# Base-Promoted Carbon−Hydrogen Bond Activation of Alkanes with Rhodium(III) Porphyrin Complexes

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Base-promoted carbon−hydrogen bond activation of alkanes was achieved in the reactions of alkanes with rhodium(III) porphyrin chlorides (Rh(por)Cl) at 120 °C to give rhodium porphyrin alkyls in moderate yields. This carbon−hydrogen activation (CHA) of alkane provided a facile synthesis of Rh(por)R. Mechanistic investigation of CHA suggested that Rh(por)H and $[Rh(por)]_2$ were key intermediates for the CHA step.

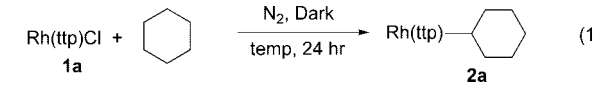
## Introduction

Carbon−hydrogen bond activation (CHA) of organic compounds by transition-metal complexes is an important area of research in organometallic chemistry.[1] The CHA of alkane is challenging, due to the lack of reactivity of alkanes.[2] Previous examples include low-valent transition-metal complexes, while more recent systems involved high-valent late-transition-metal complexes because of their added advantages of broader functional group compatibility.[3] Examples of high-valent late-transition-metal Rh(III) and Ir(III) complexes undergoing CHA are well-known.[4] Schwartz and co-workers demonstrated the Rh(III)-catalyzed chlorination of methane.[4a,b] Recently, iridium(III) pincer complexes catalyzed the dehydrogenation of cylcooctane.[4c,d] Periana and co-workers worked on the alkyl CHA with bis-bidentate O-donor iridium(III) complexes.[4e,f]

The bond activation chemistry of Rh(III) and Ir(III) is commonly accepted to occur by either $\sigma$-bond metathesis or heterolysis. However, recent reports have provided evidence for oxidative addition in which a Rh(V) or Ir(V) intermediate is formed.[5] Therefore, diverse mechanistic possibilities exist.

We have been interested in CHA by rhodium(III) porphyrin complexes. Rhodium porphyrin chloride can activate the *meta* C−H bond of benzonitrile to give (*m*-cyanophenyl)rhodium porphyrin complexes selectively via an $S_EAr$ mechanism.[6] Aryl and alkyl aldehydes also undergo selective aldehydic CHA to give rhodium porphyrin aryl and alkyl acyls.[7] Recently, we have reported the selective benzylic CHA of toluenes promoted by base.[8] These types of CHA are mechanistically puzzling, though we have suggested a heterolytic or $\sigma$-bond metathesis pathway. To explore the scope and gain further understanding of the bond activation chemistry of rhodium(III) porphyrin complexes, we have successfully discovered the base-promoted aliphatic CHA of alkanes and identified some key features of the reaction mechanism and herein report our results.

**Table 1. Effect of Temperature on CHA of Cyclohexane**




| entry | temp (°C) | yield (%) |
|---|---|---|
| 1 | 80 | trace |
| 2 | 100 | 3 |
| 3 | 120 | 31 |
| 4 | 150 | 16 |
| 5 | 200 | 18 |

## Results and Discussion

Initially, rhodium(III) tetrakis(4-tolylporphyrin) chloride (Rh(ttp)Cl; **1a**) reacted with cyclohexane at 80 and 100 °C for 24 h to give a trace amount of Rh(ttp)(*c*-hexyl) (eq 1, Table 1, entries 1 and 2). At 120 °C for 24 h, successful CHA of cyclohexane occurred and Rh(ttp)(*c*-hexyl) (**2a**) was obtained in 31% yield (Table 1, entry 3). When the temperature was further increased to 150 or 200 °C, Rh(ttp)(*c*-hexyl) (**2a**) was obtained in lower yields of 16% and 18%, respectively (Table 1, entries 4 and 5). Likely, Rh(ttp)(*c*-hexyl) (**2a**) is thermally unstable. Indeed, when Rh(ttp)(*c*-hexyl) (**2a**) was heated in cyclohexane at 120 and 150 °C for 1 day, the recovery yields were 80 and 41%, respectively. Therefore, the optimal reaction temperature was selected to be 120 °C.

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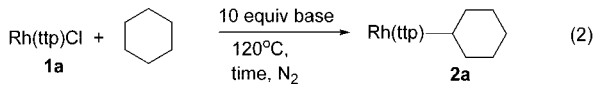
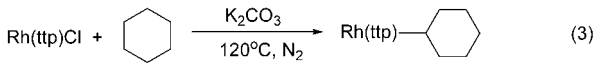
**Table 2. Base Effect in CHA**




| entry | base | time (h) | yield (%) |
|---|---|---|---|
| 1 | none | 24 | 31 |
| 2 | $PPh_3$ | 24 | 0[a] |
| 3 | 2,2′-bpy[b] | 48 | 50 |
| 4 | 2,6-dbpy[c] | 24 | 50 |
| 5 | 2,6-dppy[d] | 24 | 58 |
| 6 | 2,6-dppy[d] | 6 | 23 |
| 7 | NaOH | 6 | 47 |
| 8 | NaOAc | 6 | 51 |
| 9 | $K_2CO_3$ | 6 | 59 |
| 10 | $K_2CO_3$ | 24 | 40 |

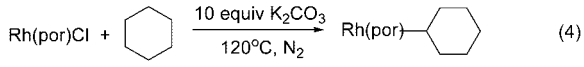
[a] Rh(ttp)Cl($PPh_3$) (**2f**) was obtained in 83% yield. [b] 2,2′-bpy = 2,2′-bipyridine. [c] 2,6-dbpy = 2,6-di-*tert*-butylpyridine. [d] 2,6-dppy = 2,6-diphenylpyridine.

**Table 3. Effect of $K_2CO_3$ Loading in CHA of Cyclohexane**




| entry | amt of $K_2CO_3$ (equiv) | time (h) | yield (%) |
|---|---|---|---|
| 1 | 0 | 24 | 31 |
| 2 | 5 | 24 | 35 |
| 3 | 10 | 6 | 59 |
| 4 | 20 | 6 | 56 |

**Table 4. CHA of Cyclohexane with Rh(por)Cl**




| entry | por | time (h) | product (yield (%)) |
|---|---|---|---|
| 1 | ttp | 6 | **2a** (59) |
| 2 | tpp | 5 | **4a** (52) |
| 3 | bocp | 1 | **4b** (61) |

With the reported base-promoted benzylic CHA of toluenes by $Rh^{III}$(ttp)Cl[8] and other examples of base-promoted CHA by transition-metal complexes,[9] we sought to examine the promoting effect of various bases. Table 2 and eq 2 give the results of the screenings. The ligand, $PPh_3$, only gave coordination complex **2f,** without any CHA product (Table 2, entry 2). On the other hand, non-coordinating bases of 2,2′-bipyridine, 2,6-di-*tert*-butylpyridine, and 2,6-diphenylpyridine gave higher yields of over 50% of Rh(ttp)(*c*-hexyl) in 1 day (eq 2, Table 2, entries 3−5). However, a shorter reaction time of 6 h resulted in the much lower yield of 23% (Table 2, entry 6).

To our delight, nucleophilic inorganic bases were found to promote both the yields and rates of CHA (Table 2, entries 7−9). When NaOH was added, the reaction only took 6 h and the yield of **2a** was 47%. NaOAc gave a slightly higher yield of 51%, and $K_2CO_3$ gave the highest yield of 59%. These nucleophilic bases required just 6 h for the reaction to be complete. Prolonged heating to 1 day with $K_2CO_3$ resulted in a lower yield of 40% (Table 2, entry 10). From these results, the optimal reaction conditions were found to require $K_2CO_3$ in 6 h.

The loading of base was further optimized (eq 3, Table 3). Five equivalents of $K_2CO_3$ increased the reaction yield slightly, but the reaction rate was not faster (Table 3, entry 2 vs 1). A higher loading of 10 equiv of $K_2CO_3$ increased both the reaction yield and the rate (Table 3, entry 3). However, a further increase to 20 equiv of $K_2CO_3$ did not result in any further enhancement in yield (Table 3, entry 4). Therefore, the optimized reaction conditions were found to require 10 equiv of $K_2CO_3$ at 120 °C. Visual inspection of the reaction mixture showed that even 5 equiv of $K_2CO_3$ did not dissolve completely at 120 °C; therefore, the reaction mixture was heterogeneous.

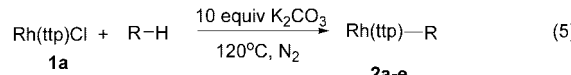
The structures of porphyrins in the rhodium porphyrin chlorides affect the rates and yields of the CHA of cyclohexane. The electronic effects of CHA were examined by three Rh(por)Cl species, including Rh(bocp)Cl (**1c**; bocp = 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(*p-tert*-butylphenyl)porphyrinato dianion), Rh(tpp)Cl (**1b**; tpp = 5,10,15,20-tetraphenylporphyrinato dianion), and Rh(ttp)Cl (**1a**) (Table 4, eq 4). The reaction rates followed the order of electron-deficient Rh(por)Cl: Rh(bocp)Cl > Rh(tpp)Cl > Rh(ttp)Cl (Table 4, entries 1−3).

The optimized $K_2CO_3$-promoted reaction conditions were successfully applied to other alkanes. Cyclopentane and cyclohexane gave the cyclopentyl and cyclohexyl complexes, in 76 and 59% yields, respectively in 6 h (eq 5, Table 5, entries 1 and 2). The straight-chain alkanes reacted with Rh(ttp)Cl (**1a**) more slowly than cyclohexane (Table 5, entries 3−5 vs 2). A longer time of 24 h was required. The yields of Rh(ttp) alkyls increased with the chain length, presumably due to the observed increasing solubility of Rh(ttp)Cl (**1a**) in longer chain hydrocarbons. Selective terminal CHA took place to give only the primary Rh(ttp) alkyls. While the thermal isomerization of $Rh(ttp)CH_2CH_2CH_3$ into $Rh(ttp)CH(CH_3)_2$ has been reported, the time to establish equilibrium requires 10 days.[10] Therefore, the isomerization of these Rh(ttp) alkyls did not occur in 24 h.

We were not able to detect any cyclohexanol, cyclohexyl chloride, cyclohexene, or cyclohexanone by GC-MS analysis of the crude reaction mixture. It may be that the concentration of these species, if formed, was low in the presence of 1000 times more cyclohexane.

In order to understand the lower yield of Rh(ttp) alkyl with longer reaction time (Table 2, entries 9 and 10), the thermal stability of Rh(ttp)(*c*-pentyl) in the presence of $K_2CO_3$ at 120 °C was examined and monitored by $^1H$ NMR spectroscopy (eq

**Table 5. Activation of Alkanes with Rh(ttp)Cl**




| entry | substrate | time (h) | product (yield (%)) |
|---|---|---|---|
| 1 | cyclopentane | 6 | **2b** (76) |
| 2 | cyclohexane | 6 | **2a** (59) |
| 3 | *n*-pentane | 24 | **2c** (29) |
| 4 | *n*-hexane | 24 | **2d** (40) |
| 5 | *n*-heptane | 24 | **2e** (58) |

**Scheme 1. Proposed Decomposition Pathway of Rh(ttp)(cyclopentyl)**

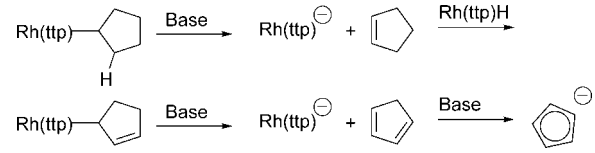



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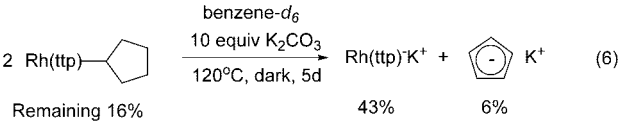
**Table 6. Selected Bond Lengths (Å) and Angles (deg) for Rh(por)R**

| entry | Rh(ttp)R | Rh−C length (Å) | dihedral angle between Ph group and mean porphyrin plane (deg) | max deviation from least-squares plane (Å) | Rh−$N_{av}$ (Å) |
|---|---|---|---|---|---|
| 1 | Rh(ttp)(cyclohexyl) (**2a**) | 2.126(7) | 80.79 (7) | 0.465(4) | 2.019 |
| 2 | Rh(ttp)(cyclopentyl) (**2b**) | 2.073(7) | 80.98 (3) | 0.452(7) | 2.017 |
| 3 | Rh(ttp)(*n*-heptyl) (**2e**) | 2.048(3) | 82.25(5) | 0.552(3) | 2.019 |
| 4 | $Rh(oep)CH_3$[12] | 1.970(4) | | | 2.027 |

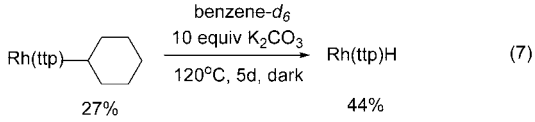
6). After the reaction mixture was heated for 30 min, the pyrrole signal of Rh(ttp)(cyclopentyl) shifted up from $\delta$ 8.99 to 8.59 ppm, assigned to be that of $Rh(ttp)^-$ (34% yield), and Rh(ttp)H was formed in 8% yield. Then after 13 h, a small amount of a cyclopentadienyl anion $^1$H NMR signal appeared ($\delta$ 5.69 ppm).[11] After 5 days, its yield increased to 6%. When dilute aqueous HCl was added into the reaction mixture, Rh(ttp)H (**1d**) ($\beta$-H at $\delta$ 9.03 ppm) was observed, further supporting the formation of $Rh(ttp)^-$.



(6)

We rationalize that $K_2CO_3$ abstracts the $\beta$-alkyl proton of Rh(ttp)(cyclopentyl) by an $E_2$ elimination to give $Rh(ttp)^-$ and cyclopentene (Scheme 1). As Rh(ttp)H is a moderately strong acid with a p$K_a$ value of about 11,[12] $Rh(ttp)^-$ is therefore a good leaving group. Similar base-induced $\beta$-elimination has also been reported.[13] Then cyclopentene can further undergo CHA at the allylic position and subsequent $\beta$-proton elimination to give cyclopentadiene, which mostly either dimerizes or polymerizes but still yields a small amount of cyclopentadienyl anion upon reaction with base.

Rh(ttp)(cyclohexyl) (**2a**) was more stable than Rh(ttp)(cyclopentyl) (**2b**) under the same basic, thermal conditions (eq 7). After 5 days, 27% remained of Rh(ttp)(cyclohexyl) together with Rh(ttp)H formed in 44% yield, presumably from the protonation of the $Rh(ttp)^-$ intermediate with some residual water present in the solvent or $K_2CO_3$.



(7)

The higher stability of Rh(ttp)(cyclohexyl) is likely due to the smaller dihedral angle of Rh−$C_\alpha$−$C_\beta$−$H_\beta$, disfavoring the antiperiplanar transition state of an $E_2$ elimination[14] (dihedral angles of Rh−$C_\alpha$−$C_\beta$−$H_\beta$ of Rh(ttp)(cyclopentyl) (**2b**) and Rh(ttp)(cyclohexyl) (**2a**) are 131 and 122°, respectively; see the Supporting Information for X-ray data).

These CHA reactions further provide a facile, convenient synthesis of Rh(por) alkyls. For comparison, a previous synthesis of rhodium porphyrin alkyl was achieved by a two-step process via reductive alkylation ($NaBH_4$/RBr) with yields from 48 to 97%.[15] This synthetic route can access a variety of rhodium porphyrin alkyls directly from alkanes in one step.

**X-ray Structure Determination.** Table 6 gives selected bond lengths and angles for complexes **2a**,**b**,**e**. Figures 1−3 show the molecular structures of **2a**,**b**,**e**, respectively (30% thermal ellipsoids). The Rh−C bond lengths of **2a**,**b**,**e** range from 2.07 to 2.13 Å (Table 6, entries 1−3) and are similar to the reported Rh−C bond lengths of Rh(oep)Me (oep = 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion) (1.97 Å)[16] (Table 6, entry 4). The Rh−$N_{av}$ bond lengths do not vary significantly (2.017−2.019 Å). The Rh−C bond lengths appear to follow the steric size of alkyls in the order cyclohexyl > cyclopentyl > *n*-heptyl (Table 6, entries 1−3). The various alkyls do not cause large distortion of the mean porphyrin plane from planarity in complexes **2a** (0.465 Å), **2b** (0.452 Å), and **2e** (0.552 Å).

**Proposed Mechanism for CHA.** Scheme 2 shows two possible pathways for the proposed mechanism of alkyl CHA with Rh(ttp)Cl (**1a**).

**Pathway $I_a$.** In the absence of base, Rh(ttp)Cl (**1a**) initially undergoes heterolysis to form Rh(ttp) cation and chloride anion, most likely as an ion pair.[6−8] An alkane then coordinates to the Rh metal center to form a C−H−Rh complex.[17] Finally, the alkyl C−H bond is cleaved to give Rh(ttp)H. The coordination of alkane to the Rh metal center is supported by the inhibition of CHA by $PPh_3$ (Table 2, entry 2). Upon addition of $PPh_3$, Rh(ttp)Cl (**1a**) did not react with cyclohexane at 120 °C in 24 h to give any Rh(ttp)(cyclohexyl) (**2a**).

Monitoring the reaction of Rh(ttp)Cl (**1a**) with cyclohexane (50 equiv) in benzene-$d_6$, a poorer hydrogen donor than cyclohexane, in a sealed NMR tube at 120 °C over the course of 12 h by $^1$H NMR spectroscopy did not reveal any intermediate, only the formation of Rh(ttp)H and Rh(ttp)(cyclohexyl) in 68 and 4% yields, respectively. No stable, long-lived intermediate likely formed, suggesting the Rh(por)Cl ion pair or C−H−Rh complex is highly reactive. Furthermore, the major product is Rh(ttp)H in benzene solvent rather than Rh(ttp)(cyclohexyl) in cyclohexane solvent. Probably, the reaction of Rh(ttp)H with a slight excess of cyclohexane is slow.

**Pathway $I_b$.** In the base-promoted reaction, Rh(ttp)Cl initially undergoes ligand substitution with MX to give Rh(ttp)X (MX = NaOH, NaOAc, $K_2CO_3$). Recently, iridium(III) hydroxide,[18a]

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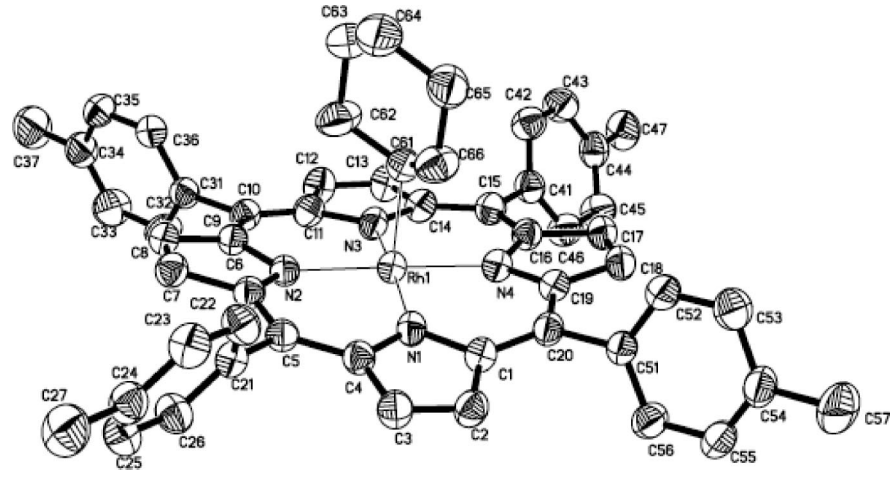



**Figure 1.** ORTEP presentation of the molecular structure with numbering scheme for complex **2a** (30% probability displacement ellipsoids).

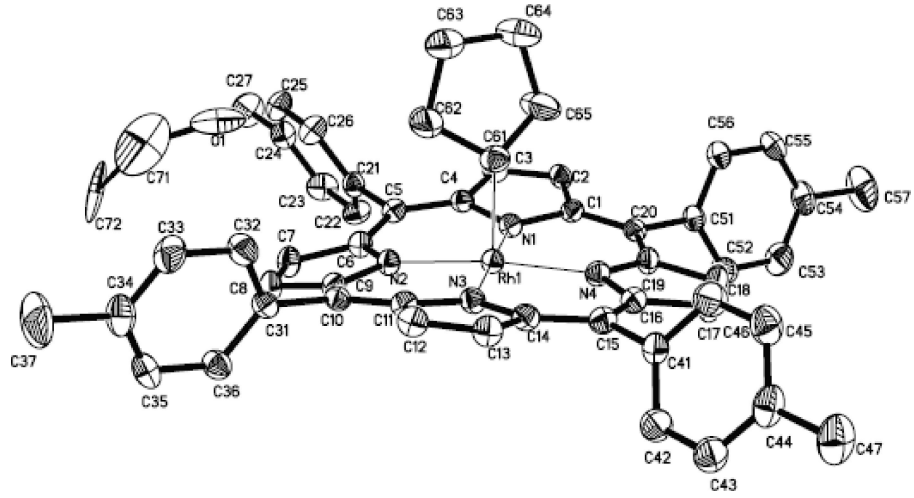



**Figure 2.** ORTEP presentation of the molecular structure with numbering scheme for complex **2b** (30% probability displacement ellipsoids).

iridium(III) alkoxide,[18b] rhodium(III) hydroxide,[18c] ruthenium(II) hydroxide,[18d] and rhodium(III) alkoxide[18e] have been reported and these ruthenium and iridium complexes can undergo C−H activation.[18a,b,d] Rh(ttp)X is then rapidly reduced by an alkane to form Rh(ttp)H (**1d**), which then yields the metal−metal-bonded $[Rh(ttp)]_2$ (**1e**)[19] quickly in basic media.

When the reaction mixture with $K_2CO_3$ in benzene-$d_6$ was followed by $^1$H NMR spectroscopy (eq 8, Figure 4), no Rh(ttp)H but only $[Rh(ttp)]_2$ was observed after 30 min. Likely, Rh(ttp)H was converted rapidly to $[Rh(ttp)]_2$ in a basic medium. After 3 h, Rh(ttp)(cyclohexyl) slowly grew in to about 15% yield and Rh(ttp)H formed quickly in up to 50% yield. The composition of the reaction mixture remained more or less the same up to 12 h with a major amount of Rh(ttp)H and small amounts of $[Rh(ttp)]_2$ and Rh(ttp)(cyclohexyl) present. It is likely that with a slight excess of cyclohexane in benzene instead of cyclohexane as the solvent, the base-promoted $E_2$ elimination of Rh(ttp)(cyclohexyl) becomes competitive to re-form $Rh(ttp)^-$ or Rh(ttp)H after protonation from the small amount of water present as well as forming the coproduct cyclohexene. Cyclohexene may also further undergo multiple CHA and $E_2$ elimination to give benzene, analogous to the case for cyclopentene. Indeed, benzene was observed by $^1$H NMR spectroscopy when cyclohexane-$d_{12}$ was used as the solvent. After 5 days of heating, the $^1$H NMR signal of benzene was observed ($\delta$ 7.21 ppm) in cyclohexane-$d_{12}$ with 8% yield. Rh(ttp)(cyclohexyl) (**2a**) decomposed, and its recovery yield was 31%. The decomposed Rh(ttp) complexes possibly precipitated and were not detected by $^1$H NMR.

$$\underset{\text{1 equiv}}{\text{Rh(ttp)Cl}} + \underset{\text{50 equiv}}{\text{benzene-}d_6} \xrightarrow[120\ ^\circ\text{C, dark, 3h}]{\text{10 equiv } K_2CO_3} \underset{\text{15\%}}{\text{Rh(ttp)}}\text{—} + \underset{\text{50\%}}{\text{Rh(ttp)H}} \qquad (8)$$

Independent experiments showed that $[Rh(ttp)]_2$ (**1e**) and presumably $H_2$ were formed quickly over 15 min at room temperature from Rh(ttp)H (**1d**) added with base (eq 9). However, Rh(ttp)H was thermally stable in the absence of base, even upon heating at 120 °C for 6 days with 90% recovery (eq 10). Therefore, both $[Rh(ttp)]_2$ and Rh(ttp)H can activate RH to give Rh(ttp)R in pathways $II_{a-c}$ (Scheme 2).

$$2\text{Rh(ttp)H} \xrightarrow[15\text{ min, }23\ ^\circ\text{C}]{\text{benzene-}d_6,\ \text{10 equiv KOH}} \underset{\text{55\%}}{[\text{Rh(ttp)}]_2} + \text{H}_2 \qquad (9)$$

$$\underset{\text{recovery yield 90\%}}{\text{Rh(ttp)H}} \xrightarrow[120\ ^\circ\text{C, 6 days}]{\text{benzene-}d_6} \text{no reaction} \qquad (10)$$

To further understand why Rh(ttp)H did not react completely with a slight excess of cyclohexane in benzene solvent, the

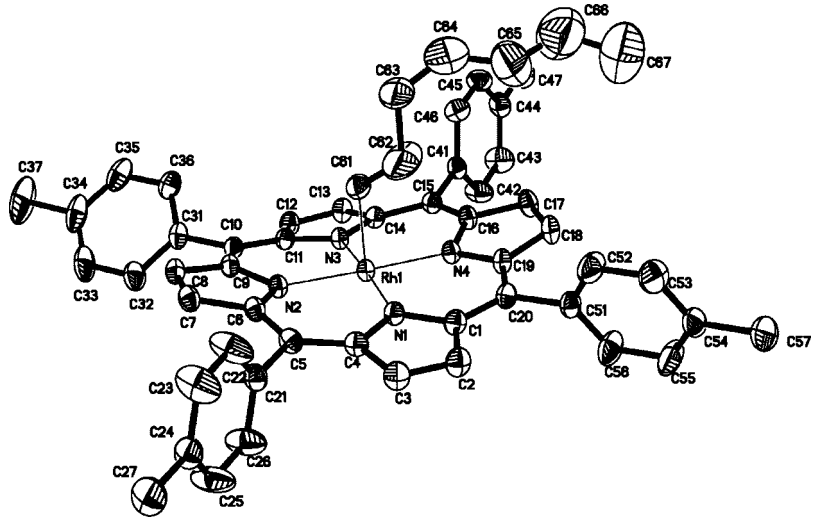
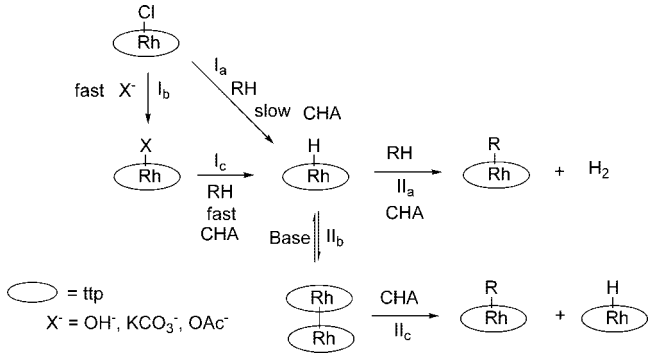



**Figure 3.** ORTEP presentation of the molecular structure with numbering scheme for complex **2e** (30% probability displacement ellipsoids).

**Scheme 2. Proposed Mechanism of Alkyl CHA with Rh(ttp)Cl**




thermal CHA reaction of Rh(ttp)H with cyclohexane at 120 °C in 3 h was carried out. Indeed, Rh(ttp)(cyclohexyl) was formed in 36% yield and supported the intermediancy of Rh(ttp)H (eq 11). The low yield of Rh(ttp)(cyclohexyl) in a slight excess of cyclohexane is probably due to the unfavorable equilibrium with limited cyclohexane as well as the base-promoted or thermal $\beta$-H elimination of Rh(ttp)(cyclohexyl).

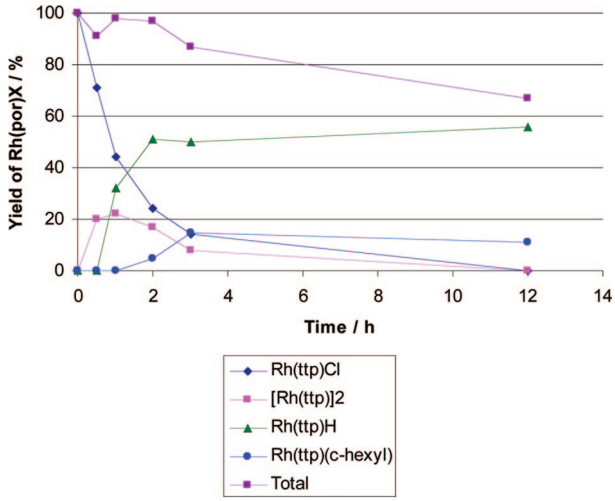
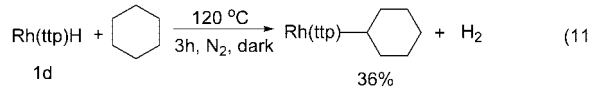
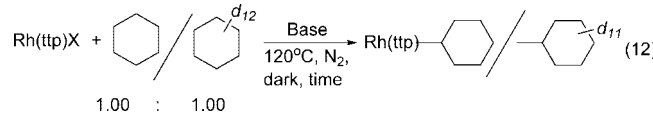



**Figure 4.** Time profile of Rh(ttp)Cl and cyclohexane with $K_2CO_3$.




(11)

**Table 7. KIE Values for Reactions of Rh(ttp)X with Cyclohexane**




(12)

| entry | Rh(ttp)X | base (amt (equiv)) | time (h) | KIE by $^1$H NMR | yield (%) |
|---|---|---|---|---|---|
| 1 | Rh(ttp)Cl | $K_2CO_3$ (10) | 6 | 9.1 ± 0.3[a] | 32 |
| 2 | Rh(ttp)H | none | 3 | 8.9 ± 0.3 | 54 |
| 3 | Rh(ttp)H | $K_2CO_3$ (10) | 3 | 8.5 ± 0.4 | 59 |
| 4 | $[Rh(ttp)]_2$ | none | 6 | 8.7 ± 0.3 | 38 |
| 5 | $[Rh(ttp)]_2$ | $K_2CO_3$ (10) | 6 | 9.0 ± 0.3 | 42 |

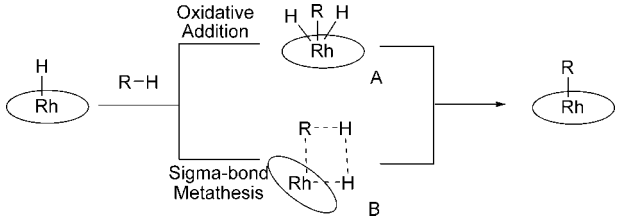
[a] The KIE determined by MS was 9.7 ± 0.2.

To gain further information about the nature of the transition state and the possible Rh species involved (pathways $I_c$ and $II_{a-c}$), the kinetic isotope effects of the CHA reaction were measured by a series of competition experiments. Rh(ttp)Cl (**1a**) was reacted with an equimolar mixture of cyclohexane and cyclohexane-$d_{12}$ in the presence of 10 equiv of $K_2CO_3$ at 120 °C over 6 h. The ratio of Rh(ttp)(cyclohexyl) (**2a**) to Rh(ttp)(cyclohexyl)-$d_{11}$ was determined to be 9.1:1.0 by $^1$H NMR spectroscopy. The large kinetic isotope effect (KIE) supported the notion that the C−H cleavage step to give Rh(ttp)(cyclohexyl) is involved in the rate-limiting step. The observed KIE is truly a kinetic value, as Rh(ttp)(cyclohexyl) did not exchange with cyclohexane-$d_{12}$ under the same conditions. Likewise, the KIEs of the CHA with Rh(ttp)H and $[Rh(ttp)]_2$ with or without $K_2CO_3$ were measured and are about 9.0 (eq 12, Table 7, entries 2 and 3 vs 4 and 5). Rh(ttp)H was also found to be more reactive than $[Rh(ttp)]_2$.

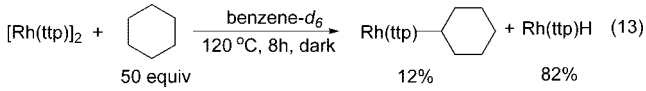
To gain further support that $[Rh(ttp)]_2$ is an intermediate, the reaction of $[Rh(ttp)]_2$ (**1e**) with cyclohexane in benzene-$d_6$ in a sealed NMR tube was monitored by $^1$H NMR spectroscopy (eq 13). After 8 h, both Rh(ttp)(cyclohexyl) (**2a**) and Rh(ttp)H (**1d**) were obtained in 12 and 82% yields, respectively (eq 13). The

(19) (a) Wayland, B. B.; Ba, S.; Sherry, A. E. *J. Am. Chem. Soc.* **1991**, *113*, 5305–5311. (b) Thibblin, A.; Sidhu, H. *J. Am. Chem. Soc.* **1992**, *114*, 7403–7407.

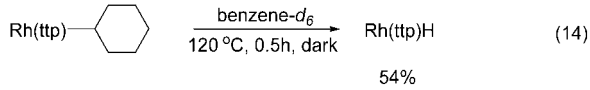
**Scheme 3. Proposed Pathways of Alkyl CHA with Rh(ttp)H**




much higher yield of Rh(ttp)H suggests that, even under thermal conditions, Rh(ttp)(cyclohexyl) still can generate Rh(ttp)H by $\beta$-H elimination, as ascertained by the independent thermal experiment shown in eq 14. Therefore, $[Rh(ttp)]_2$ is confirmed to be a viable intermediate of the CHA reaction under both neutral and basic conditions. The expected coproduct, cyclohexene, was not observed, which was rationalized by further dehydrogenation of cyclohexene to yield benzene.




(13)




(14)

Since the large values of KIEs of the CHA of $CH_4$ (8.6 at 25 °C and 5.1 at 80 °C) and of toluene (6.5 at 80 °C) with $Rh^{II}$(tmp) (tmp = 5,10,15,20-tetramesitylporphyrinato dianion) are supportive of a bimetalloradical linear, termolecular transition state,[19a] the similar magnitude of KIEs in the reaction of cyclohexane with Rh(ttp) complexes suggest that $Rh^{II}$(ttp) also undergo similar bimetalloradical activation with cyclohexane. However, the conversion of Rh(ttp)H to $[Rh(ttp)]_2$ in the absence of base is very slow; therefore, we tend to favor that both Rh(ttp)H and $[Rh(ttp)]_2$ are parallel reacting species under both neutral and basic conditions. However, we could not fully understand the high KIE value of 8.9 measured for the thermal reaction with Rh(ttp)H (Table 7, entry 2). A possible reason is the large KIE observed for a branching reaction from a common intermediate:[19b] in this case, the branching reaction of $Rh_2(ttp)_2$ with cyclohexane from the common intermediate of Rh(ttp)H.

As Rh(ttp)H was shown to be a viable intermediate of the CHA reaction (eq 11), two detailed mechanistic possibilities, oxidative addition and $\sigma$-bond metathesis, could exist (Scheme 3). For the oxidative addition, a seven-coordinated Rh(V) complex (A) formed at first with the three ligands R, H, and H on the same face of the porphyrin, which then underwent reductive elimination to give Rh(ttp)R and $H_2$. Though Rh(V) organometallic complexes are uncommon, they can be stabilized by strongly $\sigma$-donating ligands such as silyl[20] and hydride. The two *cis* dihydrides, e.g. $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiMe_3)_2]$ and $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiEt_3)_2]$,[20] are not sterically demanding enough to rule out the oxidative addition pathway. Alternatively, a concerted $\sigma$-bond metathesis or its variants such as $\sigma$-complex (B) assisted metathesis[21] could be a viable pathway.

The large KIE values of cyclohexane CHA with Rh(ttp)Cl (9.1) and with Rh(ttp)H (8.9) are not typical of "normal" $\sigma$-bond metathesis processes,[22] but they are similar to the KIE values of other CHA reactions involving methane-eliminating $\sigma$-bond metathetical events (8.7−9.1).[23a,b] As Rh(ttp)H (**1d**) reacts with cyclohexane to give Rh(ttp)(cyclohexyl) (**2a**), it may undergo $\sigma$-bond metathesis with $H_2$ elimination. Such $\sigma$-bond metathesis with $H_2$ elimination was also proposed in the alkane metathesis catalyzed by silica-supported tantalum hydride.[23c]

## Conclusions

Base-promoted aliphatic CHA of alkanes was achieved with rhodium(III) porphyrin complexes to give rhodium(III) porphyrin alkyls. Mechanistic investigations suggested that both Rh(ttp)H (**1d**) and $[Rh(ttp)]_2$ are key intermediates for the parallel CHA step. The roles of base are (i) to facilitate the formation of Rh(ttp)X, (ii) to enhance the CHA rate with alkane and generate Rh(ttp)H by a Rh(ttp)X species more reactive than Rh(ttp)Cl, and (iii) to provide a parallel CHA pathway by $[Rh(ttp)]_2$.

## Experimental Section

Unless otherwise noted, all reagents were purchased from commercial suppliers and used before purification. Hexane for chromatography was distilled from anhydrous calcium chloride. Rh(ttp)Cl (**1a**), Rh(tpp)Cl (**1b**), and Rh(bocp)Cl (**1c**) were prepared according to literature procedures. Thin-layer chromatography was performed on precoated silica gel 60 $F_{254}$ plates. Silica gel (Merck, 70−230 and 230−400 mesh) was used for column chromatography in air.

$^1$H NMR spectra were recorded on a Bruker DPX 300 (300 MHz) spectrometer. Spectra were referenced internally to the residual proton resonance in $C_6D_6$ ($\delta$ 7.15 ppm) or $CDCl_3$ ($\delta$ 7.26 ppm) or with tetramethylsilane (TMS, $\delta$ 0.00 ppm) as the internal standard. Chemical shifts ($\delta$) are reported in parts per million (ppm). $^{13}$C NMR spectra were recorded on a Bruker DPX 300 (75 MHz) spectrometer and referenced to $CDCl_3$ ($\delta$ 77.10 ppm) spectra. Coupling constants ($J$) are reported in hertz (Hz). Mass spectra (HRMS) were performed on a Thermofinnigan MAT 95 XL instrument (FABMS).

The CHA reactions were carried out in $N_2$ in the dark with Teflon-stoppered reaction tubes covered with aluminum foil. Unless otherwise stated, the reactions were duplicated and the yields are the average yields. The reactions were traced by TLC. Unless otherwise stated, all the reactions were stopped once the starting materials (Rh(por)Cl) were consumed.

**Reaction of Alkanes with Rh(ttp)Cl (1a).**[6a,c,7,24,25] **(5,10, 15,20-Tetratolylporphyrinato)(cyclohexyl)rhodium(III), [Rh-(ttp)(cyclohexyl)] (2a). Method A.** Rh(ttp)Cl (**1a**; 20.1 mg, 0.025 mmol) was added into cyclohexane (3.0 mL). The red suspension was degassed for three freeze−thaw−pump cycles and was then heated at 120 °C under $N_2$ in the dark for 24 h. After 24 h, the mixture turned dark red. Excess cyclohexane was removed by vacuum distillation. The dark red residue was then purified by column chromatography on silica gel with a hexane/$CH_2Cl_2$ solvent

(20) Ruiz, J.; Mann, B. E.; Spencer, C. M.; Taylor, B. F.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1987**, *8*, 1963–1966.

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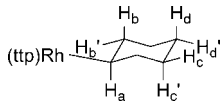
mixture (4/1) as eluent to give Rh(ttp)(cyclohexyl) (**2a**) as a red solid (6.6 mg, 0.007 mmol, 31%), which was further recrystallized from $CH_2Cl_2$/MeOH. $R_f = 0.84$ (hexane/$CH_2Cl_2$ = 1/1). $^1$H NMR




($CDCl_3$, 300 MHz): $\delta$ −4.25 (m, 5 H, $H_a$, $H_b$, and $H_b'$), −1.23 (q, 2 H, $J$ = 12.3 Hz, $H_c'$), −0.95 (tq, 1 H, $J$ = 3.3, 12.9 Hz, $H_d$), −0.58 (d, 2 H, $J$ = 12.6 Hz, $H_c$), −0.08 (d, 1 H, $J$ = 12.6 Hz, $H_d'$), 2.69 (s, 12 H, *p*-methyl), 7.52 (d, 8 H, $J$ = 7.5 Hz, *m*-phenyl), 8.01 (d, 4 H, $J$ = 8.4 Hz, *o*′-phenyl), 8.06 (d, 4 H, $J$ = 7.8 Hz, *o*-phenyl), 8.68 (s, 8 H, pyrrole). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 21.69, 25.17, 26.95, 33.36, 39.37 (d, $^1J_{Rh-C}$ = 27.6 Hz), 122.81, 127.40, 127.55, 130.88, 131.52, 131.71, 134.25, 137.23, 139.53, 143.40. HRMS: calcd *m*/*z* for $(C_{54}H_{46}N_4Rh)^+$ 854.2850, found *m*/*z* 854.2859. Anal. Calcd for $C_{54}H_{46}N_4Rh$: C, 75.87; H, 5.54; N, 6.55. Found: C, 75.41; H, 5.57; N, 6.50. Single crystals for X-ray diffraction analysis were grown from $CH_2Cl_2$/methanol.

**Method A.** Rh(ttp)Cl (**1a**; 20.2 mg, 0.025 mmol) was added into cyclohexane (3.0 mL). The red suspension was degassed for three freeze−thaw−pump cycles and was then heated at 80 °C under $N_2$ in the dark for 24 h. After 24 h, the mixture turned dark red. Excess cyclohexane was removed by vacuum distillation. The dark red residue was then purified by column chromatography on silica gel with a hexane/$CH_2Cl_2$ solvent mixture (4/1) as eluent to give Rh(ttp)(cyclohexyl) (**2a**) as a red solid (0.2 mg, 0.000 23 mmol, 1%).

**Method A.** Rh(ttp)Cl (**1a**; 19.9 mg, 0.025 mmol) was added into cyclohexane (3.0 mL). The red suspension was degassed for three freeze−thaw−pump cycles and was then heated at 100 °C under $N_2$ in the dark for 24 h. After 24 h, the mixture turned dark red. Excess cyclohexane was removed by vacuum distillation. The dark red residue was then purified by column chromatography on silica gel with a hexane/$CH_2Cl_2$ solvent mixture (4/1) as eluent to give Rh(ttp)(cyclohexyl) (**2a**) as a red solid (0.6 mg, 0.000 70 mmol, 3%).

**Method A.** Rh(ttp)Cl (**1a**; 20.0 mg, 0.025 mmol) was added into cyclohexane (3.0 mL). The red suspension was degassed for three freeze−thaw−pump cycles and was then heated at 150 °C under $N_2$ in the dark for 24 h. After 24 h, the mixture turned dark red. Excess cyclohexane was removed by vacuum distillation. The dark red residue was then purified by column chromatography on silica gel with a hexane/$CH_2Cl_2$ solvent mixture (4/1) to give Rh(ttp)(cyclohexyl) (**2a**) as a red solid (3.4 mg, 0.0040 mmol, 16%).

**Method A.** Rh(ttp)Cl (**1a**; 20.0 mg, 0.025 mmol) was added into cyclohexane (3.0 mL). The red suspension was degassed for three freeze−thaw−pump cycles and was then heated at 200 °C under $N_2$ in the dark for 24 h. After 24 h, the mixture turned dark red. Excess cyclohexane was removed by vacuum distillation. The dark red residue was then purified by column chromatography on silica gel with a hexane/$CH_2Cl_2$ solvent mixture (4/1) as eluent to give Rh(ttp)(cyclohexyl) (**2a**) as a red solid (3.8 mg, 0.0045 mmol, 18%).

**Thermal Stability of Rh(ttp)(cyclohexyl) (2a) at 120 °C.** Rh(ttp)(cyclohexyl) (**2a**; 10.9 mg, 0.013 mmol) was added into cyclohexane (3.0 mL). The red solution was degassed for three freeze−thaw−pump cycles and was heated at 120 °C under $N_2$ in the dark for 24 h. Excess cyclohexane was removed by vacuum distillation. The dark red residue was purified by column chromatography on silica gel with a hexane/$CH_2Cl_2$ solvent mixture (4/1) as eluent. Rh(ttp)(cyclohexyl) (**2a**) was obtained as a red solid (8.7 mg, 0.010 mmol, 80%).

**Thermal Stability of Rh(ttp)(cyclohexyl) (2a) at 150 °C. Method A.** Rh(ttp)(cyclohexyl) (**2a**; 10.4 mg, 0.012 mmol) was added into cyclohexane (3.0 mL). The red solution was degassed for three freeze−thaw−pump cycles and was heated at 150 °C under $N_2$ in the dark for 24 h. Excess cyclohexane was removed by vacuum distillation. The dark red residue was purified by column chromatography on silica gel with a solvent mixture of hexane/$CH_2Cl_2$ (4:1) as eluent. Rh(ttp)(cyclohexyl) (**2a**) was obtained as a red solid (4.3 mg, 0.005 mmol, 41%).

**Method B.** Rh(ttp)Cl (**1a**; 20.4 mg, 0.025 mmol) and anhydrous potassium carbonate (34.9 mg, 0.252 mmol) were added into cyclohexane (3.0 mL). The red reaction mixture was degassed for three freeze−thaw−pump cycles and was heated at 120 °C under $N_2$ for 6 h. Excess cyclohexane was removed by vacuum distillation, and the dark red crude product was extracted with $CH_2Cl_2/H_2O$. The organic layer was collected, dried, and evaporated to dryness, and the residue was purified by column chromatography on silica gel with a hexane/$CH_2Cl_2$ solvent mixture (4:1) as eluent. Rh(ttp)(cyclohexyl) (**2a**; 12.7 mg, 0.015 mmol, 59%) was collected as a red solid.

The cyclohexane fraction removed by vacuum distillation was extracted with water (3.0 mL). The colorless organic layer was diluted by dichloromethane (3.0 mL) and then was injected for GC-MS analysis.

**Method C.** Rh(ttp)Cl (**1a**; 20.4 mg, 0.025 mmol) and sodium hydroxide (10.1 mg, 0.252 mmol) were added into cyclohexane (3.0 mL). The red reaction mixture was degassed for three freeze−thaw−pump cycles and was heated at 120 °C under $N_2$ for 6 h. Excess cyclohexane was removed by vacuum distillation, and the dark red crude product was extracted with $CH_2Cl_2/H_2O$. The organic layer was collected, dried, and evaporated to dryness, and the residue was purified by column chromatography on silica gel with a hexane/$CH_2Cl_2$ solvent mixture (4:1) as eluent. Rh(ttp)(cyclohexyl) (**2a**) as a red solid was collected as the only product (10.2 mg, 0.012 mmol, 47%). The cyclohexane fraction removed by vacuum distillation was extracted with water (3.0 mL). The colorless organic layer was diluted by dichloromethane (3.0 mL) and then was injected for GC-MS analysis.

**Method D.** Rh(ttp)Cl (**1a**; 20.1 mg, 0.025 mmol) and sodium acetate (20.4 mg, 0.249 mmol) were added into cyclohexane (3.0 mL). The red reaction mixture was degassed for three freeze−thaw−pump cycles and was heated at 120 °C under $N_2$ for 6 h. Excess cyclohexane was removed by vacuum distillation, and the dark red crude product was extracted with $CH_2Cl_2/H_2O$. The organic layer was collected, dried, and evaporated to dryness, and the residue was purified by column chromatography on silica gel with a hexane/$CH_2Cl_2$ solvent mixture (4/1) as eluent to give Rh(ttp)(cyclohexyl) (**2a**) as a red solid (10.9 mg, 0.013 mmol, 51%).

**Method E.** Rh(ttp)Cl (**1a**; 20.6 mg, 0.026 mmol) and 2,2′-bipyridine (39.9 mg, 0.255 mmol) were added into cyclohexane (3.0 mL). The red reaction mixture was degassed for three freeze−thaw−pump cycles and was heated at 120 °C under $N_2$ for 48 h. Excess cyclohexane was removed by vacuum distillation, and the residue was purified by column chromatography on silica gel with a hexane/$CH_2Cl_2$ solvent mixture (4/1) as eluent to give the Rh(ttp)(cyclohexyl) (**2a**) as a red solid (11.0 mg, 0.013 mmol, 50%).

**Method F.** Rh(ttp)Cl (**1a**; 19.8 mg, 0.025 mmol) and 2,6-diphenylpyridine (57.2 mg, 0.245 mmol) were added into cyclohexane (3.0 mL). The red reaction mixture was degassed for three freeze−thaw−pump cycles and was heated at 120 °C under $N_2$ for 24 h. Excess cyclohexane was removed by vacuum distillation, and the residue was purified by column chromatography on silica gel with a hexane/$CH_2Cl_2$ solvent mixture (4/1) as eluent to give the Rh(ttp)(cyclohexyl) (**2a**) as a red solid (12.2 mg, 0.014 mmol, 58%).

**Method G.** Rh(ttp)Cl (**1a**; 19.7 mg, 0.024 mmol) and 2,6-di-*tert*-butylpyridine (46.4 mg, 54.5 $\mu$L, 0.243 mmol) were added into cyclohexane (3.0 mL). The red reaction mixture was degassed for three freeze−thaw−pump cycles and was heated at 120 °C under $N_2$ for 24 h after excess cyclohexane was removed by vacuum distillation; the residue was then purified by column chromatography

on silica gel with a hexane/$CH_2Cl_2$ solvent mixture (4/1) as eluent to give Rh(ttp)(cyclohexyl) (**2a**) as a red solid (10.3 mg, 0.012 mmol, 50%).

**Method B.** Rh(ttp)Cl (**1a**; 20.1 mg, 0.025 mmol) and anhydrous potassium carbonate (34.7 mg, 0.252 mmol) were added into cyclohexane (3.0 mL). The red reaction mixture was degassed for three freeze−thaw−pump cycles and was heated at 120 °C under $N_2$ for 24 h. Excess cyclohexane was removed by vacuum distillation, and the dark red crude product was extracted with $CH_2Cl_2/H_2O$. The organic layer was collected, dried, and evaporated to dryness, and the residue was purified by column chromatography on silica gel with a hexane/$CH_2Cl_2$ solvent mixture (4/1) as eluent to give Rh(ttp)(cyclohexyl) (**2a**) as a red solid (8.6 mg, 0.010 mmol, 40%).

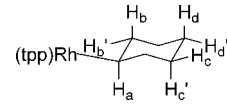
**Method F.** Rh(ttp)Cl (**1a**; 20.3 mg, 0.025 mmol) and 2,6-diphenylpyridine (57.0 mg, 0.245 mmol) were added into cyclohexane (3.0 mL). The red reaction mixture was degassed for three freeze−thaw−pump cycles and was heated at 120 °C under $N_2$ for 6 h. Excess cyclohexane was removed by vacuum distillation, and the residue was purified by column chromatography on silica gel with a hexane/$CH_2Cl_2$ solvent mixture (4/1) as eluent to give the Rh(ttp)(cyclohexyl) (**2a**) as a red solid (4.9 mg, 0.0057 mmol, 23%).

**Chloro(5,10,15,20-Tetratolylporphyrinato)(triphenylphosphine)rhodium(III), [Rh(ttp)Cl(PPh$_3$)] (2f).** Rh(ttp)Cl (**1a**; 19.9 mg, 0.025 mmol) and triphenylphosphine (64.7 mg, 0.247 mmol) were added into cyclohexane (3.0 mL). The red reaction mixture was degassed for three freeze−thaw−pump cycles and was heated at 120 °C under $N_2$ for 24 h. Excess cyclohexane was removed by vacuum distillation, and the residue was purified by column chromatography on silica gel with ethyl acetate as eluent to give Rh(ttp)Cl(PPh$_3$) (**2f**; 21.9 mg, 0.021 mmol, 83%). $R_f$ = 0.65 (ethyl acetate). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 2.68 (s, 12 H, *p*-methyl), 3.84 (dd, 6 H, $J$ = 7.6, 10.7 Hz, *m*-phenyl of PPh$_3$), 6.51 (td, 6 H, $J$ = 2.2, 7.8 Hz, *o*-phenyl of PPh$_3$), 6.90 (td, 3 H, $J$ = 5.3, 11.2 Hz, *p*-phenyl of PPh$_3$), 7.49 (d, 8 H, $J$ = 8.0 Hz, *m*-phenyl), 7.66 (d, 4 H, $J$ = 7.6 Hz, *o*′-phenyl), 8.04 (d, 4 H, $J$ = 7.49 Hz, *o*-phenyl), 8.72 (s, 8 H, pyrrole). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 21.63, 121.63, 126.79, 126.92, 127.00, 127.66, 129.36, 131.02, 131.14, 132.15, 132.65, 134.16, 135.05, 137.05, 139.31, 142.75. HRMS: calcd *m*/*z* for $(C_{66}H_{51}N_4PRh)^+$ 1033.2901, found *m*/*z* 1033.2885.

**Investigation of Base Loading in CHA of Cyclohexane. Method B.** Rh(ttp)Cl (**1a**; 20.3 mg, 0.025 mmol) and anhydrous potassium carbonate (34.9 mg, 0.126 mmol) were added into cyclohexane (3.0 mL). The red reaction mixture was degassed for three freeze−thaw−pump cycles and was heated at 120 °C under $N_2$ for 24 h. Excess cyclohexane was removed by vacuum distillation, and the dark red crude product was extracted with $CH_2Cl_2/H_2O$. The organic layer was collected, dried, and evaporated to dryness, and the residue was purified by column chromatography on silica gel with a hexane/$CH_2Cl_2$ solvent mixture (4/1) as eluent. Rh(ttp)(cyclohexyl) (**2a**) as a red solid (7.5 mg, 0.0088 mmol, 35%) was collected.

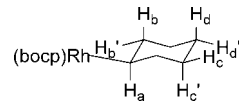
**Method B.** Rh(ttp)Cl (**1a**; 20.1 mg, 0.025 mmol) and anhydrous potassium carbonate (68.8 mg, 0.498 mmol) were added into cyclohexane (3.0 mL). The red reaction mixture was degassed for three freeze−thaw−pump cycles and was heated at 120 °C under $N_2$ for 6 h. Excess cyclohexane was removed by vacuum distillation, and the dark red crude product was extracted with $CH_2Cl_2/H_2O$. The organic layer was collected, dried, and evaporated to dryness, and the residue was purified by column chromatography on silica gel with a hexane/$CH_2Cl_2$ solvent mixture (4/1) as eluent. Rh(ttp)-(cyclohexyl) (**2a**) as a red solid (11.9 mg, 0.014 mmol, 56%) was collected.

**(5,10,15,20-Tetraphenylporphyrinato)(cyclohexyl)rhodium-(III), [Rh(tpp)(cyclohexyl)] (4a). Method B.** Rh(tpp)Cl (**1b**)[25,26] (20.2 mg, 0.027 mmol) and anhydrous potassium carbonate (37.2 mg, 0.269 mmol) were added into cyclohexane (3.0 mL) and to form a bright red reaction mixture. This reaction mixture was degassed for three freeze−thaw−pump cycles and was heated at 120 °C under $N_2$ in the dark for 5 h. After 5 h, the mixture turned dark red. Excess cyclohexane was removed by vacuum distillation. The dark red residue was extracted with $CH_2Cl_2/H_2O$. The organic layer was collected, dried, and evaporated to dryness and then purified by column chromatography on silica gel with a hexane/$CH_2Cl_2$ solvent mixture (4/1) as eluent. Rh(tpp)(cyclohexyl) (**4a**) was collected as a red solid (11.2 mg, 0.014 mmol, 52%), $R_f$ = 0.83 (hexane/$CH_2Cl_2$ 1/1). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ −4.26




(m, 5 H, H$_a$, H$_b$, and H$_b$′), −1.21 (q, 2 H, $J$ = 12.3 Hz, H$_c$′), −0.94 (tq, 1 H, $J$ = 3.3, 12.9 Hz, H$_d$), −0.56 (d, 2 H, $J$ = 11.4 Hz, H$_c$), −0.07 (d, 1 H, $J$ = 12.9 Hz, H$_d$′), 7.50 (m, 8 H, *m*-phenyl), 8.13 (d, 4 H, $J$ = 4.5 Hz, *o*′-phenyl), 8.19 (d, 4 H, $J$ = 6.6 Hz, *o*-phenyl), 8.67 (s, 8 H, pyrrole). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 25.14, 26.95, 33.39, 39.65 (d, $^1J_{Rh-C}$ = 29.5 Hz), 122.87, 126.70, 126.84, 127.69, 131.61, 133.78, 134.34, 142.39, 143.30. HRMS: calcd *m*/*z* for $(C_{50}H_{39}N_4Rh)^+$ 798.2224, found *m*/*z* 798.2171. Anal. Calcd for $C_{50}H_{39}N_4Rh$: C, 75.18; H, 4.92; N, 7.01; Found: C, 74.68; H, 4.89; N, 6.70.

**[2,3,7,8,12,13,17,18-Octachloro-5,10,15,20-tetrakis(*p*-*tert*-butylphenyl)porphyrinato](cyclohexyl)rhodium(III), Rh(bocp)(cyclohexyl) (4b). Method B.** Rh(bocp)Cl (**1c**)[25,26] (21.7 mg, 0.017 mmol) and anhydrous potassium carbonate (24.0 mg, 0.174 mmol) were added into cyclohexane (3.0 mL) to form a bright red reaction mixture. This reaction mixture was degassed for three freeze−thaw−pump cycles and was heated at 120 °C under $N_2$ in the dark for 1 h. After 1 h, the mixture turned dark red. Excess cyclohexane was removed by vacuum distillation. The dark red residue was extracted with $CH_2Cl_2/H_2O$. The organic layer was collected, dried, and evaporated to dryness and then purified by column chromatography on silica gel with a hexane/$CH_2Cl_2$ solvent mixture (4/1) as eluent to give Rh(bocp)(cyclohexyl) (**4b**) as a red solid (13.8 mg, 0.011 mmol, 61%). $R_f$ = 0.86 (hexane/$CH_2Cl_2$ 1/1). $^1$H NMR

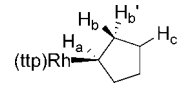



($CDCl_3$, 300 MHz): $\delta$ −3.63 (q, 2 H, $J$ = 9.6 Hz, H$_b$), −3.46 (q, 2 H, $J$ = 9.3 Hz, H$_b$′), −3.17 (td, 1 H, $J$ = 3.0, 9.0 Hz, H$_a$), −0.85 (q, 2 H, $J$ = 12.3 Hz, H$_c$′), −0.71 (t, 1 H, $J$ = 12.9 Hz, H$_d$), −0.25 (d, 2 H, $J$ = 12.0 Hz, H$_c$), 1.36 (d, 1 H, $J$ = 12.0 Hz, H$_d$′), 1.55 (s, 36 H, $^t$Bu), 7.70 (d, 8 H, $J$ = 8.7 Hz, *m*-phenyl), 8.54 (d, 4 H, $J$ = 7.2 Hz, *o*′-phenyl), 7.95 (d, 4 H, $J$ = 7.2 Hz, *o*-phenyl). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 25.18, 27.61, 29.86, 31.85, 35.11, 35.78, 122.56, 124.71, 133.02, 134.05, 134.73, 138.11, 152.76. HRMS: *m*/*z* calcd for $(C_{66}H_{63}N_4Cl_8Rh)^+$ 1298.1551, found *m*/*z* 1298.1519. Anal. Calcd for $C_{66}H_{63}N_4Cl_8Rh$: C, 61.04; H, 4.89; N, 4.31; Found: C, 61.11; H, 5.05; N, 4.19.

**(5,10,15,20-Tetratolylporphyrinato)(cyclopentyl)rhodium(III), [Rh(ttp)(cyclopentyl)] (2b). Method B.** Rh(ttp)Cl (**1a**; 20.0 mg, 0.025 mmol) and anhydrous potassium carbonate (34.2 mg, 0.248

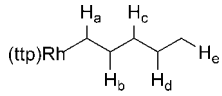
(26) (a) Buchler, J. W.; Dreher, C.; Kunzel, F. M. In *Metal Complexes with Tetrapyrrole Ligands III*; Buchler, J. W., Ed.; Springer-Verlag, Berlin, Heidelberg, 1995; Structure and Bonding *84*. (b) Mak, K. W.; Chan, K. S. *J. Am. Chem. Soc.* **1998**, *120*, 9689–9687.

mmol) were added into cyclopentane (3.0 mL). The red reaction mixture was degassed for three freeze−thaw−pump cycles and was heated at 120 °C under $N_2$ in the dark for 6 h. Excess cyclopentane was removed by vacuum distillation. The dark red crude product was extracted with $CH_2Cl_2/H_2O$. The organic layer was collected, dried, and evaporated to dryness, and the residue was purified by column chromatography on silica gel with a hexane/$CH_2Cl_2$ solvent mixture (4/1) as eluent. Rh(ttp)(cyclopentyl) (**2b**) was collected as a red solid (16.0 mg, 0.017 mmol, 75%). $R_f = 0.85$ (hexane/$CH_2Cl_2$ 1/1). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ −4.90 (m, 2 H, $H_b$), −4.37



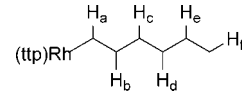

(m, 1 H, $H_a$), −3.46 (m, 2 H, $H_b'$), −1.03 (m, 4 H, $H_c$), 2.69 (s, 12 H, *p*-methyl), 7.52 (t, 8 H, $J = 6.2$ Hz, *m*-phenyl), 8.00 (d, 4 H, $J = 8.5$ Hz, *o′*-phenyl), 8.09 (d, 4 H, $J = 8.6$ Hz, *o*-phenyl), 8.69 (s, 8 H, pyrrole). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 18.87, 22.14, 29.52, 34.53, 123.20, 127.86, 127.92, 131.91, 134.19, 134.61, 137.69, 139.94, 143.93. HRMS: *m/z* calcd for $(C_{53}H_{45}N_4Rh)^+$ 840.2694, found *m/z* 840.2694. Anal. Calcd for $C_{53}H_{45}N_4Rh$: C, 75.71; H, 5.39; N, 6.66. Found: C, 75.29; H, 5.37; N, 6.53. Single crystals for X-ray diffraction analysis were grown from $CH_2Cl_2$/ethanol.

**(5,10,15,20-Tetratolylporphyrinato)(*n*-pentyl)rhodium(III), [Rh(ttp)(*n*-pentyl)] (2c). Method B.** Rh(ttp)Cl (**1a**; 20.4 mg, 0.025 mmol) and anhydrous potassium carbonate (34.9 mg, 0.252 mmol) were added into *n*-pentane (3.0 mL) to form a bright red reaction mixture. This reaction mixture was degassed for three freeze−thaw−pump cycles and was heated at 120 °C under $N_2$ in the dark for 24 h. After 24 h, the mixture turned dark red. Excess *n*-pentane was removed by vacuum distillation. The dark red residue was extracted with $CH_2Cl_2/H_2O$. The organic layer was collected, dried, and evaporated to dryness and then purified by column chromatography on silica gel with a hexane/$CH_2Cl_2$ solvent mixture (4/1) as eluent. Rh(ttp)(*n*-pentyl) (**2c**). Rh(ttp)(*n*-pentyl) (**2c**) as a red solid was collected as the major product (6.5 mg, 0.008 mmol, 31%). $R_f = 0.78$ (hexane/$CH_2Cl_2$ 1/1). $^1$H NMR ($CDCl_3$, 300 MHz):



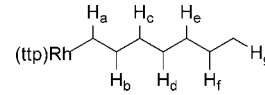

$\delta$ −4.97 (td, 2 H, $J = 2.4$, 7.5 Hz, $H_a$), −4.50 (qu, 2 H, $J = 7.2$ Hz, $H_b$), −1.59 (qu, 2 H, $J = 2.1$ Hz, $H_c$), −0.49 (q, 2 H, $J = 6.9$ Hz, $H_d$), −0.25 (t, 3 H, $J = 7.2$ Hz, $H_e$), 2.69 (s, 12 H, *p*-methyl), 7.53 (t, 8 H, $J = 6.0$ Hz, *m*-phenyl), 7.98 (d, 4 H, $J = 8.6$ Hz, *o′*-phenyl), 8.08 (d, 4 H, $J = 8.3$ Hz, *o*-phenyl), 8.70 (s, 8 H, pyrrole) (qu = quintet). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 12.81, 15.66 (d, $^1J_{Rh-C} = 27.2$ Hz), 20.72, 21.69, 26.86, 28.50, 122.51, 127.47, 127.52, 131.49, 133.81, 134.10, 137.25, 139.50, 143.37 HRMS: calcd *m/z* for $(C_{53}H_{47}N_4Rh)^+$ 840.2694, found *m/z* 840.2682. Anal. Calcd for $C_{53}H_{47}N_4Rh$: C, 75.52; H, 5.62; N, 6.64. Found: C, 75.43; H, 5.67; N, 6.36.

**(5,10,15,20-Tetratolylporphyrinato)(*n*-hexyl)rhodium(III), [Rh(ttp)(*n*-hexyl)] (2d). Method B.** Rh(ttp)Cl (**1a**; 20.6 mg, 0.026 mmol) and anhydrous potassium carbonate (35.3 mg, 0.255 mmol) were added into *n*-hexane (3.0 mL) to form a bright red reaction mixture. This reaction mixture was degassed for three freeze−thaw−pump cycles and was heated at 120 °C under $N_2$ in the dark for 24 h. After 24 h, the mixture turned dark red. Excess *n*-hexane was removed by vacuum distillation. The dark red residue was extracted with $CH_2Cl_2/H_2O$. The organic layer was collected, dried, and evaporated to dryness and then purified by column chromatography on silica gel with a hexane/$CH_2Cl_2$ solvent mixture (4/1) as eluent. Rh(ttp)(*n*-hexyl) (**2d**) was collected as the major product. Rh(ttp)(*n*-hexyl) (**2d**) was collected as a red solid (10.6 mg, 0.012 mmol, 49%). $R_f = 0.84$ (hexane/$CH_2Cl_2$ 1/1). $^1$H NMR ($CDCl_3$,




300 MHz): $\delta$ −4.96 (td, 2 H, $J = 3.0$, 9.0 Hz, $H_a$), −4.51 (qu, 2 H, $J = 7.8$ Hz, $H_b$), −1.58 (qu, 2 H, $J = 7.5$ Hz, $H_c$), −0.57 (qu, 2 H, $J = 7.5$ Hz, $H_d$), 0.10 (m, 2 H, $H_e$), 0.17 (t, 3 H, $J = 7.2$ Hz, $H_f$), 2.68 (s, 12 H, *p*-methyl), 7.52 (d, 4 H, $J = 5.7$ Hz, *m′*-phenyl), 7.54 (d, 4 H, $J = 5.7$ Hz, *m*-phenyl), 7.97 (d, 4 H, $J = 7.2$ Hz, *o′*-phenyl), 8.06 (d, 4 H, $J = 8.3$ Hz, *o*-phenyl), 8.69 (s, 8 H, pyrrole). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 13.53, 15.69 (d, $^1J_{Rh-C} = 27.2$ Hz), 21.40, 21.69, 26.06, 27.13, 29.84, 122.53, 127.47, 130.89, 131.51, 131.85, 133.83, 134.11, 137.25, 139.52, 143.39 HRMS: calcd *m/z* for $(C_{54}H_{49}N_4Rh)^+$ 856.3007, found *m/z* 856.3017. Anal. Calcd for $C_{54}H_{49}N_4Rh$: C, 75.69; H, 5.76; N, 6.54. Found: C, 75.61; H, 5.72; N, 6.53.

**(5,10,15,20-Tetratolylporphyrinato)(*n*-heptyl)rhodium(III), [Rh(ttp)(*n*-heptyl)] (2e). Method B.** Rh(ttp)Cl (**1a**; 20.9 mg, 0.026 mmol) and anhydrous potassium carbonate (35.3 mg, 0.255 mmol) were added into *n*-heptane (3.0 mL) to form a bright red reaction mixture. This reaction mixture was degassed for three freeze−thaw−pump cycles and was heated at 120 °C under $N_2$ in the dark for 24 h. After 24 h, the mixture turned dark red. Excess *n*-heptane was removed by vacuum distillation. The dark red residue was extracted with $CH_2Cl_2/H_2O$. The organic layer was collected, dried, and evaporated to dryness and then purified by column chromatography on silica gel with a hexane/$CH_2Cl_2$ solvent mixture (4/1) as eluent. Rh(ttp)(*n*-heptyl) (**2e**) was collected as the major product as a red solid (13.2 mg, 0.015 mmol, 59%). $R_f = 0.83$ (hexane/$CH_2Cl_2$ 1/1). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ −4.97 (td, 2




H, $J = 3.0$, 8.7 Hz, $H_a$), −4.53 (qu, 2 H, $J = 7.2$ Hz, $H_b$), −1.63 (qu, 2 H, $J = 7.2$ Hz, $H_c$), −0.55 (qu, 2 H, $J = 7.2$ Hz, $H_d$), −0.04 (d, 2 H, $J = 9.0$ Hz, $H_e$), 0.45 (q, 3 H, $J = 6.0$ Hz, $H_g$), 0.52 (qu, 2 H, $J = 7.2$ Hz, $H_f$), 2.69 (s, 12 H, *p*-methyl), 7.51 (d, 4 H, $J = 6.6$ Hz, *m′*-phenyl), 7.53 (d, 4 H, $J = 6.3$ Hz, *m*-phenyl), 7.98 (d, 4 H, $J = 6.9$ Hz, *o′*-phenyl), 8.08 (d, 4 H, $J = 7.2$ Hz, *o*-phenyl), 8.70 (s, 8 H, pyrrole). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 13.89, 15.71 (d, $^1J_{Rh-C} = 27.5$ Hz), 21.69, 22.10, 26.25, 27.06, 27.24, 30.57, 122.52, 126.22, 127.45, 127.52, 131.49, 133.80, 134.11, 137.23, 139.51, 143.38 HRMS: calcd *m/z* for $(C_{55}H_{51}N_4Rh)^+$ 870.3163, found *m/z* 870.3167. Anal. Calcd for $C_{55}H_{51}N_4Rh$: C, 75.85; H, 5.90; N, 6.43. Found: C, 75.77; H, 5.96; N, 6.31. Single crystals for X-ray diffraction analysis were grown from $CH_2Cl_2$/methanol.

**Decomposition of Rh(ttp)(cyclopentyl) (2b) with $K_2CO_3$ in Benzene-$d_6$.** Rh(ttp)(cyclopentyl) (6.7 mg, 0.0080 mmol) and potassium carbonate (11.0 mg, 0.080 mmol) were added into benzene-$d_6$ (520 $\mu$L) in an NMR tube. The red reaction mixture was degassed for three freeze−thaw−pump cycles, and the NMR tube was sealed under vacuum. It was heated to 120 °C, the reaction mixture was monitored with $^1$H NMR spectroscopy, and NMR yields were determined.

For the observation of Rh(ttp)H, a dilute HCl solution was added into the NMR tube with shaking. A $^1$H NMR spectrum was measured immediately after the addition of dilute HCl.

**Decomposition of Rh(ttp)(cyclohexyl) (2a) with $K_2CO_3$ in Benzene-$d_6$.** Rh(ttp)(cyclohexyl) (6.9 mg, 0.0081 mmol) and potassium carbonate (11.0 mg, 0.080 mmol) were added into benzene-$d_6$ (520 $\mu$L) in an NMR tube. The red reaction mixture was degassed for three freeze−thaw−pump cycles, and the NMR tube was sealed under vacuum. It was heated to 120 °C, the reaction mixture was monitored with $^1$H NMR spectroscopy, and NMR yields were determined.

**Sealed NMR Tube Experiment of Rh(ttp)Cl and Cyclohexane in Benzene-$d_6$.** Rh(ttp)Cl (**1a**; 5.1 mg, 0.0066 mmol) and cyclohexane (34 $\mu$L, 0.316 mmol) were added into benzene-$d_6$ (520 $\mu$L) in an NMR tube. The red mixture was degassed for three freeze−thaw−pump cycles, and the NMR tube was sealed under vacuum. It was heated at 120 °C in the dark. It was monitored with $^1$H NMR spectroscopy at particular time intervals, and the NMR yields were determined.

**Sealed NMR Tube Experiment of Rh(ttp)Cl and Cyclohexane with $K_2CO_3$ in Benzene-$d_6$.** Rh(ttp)Cl (**1a**; 5.1 mg, 0.0066 mmol), cyclohexane (34 $\mu$L, 0.316 mmol), and $K_2CO_3$ (8.7 mg, 0.063 mmol) were added into benzene-$d_6$ (520 $\mu$L) in an NMR tube. The red mixture was degassed for three freeze−thaw−pump cycles, and the NMR tube was sealed under vacuum. It was heated at 120 °C in the dark. It was monitored with $^1$H NMR spectroscopy at particular time intervals, and the NMR yields were determined.

**Reaction of Rh(ttp)H with KOH.**[11] Rh(ttp)H (**1d**; 8.0 mg, 0.010 mmol) and potassium hydroxide (14.3 mg, 0.104 mmol) were added into degassed benzene-$d_6$ (520 $\mu$L) in an NMR tube. The reaction mixture was degassed for three freeze−thaw−pump cycles, and the NMR tube was sealed under vacuum. The reaction mixture was then warmed to 23 °C in a water bath for 15 min. It was monitored by $^1$H NMR spectroscopy. $[Rh(ttp)]_2$ was obtained (55% NMR yield).

**Thermal Stability of Rh(ttp)H.** Rh(ttp)H (**1d**; 7.9 mg, 0.010 mmol) was added into degassed benzene-$d_6$ (520 $\mu$L) in an NMR tube. The reaction mixture was degassed for three freeze−thaw−pump cycles, and the NMR tube was sealed under vacuum. The reaction mixture was then heated to 120 °C for 6 days. It was monitored by $^1$H NMR spectroscopy. The NMR yield of Rh(ttp)H was found to be 90%.

**Reaction of Alkanes with Rh(ttp)H (1d).**[7,25] **Method A.** Rh(ttp)H (**1d**; 10.0 mg, 0.013 mmol) was added into cyclohexane (3.0 mL). The red suspension was degassed for three freeze−thaw−pump cycles and was then heated at 120 °C under $N_2$ in the dark for 3 h. After 3 h, the mixture turned red. Excess cyclohexane was removed by vacuum distillation. The dark red residue was then purified by column chromatography on silica gel with a hexane/$CH_2Cl_2$ solvent mixture (4/1) as eluent to give Rh(ttp)(cyclohexyl) (**2a**) as a red solid (4.0 mg, 0.0047 mmol, 36%).

**Competition Reaction of Cyclohexane and Cyclohexane-$d_{12}$ with Rh(ttp)Cl (1a) and $K_2CO_3$. Method B.** Rh(ttp)Cl (**1a**; 19.6 mg, 0.021 mmol) and potassium carbonate (33.6 mg, 0.243 mmol) were added into a mixture of cyclohexane (1.50 mL, 14.000 mmol) and cyclohexane-$d_{12}$ (1.49 mL, 14.000 mmol). The red mixture was degassed for three freeze−thaw−pump cycles and was heated at 120 °C under $N_2$ in the dark for 6 h. Then the excess cycloxane/cyclohexane-$d_{12}$ mixture was removed by vacuum distillation. Part of the red residue (0.2 mg) was examined by mass spectroscopy to obtain the ratio of the two products. The remaining crude product was monitored by $^1$H NMR spectroscopy to determine the product ratio. It was then extracted with $CH_2Cl_2/H_2O$ and purified by column chromatography on silica gel with a hexane/$CH_2Cl_2$ solvent mixture (4/1) as eluent. The red fraction was collected. After rotary evaporation, the product mixture of Rh(ttp)(cyclohexyl) (**2a**) and Rh(ttp)(cyclohexyl)-$d_{11}$ was obtained as a red solid (6.7 mg, 0.0078 mmol, 32%).

The product ratio was calculated as follows.

**(i) $^1$H NMR Method.** Integration of the alkyl protons of Rh(ttp)(cyclohexyl) at $\delta$ −4.26 (observed $\delta$ 5.193) and integration of the alkyl protons of Rh(ttp)(cyclohexyl)/Rh(ttp)(cyclohexyl)-$d_{11}$ at $\delta$ −4.26 (observed $\delta$ 4.680) were used to calculate the ratio with the integration of the pyrrole signal of **2a** ($\delta$ 8.63) being taken as 8. Let the integration of that alkyl deuterium be *Y*. *Y* is equal to the integration of that alkyl proton without deuterium incorporation (5.193) minus the observed integration of that alkyl proton with deuterium incorpation (4.680). $k_H/k_D$ is equal to the integration of alkyl proton ($\delta$ 4.680) over the integration of alkyl deuterium ($\delta$ 5.193−4.680). The calculated $k_H/k_D$ is 9.1 ± 0.3.

**(ii) MS Method.** The product ratio is calculated to be the molecular peak intensity of Rh(ttp)(cyclohexyl) (observed to be 60.0) over the molecular peak intensity of Rh(ttp)(cyclohexyl)-$d_{11}$ (observed to be 6.1). The product ratio is calculated to be 9.7 ± 0.2.

**Alkyl Exchange of Rh(ttp)(cyclohexyl) (2a) with Cyclohexane-$d_{12}$ at 120 °C.** Rh(ttp)(cyclohexyl) (**2a**; 5.4 mg, 0.0063 mmol) was added into cyclohexane-$d_{12}$ (0.5 mL) in a Teflon screw capped NMR tube. The red solution was degassed for three freeze−thaw−pump cycles. The NMR tube was sealed under vacuum. It was heated at 120 °C in the dark, and the reaction was monitored by $^1$H NMR. The product ratio was calculated as follows.

For the case of a 3 h reaction, the integration of the alkyl proton at $\delta$ −4.171 (observed $\delta$ 5.370) was used to calculate the ratio, with the integration of the pyrrole signal of **2a** ($\delta$ 8.63) being taken as 8. Let the integration of that alkyl deuterium be *Y*. *Y* is equal to the integration of that alkyl proton without deuterium incorporation ($\delta$ 5.370) minus the observed integration of that alkyl proton with deuterium incorpation ($\delta$ 5.144). $k_H/k_D$ is equal to the integration of alkyl proton over the integration of alkyl deuterium. $k_H/k_D$ is calculated to be 22.8.

For the case of a 42 h reaction, $k_H/k_D$ is equal to the integration of the alkyl proton ($\delta$ 5.191) over the integration of alkyl deuterium ($\delta$ 5.370−5.191). The calculated $k_H/k_D$ is 22.9.

**Competition Reaction of Cyclohexane and Cyclohexane-$d_{12}$ with Rh(ttp)H (1d). Method A.** Rh(ttp)H (**1d**; 10.1 mg, 0.013 mmol) was added into a mixture of cyclohexane (1.50 mL, 14.000 mmol) and cyclohexane-$d_{12}$ (1.49 mL, 14.000 mmol). The red mixture was degassed for three freeze−thaw−pump cycles and was heated at 120 °C under $N_2$ in the dark for 3 h. Then the excess cyclohexane/cyclohexane-$d_{12}$ mixture was removed by vacuum distillation. The dark red residue was examined by $^1$H NMR spectroscopy. It was then purified by column chromatography on silica gel with a hexane/$CH_2Cl_2$ solvent mixture (4/1) as eluent. The red fraction was collected. After rotary evaporation, the product mixture of Rh(ttp)(cyclohexyl) (**2a**) and Rh(ttp)(cyclohexyl)-$d_{11}$ was obtained as a red solid (6.0 mg, 0.0070 mmol, 54%). Integration of the alkyl proton of the Rh(ttp)(cyclohexyl)/Rh(ttp)(cyclohexyl)-$d_{11}$ mixture ($\delta$ −4.26) was found to be 4.668. The calculated $k_H/k_D$ was 8.9 ± 0.3.

**Competition Reaction of Cyclohexane and Cyclohexane-$d_{12}$ with Rh(ttp)H (1d) and $K_2CO_3$. Method B.** Rh(ttp)H (**1d**; 10.0 mg, 0.013 mmol) and potassium carbonate (17.9 mg, 0.130 mmol) were added into a mixture of cyclohexane (1.50 mL, 14.000 mmol) and cyclohexane-$d_{12}$ (1.49 mL, 14.000 mmol). The red mixture was degassed for three freeze−thaw−pump cycles and was heated at 120 °C under $N_2$ in the dark for 3 h. Then the excess cyclohexane/cyclohexane-$d_{12}$ mixture was removed by vacuum distillation. The dark red residue was examined by $^1$H NMR spectroscopy to determine the product ratio. It was then extracted with $CH_2Cl_2/H_2O$ and purified by column chromatography on silica gel with a hexane/$CH_2Cl_2$ solvent mixture (4/1) as eluent. The red fraction was collected. After rotary evaporation, the product mixture of Rh(ttp)(cyclohexyl) (**2a**) and Rh(ttp)(cyclohexyl)-$d_{11}$ was obtained as a red solid (6.2 mg, 0.0073 mmol, 56%). Integration of the alkyl proton of the Rh(ttp)(cyclohexyl)/Rh(ttp)(cyclohexyl)-$d_{11}$ mixture ($\delta$ −4.26) was found to be 4.647. The calculated $k_H/k_D$ was 8.5 ± 0.4.

**Competition Reaction of Cyclohexane and Cyclohexane-$d_{12}$ with $[Rh(ttp)]_2$ (1e).**[11] **Method A.** $[Rh(ttp)]_2$ (**1e**; 10.3 mg, 0.0067 mmol) was added into a mixture of cyclohexane (1.50 mL, 14.000 mmol) and cyclohexane-$d_{12}$ (1.49 mL, 14.000 mmol). The red mixture was degassed for three freeze−thaw−pump cycles and was heated at 120 °C under $N_2$ in the dark for 6 h. Then the excess

cyclohexane/cyclohexane-$d_{12}$ mixture was removed by vacuum distillation. The dark red residue was examined by $^1$H NMR spectroscopy. It was then purified by column chromatography on silica gel with a hexane/$CH_2Cl_2$ solvent mixture (4/1) as eluent. The red fraction was collected. After rotary evaporation, the product mixture of Rh(ttp)(cyclohexyl) (**2a**) and Rh(ttp)(cyclohexyl)-$d_{11}$ was obtained as a red solid (4.3 mg, 0.0050 mmol, 38%). Integration of the alkyl proton of the Rh(ttp)(cyclohexyl)/Rh(ttp)(cyclohexyl)-$d_{11}$ mixture ($\delta$ −4.26) was found to be 4.659. The calculated $k_H/k_D$ was 8.7 ± 0.3.

**Competition Reaction of Cyclohexane and Cyclohexane-$d_{12}$ with [Rh(ttp)]$_2$ (1e) and $K_2CO_3$.[11] Method A.** [Rh(ttp)]$_2$ (**1e**; 10.1 mg, 0.0065 mmol) and potassium carbonate (9.0 mg, 0.065 mmol) were added into a mixture of cyclohexane (1.50 mL, 14.000 mmol) and cyclohexane-$d_{12}$ (1.49 mL, 14.000 mmol). The red mixture was degassed for three freeze−thaw−pump cycles and was heated at 120 °C under $N_2$ in the dark for 6 h. Then the excess cyclohexane/cyclohexane-$d_{12}$ mixture was removed by vacuum distillation. The dark red residue was examined by $^1$H NMR spectroscopy. It was then purified by column chromatography on silica gel with a hexane/$CH_2Cl_2$ solvent mixture (4/1) as eluent. The red fraction was collected. After rotary evaporation, the product mixture of Rh(ttp)(cyclohexyl) (**2a**) and Rh(ttp)(cyclohexyl)-$d_{11}$ was obtained as a red solid (4.7 mg, 0.0055 mmol, 42%). Integration of the alkyl proton of the Rh(ttp)(cyclohexyl)/Rh(ttp)(cyclohexyl)-$d_{11}$ mixture ($\delta$ −4.26) was found to be 4.673. The calculated $k_H/k_D$ was 9.0 ± 0.3.

**Sealed NMR Tube Experiment with [Rh(ttp)]$_2$ (1e) and Cyclohexane in Benzene-$d_6$.[11]** [Rh(ttp)]$_2$ (**1e**; 5.1 mg, 0.0033 mmol) and cyclohexane (34 $\mu$L, 0.316 mmol) were added into benzene-$d_6$ (520 $\mu$L) in an NMR tube. The red mixture was degassed for three freeze−thaw−pump cycles, and the NMR tube was sealed under vacuum. It was heated at 120 °C in the dark. It was monitored with $^1$H NMR spectroscopy at particular time intervals, and the NMR yields were determined.

***β*-Hydride Elimination of Rh(ttp)(cyclohexyl) (2a).** Rh(ttp)(cyclohexyl) (6.8 mg, 0.0081 mmol) was added into benzene-$d_6$ (520 $\mu$L) in an NMR tube. The red reaction mixture was degassed for three freeze−thaw−pump cycles, and the NMR tube was sealed under vacuum. It was heated to 120 °C, the reaction mixture was monitored with $^1$H NMR spectroscopy, and NMR yields were detemined.

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**Supporting Information Available:** Figures giving spectroscopic data for compounds **2a**−**f** and **4a**,**b** and text, tables, figures, and CIF files giving crystallographic data for complexes **2a**,**b**,**e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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