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Reactivity Studies of Rhodium(III) Porphyrins with Methanol in Alkaline Media

Hong Sang Fung, Yun Wai Chan, Chi Wai Cheung, Kwong Shing Choi, Siu Yin Lee, Ying Ying Qian, and Kin Shing Chan*

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

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Rh(ttp)Cl (**1a**) (ttp = 5,10,15,20-tetrakistolylporphyrinato dianion) was found to react with methanol at a high temperature of 150 °C in the presence of inorganic bases to give a high yield of $Rh(ttp)CH_3$ (**2a**), up to 87%. Rh(ttp)H (**1d**) is suggested to be the key intermediate for the carbon−oxygen bond cleavage.

Introduction

The efficient, catalytic, and selective conversion of methane into methanol provides an attractive alternative energy source to diminishing oil and gas resources.[1] In the catalysis, besides the efficient activation of the inert carbon−hydrogen bond, one of the key difficulties is the selective formation of methanol without formaldehyde and other overoxidation products, posing stringent requirements on the catalyst and reaction conditions.

Transition metal complexes play important roles in catalytic methane oxidation. In nature, methane monooxygenanse[2] and cytochrome P450[2,3] are known to catalyze hydroxylation of alkanes. Artificially, Shilov et al. in the 1960s reported catalytic methane oxidation by $[PtCl_4]^{2-}$.[4] In the 1990s, Periana et al. further modified the platinum system to afford high yields of CH_3OSO_3H, but required high concentrations of H_2SO_4 and a high temperature of 200 °C.[5] As a biomimetic system, metalloporphyrins were found to catalyze the hydroxylation of various organic compounds.[6] The first example was reported by Groves et al. on the alkane hydroxylation by iron(III) porphyrin systems using iodosylbenzene as an oxygen source at room temperature in the late 1970s.[7] In the late transition metalloporphyrin system, Rh^{II}(por) was found to activate the carbon−hydrogen bond of methane under ambient conditions.[8] Using more stable Rh^{III}(por) complexes, we previously discovered that benzylic carbon hydrogen bonds of toluenes were activated at 120 °C under basic media.[9]

However, the alkane oxidation product alcohol is usually more reactive than alkane.[10] Transition metal complexes are well known to react with alcohols in both a stoichiometric and catalytic manner. $[Cp^*IrCl_2]_2$ and $[Cp^*RhCl_2]_2$ were found to oxidize benzyl alcohols in the presence of K_2CO_3 at room temperature in a catalytic manner.[11] $(Me_4N)[Co(L)]\cdot nH_2O$ (where L = *o*-phenylenebis(*N*′-methyloxamidate) (Me_2opba (n = 2)), *o*-phenylene(*N*′-methyloxamidate)oxamate (Meopba (n = 3)), and *o*-phenylenebis(oxamate) (opba (n = 4))) also catalyzed the oxidation of α-alkylbenzyl alcohols in the presence of oxygen and aldehyde at room temperature.[12] At an elevated temperature, rhodium trichloride reacted with refluxing *n*-propanol to generate rhodium hydride to catalyze the isomerization of *N*-allyl amides to corresponding enamides.[13] Saito et al. reported the formation of ketones and dihydrogen from the photolytic reaction of cyclohexanol or isopropanol with rhodium porphyrin chloride at refluxing conditions under irradiation using a 500 W xenon lamp (λ > 360 nm) in the 1980s[14] and with a trace amount of rhodium alkyls as byproduct observed in alkaline medium under similar conditions.[15] Wayland et al. recently reported the chemistry between rhodium(II) porphyrin and methanol to form $Rh(por)OCH_3$ and Rh(por)H.[16]

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

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We have been interested in the carbon−hydrogen bond activation chemistry with rhodium porphyrins.[9,17,20] Recently, we have observed the base-promoted benzylic carbon−hydrogen bond activation by Rh(por)Cl (por = porphyrinato dianion).[9] We here define the reaction conditions under which methanol can react with rhodium porphyrin complexes in H−CH_2OH, H−OCH_3, and CH_3−OH cleavage reactions to aid the further design of reaction conditions and catalysts for catalytic methane oxidation. Herein, we report that Rh(ttp)Cl reacts with methanol in the presence of inorganic bases at a high temperature of 150 °C to give Rh(ttp)CH_3 as a result of both carbon−hydrogen and carbon−oxygen cleavage.

Results and Discussion

Base Effects. Initially, when Rh(ttp)Cl (**1a**) (ttp = 5,10,15,20-tetrakistolylporphyrinato dianion) was heated in methanol at 150 °C for 4 days, only lower yields of Rh(ttp)CH_3 (**2a**) (carbon−oxygen bond cleavage) and Rh(ttp)CH_2OCH_3 (**3**) (carbon−hyrogen/oxygen−hydrogen bond cleavage) were isolated, in 7% and 5% yield, respectively (eq 1, Table 1, entry 1). We sought to enhance the product yield and selectivity by examining the promoting effect of base.[9] The reactions were then examined at 150 °C with 10 equiv of base added. The organic base, 2,2′-bipyridyl, was not effective with Rh(ttp)CH_3 and Rh(ttp)CH_2OCH_3; both formed in only 2% yield (Table 1, entry 2). To our delight, various inorganic bases used are beneficial, with Rh(ttp)CH_3 produced in higher yields, from 45% to 87% (Table 1, entries 3−11). Regardless of the inorganic bases used, Rh(ttp)Cl was consumed within 1 h with only a small amount of Rh(ttp)CH_3 observed. The carbon−oxygen bond cleavage is therefore likely the slowest reaction step. Stronger bases such as KOH and NaOH gave only 45% and 61% yields of Rh(ttp)CH_3, respectively (Table 1, entries 3 and 4). Rh(ttp)CH_3 was obtained in higher yields with weaker bases of K_2CO_3 and NaOAc (Table 1, entries 5−11). Strong bases likely cause the decomposition of rhodium porphyrin intermediates.[25d] Rh(ttp)CH_2OCH_3 usually formed in a trace amount when a weak base was used. Therefore, K_2CO_3 was chosen to be the optimal base since it gave the highest yield of Rh(ttp)CH_3 with a better selectivity.

Effects of Base Loadings. The optimization of K_2CO_3 loading in the reaction of Rh(ttp)Cl with methanol was carried out at 150 °C (eq 2, Table 2). Higher loadings of K_2CO_3 (20 and 30 equiv) gave lower yields of Rh(ttp)CH_3 of 43% and 36%, respectively (Table 2, entries 3 and 4). Alternatively, a lower loading of K_2CO_3 (5 equiv) gave a slightly lower yield of Rh(ttp)CH_3 of 80% together with a trace amount of Rh(ttp)CH_2OCH_3 (Table 2, entry 1). Therefore, the optimized amount of K_2CO_3 was found to be 10 equiv (Table 2, entry 2).

Temperature and Time Effects. We then examined the temperature effect on the reaction (eq 3, Table 3). At lower reaction temperatures of 80 and 120 °C, lower product yields of Rh(ttp)CH_3 of 6% and 47%, respectively, together with a trace amount of Rh(ttp)CH_2OCH_3 (Table 3, entries 1 and 2) were obtained. It was observed that Rh(ttp)Cl was consumed rapidly even at 80 °C after 1 h without any Rh(ttp)CH_3 observed. Likely, Rh(ttp)Cl reacts rapidly to give an intermediate, which then reacts with methanol to produce Rh(ttp)CH_3 in a slower step. A high temperature of 150 °C was required for a high yield of Rh(ttp)CH_3. Furthermore, the reaction required 1 day at 150 °C for completeness, as in half a day, only 56% yield of Rh(ttp)CH_3 was obtained (Table 3, entries 3 and 4).

Therefore, the optimal conditions for carbon−oxygen bond cleavage of methanol by Rh(ttp)Cl was found to be 150 °C in the presence of 10 equiv of K_2CO_3 for 1 day and 87% yield of Rh(ttp)CH_3 was obtained (eq 4).

$$\underset{\mathbf{1a}}{\text{Rh(ttp)Cl}} + \text{CH}_3\text{OH} \xrightarrow[\text{N}_2,\ 150^\circ\text{C},\ 1\text{ d}]{10\text{ equiv }\text{K}_2\text{CO}_3} \underset{87\%\ \mathbf{2a}}{\text{Rh(ttp)CH}_3} \quad (4)$$

Porphyrin Effects. By installing different aryls at the meso-positions, we sought to study the effects of porphyrin ligands

Table 1. Base Effects on the Reaction of Rh(ttp)Cl with MeOH

$$\underset{\mathbf{1a}}{\text{Rh(ttp)Cl}} + \text{CH}_3\text{OH} \xrightarrow[\text{N}_2,\ 150^\circ\text{C},\ 1\text{ d}]{10\text{ equiv base}} \underset{\mathbf{2a}}{\text{Rh(ttp)CH}_3} + \underset{\mathbf{3}}{\text{Rh(ttp)CH}_2\text{OCH}_3} \quad (1)$$

entry	base	time/days	**2a** yield/%[a]	**3** yield/%[a]
1	none	4	7	5
2	bpy	4	2	2
3	KOH	1	45	none[b]
4	NaOH	1	61	none
5	Cs_2CO_3	1	51	none
6	K_2CO_3	1	87	none
7	Na_2CO_3	1	77	6
8	$KHCO_3$	1	61	trace[b]
9	K_3PO_4	1	67	none
10	KOAc	1	84	none
11	NaOAc	1	87	6

[a] Isolated yield. [b] Less than 1% by NMR yield.

Table 2. Effects of Base Loading on the Reaction of Rh(ttp)Cl with MeOH

$$\underset{\mathbf{1a}}{\text{Rh(ttp)Cl}} + \text{CH}_3\text{OH} \xrightarrow[\text{N}_2,\ 150^\circ\text{C},\ 1\text{ d}]{\text{K}_2\text{CO}_3\text{ equiv}} \underset{\mathbf{2a}}{\text{Rh(ttp)CH}_3} \quad (2)$$

entry	K_2CO_3 equiv	**2a** yield/%[a]
1	5	80[b]
2	10	87
3	20	43
4	30	36

[a] Isolated yield. [b] With trace of Rh(ttp)CH_2OCH_3.

Table 3. Temperature and Time Effects on the Reaction of Rh(ttp)Cl with MeOH

$$\underset{\mathbf{1a}}{\text{Rh(ttp)Cl}} + \text{CH}_3\text{OH} \xrightarrow[\text{N}_2,\ \text{temp},\ \text{time}]{10\text{ equiv }\text{K}_2\text{CO}_3} \underset{\mathbf{2a}}{\text{Rh(ttp)CH}_3} + \underset{\mathbf{3}}{\text{Rh(ttp)CH}_2\text{OCH}_3} \quad (3)$$

entry	temp/°C	time/days	**2a** yield/%[a]	**3** yield/%[a]
1	80	5	6	trace[b]
2	120	3	47	trace[b]
3	150	0.5	56	none
4	150	1	87	none

[a] Isolated yield. [b] Less than 1% by NMR.

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Table 4. Porphyrin Effects on the Reaction of Rh(por)Cl with MeOH

$$\underset{\textbf{1a-c}}{\text{Rh(por)Cl}} + \text{CH}_3\text{OH} \xrightarrow[\text{N}_2,\ 150\ ^\circ\text{C},\ 1\ \text{d}]{10\ \text{equiv}\ \text{K}_2\text{CO}_3} \underset{\textbf{2a-c}}{\text{Rh(por)CH}_3} \quad (5)$$

entry	por	**2a**−**c** yield/%[a]
1	ttp	**2a** 87
2	tpp	**2b** 52
3	tmp	**2c** 69

[a] Isolated yield.

on the carbon−oxygen bond cleavage of methanol (eq 5, Table 4). There was a slight difference in product yields in the reactions of methanol with Rh(tpp)Cl (**1b**) (tpp = 5,10,15,20-tetrakisphenylporphyrinato dianion), Rh(ttp)Cl, or Rh(tmp)Cl (**1c**) (tmp = 5,10,15,20-tetrakismesitylporphyrinato dianion). The less electron-rich Rh(tpp)Cl and the more bulky Rh(tmp)Cl reacted slightly less efficiently to give Rh(tpp)CH_3 (**2b**) in 52% yield (Table 4, entry 2) and Rh(tmp)CH_3 (**2c**) in 69% yield, respectively (Table 4, entry 3).

These new convenient syntheses of Rh(por)CH_3 employ cheap methanol as the methylating agent without the use of expensive and toxic iodomethane. In contrast, the conventional syntheses of rhodium porphyrin methyls were carried out by the reduction of Rh(por)Cl (por = porphyrinato dianion) with $NaBH_4$ followed by methylation with iodomethane.[18] Rh(ttp)CD_3 (**2a**−d_3) was also easily accessible in 91% yield from methanol-d_4 (eq 6).

$$\underset{\textbf{1a}}{\text{Rh(ttp)Cl}} + \text{CD}_3\text{OD} \xrightarrow[\text{N}_2,\ 150\ ^\circ\text{C},\ 1\ \text{d}]{10\ \text{equiv}\ \text{K}_2\text{CO}_3} \underset{\textbf{2a-}d_3\ 91\%}{\text{Rh(ttp)CD}_3} \quad (6)$$

Figures 1 and 2 show the X-ray structures of Rh(ttp)CH_2OCH_3 and Rh(ttp)CD_3. Table 5 lists some selected bond lengths and maximum deviations of the core atoms and rhodium from the 24-atom least-squares plane of Rh(ttp)CH_2OCH_3 and Rh(ttp)CD_3. The Rh−C_α bond lengths of Rh(ttp)CH_2OCH_3 and Rh(ttp)CD_3 are 2.059(16) and 2.022 (7) Å, respectively (Table 5, entries 1 and 2), which are similar to the reported Rh−C_α bond length (2.031(6) Å) of Rh(oep)CH_3 (oep = 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion)[19] (Table 5, entry 3). The average Rh−N bond lengths in Rh(ttp)CH_2OCH_3 and Rh(ttp)CD_3 do not have any significant difference, which are 2.021 and 2.029 Å, respectively (Table 5, entries 1 and 2). On the other hand, the more bulky axial ligand −CH_2OCH_3 likely forces the porphyrin to adopt a geometry with a smaller out-of-plane distance (Table 5, entries 1 and 2).

Mechanistic Studies

Mechanism. Scheme 1 illustrates the proposed mechanism of carbon−oxygen bond cleavage of methanol with Rh(ttp)Cl.

No Base. In the absence of base, Rh(ttp)Cl likely undergoes heterolysis to form $Rh(ttp)^+$ and Cl^-.[9,20] The rhodium center is then coordinated with methanol, and after the abstraction of a proton by chloride anion, Rh(ttp)OCH_3 is produced (Scheme 1, pathway Ia). Rh(ttp)OCH_3 is then converted to Rh(ttp)H and formaldehyde via β-hydride elimination (Scheme 1, pathway IIa).[21] Rh(ttp)H cleaves the carbon−oxygen bond of methanol to give Rh(ttp)CH_3 (Scheme 1, pathway III, and Table 7, entry 3). The intermediate Rh(ttp)OCH_3 can also undergo isomerization to give Rh(ttp)CH_2OH (Scheme 1, pathways IIa and IV). The isomerization of Rh(ttp)OCH_3 to Rh(ttp)CH_2OH through β-hydride elimination and subsequent reinsertion is reported.[16,22,23] We did not observe the formation of Rh(ttp)CH_2OH from Rh(ttp)OCH_3, but the insertion of Rh(ttp)H to formaldehyde (paraformaldehyde as a precursor) to give Rh(ttp)CH_2OH was observed (Scheme 1, pathway IV, and eq 7). This insertion process under dihydrogen has been reported by Wayland et al.[23]

$$\text{Rh(ttp)H} + \underset{10\ \text{equiv}}{(\text{HCHO})_n} \xrightarrow[\text{C}_6\text{D}_6]{\text{rt},\ 5\ \text{min}} \underset{\text{quantitative}}{\text{Rh(ttp)CH}_2\text{OH}} \quad (7)$$

Rh(ttp)CH_2OH formation through intermolecular carbon−hydrogen bond activation of methanol by Rh(ttp)H is also possible, which further condenses with methanol to yield Rh(ttp)CH_2OCH_3 (Scheme 1, pathway V). We have attempted to illustrate the condensation of Rh(ttp)CH_2OH with methanol. The reaction gave Rh(ttp)CH_3 in 94% yield with a trace amount of Rh(ttp)CH_2OCH_3 at 150 °C (eq 8). The unexpected result was probably due to the formation of Rh(ttp)H from Rh(ttp)CH_2OH through β-hydride elimination with subsequent carbon−oxygen bond cleavage of methanol. Nonetheless, a similar ether condensation of two Rh(tpp)CH_2OH to give (Rh(tpp)CH_2)$_2$O in benzene was reported by Wayland et al.[23] In excess methanol, it is believed that Rh(ttp)CH_2OH condenses with methanol rather than undergoing self-condensation.

$$\text{Rh(ttp)CH}_2\text{OH} + \text{CH}_3\text{OH} \xrightarrow[\text{N}_2,\ 1\ \text{d}]{150\ ^\circ\text{C}} \underset{\substack{94\%\\ \textbf{2a}}}{\text{Rh(ttp)CH}_3} + \underset{\substack{\text{trace}\\ \textbf{3}}}{\text{Rh(ttp)CH}_2\text{OCH}_3} \quad (8)$$

. **Base-Promoted.** In the presence of a base, Rh(ttp)Cl first undergoes ligand substitution with X (X = OH and CO_3K, etc.) (Scheme 1, pathway Ib). The ligand substitution of Rh(ttp)Cl with base has been reported previously,[24,25d] and we proposed that it is the same case in methanol. For X = OH, transition metal hydroxides have been reported to be reactive in bond activation.[25] Rh(ttp)X reacts with

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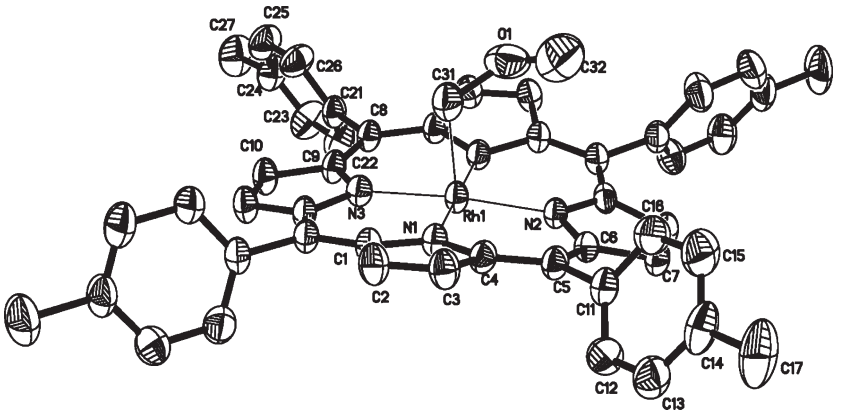

Figure 1. ORTEP presentation of the molecular structure with numbering scheme for Rh(ttp)CH_2OCH_3 (**3**) with solvent molecules omitted for clarity (30% probability displacement ellipsoids).

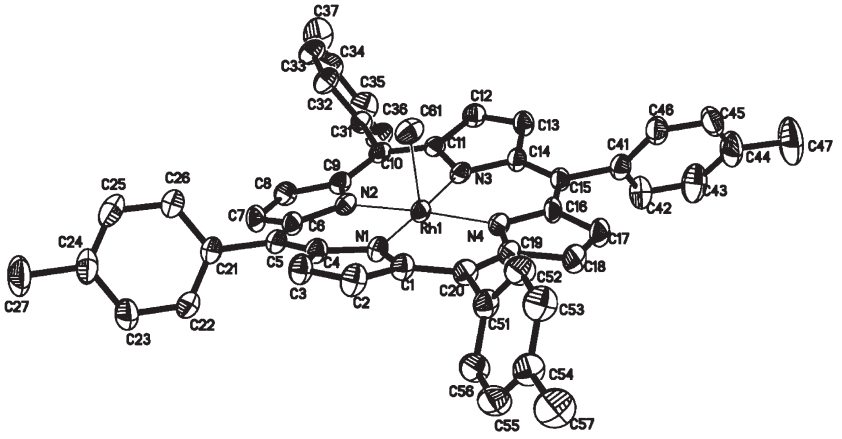

Figure 2. ORTEP presentation of the molecular structure with numbering scheme for Rh(ttp)CD_3 (**2a**-d_3) with solvent molecules omitted for clarity (30% probability displacement ellipsoids).

Table 5. Selected Bond Lengths (Å) and Max. Deviation of Rh(ttp)CD_3 and Rh(ttp)CH_2OCH_3

entry	Rh(ttp)R	Rh−C length (Å)	max. deviation from the least-squares plane (Å)	Rh−N_{av} (Å)
1	Rh(ttp)CD_3 (**2a**-d_3)	2.022(7)	0.495(6)	2.029
2	Rh(ttp)CH_2OCH_3 (**3**)	2.059(16)	0.335(7)	2.021
3	Rh(oep)CH_3[19]	2.031(6)		

CH_3O-H to give Rh(ttp)OCH_3. Deprotonation of the coordinated methanol by a base provides an alternative pathway to Rh(ttp)OCH_3. Rh(ttp)OCH_3 then converts to Rh(ttp)H and formaldehyde through β-proton elimination/protonation[21] (Scheme 1, pathway IIb). Rh(ttp)H once formed cleaves the carbon−oxygen bond of methanol to give Rh(ttp)CH_3 (Scheme 1, pathway III, and Table 7, entry 3) and in a minor pathway inserts to formaldehyde to give Rh(ttp)CH_2OH[23] (Scheme 1, pathway IV). Rh(ttp)CH_2OCH_3 is finally formed from the condensation of Rh(ttp)CH_2OH with methanol[23] (Scheme 1, pathway V). The addition of base significantly enhances the reaction rate and yield, probably the base-promoted formation of Rh(ttp)OCH_3 (Scheme 1, pathway Ib) and Rh(ttp)H (Scheme 1, pathway IIb).

However, low yields of Rh(ttp)CH_2OCH_3 were obtained in most studies (Tables 1, 2, and 3). Probably, Rh(ttp)CH_2OH, as a precursor for the Rh(ttp)CH_2OCH_3 formation, converts more competitively back to Rh(ttp)H.[23] Furthermore, Rh(ttp)CH_2OCH_3 was found to be unstable at 150 °C in methanol in the presence of 10 equiv of K_2CO_3 to give a 84% yield of Rh(ttp)$^-$ and a 10% yield of Rh(ttp)CH_2OCH_3 after 36 h, respectively (eq 9, Table 6, entry 1). Likely, Rh(ttp)CH_2OCH_3 is converted to Rh(ttp)$^-$ slowly in the presence of a nucleophilic base in the polar methanol by nucleophilic substitution at the α-carbon (Scheme 2, pathway VIII).[26] This observation agrees with the absence of Rh(ttp)CH_2OCH_3 under strongly basic media. The Rh(ttp)$^-$ formed is then reprotonated to give Rh(ttp)H[27] (Scheme 2, pathway VI) for further reactions. It is worth noting that the nucleophilic attack of Rh(ttp)CH_2OCH_3 (36 h) is slower than the formation of Rh(ttp)CH_3 (24 h). Therefore, Rh(ttp)CH_2OCH_3 is not a major productive intermediate for Rh(ttp)CH_3. However, the nucleophilic attack requires both base and polar solvent. Rh(ttp)CH_2OCH_3 was found thermally stable in benzene-d_6 with 10 equiv of K_2CO_3 and in methanol-d_4 without base (Table 6, entries 2 and 3).

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Scheme 1. Proposed Mechanism of the Reaction of MeOH with Rh(ttp)Cl

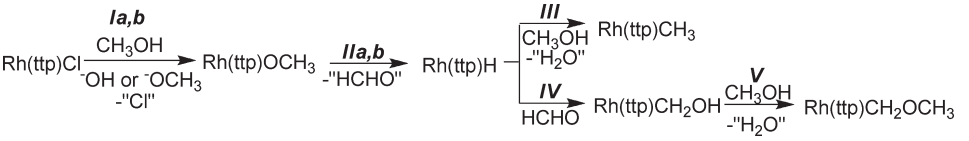


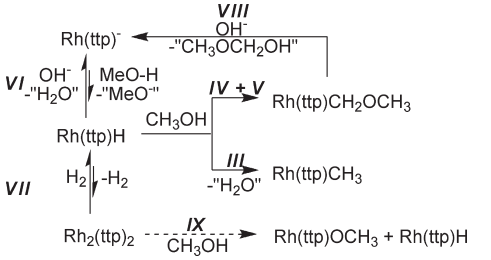
Table 6. Thermal Stability of $Rh(ttp)CH_2OCH_3$ in C_6D_6 and CD_3OD

$$\underset{\textbf{2b}}{Rh(ttp)CH_2OCH_3} \xrightarrow[150\ ^\circ C,\ time]{K_2CO_3\ equiv} Rh(ttp)R \qquad (9)$$

entry	solvent	K_2CO_3 equiv	time	Rh(ttp)R(% yield[a])
1	CD_3OD	10	36 h	$Rh(ttp)^-$ (84);$Rh(ttp)CH_2OCH_3$ (10)
2	CD_3OD	0	20 d	$Rh(ttp)^-$ (trace);$Rh(ttp)CH_2OCH_3$ (77)
3	C_6D_6	10	19 d	$Rh(ttp)CH_2OCH_3$ (100)

[a] Estimated by ^1H NMR spectroscopy.

Scheme 2. Equilibrium between Rh(I), Rh(II), and Rh(III)



Although Rh(ttp)H is known to equilibrate with $Rh(ttp)^-$ and $Rh_2(ttp)_2$ (Scheme 2, pathways VI and VII),[23,27] only Rh(ttp)H plays a role of the active intermediate that directly cleaves the carbon−oxygen bond of methanol, as further supporting experiments shown below disfavor other possibilities.

Reaction with $Rh(ttp)^-$ Anion. Indeed, $Rh(ttp)^-$ was observed as a major intermediate when the reaction sequence of methanol with Rh(ttp)Cl in the presence of K_2CO_3 (10 equiv) at 150 °C was monitored by ^1H NMR spectroscopy in the course of 2 days (eq 10). The β-pyrrole signals are very diagnostic of the rhodium porphyrin species. Initially, Rh(ttp)Cl (**1a**) ($\delta = 8.72$ ppm) was transformed to $Rh(ttp)^-$ anion (**1f**) ($\delta = 8.05$ ppm) at 40 °C in 1 h in approximately 81% yield. The intensity of the β-pyrrole signal corresponding to $Rh(ttp)^-$ decreased gradually upon further heating the mixture at 150 °C for 2 days. Since $Rh(ttp)CD_3$ was sparingly soluble in methanol-d_4, it could not be accurately monitored by ^1H NMR spectroscopy. However, upon workup and purification by column chromatography, a 94% yield of $Rh(ttp)CD_3$ was isolated.

$$\underset{\textbf{1a}}{Rh(ttp)Cl} \xrightarrow[40\ ^\circ C,\ CD_3OD,\ 1\ h]{10\ equiv\ K_2CO_3} \underset{\sim 81\%}{Rh(ttp)^-}$$
$$+\ \underset{\sim 6\%}{Rh(ttp)Cl} \xrightarrow[150^\circ C,\ CD_3OD,\ 2\ d]{10\ equiv\ K_2CO_3} \underset{94\%\ \textbf{2a}\text{-}d_3}{Rh(ttp)CD_3} \qquad (10)$$

Likewise, the reaction of Rh(tmp)Cl (**1c**) ($\delta = 8.56$ ppm) with CD_3OD at 40 °C in the presence of 10 equiv of K_2CO_3 in a sealed NMR tube was monitored by ^1H NMR spectroscopy (eq 11). $Rh(tmp)^-$ anion ($\delta = 7.84$ ppm) was observed within 30 min. The yield of $Rh(tmp)^-$ anion could not be estimated accurately since Rh(tmp)Cl is sparingly soluble in methanol-d_4. Then the mixture was heated at 150 °C for 1 day, and after workup, $Rh(tmp)CD_3$ was isolated in 75% yield.

$$\underset{\textbf{1c}}{Rh(tmp)Cl} \xrightarrow[40\ ^\circ C,\ CD_3OD,\ 30\ min]{10\ equiv\ K_2CO_3}$$
$$Rh(tmp)^- \xrightarrow[150\ ^\circ C,\ CD_3OD,\ 2\ days]{10\ equiv\ K_2CO_3} \underset{75\%\ \textbf{2c}\text{-}d_3}{Rh(tmp)CD_3} \qquad (11)$$

Independent reaction of Rh(ttp)Na (sodium [5,10,15,20-tetratolylporphyrinato]rhodate(I)) (**1f**), generated from the reduction of Rh(ttp)Cl with sodium amalgam,[33] with methanol in both the absence and the presence of K_2CO_3 gave $Rh(ttp)CH_3$ in 37% and 47% yields, respectively (eq 13, Table 7, entries 1 and 2). While all these experiments point to the possibility of carbon−oxygen bond cleavage of methanol by $Rh(ttp)^-$, the implied nucleophilic substitution is highly unlikely because hydroxide anion is a very poor leaving group. We suggest that the equilibrium amount of Rh(ttp)H ($pK_a \sim 11$)[28] is more likely the active intermediate. We did not observe Rh(ttp)H formed by ^1H NMR spectroscopy because it is formed in trace amount and is not very soluble in methanol.

Reaction with $Rh_2(ttp)_2$. Since the bimetalloradical activation of methanol by $Rh^{II}(tmp)$ to give the OH activation products of $Rh(tmp)OCH_3$ and Rh(tmp)H is known,[16] the possibility of $Rh(ttp)CH_3$ formation by $Rh_2(ttp)_2$ is investigated. $Rh_2(ttp)_2$ indeed reacted with methanol at 150 °C, but gave only 9% yield of $Rh(ttp)CH_3$ and 5% yield of $Rh(ttp)CH_2OCH_3$, respectively (Scheme 2, pathway IX, and Table 7, entry 3). While an equilibrium concentration Rh(ttp) monomer exists in benzene due to the weak Rh−Rh bond,[29] the poor solubility of $Rh_2(ttp)_2$ in the more polar MeOH solvent even reduces the concentration of Rh(ttp). The direct C−O cleavage by Rh(ttp) monomer or $Rh_2(ttp)_2$ is not likely. Furthermore, the more reactive, monomeric Rh(tmp) does not react with MeOH (5 M in benzene or neat) at room temperature to give any C−O cleavage product but only yields the OH activation products. Rh(II) does not appear to be the direct species, at least the major one, in activating the C−O bond. Moreover, the chemistry involving the direct C−O cleavage of MeOH by Rh(II) implies the very unlikely homolytic bimolecular substitution on the carbon center to give a very energetic hydroxyl radical. The endothermicity is estimated to be prohibitively high, about 35 kcal/mol, based on the bond dissociation

(28) (a) Nelson, A. P.; DiMagno, S. G. *J. Am. Chem. Soc.* **2000**, *122*, 8569–8570. (b) The $pK_a \sim 11$ supports that Rh(ttp)H is in equilibrium with $Rh(ttp)^-$ in DMSO, while the equilibrium in MeOH was observed in the H/D exchange reaction of Rh(ttp)H even with 100 equiv MeOH in benzene (eq 19) where rapid proton exchange offers the most reasonable explanation.

(29) (a) Wayland, B. B.; Coffin, V. L.; Farnos, M. D. *Inorg. Chem.* **1988**, *27*, 2745–2747. (b) Wayland, B. B. *Polyhedron* **1988**, *7*, 1545–1555. (c) Wayland, B. B.; Ba, S.; Sherry, A. E. *J. Am. Chem. Soc.* **1991**, *113*, 5305–5311.

energies of the Me−OH and Rh(ttp)−Me of 92 and 57 kcal/mol, respectively.[29c]

With K_2CO_3 added, $Rh_2(ttp)_2$ reacted with methanol to give a much higher yield of $Rh(ttp)CH_3$ of 73% (Table 7, entry 4). Probably, K_2CO_3 promotes the product formation by converting $Rh_2(ttp)_2$ into Rh(ttp)OH or $Rh(ttp)CO_3K$ and $Rh(ttp)^-$ (eq 12).[30] These species are more soluble in methanol and gave a higher yield of $Rh(ttp)CH_3$. Therefore, $Rh_2(ttp)_2$ is unlikely an active direct intermediate for the carbon−oxygen bond cleavage of methanol because (1) it gave only a low yield of $Rh(ttp)CH_3$ of 9%, and (2) Rh^{II}(por) is reported to cleave the O−H bond rapidly,[16] which makes C−O cleavage by Rh^{II}(por) not very competitive. $Rh_2(ttp)_2$, at most, provides a minor pathway to afford Rh(ttp)H and $Rh(ttp)OCH_3$ (Scheme 2, pathway IX), which further react to give $Rh(ttp)CH_3$ and $Rh(ttp)CH_2OCH_3$, respectively.

$$\underset{Nu^- = OH^-,\, CO_3K^-}{Rh_2(ttp)_2} + Nu^- \longrightarrow Rh(ttp)Nu + Rh(ttp)^- \qquad (12)$$

Table 7. Reactions of MeOH with Rh(I), Rh(II), and Rh(III)

$$\underset{\textbf{1d-f}}{Rh(ttp)X} + CH_3OH \xrightarrow[150\ ^oC,\ N_2,\ 1\ d]{K_2CO_3\ equiv} \underset{\textbf{2a}}{Rh(ttp)CH_3} + \underset{\textbf{3}}{Rh(ttp)CH_2OCH_3} \qquad (13)$$

entry	Rh(ttp)X	K_2CO_3 equiv	**2a** yield/ %	**3** yield/ %
1	Rh(ttp)Na	0	37	none
2	Rh(ttp)Na	10	47	none
3	$Rh_2(ttp)_2$	0	9	5
4	$Rh_2(ttp)_2$	10	73	none
5	Rh(ttp)H	0	33	15
6	Rh(ttp)H	10	42	4

Reaction with Rh(ttp)H. We favor Rh(ttp)H as the more likely intermediate for carbon−oxygen bond cleavage in thermodynamic terms; the formation of a strong oxygen−hydrogen bond in the coproduct water drives the reaction. The carbon−oxygen bond cleavage step via Rh(ttp)H is supported by the independent reaction between Rh(ttp)H and methanol, which gave $Rh(ttp)CH_3$ in 33% yield and $Rh(ttp)CH_2OCH_3$ in 15% yield (Table 7, entry 5). With K_2CO_3 added, Rh(ttp)H quickly yields $Rh(ttp)^-$ anion[23] in methanol (Scheme 2, pathway VI) before finally producing $Rh(ttp)CH_3$ in 42% yield and $Rh(ttp)CH_2OCH_3$ in 4% yield (Table 7, entry 6).

Kinetic Isotope Effects. Since $Rh(ttp)CH_3$ does not undergo significant methyl group exchange with methanol-d_4 at 150 °C for 1 day in the presence of K_2CO_3 (eq 14), even with a stronger base of KOH (eq 15), kinetic isotope effects on the carbon−oxygen bond cleavage were carried out by a competition experiment using an equimolar mixture of methanol and methanol-d_4 with Rh(ttp)Cl (eq 16). The value of the kinetic isotope effect of the formation of $Rh(ttp)CH_3$ from Rh(ttp)Cl was found to be 1.19 ± 0.05 by ^{1}H NMR spectroscopy. The relaxation time for KIE analysis by ^{1}H NMR spectroscopy is sufficiently long, as the same KIE value was obtained independently by MS analysis (eq 16). The KIE value from Rh(ttp)Cl agreed with KIE values from Rh(ttp)H and Rh(ttp)D, which were 1.21 ± 0.09 (eq 17) and 1.07 ± 0.09 (eq 18), respectively. These small values could be interpreted as the secondary KIE initially.

However, Rh(ttp)H in the presence of 100 equiv of CD_3OD in benzene at room temperature exchanged to give Rh(ttp)D quantitatively within 5 min (eq 19). Fast proton exchanges of Rh(ttp)H/Rh(ttp)D with methanol had occurred. The small KIE values could not be interpreted easily, as they are the combined results of two processes.

$$\underset{\textbf{2a}}{Rh(ttp)CH_3} + CD_3OD \xrightarrow[150\ ^oC,\ N_2,\ 1\ d]{10\ equiv\ K_2CO_3} \underset{\textbf{2a}\ 93\%\ recovery}{Rh(ttp)CH_3} \qquad (14)$$

$$\underset{\textbf{2a-}d_3}{Rh(ttp)CD_3} + CH_3OH \xrightarrow[150\ ^oC,\ N_2,\ 1\ d]{10\ equiv\ KOH} \underbrace{\underset{\textbf{2a}}{Rh(ttp)CH_3} + \underset{\textbf{2a-}d_1}{Rh(ttp)CH_2D} + \underset{\textbf{2a-}d_2}{Rh(ttp)CHD_2}}_{1\%} \qquad (15)$$

85% recovery

$$\underset{\textbf{1a}}{Rh(ttp)Cl} + \underset{1.0}{CH_3OH} / \underset{1.0}{CD_3OD} \xrightarrow[150\ ^oC,\ N_2,\ 1\ d]{10\ equiv\ K_2CO_3} \underset{28\%\ \textbf{2a}}{Rh(ttp)CH_3} + \underset{24\%\ \textbf{2a-}d_3}{Rh(ttp)CD_3} \qquad (16)$$

$(k_H/k_D)_{obs} = 1.19 \pm 0.05$ average of 2 runs(duplicate)

$$\underset{\textbf{1d}}{Rh(ttp)H} + \underset{1.0}{CH_3OH} + \underset{1.0}{CD_3OD} \xrightarrow[N_2,\ 1\ d]{150\ ^oC} \underset{25\%\ \textbf{2a}}{Rh(ttp)CH_3} + \underset{23\%\ \textbf{2a-}d_3}{Rh(ttp)CD_3} + \underset{(D_2)\ \sim 12\%}{Rh(ttp)CH_2OCH_3} \qquad (17)$$

$(k_H/k_D)_{obs} = 1.21 \pm 0.09$ $(k_H/k_D)_{obs} = 1.38 \pm 0.08$ for CH_2

average of 2 runs(duplicate) $(k_H/k_D)_{obs} = 0.44 \pm 0.03$ for CH_3

$$\underset{\textbf{1d-}d_1}{Rh(ttp)D} + \underset{1.0}{CH_3OH} + \underset{1.0}{CD_3OD} \xrightarrow[N_2,\ 1\ d]{150\ ^oC} \underset{27\%\ \textbf{2a}}{Rh(ttp)CH_3} + \underset{25\%\ \textbf{2a-}d_3}{Rh(ttp)CD_3} \qquad (18)$$

$(k_H/k_D)_{obs} = 1.07 \pm 0.09$

average of 2 runs(duplicate)

$$\underset{\textbf{1d}\ \text{trace recovery}}{Rh(ttp)H} + \underset{100\ equiv}{CD_3OD} \xrightarrow[r.t.,\ 5\ min]{C_6D_6} \underset{\textbf{1d-}d_1\ \sim 100\%\ \text{estimated by}\ ^1\text{H NMR}}{Rh(ttp)D} \qquad (19)$$

While lacking a direct piece of evidence, however, we do believe the slowest step of the reaction is the carbon−oxygen bond cleavage step by Rh(ttp)H because Rh(ttp)Cl quickly was converted to $Rh(ttp)^-$ within 5 min at 150 °C in the presence of K_2CO_3 (10 equiv), while further transformation to $Rh(ttp)CH_3$ required 1 day.

For the $Rh(ttp)CH_2OCH_3$ obtained from the competitive reaction by Rh(ttp)H, it is likely a mixture of Rh(ttp)CH_2OCH_3, Rh(ttp)CD_2OCD_3, Rh(ttp)CH_2OCD_3, and Rh(ttp)CD_2OCH_3. The observed values of the kinetic isotope effect for the methine (CH_2) and methyl (CH_3) groups were 1.38 ± 0.08 and 0.44 ± 0.03, respectively. A simple interpretation seems inappropriate due to the complex steps involved.

Conclusions

Rhodium porphyrin chlorides were found to react with methanol at a high temperature of 150 °C in the presence of

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(31) (a) Alder, A. D.; Logon, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakof, L. *J. Org. Chem.* **1967**, *32*, 476. (b) Wagner, R. W.; Lawrence, D. S.; Lindsey, J. S. *Tetrahedron Lett.* **1987**, *28*, 3069–3070.

base to give high yields of rhodium porphyrin methyls. Mechanistic studies suggest that Rh(ttp)H is the key intermediate for the carbon−oxygen bond cleavage. The roles of base are (i) to facilitate the formation of the more reactive Rh(ttp)X (X = OH or CO_3K), (ii) to enhance the rate of formation of Rh(ttp)OCH_3 and hence Rh(ttp)H for carbon−oxygen bond cleavage, and (iii) to convert the side product, Rh(ttp)CH_2OCH_3, to Rh(ttp)CH_3 via Rh(ttp)$^-$ anion. In order to achieve an efficient rhodium porphyrin-based methane oxidation, it would be necessary (i) to remove the methanol continuously or (ii) to carry out the reaction at a lower conversion. Further studies are ongoing.

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 Telfon screw-capped tubes under N_2 with the mixture degassed for three freeze−thaw−pump cycles and wrapped with aluminum foil to prevent undesired photochemical reactions. After the crude mixture was dried under high vacuum, extraction was performed using CH_2Cl_2/H_2O in case bases were used. The products were further purified by silica gel column chromatography eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1). The known compounds H_2(ttp),[31a] H_2(tpp),[31a] H_2(tmp),[31b] Rh(ttp)Cl (**1a**); ^{1}H NMR (CD_3OD, 300 MHz) δ 2.66 (s, 12 H), 7.53 (d, 8 H, J = 8.1 Hz), 8.09 (d, 8 H, J = 7.8 Hz), 8.73 (s, 8 H),[20] Rh(tpp)Cl (**1b**),[20] Rh(tmp)Cl (**1c**),[20] Rh(ttp)H (**1d**),[23] and Rh_2(ttp)$_2$ (**1e**)[23,32] were synthesized according to literature procedures.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-300 at 300 and 75 MHz or Bruker AV- 400 MHz at 400 MHz and 100 MHz, respectively. Chemical shifts were referenced with the residual solvent protons in CD_3OD (δ = 3.31 ppm) and $CDCl_3$ (δ = 7.26 ppm) or tetramethylsilane (δ = 0.00 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.

1. Preparation of Starting Materials. Preparation of Sodium [5,10,15,20-tetratolylporphyrinato]rhodate(I) [Rh(ttp)]Na (1f). The synthesis of [Rh(ttp)]$^-$Na$^+$ follows a literature method except the solvent used was changed to methanol.[33] ^{1}H NMR (CD_3OD, 300 MHz): δ 2.55 (s, 12 H), 7.36 (d, 8 H, J = 7.7 Hz), 7.78 (d, 8 H, J = 7.6 Hz), 8.02 (s, 8 H).

2. Reaction between Rh(ttp)Cl and Methanol with Various Bases. Without Base. Rh(ttp)Cl (**1a**) (20.1 mg, 0.025 mmol) and methanol (3.0 mL) were heated at 150 °C under N_2 for 1 day. Two red products, Rh(ttp)CH_3 (**2a**)[34] (1.4 mg, 0.001 mmol, 7%) and Rh(ttp)CH_2OCH_3 (**3**) (1.0 mg, 0.001 mmol, 5%), with R_f = 0.72 and R_f = 0.51 (hexane/CH_2Cl_2, 1:1), were collected, respectively. Rh(ttp)CH_3 (**2a**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ −5.82 (d, 3 H, J = 3.0 Hz), 2.69 (s, 12 H), 7.53 (d, 8 H, J = 7.5 Hz), 8.01 (dd, 4 H, J = 2.4, 8.4 Hz), 8.07 (dd, 4 H, J = 2.4, 8.4 Hz), 8.73 (s, 8 H); ^{1}H NMR (CD_3OD, 300 MHz) δ −6.62 (d, 3 H, J = 2.7 Hz), 2.69 (s, 12 H), 7.56 (d, 8 H, J = 8.1 Hz), 8.00 (dd, 4 H, J = 1.5, 8.1 Hz), 8.05 (dd, 4 H, J = 1.5, 8.4 Hz), 8.63 (s, 8 H); HRMS (FABMS) calcd for $C_{49}H_{39}N_4Rh^+$ m/z 786.2224, found m/z 786.2227. Rh(ttp)CH_2OCH_3 (**3**) (< 1%, NMR yield) with R_f = 0.51 (hexane/CH_2Cl_2, 1:1) was observed in the ^{1}H NMR. Rh(ttp)CH_2OCH_3 (**3**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ −2.20 (d, 2 H, J = 3.3 Hz), δ −0.70 (s, 3 H), δ 2.69 (s, 12 H), δ 7.52 (t, 8 H, J = 6 Hz), δ 7.98 (dd, 4 H, J = 2.1, 7.5 Hz), δ 8.07 (dd, 4 H, J = 2.1, 8.0 Hz), δ 8.71 (s, 8 H); ^{1}H NMR (CD_3OD, 300 MHz) δ −2.74 (d, 2 H, J = 3.3 Hz), −0.74 (s, 3H), 2.68 (s, 12 H), 7.56 (d, 8 H, J = 7.8 Hz), 7.98 (dd, 4 H, J = 1.5, 8.0 Hz), 8.05 (dd, 4 H, J = 2.1, 7.7 Hz), 8.66 (s, 8 H); ^{1}H NMR (C_6D_6, 300 MHz) δ −1.88 (d, 2 H, J = 3.6 Hz), −0.64 (s, 3H), 2.41 (s, 12 H), 7.26 (d, 8 H, J = 7.8 Hz), 7.34 (d, 4 H, J = 7.8 Hz), 8.04 (dd, 4 H, J = 1.2, 7.35 Hz), 8.19 (dd, 4 H, J = 1.5, 8.5 Hz), 8.98 (s, 8 H); ^{13}C NMR (C_6D_6, 75 MHz) δ 21.82 (d, $^1J_{Rh-C}$ = 26.6 Hz), 30.56, 56.35, 34.48, 65.53 (d, J = 26.8 Hz), 123.17, 132.14, 134.64 (d, J = 25.7 Hz), 137.52, 140.53, 144.16; HRMS (FABMS) calcd for $C_{50}H_{41}N_4ORh^+$ m/z 816.2330, found m/z 816.2315.

Addition of 10 equiv of KOH. Rh(ttp)Cl (**1a**) (20.0 mg, 0.025 mmol), methanol (3.0 mL), and KOH (15.1 mg, 0.26 mmol) were heated at 150 °C under N_2 for 1 day. A red product, Rh(ttp)CH_3 (**2a**) (8.7 mg, 0.011 mmol, 45%), was collected. Rh(ttp)CH_2OCH_3 (**3**) (< 1%, NMR yield) was observed in the ^{1}H NMR.

Addition of 10 equiv of NaOH. Rh(ttp)Cl (**1a**) (20.2 mg, 0.025 mmol), methanol (3.0 mL), and NaOH (10.1 mg, 0.25 mmol) were heated at 150 °C under N_2 for 1 day. A red product, Rh(ttp)CH_3 (**2a**) (11.9 mg, 0.015 mmol, 61%), was collected.

Addition of 10 equiv of Cs_2CO_3. Rh(ttp)Cl (**1a**) (19.9 mg, 0.025 mmol), methanol (3.0 mL), and Cs_2CO_3 (82.2 mg, 0.25 mmol) were heated at 150 °C under N_2 for 1 day. A red product, Rh(ttp)CH_3 (**2a**) (10.0 mg, 0.011 mmol, 51%), was collected.

Addition of 10 equiv of K_2CO_3. Rh(ttp)Cl (**1a**) (20.3 mg, 0.025 mmol), methanol (3.0 mL), and K_2CO_3 (35.1 mg, 0.25 mmol) were heated at 150 °C under N_2 for 1 day. A red product, Rh(ttp)CH_3 (**2a**) (17.1 mg, 0.022 mmol, 87%), was collected.

Addition of 10 equiv of Na_2CO_3. Rh(ttp)Cl (**1a**) (20.2 mg, 0.025 mmol), methanol (3.0 mL), and Na_2CO_3 (27.2 mg, 0.25 mmol) were heated at 150 °C under N_2 for 1 day. Two red products, Rh(ttp)CH_3 (**2a**) (17.0 mg, 0.022 mmol, 87%) and Rh(ttp)CH_2OCH_3 (**3**) (1.2 mg, 0.001 mmol, 6%), were collected, respectively.

Addition of 10 equiv of $KHCO_3$. Rh(ttp)Cl (**1a**) (19.8 mg, 0.025 mmol), methanol (3.0 mL), and $KHCO_3$ (25.1 mg, 0.25 mmol) were heated at 150 °C under N_2 for 1 day with the reaction protected from light by aluminum foil. A red product, Rh(ttp)CH_3 (**2a**) (11.2 mg, 0.014 mmol, 57%), was collected. Rh(ttp)CH_2OCH_3 (**3**) (< 1%, NMR yield) was observed in the ^{1}H NMR.

Addition of 10 equiv of K_3PO_4. Rh(ttp)Cl (**1a**) (20.1 mg, 0.025 mmol), methanol (3.0 mL), and NaOAc (20.1 mg, 0.24 mmol) were heated at 150 °C under N_2 for 1 day. A red product, Rh(ttp)CH_3 (**2a**) (13.2 mg, 0.017 mmol, 67%), was collected.

Addition of 10 equiv of KOAc. Rh(ttp)Cl (**1a**) (20.1 mg, 0.025 mmol), methanol (3.0 mL), and NaOAc (16.5 mg, 0.21 mmol) were heated at 150 °C under N_2 for 1 day. A red product, Rh(ttp)CH_3 (**2a**) (13.2 mg, 0.017 mmol, 84%), was collected.

Addition of 10 equiv of NaOAc. Rh(ttp)Cl (**1a**) (20.1 mg, 0.025 mmol), methanol (3.0 mL), and NaOAc (20.1 mg, 0.24 mmol) were heated at 150 °C under N_2 for 1 day. Two red products, Rh(ttp)CH_3 (**2a**) (17.0 mg, 0.022 mmol, 87%) and Rh(ttp)CH_2OCH_3 (**3**) (1.2 mg, 0.001 mmol, 6%), were collected, respectively.

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(33) (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.

(34) 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.

Addition of 10 equiv of 2,2′-Bipyridyl. Rh(ttp)Cl (**1a**) (20.0 mg, 0.025 mmol), methanol (3.0 mL), and 2,2′-bipyridyl (40.2 mg, 0.26 mmol) were heated at 150 °C under N_2 for 1 day. A mixture of red products, Rh(ttp)CH_3 (**2a**) (~2%, NMR yield) and Rh(ttp)CH_2OCH_3 (**3**) (~2%, NMR yield), was collected.

3. Base Loading Effects on the Reaction between Rh(ttp)Cl and Methanol. Addition of 5 equiv of K_2CO_3. Rh(ttp)Cl (**1a**) (20.2 mg, 0.025 mmol), methanol (3.0 mL), and K_2CO_3 (17.3 mg, 0.125 mmol) were heated at 150 °C under N_2 for 1 day. A red product, Rh(ttp)CH_3 (**2a**) (15.7 mg, 0.021 mmol, 80%), was collected. Rh(ttp)CH_2OCH_3 (**3**) (<1%, NMR yield) was observed by ^{1}H NMR.

Addition of 20 equiv of K_2CO_3. Rh(ttp)Cl (**1a**) (20.1 mg, 0.025 mmol), methanol (3.0 mL), and K_2CO_3 (69.2 mg, 0.50 mmol) were heated at 150 °C under N_2 for 1 day. A Red product, Rh(ttp)CH_3 (**2a**) (8.5 mg, 0.011 mmol, 43%) was collected.

Addition of 30 equiv of K_2CO_3. Rh(ttp)Cl (**1a**) (20.2 mg, 0.025 mmol), methanol (3.0 mL), and K_2CO_3 (104.2 mg, 0.75 mmol) were heated at 150 °C under N_2 for 1 day. A Red product, Rh(ttp)CH_3 (**2a**) (7.1 mg, 0.009 mmol, 36%) was collected.

4. Temperature Effects on the Reaction between Rh(ttp)Cl and Methanol. Reaction at 80 °C. Rh(ttp)Cl (**1a**) (20.3 mg, 0.025 mmol), methanol (3.0 mL), and K_2CO_3 (35.0 mg, 0.25 mmol) were heated at 80 °C under N_2 for 5 days. A red product, Rh(ttp)CH_3 (**2a**) (1.2 mg, 0.002 mmol, 6%), was collected.

Reaction at 120 °C. Rh(ttp)Cl (**1a**) (19.9 mg, 0.025 mmol), methanol (3.0 mL), and K_2CO_3 (34.8 mg, 0.25 mmol) were heated at 120 °C under N_2 for 3 days. A red product, Rh(ttp)CH_3 (**2a**) (9.2 mg, 0.012 mmol, 47%), was collected. Rh(ttp)CH_2OCH_3 (**3**) (<1%, NMR yield) was observed by ^{1}H NMR.

5. Time Effects on the Reaction between Rh(ttp)Cl and Methanol. Half a Day. Rh(ttp)Cl (**1a**) (20.1 mg, 0.025 mmol), methanol (3.0 mL), and K_2CO_3 (35.2 mg, 0.25 mmol) were heated at 150 °C under N_2 for 0.5 day. Red Rh(ttp)CH_3 (**2a**) (11.0 mg, 0.014 mmol, 56%) was collected.

6. Reaction between Rh(por)Cl and Methanol. Reaction between Rh(tpp)Cl and Methanol. Rh(tpp)Cl (**1b**) (19.1 mg, 0.025 mmol), methanol (3.0 mL), and K_2CO_3 (34.9 mg, 0.25 mmol) were heated at 150 °C under N_2 for 1 day. A red product, Rh(tpp)CH_3 (**2b**)[23] (10.3 mg, 0.014 mmol, 52%), with R_f = 0.72 (hexane/ CH_2Cl_2, 1:1) was collected. ^{1}H NMR ($CDCl_3$, 300 MHz): δ −5.80 (d, 3 H, J = 2.7 Hz), 7.75 (s, 12 H), 8.14 (d, 4 H, J = 6.3 Hz), 8.19 (d, 4 H, J = 5.7 Hz), 8.72 (s, 8 H).

Reaction between Rh(tmp)Cl and Methanol. Rh(tmp)Cl (**1c**) (22.6 mg, 0.025 mmol), methanol (3.0 mL), and K_2CO_3 (35.1 mg, 0.25 mmol) were heated at 150 °C under N_2 for 1 day. A red product, Rh(tmp)CH_3 (**2c**)[35] (13.6 mg, 0.015 mmol, 69%), with R_f = 0.72 (hexane/ CH_2Cl_2, 1:1) was collected. ^{1}H NMR (C_6D_6, 300 MHz): δ −5.17 (d, 3 H, J = 3 Hz), 1.81 (s, 12 H), 2.34 (s, 12 H), 2.52 (s, 12 H), 7.15 (s, 4 H), 7.29 (s, 4 H), 8.83 (s, 8 H).

7. Reaction between Rh(ttp)Cl and Methanol-d_4. Rh(ttp)Cl (**1a**) (20.0 mg, 0.025 mmol), methanol-d_4 (3.0 mL), and K_2CO_3 (35.1 mg, 0.25 mmol) were heated at 150 °C under N_2 for 1 day. Red Rh(ttp)CD_3 (**2a-d_3**)[36] (18.0 mg, 0.015 mmol, 91%) was collected. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.69 (s, 12 H), 7.53 (d, 8 H, J = 7.1 Hz), 8.01 (dd, 4 H, J = 2.4, 8.4 Hz), 8.07 (dd, 4 H, J = 2.1, 8.0 Hz), 8.72 (s, 8 H). HRMS (FABMS): calcd for $C_{49}H_{36}N_4D_3Rh^+$ m/z 789.2413; found m/z 789.2427.

8. Mechanistic Studies. NMR Experiment between Rh(ttp)Cl and Methanol-d_4. Rh(ttp)Cl (**1a**) (3.6 mg, 0.0045 mmol), methanol-d_4 (500 μL), and K_2CO_3 (6.2 mg, 0.045 mmol) were added into a Telfon screw-capped NMR tube. The red mixture was degassed for three freeze−thaw−pump cycles, and the NMR tube was flame-sealed under vacuum. The reaction was monitored by ^{1}H NMR at certain time intervals in the course of the reaction. It was heated at 40 °C for 1 h, and Rh(ttp)Cl and Rh(ttp)$^-$ in estimated 6% and 81% yields, respectively, were observed. The estimations were done by taking the solvent peak as an internal standard, and the yields were determined from the integrations by ^{1}H NMR spectroscopy. The mixture was further heated at 40 °C for 4 days, and there was no significant change in ^{1}H NMR signals. Further heating the mixture at 150 °C for 2 days caused a decrease in intensity of the β-signal corresponding to Rh(ttp)$^-$. No Rh(ttp)CD_3 was observed since Rh(ttp)CD_3 is sparingly soluble in CD_3OD. The crude mixture was dried by rotary evaporation and purified by silica gel column chromatography eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1). A red product of Rh(ttp)CD_3 (**2a-d_3**) (3.3 mg, 0.0042 mmol, 94%) with R_f = 0.72 (hexane/CH_2Cl_2, 1:1) was collected.

NMR Experiment between Rh(tmp)Cl and Methanol-d_4. Rh(tmp)Cl (**1c**) (4.1 mg, 0.0045 mmol), methanol-d_4 (500 μL), and K_2CO_3 (6.3 mg, 0.045 mmol) were added into a Telfon screw-capped NMR tube. Rh(tmp)Cl: ^{1}H NMR (CD_3OD, 300 MHz) δ 1.91 (s, 24 H), 2.60 (s, 12 H), 7.28 (s, 8 H), 8.59 (s, 8 H). The red mixture was degassed for three freeze−thaw−pump cycles, and the NMR tube was flame-sealed under vacuum. The reaction was monitored by ^{1}H NMR at certain time intervals in the course of the reaction. It was heated at 40 °C for 30 min, and Rh(tmp)$^-$ was observed. Rh(tmp)$^-$: ^{1}H NMR (CD_3OD, 300 MHz) δ 1.98 (s, 24 H), 2.51 (s, 12 H), 7.13 (s, 8 H), 7.84 (s, 8 H). No estimation on the yield of Rh(tmp)$^-$ could be done probably because Rh(tmp)Cl was poorly soluble in methanol-d_4. The mixture was further heated at 40 °C for 2 days, and there was no significant change in the ^{1}H NMR signals. Further heating the mixture at 150 °C for 1 day caused a decrease in intensity of the β-signals corresponding to Rh(tmp)$^-$. No Rh(tmp)CD_3 was observed since it is sparingly soluble in CD_3OD. The crude mixture was dried by rotary evaporation and purified by silica gel column chromatography eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1). A red product of Rh(tmp)CD_3 (**2c-d_3**)[37] (3.1 mg, 0.0034 mmol, 75%) with R_f = 0.72 (hexane/CH_2Cl_2, 1:1) was collected.

NMR Experiment of Rh(ttp)CH_2OCH_3 without Base in Methanol-d_4. Rh(ttp)CH_2OCH_3 (**3**) (3.7 mg, 0.0045 mmol) and methanol-d_4 (500 μL) were added into a Telfon screw-capped NMR tube. The red mixture was degassed for three freeze−thaw−pump cycles, and the NMR tube was flame-sealed under vacuum. It was heated at 150 °C for 20 days in the dark and monitored with ^{1}H NMR spectroscopy at particular time intervals. Rh(ttp)CH_2OCH_3 was recovered in 77% yield approximately, the estimation was done by taking the solvent peak as an internal standard, and the yield was determined from the integrations by ^{1}H NMR spectroscopy.

NMR Experiment of Rh(ttp)CH_2OCH_3 with K_2CO_3 in Methanol-d_4. Rh(ttp)CH_2OCH_3 (**3**) (3.7 mg, 0.0045 mmol), methanol-d_4 (500 μL), and K_2CO_3 (6.2 mg, 0.045 mmol) were added into a Telfon screw-capped NMR tube. The red mixture was degassed for three freeze−thaw−pump cycles, and the NMR tube was flame-sealed under vacuum. It was heated at 150 °C for 36 h in the dark and monitored with ^{1}H NMR spectroscopy at particular time intervals. Rh(ttp)CH_2OCH_3 was converted to Rh(ttp)$^-$ in 84% yield, and 10% yield of Rh(ttp)CH_2OCH_3 was recovered in 36 h. The estimations were done by taking the solvent peak as an internal standard, and the yields were determined from the integrations by ^{1}H NMR spectroscopy.

NMR Experiment of Rh(ttp)CH_2OCH_3 with Base in Benzene-d_6. Rh(ttp)CH_2OCH_3 (**3**) (3.7 mg, 0.0045 mmol), benzene-d_6 (500 μL, 0.316 mmol), and K_2CO_3 were added into a Telfon screw-capped NMR tube. The red mixture was degassed for three freeze−thaw−pump cycles, and the NMR tube was

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flame-sealed under vacuum. It was heated at 150 °C for 19 days in the dark and monitored with ^{1}H NMR spectroscopy at particular time intervals. Rh(ttp)CH_2OCH_3 was recovered in quantitative yield, the estimation was done by taking the solvent peak as an internal standard, and the yield was determined from the integrations by ^{1}H NMR spectroscopy.

Reaction between Rh(ttp)Na and Methanol without Base. Rh(ttp)Na (**1f**) was prepared from Rh(ttp)Cl as described. Rh(ttp)Na (0.025 mmol) and methanol (3.0 mL) were heated at 150 °C under N_2 for 1 day. A red product, Rh(ttp)CH_3 (**2a**) (7.3 mg, 0.009 mmol, 37%), with R_f = 0.72 (hexane/CH_2Cl_2, 1:1) was collected.

Reaction between Rh(ttp)Na and Methanol with K_2CO_3. Rh(ttp)Na (**1f**) was prepared from Rh(ttp)Cl as described. Rh(ttp)Na (0.025 mmol), methanol (3.0 mL), and K_2CO_3 (35.2 mg, 0.25 mmol) were heated at 150 °C under N_2 for 1 day. A red product, Rh(ttp)CH_3 (**2a**) (9.2 mg, 0.012 mmol, 47%). was collected.

Reaction between Rh(ttp)H and Methanol without Base. Rh(ttp)H (**1d**) was prepared from Rh(ttp)Cl according to the literature procedure.[23] Rh(ttp)H (0.025 mmol) and methanol (3.0 mL) were heated at 150 °C under N_2 for 1 day. Two red products, Rh(ttp)CH_3 (**2a**) (6.5 mg, 0.008 mmol, 33%) and Rh(ttp)CH_2OCH_3 (**3**) (3.1 mg, 0.004 mmol, 15%), were collected, respectively.

Reaction between Rh(ttp)H and Methanol with K_2CO_3. Rh(ttp)H (**1d**) was prepared from Rh(ttp)Cl according to the literature procedure.[23] Rh(ttp)H (0.025 mmol), methanol (3.0 mL), and K_2CO_3 (34.7 mg, 0.25 mmol) were heated at 150 °C under N_2 for 1 day. Two red products, Rh(ttp)CH_3 (**2a**) (8.3 mg, 0.011 mmol, 42%) and Rh(ttp)CH_2OCH_3 (**3**) (0.8 mg, 0.001 mmol, 4%), were collected, respectively.

Reaction between $Rh_2(ttp)_2$ and Methanol without Base. $Rh_2(ttp)_2$ (**1e**) was prepared from Rh(ttp)H according to the literature procedure.[23,32] $Rh_2(ttp)_2$ (0.025 mmol) and methanol (3.0 mL) were heated at 150 °C under N_2 for 1 day. Two red products, Rh(ttp)CH_3 (**2a**) (1.8 mg, 0.002 mmol, 9%) and Rh(ttp)CH_2OCH_3 (**3**) (1.0 mg, 0.001 mmol, 5%), were collected, respectively.

Reaction between $Rh_2(ttp)_2$ and Methanol with K_2CO_3. $Rh_2(ttp)_2$ (**1e**) was prepared from Rh(ttp)H according to the literature procedure.[23,32] $Rh_2(ttp)_2$ (0.025 mmol), methanol (3.0 mL), and K_2CO_3 (0.25 mmol) were heated at 150 °C under N_2 for 1 day. A red product, Rh(ttp)CH_3 (**2a**) (14.4 mg, 0.018 mmol, 73%), was collected.

Insertion of Rh(ttp)H to Formaldehyde. Rh(ttp)H (**1d**) was prepared from Rh(ttp)Cl (4.3 mg, 0.006 mmol) according to the literature procedure.[23] Rh(ttp)H, benzene-d_6 (500 μL), and paraformaldehyde (2.1 mg, 0.06 mmol) were prepared in a sealed NMR tube. A red solution was formed. The mixture was analyzed by ^{1}H NMR spectroscopy after approximately 5 min, and Rh(ttp)CH_2OH was observed quantitatively. The spectrum was compared with that reported in the literature.[23]

Reaction of Rh(ttp)CH_2OH (0.025 mmol) with Methanol. Rh(ttp)CH_2OH and methanol (3.0 mL) were heated at 150 °C under N_2 for 1 day. Two red products, Rh(ttp)CH_3 (**2a**) (18.5 mg, 0.023 mmol,94%) and Rh(ttp)CH_2OCH_3 (**3**) (< 1%, NMR yield), were collected, respectively.

Methyl Group Exchange Experiment, K_2CO_3. Rh(ttp)CH_3 (19.6 mg, 0.025 mmol), methanol-d_4 (3 mL), and K_2CO_3 (35.1 mg, 0.25 mmol) were heated at 150 °C under N_2 for 1 day. A red starting material of Rh(ttp)CH_3 (**2a**) (18.2 mg, 0.023 mmol, 93%) was recovered.

Methyl Group Exchange Experiment, KOH. Rh(ttp)CD_3 (10.0 mg, 0.013 mmol), methanol (1.5 mL), and KOH (7.1 mg, 0.13 mmol) were heated at 150 °C under N_2 for 1 day. A red mixture of Rh(ttp)CD_3 (**2a**) (8.7 mg, 0.011 mmol, 93%), Rh(ttp)CHD_2, Rh(ttp)CH_2D, and Rh(ttp)CH_3 (~1%, NMR yield) was collected.

Kinetic Isotope Effects: Reaction between Rh(ttp)Cl, Methanol, and Methanol-d_4. Rh(ttp)Cl (20.2 mg, 0.025 mmol) and a premixed equimolar mixture of methanol (1.5 mL, 37.03 mmol), methanol-d_4 (1.5 mL, 36.94 mmol), and K_2CO_3 (34.9 mg, 0.25 mmol) were heated at 150 °C under N_2 for 1 day. A mixture of red products of Rh(ttp)CH_3 (**2a**) (5.7 mg, 0.007 mmol, 28%, NMR yield) and Rh(ttp)CD_3 (**2a**-d_3) (4.8 mg, 0.006 mmol, 24%, NMR yield) with the same R_f = 0.72 (hexane/CH_2Cl_2, 1:1) was collected, respectively. Observed kinetic isotope effects $(k_H/k_D)_{obs}$ were found to be 1.19 ± 0.05 by both ^{1}H NMR and mass spectrometry in an average of 2 runs, respectively.

Kinetic Isotope Effects: Reaction between Rh(ttp)H, Methanol, and Methanol-d_4. Rh(ttp)H (19.4 mg, 0.025 mmol) and a premixed equimolar mixture of methanol (1.5 mL, 37.03 mmol) and methanol-d_4 (1.5 mL, 36.94 mmol) were heated at 150 °C under N_2 for 1 day. A mixture of red products of Rh(ttp)CH_3 (**2a**) (4.9 mg, 0.006 mmol, 25%, NMR yield), Rh(ttp)CD_3 (**2a**-d_3) (4.4 mg, 0.006 mmol, 23%, NMR yield), and Rh(ttp)CH_2OCH_3 (**3**) (2.5 mg, 0.003 mmol, 12%, NMR yield) with R_f = 0.72 and 0.51 (hexane/CH_2Cl_2, 1:1) was collected, respectively. The observed kinetic isotope effect $(k_H/k_D)_{obs}$ was found to be 1.21 ± 0.09 for Rh(ttp)CH_3 and Rh(ttp)CD_3 by ^{1}H NMR in an average of 2 runs. For Rh(ttp)CH_2OCH_3, there was likely a mixture of Rh(ttp)CH_2OCH_3, Rh(ttp)CD_2OCD_3, Rh(ttp)CH_2OCD_3, and Rh(ttp)CD_2OCH_3, and the observed kinetic isotope effects $(k_H/k_D)_{obs}$ were found to be 1.38 ± 0.08 and 0.44 ± 0.03 for the methine (CH_2) and methyl (CH_3) groups, respectively, by ^{1}H NMR spectroscopy in an average of 2 runs.

Kinetic Isotope Effects: Reaction between Rh(ttp)D, Methanol, and Methanol-d_4. Rh(ttp)D (19.6 mg, 0.025 mmol) and a premixed equimolar mixture of methanol (1.5 mL, 37.03 mmol) and methanol-d_4 (1.5 mL, 36.94 mmol) were heated at 150 °C under N_2 for 1 day. A mixture of red products of Rh(ttp)CH_3 (**2a**) (5.3 mg, 0.007 mmol, 27%, NMR yield) and Rh(ttp)CD_3 (**2a**-d_3) (4.9 mg, 0.006 mmol, 25%, NMR yield) with R_f = 0.72 (hexane/CH_2Cl_2, 1:1) was collected. The observed kinetic isotope effect $(k_H/k_D)_{obs}$ was found to be 1.07 ± 0.09 for Rh(ttp)CH_3 and Rh(ttp)CD_3 by ^{1}H NMR in an average of 2 runs.

Proton Exchange of Rh(ttp)H with Methanol-d_4. Rh(ttp)H (**1d**) (3.5 mg, 0.0045 mmol), methanol-d_4 (18 μL, 0.44 mmol), and benzene-d_6 (480 μL) were added into a Telfon screw-capped NMR tube. The red mixture was degassed for three freeze−thaw−pump cycles, and the NMR tube was flame-sealed under vacuum. The mixture was analyzed by ^{1}H NMR spectroscopy. Rh(ttp)D (**1d**-d_1) (~100%) and Rh(ttp)H (**1d**) (trace) were observed. Due to the presence of methanol-d_4, the chemical shifts were slightly different from the spectrum obtained in pure benzene-d_6.[23] ^{1}H NMR (C_6D_6, 400 MHz): δ 2.40 (s, 12 H), 7.2 (d, 8 H, J = 7.2 Hz), 7.33 (d, 4 H, J = 7.2 Hz), 7.94 (d, 4 H, J = 7.2 Hz), 8.19 (d, 4 H, J = 6.8 Hz), 8.98 (s, 8 H). The hydridic signal appeared at δ −38.80 (d, J = 38.0 Hz).

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Supporting Information Available: Tables and figures of crystallographic data for complexes **2a**-d_3 and **3** (CIF and PDF), sequence of reactions monitored by ^{1}H NMR and ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.