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Alkylation of Rhodium Porphyrin Complexes with Primary Alcohols under Basic Conditions

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ABSTRACT: Primary alcohols were successfully utilized as the alkylating reagents to conveniently access rhodium porphyrin alkyl complexes in up to 91% yields under basic conditions. Mechanistic investigations suggest two possible pathways for the C−O bond cleavage: (1) nucleophilic substitution with rhodium(I) porphyrin anion and (2) a borrowing hydrogen pathway via rhodium(III) porphyrin hydride.

$Rh^{III}(ttp)Cl + ROH \xrightarrow[PhCN,\ N_2,\ 120\ ^\circ C,\ 1\text{-}24\ h]{K_2CO_3\ (10\ equiv)} Rh^{III}(ttp)R$

R = 1° alkyl, benzyl — up to 91%

INTRODUCTION

Rhodium porphyrin alkyl complexes, $Rh^{III}(por)R$ (por = porphyrinato dianion ligand), are convenient and air-stable precursors to rhodium(II) porphyrin metalloradicals, which display distinct reactivity on C−H and C−C bond activation of various organic substrates under mild reaction conditions.[1,2] $Rh^{III}(ttp)R$ (ttp = 5,10,15,20-tetratolylporphyrinato dianion) has been used as a precatalyst in the catalytic transfer hydrogenation of [2.2]paracyclophane,[2d,e] catalytic anaerobic oxidation of ketones,[3] and hydrodebromination of allylic and benzylic bromides with water by hydrolysis or photolysis of the Rh−R bond.[4] Rhodium porphyrin alkyl complexes allow the access of air-sensitive intermediates from benchtop-stable materials for the activation of inert chemical bonds. The first systematic synthesis of rhodium porphyrin alkyl complexes was reported by Ogoshi in 1975.[5] $Rh^{III}(oep)Cl$ (oep = 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion) was first treated with $NaBH_4$ and aqueous NaOH in EtOH at 60 °C to first generate the $Rh^{I}(oep)^-$ anion. The $Rh^{I}(oep)^-$ anion then reacted with alkyl bromides or iodides, R−X (R = 1°, 2° alkyl, X = Br, I), to give the corresponding $Rh^{III}(oep)R$ via nucleophilic substitution (Scheme 1a). In 2014, Dong utilized tetraalkylammonium and alkylquinolinium salts as the alkylating agents for $Rh^{III}(tpp)Cl$ (tpp = tetraphenylporphyrinato dianion).[6] This air-tolerant transformation also takes advantage of the nucleophilicity of the $Rh^{I}(tpp)^-$ anion generated in situ under basic conditions. Our group has communicated the alkylation of $Rh^{III}(ttp)Cl$ with alkyl halides under basic conditions.[7] Both the $Rh^{II}(ttp)$ metalloradical and $Rh^{I}(ttp)^-$ anion generated in situ from $Rh^{III}(ttp)Cl$ are responsible for cleaving the alkyl R−X bond (X = Cl, Br, I) by halogen atom abstraction and nucleophilic substitution, respectively (Scheme 1c). This alkylation protocol gives access to $Rh^{III}(ttp)R$ with 1°, 2°, and even 3° alkyl ligands in air.

Alkyl alcohols are poor alkylating agents because direct nucleophilic substitution leads to hydroxide as a poor leaving group under neutral or basic conditions. We have previously disclosed the cleavage of the alkyl PhO−Me bond in anisole with $Rh^{I}(ttp)^-$ anion via a nucleophilic substitution process to give $Rh^{III}(ttp)Me$.[8] In this scenario phenoxide is the leaving group (pK_a of $Rh^{III}(ttp)H$ = 11 in DMSO, and pK_a of PhOH = 9.95 in H_2O).[9] Alternatively, the C−O bond is relatively strong with BDE values of 92.0 kcal/mol in Me−OH and 79.9 kcal/mol in $PhCH_2$−OH.[10] Our group has reported the C−O bond cleavage of MeOH with $Rh^{III}(ttp)Cl$ under basic conditions to give $Rh^{III}(ttp)Me$.[11] $Rh^{III}(ttp)H$ is proposed as the active intermediate and cleaves the C−O bond in MeOH via σ-bond metathesis to yield $Rh^{III}(ttp)Me$ and H_2O. Other C−O cleavage strategies involve the Lewis acid promoted S_N1-type nucleophilic reaction of alcohol,[12a] conversion of the hydroxy group into a better leaving group followed by substitution,[12b] and a borrowing hydrogen strategy.[12c] In this work, we have successfully expanded the scope of the alcohol from MeOH. Herein, we report the reaction of $Rh^{III}(ttp)Cl$ with primary alkyl alcohols under basic conditions to access a series of $Rh^{III}(ttp)R$ species in benzonitrile solvent as a result of C−O bond cleavage (Scheme 1d). Mechanistic investigations suggest that both $Rh^{III}(ttp)H$ and $Rh^{I}(ttp)^-$ anion are viable intermediates for the C−O cleavage.

RESULTS AND DISCUSSION

Initial Discovery. Initially, we employed the previously reported conditions[11] and examined the C−O cleavage of benzyl alcohol (**2a**) with $Rh^{III}(ttp)Cl$ (**1**). To our delight, $Rh^{III}(ttp)Cl$ (**1**) reacted with $PhCH_2OH$ (**2a**) in the presence of 10 equiv of K_2CO_3 under solventless conditions at 150 °C to afford the C−O cleavage product $Rh^{III}(ttp)CH_2Ph$ (**3a**) in 50% yield in 1 day (eq 1). We then further pursued the optimization of reaction conditions.

$$\underset{\mathbf{1}}{Rh^{III}(ttp)Cl} + \underset{\mathbf{2}}{PhCH_2OH} \xrightarrow[N_2,\ dark,\ 150\ ^\circ C,\ 24\ h]{K_2CO_3\ (10\ equiv)} \underset{\mathbf{3a},\ 50\%}{Rh^{III}(ttp)CH_2Ph} \quad (1)$$

Temperature Effects. The reaction temperature was first screened (Table 1). At lower reaction temperatures of 80 and

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Scheme 1. Alkylation of Rh^{III}(por)Cl To Give Rh^{III}(por)R

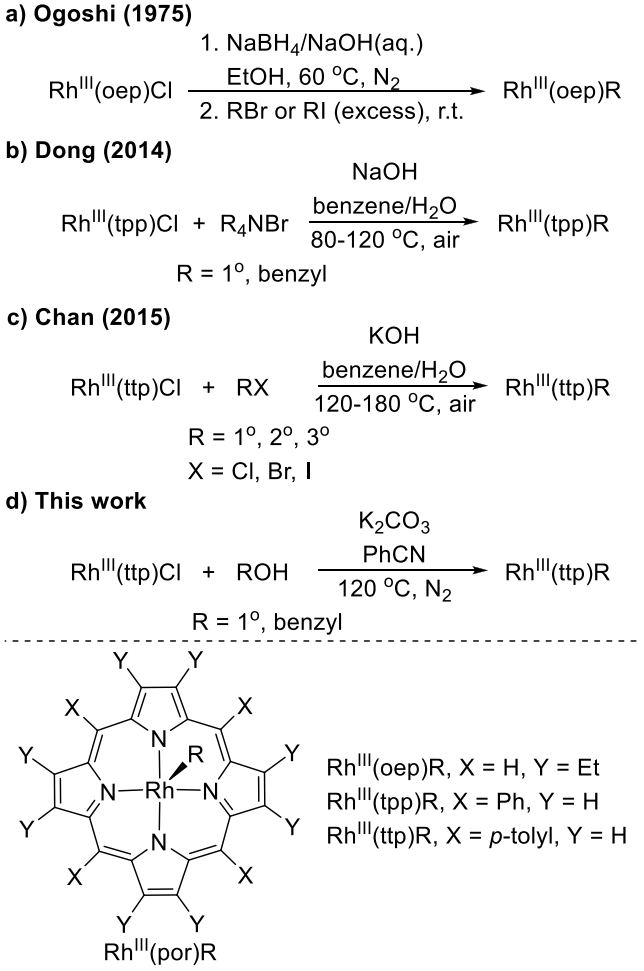
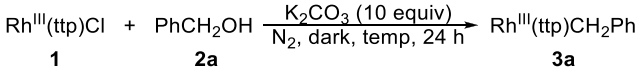


Table 1. Temperature Effects on the C−O Cleavage of Benzyl Alcohol



1 2a 3a

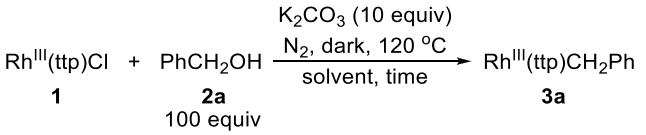
entry	temp/°C	yield/%[a]
1	80	19[b]
2	100	38[b]
3	120	85
4	150	50

[a]Isolated yield. [b]^{1}H NMR yield with DCE (1,2-dichloroethane) as the internal standard.

100 °C, Rh^{III}(ttp)CH_2Ph (**3a**) was produced in poor yields of 19% and 38%, respectively, after 1 day. Increasing the temperature to 120 °C afforded Rh^{III}(ttp)CH_2Ph (**3a**) in 85% yield. The reduction in product yield at 150 °C was probably due to the partial decomposition of Rh^{III}(ttp)CH_2Ph (**3a**) at elevated temperature. Therefore, 120 °C was chosen to be the optimal reaction temperature.

Solvent Effect. We then examined the use of various solvents to reduce the loading of benzyl alcohol (**2a**) from solventless to 100 equiv with respect to Rh^{III}(ttp)Cl (**1**) (Table 2). When isopropyl alcohol was used as the solvent, Rh^{III}(ttp)Bn (**3a**) was formed in 31% yield after 15 h (Table 2, entry 1). The yield was increased to 57% when the reaction time was prolonged to 24 h (Table 2, entry 2). There were

Table 2. Solvent Effects on the C−O Cleavage of Benzyl Alcohol



1 2a 3a
100 equiv

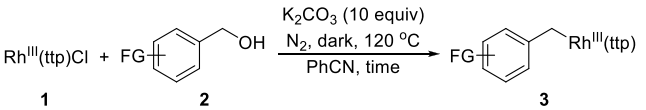
entry	solvent	time/h	yield/%[a]
1	^{i}PrOH	15	31
2	^{i}PrOH	24	57[b]
3	MeOH	24	<5[b,c]
4	EtOH	24	<5[b]
5	PhCN	2	88
6	PhCN	13	81[d]
7	CH_3CN	4	65
8	$HOCH_2CH_2OH$	24	36[b]
9	DMF	24	30
10	pyridine	24	<5[b]
11	CH_3NO_2	4	<5[b]

[a]Isolated yield, [b]^{1}H NMR yield. [c]A 28% yield of Rh^{III}(ttp)Me was isolated. [d]80 °C.

negligible yields of Rh^{III}(ttp)Bn (**3a**) when the reaction was conducted in methanol or ethanol solvent (Table 2, entries 3 and 4). The optimal result was obtained by employing benzonitrile as the solvent, and Rh^{III}(ttp)CH_2Ph (**3a**) was formed in 88% yield after 2 h (Table 2, entry 5). The reaction also proceeded smoothly at 80 °C in PhCN to give Rh^{III}(ttp)CH_2Ph (**3a**) in 81% yield in 13 h (Table 2, entry 6). Acetonitrile was a suitable solvent and afforded a 65% yield of **3a** in 4 h (Table 2, entry 7). Other polar solvents such as ethylene glycol, DMF, pyridine and nitromthane gave poor to negligible yields of Rh^{III}(ttp)CH_2Ph **3a** (Table 2, entries 8−11). At this stage we could not observe the clear relationships between product yields and solvent properties except that nitrile solvents were promising. Therefore, benzonitrile was chosen to be the optimal solvent for the screening of alcohol substrates.

Substrate Scope. Rh^{III}(ttp)Cl (**1**) reacted smoothly with electron-rich and electron-poor benzyl alcohols **2a−g** under the optimized reaction conditions to afford the corresponding C−O cleavage product Rh^{III}(ttp)$CH_2C_6H_4$(FG) (**3**) in good yields in 2−4 h (Table 3). 4-Fluoro- and 4-chloro-substituted

Table 3. Scope of Substituted Benzyl Alcohols



1 2 3
100 equiv

entry	FG	time/h	yield/%[a]
1	H (**2a**)	2	88 (**3a**)
2	4-F (**2b**)	2	81 (**3b**)
3	4-Cl (**2c**)	2	63 (**3c**)
5	4-CF_3 (**2d**)	3	65 (**3d**)
4	4-^{t}Bu (**2e**)	2	91 (**3e**)
5	4-Me (**2f**)	2	78 (**3f**)
6	2-Me (**2g**)	4	73 (**3g**)
7	4-OMe (**2h**)	2	62 (**3h**)
8	4-NO_2 (**2i**)	0.5	19 (**3i**)

[a]Isolated yield.

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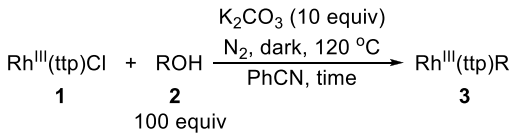
benzyl alcohols gave $Rh^{III}(ttp)CH_2C_6H_4(4\text{-}F)$ (**3b**(and $Rh^{III}(ttp)CH_2C_6H_4(4\text{-}Cl)$ (**3c**) in 81% and 63% yields, respectively (Table 3, entries 2 and 3). No C−F or C−Cl cleavage products were observed.[13] Alkylation of $Rh^{III}(ttp)Cl$ (**1**) with 4-trifluoromethylbenzyl alcohol (**2d**) successfully afforded $Rh^{III}(ttp)CH_2C_6H_4(4\text{-}CF_3)$ (**3d**) in 65% yield in 3 h. The reactions with benzyl alcohols bearing 4-^{t}Bu and 4-Me substituents were completed in 2 h to give $Rh^{III}(ttp)$-$CH_2C_6H_4(4\text{-}^tBu)$ (**3e**) and $Rh^{III}(ttp)CH_2C_6H_4(4\text{-}Me)$ (**3f**) in 81% and 63% yields, respectively (Table 3, entries 4 and 5). 2-Methylbenzyl alcohol (**2g**) required a longer reaction time of 4 h to yield 73% of $Rh^{III}(ttp)CH_2C_6H_4(2\text{-}Me)$ (**3g**) due to the steric hindrance. No benzylic C−H activation products were observed.[1d] Electron-rich *p*-methoxybenzyl alcohol (**2h**) underwent regioselective C−O cleavage to produce $Rh^{III}(ttp)$-$CH_2C_6H_4(4\text{-}OMe)$ (**3g**) in 62% yield in 2 h (Table 3, entry 6). *p*-Nitrobenzyl alcohol was a poor candidate and only led to a 19% yield of $Rh^{III}(ttp)CH_2C_6H_4(4\text{-}NO_2)$ (**3i**) presumably due to the reduction of the nitro group (Table 3, entry 7).[14]

To expand the synthetic utility of this alkylating protocol, we then explored the C−O cleavage reaction with other primary alkyl alcohols (Table 4). Under the optimized reaction

Table 4. Scope of Primary Alkyl Alcohols

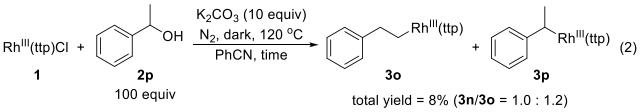


entry	R	time/h	yield/%[a]
1	Me (**2j**)	24	69 (**3j**)
2	Et (**2k**)	24	37 (**3k**)
3	^{n}Pr (**2l**)	24	12 (**3l**)
4	^{n}Bu (**2m**)	24	9 (**3m**)
5	$CNCH_2CH_2$ (**2n**)	1	63(**3n**)
6	2-phenylethyl (**2o**)	24	29 (**3o** + **3p**)[b]

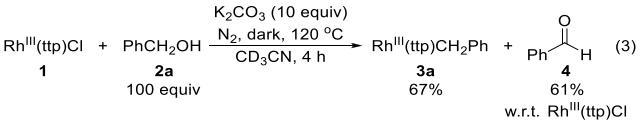
[a]Isolated yield. [b]$Rh^{III}(ttp)CH_2CH_2Ph$ (**3o**) and $Rh^{III}(ttp)CH(CH_3)$-Ph (**3p**) in a 2.2:1.0 ratio.

conditions, methanol (**2j**) without *β*-hydrogens reacted with $Rh^{III}(ttp)Cl$ (**1**) to afford the desired product $Rh^{III}(ttp)Me$ (**3j**) in 69% yield after 24 h (Table 4, entry 1). This yield is similar to that with the previously reported solventless conditions.[11] To our delight, the C−O cleavage of ethanol (**2k**) took place to give a 37% yield of $Rh^{III}(ttp)Et$ (**3k**) in 24 h (Table 4, entry 2). Both *n*-propanol (**2l**) and *n*-butanol (**2m**) were poor alkylating candidates to afford $Rh^{III}(ttp)^nPr$ (**3l**) and $Rh^{III}(ttp)^nBu$ (**3m**) in 12% and 9% yields, respectively (Table 4, entries 3 and 4). The low yields were presumably due to the product decomposition by the facile *β*-hydride elimination to give $Rh^{III}(ttp)H$ and gaseous olefins. To our delight, the cyano group in 2-cyanoethanol (**2n**) effectively suppressed the *β*-hydride elimination and afforded a 63% yield of $Rh^{III}(ttp)$-CH_2CH_2CN (**3n**) in 1 h (Table 4, entry 5). When 2-phenylethanol (**2o**) was employed as the substrate, a mixture of $Rh^{III}(ttp)CH_2CH_2Ph$ (**3o**) and $Rh^{III}(ttp)CH(CH_3)Ph$ (**3p**) was obtained in 29% total yield in a 2.2:1.0 ratio (Table 3, entry 6). The formation of $Rh^{III}(ttp)CH_2CH_2Ph$ (**3o**) can be accounted for by the C−O cleavage of 2-phenylethanol (**2o**), while the formation of branched $Rh^{III}(ttp)CH(CH_3)Ph$ (**3p**) is likely derived from the *β*-hydride elimination of $Rh^{III}(ttp)$-CH_2CH_2Ph (**3o**) to give $Rh^{III}(ttp)H$ and styrene followed by the reinsertion.[15]

To further examine whether this C−O cleavage protocol is applicable to secondary alcohols, the reaction of 1-phenylethanol (**2p**) with $Rh^{III}(ttp)Cl$ (**1**) was carried out. However, this reaction proceeded sluggishly to give the products $Rh^{III}(ttp)CH_2CH_2Ph$ (**3o**) and $Rh^{III}(ttp)CH(CH_3)Ph$ (**3p**) in 8% total yield with a **3o**:**3p** ratio of 1.0:1.2 (eq 2). Therefore, we did not pursue other secondary alcohols.



Mechanistic Studies. It has been reported that $Rh^{III}(ttp)$Cl readily reacts with K_2CO_3 to give $Rh^{III}(ttp)CO_3K$ via ligand substitution in MeOH,[11] and we proposed that it is the same case in benzonitrile solvent, given its polar nature. $Rh^{III}(ttp)$-CO_3K might then react with $PhCH_2OH$ to give $Rh^{III}(ttp)$-OCH_2Ph. Alternatively, deprotonation of coordinated benzyl alcohol gives $Rh^{III}(ttp)OCH_2Ph$ as well (pK_a of $PhCH_2OH$ = 15.4). $Rh^{III}(ttp)OCH_2Ph$ then converts to $Rh^{III}(ttp)H$ and benzaldehyde via *β*-H elimination,[16] in a pathway analogous to that proposed in the C−O activation of MeOH. To probe this possibility, we attempted to detect any organic coproducts formed in the C−O cleavage of benzyl alcohol. The reaction of $Rh^{III}(ttp)Cl$ (**1**) with 100 equiv of $PhCH_2OH$ (**2a**) and 10 equiv of K_2CO_3 was conducted in CD_3CN at 120 °C. The reaction gave $Rh^{III}(ttp)CH_2Ph$ (**3a**) in 67% yield and benzaldehyde (**4**) in 61% yield with respect to $Rh^{III}(ttp)Cl$ (**1**) (eq 3). This suggests that the benzyl alcohol plays a dual



role in the reaction: as a reductant for $Rh^{III}(ttp)Cl$ (**1**) to $Rh^{III}(ttp)H$ via an analogous $Rh^{III}(ttp)OCH_2Ph$ intermediate and as an alkylating agent. Therefore, the reaction stoichiometry for benzyl alcohol (**2a**) and $Rh^{III}(ttp)Cl$ (**1**) is 2:1.

In principle, $Rh^{III}(ttp)H$ generated from the reduction of $Rh^{III}(ttp)Cl$ could be deprotonated by K_2CO_3 to give an equilibrium mixture of $Rh^{I}(ttp)^-$ anion and $Rh^{III}(ttp)H$ (pK_a of $Rh^{III}(ttp)H$ = 11 in DMSO and pK_a of $KHCO_3$ = 10.25 in H_2O).[17] To identify which species is the active intermediate for C−O cleavage, independent reactions between benzyl alcohol and $Rh^{III}(ttp)H$ with and without K_2CO_3 were performed.

In the absence of K_2CO_3, $Rh^{III}(ttp)H$ (**5**) reacted with 100 equiv of benzyl alcohol (**2a**) in CD_3CN at 120 °C for 4 h to give only a trace amount of $Rh^{III}(ttp)CH_2Ph$ (**3a**) (Scheme 2a). Therefore, $Rh^{III}(ttp)H$ (**5**) is unlikely the active intermediate for the C−O bond cleavage. The lack of reaction is likely due to the formation of coordinatively saturated $(CD_3CN)Rh^{III}(ttp)H$. At the same time, $Rh^{III}(ttp)H$ underwent dehydrogenation to give $[Rh^{II}(ttp)]_2$,[18] which is in thermal equilibrium with the $Rh^{II}(ttp)$ metalloradical (BDE of Rh−Rh = 12 kcal/mol).[19] The estimated equilibrium constant at 120 °C is 1.53 M. Therefore, the direct cleavage of the C−O bond in benzyl alcohol by $[Rh^{II}(ttp)]_2$ or $Rh^{II}(ttp)$ metal-

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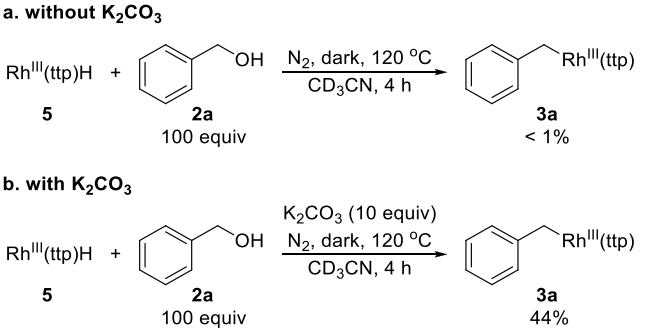
Scheme 2. Reactivity of Rh^{III}(ttp)H toward C−O Bond Cleavage

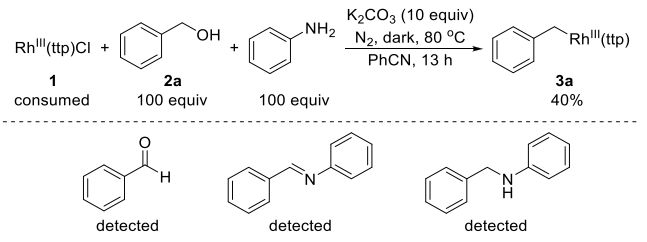


loradical is unlikely as well, in agreement with the estimated endothermicity of about 8.8 kcal/mol.[20]

When 10 equiv of K_2CO_3 was added into the reaction mixture containing Rh^{III}(ttp)H (**5**) and benzyl alcohol (**2a**) in CD_3CN to generate $Rh^{I}(ttp)^-$ in situ, $Rh^{III}(ttp)CH_2Ph$ (**3a**) was formed in 44% yield after heating at 120 °C for 4 h (Scheme 2b). These results point to two possible mechanistic possibilities: (1) $Rh^{I}(ttp)^-$ anion is responsible for the direct C−O cleavage of benzyl alcohol, likely via nucleophilic substitution and (2) K_2CO_3 is essential and plays a promoting role in the C−O cleavage reaction with Rh^{III}(ttp)H. We favor the latter mechanistic proposal over the former because the direct nucleophilic substitution of alcohol with a nucleophile weaker than hydroxide is unlikely to be feasible under basic conditions.

We reason that, in addition to the nucleophilic substitution with $Rh^{I}(ttp)^-$ anion, other K_2CO_3-dependent C−O cleavage pathways were concurrently operating. We examined the C−O cleavage of benzyl alcohol in the presence of aniline to probe whether the borrowing hydrogen pathway was operating. When Rh^{III}(ttp)Cl (**1**) was treated with 100 equiv of $PhCH_2OH$ (**2a**) and 100 equiv of $PhNH_2$ at 80 °C for 13 h, $Rh^{III}(ttp)CH_2Ph$ (**3a**) was isolated in 40% yield (Scheme 3).

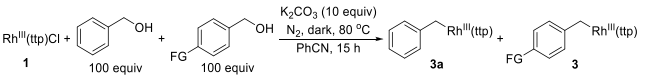
Scheme 3. Probing for the Borrowing Hydrogen Mechanism



Analysis of the reaction aliquot with GC-MS revealed the formation of benzaldehyde, *N*-benzylideneaniline, and *N*-benzylaniline. The formation of *N*-benzylideneaniline is accounted for by the condensation of benzaldehyde with aniline with the elimination of H_2O. Subsequently, hydrogenation of *N*-benzylideneaniline can yield *N*-benzylaniline. The observation of all these organic coproducts suggests that the borrowing hydrogen pathway is likely operating for the C−O cleavage reaction.

Finally, to gain some mechanistic insights from the electronic effects of C−O bond cleavage in para-substituted benzyl alcohols, competition experiments using an equimolar ratio of benzyl alcohol and para-substituted benzyl alcohol with Rh^{III}(ttp)Cl were carried out (Table 5). The Hammett plot from these experiments shows that both electron-donating and

Table 5. Competition Experiment of C−O Activation



			yield/%[a]		
entry	FG	σ_p	**3a**	**3**	$\log(k_{FG}/k_H)$
1	OMe	−0.27	23	66	0.45
2	Me	−0.17	40	53	0.12
3	H	0	81		
4	F	0.06	27	63	0.38
5	Cl	0.23	15	44	0.46
6	CF_3	0.54	20	70	0.54

[a]NMR yield.

-withdrawing substituents promoted the rate of C−O cleavage (Figure 1). Due to the different sensitivities of each reaction

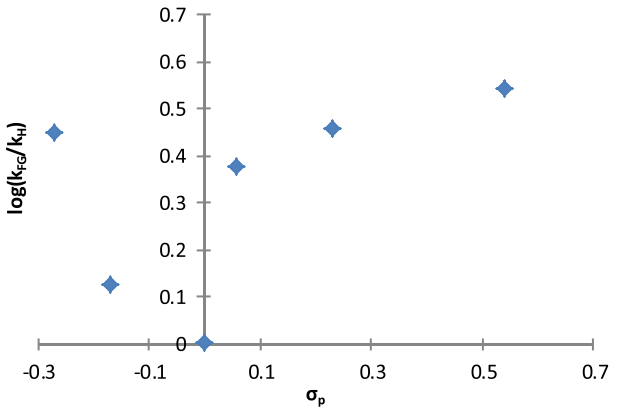


Figure 1. Hammett plot of C−O cleavage of benzyl alcohols using the Hammett constant σ_p.

step to the electronic effects and the possibilities of two C−O bond activation pathways, this concave upward Hammett plot could not be interpreted easily.

On the basis of the previous studies on C−O cleavage of MeOH[11] and current experimental findings, Scheme 4 illustrates the proposed mechanism of C−O bond cleavage in primary alcohols using benzyl alcohol as an example. Initially, K_2CO_3 deprotonates benzyl alcohol to generate a small amount of $PhCH_2O^-$ anion, which reacts with Rh^{III}(ttp)Cl via ligand substitution to give the $Rh^{III}(ttp)OCH_2Ph$ intermediate. Alternatively, $Rh^{III}(ttp)OCH_2Ph$ can be produced from the ligand substitution of Rh^{III}(ttp)Cl with K_2CO_3 followed by the reaction with benzyl alcohol. Then $Rh^{III}(ttp)OCH_2Ph$ undergoes β-H elimination to yield Rh^{III}(ttp)H and benzaldehyde.[16] In PhCN solvent, $(PhCN)Rh^{III}(ttp)^-$ anion is rapidly produced from the deprotonation of Rh^{III}(ttp)H by K_2CO_3 followed by the solvent ligation (pK_a of Rh^{III}(ttp)H = 11 in DMSO and pK_a of $KHCO_3$ = 10.25 in H_2O). The $(PhCN)Rh^{III}(ttp)^-$ anion is more nucleophilic than the $Rh^{I}(ttp)^-$ anion.[21] Then, $(PhCN)Rh^{I}(ttp)^-$ attacks the carbonyl carbon of benzaldehyde, which leads to the α-hydroxyalkyl complex $Rh^{III}(ttp)CH(OH)Ph$ upon protonation.[17,22] $Rh^{III}(ttp)CH(OH)Ph$ is then reduced by Rh^{III}(ttp)H to afford the final product $Rh^{III}(ttp)CH_2Ph$ (**3a**) and

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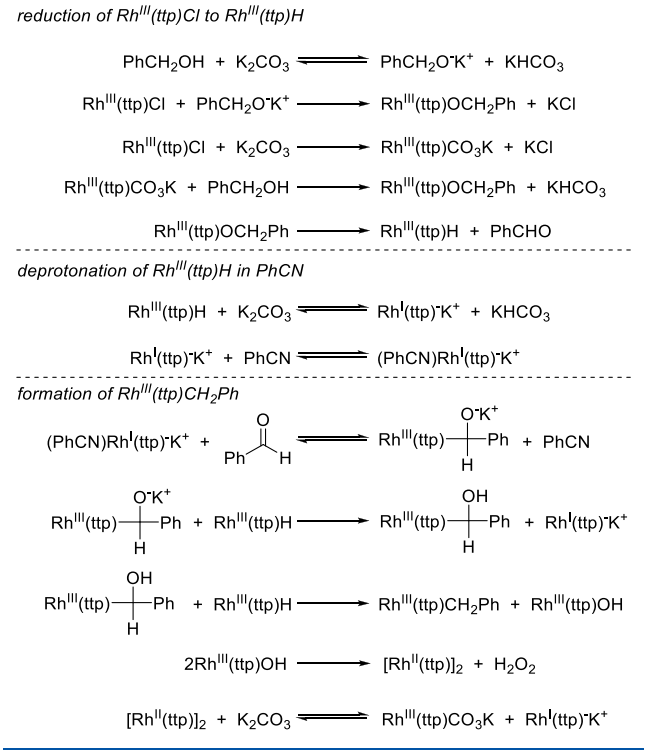
Scheme 4. Proposed Reaction Mechanism



Rh^{III}(ttp)OH, likely via σ-bond metathesis. Rh^{III}(ttp)OH then undergoes rapid reductive dimerization to produce $[Rh^{II}(ttp)]_2$ and H_2O_2 at 120 °C.[23] Under basic conditions and polar medium, K_2CO_3 promotes the conversion of $[Rh^{II}(ttp)]_2$ to $Rh^{I}(ttp)^{-}K^{+}$ anion and $Rh^{III}(ttp)CO_3K$,[24] which can participate in the C−O cleavage reaction. At the same time, H_2O_2 is decomposed rapidly to H_2O and O_2.[25] We do not consider the direct nucleophilic substitution pathway because hydroxide is a very poor leaving group.

CONCLUSION

In summary, Rh^{III}(ttp)Cl reacted with primary alcohols at 80−120 °C in the presence of base to give moderate to good yields of Rh^{III}(ttp)(alkyl) complexes in PhCN. Mechanistic studies suggest that the base-promoted borrowing hydrogen pathway with Rh^{III}(ttp)H as the key intermediate is operating. Further studies to look for more evidence for the nucleophilic substitution pathway 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 (TLC) was performed on precoated silica gel 60 F_{254} plates. Silica gel (Merck, 70−230 mesh) was used for column chromatography. All reactions were protected from light by wrapping with aluminum foil. The reaction mixtures in Teflon screw-capped pressure tubes were heated in heating blocks on heaters and monitored by TLC. Rh^{III}(ttp)Cl (**1**)[26] and Rh^{III}(ttp)H (**5**)[17] have been characterized and were prepared according to the literature process.

^{1}H NMR spectra were recorded on a Bruker AV400 instrument at 400 MHz. Chemical shifts were referenced with the residual solvent protons in $CDCl_3$ (δ 7.26 ppm) and CD_3CN (δ 1.94 ppm). Unless otherwise specified, the coupling constant J refers to H−H coupling.

Reaction of Rh^{III}(ttp)Cl and Benzyl Alcohol with K_2CO_3 at 150 °C. In a Teflon screw-capped tube, a mixture of Rh^{III}(ttp)Cl (**1**) (20.2 mg, 0.025 mmol), K_2CO_3 (34.5 mg, 0.25 mmol) and benzyl alcohol (**2a**) (3.0 mL) was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 150 °C for 24 h. After the excess benzyl alcohol was removed by vacuum distillation, the mixture was worked up by extraction with CH_2Cl_2 and H_2O. The organic extract was dried by anhydrous Na_2SO_4, filtered, and rotary evaporated. The red residue was purified by column chromatography over silica gel with a solvent mixture of hexane/CH_2Cl_2 (1/1) as eluent to give Rh^{III}(ttp)Bn (**3a**)[1d] (10.7 mg, 0.013 mmol, 50%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ −3.77 (d, 2 H, $^3J_{Rh-H}$ = 3.7 Hz), 2.72 (s, 12 H), 2.98 (d, 2 H, J = 7.5 Hz), 5.89 (t, 2 H, J = 7.6 Hz), 6.43 (t, 1 H, J = 7.3 Hz), 7.56 (t, 8 H, J = 6.4 Hz), 8.02 (d, 4 H, J = 7.0 Hz), 8.09 (d, 4 H, J = 6.8 Hz), 8.69 (s, 8 H).

Reaction of Rh^{III}(ttp)Cl and Benzyl Alcohol with K_2CO_3 at 120 °C. In a Teflon screw-capped tube, a mixture of Rh^{III}(ttp)Cl (**1**) (20.2 mg, 0.025 mmol), K_2CO_3 (34.5 mg, 0.25 mmol) and benzyl alcohol (**2a**) (3.0 mL) was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 24 h. After the excess benzyl alcohol was removed by vacuum distillation, the mixture was worked up by extraction with CH_2Cl_2 and H_2O. The organic extract was dried by anhydrous Na_2SO_4, filtered, and rotary evaporated. The residue was washed twice with hexane to give Rh^{III}(ttp)Bn (**3a**) (18.4 mg, 0.021 mmol, 85%).

Reaction of Rh^{III}(ttp)Cl and Benzyl Alcohol with K_2CO_3 at 100 °C. In a Teflon screw-capped tube, a mixture of Rh^{III}(ttp)Cl (**1**) (20.2 mg, 0.025 mmol), K_2CO_3 (34.5 mg, 0.25 mmol) and benzyl alcohol (**2a**) (3.0 mL) was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 100 °C for 24 h. After the excess benzyl alcohol was removed by vacuum distillation, the mixture was worked up by extraction with CH_2Cl_2 and H_2O. The organic extract was dried by anhydrous Na_2SO_4, filtered, and rotary evaporated. Then $CDCl_3$ and a smaller amount of 1,2-dichloroethane (DCE) were added to measure the NMR yield of Rh^{III}(ttp)Bn (**3a**) (38%).

Reaction of Rh^{III}(ttp)Cl and Benzyl Alcohol with K_2CO_3 at 80 °C. In a Teflon screw-capped tube, a mixture of Rh^{III}(ttp)Cl (**1**) (20.2 mg, 0.025 mmol), K_2CO_3 (34.5 mg, 0.25 mmol), and benzyl alcohol (**2a**) (3.0 mL) was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 100 °C for 24 h. After the excess benzyl alcohol was removed by vacuum distillation, the mixture was worked up by extraction with CH_2Cl_2 and H_2O. The organic extract was dried by anhydrous Na_2SO_4, filtered, and rotary evaporated. Then $CDCl_3$ and a smaller amount of 1,2-dichloroethane (DCE) were added to measure the NMR yield of Rh^{III}(ttp)Bn (**3a**) (19%).

Reaction of Rh^{III}(ttp)Cl and Benzyl Alcohol with K_2CO_3 in Isopropyl Alcohol for 15 h. Rh^{III}(ttp)Cl (**1**) (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and benzyl alcohol (**2a**) (135.2 mg, 1.25 mmol) were added to isopropyl alcohol (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 15 h. After the isopropyl alcohol was removed by vacuum distillation, the mixture was worked up by extraction with CH_2Cl_2 and H_2O. The organic extract was dried by anhydrous Na_2SO_4, filtered, and rotary evaporated. The residue was purified by column chromatography over silica gel with a solvent mixture of hexane/CH_2Cl_2 (1/1) as eluent to give Rh^{III}(ttp)Bn (**3a**) (3.3 mg, 0.0038 mmol, 31%).

Reaction of Rh^{III}(ttp)Cl and Benzyl Alcohol with K_2CO_3 in Isopropyl Alcohol for 24 h. Rh^{III}(ttp)Cl (**1**) (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and benzyl alcohol (**2a**; 135.2 mg, 1.25 mmol) were added to isopropyl alcohol (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 24 h. After the isopropyl alcohol was removed by vacuum distillation, the mixture was worked up by extraction with CH_2Cl_2 and H_2O. The organic extract was dried by anhydrous Na_2SO_4, filtered, and rotary evaporated. The residue was purified by column chromatography over silica gel with a solvent mixture of hexane/CH_2Cl_2 (1/1) as eluent to give Rh^{III}(ttp)Bn (**3a**) (6.1 mg, 0.0071 mmol, 57%).

Reaction of Rh^{III}(ttp)Cl and 50 equiv of Benzyl Alcohol with K_2CO_3 in Isopropyl Alcohol. Rh^{III}(ttp)Cl (**1**) (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and benzyl alcohol (**2a**) (67.5 mg, 0.625 mmol) were added to isopropyl alcohol (1.5 mL) in a

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Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 24 h. After the isopropyl alcohol was removed by vacuum distillation, the mixture was worked up by extraction with CH_2Cl_2 and H_2O. The organic extract was dried by anhydrous Na_2SO_4, filtered, and rotary evaporated. Then $CDCl_3$ and a smaller amount of DCE were added to measure the NMR yield of Rh^{III}(ttp)Bn (**3a**) (38%).

Reaction of Rh^{III}(ttp)Cl and 10 equiv of Benzyl Alcohol with K_2CO_3 in Isopropyl Alcohol. Rh^{III}(ttp)Cl (**1**) (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and benzyl alcohol (**2a**) (13.5 mg, 0.125 mmol) were added to isopropyl alcohol (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 24 h. After the isopropyl alcohol was removed by vacuum distillation, the mixture was worked up by extraction with CH_2Cl_2 and H_2O. The organic extract was dried by anhydrous Na_2SO_4, filtered, and rotary evaporated. Then $CDCl_3$ and a smaller amount of DCE were added to measure the NMR yield of Rh^{III}(ttp)Bn (**3a**) (9%).

Reaction of Rh^{III}(ttp)Cl and Benzyl Alcohol with K_2CO_3 in Methanol. Rh^{III}(ttp)Cl (**1**) (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and benzyl alcohol (**2a**) (135.2 mg, 1.25 mmol) were added to methanol (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 24 h. After the methanol was removed by vacuum distillation, the mixture was worked up by extraction with CH_2Cl_2 and H_2O. The organic extract was dried by anhydrous Na_2SO_4, filtered, and rotary evaporated. Then $CDCl_3$ and a smaller amount of DCE were added to measure the NMR yield of Rh^{III}(ttp)Bn (**3a**) (<5%).

Reaction of Rh^{III}(ttp)Cl and Benzyl Alcohol with K_2CO_3 in Ethanol. Rh^{III}(ttp)Cl (**1**) (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and benzyl alcohol (**2a**) (135.2 mg, 1.25 mmol) were added to ethanol (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 24 h. After the ethanol was removed by vacuum distillation, the mixture was worked up by extraction with CH_2Cl_2 and H_2O. The organic extract was dried by anhydrous Na_2SO_4, filtered, and rotary evaporated. Then $CDCl_3$ and a smaller amount of DCE were added to measure the NMR yield of Rh^{III}(ttp)Bn (**3a**) (<5%).

Reaction of Rh^{III}(ttp)Cl and Benzyl Alcohol with K_2CO_3 in Benzonitrile. Rh^{III}(ttp)Cl (**1**) (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and benzyl alcohol (**2a**) (135.2 mg, 1.25 mmol) were added to benzonitrile (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 2 h. After the benzonitrile was removed by vacuum distillation, the mixture was worked up by extraction with CH_2Cl_2 and H_2O. The organic extract was dried by anhydrous Na_2SO_4, filtered, and rotary evaporated. The residue was purified by column chromatography over silica gel with a solvent mixture of hexane/CH_2Cl_2 (1/1) as eluent to give Rh^{III}(ttp)Bn (**3a**) (9.5 mg, 0.011 mmol, 88%).

Reaction of Rh^{III}(ttp)Cl and Benzyl Alcohol with K_2CO_3 in Benzonitrile at 80 °C. Rh^{III}(ttp)Cl (**1**) (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and benzyl alcohol (**2a**) (135.2 mg, 1.25 mmol) were added to benzonitrile (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 80 °C for 13 h. After the benzonitrile was removed by vacuum distillation, the mixture was worked up by extraction with CH_2Cl_2 and H_2O. The organic extract was dried by anhydrous Na_2SO_4, filtered, and rotary evaporated. The residue was purified by column chromatography over silica gel with a solvent mixture of hexane/CH_2Cl_2 (1/1) as eluent to give Rh^{III}(ttp)Bn (**3a**) (8.7 mg, 0.010 mmol, 81%).

Reaction of Rh^{III}(ttp)Cl and Benzyl Alcohol with K_2CO_3 in Acetonitrile. Rh^{III}(ttp)Cl (**1**) (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and benzyl alcohol (**2a**) (135.2 mg, 1.25 mmol) were added to acetonitrile (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 4 h. After the acetonitrile and excess benzyl alcohol were removed by vacuum distillation, the mixture was worked up by extraction with CH_2Cl_2 and H_2O. The organic extract was dried by anhydrous Na_2SO_4, filtered, and rotary evaporated. The residue was purified by column chromatography over silica gel with a solvent mixture of hexane/CH_2Cl_2 (1/1) as eluent to give Rh^{III}(ttp)Bn (**3a**) (7.0 mg, 0.008 mmol, 65%).

Reaction of Rh^{III}(ttp)Cl and Benzyl Alcohol with K_2CO_3 in Ethylene Glycol. Rh^{III}(ttp)Cl (**1**) (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and benzyl alcohol (**2a**) (135.2 mg, 1.25 mmol) were added to ethylene glycol (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 24 h. After the ethylene glycol and excess benzyl alcohol were removed by vacuum distillation, the mixture was worked up by extraction with CH_2Cl_2 and H_2O. The organic extract was dried by anhydrous Na_2SO_4, filtered, and rotary evaporated. Then $CDCl_3$ and a smaller amount of DCE were added to measure the NMR yield of Rh^{III}(ttp)Bn (**3a**) (36%).

Reaction of Rh^{III}(ttp)Cl and Benzyl Alcohol with K_2CO_3 in Pyridine. Rh^{III}(ttp)Cl (**1**) (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and benzyl alcohol (**2a**) (135.2 mg, 1.25 mmol) were added to pyridine (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 24 h. After the pyridine and excess benzyl alcohol were removed by vacuum distillation, the mixture was worked up by extraction with CH_2Cl_2 and H_2O. The organic extract was dried by anhydrous Na_2SO_4, filtered, and rotary evaporated. Then $CDCl_3$ and a smaller amount of DCE were added to measure the NMR yield of Rh^{III}(ttp)Bn (**3a**) (<5%).

Reaction of Rh^{III}(ttp)Cl and Benzyl Alcohol with K_2CO_3 in *N*,*N*-Dimethylformamide. Rh^{III}(ttp)Cl (**1**) (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and benzyl alcohol (**2a**) (135.2 mg, 1.25 mmol) were added to DMF (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 24 h. After DMF and excess benzyl alcohol were removed by vacuum distillation, the mixture was worked up by extraction with CH_2Cl_2 and H_2O. The organic extract was dried by anhydrous Na_2SO_4, filtered, and rotary evaporated. The residue was purified by column chromatography over silica gel with a solvent mixture of hexane/CH_2Cl_2 (1/1) as eluent to give Rh^{III}(ttp)Bn (**3a**) (3.2 mg, 0.0037 mmol, 30%).

Reaction of Rh^{III}(ttp)Cl and Benzyl Alcohol with K_2CO_3 in Nitroethane. Rh^{III}(ttp)Cl (**1**) (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and benzyl alcohol (**2a**) (135.2 mg, 1.25 mmol) were added to nitroethane (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 4 h. After nitroethane and excess benzyl alcohol were removed by vacuum distillation, the mixture as worked up by extraction with CH_2Cl_2 and H_2O. The organic extract was dried by anhydrous Na_2SO_4, filtered, and rotary evaporated. Then $CDCl_3$ and a smaller amount of DCE were added to measure the NMR yield of Rh^{III}(ttp)Bn (**3a**) (<5%).

Reaction of Rh^{III}(ttp)Cl and 4-Fluorobenzyl Alcohol. Rh^{III}(ttp)Cl (**1**) (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and 4-fluorobenzyl alcohol (**2b**) (157.7 mg, 1.25 mmol) were added to benzonitrile (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 2 h. After benzonitrile and excess 4-fluorobenzyl alcohol were removed by vacuum distillation, the residue was quickly purified by column chromatography over silica gel with a solvent mixture of hexane/CH_2Cl_2 (1/1) as eluent to give Rh^{III}(ttp)Bn(4-F) (**3b**)[1d] (8.9 mg, 0.0101 mmol, 81%). R_f = 0.60 (hexane/CH_2Cl_2 = 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ −3.81 (d, 2 H, $^3J_{Rh-H}$ = 3.7 Hz), 2.73 (s, 12 H), 2.93−2.89 (m, 2 H), 5.57 (t, 2 H, J = 8.7 Hz), 7.58 (t, 8 H, J = 7.9 Hz), 8.00 (dd, 4 H, J = 7.5, 1.6 Hz), 8.09 (dd, 4 H, J = 7.5, 1.6 Hz), 8.71 (s, 8 H).

Reaction of Rh^{III}(ttp)Cl and 4-Chlorobenzyl Alcohol. Rh^{III}(ttp)Cl (**1**) (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and 4-chlorobenzyl alcohol (**2c**) (178.2 mg, 1.25 mmol) were added to benzonitrile (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 2 h. After benzonitrile was removed by vacuum

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distillation, the residue was quickly purified by column chromatography over silica gel with a solvent mixture of hexane/CH_2Cl_2 (1/1) as eluent to give Rh^{III}(ttp)Bn(4-Cl) **3c**[1d] (7.1 mg, 0.0079 mmol, 63%). R_f = 0.58 (hexane/CH_2Cl_2 = 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ −3.74 (d, 2 H, $^3J_{Rh-H}$ = 3.7 Hz), 2.73 (s, 12 H), 2.90 (d, 2 H, J = 7.9 Hz), 5.68 (d, 2 H, J = 7.8 Hz), 7.56 (t, 8 H, J = 11.2 Hz), 8.00−7.97 (m, 4 H), 8.10−8.07 (m, 4 H), 8.69 (s, 8 H).

Reaction of Rh^{III}(ttp)Cl and 4-Trifluoromethylbenzyl Alcohol. Rh^{III}(ttp)Cl (**1**) (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol) and 4-trifluoromethylbenzyl alcohol (**2d**) (220.2 mg, 1.25 mmol) were added to benzonitrile (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 3 h. After benzonitrile was removed by vacuum distillation, the residue was quickly purified by column chromatography over silica gel with a solvent mixture of hexane/CH_2Cl_2 (1/1) as eluent to give Rh^{III}(ttp)Bn(4-CF_3) **3d**[1d] (7.6 mg, 0.0081 mmol, 65%). R_f = 0.58 (hexane/CH_2Cl_2 = 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ −3.82 (d, 2 H, $^3J_{Rh-H}$ = 4.0 Hz), 2.71 (s, 12 H), 2.96 (d, 2 H, J = 8.0 Hz), 6.08 (d, 2 H, J = 8.1 Hz), 7.54 (d, 4 H, J = 7.8 Hz), 7.55 (d, 4 H, J = 7.6 Hz), 7.94 (d, 4 H, J = 8.0 Hz), 8.05 (d, 4 H, J = 8.0 Hz), 8.70 (s, 8 H).

Reaction of Rh^{III}(ttp)Cl and 4-*tert*-Butylbenzyl Alcohol. Rh^{III}(ttp)Cl (**1**) (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and 4-*tert*-butylbenzyl alcohol (**2e**) (205.3 mg, 1.25 mmol) were added to benzonitrile (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 2 h. After benzonitrile was removed by vacuum distillation, the residue was quickly purified by column chromatography over silica gel with a solvent mixture of hexane/CH_2Cl_2 (1/1) as eluent to give Rh^{III}(ttp)Bn(4-^{t}Bu)[1d] (**3e**) (10.5 mg, 0.0114 mmol, 91%). R_f = 0.77 (hexane/CH_2Cl_2 = 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ −3.75 (d, 2 H, $^3J_{Rh-H}$ = 3.7 Hz), 0.99 (s, 9 H), 2.73 (s, 12 H), 2.97 (d, 2 H, J = 8.2 Hz), 5.92 (d, 2 H, J = 8.2 Hz), 7.57 (t, 8 H, J = 6.6 Hz), 8.10−8.05 (m, 8 H), 8.68 (s, 8 H).

Reaction of Rh^{III}(ttp)Cl and 4-Methylbenzyl Alcohol. Rh^{III}(ttp)Cl (**1**) (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and 4-methylbenzyl alcohol (**2f**) (152.5 mg, 1.25 mmol) were added to benzonitrile (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 2 h. After benzonitrile was removed by vacuum distillation, the residue was quickly purified by column chromatography over silica gel with a solvent mixture of hexane/CH_2Cl_2 (1/1) as eluent to give Rh^{III}(ttp)Bn(4-Me) (**3f**)[1d] (8.5 mg, 0.0093 mmol, 78%). R_f = 0.72 (hexane/CH_2Cl_2 = 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ −3.74 (d, 2 H, $^3J_{Rh-H}$ = 3.7 Hz), 1.71 (s, 3 H), 2.73 (s, 12 H), 2.90 (d, 2 H, J = 7.9 Hz), 5.68 (d, 2 H, J = 7.8 Hz), 7.57 (t, 8 H, J = 5.8 Hz), 8.02−7.98 (m, 4 H), 8.11−8.08 (m, 4 H), 8.70 (s, 8 H).

Reaction of Rh^{III}(ttp)Cl and 2-Methylbenzyl Alcohol. Rh^{III}(ttp)Cl (**1**) (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and 2-methylbenzyl alcohol (**2g**) (152.5 mg, 1.25 mmol) were added into benzonitrile (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 4 h. After benzonitrile was removed by vacuum distillation, the residue was quickly purified by column chromatography over silica gel with a solvent mixture of hexane/CH_2Cl_2 (1/1) as eluent to give Rh^{III}(ttp)Bn(2-CH_3) (**3g**)[1d] (8.0 mg, 0.0091 mmol, 73%). R_f = 0.69 (hexane/CH_2Cl_2 = 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ −3.54 (d, 2 H, $^3J_{Rh-H}$ = 3.7 Hz), −0.88 (s, 3 H), 2.58 (d, 1 H, J = 7.4 Hz), 2.73 (s, 12 H), 5.68 (t, 1 H, J = 7.4 Hz), 5.75 (d, 1 H, J = 7.4 Hz), 6.33 (t, 1 H, J = 7.3 Hz), 7.57 (t, 8 H, J = 11.6 Hz), 8.00−7.98 (m, 4 H), 8.10−8.07 (m, 4 H), 8.71 (s, 8 H).

Reaction of Rh^{III}(ttp)Cl and 4-Methoxylbenzyl Alcohol. Rh^{III}(ttp)Cl (**1**) (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and 4-methoxylbenzyl alcohol (**2h**) (172.5 mg, 1.25 mmol) were added to benzonitrile (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 2 h. After benzonitrile was removed by vacuum distillation, the residue was quickly purified by column chromatography over silica gel with a solvent mixture of hexane/CH_2Cl_2 (1/1) as eluent to give Rh^{III}(ttp)Bn(4-OMe) (**3h**)[20] (6.9 mg, 0.0077 mmol, 62%). R_f = 0.52 (hexane/CH_2Cl_2 = 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ −3.74 (d, 2 H, $^3J_{Rh-H}$ = 3.7 Hz), 2.73 (s, 12 H), 2.95 (d, 2 H, J = 8.6 Hz), 3.45 (s, 3 H), 5.44 (d, 2 H, J = 8.6 Hz), 7.57−7.55 (m, 8 H), 8.02−7.98 (m, 4 H), 8.10−8.08 (m, 4 H), 8.70 (s, 8 H).

Reaction of Rh^{III}(ttp)Cl and 4-Nitrobenzyl Alcohol. Rh^{III}(ttp)Cl (**1**) (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and 4-nitrobenzyl alcohol (**2i**) (191.3 mg, 1.25 mmol) were added to benzonitrile (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 0.5 h. After benzonitrile was removed by vacuum distillation, the residue was quickly purified by column chromatography over silica gel with a solvent mixture of hexane/CH_2Cl_2 (1/1) as eluent to give Rh^{III}(ttp)Bn(4-NO_2) (**3i**)[20] (2.1 mg, 0.0023 mmol, 19%). R_f = 0.55 (hexane/CH_2Cl_2 = 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ −3.81 (d, 2 H, $^3J_{Rh-H}$ = 3.9 Hz), 2.73 (s, 12 H), 2.92 (d, 2 H, J = 8.6 Hz), 6.71 (d, 2 H, J = 8.6 Hz), 7.58 (t, 8 H, J = 17.8 Hz), 7.98 (d, 4 H, J = 8.8 Hz), 8.07 (d, 4 H, J = 7.6 Hz), 8.74 (s, 8 H).

Reaction of Rh^{III}(ttp)Cl and Methanol. Rh^{III}(ttp)Cl (**1**) (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and methanol (**2j**) (40.0 mg, 1.25 mmol) were added to benzonitrile (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 24 h. After benzonitrile was removed by vacuum distillation, the residue was quickly purified by column chromatography over silica gel with a solvent mixture of hexane/CH_2Cl_2 (1/1) as eluent to give Rh^{III}(ttp)Me (**3j**)[17] (6.8 mg, 0.0086 mmol, 69%). R_f = 0.74 (hexane/CH_2Cl_2 = 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ −5.79 (d, 3 H, $^3J_{Rh-H}$ = 2.9 Hz), 2.72 (s, 12 H), 7.56 (t, 8 H, J = 5.1 Hz), 8.05 (d, 4 H, J = 7.3 Hz), 8.10 (d, 4 H, J = 7.2 Hz), 8.73 (s, 8 H).

Reaction of Rh^{III}(ttp)Cl and Ethanol. Rh^{III}(ttp)Cl (**1**) (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and ethanol (**2k**) (57.5 mg, 1.25 mmol) were added to benzonitrile (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 24 h. After benzonitrile was removed by vacuum distillation, the residue was quickly purified by column chromatography over silica gel with a solvent mixture of hexane/CH_2Cl_2 (1/1) as eluent to give Rh^{III}(ttp)Et (**3k**)[27] (3.7 mg, 0.0046 mmol, 37%). R_f = 0.72 (hexane/CH_2Cl_2 = 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ −4.84 (qd, 2 H, J = 7.3, 3.0 Hz), −4.42 (td, 3 H, J = 7.4, 1.6 Hz), 2.72 (s, 12 H), 7.55 (t, 8 H, J = 7.3 Hz), 8.02 (d, 4 H, J = 7.6 Hz), 8.10 (d, 4 H, J = 7.6 Hz), 8.76 (s, 8 H).

Reaction of Rh^{III}(ttp)Cl and *n*-Propanol. Rh(ttp)Cl **1** (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and *n*-propanol (**2l**) (75.1 mg, 1.25 mmol) were added to benzonitrile (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 24 h. After benzonitrile was removed by vacuum distillation, the residue was quickly purified by column chromatography over silica gel with a solvent mixture of hexane/CH_2Cl_2 (1/1) as eluent to give Rh^{III}(ttp)^{n}Pr (**3l**)[27] (1.2 mg, 0.0015 mmol, 12%). R_f = 0.60 (hexane/CH_2Cl_2 4/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ −4.94 to −4.98 (m, 2 H), −4.37 to −4.47 (m, 2 H), −1.72 (t, 2 H, J = 7.4 Hz), 2.72 (s, 12 H), 7.55 (t, 8 H, J = 6.4 Hz), 8.03 (d, 4 H, J = 7.4 Hz), 8.09 (d, 4 H, J = 7.4 Hz), 8.73 (s, 8 H).

Reaction of Rh^{III}(ttp)Cl and *n*-Butanol. Rh^{III}(ttp)Cl (**1**) (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and *n*-butanol (**2m**) (92.6 mg, 1.25 mmol) were added to benzonitrile (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 24 h. After benzonitrile was removed by vacuum distillation, the residue was quickly purified by column chromatography over silica gel with a solvent mixture of hexane/CH_2Cl_2 (1/1) as eluent to give Rh^{III}(ttp)^{n}Bu (**3m**)[27] (0.9 mg, 0.0011 mmol, 9%). R_f = 0.84 (hexane/CH_2Cl_2 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ −4.91 to −4.95 (m, 2 H), −4.44 to −4.52 (m, 2 H), −1.56 (q, 2 H, J = 7.4 Hz), −0..81 (t, 3 H, J = 7.3 Hz), 2.72 (s, 12 H), 7.55 (t, 8 H, J = 7.3 Hz), 8.01 (d, 4 H, J = 7.6 Hz), 8.10 (d, 4 H, J = 7.4 Hz), 8.73 (s, 8 H).

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Reaction of Rh^{III}(ttp)Cl and 2-Cyanoethanol. Rh^{III}(ttp)Cl (**1**) (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and 2-cyanoethanol (**2n**) (88.8 mg, 1.25 mmol) were added to benzonitrile (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 1 h. After benzonitrile was removed by vacuum distillation, the residue was quickly purified by column chromatography over silica gel with a solvent mixture of hexane/CH_2Cl_2 (1/1) as eluent to give Rh^{III}(ttp)CH_2CH_2CN (**3n**)[28] (6.5 mg, 0.0078 mmol, 63%). R_f = 0.46 (hexane/CH_2Cl_2 1/2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ −4.97 to −5.02 (m, 2 H), −3.69 (t, 2 H, J = 8.4 Hz), 2.73 (s, 12 H), 7.58 (d, 8 H, J = 7.4 Hz), 8.07 (t, 8 H, J = 9.4 Hz), 8.81 (s, 8 H).

Reaction of Rh^{III}(ttp)Cl and 2-Phenylethanol. Rh^{III}(ttp)Cl (**1**) (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and 2-phenylethanol (**2o**) (152.5 mg, 1.25 mmol) were added to benzonitrile (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 24 h. After benzonitrile was removed by vacuum distillation, the residue was quickly purified by column chromatography over silica gel with a solvent mixture of hexane/CH_2Cl_2 (1/1) as eluent to give a mixture of Rh^{III}(ttp)CH_2CH_2Ph (**3o**)[29] and Rh^{III}(ttp)$CH(CH_3)Ph$ (**3p**)[29] in a total yield of 29%, and the ratio of **3n** to **3o** was measured to be 2.2:1 by an ^{1}H NMR spectrum.

Reaction of Rh^{III}(ttp)Cl and 1-Phenylethanol. Rh^{III}(ttp)Cl (**1**) (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and 1-phenylethanol (**2p**) (152.5 mg, 1.25 mmol) were added to benzonitrile (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 75 h. After benzonitrile was removed by vacuum distillation, the residue was quickly purified by column chromatography over silica gel with a solvent mixture of hexane/CH_2Cl_2 (1/1) as eluent to give a mixture of Rh^{III}(ttp)CH_2CH_2Ph (**3o**) and Rh^{III}(ttp)$CH(CH_3)Ph$ (**3p**) in a total yield of 8%, and the ratio of **3o** to **3p** was measured to be 1.2:1 by an ^{1}H NMR spectrum.

Reaction of Rh^{III}(ttp)Cl and Benzyl Alcohol in CD_3CN. Rh^{III}(ttp)Cl (**1**) (10.1 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and benzyl alcohol (**2a**) (135.2 mg, 1.25 mmol) were added to CD_3CN (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 4 h. After CD_3CN was removed by vacuum distillation, $CDCl_3$ and DCE as an internal standard were added to measure the NMR yields. The yields of Rh^{III}(ttp)Bn (**3a**) and benzaldehyde (**4**) were determined to be 67% and 61% based on metal Rh, respectively.

Reaction of Rh^{III}(ttp)H and Benzyl Alcohol in CD_3CN. Rh^{III}(ttp)H (**5**) (9.7 mg, 0.0125 mmol) and benzyl alcohol (**2a**) (135.2 mg, 1.25 mmol) were added to CD_3CN (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 4 h. After CD_3CN was removed by vacuum distillation, the mixture was worked up by extraction with CH_2Cl_2 and H_2O. The organic extract was dried by anhydrous Na_2SO_4, filtered, and rotary evaporated. The residue was purified by column chromatography over silica gel with a solvent mixture of hexane/CH_2Cl_2 (1/1) as eluent to give Rh^{III}(ttp)Bn (**3a**) (<1%).

Reaction of Rh^{III}(ttp)H and Benzyl Alcohol with K_2CO_3 in CD_3CN. Rh^{III}(ttp)H (**5**) (9.7 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), and benzyl alcohol (**2a**) (135.2 mg, 1.25 mmol) were added to CD_3CN (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 120 °C for 4 h. After CD_3CN was removed by vacuum distillation, the mixture was worked up by extraction with CH_2Cl_2 and H_2O. The organic extract was dried by anhydrous Na_2SO_4, filtered, and rotary evaporated. The residue was purified by column chromatography over silica gel with a solvent mixture of hexane/CH_2Cl_2 (1/1) as eluent to give Rh^{III}(ttp)Bn (**3a**) (4.7 mg, 0.0054 mmol, 44%).

Reaction of Rh^{III}(ttp)Cl and Benzyl Alcohol with K_2CO_3 in the Presence of Aniline in PhCN. Rh^{III}(ttp)Cl (**1**) (10.0 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), benzyl alcohol (**2a**) (135.2 mg, 1.25 mmol), and aniline (113.0 μL, 1.25 mmol) were added to PhCN (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 80 °C for 13 h. The reaction aliquot was analyzed by GC-MS. After the removal of PhCN by vacuum distillation, the crude mixture was worked up by extraction with CH_2Cl_2 and H_2O. The organic extract was dried by anhydrous Na_2SO_4, filtered, and rotary evaporated. The residue was purified by column chromatography over silica gel with a solvent mixture of hexane/CH_2Cl_2 (1/1) as eluent to give Rh^{III}(ttp)Bn (**3a**) (4.3 mg, 0.0050 mmol, 40%).

General Procedures for the Competition Experiments. Rh^{III}(ttp)Cl (**1**) (10.0 mg, 0.0125 mmol), K_2CO_3 (17.3 mg, 0.125 mmol), benzyl alcohol (**2a**) (135.2 mg, 1.25 mmol), and substituted benzyl alcohol (1.25 mmol) were added to PhCN (1.5 mL) in a Teflon screw-capped tube and degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 80 °C for 15 h. After the completion of the reaction and removal of solvent, the ^{1}H NMR spectrum of the crude reaction mixture was taken and the yields were measured using DCE as the internal standard.

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Notes

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