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Journal of Organometallic Chemistry 691 (2006) 3782–3787
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Aliphatic carbon—carbon bond activation of ketones by rhodium(II) porphyrin radical

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Received 4 March 2006; received in revised form 8 May 2006; accepted 16 May 2006
Available online 27 May 2006

Abstract

Aliphatic carbon—carbon bond activation of both enolizable and non-enolizable ketones occurred successfully with rhodium(II) porphyrin radical to give rhodium(III) porphyrin alkyls. Added Ph_3P promoted the yields of products.

Keywords: Rhodium(II) porphyrin; Ketones; Carbon—carbon bond activation

1. Introduction

The activations of inert chemical bonds are of fundamental importance in basic chemical research and industrial applications [1–3]. Activations of aliphatic carbon—carbon bond (CCA) are among the most challenging reactions. The potential applications of new methods to carbon—carbon bond activation may provide more energy-efficient routes in the breakdown of long chain hydrocarbons such as the catalytic cracking of fuels [4], depolymerization of polymer waste [5], and enzymatic degradation of hydrocarbons for methane production [6].

Several reported examples of CCA by transition metal require extra driving force to realize the activation, including ring strain relief [7–9], aromatization [10,11], the presence of an activating functionality [12,13] or in chelation assisted system [14], etc. The activation of unstrained aliphatic carbon—carbon bonds is very challenging [15]. The difficulty is in the more facile activation of sterically more accessible carbon—hydrogen over carbon—carbon bonds. The intramolecular activations of C(aryl)—C(alkyl) [16] and C(alkyl)—C(alkynl) [17] bonds have also been observed. However, the intermolecular activation of the C_{alkyl}—C_{alkyl} bond by a transition metal complex in solution has remained a challenge, most likely due to steric factors of the shielded carbon—carbon bonds.

Our group has reported the activation of aliphatic carbon—carbon bonds of nitroxide radicals by 5,10,15,20-tetra(2,4,6-trimethylphenyl)porphyrinate rhodium(II) [Rh(tmp)] [18]. We have extended our studies in the activation of carbon—carbon bond of less coordinating ketones. While carbon—carbon bond activations of carbonyls have been reported, they are in the category of C(carbonyl)—C(alkyl) bonds [19,20]. Hence, in this paper, we report the successful activation of aliphatic carbon—carbon bond alpha to carbonyl groups in ketones by Rh(tmp) radical.

2. Results and discussion

The metal centered radical Rh^{II}(tmp) [21] (**2**) was generated in about 80% yield by the photolytic cleavage of Rh(tmp)CH_3 (**1**) in benzene at 6–10 °C for ~8 h (Eq. (1); see Fig. 1):

$$\underset{\mathbf{1}}{Rh(tmp)CH_3} \xrightarrow[8\ h,\ N_2]{C_6H_6,\ h\nu,\ 6\text{–}10\ ^\circ C} \underset{\mathbf{2}}{Rh(tmp)} \qquad (1)$$

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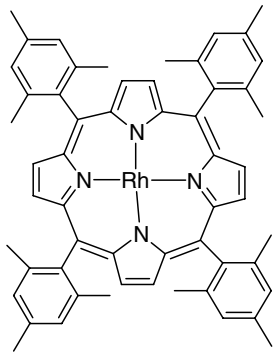
doi:10.1016/j.jorganchem.2006.05.032



Rh(tmp)

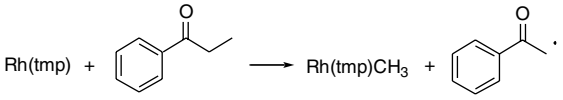
Fig. 1. Structure of Rh(tmp).

2.1. Reactions of Rh(tmp) and enoliazble ketones under solvent-free conditions

$$\underset{\mathbf{2}}{\mathrm{Rh(tmp)}} + \mathrm{ketone} \xrightarrow[\text{temp. time}]{\text{solvent-free, } Ph_3P} \mathrm{products} \qquad (2)$$

First, the ketones containing α-protons were examined (Table 1). When Rh(tmp) was reacted with acetophenone (**3a**) at 130 °C for 1 day under solvent-free conditions in the presence of 1 equiv. of Ph_3P, a mixture products were observed, and a carbon—hydrogen bond activation product Rh(tmp)CH_2COPh (**4**) was tentatively identified (Table 1, entry 1). However this compound proved to be unstable to be purified by chromatography even for a sample prepared by independent synthesis from Rh(tmp) anion and $ClCH_2COph$. Although the bond energy of α-C(carbonyl)—C(methyl) bond ($BDE_{C-C} = 85\ kcal\,mol^{-1}$) [22] is lower than that of C(carbonyl)—hydrogen bond ($BDE_{C-H} = 96\ kcal\,mol^{-1}$) [22], no C(carbonyl)—C(methyl) bond activation occurred, therefore, kinetically favored CHA was more facile.

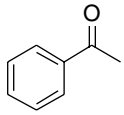
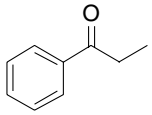
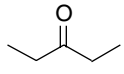
For the case of propiophenone (**3b**), the $C(sp^3)$—$C(sp^3)$ activation product Rh(tmp)CH_3 (**1**), and CHA product Rh(tmp)$CH_2CH_2C(O)C_6H_5$ (**5**) were observed at 130 °C. At a lower reaction temperature of 100 °C, no Rh(tmp)CH_3 was formed, even the reaction time was lengthened to 5 days (Table 1, entries 2–4). The CCA was proposed to occur via hemolytic bimolecular substitution (S_H2) mechanism (Eq. (3)) [23,24]. However no Rh(tmp)$CH_2C(O)Ph$ was observed, it may due to the instability of radical **A**:



A (3)

When diethyl ketone (**3c**) was used, multiple activation products were observed. $C(sp^3)$—$C(sp^3)$ activation product, Rh(tmp)CH_3 (**1**), $C(sp^2)$—$C(sp^3)$ activation product Rh(tmp)$C(O)CH_2CH_3$ (**6**), and CHA product Rh(tmp)$CH_2CH_2C(O)CH_2CH_3$ (**7**) were formed (Table 1, entry 5). The lower bond energy of α-C(carbonyl)—C(ethyl) bond ($BDE_{C-C} = 82\ kcal\,mol^{-1}$) than α-C(methyl)—C(methyl) bond ($BDE_{C-C} = 86\ kcal\,mol^{-1}$) [22] is consistent with the higher yield of **6** than **1**. Furthermore, the sterically more accessible carbonyl carbon may favor the formation of **6**.

Table 1
The reactions of Rh(tmp) (**2**) and enolizable ketones

Entry	Substrate	Temperature (°C)	Time (d)	Rh(tmp)R (Yield [%]),[a] R =	
				CCA	CHA
1	 **3a**	130	1	Complex mixture pf products[b]	
2	 **3b**	130	1	CH_3 **1** (3)	CH_2CH_2COPh **5** (26)
3		100	2		CH_2CH_2COPh **5** (trace)
4		100	5		CH_2CH_2COPh **5** (11)
5	 **3c**	100	2	CH_3 **1** (6) COC_2H_5 **6** (11)	$CH_2CH_2COC_2H_5$ **7** (33)

[a] % Yield was based on 80% of Rh(tmp) generated through photolysis.
[b] Rh(tmp)CH_2COPh was tentatively identified.

The enolizable ketones in Table 1 exhibit minor CCA and major CHA. Only in the case of **3b**, an increase of reaction temperature favored CCA slightly but was not very efficient. The formation of carbon—hydrogen bond activation products suggested that Rh(tmp) might react with the enol tautomers [25]. To prevent this competitive CHA, non-enolizable carbonyls were then examined.

2.2. Reactions of Rh(tmp) and non-enolizable ketones

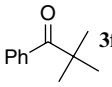
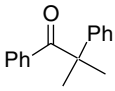
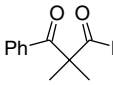
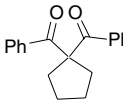
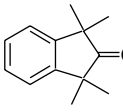
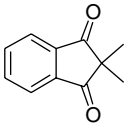
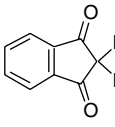
$$\underset{\mathbf{2}}{\mathrm{Rh(tmp)}} + \mathrm{ketone} \xrightarrow[\text{benzene 130 °C, time}]{\text{ligand}} \mathrm{Rh(tmp)R} \qquad (4)$$

A series of non-enolizable ketones were examined. The solvent-free conditions was first examined using **3f**. In solvent-free conditions, **3f** (~680 equiv.) reacted with Rh(tmp) at 130 °C in 1 day to give the CCA produt $Rh(tmp)CH_3$ in 16%. When 5 equiv. of **3f** was used and the reaction was carried out in benzene solvent, $C(sp^3)$—$C(sp^3)$ activation product $Rh(tmp)CH_3$ was obtained in 18%, with nearly equal efficiency as that in solvent-free conditions. So, subsequent studies were carried out in benzene solution.

Rh(tmp) (**2**) also successfully activated carbon—carbon bond of 2,2,4,4-tetramethyl-pentan-3-one (**3d**) in benzene solution to produce $Rh(tmp)CH_3$ (**1**) as the CCA product.

To improve the yield, the effect of added ligand was examined. Rh(II) radicals typically react as metalloradicals with a variety of ligands (L = σ donor and π acceptor), e.g. triphenylphosphine and pyridine, to form adducts, which are more electron-rich and reactive [31]. Ligand (triphenylphosphine and pyridine) effects were therefore investigated. To our delight, the CCA product yield was increased to 31% when triphenylphosphine was used as the ligand (Table 2, entry 2). Addition of pyridine ligand, however, did not promote CCA. It has been known that pyridine ligand induces the disproportionation of Rh(tmp) to yield $[pyRh^{III}(tmp)]^+$ and $[pyRh^{I}(tmp)]^-$, [32,33]; therefore,

Table 2
CCA results between Rh(tmp) and ketones

Entry	Ketone[a]	Ligand	Time (d)	Product (Yield [%][d])
1	 **3d**	None		$Rh(tmp)CH_3$ **1** (20)
2		Ph_3P[b]	1	$Rh(tmp)CH_3$ **1** (31)
3		py[c]		$Rh(tmp)CH_3$ **1** (22)
4	 **3e**	Ph_3P[b]	3	$Rh(tmp)CH_3$ **1**(trace)
5	 **3f**	Ph_3P[b]	1	$Rh(tmp)CH_3$ **1** (18, 16[e])
6	 **3g** [26]	Ph_3P[b]	1	$Rh(tmp)CH_3$ **1** (24)
7	 **3h** [27]	Ph_3P[b]	1	$Rh(tmp)CH_3$ **1** (14)
8	 **3i** [28]	Ph_3P[b]	3	No reaction
9	 **3j** [29]	Ph_3P[b]	1	$Rh(tmp)CH_3$ **1** (25)
10	 **3k** [30]	Ph_3P[b]	1	$Rh(tmp)CH_3$ **1** (30)
11	 **3l** [30]	Ph_3P[b]	3	Rh(tmp)Bn **10** (6)

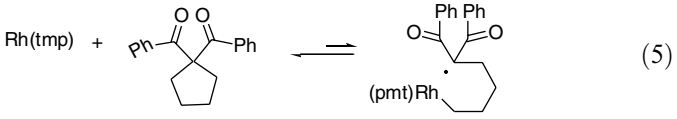
[a] 5 equiv. of ketone added to Rh(tmp).
[b] 1 equiv. of Ph_3P based on Rh(tmp).
[c] 2 equiv. of pyridine based on Rh(tmp).
[d] % Yield was based on 80% of Rh(tmp) generated through photolysis.
[e] Under solvent-free conditions.

pyridine is not good promoter. Hence, triphenylphosphine was chosen as the promoter ligand for the CCA of Rh(tmp) and ketones.

Though, the acyclic ketone **3d** (BDE(α(c)-α(methyl)) = 84 kcal mol^{-1}) [22] underwent successful carbon—carbon bond activation with Rh(tmp) (Table 2, entry 2) to give Rh(tmp)CH_3 in 31%, the cyclic ketone 2,2,5,5-tetramethyl-cyclopentanone (**3e**; entry 4) almost did not react. It suggests that a cyclic substrate may be less reactive than an acyclic one.

2,2-Dimethyl-1-phenyl-propan-1-one (**3f**; entry 5) and 2-methyl-1, 2-diphenyl-propen-1-one (**3g**; entry 6) were activated with Rh(tmp) to produce Rh(tmp)CH_3 in 18% and 24% yield, respectively. Only a slight increase of activity was observed by changing a methyl to phenyl substituent adjacent to the site of bond cleavage. We rationalize that if a co-product carbon-centered radical is formed [18], slight stabilization is gained through resonance with the phenyl ring to account for the high yield.

In the hope of stronger ketone binding to Rh(tmp) to give higher yield of product, 1,3-dicarbonyl substrates were examined. However 2,2-dimethyl-1,3-diphenyl-propane-1,3-dione (**3h**; Table 2, entry 7) only gave Rh(tmp)CH_3 (**1**) in 14% yield. No improvement was made over **3f**. It might be due to the increased steric hindrance of benzoyl over methyl group in blocking the access of carbon—carbon bond to the metal center of Rh(tmp). When 1,1-dibenzoylcyclopentane (**3i**; entry 8) was used as the substrate, no CCA occurred even after heating at 130 °C for 3 days. Rh(tmp) may not be reactive enough to open the ring. Alternatively, the ring opening occurs but is reversible and unfavorable due to the instability of the carbon centered radical formed. Facile reverse reaction gives back the starting materials likely via homolytic bimolecular substitution (Eq. (5)) [34]:



(5)

When 1,1,3,3-tetramethyl-indan-2-one (**3j**; entry 9) reacted with Rh(tmp), 25% yield of Rh(tmp)CH_3 (**1**) was produced. However, 2,2-dimethyl-indan-1,3-dione (**3k**; entry 10) was more high-yielding. We speculate that **3k** gives a more stable co-product radical, which is symmetrical and more resonance-stabilized through conjugation with the two cabonyls.

Even benzyl-methine carbon—carbon bond activation was observed in case of 2,2-dibenzyl-indan-1,3-dione (**3l**; entry 11), to give Rh(tmp)Bn (**10**), though in a lower yield of 6% after 130 °C for 3 days. Presumably, the lower yield is due to the steric hindrance of an adjacent benzyl group.

2.3. Sealed tube experiment

The product yields of Rh(tmp) alkyls were low. To ascertain that Rh(tmp)CH_3 was formed from the CCA but not from incomplete photolysis, the progress of the reaction was also monitored by ^{1}H NMR in a sealed tube experiment. Mixture of solution of Rh(tmp), 1 equiv. of Ph_3P and 10 equiv. of **3d** in C_6D_6 was placed in a NMR tube, then sealed under vacuo and was heated at 130 °C for 30 h. Initially, no signal due to Rh(tmp)CH_3 was observed. Then, characteristic peak of Rh—CH_3 (doublet, $^2J_{Rh-H} = 3.0$ Hz, δ: −5.25 ppm) appeared after heating. Therefore, Rh(tmp)CH_3 was a true product of CCA. Furthermore, the formation of Rh(tmp)Bn further supported that CCA had occurred.

3. Summary

In conclusion, enolizable ketones underwent carbon—carbon bond and carbon hydrogen bond activation with Rh(tmp) with low selectivity to give Rh(tmp)CH_3 and Rh(tmp) acyl. Non-enolizable ketones underwent selective α-carbonyl CCA with Rh(tmp) to give Rh(tmp)CH_3 and Rh(tmp)Bn.

4. Experimental

All materials were obtained from commercial suppliers and used without further purification unless otherwise specified. Benzene was distilled from sodium. Benzene-d_6 was vacuum distilled from sodium, degassed thrice by freeze–thaw–pump cycle and store in a Teflon scrawhead stoppered flask. Pyridine was distilled over KOH under N_2. Triphenylphosphine was recrystallized from EtOH. Thin layer chromatography was performed on Merck pre-coated silica gel 60 F_{254} plates. Silica gel (Merck, 70–230 and 230–400 mesh) or neutral aluminum oxide (Merck, activity I, 70–230 mesh) was used for column chromatography.

^{1}H NMR spectra were recorded on a Brüker DPX 300 (300 MHz) spectrometer. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm), tetramethylsilane (TMS, δ 0.00 ppm), tetrakistrimethylsilysilane ((TMS)$_4$Si, δ 0.00 ppm) or with C_6D_6 (δ 7.15 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS or (TMS)$_4$Si.

4.1. Preparation of 5,10,15,20-tetramesitylporphyrinatorhodium(II) [Rh(tmp)] (2) [21]

To a Teflon screwheaded stoppered flask, Rh(tmp)CH_3 [21] (**1**) (10.0 mg, 0.011 mmol) was charged and dissolved in C_6H_6 (4.0 mL) to obtain a clear orange solution. The reaction mixture was then degassed by the freeze–pump–thaw method (3 cycles) and refilled with N_2. The reaction mixture was irradiated under a 400 W Hg-lamp at 6–10 °C until all the starting material was consumed as indicated by TLC (~8 h) to give Rh(tmp) (**2**).

4.2. Reaction of Rh(tmp) (2) and acetophenone (3a) under solvent-free conditions

Triphenylphosphine (0.1 mL, 0.01 mmol, 0.1 M in benzene) was added to the benzene solution of Rh(tmp) at r.t. The mixture was then stirred for 0.5 h, and subsequently the solvent was removed. Acetophenone (1.0 mL, 8.57 mmol) which was degassed by the freeze–pump–thaw method (3 cycles), was added via a micro-syringe to Rh(tmp) (0.0088 mmol) and the reaction mixture was stirred at 130 °C for 1 day under N_2 in the absence of light. A complex mixture of products were formed by TLC analysis. From the ^{1}H NMR spectrum of the crude reaction mixture, the methylene signal of the complex Rh(tmp)-$CH_2COC_6H_5$ (**4**) was observed as a doublet at −3.88 ppm ($J = 4.2$ Hz). Other signals could not be assigned due to overlapping peaks. The compound was unstable towards chromatography for purification. HRMS (FAB) verified the formation of Rh(tmp)$CH_2COC_6H_5$. HRMS (FAB): Calcd. for $(C_{64}H_{59}N_4ORh)^+$: *m/z* 1002.3738. Found: *m/z* 1002.3696.

4.3. Reaction of Rh(tmp) (2) and propiophenone (3b) under solvent-free conditions

Triphenylphosphine (0.1 mL, 0.01 mmol, 0.1 M in benzene) was added to the solution of Rh(tmp) at r.t. The mixture was stirred for 0.5 h, then the solvent was removed. Propiophenone (1.0 mL, 6.94 mmol) which was degassed by the freeze–pump–thaw method (3 cycles) was added via a micro-syringe to Rh(tmp) (0.0088 mmol) and the reaction mixture was stirred at 130 °C for 1 day under N_2 in the absence of light. The crude product was purified by chromatography on silica gel using a solvent mixture hexane:CH_2Cl_2 (10:1) to hexane:CH_2Cl_2 (1:1) as the gradient eluent. Red solids of Rh(tmp)CH_3 (**1**) (0.2 mg, 0.0003 mmol, 3%) $R_f = 0.57$ (hexane:$CH_2Cl_2 = 5$:1); ^{1}H NMR (C_6D_6, 300 MHz) δ −5.26 (d, 3H, $^2J_{RhH} = 2.7$ Hz), 1.72 (s, 12H), 2.25 (s, 12H), 2.43(s, 12H), 7.07 (s, 4H), 7.20 (s, 4H), 8.75 (s, 8H), and Rh(tmp)$CH_2CH_2COC_6H_5$ (**5**) (2.3 mg, 0.0023 mmol, 26%) were obtained. $R_f = 0.45$ (hexane:$CH_2Cl_2 = 1$:1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ −4.63 (td, 2H, $J_1 = 9.6$ Hz, $J_{Rh-H} = 3.0$ Hz), −2.85 (t, 2H, $J = 9.6$ Hz), 2.01 (s, 12H), 2.04 (s, 12H), 2.61 (s, 12H), 5.75 (d, 2H, $J = 7.6$ Hz), 6.75 (t, 2H, $J = 7.9$ Hz), 7.03 (t, 1H, $J = 7.7$ Hz), 7.21 (s, 8H), 8.63 (s, 8H). HRMS (FAB): Calcd. for $(C_{65}H_{61}N_4ORh)^+$: *m/z* 1016.3895. Found: *m/z* 1016.3924. IR (KBr, cm^{-1}) ν(C=O) 1600. Some unidentified products were observed.

4.4. Reaction of Rh(tmp) (2) and diethyl ketone (3c) under solvent-free conditions

Triphenylphosphine (0.1 mL, 0.01 mmol, 0.1 M in benzene) was added to the solution of Rh(tmp) at r.t. The mixture was stirred for 0.5 h, then the solvent was removed. Diethyl ketone (1.0 mL, 9.46 mmol) which was degassed by the freeze–pump–thaw method (3 cycles) was added via a micro-syringe to Rh(tmp) (0.0088 mmol) and the reaction mixture was stirred at 100 °C for 2 days under N_2 in the absence of light. The crude product was purified by chromatography on silica gel using a solvent mixture hexane:CH_2Cl_2 (10:1) to hexane:CH_2Cl_2 (3:1) as the gradient eluent. Red solids of Rh(tmp)CH_3 (**1**) (0.5 mg, 0.0006 mmol, 6%), and Rh(tmp)$COCH_2CH_3$ (**6**) (0.9 mg, 0.0009 mmol, 11%) were obtained; $R_f = 0.14$ (hexane:$CH_2Cl_2 = 5$:1); ^{1}H NMR (C_6D_6, 300 MHz) δ −2.73 (q, 3H, $J_1 = 7.5$ Hz, $J_2 = 7.2$ Hz), −1.53 (t, 3H, $J = 7.2$ Hz), 1.84 (s, 12H), 2.14 (s, 12H), 2.44 (s, 12H), 7.09 (s, 4H), 7.19 (s, 4H), 8.79 (s, 8H). HRMS (FAB): Calcd. for $(C_{59}H_{57}N_4ORh)^+$: *m/z* 940.5123. Found: *m/z* 940.5130. IR (KBr, cm^{-1}) ν(C=O) 1600. Another orange solid of Rh(tmp)$CH_2CH_2COCH_2CH_3$ (**7**) (2.8 mg, 0.0029 mmol, 33%) was produced. $R_f = 0.42$ (hexane:$CH_2Cl_2 = 1$:1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ −4.74 (td, 2H, $J = 7.5$ Hz, $J_{Rh-H} = 3.0$ Hz), −3.35 (t, 2H, $J = 9.0$ Hz), −0.15 (t, 3H, $J = 7.5$ Hz), 0.40 (q, 2H, $J = 7.5$ Hz), 2.04 (s, 24H), 2.61 (s, 12H), 8.50 (s, 8H). HRMS (FAB): Calcd. for $(C_{61}H_{61}N_4ORh)^+$: *m/z* 968.3895. Found: *m/z* 968.3883. IR (KBr, cm^{-1}) ν(C=O) 1600. Some unidentified products were observed.

4.5. Reactions of [Rh(tmp)] (2) and ketones 3d–3k with Ph_3P added

Triphenylphosphine (0.1 mL, 0.01 mmol, 0.1 M in C_6H_6, 1 equiv.) solution (2 μL, 0.02 mmol, 2 equiv.) was added to the solution of [Rh(tmp)] (**2**) at r.t. Degassed ketone solution (5 equiv.) in benzene was then added, and the mixture was heated at 130 °C under N_2 in the absence of light. Pure products were obtained after purification on silica gel column chromatography.

4.6. Reaction of Rh(tmp) (2) and 2,2-dibenzyl-indan-1,3-dione (3l) with Ph_3P added

Triphenylphosphine (0.1 mL, 0.01 mmol, 0.1 M in benzene) was added to the solution of Rh(tmp) at r.t.. Degassed (**3i**) solution (5 equiv.) in benzene was then added, and the mixture was heated at 130 °C for 3 days under N_2 in the absence of light. The crude product was purified by chromatography on silica gel to give a red solid of Rh(tmp)Bn (**10**) (0.5 mg, 0.0005 mmol, 6%). $R_f = 0.54$ (hexane:$CH_2Cl_2 = 5$:1); ^{1}H NMR (300 MHz, C_6D_6) δ −3.15 (d, 2H, $J = 3.9$ Hz), 1.79 (s, 12H), 1.93 (s, 12H), 2.45 (s, 12H), 3.66 (d, 2H, $J = 7.2$ Hz), 5.76 (t, 2H, $J = 7.8$ Hz), 6.22 (t, 1H, $J = 7.8$ Hz), 8.80 (s, 8H). ^{13}C NMR (C_6D_6, 75 MHz) 14.29, 21.93, 22.45, 22.80, 120.00, 123.56, 125.44, 126.66, 127.80, 127.86, 130.82, 137.53, 138.58, 138.73, 139.57, 142.76. HRMS (FAB): Calcd. for $(C_{63}H_{59}N_4Rh)^+$: *m/z* 974.3789. Found: *m/z* 974.3806.

4.7. Reactions of [Rh(tmp)] (2) and ketones 3d with pyridine added

Pyridine (2 μL, 0.02 mmol, 2 equiv.) was added to the solution of [Rh(tmp)] (**2**) at r.t. Degassed ketone solution (5 equiv.) in benzene was added to the adduct solution, and the mixture was heated at 130 °C under N_2 in the absence of light. The crude product was purified by chromatography on silica gel to give Rh(tmp)CH3 (1.7 mg, 1.9 μmol, 22%).

4.8. Sealed NMR tube experiment

Triphenylphosphine (0.01 mL, 0.001 mmol, 0.1 M in C_6D_6, 1 equiv.) was added to the solution of [Rh(tmp)] (**2**) in a NMR tube at r.t. Degassed ketone solution (10 equiv.) in C_6D_6 was then added, then the NMR tube was Hame-sealed under vacuum. The initial ^1H NMR spectrum was taken. No $Rh(tmp)CH_3$ was observed. After the mixture was heated at 130 °C for 30 h under N_2 in the absence of light. $Rh(tmp)CH_3$ signal was observed.

Acknowledgment

We thank the Research Grants Council of Hong Kong of the SAR of China for financial support (No. 400203).

References

[1] (a) R.H. Crabtree, Chem. Rev. 95 (1995) 987;
(b) R.H. Crabtree, Chem. Rev. 85 (1985) 245.
[2] W.D. Jones, Nature 364 (1993) 676.
[3] B.A. Arndtsen, R.G. Bergman, T.H. Mobley, Acc. Chem. Res. 28 (1995) 154.
[4] J.G. Speight, The Chemistry and Technology of Petroleum, third ed., Marcel Dekker, New York, 1998.
[5] V. Dufaud, J.-M. Basset, Angew. Chem., Int. Ed. 37 (1998) 1433.
[6] K. Zengler, H.H. Richnow, R. Rossello-Mora, W. Michaelis, F. Widdel, Nature 401 (1999) 266.
[7] (a) L. Cassar, P.E. Eaton, J. Halpern, J. Am. Chem. Soc. Chem. 92 (1970) 3515;
(b) L. Cassar, P.E. Eaton, J. Halpern, J. Am. Chem. Soc. 92 (1970) 6366.
[8] C. Perthuisot, B.L. Edelbach, D.L. Zubris, W.D. Jones, Organometallics 16 (1997) 2016.
[9] Z. Lu, C.-H. Jun, S.R. de Gala, M. Sigalas, O. Eisenstein, R.H. Crabtree, J. Chem. Soc., Chem. Commun. (1993) 1877.
[10] R.C. Hemond, R.P. Hughes, H.B. Locker, Organometallics 5 (1986) 2391.
[11] W.D. Jones, J.A. Maguire, Organometallics 6 (1987) 1301.
[12] (a) M. Murakami, H. Amii, Y. Ito, Nature 370 (1994) 541;
(b) M. Murakami, T. Tsuruta, Y. Ito, Angew. Chem., Int. Ed. 39 (2000) 2484.
[13] (a) C.-H. Jun, Chem. Soc. Rev. 33 (2004) 610;
(b) C.-H. Jun, C.W. Moon, D.-Y. Lee, Chem. Eur. J. 8 (2002) 2422;
(c) D.-H. Chang, D.-Y. Lee, B.-S. Hong, J.-H. Choi, C.-H. Jun, J. Am. Chem. Soc. 126 (2004) 424.
[14] (a) B. Rybtchinski, A. Vigalok, Y. Ben-David, D. Milstein, J. Am. Chem. Soc. 118 (1999) 12406;
(b) B. Rybtchinski, S. Oevers, M. Montag, A. Vigalok, H. Rozenberg, J.M.L. Martin, D. Milstein, J. Am. Chem. Soc. 123 (2001) 9064.
[15] B. Rybtchinski, D. Milstein, Angew. Chem., Int. Ed. 38 (1999) 871.
[16] R.H. Crabtree, R.P. Dion, D.J. Gibboni, D.V. McGrath, E.M. Holt, J. Am. Chem. Soc. 108 (1986) 7222.
[17] K. McNeill, R.A. Andersen, R.G. Bergman, J. Am. Chem. Soc. 119 (1997) 11244.
[18] M.K. Tse, K.S. Chan, J. Chem. Soc., Dalton Trans. (2001) 510.
[19] J.W. Suggs, C.-H. Jun, J. Chem. Soc., Chem. Commun. (1985) 92.
[20] N. Chatanik, Y. Ie, F. Kakiuchi, S. Murai, J. Am. Chem. Soc. 121 (1999) 8645.
[21] B.B. Wayland, A.E. Sherry, G. Poszmik, A.G. Bunn, J. Am. Chem. Soc. 114 (1992) 1673.
[22] Y.-R. Luo, Handbook of Bond Dissociation Energies in Organic Compounds, CRC Press, Boca Raton, FL, 2003.
[23] K.J. Kulicke, C. Chatgilialoglu, B. Kopping, B. Giese, Helv. Chim. Acta 75 (1992) 935.
[24] M.D. Johnson, Acc. Chem. Res. 16 (1983) 343.
[25] R. Del, J. Kenneth, X.-X. Zhang, B.B. Wayland, J. Organomet. Chem. 504 (1995) 47.
[26] I. Artavd, G. Torossian, P. Viout, Tetrahedron 21 (1985) 5031.
[27] A. Chardhary, L. Baumstark, Synthesis 9 (1989) 688.
[28] A. Waldemar, H. Thomas, S. Coskun, Synthesis 9 (1995) 1163.
[29] A.S. Kende, K. Koch, C.A. Smith, J. Am. Chem. Soc. 110 (1988) 2210.
[30] P. Maslask, S. Varadarajan, J. Org. Chem. 64 (1999) 8201.
[31] B.B. Wayland, A.E. Sherry, A.G. Bunn, J. Am. Chem. Soc. 115 (1993) 7675.
[32] (a) T. Nishimura, H. Araki, Y. Maeda, S. Uemura, Org. Lett. 5 (2003) 2997;
(b) T. Nishimura, K. Ohe, S. Uemura, J. Am. Chem. Soc. 121 (1999) 2645.
[33] R.A. Periana, R.G. Bergman, J. Am. Chem. Soc. 106 (1984) 7272.
[34] (a) A.G. Davis, B.P. Robers, in: J.K. Kochi (Ed.), Free Radicals, vol. 2, Wiley, New York, 1973;
(b) J. Fossey, D. Lefort, J. Sorba, Free Radicals in Organic Chemistry, Wiley, New York, 1995.