at 200 °C under N_2 for 1 day. A red product Rh(ttp)COPh **3a** (2.3 mg, 0.003 mmol, 12%) was purified and collected by column chromatography.

Reaction between Rh(ttp)Me and Isobutyrophenone at 200 °C for 1 Day. Rh(ttp)Me **1c** (17.5 mg, 0.022 mmol) and isobutyrophenone (1.5 mL) were heated at 200 °C under N_2 for 1 day. A red product Rh(ttp)COPh **3a** (18.7 mg, 0.021 mmol, 97%) was purified and collected by column chromatography.

Reaction between Rh(ttp)Me and Isobutyrophenone at 50 °C for 3 Days. Rh(ttp)Me **1c** (17.6 mg, 0.022 mmol) and isobutyrophenone (1.5 mL) were heated at 50 °C under N_2 for 3 days. A red product Rh(ttp)COPh **3a** (7.9 mg, 0.018 mmol, 41%) was purified and collected by column chromatography. Rh(ttp)Me (5.6 mg, 0.007 mmol, 32%) was recovered.

Reaction between Rh(ttp)Cl and Acetone at 200 °C for 26 Days. Rh(ttp)Cl **1b** (17.5 mg, 0.022 mmol) and acetone (1.5 mL) were heated at 200 °C under N_2 for 26 days. A red product Rh(ttp)COMe **3f**[29b] (6.1 mg, 0.007 mmol, 34%) with R_f = 0.38 (hexane/CH_2Cl_2 = 1:1) was purified and collected by column chromatography. Rh(ttp)COMe **3f**. ^{1}H NMR ($CDCl_3$, 300 MHz): δ −2.79 (s, 3H), 2.70 (s, 12H), 7.54 (t, 8H, J = 7.8 Hz), 8.06 (dd, 8H, J = 3, 6.6 Hz), 8.01 (s, 8H).

Reaction between Rh(ttp)Me and Acetone at 200 °C for 17 Days. Rh(ttp)Me **1c** (17.5 mg, 0.022 mmol) and acetone (1.5 mL) were heated at 200 °C under N_2 for 17 days. A red product Rh(ttp)COMe **3f** (3.6 mg, 0.004 mmol, 20%) was purified and collected by column chromatography.

Reaction between Rh(ttp)Cl and Diethyl Ketone at 200 °C for 20 Days. Rh(ttp)Cl **1b** (17.5 mg, 0.022 mmol) and diethyl ketone (1.5 mL) were heated at 200 °C under N_2 for 20 days. A red product Rh(ttp)COEt **3g**[29a] (4.2 mg, 0.005 mmol, 23%) with R_f = 0.52 (hexane/CH_2Cl_2 = 1:1) was purified and collected by column chromatography. Rh(ttp)COEt **3g**. ^{1}H NMR (300 MHz, $CDCl_3$): δ −3.14 (q, 2H, J = 7.5 Hz), −1.69 (t, 3H, J = 7.2 Hz), 2.70 (s, 12H), 7.26 (d, 8H, J = 7.8 Hz), 8.05 (d, 8H, J = 6.3 Hz), 8.80 (s, 8H).

Reaction between Rh(ttp)Me and Diethyl Ketone at 200 °C for 16 Days. Rh(ttp)Me **1c** (17.4 mg, 0.022 mmol) and diethyl ketone (1.5 mL) were heated at 200 °C under N_2 for 16 days. A red product Rh(ttp)COEt **3g** (8.2 mg, 0.010 mmol, 45%) was purified and collected by column chromatography.

Reaction between Rh(ttp)Cl and Diisopropyl Ketone at 200 °C for 1 Day. Rh(ttp)Cl **1b** (17.5 mg, 0.022 mmol) and diisopropyl ketone (1.5 mL) were heated at 200 °C under N_2 for 1 day. A red product Rh(ttp)CO^{i}Pr **3h** (4.4 mg, 0.005 mmol, 24%) with R_f = 0.57 (hexane/CH_2Cl_2 = 1:1) was purified and collected by column chromatography. Rh(ttp)CO^{i}Pr **3h**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ

dx.doi.org/10.1021/om200788p | *Organometallics* 2012, 31, 570−579

−3.68 (hept, 1H, J = 6.8 Hz), −2.14 (d, 6H, J = 6.8 Hz), 2.69 (s, 12H), 7.53 (t, 8H, J = 8.4 Hz), 7.99 (d, 4H, J = 7.4 Hz), 8.09 (d, 4H, J = 7.6 Hz), 8.79 (s, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 12.4, 19.3, 21.6, 29.4, 31.5, 42.6, 48.9, 122.8, 127.4, 127.5, 131.6, 133.7, 134.1, 137.3, 139.1, 143.3, 207.4 (d, $^1J_{Rh-C}$ = 29.8 Hz), 208.1. HRMS (FABMS): Calcd for $C_{50}H_{41}N_4ORh^+$: m/z 843.2565. Found: m/z 843.2559.

Reaction between Rh(ttp)Me and Diisopropyl Ketone at 200 °C for 30 min. Rh(ttp)Me **1c** (17.5 mg, 0.022 mmol) and diisopropyl ketone (1.5 mL) were heated at 200 °C under N_2 for 30 min. At the end of the reaction, an aliquot of the reaction mixture was added to benzene-d_6 for ^{1}H NMR analysis. Acetone (δ = 1.5 ppm) was observed in quantitative yield. A red product Rh(ttp)CO^{i}Pr **3h** (15.9 mg, 0.019 mmol, 86%) was purified and collected by column chromatography.

Reaction between Rh(ttp)Me and Diisopropyl Ketone at 50 °C for 1 day. Rh(ttp)Me **1c** (17.5 mg, 0.022 mmol) and diisopropyl ketone (1.5 mL) were heated at 50 °C under N_2 for 1 day. A red product Rh(ttp)CO^{i}Pr **3h** (17.4 mg, 0.021 mmol, 94%) was purified and collected by column chromatography.

Reaction between Rh(ttp)Me and Diisopropyl Ketone (100 equiv) in Benzene at 50 °C for 2 Days. Rh(ttp)Me **1c** (8.7 mg, 0.011 mmol) and diisopropyl ketone (160 μL, 1.1 mmol) were heated in benzene (590 μL) at 50 °C under N_2 for 2 days. A red product Rh(ttp)CO^{i}Pr **3h** (7.1 mg, 0.008 mmol, 77%) was purified and collected by column chromatography. Rh(ttp)Me **1c** (1.6 mg, 0.002 mmol, 18%) was recovered.

Reaction between Rh(ttp)Me and Diisopropyl Ketone (200 equiv) in Benzene at 50 °C for 1 Day. Rh(ttp)Me **1c** (8.6 mg, 0.011 mmol) and diisopropyl ketone (320 μL, 2.2 mmol) were heated in benzene (430 μL) at 50 °C under N_2 for 1 day. A red product Rh(ttp)CO^{i}Pr **3h** (8.1 mg, 0.010 mmol, 87%) was purified and collected by column chromatography.

Reaction between Rh(ttp)Me and Diisopropyl Ketone (100 equiv) in THF at 50 °C for 2 Days. Rh(ttp)Me **1c** (8.7 mg, 0.011 mmol) and diisopropyl ketone (160 μL, 1.1 mmol) were heated in THF (590 μL) at 50 °C under N_2 for 2 days. A red product Rh(ttp)CO^{i}Pr **3h** (7.0 mg, 0.008 mmol, 75%) was purified and collected by column chromatography. Rh(ttp)Me **1c** (2.1 mg, 0.003 mmol, 24%) was recovered.

Reaction between Rh(ttp)Me and Diisopropyl Ketone (200 equiv) in THF at 50 °C for 1 Day. Rh(ttp)Me **1c** (8.7 mg, 0.011 mmol) and diisopropyl ketone (320 μL, 2.2 mmol) were heated in THF (430 μL) at 50 °C under N_2 for 1 day. A red product Rh(ttp)CO^{i}Pr **3h** (8.3 mg, 0.010 mmol, 89%) was purified and collected by column chromatography.

Reaction between Rh(ttp)Me and Diisopropyl Ketone (100 equiv) in Acetone at 50 °C for 2 Days. Rh(ttp)Me **1c** (8.7 mg, 0.011 mmol) and diisopropyl ketone (160 μL, 1.1 mmol) were heated in acetone (590 μL) at 50 °C under N_2 for 2 days. A red product Rh(ttp)CO^{i}Pr **3h** (8.3 mg, 0.010 mmol, 90%) was purified and collected by column chromatography. Rh(ttp)Me (0.5 mg, 0.001 mmol, 6%) was recovered.

Reaction between Rh(ttp)Me and Diisopropyl Ketone (200 equiv) in THF at 50 °C for 1 Day. Rh(ttp)Me **1c** (8.7 mg, 0.011 mmol) and diisopropyl ketone (320 μL, 2.2 mmol) were heated in acetone (430 μL) at 50 °C under N_2 for 1 day. A red product Rh(ttp)CO^{i}Pr **3h** (8.8 mg, 0.010 mmol, 95%) was purified and collected by column chromatography.

Reaction between Rh(ttp)Me, Diisopropyl Ketone (200 equiv), and Water (50 equiv) in Acetone at 50 °C for 3 h. Rh(ttp)Me **1c** (8.7 mg, 0.011 mmol), water (10 μL, 0.55 mmol), and diisopropyl ketone (320 μL, 2.2 mmol) were heated in acetone (430 μL) at 50 °C under N_2 for 3 h. A red product Rh(ttp)CO^{i}Pr **3h** (8.5 mg, 0.010 mmol, 92%) was purified and collected by column chromatography.

Reaction between Rh(ttp)Me, Diisopropyl Ketone (200 equiv), and Water (100 equiv) in Acetone at 50 °C for 3 h. Rh(ttp)Me **1c** (8.7 mg, 0.011 mmol), water (20 μL, 1.1 mmol), and diisopropyl ketone (320 μL, 2.2 mmol) were heated in acetone (430 μL) at 50 °C under N_2 for 3 h. A red product Rh(ttp)CO^{i}Pr **3h** (8.8 mg, 0.010 mmol, 95%) was purified and collected by column chromatography.

Reaction between Rh(ttp)Me, Diisopropyl Ketone (200 equiv), and Water (200 equiv) in Acetone at 50 °C for 3 h. Rh(ttp)Me **1c** (8.7 mg, 0.011 mmol), water (40 μL, 2.2 mmol), and diisopropyl ketone (320 μL, 2.2 mmol) were heated in acetone (430 μL) at 50 °C under N_2 for 3 h. A red product Rh(ttp)CO^{i}Pr **3h** (8.6 mg, 0.010 mmol, 93%) was purified and collected by column chromatography.

Reaction between Rh(ttp)Cl and Methyl Isopropyl Ketone at 200 °C for 8 Days. Rh(ttp)Cl **1b** (17.6 mg, 0.022 mmol) and methyl isopropyl ketone (1.5 mL) were heated at 200 °C under N_2 for 8 days. A red product Rh(ttp)COMe **3f** (2.5 mg, 0.003 mmol, 14%) was purified and collected by column chromatography.

Reaction between Rh(ttp)Me and Methyl Isopropyl Ketone at 200 °C for 1 Day. Rh(ttp)Me **1c** (17.6 mg, 0.022 mmol) and methyl isopropyl ketone (1.5 mL) were heated at 200 °C under N_2 for 1 day. A red product Rh(ttp)COMe **3f** (17.0 mg, 0.021 mmol, 95%) was purified and collected by column chromatography.

Reaction between Rh(ttp)Me and Methyl Isopropyl Ketone at 50 °C for 3 Days. Rh(ttp)Me **1c** (17.6 mg, 0.022 mmol) and methyl isopropyl ketone (1.5 mL) were heated at 50 °C under N_2 for 3 days. A red product Rh(ttp)COMe **3f** (10.2 mg, 0.013 mmol, 57%) was purified and collected by column chromatography. Rh(ttp)Me **1c** (6.8 mg, 0.009 mmol, 39%) was recovered.

Reaction between Rh(ttp)Me and 2,6-Dimethylcyclohexanone at 100 °C for 4 Days. Rh(ttp)Me **1c** (17.5 mg, 0.022 mmol) and 2,6-dimethylcyclohexanone (1.5 mL) were heated at 100 °C under N_2 for 4 days. A red product Rh(ttp)COCHMe$(CH_2)_3$COMe **3i** (17.1 mg, 0.019 mmol, 85%) with R_f = 0.03 (hexane/CH_2Cl_2 = 1:1) was purified and collected by column chromatography. Rh(ttp)Me (2.4 mg, 0.003 mmol, 14%) was recovered. Rh(ttp)COCHMe$(CH_2)_3$COMe **3i**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ −3.61 (sext, 1H, J = 5.6 Hz), −2.34 (d, 3H, J = 6.8 Hz), −1.65 (q, 1H, J = 7.8 Hz), −1.39 (m, 2H), −0.92 (quint, 1H, J = 8.6 Hz), 1.13 (m, 2H), 1.72 (s, 3H), 2.72 (s, 12H), 7.56 (d, 8H, J = 7.9 Hz), 8.04 (dd, 8H, J = 2.0, 7.4 Hz), 8.10 (dd, 8H, J = 2.1, 7.4 Hz), 8.84 (s, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 15.6, 21.7, 29.8, 43.5, 122.8, 127.5, 127.6, 131.6, 133.7, 134.3, 137.4, 139.3, 143.3, 207.4 (d, $^1J_{Rh-C}$ = 29.8 Hz), 208.1. HRMS (FABMS): Calcd for $C_{56}H_{49}N_4O_2Rh^+$: m/z 912.2905. Found: m/z 912.2924.

Reaction between $Rh_2(ttp)_2$ and 2,6-Dimethylcyclohexanone at 100 °C for 5 Days. $Rh_2(ttp)_2$ **1f**, freshly prepared from Rh(ttp)Cl **1b** (17.4 mg, 0.022 mmol), and 2,6-dimethylcyclohexanone (1.5 mL) were heated at 100 °C under N_2 for 5 days. A red product Rh(ttp)COCHMe$(CH_2)_3$COMe **3i** (8.2 mg, 0.010 mmol, 40%) was purified and collected by column chromatography.

Reaction between Rh(ttp)H and 2,6-Dimethylcyclohexanone at 100 °C for 5 Days. Rh(ttp)H **1g**, freshly prepared from Rh(ttp)Cl **1b** (17.5 mg, 0.022 mmol), and 2,6-dimethylcyclohexanone (1.5 mL) were heated at 100 °C under N_2 for 5 days. A red product Rh(ttp)COCHMe$(CH_2)_3$COMe **3i** (8.0 mg, 0.009 mmol, 40%) was purified and collected by column chromatography.

Reaction between Rh(ttp)$^-$Na$^+$ and 2,6-Dimethylcyclohexanone at 100 °C for 5 Days. Rh(ttp)$^-$Na$^+$ **1h**, freshly prepared from Rh(ttp)Cl **1b** (17.4 mg, 0.022 mmol), and 2,6-dimethylcyclohexanone (1.5 mL) were heated at 100 °C under N_2 for 5 days. The reaction mixture gradually turned dark, and no product was isolated.

Reaction between Rh(ttp)Me and 2-Methylcyclohexanone at 100 °C for 7 Days. Rh(ttp)Me **1c** (17.6 mg, 0.022 mmol) and 2-methylcyclohexanone (1.5 mL) were heated at 100 °C under N_2 for 7 days. A red product Rh(ttp)CO$(CH_2)_4$COMe **3j** (13.2 mg, 0.015 mmol, 67%) with R_f = 0.04 (hexane/CH_2Cl_2 = 1:1) was purified and collected by column chromatography. Rh(ttp)Me (5.3 mg, 0.007 mmol, 30%) was recovered. Rh(ttp)CO$(CH_2)_4$COMe **3j**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ −3.11 (t, 2H, J = 7.0 Hz), −1.30 (quin, 2H, J = 7.3 Hz), −0.58 (quin, 2H, J = 7.5 Hz), 0.96 (t, 2H, J = 7.6 Hz), 1.62 (s, 3H), 2.69 (s, 12H), 7.53 (d, 8H, J = 7.8 Hz), 8.04 (t, 8H, J = 8.3 Hz), 8.80 (s, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.0, 21.7, 22.2, 29.6, 41.7, 43.1, 122.8, 127.6, 131.7, 133.9, 134.2, 137.5, 139.2, 143.2, 202.0 (d, $^1J_{Rh-C}$ = 30.0 Hz), 208.1. HRMS (FABMS): Calcd for $[C_{55}H_{47}N_4O_2Rh + H]^+$: m/z 899.2827. Found: m/z 899.2854.

Carbon−Hydrogen Bond Activation of Acetophenone by Rh(ttp)Me. Rh(ttp)Me **1c** (4.0 mg, 0.005 mmol), acetophenone (60 uL,

dx.doi.org/10.1021/om200788p | Organometallics 2012, 31, 570−579

0.5 mmol), and benzene-d_6 (500 uL) were added to an NMR tube with a Telfon screw cap. The reaction mixture was degassed for three freeze−thaw−pump cycles and flame-sealed. The tube was heated at 200 °C in the dark for 30 min and analyzed by ^{1}H NMR spectroscopy. A 66% yield of Rh(ttp)CH_2COPh **4a**, 33% yield of Rh(ttp)H **1g**, and 87% yield of methane were observed in 30 min.

Hydrolysis of Rh(ttp)Me. Rh(ttp)Me **1c** (4.0 mg, 0.005 mmol), water (10 uL, 0.5 mmol), and benzene-d_6 (500 uL) were added to an NMR tube with a Telfon screw cap. The reaction mixture was degassed for three freeze−thaw−pump cycles and flame-sealed. The tube was heated at 200 °C in the dark for 30 min and analyzed by ^{1}H NMR spectroscopy. A 34% yield of Rh_2(ttp)$_2$ **1g**, a trace amount of Rh(ttp)H **1f**, and 11% of methane were observed in 30 min with a 60% yield of Rh(ttp)Me **1c** remained.

Hydrolysis of Rh(ttp)CH_2COPh. Rh(ttp)CH_2COPh **4a** (4.0 mg, 0.004 mmol), H_2O (100 equiv, 8.0 uL, 0.45 mmol), and benzene-d_6 (500 uL) were added to an NMR tube with a Telfon screw cap. The reaction mixture was degassed for three freeze−thaw−pump cycles and flame-sealed. The tube was heated at 200 °C in the dark for 5 min and analyzed by ^{1}H NMR spectroscopy. A 42% yield of Rh(ttp)H **1g**, 13% yield of Rh_2(ttp)$_2$ **1f**, 57% yield of acetophenone, and 42% recovery yield of Rh(ttp)CH_2COPh **4b** were obtained in 5 min.

Hydrolysis of Rh(ttp)CH_2CH_2COPh. Rh(ttp)CH_2CH_2COPh **4b** (4.0 mg, 0.004 mmol), H_2O (100 equiv, 8.0 uL, 0.45 mmol), and benzene-d_6 (500 uL) were added to an NMR tube with a Telfon screw cap. The reaction mixture was degassed for three freeze−thaw−pump cycles and flame-sealed. The tube was heated at 200 °C in the dark for 5 min and analyzed by ^{1}H NMR spectroscopy. A 9% yield of Rh(ttp)H **1g**, 18% yield of Rh_2(ttp)$_2$ **1f**, 29% yield of propiophenone, and 71% recovery yield of Rh(ttp)CH_2CH_2COPh **4b** were obtained in 5 min.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables and figures of crystallographic data for complexes **3b**, **3c**, **3f**, **3h**−**3j**, **4a**, and **4b** (CIF and PDF), and ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ksc@cuhk.edu.hk.

■ ACKNOWLEDGMENTS

We are grateful to the Research Grants Council of Hong Kong of the SAR of China for financial support (No. 400308).

■ REFERENCES

(1) Murakami, M.; Ito, Y. Cleavage of Carbon-Carbon Single Bonds by Transition Metals. In *Topics in Organometallic Chemistry*; Murai, S., Ed.; Springer-Verlag: Berlin, 1999; Vol. 3, 97−129.
(2) Taw, F. L.; Mueller, A. H.; Bergman, R. G.; Brookhart, M. *J. Am. Chem. Soc.* **2003**, *125*, 9808−9813.
(3) Chan, Y. W.; Chan, K. S. *J. Am. Chem. Soc.* **2010**, *132*, 6920−6922.
(4) Lee, S. Y.; Lai, T. H.; Choi, K. S.; Chan, K. S. *Organometallics* **2011**, *30*, 3691−3693.
(5) Li, B. Z.; Fung, H. S.; Song, X.; Chan, K. S. *Organometallics* **2011**, *30*, 1984−1990.
(6) Fung, H. S.; Li, B. Z.; Chan, K. S. *Organometallics* **2010**, *29*, 4421−4423.
(7) We would like to make an amendment to our previous report in ref 6. Rh^{III}(ttp)Me catalyzed the aldol condensation of acetophenone at 200 °C to give 4% yield (wrt PhCOMe) or 700% yield (wrt Rh) of 1,3,5-triphenylbenzene in 12 days, not 28% yield (wrt PhCOMe).
(8) Luo, Y. R. *Comprehensive Handbook of Chemical Bond Energies*; CRC Press: Boca Raton, FL, 2007.
(9) The absence of heptanoic acid was confirmed with an authentic sample by GC/MS.
(10) (a) Aoyama, Y.; Yoshida, T.; Ogoshi, H. *Tetrahedron Lett.* **1985**, *26*, 6107−6108. (b) Aoyama, Y.; Tanaka, Y.; Yoshida, T.; Toi, H.; Ogoshi, H. *J. Organomet. Chem.* **1987**, *329*, 251−266.
(11) Fumiaki, O.; Yuichi, I.; Yuusuke, T.; Masato, E.; Tsuneo, S. *Synlett* **2008**, *15*, 2365−2367.
(12) (a) Mak, K. W.; Chan, K. S. *J. Am. Chem. Soc.* **1998**, *120*, 9686−9687. (b) Mak, K. W.; Xue, F.; Mak, T. C. W.; Chan, K. S. *J. Chem. Soc., Dalton Trans.* **1999**, 3333−3334.
(13) Hanson, S. K.; Heinekey, D. M.; Goldberg, K. I. *Organometallics* **2008**, *27*, 1454−1463.
(14) Choi, K. S.; Lai, T. H.; Lee, S. Y.; Chan, K. S. *Organometallics* **2011**, *30*, 2633−2635.
(15) Wayland, B. B.; Balkus, K. J. Jr.; Farnos, M. D. *Organometallics* **1989**, *8*, 950−955.
(16) Fu, X.; Wayland, B. B. *J. Am. Chem. Soc.* **2004**, *126*, 2626−2631.
(17) Choi, K. S.; Chiu, P. F.; Chan, K. S. *Organometallics* **2010**, *29*, 624−629.
(18) Vidal, V.; Tholier, A.; Thivolle-Cazat, J.; Basset, J. M. *Science* **1997**, *276*, 99−102.
(19) Wypych, G. *Handbook of Solvents*; ChemTec Publishing: Toronto, 2000.
(20) Lide, D. R., Ed. *Handbook of Chemistry and Physics*, 84th ed.; CRC Press: Boca Raton, FL, 2004.
(21) Wayland et al. reported that the bond strength of Rh^{III}(tmp)−OMe is 46 kcal mol^{-1}. It is assumed that the Rh^{III}(por)−OH bond is similar in strength. See: Sarkar, S.; Li, S.; Wayland, B. B. *J. Am. Chem. Soc.* **2010**, *132*, 13569−13571.
(22) Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832−2838.
(23) Collman, J. P.; Boulatov, R. *Inorg. Chem.* **2001**, *40*, 560−563.
(24) Liu, L.; Yu, M.; Wayland, B. B.; Fu, X. *Chem. Commun.* **2010**, *46*, 6353−6355.
(25) (a) Zhou, X.; Li, Q.; Mak, T. C. W.; Chan, K. S. *Inorg. Chim. Acta* **1998**, *270*, 551−554. (b) Zhou, X.; Wang, R. J.; Xue, F.; Mak, T. C. W.; Chan, K. S. *J. Organomet. Chem.* **1999**, *580*, 22−25.
(26) (a) Chan, K. S.; Mak, K. W.; Tse, M. K.; Yeung, S. K.; Li, B. Z.; Chan, Y. W. *J. Organomet. Chem.* **2008**, *693*, 399−407. (b) Fung, H. S.; Chan, Y. W.; Cheung, C. W.; Choi., K. S.; Lee, S. Y.; Qian, Y. Y.; Chan, K. S. *Organometallics* **2009**, *28*, 3981−3989.
(27) Wayland, B. B.; Van Voorhees, S. L.; Wilker, C. *Inorg. Chem.* **1986**, *25*, 4039−4042.
(28) (a) Tse, A. K. S.; Wu, B. M.; Mak, T. C. W.; Chan, K. S. *J. Organomet. Chem.* **1998**, *568*, 257−261. (b) Dolphin, D.; Halko, D. J.; Johnson, E. *Inorg. Chem.* **1981**, *20*, 4348−4351.
(29) (a) Chan, K. S.; Lau, C. M. *Organometallics* **2006**, *25*, 260−265. (b) Wayland, B. B.; Van Voorhees, S. L.; Wilker, C. *Inorg. Chem.* **1986**, *25*, 4039−4042.