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Hydroxide-promoted selective C(α)–C(β) bond activation of aliphatic ethers by rhodium(III) porphyrins

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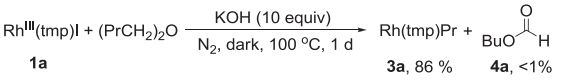
ABSTRACT

The selective aliphatic C(α)–C(β) bond activation (CCA) of ethers by rhodium(III) porphyrin halides in the presence of KOH was achieved to give Rh–C(β) alkyls up to 88% yield. The addition of H_2O and a phase transfer agent Ph_4PBr improved the homogeneity of the reaction mixture and significantly brought down the reaction temperature to 60 °C. At this mild temperature, the C(α) co-product was oxidized to the corresponding esters in up to 89% yield. KOH promotes the bond activation by transferring the hydroxyl group to rhodium porphyrin to generate the key intermediate Rh^{III}(ttp)OH (ttp = 5,10,15,20-tetratolylporphyrinate dianion).

Introduction

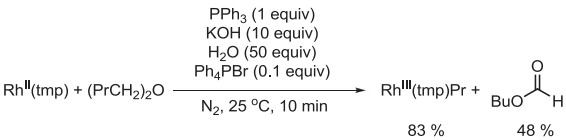
The aliphatic carbon–carbon bond activation (CCA) by transition metal complexes is a challenging reaction due to the sterical hindrance imposed by surrounding carbon–hydrogen bonds in hydrocarbons [1]. Strategies to achieve CCA include ring strain release of cubanes [2], cyclopropane [3], biphenylenes [4] and cyclobutanone [5] or chelation assistance with pincer-type ligands (Scheme 1) [1c,6]. However, the activation of unstrained, aliphatic C–C bonds remains rare in examples and an important problem to tackle.

In our continuous and systematic investigation of carbon–carbon bond activation by group 9 metalloporphyrin complexes, we have earlier communicated that the CCA of various ethers can be achieved by rhodium(III) 5,10,15,20-tetrakis(mesitylporphyrin) iodide (Rh^{III}(tmp)I; **1a**) in the basic medium (Eq. (1)) [7]. However, a high temperature of 100 °C was required to increase the solubility of KOH in ethers. At this elevated temperature, the organic co-product that could establish the stoichiometry decomposed extensively with less than 1% of butyl formate observed. Therefore, mechanistic understandings are not complete.



(1)

When the more reactive Rh^{II}(tmp) (**2**) was used instead of Rh^{III}(tmp)I (**1a**), water was found to assist the same selective cleavage of the C(α)–C(β) bond of ethers occurring at room temperature to generate Rh^{III}(tmp)R (**3**) and the corresponding functionalized esters (**4**) (Eq. (2)) [8]. We reasoned that water-induced disproportionation of Rh^{II}(tmp) (**2**) generates Rh^{III}(tmp)OH as the key intermediate for the CCA of ethers. The mild room temperature reactions further allow the identification of labile organic products formed from the cleaved C(α) fragment of ethers to establish the stoichiometry. Though Rh^{II}(tmp) works very well, the preparation of Rh^{II}(tmp) requires controlled temperature photolysis of Rh(tmp)Me and it is very air-sensitive [9]. We now report our full results that the more user-friendly, air-stable rhodium(III) porphyrin halides can also selectively cleave the C(α)–C(β) bond of ethers successfully with the assistance of H_2O and the phase transfer agent Ph_4PBr under milder conditions to give both the Rh(por) C(β)alkyls and organic products in good yields.



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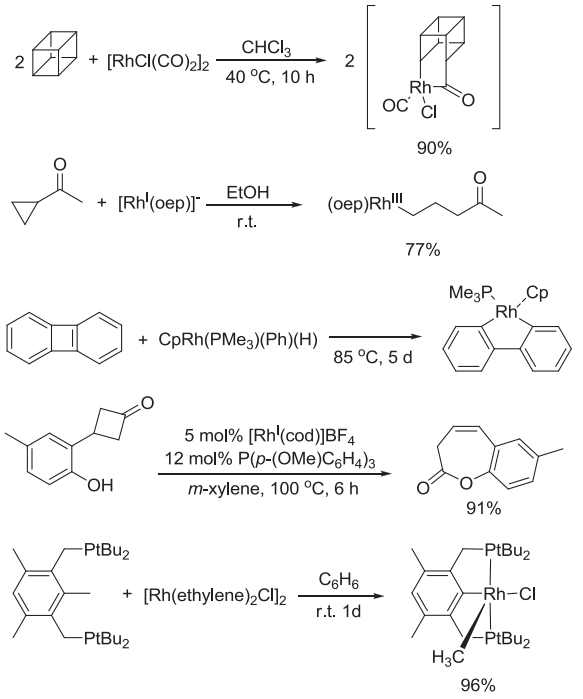
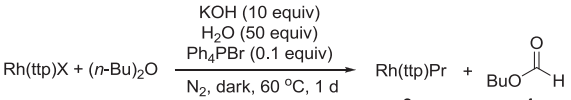


Scheme 1. Carbon–carbon bond activation examples.

Results and discussions

Stoichiometry

Initially, Rh(ttp)Cl (**5**) cleaved the C(α)–C(β) bond of *n*-butyl ether selectively in the presence of KOH (10 equiv), H_2O (50 equiv) and a phase transfer agent Ph_4PBr (0.1 equiv) to give Rh(ttp)Pr (**3b**) in 45% yield at 60 °C (Eq. (3)). At this lower temperature, the oxidized α-alkyl fragment can be retained according to the stoichiometry. Butyl formate was also observed by GC/MS analysis in 32% yield (Eq. (3)).



(3)

X = Cl, **5**	45 %	32 %
= I, **1b**	70 %	47 %

The axial ligand of Rh(ttp)X (X = I, Cl) strongly affects the CCA yield. Rh(ttp)I (**1b**) reacted with di-*n*-butyl ether to give higher yield of Rh(ttp)Pr (**3b**) compared to Rh(ttp)Cl (**5**) (Eq. (3)). We reason that the more soluble Rh(ttp)I (**1b**) undergoes more facile substitution with KOH to generate Rh(ttp)OH for further CCA reaction [10].

Optimization of conditions

To further optimize the reaction efficiency, we carried out extensive investigation on the C(α)–C(β) bond activation of di-*n*-butyl ether by Rh(ttp)I (**1b**). In the absence of KOH, only 5% of Rh(ttp)Pr (**3b**) was obtained (Table 1, entry 1). Addition of KOH (1–10 equiv) enhanced the yields of Rh(ttp)Pr (**3b**) and butyl formate (**4a**) up to 72% and 66%, respectively (Table 1, entries 2–4). However, a higher KOH loading (10 equiv) resulted in a similar yield of Rh(ttp)Pr (**3b**) but a lower yield of butyl formate (**4a**) likely due to the alkaline hydrolysis of ester (Table 1, entry 4). Indeed, the alkaline hydrolysis of butyl formate is a known process that has previously been reported [8].

To increase the solubility of KOH, H_2O was also added. Higher H_2O loadings improved both the yields of Rh(ttp)Pr (**3b**) and butyl formate (**4a**) (Table 1, entries 5–6). Further increase in the water loading showed no further yield enhancement due to the limited solubility of H_2O in di-*n*-butyl ether (Table 1, entry 7). To our surprise, elevated temperature did not enhance the yields. At temperature higher than 60 °C, alkaline hydrolysis of ester becomes significant and no organic product was obtained (Table 1, entries 8–9). Reactions that were carried out in benzene or THF solvent were also non-productive (Table 1, entry 10). We reason that the highly unstable Rh^{III}(ttp)OH rapidly dimerizes to give Rh^{II}_2(ttp)$_2$ that is inactive in CCA [11]. Thus, solvent-free conditions favors the C–C bond cleavage of ethers.

Porphyrin ligand effect

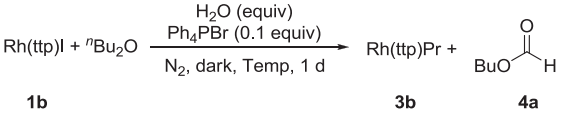
As various electronically different rhodium porphyrin iodides gave similar yields of Rh(por)Pr (**3**) and butyl formate (**4a**) (Table 2), the porphyrin electronic effect is thus not significant.

Surprising, the sterically hindered Rh(tmp)I reacted to give slightly higher yields of Rh(tmp)Pr (**3a**) (Table 3, entry 1). Likely, the formation of Rh$_2$(ttp)$_2$ dimer from Rh^{III}(ttp)OH [11] can be prevented using the bulkier tmp ligand.

Scope of the reaction

Without a phase transfer agent, Rh(por)I reacted to give good yields of Rh(por)R but little organic coproducts (Table 3, Conditions 1, entries 1–4). In the presence of H_2O and Ph_4PBr, the reactions of Rh(ttp)I (**1b**) with di-*n*-butyl ether, di-*n*-pentyl ether and diisopropyl ether occurred at a lower temperature of 60 °C and yielded both Rh(por)R and the corresponding alkyl formates or alkyl acetate, respectively in good yields (Table 3, Conditions 2, entries 2–4). The extra oxygen incorporated in the organics is consistent with the proposed Rh(ttp)OH intermediate in the CCA of ethers. Unfortunately, we could not detect the corresponding ester in lower molecular weight di-*n*-propyl ether likely due to either lower product yield or mechanical loss of high volatility (Table 3, Conditions 2, entry 1).

Table 1
Optimization of CCA of *n*-butyl ether.

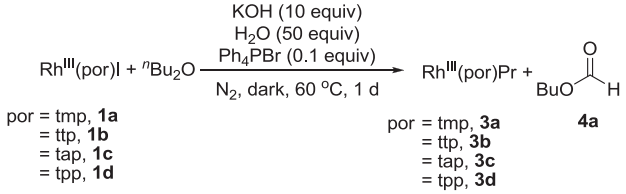


1b **3b** **4a**

Entry	Conditions			Yield (%)[a]	
	KOH (equiv)	H_2O (equiv)	Temp (°C)	**3b**	**4a**
1	0	50	60	5	0
2	1	50	60	60	40
3	5	50	60	72	66
4	10	50	60	70	47
5	5	100	60	83	56
6	5	200	60	70	89
7	5	300	60	74	89
8	5	200	80	66	0
9	5	200	100	68	0
10[b]	5	200	60	0	0

[a] Average of at least duplicate runs.
[b] Benzene or THF were employed as solvent with 100 equiv of $^nBu_2O$ added. Rh(ttp)I was recovered in 54%.

Table 2
Electronic effect of porphyrin ligand.



Entry	Rh^{III}(por)I[a]	Yield (%)[a]	
		3a–d	**4a**
1	Rh(tmp)I (**1a**)	**3a** (80)	63
2	Rh(tap)I (**1c**)	**3c** (62)	63
3	Rh(ttp)I (**1b**)	**3b** (72)	66
4	Rh(tpp)I (**1d**)	**3d** (75)	76

[a] tap = 5,10,15,20-tetra-4-anisylporphyrinato dianion; tpp = 5,10,15,20-tetraphenylporphyrinato dianion.

Proposed mechanism

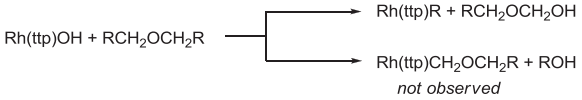
Scheme 2 shows the overall proposed reaction mechanism. Initially, Rh(ttp)OH is generated from the ligand substitution of Rh(ttp)I with KOH. Rh(ttp)OH then cleaves the C–C bond of ether by sigma-bond metathesis [8] to yield Rh(ttp)Pr and $BuOCH_2OH$. $BuOCH_2OH$ then condenses with Rh(ttp)OH to give Rh(ttp)OCH_2OBu [12]. The other mechanism that Rh^{II}(ttp) reacts with *n*-butyl ether at the C(α)–H bond to give Rh(ttp)CH(OH)(OBu) is less likely due to the rapid and favorable disproportionation of Rh^{II}(ttp) [13]. Subsequent β-hydride elimination affords Rh(ttp)H and butyl formate. β-Proton elimination can also occur to give $Rh(ttp)^-$ and butyl formate, followed by reaction of $Rh(ttp)^-$ with H_2O to generate Rh(ttp)H. The regenerated Rh(ttp)H is then recycled back to Rh(ttp) and H_2 through the proposed base-promoted and thermal [14,15] dehydrogenation. The individual reaction steps will be discussed as follows.

Generation of Rh(ttp)OH (Eq. (i))

Rh(ttp)X (X = I, Cl) reacted with ether poorly in the absence of KOH (Table 1, entry 1). Reaction promoted by the addition of KOH supports the ligand substitution of Rh(ttp)X to give Rh(ttp)OH. Furthermore, Rh(ttp)X reacted in th order of I > Cl. It supports that the better leaving group reacts faster.

CCA of ether by Rh(ttp)OH (Eq. (ii))

Rh(ttp)OH activates the C(α)–C(β) bond of ether selectively to form a Rh–C(β) bond and a C(α)–OH bond through sigma-bond metathesis (Eq. (4)). The selective cleavage of the weaker internal C(α)–C(β) bond (83 kcal mol^{-1}) [16] occurred preferentially over the stronger and less hindered terminal C–CH_3 bond (89 kcal mol^{-1}) [16] of ether. The Rh–C(β) bond is regioselectively formed rather than the Rh–C(α) bond due to the less sterically hindered transition state involved (Fig. 1).



(4)

The selective formation of Rh–C(β) bond can also be explained by the electrostatic interaction. We propose that Rh(ttp)OH pre-organizes to C(α)–C(β) bond in ether and forms a cyclic structure with neighboring atoms featuring opposite polarities (Fig. 2). The 6-membered-ring-like structure can be facilitated by the formation of H-bonding with the oxygen atom in ether. The pre-organized molecules then converts into a 4-membered cyclic transition state and C–C bond activation occurs (Fig. 2a). In contrast, formation of Rh–C(α) bond is electronically less favorable due to electrostatic repulsion on the like-charged neighboring atom (Fig. 2b).

Dehydrogenation of alcohol (Eqs. (iiia) and (iiib))

The alcohol that is formed from sigma-bond metathesis of Rh(ttp)OH with C(α)–C(β) of ether is dehydrogenated by Rh(ttp)OH to generate the observed ester. Similar mechanism has been proposed by Collman [17] and Fu et al. [18] in the alcohol oxidation to ketone through Rh-alkoxide species.

Base-promoted disproportionation (Eqs. (iva)–(c))

Dehydrogenation of Rh^{III}(ttp)H in basic media can give Rh^{II}(ttp) and H_2 [14]. Rh^{II}(ttp) then disproportionates with KOH to generate $Rh^{I}(ttp)^-$ and Rh^{III}(ttp)OH [19]. $Rh^{I}(ttp)^-$ can be further protonated with H_2O to regenerate Rh^{III}(ttp)H [14]. Thus, Rh^{III}(ttp)H, Rh^{II}(ttp) and Rh^{III}(ttp)OH can exist in equilibrium during the course of reaction [20].

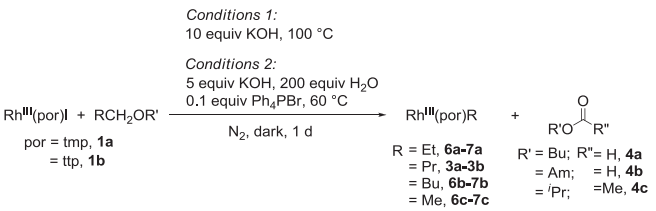
Conclusions

In summary, we have carried out a comprehensive investigation on the carbon–carbon bond activation of ethers by rhodium(III) porphyrin iodides under mild conditions of 60 °C. The promoting role of water, base and phase transfer agent in generating the key intermediate Rh^{III}(ttp)OH from Rh^{III}(ttp)I for the CCA of ethers has also been established. The stoichiometric CCA product of Rh^{III}(ttp)R (R = alkyls) and the corresponding esters were observed in high yields.

Experimental section

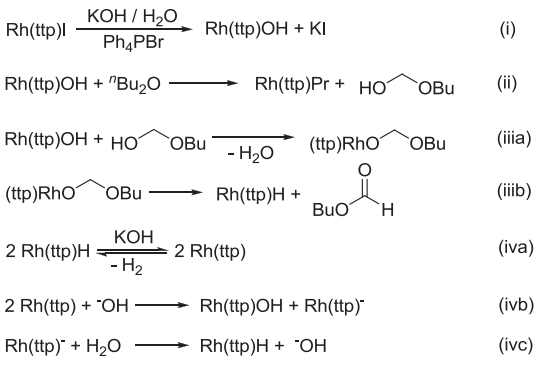
All materials were obtained from commercial suppliers and used without further purification unless otherwise specified. Benzene was distilled from sodium under nitrogen. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl under N_2. All ether solutions were distilled prior to use. All solutions used were degassed thrice by freeze-thaw-pump cycle and stored in a Teflon screwhead stoppered flask. Thin layer chromatography was performed on Merck pre-coated silica gel 60 F_{254} plates. Silica gel (Merck, 70–230 mesh) was used for column chromatography. All reactions were run in Teflon screw capped flask, which was

Table 3
Comparison on CCA of ethers under two different conditions.



Entry	Ether	Conditions 1		Conditions 2	
		Yield (%)		Yield (%)	
		Rh(tmp) R **3a**, **6a–c**	Ester	Rh(ttp) R **3b**, **7a–c**	Ester **4a**, **b**
1	$(EtCH_2)_2O$	**6a** (30)	–	**7a** (30)	n.d.[a]
2	$(PrCH_2)_2O$	**3a** (86)	–	**3b** (70)	**4a** (89)
3	$(BuCH_2)_2O$	**6b** (88)	–	**7b** (76)	**4b** (76)
4	$(Me_2CH)_2O$	**6c** (42)	–	**7c** (56)	**4c** (29)

[a] n.d. = not determined.



Scheme 2. Proposed mechanism.

wrapped with aluminum foils to protect from light. Rh(ttp)Cl, Rh(ttp)I, Rh(tmp)I, Rh(tap)I and Rh(tpp)I were prepared according to the literature procedures [21,22] and they had been characterized.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 instrument at 400 and 100 MHz or a Bruker Avance III 700 instrument at 175 MHz, respectively. Chemical shifts were referenced internally to the residual proton resonance in C_6D_6 (δ = 7.15 ppm) or $CDCl_3$ (δ = 7.26 ppm) in ^{1}H NMR spectra, and $CDCl_3$ (δ = 77.16 ppm) in ^{13}C NMR spectra as the internal standard. Chemical shifts (δ) were reported as part 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 preformed with 3-nitrobenzyl alcohol (NBA) as the matrix.

GC–MS analysis was conducted on a GCMS-QP2010 Plus system using Rtx-5MS column (30 m × 0.25 mm). Details of GC program are as follows: The column oven injection temperatures were respectively 50.0 and 250 °C. Helium was used as carrier gas. Flow control mode was chosen as linear velocity (36.3 cm s^{-1}) with pressure 53.5 kPa. The total flow, column flow and purge flow were 24.0, 1.0 and 3.0 mL min^{-1}, respectively. Split mode inject with split ratio 20.0 was applied. After injection, the column oven temperature was kept at 50 °C for 5 min and was then elevated at a rate of 20 °C min^{-1} for 10 min until 250 °C. The temperature of 250 °C was kept for 5 min.

General procedure for CCA of ethers. n-Butyl ether as an example

Rh(tmp)I (**1a**), KOH, H_2O and Ph_4PBr were dissolved in *n*-butyl ether. The reaction mixture was degassed thrice by freeze-thaw-pump cycle and was heated at desired temperature under nitrogen for 1 day. Excess *n*-butyl ether was removed, the dark red crude product was then purified by column chromatography on silica gel eluting with hexane/CH_2Cl_2 (3:1) to give the reddish purple solid of Rh(tmp)Pr (**3a**) [8,23]. R_f = 8.0 (CH_2Cl_2:Hexane = 2:1); ^{1}H NMR (400 MHz, C_6D_6) δ −4.43 (dt, 2H, $^2J_{Rh-H}$ = 3.0 Hz, $^3J_{H-H}$ = 7.5 Hz), −3.87 (sextet, 2H, J = 7.6 Hz), −1.43 (t, 3H, J = 7.5 Hz), 1.87 (s, 12H), 2.17 (s, 12H), 2.43 (s, 12H), 7.09 (s, 4H), 7.19 (s, 4H), 8.74 (s, 8H).

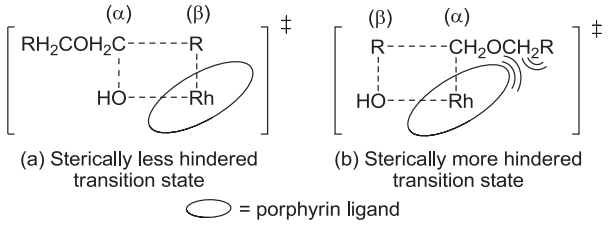


Fig. 1. Selective generation of Rh(por)R.

Reaction of Rh(tmp)I and n-butyl ether with 10 equiv of KOH at 100 °C for 1 day

Rh(tmp)I (10.0 mg, 0.010 mmol), KOH (5.5 mg, 0.098 mmol) and *n*-butyl ether (2.0 mL) were heated at 100 °C under nitrogen for 1 day. The dark red crude product was purified by column chromatography to give the reddish purple solid of Rh(tmp)Pr (**3a**) [8] (7.9 mg, 0.0085 mmol, 86%). Butyl formate (**4a**) [8] (<1%) was observed in crude reaction mixture from GC/MS using naphthalene as internal standard.

Reaction of Rh(ttp)Cl and n-butyl ether with 10 equiv of KOH, 50 equiv H_2O and 0.1 equiv Ph_4PBr at 60 °C for 1 day

Rh(ttp)Cl (**5**) (10.0 mg, 0.012 mmol), KOH (6.9 mg, 0.123 mmol), H_2O (11 μL, 0.61 mmol), Ph_4PBr (0.5 mg, 0.0012 mmol) and *n*-butyl ether (2.0 mL) were heated at 60 °C under nitrogen for 1 day. The dark red crude product was purified by column chromatography to give the reddish purple solid of Rh(ttp)Pr (**3b**) [24–26] (5.2 mg, 0.0056 mmol, 45%). R_f = 0.79 (CH_2Cl_2:Hexane = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ −4.98 (dt, 2H, $^2J_{Rh-H}$ = 3.3 Hz, $^3J_{H-H}$ = 8.3 Hz), −4.46 (sixtet, 2H, J = 8.7 Hz), −1.75 (t, 3H, J = 7.2 Hz), 2.69 (s, 12H), 7.53 (t, 4H, J = 5.7 Hz), 8.00 (dd, 4H, J = 2.1 Hz, 5.7 Hz), 8.07 (dd, 4H, J = 2.1 Hz, 7.5 Hz), 8.71 (d, 4H, J = 7.3 Hz), 8.76 (s, 8H). Butyl formate (**4a**) [8] (32%) was observed in crude reaction mixture from GC/MS using naphthalene as internal standard.

Reaction of Rh(ttp)I and n-butyl ether with 10 equiv of KOH, 50 equiv H_2O and 0.1 equiv Ph_4PBr at 60 °C for 1 day

Rh(ttp)I (**1b**) (10.0 mg, 0.011 mmol), KOH (6.6 mg, 0.111 mmol), H_2O (10 μL, 0.56 mmol), Ph_4PBr (0.5 mg, 0.0012 mmol) and *n*-butyl ether (2.0 mL) were heated at 60 °C under nitrogen for 1 day. The dark red crude product was purified by column chromatography to give the reddish purple solid of Rh(ttp)Pr (**3b**) (6.3 mg, 0.0078 mmol, 70%). Butyl formate (**4a**) [8] (47%) was observed in crude reaction mixture from GC/MS using naphthalene as internal standard.

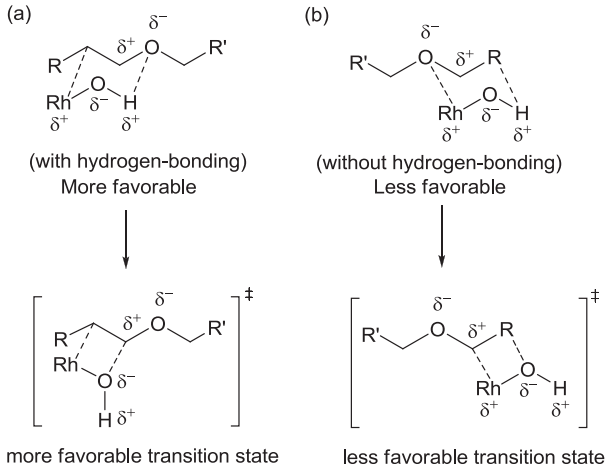


Fig. 2. Pre-organization of ether to Rh–OH with hydrogen bonding.

Conditions optimization

Reaction of Rh(ttp)I and n-butyl ether with various additives at 60 °C for 1 day

i. H_2O (50 equiv), Ph_4PBr (0.1 equiv). Rh(ttp)I (**1b**) (10.0 mg, 0.011 mmol), H_2O (10 μL, 0.56 mmol), Ph_4PBr (0.5 mg, 0.0012 mmol) and *n*-butyl ether (2.0 mL) were heated at 60 °C under nitrogen for 1 day. Reddish purple solid Rh(ttp)Pr (**3b**) (0.5 mg, 0.0006 mmol, 5%) was purified and collected.

ii. KOH (1 equiv), H_2O (50 equiv), Ph_4PBr (0.1 equiv). Rh(ttp)I (**1b**) (10.0 mg, 0.011 mmol), KOH (0.66 mg, 0.011 mmol), H_2O (10 μL, 0.56 mmol), Ph_4PBr (0.5 mg, 0.0012 mmol) and *n*-butyl ether (2.0 mL) were heated at 60 °C under nitrogen for 1 day. Reddish purple solid Rh(ttp)Pr (**3b**) (5.4 mg, 0.0067 mmol, 60%) was purified and collected. Butyl formate (**4a**) (40%) was observed in crude reaction mixture from GC/MS using naphthalene as internal standard.

iii. KOH (5 equiv), H_2O (50 equiv), Ph_4PBr (0.1 equiv). Rh(ttp)I (**1b**) (10.0 mg, 0.011 mmol), KOH (3.3 mg, 0.056 mmol), H_2O (10 μL, 0.56 mmol), Ph_4PBr (0.5 mg, 0.0012 mmol) and *n*-butyl ether (2.0 mL) were heated at 60 °C under nitrogen for 1 day. Reddish purple solid Rh(ttp)Pr (**3b**) (6.5 mg, 0.0080 mmol, 72%) was purified and collected. Butyl formate (**4a**) (66%) was observed in crude reaction mixture from GC/MS using naphthalene as internal standard.

iv. KOH (5 equiv), H_2O (100 equiv), Ph_4PBr (0.1 equiv). Rh(ttp)I (**1b**) (10.0 mg, 0.011 mmol), KOH (3.3 mg, 0.056 mmol), H_2O (20 μL, 1.11 mmol), Ph_4PBr (0.5 mg, 0.0012 mmol) and *n*-butyl ether (2.0 mL) were heated at 60 °C under nitrogen for 1 day. Reddish purple solid Rh(ttp)Pr (**3b**) (7.8 mg, 0.0096 mmol, 83%) was purified and collected. Butyl formate (**4a**) (56%) was observed in crude reaction mixture from GC/MS using naphthalene as internal standard.

v. KOH (5 equiv), H_2O (200 equiv), Ph_4PBr (0.1 equiv). Rh(ttp)I (**1b**) (10.0 mg, 0.011 mmol), KOH (3.3 mg, 0.056 mmol), H_2O (40 μL, 2.22 mmol), Ph_4PBr (0.5 mg, 0.0012 mmol) and *n*-butyl ether (2.0 mL) were heated at 60 °C under nitrogen for 1 day. Reddish purple solid Rh(ttp)Pr (**3b**) (6.3 mg, 0.0078 mmol, 70%) was purified and collected. Butyl formate (**4a**) (89%) was observed in crude reaction mixture from GC/MS using naphthalene as internal standard.

vi. KOH (5 equiv), H_2O (300 equiv), Ph_4PBr (0.1 equiv). Rh(ttp)I (**1b**) (10.0 mg, 0.011 mmol), KOH (3.3 mg, 0.056 mmol), H_2O (60 μL, 3.33 mmol), Ph_4PBr (0.5 mg, 0.0012 mmol) and *n*-butyl ether (2.0 mL) were heated at 60 °C under nitrogen for 1 day. Reddish purple solid Rh(ttp)Pr (**3b**) (6.7 mg, 0.0082 mmol, 74%) was purified and collected. Butyl formate (**4a**) (89%) was observed in crude reaction mixture from GC/MS using naphthalene as internal standard.

vii. 5 equiv KOH, 200 equiv H_2O, 0.1 equiv Ph_4PBr at 80 °C for 1 day. Rh(ttp)I (**1b**) (10.0 mg, 0.011 mmol), KOH (3.3 mg, 0.056 mmol), H_2O (40 μL, 2.22 mmol), Ph_4PBr (0.5 mg, 0.0012 mmol) and *n*-butyl ether (2.0 mL) were heated at 80 °C under nitrogen for 1 day. Reddish purple solid Rh(ttp)Pr (**3b**) (6.0 mg, 0.0073 mmol, 66%) was purified and collected. No new organics was observed in GC/MS.

viii. 5 equiv KOH, 200 equiv H_2O, 0.1 equiv Ph_4PBr at 100 °C for 1 day. Rh(ttp)I (**1b**) (10.0 mg, 0.011 mmol), KOH (3.3 mg, 0.056 mmol), H_2O (40 μL, 2.22 mmol), Ph_4PBr (0.5 mg, 0.0012 mmol) and *n*-butyl ether (2.0 mL) were heated at 100 °C under nitrogen for 1 day. Reddish purple solid Rh(ttp)Pr (**3b**) (6.2 mg, 0.0076 mmol, 68%) was purified and collected. No new organics was observed in GC/MS.

ixa. 5 equiv of KOH, 200 equiv H_2O and 0.1 equiv Ph_4PBr in THF at 60 °C for 1 day. Rh(ttp)I (**1b**) (10.0 mg, 0.011 mmol), KOH (3.3 mg, 0.056 mmol), H_2O (40 μL, 2.22 mmol), Ph_4PBr (0.5 mg, 0.0012 mmol), *n*-butyl ether (188 μL, 1.112 mmol) and THF (1.8 mL) were heated at 60 °C under nitrogen for 1 day. No product was obtained.

ixb. 5 equiv of KOH, 200 equiv H_2O and 0.1 equiv Ph_4PBr in benzene at 60 °C for 1 day. Rh(ttp)I (**1b**) (10.0 mg, 0.011 mmol), KOH (3.3 mg, 0.056 mmol), H_2O (40 μL, 2.22 mmol), Ph_4PBr (0.5 mg, 0.0012 mmol), *n*-butyl ether (188 μL, 1.112 mmol) and benzene (1.8 mL) were heated at 60 °C under nitrogen for 1 day. No product was obtained.

Reaction of different Rh(por)I and n-butyl ether with 5 equiv KOH, 50 equiv H_2O, 0.1 equiv Ph_4PBr at 60 °C for 1 day

i. Rh(tmp)I. Rh(tmp)I (**1a**) (10.0 mg, 0.0099 mmol), KOH (3.0 mg, 0.051 mmol), H_2O (10 μL, 0.55 mmol), Ph_4PBr (0.5 mg, 0.0012 mmol) and *n*-butyl ether (2.0 mL) were heated at 60 °C under nitrogen for 1 day. Reddish purple solid Rh(tmp)Pr (**3a**) (7.3 mg, 0.0079 mmol, 80%) was purified and collected. Butyl formate (**4a**) (63%) was observed in crude reaction mixture from GC/MS using naphthalene as internal standard.

ii. Rh(tap)I. Rh(tap)I (**1c**) (10.0 mg, 0.0104 mmol), KOH (3.4 mg, 0.058 mmol), H_2O (10 μL, 0.55 mmol), Ph_4PBr (0.5 mg, 0.0012 mmol) and *n*-butyl ether (2.0 mL) were heated at 60 °C under nitrogen for 1 day. Reddish purple solid Rh(tap)Pr (**3c**) [24] (5.7 mg, 0.0064 mmol, 62%) was purified and collected. Rh(tap)Pr (**3c**). $R_f = 0.72$ (CH_2Cl_2:Hexane = 2:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ −4.97 (dt, 2H, $^2J_{Rh-H} = 3.7$ Hz, $^3J_{H-H} = 6.6$ Hz), −4.44 (sextet, 2H, $J = 7.8$ Hz), −1.74 (t, 3H, $J = 7.1$ Hz), 4.09 (s, 12H), 8.04 (d, 4H, $J = 7.0$ Hz), 8.10 (d, 4H, $J = 7.9$ Hz), 8.73 (s, 8H). *o*-Phenyl hydrogens are obscured by solvent (7.26). ^{13}C NMR (176 MHz, $CDCl_3$) δ 10.98, 17.73, 20.53, 55.70, 112.23, 122.18, 131.49, 134.77, 134.85, 135.14, 143.58, 159.35. HRMS Calcd for $C_{47}H_{35}N_4O_4Rh$ 879.2421; Found, 879.2419. Butyl formate (**4a**) (63%) was observed in crude reaction mixture from GC/MS using naphthalene as internal standard.

iii. Rh(tpp)I. Rh(tpp)I (**1d**) (10.0 mg, 0.0118 mmol), KOH (3.5 mg, 0.059 mmol), H_2O (10 μL, 0.55 mmol), Ph_4PBr (0.5 mg, 0.0012 mmol) and *n*-butyl ether (2.0 mL) were heated at 60 °C under nitrogen for 1 day. Reddish purple solid Rh(tpp)Pr (**3d**) [24] (6.7 mg, 0.0089 mmol, 75%) was purified and collected. Rh(tpp)Pr (**3d**). $R_f = 0.75$ (CH_2Cl_2:Hexane = 2:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ −4.96 (dt, 2H, $^2J_{Rh-H} = 3.7$ Hz, $^3J_{H-H} = 6.9$ Hz), −4.43 (sextet, 2H, $J = 7.8$ Hz), −1.72 (t, 3H, $J = 7.4$ Hz), 7.75 (m, 12H), 8.13 (d, 4H, $J = 6.9$ Hz), 8.20 (d, 4H, $J = 6.8$ Hz), 8.70 (s, 8H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 10.99, 17.98, 20.55, 122.58, 126.75, 127.72, 131.60, 133.90, 142.31, 143.25. HRMS Calcd for $C_{47}H_{35}N_4Rh$ 758.1911; Found, 758.1920. Butyl formate (**4a**) (76%) was observed in crude reaction mixture from GC/MS using naphthalene as internal standard.

Reaction of different Rh(ttp)I and different ethers with 5 equiv KOH, 200 equiv H_2O, 0.1 equiv Ph_4PBr at 60 °C for 1 day

i. Di-*n*-propyl ether. Rh(ttp)I (**1b**) (10.0 mg, 0.0111 mmol), KOH (3.29 mg, 0.0557 mmol), H_2O (40 μL, 2.22 μmol), Ph_4PBr (0.5 mg, 0.0012 mmol) and di-*n*-propyl ether (2.0 mL) were stirred at 60 °C under N_2 for 1 d. Reddish purple solid Rh(ttp)

Et (**7a**) [25] (2.67 mg, 0.0033 mmol, 30%) was purified and collected. Rh(ttp)Et (**7a**). $R_f = 0.75$ (CH_2Cl_2:Hexane = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ −4.85 (dq, 2H, $^2J_{Rh-H} = 2.9$ Hz, $^3J_{H-H} = 7.3$ Hz), −4.44 (t, 3H, $J = 6.4$ Hz), 2.69 (s, 12H), 7.52 (d, 4H, $J = 7.4$ Hz), 7.54 (d, 4H, $J = 7.3$ Hz), 8.00 (d, 4H, $J = 7.6$ Hz), 8.08 (d, 4H, $J = 7.3$ Hz), 8.71 (s, 8H). No organics were observed in GC–MS.

ii. Di-*n*-pentyl ether. Rh(ttp)I (**1b**) (10.0 mg, 0.0111 mmol), KOH (3.29 mg, 0.0557 mmol), H_2O (40 μL, 2.22 μmol), Ph_4PBr (0.5 mg, 0.0012 mmol) and di-*n*-pentyl ether (2.0 mL) were stirred at 60 °C under N_2 for 1 d. Reddish purple solid Rh(ttp)Bu (**7b**) [27] (6.99 mg, 0.0084 mmol, 76%) was purified and collected. Rh(ttp)Bu (**7b**). $R_f = 0.80$ (CH_2Cl_2:Hexane = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ −4.86 (dt, 2H, $^2J_{Rh-H} = 3.0$ Hz, $^3J_{H-H} = 8$ Hz), −4.45 (qu, 2H, $J = 7.4$ Hz), −1.53 (sextet, 2H, $J = 6.6$ Hz), −0.80 (t, 3H, $J = 7.3$ Hz), 2.71 (s, 12H), 7.54 (t, 8H, $J = 6.2$ Hz), 8.00 (d, 4H, $J = 6.2$ Hz), 8.08 (d, 4H, $J = 6.2$ Hz), 8.73 (s, 8H). Pentyl formate (**4b**) [8] (76%) was observed in crude reaction mixture from GC/MS using naphthalene as internal standard.

iii. Diisopropyl ether. Rh(ttp)I (**1b**) (10.0 mg, 0.0111 mmol), KOH (3.29 mg, 0.0557 mmol), H_2O (40 μL, 2.22 μmol), Ph_4PBr (0.5 mg, 0.0012 mmol) and diisopropyl ether (2.0 mL) were stirred at 60 °C under N_2 for 1 d. Reddish purple solid Rh(ttp)Me (**7c**) [25] (4.90 mg, 0.0062 mmol, 56%) was purified and collected. Rh(ttp)Me (**7c**). $R_f = 0.80$ (CH_2Cl_2:Hexane = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ −5.82 (s, 3H), 2.69 (s, 12H), 7.53 (t, 8H, $J = 5.4$ Hz), 8.00 (d, 4H, $J = 7.3$ Hz), 8.07 (d, 4H, $J = 7.3$ Hz), 8.72 (s, 8H). Isopropyl acetate (**4c**) [8] (29%) was observed in crude reaction mixture from GC/MS using naphthalene as internal standard.

Notes

The authors declare no competing financial interest.

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