

Base-Promoted, Selective Aliphatic Carbon–Carbon Bond Cleavage of Ethers by Rhodium(III) Porphyrin Complexes

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Summary: Base-promoted, selective aliphatic carbon(α)–carbon(β) bond activation (CCA) of ethers by (5,10,15,20-tetramesitylporphyrinato)rhodium(III) iodide was achieved.

Carbon–carbon bond activation (CCA) by late-transition-metal complexes is important and challenging in the field of organometallic chemistry.¹ Most examples involve ring-strained cubane,^{2a} cyclopropane,^{2b} cyclobutanone,^{2c} and biphenylene^{2d} or chelating substrates of pincer type ligands,^{2e,f} amine,^{2g} and cycloalkanone imine^{2h} with low-valent group 9 transition-metal complexes.

Examples with high-valent group 9 transition-metal complexes are still rarely documented. Bergman and co-workers have reported the activations of aliphatic nitrile bonds by rhodium(III) complexes^{3a,b} and cyclopropane carbon–carbon bonds by iridium(III) complexes,^{3c} respectively.

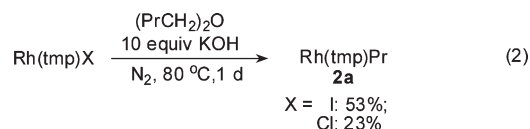
Additionally, the intermediate valency of rhodium(II) mesotetramesitylporphyrin Rh(tmp) is also known to activate the aliphatic carbon–carbon bonds of unstrained ketone,⁴ amide,⁵ ester,⁵ nitroxide,⁶ and nitrile.⁷

Recently, we have reported mild carbon–hydrogen bond activation (CHA) of benzaldehyde by using (5,10,15,20-tetratolylporphyrinato)(β -hydroxyethyl)rhodium(III) with a rhodium hydroxo porphyrin complex, Rh(ttp)(OH)–

(C₂H₄), as the proposed intermediate to afford the rhodium acyl porphyrin complexes.^{8a} In addition, the base-promoted benzylic CHA of toluenes^{8b} and CHA of alkane⁹ by rhodium(III) porphyrins have also been documented. Therefore, we sought to examine the reactivities of rhodium hydroxo porphyrin complexes by reacting Rh(tmp)I (**1a**) with KOH in ether solvents. To our delight, the unstrained, aliphatic C(α)–C(β) bonds of ethers were cleaved and the β -alkyl groups were transferred to rhodium porphyrins to yield Rh(tmp) alkyls. We now report the discovery of the new reactivity pattern in organometallic chemistry.

Initially, Rh(tmp)I reacted with *n*-butyl ether solvent at 40 °C in 1 day to give a low yield of 4% Rh(tmp)Pr as the selective C(α)–C(β) bond activation product (Table 1, entry 1). We then examined the promoting effect of bases (Table 1, eq 1). The weak base Cs₂CO₃ was not advantageous (Table 1, entry 2). Stronger bases such as KO^tBu, NaOMe, NaOH, and KOH were much more effective, with KOH producing the highest product yield (Table 1, entries 3–5 vs 7). A lower loading of KOH (5 equiv) gave a lower yield, while a higher loading (20 equiv) resulted in little enhancement over the use of 10 equiv (Table 1, entries 6 and 8). In benzene solvent, *n*-butyl ether (50 equiv) yielded less than 1% of Rh(tmp)Pr at 40 °C in 1 day. Therefore, base and neat ether are necessary.

The counteranion of Rh(tmp)X (X = I, Cl) strongly affected the yield of CCA (eq 2). In the presence of KOH (10 equiv), Rh(tmp)I gave Rh(tmp)Pr in 53% yield while Rh(tmp)Cl produced Rh(tmp)Pr in 23% yield. It is likely that Rh(tmp)I undergoes much more facile ligand substitution with KOH for further CCA reaction. Furthermore, Rh(tmp)Cl, being less soluble than Rh(tmp)I in ether, gave a lower CCA yield.



The reaction temperature for CCA of straight-chain ethers with Rh(tmp)I was varied from 40 to 100 °C (Table 2, eq 3). The lower yields for *n*-propyl ether as compared to those for *n*-butyl ether (Table 2, entries 1 and 2 vs 3–5) were due to the poorer solubility of Rh(tmp)I in *n*-propyl ether. The highest product yield was observed for the more soluble *n*-butyl ether in 86% yield at 100 °C (Table 2, entry 5). Therefore, the optimal reaction temperature was found to be 100 °C.

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Table 1. Base and Base Loading Effect in CCA

$$\text{Rh(tmp)I} \xrightarrow[\text{N}_2, 40^\circ\text{C}, 1\text{ d}]{\text{Base}} \text{Rh(tmp)Pr} \quad (1)$$

1a **2a**

entry	base	amt of base (equiv)	yield of 2a (%)
1			4
2	CS ₂ CO ₃	10	4
3	KO ^t Bu	10	22
4	NaOMe	10	20
5	NaOH	10	18
6	KOH	5	17
7	KOH	10	33
8	KOH	20	35

Table 2. Temperature Effect in CCA

$$\text{Rh(tmp)I} \xrightarrow[\text{N}_2, \text{Temp}, 1\text{ d}]{\text{(RCH}_2)_2\text{O}, 10\text{ equiv KOH}} \text{Rh(tmp)R} \quad (3)$$

1a **2a - 2b**

entry	(RCH ₂) ₂ O	temp (°C)	Rh(tmp)R	yield (%)
1	(EtCH ₂) ₂ O	40	Rh(tmp)Et (2b)	23
2	(EtCH ₂) ₂ O	80	Rh(tmp)Et (2b)	34
3	(PrCH ₂) ₂ O	40	Rh(tmp)Pr (2a)	33
4	(PrCH ₂) ₂ O	80	Rh(tmp)Pr (2a)	53
5	(PrCH ₂) ₂ O	100	Rh(tmp)Pr (2a)	86

To explore the substrate scope, various ethers were then investigated at 100 °C for 1 day with KOH (10 equiv) (Table 3, eq 4). The reactions were highly selective in the cleavage of C(α)–C(β) bonds of ethers to give Rh(tmp)R without any carbon–oxygen bond cleaved product of Rh(tmp)CH₂R. In general, linear ethers were more reactive than branched ones (Table 3, entries 2–5 vs 1 and 6) likely due to sterics. The steric effect is also evident in the activation of 2-ethoxyethyl ether (Table 3, entry 7). Even though the internal C(α)–C(β) bond is weaker than the terminal one by around 6 kcal/mol,¹⁰ only the terminal, least hindered C(α)–C(β) bond was cleaved to give Rh(tmp)Me, though in lower yield.

To gain an idea of the reaction mechanism, we monitored the progress of the reaction of Rh(tmp)I with *n*-butyl ether (50 equiv) and KOH (10 equiv) in benzene-*d*₆ at 100 °C by ¹H

(10) The internal C(α)–C(β) bond of 1,2-methoxyethane is 81 kcal/mol, while the C(α)–C(β) bond of ethyl methyl ether is 87 kcal/mol: Luo, Y. R. *Handbook of Bond Dissociation Energies in Organic Compounds*; CRC Press: Boca Raton, FL, 2003.

Table 3. CCA of Aliphatic Ethers

$$\text{Rh(tmp)I} \xrightarrow[\text{N}_2, 100^\circ\text{C}, 1\text{ d}]{\text{(RCH}_2)_2\text{O}, 10\text{ equiv KOH}} \text{Rh(tmp)R} \quad (4)$$

1a **2a - 2f**

entry	(RCH ₂) ₂ O	Rh(tmp)R	yield (%)
1	Me ₂ CHOCHMe ₂	Rh(tmp)Me (2c)	32
2	EtCH ₂ OCH ₂ Et	Rh(tmp)Et (2b)	30
3	PrCH ₂ OCH ₂ Pr	Rh(tmp)Pr (2a)	86
4	BuCH ₂ OCH ₂ Bu	Rh(tmp)Bu (2d)	88
5	PentCH ₂ OCH ₂ Pent	Rh(tmp)Pent (2e)	58
6	ⁱ BuCH ₂ OCH ₂ ⁱ Bu	Rh(tmp) ⁱ Bu (2f)	trace
7 ^a	(MeCH ₂ OCH ₂) ₂	Rh(tmp)Me (2c)	19

^a Conditions: N₂, 80 °C, 1 day.

NMR spectroscopy. After the complete consumption of Rh(tmp)I in 14 h, Rh(tmp)H (10%), Rh^{II}(tmp) (8%), and Rh(tmp)Pr (10%) were formed. Prolonged heating led to the disappearance of Rh(tmp)H and Rh^{II}(tmp) with a concomitant increase of Rh(tmp)Pr to 37% yield in 6 days. Therefore, Rh(tmp)H and Rh^{II}(tmp) are likely the intermediates. We then examined the reactivities of Rh(tmp)H and Rh^{II}(tmp) toward *n*-butyl ether separately. In the absence of KOH, both Rh(tmp)H and Rh^{II}(tmp) reacted with *n*-butyl ether at 100 °C in 1 day to give only 10% and 37% yields of Rh(tmp)Pr, respectively. However, in the presence of KOH (10 equiv), Rh(tmp)H and Rh^{II}(tmp) reacted with *n*-butyl ether at 100 °C in 1 day to give Rh(tmp)Pr in higher yields of 54% and 56%, respectively. We do not fully understand the mechanistic details at this moment. KOH may play an important roles in assisting the C–C bond cleavage step.

In conclusion, we have discovered the base-promoted, selective aliphatic C(α)–C(β) bond cleavage of ethers by Rh(tmp)I. Investigations of the scope and mechanistic details of rhodium porphyrin complexes in bond activation are ongoing.

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Supporting Information Available: Text and figures giving experimental details and characterization data for the compounds prepared in this paper. This material is available free of charge via the Internet at <http://pubs.acs.org>.