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Facile Aerobic Alkylation of Rhodium Porphyrins with Alkyl Halides

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Supporting Information

ABSTRACT: Alkylation of rhodium porphyrins was achieved in moderate to high yields in the presence of air and water. With this facile alkylation method, various alkyl Rh^{III}(por) species, including those with tertiary alkyl, were synthesized. Mechanistic investigations suggest a parallel S_N2 via $[Rh^{I}(ttp)]^-$ with halogen atom transfer pathway via $[Rh^{II}(ttp)]^{\bullet}$.

$Rh^{III}(por)Cl \xrightarrow[\text{air, dark, 120-180 °C}]{\text{R-X (X = Cl, Br, I)}, \text{KOH (aq)}, C_6H_6} Rh^{III}(por)R$ up to 86%

Facile: Air and water tolerated

Wide scope: Various R, including 1°, 2°, 3° alkyl

INTRODUCTION

Rhodium porphyrin alkyls (Figure 1) play an important role in catalysis. They are precursors of $[Rh^{II}(por)]^{\bullet}$ (por = porphyrinato dianion) metalloradicals for carbon−hydrogen bond[1] and carbon−carbon single bond activation.[1d,2] Activation of these strong bonds has gained much current interest for more efficient utilization of hydrocarbons.[3] To the best of our knowledge, only primary and secondary alkyl Rh^{III}(por) species have been reported so far. Tertiary alkyl Rh^{III}(por) species remain unknown, which may be of great interest in investigating its role in catalysis. Hence, developing robust methods to access alkyl Rh^{III}(por) species, especially tertiary alkyl Rh^{III}(por) species, is important.

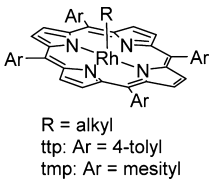

Figure 1. Structure of rhodium porphyrin alkyls.

The synthesis of rhodium porphyrin alkyls was first reported by Ogoshi in 1972 by the reaction between Rh^{III}(oep)Cl (oep =2,3,7,8,12,13,17,18-octaethylporphyrinato dianion) and MeLi (Scheme 1a).[4] A more versatile method involves the reduction of Rh^{III}(por)Cl by $NaBH_4$ to generate $[Rh^{I}(por)]^-$. $[Rh^{I}(por)]^-$ then undergoes nucleophilic substitution with alkyl halides to give the corresponding rhodium porphyrin alkyls (Scheme 1b).[5] In 1986, Kadish and co-workers reported the Rh−C bond formation by the electrochemically generated monomeric species $[Rh^{II}(tpp)]^{\bullet}$ (tpp = 5,10,15,20-tetraphenylporphyrinato dianion) (Scheme 1c).[6] In 1990, Wayland discovered the formation of Rh−C bond by carbon−hydrogen bond activation of CH_4 and toluene to give Rh(por)Me and Rh(por)Bn (Scheme 1d).[1a,b] The carbon−oxygen bond cleavage of methanol by Rh^{III}(ttp)Cl (ttp =5,10,15,20-tetratolylporphyrinato dianion) in alkaline media was discovered to give a high yield of Rh^{III}(ttp)Me and was reported by Chan in 2009 (Scheme 1e).[7] In 2010, Chan and co-workers found the formation of the Rh−C bonds by carbon−nitrogen bond activation (CNA) of amines (Scheme 1f).[8] This CNA method, further developed by the Dong group, tolerates air and water by utilizing ammonium salts as the alkylating agents (Scheme 1g). An S_N2-like reaction pathway involving a $[Rh^{I}(por)]^-$ intermediate was proposed.[9] These reported methods are unlikely to prepare a tertiary alkyl Rh^{III}(por) species due to the steric hindrance. Herein, we disclose a facile

Scheme 1. Synthesis of Rhodium Porphyrin Alkyls

Ogoshi (1972)

a) $Rh^{III}(oep)Cl \xrightarrow{RLi} Rh^{III}(oep)R$ (R = 1°, 2° alkyl)

b) $Rh^{III}(por)Cl \xrightarrow[\text{2) RBr or RI (excess), } N_2\text{, 0 °C}]{\text{1) } NaBH_4/NaOH\text{ (aq), EtOH, } N_2\text{, 50 °C}} Rh^{III}(por)R$ (R = 1°, 2° alkyl)

Kadish (1986)

c) $[(tpp)Rh^{III}(L)_2]^+ \xrightarrow[-2L]{e} [(tpp)Rh^{II}]\bullet \xrightarrow{RX} (tpp)Rh\text{-}R + X\bullet$ (R = 1° alkyl)

Wayland (1990)

d) $[Rh^{II}(por)]\bullet \xrightarrow[N_2\text{, r.t.}]{R\text{-}H} Rh^{III}(por)R$ (R = 1°, 2° alkyl)

Chan (2009-2010)

e) $Rh^{III}(ttp)Cl + MeOH \xrightarrow[N_2\text{, 150 °C}]{K_2CO_3} Rh^{III}(ttp)Me$

f) $Rh^{III}(ttp)Cl + R_3N \xrightarrow{N_2\text{, 120 °C}} Rh^{III}(ttp)R$ (R = 1° alkyl)

Dong (2014)

g) $Rh^{III}(por)X \xrightarrow[C_6H_6\text{, 80-120 °C, air}]{\oplus NR_4, \text{"}\ominus OH\text{"}, H_2O} Rh^{III}(por)R$ (R = 1° alkyl)

This work

h) $Rh^{III}(por)Cl + R\text{-}X \xrightarrow[\text{dark, } C_6H_6\text{, 120-180 °C}]{KOH,\ H_2O,\ air} Rh^{III}(por)R$ (R = 1°, 2°, 3° alkyl)

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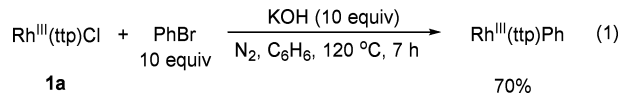
Organometallics XXXX, XXX, XXX−XXX

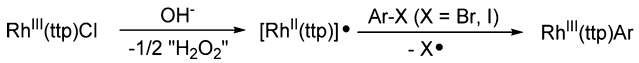
alkylation method with alkyl halides to afford various alkyl Rh^{III}(por) species, including a tertiary alkyl Rh^{III}(por) complex, Rh(ttp)(1-adamantyl), in moderate to high yields (Scheme 1h).

RESULTS AND DISCUSSION

Reaction Discovery. Previously, Rh^{III}(ttp)Ph was synthesized by the treatment of Rh^{III}(ttp)Cl (**1a**) with PhBr under basic conditions (eq 1). $[Rh^{II}(ttp)]^{\bullet}$ was proposed to be the key intermediate for Ar-X (X = I, Br) cleavage via metalloradical ipso substitution (Scheme 2).[10]

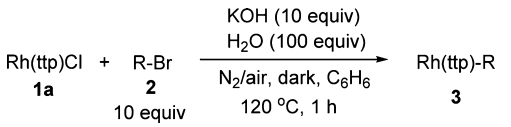


Scheme 2. Proposed Mechanism for the Generation of Rh^{III}(ttp)Ar



We have extended the substrates from aryl halides to alkyl halides to systematically explore the synthetic scope and mechanistic features. Rh(ttp)(alkyl) complexes were accessed in high yields with both primary and secondary alkyl bromides under an inert N_2 atmosphere in the presence of water (Table 1, entries 1 and 2). To our delight, the reaction tolerated air

Table 1. Atmosphere Effects on the Alkylation with Alkyl Bromides

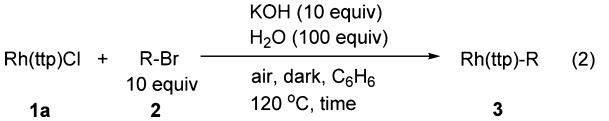


entry	R	atmosphere	yield (%)[a]
1	c-C_6H_{11} (**2a**)	N_2	86 (**3a**)
2	*n*-C_5H_{11} (**2b**)	N_2	78 (**3b**)
3	c-C_6H_{11} (**2a**)	air	83 (**3a**)
4	*n*-C_5H_{11} (**2b**)	air	81 (**3b**)

[a]Average isolated yield of duplicate runs.

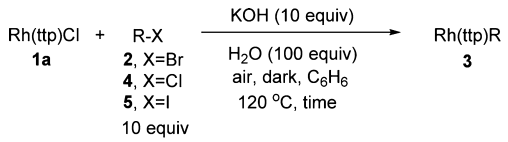
(Table 1, entries 3 and 4). Therefore, this alkylation reaction was found to tolerate water and oxygen and thus was user-friendly.

With this initial success, the reaction conditions of temperature (90, 120, 150 °C) (Table S1 in the Supporting Information), base (NaOH, KOH, K_2CO_3, KOAc) (Table S2 in the Supporting Information), KOH loading (0, 5, 10, 40 equiv) (Table S3 in the Supporting Information), H_2O loading (0, 100, 200, 600 equiv) (Table S4 in the Supporting Information), and solvent (C_6H_6, THF, acetone) (Table S5 in the Supporting Information) were optimized. The optimal conditions are shown in eq 2.



Substrate Scope. With the optimal conditions in hand, the substrate scope was examined. Alkyl chlorides, bromides, and iodides were good alkylation agents that gave high yields of Rh(ttp)R (**3**; R = alkyl) (Table 2). Alkylations with both

Table 2. Substrate Scope in Alkylation of Rh(ttp)Cl with Alkyl Halides



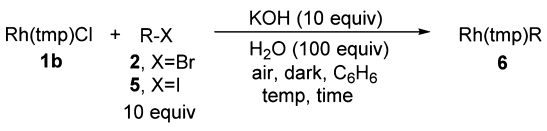
entry	R-X	time (h)[a]	yield (%)[b]
1	c-C_6H_{11}-Cl (**4a**)	3	74 (**3a**)
2	c-C_6H_{11}-Br (**2a**)	1	83 (**3a**)
3	c-C_6H_{11}-I (**5a**)	24	74 (**3a**)
4	*n*-C_8H_{15}-Cl (**4b**)	3	81 (**3c**)
5	*n*-C_5H_{11}-Br (**2b**)	1	81 (**3b**)
6	*n*-C_4H_7-I (**5b**)	24	76 (**3d**)
7	Bn-Br (**2c**)	1	60 (**3e**)
8	$(CH_3)_3CCH_2$-Br (**2d**)	5	43 (**3f**)
9	Me-I (**5c**)	24	54 (**3g**)

[a]The reaction was monitored by TLC until the complete consumption of Rh(ttp)Cl. [b]Average isolated yield of duplicate runs.

primary and secondary alkyl halides were achieved in moderate to high yields. As the reaction was conducted in sealed glass vessels, we were glad to find out that low-boiling alkyl halides, such as MeI, worked well (Table 2, entry 9). The alkylation also took place with the sterically hindered neopentyl bromide (Table 2, entry 8), although the reaction required a longer time. The reactivity of c-hexyl-X followed the order X = Br > Cl > I (Table 2, entries 1−3). This result indicates that the pathway is not purely $[Rh^{I}(ttp)]^{-}$-mediated bimolecular nucleophilic substitution (S_N2), in which the rate should follow the order X = I > Br > Cl.[11]

Sterically more hindered Rh(tmp)Cl (**1b**; tmp = 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrinato dianion) also reacted smoothly with MeI to give Rh(tmp)Me in 51% yield, together with Rh(tmp)I in 33% yield at 120 °C for 84 h, which is much longer than that of Rh(ttp)Cl (Table 3, entry 1 and Table 2, entry 9). The reaction at 150 °C for 10 h enhanced the yield of Rh(tmp)Me (**6a**) to 86% (Table 3, entry 2). Therefore, a higher temperature is needed for bulky Rh(tmp)Cl. A temperature of 150 °C was chosen for further substrate scope

Table 3. Substrate Scope in Alkylation of Rh(tmp)Cl with Alkyl Halides



entry	temp (°C)	R-X	time (h)[a]	yield (%)[b]
1[c]	120	Me-I (**5c**)	84	51 (**6a**)
2	150	Me-I (**5c**)	10	86 (**6a**)
3	150	Bn-Br (**2c**)	3	49 (**6b**)
4	150	*n*-C_4H_7-Br (**2e**)	5	59 (**6c**)

[a]The reaction was monitored by TLC until the complete consumption of Rh(tmp)Cl. [b]Average isolated yield of duplicate runs. [c]Rh(tmp)I was obtained in 33% yield (calculated according to the ratio of the ^1H NMR integrations between Rh(tmp)Me and Rh(tmp)I of the crude reaction mixtures).

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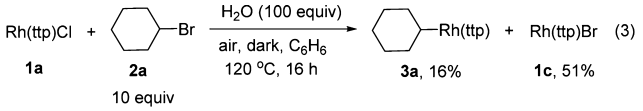
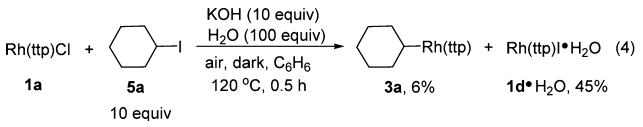
Organometallics XXXX, XXX, XXX−XXX

examination with Rh(tmp)Cl. Rh(tmp)Bn (**6b**) was obtained in 49% yield at 150 °C for 3 h (Table 3, entry 3). Alkylation with *n*-C_4H_7-Br (**2e**) occurred readily to give Rh(tmp)(*n*-butyl) (**6c**) in 59% yield at 150 °C for 5 h (Table 3, entry 4).

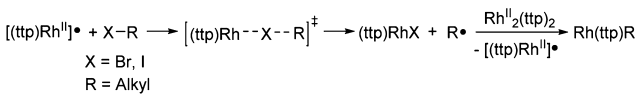
Mechanistic Investigations. *Discovery of the Intermediate Rh(ttp)Br and Rh(ttp)I.* To gain a mechanistic understanding of the alkylation, we carried out the alkylation in the absence of base to slow the ligand substitution of Rh^{III}(ttp)Cl into Rh^{III}(ttp)OH. Therefore, $Rh^{II}_2(ttp)_2$ from the thermal conversion of Rh^{III}(ttp)OH[12] can remain stable without undergoing reaction with hydroxide to give $[Rh^{I}(ttp)]^-$ and Rh^{III}(ttp)OH. $Rh^{II}_2(ttp)_2$ can then remain as the dominant species in C_6H_6. Rh(ttp)Br (**1c**) was isolated in 51% yield together with Rh(ttp)(cyclohexyl) (**3a**) in 16% yield in the reaction without base over a prolonged reaction time of 16 h (eq 3) and could only be generated through a metalloradical





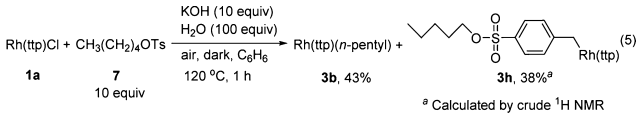
pathway by halogen atom transfer via $[Rh^{II}(ttp)]^\bullet$ (Scheme 3).[10] Under the optimal conditions, Rh(ttp)I·H_2O (**1d**·H_2O)

Scheme 3. Metalloradical-Mediated Halogen Atom Transfer



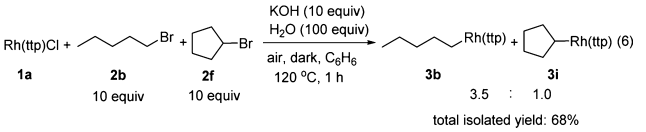
was isolated in 45% yield together with **3a** in 6% yield at 120 °C for 0.5 h when the less reactive *c*-C_6H_{11}-I substrate was utilized (eq 4). The isolation of Rh(ttp)Br and Rh(ttp)I·H_2O supports the presence of halogen atom transfer via $[Rh^{II}(ttp)]^\bullet$. In addition, Rh(tmp)I was obtained in 33% yield through halogen atom transfer via $[Rh^{II}(tmp)]^\bullet$ (Table 3, entry 1).

$CH_3(CH_2)_4OTs$ Substrate. Alkyl tosylate was employed to test whether an S_N2 pathway via $[Rh^{I}(ttp)]^-$ is also operating. Alkyl tosylate seems unlikely to react by a free radical path in the C–O cleavage. To the best of our knowledge, such radical pathways have not been observed in the reactions of transition-metal complexes with alkyl tosylates.[13] As expected, Rh(ttp)(*n*-pentyl) (**3b**) was generated rapidly in 43% isolated yield at 120 °C for 1 h under the optimal conditions by employing *n*-pentyl tosylate through an S_N2 pathway via $[Rh^{I}(ttp)]^-$. To our surprise, the benzylic carbon–hydrogen bond activation product **3h** was also obtained in 38% yield (eq 5). As



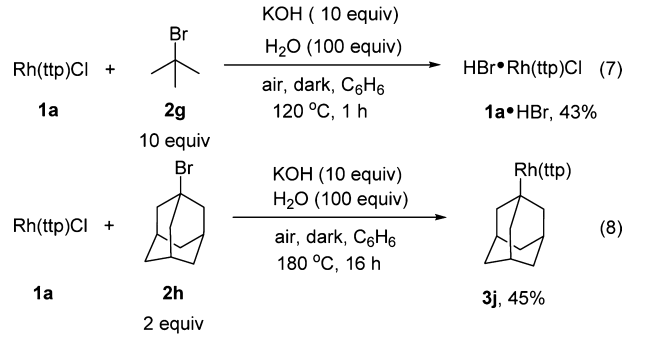
previously reported, $[Rh^{II}(ttp)]^\bullet$ was discovered to be a key intermediate for the benzylic carbon–hydrogen bond activation of toluene by Rh(ttp)Cl under basic conditions.[14] Therefore, this result suggests that both $[Rh^{I}(ttp)]^-$ and $[Rh^{II}(ttp)]^\bullet$ coexist in the reaction process under the optimal conditions.

Competition Reaction. To further quantify the relative rate of alkylation with alkyl halides, a competition reaction between primary and secondary alkyl bromides was carried out (eq 6).



The **3b** to **3i** product ratio is 3.5:1.0, with a total isolated yield of 68% for the reaction at 120 °C for 1 h. Thus, *n*-pentyl bromide (**2b**) reacted more quickly than cyclopentyl bromide (**2f**), which suggests an S_N2 pathway via $[Rh^{I}(ttp)]^-$, but the reaction was not as fast in comparison to the typical relative S_N2 rate of 16 between *n*-propyl- and isopropyl-substituted alkyl halides,[11,15] which might imply the coexistence of a metalloradical pathway by halogen atom transfer that favors **2f**.

Extension to Tertiary Alkyl Bromide Substrates. To further verify the coexistence of the metalloradical pathway, alkylation reactions with tertiary alkyl bromide substrates, which cannot react by an S_N2 pathway, were carried out. For ^{t}Bu-Br (**2g**), the base-promoted elimination occurred rapidly to generate 2-methylpropene and HBr, which then formed the product HBr·Rh(ttp)Cl (**1a**·HBr) (eq 7). The crystal structure is illustrated



in Figure S2 in the Supporting Information. Alkylation with 1-bromoadamantane (**2h**) was then attempted; the desired product Rh(ttp)(1-adamantyl) (**3j**) was obtained in a trace amount at 120 °C over 5 h. When the reaction temperature was increased to 180 °C, **3j** was isolated in 45% yield after 16 h (eq 8). The moderate isolated yield is likely due to the air sensitivity of **3j**. Higher temperature is favorable for promoting the thermal dissociation of $Rh^{II}_2(ttp)_2$ into $[Rh^{II}(ttp)]^\bullet$ metalloradical species.[10,16] To the best of our knowledge, this is the first reported tertiary alkyl Rh(por) species. The tertiary alkyl rhodoxime *tert*-butylrhodoxime was reported in 1992.[17] For 1-bromoadamantane (**2h**), back-side attack by S_N2 is impossible due to the steric hindrance. An alternative metalloradical-mediated bromine atom abstraction operates to yield the product **3j** (Scheme 3). Therefore, this result further validates the existence of the metalloradical pathway.

Proposed Mechanism for the Alkylation Reaction. The known equilibria among rhodium porphyrin species in C_6H_6 have been reported, as shown in Scheme 4. First, Rh(ttp)Cl undergoes ligand substitution with OH^- to give Rh(ttp)OH, which serves as a precursor to $Rh^{II}_2(ttp)_2$ by reductive elimination.[12] This $Rh^{II}_2(ttp)_2$ dimer is in an equilibrium with the monomeric $[Rh^{II}(ttp)]^\bullet$ metalloradical.[1d,18] The $[Rh^{II}(ttp)]^\bullet$ metalloradical then cleaves the R-X (X = Br, I) bond by halogen atom transfer to afford Rh(ttp)R (R = alkyl) and Rh(ttp)X (pathway *B*).[19] Rh(ttp)X (X = Br, I), which is

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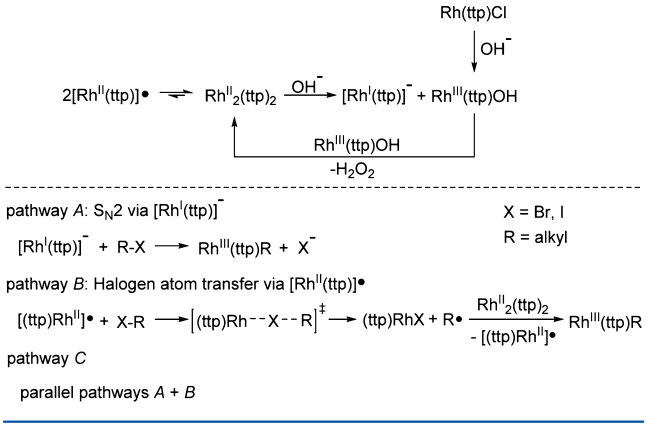
Organometallics XXXX, XXX, XXX–XXX

Scheme 4. Proposed Mechanistic Pathways for the Alkylation Reaction with R-X (R = Alkyl, X = Br, I)



chemically equivalent to Rh(ttp)Cl, recycles back to Rh(ttp)-OH by ligand substitution with OH^-. The slower reaction rate of Rh(ttp)Cl with R-I (R = alkyl) in comparison to that of R-Br implies the slower ligand substitution with OH^- of Rh(ttp)I, which is likely due to the lower electrophilicity of the rhodium center in Rh(ttp)I.[20] Alternatively, disproportionation of $Rh^{II}_2(ttp)_2$ with OH^- generates $Rh^{III}(ttp)OH$ and $[Rh^I(ttp)]^-$.[20c,21] $[Rh^I(ttp)]^-$ then undergoes a bimolecular nucleophilic substitution (S_N2) reaction with alkyl halides to afford Rh(ttp)R (pathway *A*).

On the basis of the reported known equilibria, three possible mechanisms are proposed (Scheme 4): pathway *A*, S_N2 via $[Rh^I(ttp)]^-$; pathway *B*, halogen atom transfer via $[Rh^{II}(ttp)]^•$; pathway *C*, parallel pathways *A* and *B*.

Pathway A: Sole S_N2 via $[Rh^I(ttp)]^-$. *n*-Pentyl bromide reacted more quickly than cyclopentyl bromide by 3.5-fold (eq 6). This competition reaction result supports the existence of the S_N2 via $[Rh^I(ttp)]^-$ approach. However, when 1-bromoadamantane was employed, which is unlikely to react by an S_N2 pathway due to the steric hindrance, Rh(ttp)(1-adamantyl) (**3j**) was accessed in 45% isolated yield (eq 8. In addition, cyclohexyl iodide (**5a**) reacted more slowly than cyclohexyl bromide (**2a**) and cyclohexyl chloride (**4a**). (Table 2, entries 1−3). This result is contradictory to a pure S_N2 pathway, in which cyclohexyl iodide reacts the fastest due to the highest leaving group stability. Thus, a pure S_N2 via $[Rh^I(ttp)]^-$ (pathway *A*) is not likely to be operating.

Pathway B: Sole Halogen Atom Transfer via $[Rh^{II}(ttp)]^•$. The discovery of Rh(ttp)I·H_2O (**1d**·H_2O) and Rh(tmp)I under optimal conditions strongly supports the existence of the halogen atom transfer pathway. However, a competition reaction between *n*-pentyl bromide and cyclopentyl bromide revealed that cyclopentyl bromide reacted more slowly than *n*-pentyl bromide (eq 6). This result is contradictory to the halogen atom transfer pathway, in which cyclopentyl bromide reacts more quickly than *n*-pentyl bromide for the formation of the more stable cyclopentyl radical. Therefore, a pure halogen atom transfer (pathway *B*) is ruled out.

Pathway C: Parallel S_N2 via $[Rh^I(ttp)]^-$ with Halogen Atom Transfer via $[Rh^{II}(ttp)]^•$. We thus rationalize the coexistence of S_N2 and halogen atom transfer from the above analyses of pathways *A* and *B*. This is supported by the following observations:. First, the alkylation experiment with *n*-pentyl tosylate reveals the coexistence of $[Rh^I(ttp)]^-$ and $[Rh^{II}(ttp)]^•$. Second, the faster reaction rate of *n*-pentyl bromide in comparison to that of cyclopentyl bromide suggests an S_N2 pathway via $[Rh^I(ttp)]^-$. The existence of halogen atom transfer is supported by the discovery of the Rh(ttp)I·H_2O (**1d**·H_2O) intermediate under the optimal conditions. The formation of Rh(ttp)(1-adamantyl) (**3j**) also suggests the existence of halogen atom transfer via $[Rh^{II}(ttp)]^•$. Therefore, Rh(ttp)R (R = alkyl) is concluded to be accessed by a parallel S_N2 with halogen atom transfer pathway via $[Rh^I(ttp)]^-$ and $[Rh^{II}(ttp)]^•$, respectively (pathway *C*).

CONCLUSION

In summary, a facile alkylation method was developed to achieve moderate to high yields of various alkyl Rh^{III}(por) species, including Rh^{III}(ttp)(1-adamantyl), in the presence of air and water, which is convenient and user-friendly. Mechanistic investigations suggest a parallel S_N2 via $[Rh^I(ttp)]^-$ and a halogen atom transfer via $[Rh^{II}(ttp)]^•$ mechanism.

EXPERIMENTAL SECTION

General Procedures. Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. Benzene was distilled over sodium under nitrogen. All reactions were protected from light by wrapping with aluminum foil. The reaction mixtures in Teflon screw capped pressure tubes were heated in heat blocks on heaters and monitored by TLC until complete consumption of Rh(ttp)Cl. Rh(ttp)Cl (**1a**) was prepared according to the literature procedures.[22] Thin-layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates. Silica gel (Merck, 70−230 and 230−400 mesh) or alumina (90 active neutral, 70−230 mesh) was used for column chromatography in air. Yields are reported as the average of duplicate runs.

^{1}H NMR spectra were recorded on a Bruker AV400 instrument (400 MHz). Chemical shifts were reported with reference to the residual solvent protons in C_6D_6 (δ 7.15 ppm) or in $CDCl_3$ (δ 7.26 ppm) as the internal standard. Coupling constants (*J*) are reported in hertz (Hz). ^{13}C NMR spectra were recorded on a Bruker AV400 (100 MHz) spectrometer and referenced to $CDCl_3$ (δ 77.1 ppm) or C_6D_6 (δ 128.1 ppm). High-resolution mass spectrometry (HRMS) was performed on a Thermofinnigan MAT 95 XL instrument in FAB mode (3-nitrobenzyl alcohol (NBA) as the matrix and CH_2Cl_2 as the solvent) and an ESI instrument (MeOH/CH_2Cl_2 1/1 as the solvent).

Reaction of Rh(ttp)Cl with Cyclohexyl Bromide and KOH under N_2. Rh(ttp)Cl (**1a**; 7.7 mg, 0.0095 mmol), aqueous KOH (5.5 M, 0.0175 mL, 0.096 mmol), and cyclohexyl bromide (**2a**; 0.012 mL, 0.097 mmol) were added to benzene (2.0 mL). The mixture was degassed for three freeze−pump−thaw cycles, purged with N_2, and heated to 120 °C for 1 h. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. The red solid Rh(ttp)(cyclohexyl)[23] (**3a**; 7.0 mg, 0.0082 mmol, 86%) was collected. R_f = 0.76 (hexane/CH_2Cl_2 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ −4.33 to −4.17 (m, 5H), −1.22 (q, *J* = 12.4 Hz, 2H), −0.94 (tq, *J* = 3.3, 12.9 Hz, 1H), −0.57 (d, *J* = 12.5 Hz, 2H), −0.08 (d, *J* = 12.7 Hz, 1H), 2.70 (s, 12H), 7.53 (t, *J* = 5.8 Hz, 8H), 8.01 (d, *J* = 7.2 Hz, 4H), 8.07 (d, *J* = 7.3 Hz, 4H), 8.69 (s, 8H).

Reaction of Rh(ttp)Cl with *n*-Pentyl Bromide and KOH under N_2. Rh(ttp)Cl (**1a**; 7.8 mg, 0.0097 mmol), aqueous KOH (5.5 M, 0.0175 mL, 0.096 mmol), and *n*-pentyl bromide (**2b**; 0.012 mL, 0.097 mmol) were added to benzene (2.0 mL). The mixture was degassed for three freeze−pump−thaw cycles, purged with N_2, and heated to 120 °C for 1 h. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. The red solid Rh(ttp)(*n*-pentyl)[23] (**3b**; 6.4 mg, 0.0076 mmol, 78%) was collected. R_f = 0.85 (hexane/CH_2Cl_2 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ −4.95 (td, *J* = 2.9, 8.0 Hz, 2H), −4.48 (quint, *J* = 7.8 Hz, 2H), −1.60 (quint, *J* = 7.4 Hz, 2H), −0.50 (sext, *J* = 7.4 Hz, 2H), −0.26 (t, *J* = 7.3 Hz,

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Organometallics XXXX, XXX, XXX−XXX

3H), 2.70 (s, 12H), 7.53 (t, J = 6.7 Hz, 8H), 8.00 (d, J = 8.0 Hz, 4H), 8.08 (d, J = 7.5 Hz, 4H), 8.71 (s, 8H).

Typical Procedures for the Reaction of Rh(ttp)Cl with Cyclohexyl Bromide and KOH in Air. Rh(ttp)Cl (**1a**; 7.8 mg, 0.0097 mmol), aqueous KOH (5.5 M, 0.0175 mL, 0.096 mmol), and cyclohexyl bromide (**2a**; 0.012 mL, 0.097 mmol), were added to benzene (2.0 mL). The mixture was heated to 120 °C for 1 h. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. The red solid Rh(ttp)(cyclohexyl)[23] (**3a**) (6.9 mg, 0.0081 mmol, 83%) was collected.

Reaction of Rh(ttp)Cl with *n*-Pentyl Bromide and KOH in Air. The typical procedures above were followed. The starting materials Rh(ttp)Cl (**1a**) (7.8 mg, 0.0097 mmol), aqueous KOH (5.5 M, 0.0175 mL, 0.096 mmol), and *n*-pentyl bromide (**2b**) (0.012 mL, 0.097 mmol) gave Rh(ttp)(*n*-pentyl)[23] (**3b**; 6.6 mg, 0.0078 mmol, 81%) as a red solid.

Optimization of Temperature. *Reaction of Rh(ttp)Cl with Cyclohexyl Bromide and KOH in Air at 90 °C.* Rh(ttp)Cl (**1a**); 7.8 mg, 0.0097 mmol), aqueous KOH (5.5 M, 0.0175 mL, 0.096 mmol), and cyclohexyl bromide (**2a**; 0.012 mL, 0.097 mmol) were added to benzene (2.0 mL). The mixture was heated to 90 °C for 24 h. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. The red solid Rh(ttp)(cyclohexyl)[23] (**3a**; 0.2 mg, 0.0002 mmol, trace) was collected.

Reaction of Rh(ttp)Cl with Cyclohexyl Bromide and KOH in Air at 150 °C. Rh(ttp)Cl (**1a**; 7.8 mg, 0.0097 mmol), aqueous KOH (5.5 M, 0.0175 mL, 0.096 mmol), and cyclohexyl bromide (**2a**) (0.012 mL, 0.097 mmol) were added to benzene (2.0 mL). The mixture was heated to 150 °C for 0.25 h. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. The red solid Rh(ttp)(cyclohexyl)[23] (**3a**; 7.7 mg, 0.0090 mmol, 93%) was collected.

Optimization of Base. *Reaction of Rh(ttp)Cl with Cyclohexyl Bromide and NaOH in Air at 120 °C.* Rh(ttp)Cl (**1a**; 7.8 mg, 0.0097 mmol), aqueous NaOH (5.5 M, 0.0175 mL, 0.096 mmol), and cyclohexyl bromide (**2a**; 0.012 mL, 0.097 mmol) were added to benzene (2.0 mL). The mixture was heated to 120 °C for 1 h. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. The red solid Rh(ttp)(cyclohexyl)[23] (**3a**; 5.8 mg, 0.0068 mmol, 71%) was collected.

Reaction of Rh(ttp)Cl with Cyclohexyl Bromide and K_2CO_3 in Air at 120 °C. Rh(ttp)Cl (**1a**; 7.8 mg, 0.0097 mmol), aqueous K_2CO_3 (5.5 M, 0.0175 mL, 0.096 mmol), and cyclohexyl bromide (**2a**; 0.012 mL, 0.097 mmol) were added to benzene (2.0 mL). The mixture was heated to 120 °C for 8 h. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. The red solid Rh(ttp)(cyclohexyl)[23] (**3a**; 1.9 mg, 0.0022 mmol, 23%) was collected.

Reaction of Rh(ttp)Cl with Cyclohexyl Bromide and KOAc in Air at 120 °C. Rh(ttp)Cl (**1a**; 7.8 mg, 0.0097 mmol), aqueous KOAc (5.5 M, 0.0175 mL, 0.096 mmol), and cyclohexyl bromide (**2a**; 0.012 mL, 0.097 mmol) were added to benzene (2.0 mL). The mixture was heated to 120 °C for 8 h. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. The red solid Rh(ttp)(cyclohexyl)[23] (**3a**; 1.9 mg, 0.0022 mmol, 23%) was collected.

Optimization of KOH Loading. *Reaction of Rh(ttp)Cl with Cyclohexyl Bromide and KOH (0 equiv) in Air at 120 °C.* Rh(ttp)Cl (**1a**; 7.8 mg, 0.0097 mmol), water (0.0175 mL, 0.97 mmol), and cyclohexyl bromide (**2a**; 0.012 mL, 0.097 mmol) were added to benzene (2.0 mL). The mixture was heated to 120 °C for 16 h. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. The red solid Rh(ttp)(cyclohexyl)[23] (**3a**; 1.5 mg, 0.0017 mmol, 18%) was collected.

Reaction of Rh(ttp)Cl with Cyclohexyl Bromide and KOH (5 equiv) in Air at 120 °C. Rh(ttp)Cl (**1a**; 7.7 mg, 0.0095 mmol), aqueous KOH (2.75 M, 0.0175 mL, 0.048 mmol), cyclohexyl bromide (**2a**; 0.012 mL, 0.097 mmol) were added to benzene (2.0 mL). The mixture was heated to 120 °C for 1 h. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. The red solid Rh(ttp)(cyclohexyl)[23] (**3a**; 5.5 mg, 0.0064 mmol, 67%) was collected.

Reaction of Rh(ttp)Cl with Cyclohexyl Bromide and KOH (40 equiv) in Air at 120 °C. Rh(ttp)Cl (**1a**; 7.8 mg, 0.0097 mmol), aqueous KOH (22 M, 0.0175 mL, 0.385 mmol), and cyclohexyl bromide (**2a**; 0.012 mL, 0.097 mmol) were added to benzene (2.0 mL). The mixture was heated to 120 °C for 1 h. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. The red solid Rh(ttp)(cyclohexyl)[23] (**3a**; 6.2 mg, 0.0072 mmol, 74%) was collected.

Optimization of H_2O Loading. *Reaction of Rh(ttp)Cl with Cyclohexyl Bromide, KOH, and H_2O (0 equiv) in Air at 120 °C.* Rh(ttp)Cl (**1a**; 7.8 mg, 0.0097 mmol), solid KOH (5.6 mg, 0.10 mmol), and cyclohexyl bromide (**2a**; 0.012 mL, 0.097 mmol) were added to benzene (2.0 mL). The mixture was heated to 120 °C for 1 h. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. The red solid Rh(ttp)(cyclohexyl)[23] (**3a**; 6.4 mg, 0.0075 mmol, 77%) was collected.

Reaction of Rh(ttp)Cl with Cyclohexyl Bromide, KOH, and H_2O (200 equiv) in Air at 120 °C. Rh(ttp)Cl (**1a**; 7.8 mg, 0.0097 mmol), aqueous KOH (2.75 M, 0.035 mL, 0.096 mmol), and cyclohexyl bromide (**2a**; 0.012 mL, 0.097 mmol) were added to benzene (2.0 mL). The mixture was heated to 120 °C for 1 h. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. The red solid Rh(ttp)(cyclohexyl)[23] (**3a**; 6.8 mg, 0.0079 mmol, 81%) was collected.

Reaction of Rh(ttp)Cl with Cyclohexyl Bromide, KOH, and H_2O (600 equiv) in Air at 120 °C. Rh(ttp)Cl (**1a**; 7.8 mg, 0.0097 mmol), aqueous KOH (0.91 M, 0.105 mL, 0.096 mmol), and cyclohexyl bromide (**2a**) (0.012 mL, 0.097 mmol) were added to benzene (2.0 mL). The mixture was heated to 120 °C for 1 h. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. The red solid Rh(ttp)(cyclohexyl)[23] (**3a**; 2.2 mg, 0.0026 mmol, 27%) was collected.

Optimization of Solvent. *Reaction of Rh(ttp)Cl with Cyclohexyl Bromide and KOH in Air at 120 °C in THF.* Rh(ttp)Cl (**1a**; 7.8 mg, 0.0097 mmol), aqueous KOH (5.5 M, 0.0175 mL, 0.096 mmol), and cyclohexyl bromide (**2a**; 0.012 mL, 0.097 mmol) were added to THF (2.0 mL). The mixture was heated to 120 °C for 1 h. Excess THF was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. The red solid Rh(ttp)(cyclohexyl)[23] (**3a**; 5.3 mg, 0.0062 mmol, 64%) was collected.

Reaction of Rh(ttp)Cl with Cyclohexyl Bromide and KOH in Air at 120 °C in Acetone. Rh(ttp)Cl (**1a**; 7.8 mg, 0.0097 mmol), aqueous KOH (5.5 M, 0.0175 mL, 0.096 mmol), and cyclohexyl bromide (**2a**; 0.012 mL, 0.097 mmol) were added to acetone (2.0 mL). The mixture was heated to 120 °C for 1 h. Excess acetone was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. A trace amount of the red solid Rh(ttp)(cyclohexyl)[23] (**3a**) was collected.

Reaction of Rh(ttp)Cl with Cyclohexyl Chloride and KOH in Air. Rh(ttp)Cl (**1a**; 7.8 mg, 0.0097 mmol), aqueous KOH (5.5 M, 0.0175 mL, 0.096 mmol), and cyclohexyl chloride (**4a**; 0.0115 mL, 0.097 mmol) were added to benzene (2.0 mL). The mixture was heated to 120 °C for 3 h. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatog-

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Organometallics XXXX, XXX, XXX−XXX

raphy on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. The red solid Rh(ttp)(cyclohexyl)[23] (**3a**; 6.2 mg, 0.0072 mmol, 74%) was collected.

Reaction of Rh(ttp)Cl with Cyclohexyl Iodide and KOH in Air. Rh(ttp)Cl (**1a**; 7.8 mg, 0.0097 mmol), aqueous KOH (5.5 M, 0.0175 mL, 0.096 mmol), and cyclohexyl iodide (**5a**; 0.0125 mL, 0.097 mmol) were added to benzene (2.0 mL). The mixture was heated to 120 °C for 24 h. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. The red solid Rh(ttp)(cyclohexyl)[23] (**3a**; 6.2 mg, 0.0072 mmol, 74%) was collected.

Reaction of Rh(ttp)Cl with *n*-Octyl Chloride and KOH in Air. Rh(ttp)Cl (**1a**; 7.7 mg, 0.0095 mmol), aqueous KOH (5.5 M, 0.0175 mL, 0.096 mmol), and *n*-octyl chloride (**4b**; 0.0165 mL, 0.097 mmol) were added to benzene (2.0 mL). The mixture was heated to 120 °C for 3 h. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. The red solid Rh(ttp)(*n*-octyl)[1d] (**3c**; 6.8 mg, 0.0077 mmol, 81%) was collected.

Reaction of Rh(ttp)Cl with *n*-Butyl Iodide and KOH in Air. Rh(ttp)Cl (**1a**; 7.8 mg, 0.0097 mmol), aqueous KOH (5.5 M, 0.0175 mL, 0.096 mmol), and *n*-butyl iodide (**5b**; 0.011 mL, 0.097 mmol) were added to benzene (2.0 mL). The mixture was heated to 120 °C for 24 h. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. The red solid Rh(ttp)(*n*-butyl)[8] (**3d**; 6.1 mg, 0.0074 mmol, 76%) was collected.

Reaction of Rh(ttp)Cl with BnBr and KOH in Air. Rh(ttp)Cl (**1a**; 7.8 mg, 0.0097 mmol), aqueous KOH (5.5 M, 0.0175 mL, 0.096 mmol), and benzyl bromide (**2c**; 0.0115 mL, 0.096 mmol) were added to benzene (2.0 mL). The mixture was heated to 120 °C for 1 h. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. The red solid Rh(ttp)Bn[24] (**3e**; 5.0 mg, 0.0058 mmol, 60%) was collected.

Reaction of Rh(ttp)Cl with Neopentyl Bromide and KOH in Air. Rh(ttp)Cl (**1a**; 7.9 mg, 0.0098 mmol), aqueous KOH (5.5 M, 0.0175 mL, 0.096 mmol), and neopentyl bromide (**2d**; 0.012 mL, 0.096 mmol) were added to benzene (2.0 mL). The mixture was heated to 120 °C for 5 h. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. The red solid Rh(ttp)(neopentyl) (**3f**; 3.5 mg, 0.0042 mmol, 43%) was collected. R_f = 0.80 (hexane/CH_2Cl_2 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ −4.99 (d, $^2J_{Rh-H}$ = 2.8 Hz, 2H), −2.49 (s, 9H), 2.69 (s, 12H), 7.53 (t, J = 6.6 Hz, 8H), 7.99 (d, J = 7.5 Hz, 4H), 8.06 (d, J = 7.4 Hz, 4H), 8.70 (s, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.7, 26.1, 32.5 ($^1J_{Rh-C}$ = 27.0 Hz), 32.5, 122.9, 127.4, 127.5, 131.5, 133.7, 134.1, 137.3, 139.4, 143.7. HRMS (FABMS): calcd for $C_{53}H_{47}N_4Rh$ $[M]^+$ m/z 842.2850, found m/z 842.285632.

Reaction of Rh(ttp)Cl with Methyl Iodide and KOH in Air. Rh(ttp)Cl (**1a**; 7.8 mg, 0.0097 mmol), aqueous KOH (5.5 M, 0.0175 mL, 0.096 mmol), and methyl iodide (**5c**; 0.006 mL, 0.096 mmol) were added to benzene (2.0 mL). The mixture was heated to 120 °C for 24 h. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. The red solid Rh(ttp)Me[7] (**3g**; 4.1 mg, 0.0052 mmol, 54%) was collected.

Reaction of Rh(tmp)Cl with Methyl Iodide and KOH in Air at 120 °C. Rh(tmp)Cl (**1b**; 8.9 mg, 0.0097 mmol), aqueous KOH (5.5 M, 0.0175 mL, 0.096 mmol), and methyl iodide (**5c**; 0.006 mL, 0.096 mmol) were added to benzene (2.0 mL). The mixture was heated to 120 °C for 84 h. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. The red solid Rh(tmp)Me[25] (**6a**; 4.4 mg, 0.0049 mmol, 51%) was collected.

Reaction of Rh(tmp)Cl with Methyl Iodide and KOH in Air at 150 °C. Rh(tmp)Cl (**1b**; 8.9 mg, 0.0097 mmol), aqueous KOH (5.5 M, 0.0175 mL, 0.096 mmol), and methyl iodide (**5c**; 0.006 mL, 0.096 mmol) were added to benzene (2.0 mL). The mixture was heated to 150 °C for 10 h. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. The red solid Rh(tmp)Me[25] (**6a**; 7.5 mg, 0.0083 mmol, 86%) was collected.

Reaction of Rh(tmp)Cl with BnBr and KOH in Air at 150 °C. Rh(tmp)Cl (**1b**; 8.9 mg, 0.0097 mmol), aqueous KOH (5.5 M, 0.0175 mL, 0.096 mmol), and benzyl bromide (**2c**; 0.0115 mL, 0.096 mmol) were added to benzene (2.0 mL). The mixture was heated to 150 °C for 3 h. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. The red solid Rh(tmp)Bn[1b,25b] (**6b**; 4.6 mg, 0.0047 mmol, 49%) was collected.

Reaction of Rh(tmp)Cl with *n*-BuBr and KOH in Air at 150 °C. Rh(tmp)Cl (**1b**; 8.9 mg, 0.0097 mmol), aqueous KOH (5.5 M, 0.0175 mL, 0.096 mmol), and *n*-butyl bromide (**2e**; 0.0105 mL, 0.098 mmol) were added to benzene (2.0 mL). The mixture was heated to 150 °C for 5 h. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. The red solid Rh(tmp)(*n*-butyl)[2b] (**6c**; 5.4 mg, 0.0057 mmol, 59%) was collected.

Reaction of Rh(ttp)Cl with *n*-Pentyl Tosylate and KOH in Air. Rh(ttp)Cl (**1a**; 11.3 mg, 0.014 mmol), aqueous KOH (5.5 M, 0.026 mL, 0.14 mmol), and *n*-pentyl tosylate (**7**; 0.031 mL, 0.14 mmol) were added to benzene (2.0 mL). The mixture was heated to 120 °C for 1 h. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. The first band was collected to give the red solid Rh(ttp)(*n*-pentyl)[23] (**3b**; 5.1 mg, 0.0060 mmol, 43%).

Synthesis of *n*-Pentyl 4-(Rh(ttp)CH_2)benzenesulfonate (3h). Rh(ttp)Cl (**1a**; 15.5 mg, 0.019 mmol), aqueous KOH (5.5 M, 0.035 mL, 0.19 mmol), and *n*-pentyl tosylate (**7**; 0.004 mL, 0.018 mmol) were added to benzene (2.0 mL). The mixture was heated to 150 °C for 15 min. Excess benzene was removed by rotary evaporation. The residue was purified by column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (1/1) as eluent. The major red band was collected to give the red solid *n*-pentyl 4-(Rh(ttp)CH_2)-benzenesulfonate (**3h**; 4.6 mg, 0.0045 mmol, 24%). R_f = 0.32 (hexane/CH_2Cl_2 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ −3.85 (d, $^2J_{Rh-H}$ = 3.5 Hz, 2H), 0.81 (t, J = 6.9 Hz, 3H), 1.21−1.15 (m, 4H), 1.48 (t, J = 7.0 Hz, 2H), 2.71 (s, 12H), 2.99 (d, J = 7.9 Hz, 2H), 3.65 (t, J = 6.6 Hz, 2H), 6.39 (d, J = 8.1 Hz, 2H), 7.55 (d, J = 7.7 Hz, 4H), 7.58 (d, J = 7.7 Hz, 4H), 7.99 (d, J = 7.6 Hz, 4H), 8.05 (d, J = 7.5 Hz, 4H), 8.71 (s, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 9.0 ($^1J_{Rh-C}$ = 28.0 Hz), 13.9, 21.7, 22.2, 27.5, 28.6, 70.6, 122.9, 124.7, 125.5, 127.6, 127.7, 130.0, 131.8, 133.9, 134.0, 137.6, 139.1, 143.2, 148.5. HRMS (FABMS): calcd for $C_{60}H_{53}N_4O_3RhS$ $[M + H]^+$ m/z 1013.2966, found m/z 1013.296177.

Competition Reaction of *n*-Pentyl Bromide and Cyclopentyl Bromide with Rh(ttp)Cl. Rh(ttp)Cl (**1a**; 7.8 mg, 0.0097 mmol), aqueous KOH (5.5 M, 0.0175 mL, 0.096 mmol), *n*-pentyl bromide (**2b**; 0.012 mL, 0.097 mmol), and cyclopentyl bromide (**2f**; 0.012 mL, 0.097 mmol) were added to benzene (2.0 mL). The mixture was heated to 120 °C for 1 h. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (7/1) as eluent. The red solids Rh(ttp)(*n*-pentyl)[23] (**3b**; 4.4 mg, 0.0052 mmol, 54%) and Rh(ttp)(cyclopentyl)[23] (**3i**; 1.2 mg, 0.0014 mmol, 14%) were collected in a single fraction. The ratio was determined by the integrations of proton signals of their products by ^{1}H NMR spectroscopy (Table S7 in the Supporting Information).

Reaction of Rh(ttp)Cl with ^{t}BuBr and KOH in Air. Rh(ttp)Cl (**1a**; 7.9 mg, 0.0098 mmol), aqueous KOH (5.5 M, 0.0175 mL, 0.096 mmol), and ^{t}Bu-Br (**2g**; 0.011 mL, 0.098 mmol), were added to benzene (2.0 mL). The mixture was heated to 120 °C for 1 h. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (1/3) as eluent. The red solid HBr·Rh(ttp)Cl (**1a**·HBr; 3.7 mg, 0.0042 mmol, 43%) was collected. R_f = 0.26 (hexane/CH_2Cl_2 1/3). ^{1}H NMR ($CDCl_3$, 400 MHz): δ −0.28 (br, 8H, ligated

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Organometallics XXXX, XXX, XXX−XXX

H_2O), 2.71 (s, 12H), 7.55 (t, J = 5.9 Hz, 8H), 8.08 (t, J = 5.8 Hz, 8H), 8.91 (s, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.7, 121.9, 127.4, 127.7, 132.7, 133.9, 134.8, 137.5, 139.3, 143.5. HRMS (ESIMS): calcd for $C_{48}H_{36}BrClN_4Rh$ [M-Cl]$^+$ m/z 850.1173, found m/z 850.117473.

Reaction of Rh(ttp)Cl with 1-Bromoadamantane and KOH in Air. Rh(ttp)Cl (**1a**; 15.5 mg, 0.019 mmol), aqueous KOH (5.5 M, 0.035 mL, 0.19 mmol), and 1-bromoadamantane (**2h**; 8.2 mg, 0.038 mmol) were added to benzene (2.0 mL). The mixture was heated to 180 °C for 16 h. Excess benzene was removed by rotary evaporation. The residue was washed with MeOH (2 mL × 3) and then purified by flash pipet column chromatography on alumina with a hexane/CH_2Cl_2 solvent mixture (4/1) as eluent under N_2. The red solid Rh(ttp)(1-adamantyl) (**3j**; 7.8 mg, 0.0086 mmol, 45%) was collected. R_f = 0.30 (hexane/CH_2Cl_2 4/1). ^1H NMR (C_6D_6, 400 MHz): δ −3.33 (s, 6H), −0.21 (d, J = 11.1 Hz 3H), −0.04 (s, 3H), 0.06 (d, J = 11.4 Hz, 3H), 2.41 (s, 12H), 7.33 (d, J = 7.3 Hz, 8H), 8.16 (d, J = 7.4 Hz, 4H), 8.25 (d, J = 7.0 Hz, 4H), 8.98 (s, 8H). ^{13}C NMR (C_6D_6, 100 MHz): δ 21.5, 33.0, 36.1, 46.1, 50.9 ($^1J_{Rh-C}$ = 30.0 Hz), 123.8, 127.7, 132.0, 133.9, 134.7, 137.2, 140.4, 144.1. HRMS (ESIMS): calcd for $C_{58}H_{51}N_4Rh$ [M]$^+$ m/z 906.3169, found m/z 906.316497.

■ ASSOCIATED CONTENT

Supporting Information

Tables, figures, and a CIF file giving X-ray crystallographic data for HBr·Rh(ttp)Cl (**1a**·HBr), reaction conditions optimization, competition experiment ratio of Rh(ttp)(*n*-pentyl) to Rh(ttp)(cyclopentyl), and ^1H NMR and ^{13}C NMR spectra. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00488.

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Notes

The authors declare no competing financial interest.

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Organometallics XXXX, XXX, XXX−XXX