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K_2CO_3-Promoted Consecutive Carbon−Hydrogen and Carbon−Carbon Bond Activation of Cycloheptane with Rhodium(III) Porphyrin Complexes: Formation of Rhodium Porphyrin Cycloheptyl and Benzyl

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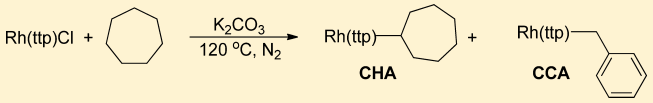
Supporting Information

ABSTRACT: K_2CO_3-promoted carbon−hydrogen and carbon−carbon bond activations of cycloheptane are achieved with rhodium(III) tetrakis(4-tolyl)porphyrin chloride (Rh(ttp)Cl) at 120 °C to give Rh(ttp) cycloheptyl and benzyl complexes. On the basis of mechanistic studies, Rh(ttp)Cl first reacts by ligand substitution to give Rh(ttp)OH, which then undergoes reductive elimination to give $Rh^{II}_2(ttp)_2$. The metalloradical $Rh^{II}(ttp)$, formed via dissociation of $Rh^{II}_2(ttp)_2$, activates the CH bond of cycloheptane to form Rh(ttp)(cycloheptyl) and Rh(ttp)H. Rh(ttp)(cycloheptyl) slowly yields Rh(ttp)(cycloheptatrieneyl) by successive β-hydride elimination to olefins and Rh(ttp)H. K_2CO_3 promoted the dehydrogenation of Rh(ttp)H to give $Rh^{II}_2(ttp)_2$ and H_2. Both Rh(ttp)H and $Rh^{II}_2(ttp)_2$ activate the cycloheptatriene to give Rh(ttp)(cycloheptatrienyl), which further undergoes a Rh^{II}(ttp)-catalyzed skeletal rearrangement to form Rh(ttp)Bn with rate enhancement much faster than that of the analogous organic isomerization of cycloheptatriene to toluene.



INTRODUCTION

Carbon−hydrogen bond activation (CHA) of organic compounds by transition-metal complexes, especially the late-transition-metal complexes, is an important research area in organometallic chemistry.[1] The CHA of alkane is difficult due to the low reactivity of nonpolar and strong CH bonds in alkanes.[2] Great efforts have been undertaken to achieve CHA. Previous successful examples include low-valent transition-metal complexes, while more recent systems involve high-valent late-transition-metal complexes because of their added advantages of broader functional group compatibility and catalytic application.[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 were shown to catalyze the dehydrogenation of cyclooctane.[4c,d] The alkyl CHA with bis-bidentate O-donor iridium(III) complexes was also reported.[4e,f]

Bond activation chemistry of Rh(III) and Ir(III) are commonly accepted to occur by either σ-bond metathesis or heterolysis.[4] However, recent reports provide evidence for the oxidative addition mechanism in which a Rh(V) or Ir(V) intermediate is formed and isolated.[5] The isolation of oxidative addition intermediates of strongly electron donating silyl Ir(V) complexes provides further supporting evidence for such a pathway;[6] therefore, diverse mechanistic possibilities exist for group 9 metal complexes undergoing CH activation.

We have reported examples of CHA by rhodium(III) porphyrin (por) complexes. Rhodium(III) porphyrin chlorides activate the meta C−H bond of benzonitrile to give *m*-cyanophenyl rhodium porphyrin complexes selectively by an S_EAr mechanism via a Rh(III) porphryin cation intermediate.[7] Aryl and alkyl aldehydes also undergo selective aldehydic CHA with Rh(III) porphyrin chloride or methyl to give rhodium porphyrin aryl and alkyl acyls.[8] A σ bond metathesis mechanism was proposed.[8] Recently, we have reported the selective benzylic CHA of toluenes promoted by base.[9] Initial ligand substitution of Rh(por)Cl with hydroxide gives Rh(por)OH, which at high temperature by reductive elimination gives H_2O_2 and Rh^{II}(por).[10] Then Rh^{II}(por) undergoes bimetalloradical benzylic CHA on the basis of Wayland's proposed mechanism.[11] The unique hydroxide reduction of easily handled Rh^{III}(por) halides to highly reactive Rh^{II}(por) metalloradical provides a facile, alternative entry to Rh^{II}(por). Similar hydroxide-promoted alkane CH activation of *n*-alkanes, cyclopentane,[12] cyclohexane,[12] and cyclooctane[13] was reported with a Rh(II) porphyrin intermediate detected.[9,12,13] To explore the scope and gain further understanding of the base-promoted bond activation chemistry with rhodium(III) porphyrin complexes in alkane CHA, we have successfully discovered the base-promoted aliphatic CHA of cycloheptane with Rh^{III}(ttp)Cl (ttp = 5,10,15,20-tetratolylporphyrinato dianion; Figure 1) to give Rh^{III}(ttp)(cycloheptyl) as a CHA product and Rh(ttp)Bn as an unexpected carbon−carbon bond activation (CCA)[13] and CHA product. Mechanistic studies reveal that metalloradical CHA is operating to initially produce Rh(ttp)H and Rh(ttp)(cycloheptyl). Rh(ttp)(cycloheptyl) further undergoes Rh^{II}(ttp)-catalyzed dehydrogenation to yield Rh(ttp)(cycloheptatrienyl), which further isomerizes into Rh(ttp)Bn

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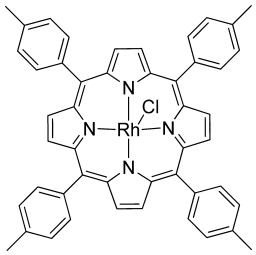


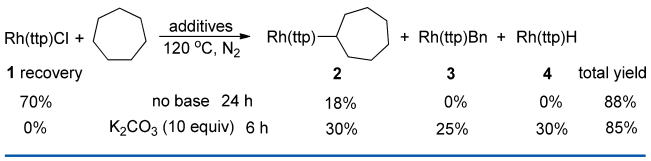
Figure 1. Structure of Rh(ttp)Cl.

via a Rh^{II}(ttp)-catalyzed skeletal rearrangement. We have communicated that the metalloradical-catalyzed isomerization is 10^{10} times faster than the analogous organic isomerization of cycloheptatriene into toluene.[14] We now report the full scope of the K_2CO_3-promoted CHA and CCA[13] of cycloheptane with Rh(ttp)Cl.

RESULTS AND DISCUSSION

Initially, cycloheptane was found to react with Rh(ttp)Cl (**1**) (Figure 1) to give Rh(ttp)(cycloheptyl) (**2**) in 18% yield as the sole CHA product, while 70% of Rh(ttp)Cl was recovered (Scheme 1). However, when K_2CO_3 (10 equiv) was

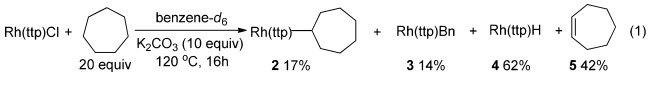
Scheme 1. Reaction of Rh(ttp)Cl with Cycloheptane



added,[9,12,14,15] Rh(ttp)(cycloheptyl) (**2**), Rh(ttp)H (**4**), and surprisingly the CCA product Rh(ttp)Bn (**3**)[13] were formed in 30, 30, and 25% yields, respectively.

Since the thermal catalytic dehydrogenation of cycloheptane to toluene in the presence of selenium takes place slowly at the much higher temperature of 360 °C,[16] Rh(ttp)Bn (**3**) most likely comes from Rh(ttp)(cycloheptyl) (**2**) rather from the benzylic CHA of isomerized toluene.

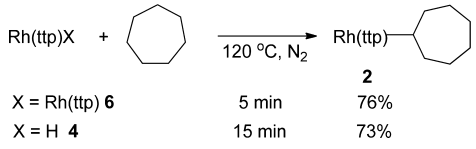
Reaction Profile. To gain further mechanistic understanding, the reaction of Rh(ttp)Cl with excess cycloheptane at 120 °C in benzene-d_6 in the presence of K_2CO_3 was monitored by ^{1}H NMR spectroscopy in a NMR tube (Table S1 and Figure S1 (Supporting Information)). After 2 h, only 15% of Rh(ttp)Cl (**1**) remained while Rh(ttp)Bn (**3**), Rh(ttp)H (**4**), and Rh_2(ttp)$_2$ (**6**) were formed in 13, 64, and 7% yields, respectively. After 16 h, Rh(ttp)Cl (**1**) and Rh_2(ttp)$_2$ (**6**) completely reacted; Rh(ttp)H (**4**) and Rh(ttp)Bn (**3**) still remained unchanged while Rh(ttp)(cycloheptyl) (**2**) formed in 17% yield and cycloheptene (**5**) was observed in 42% yield (eq 1). Since the complete consumption of Rh_2(ttp)$_2$ (**6**)



significantly slowed down further conversion of Rh(ttp)(cycloheptyl) (**2**) to Rh(ttp)Bn (**3**), Rh_2(ttp)$_2$ (**6**) likely has a promoting role in the transformation. Therefore, both Rh_2(ttp)$_2$ and Rh(ttp)H are possible intermediates.

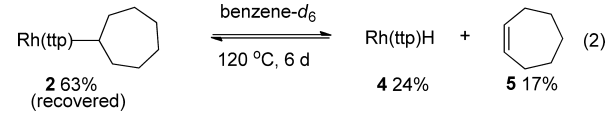
Rh_2(ttp)$_2$ and Rh(ttp)H were then reacted with cycloheptane separately. Indeed, both Rh_2(ttp)$_2$ and Rh(ttp)H each gave only Rh(ttp)(cycloheptyl) (**2**) in 76 and 73% yields, respectively, in less than 15 min (Scheme 2). Therefore, they are intermediates for the CHA product **2** only.

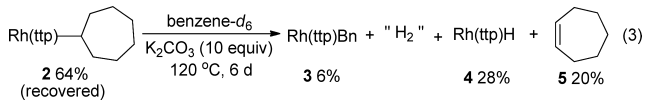
Scheme 2. Reactions of Rh_2(ttp)$_2$ and Rh(ttp)H with Cycloheptane



Mechanism of CHA. As the mechanism of aliphatic CHA has been proposed by Wayland via a bimetalloradical mechanism[11] and shown to operate analogously in our previous reports,[12,13] we therefore did not pursue its study in great detail in this report. The Rh_2(ttp)$_2$ intermediate has also been observed by ^{1}H NMR (Table S1 and Figure S1 (Supporting Information)).

Conversion of Rh(ttp)(cycloheptyl) to Rh(ttp)Bn. We reasoned that the CHA and CCA product Rh(ttp)Bn (**3**) is formed from Rh(ttp)(cycloheptyl) (**2**). Rh(ttp)(cycloheptyl) (**2**) was then heated under neutral and basic conditions separately (eqs 2 and 3). Under neutral conditions, Rh(ttp)-

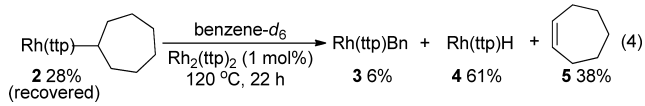




(cycloheptyl) (**2**) yielded only Rh(ttp)H (**4**) and cycloheptene (**5**) in 24 and 17% yields, respectively, after 6 days (eq 2 and Table S2 and Figure S2 (Supporting Information)). Rh(ttp)H and cycloheptene likely stem from the β-hydride elimination of Rh(ttp)(cycloheptyl). In fact, the β-hydride elimination of transition-metal alkyls[17] and transition-metal metalloporphyrin alkyls[18] is well-known to give metal hydride and olefin. The resultant metal hydrides and olefins can either undergo reverse 1,2-addition to give the metal alkyl or dissociation to produce free alkene.

However, under basic conditions, Rh(ttp)Bn (**3**) was observed in 6% yield over an extended time of 6 days, together with a 28% yield of Rh(ttp)H and a 20% yield of cycloheptene (eq 3). The conversion of Rh(ttp)(cycloheptyl) (**2**) to Rh(ttp)Bn (**3**) occurs therefore only in the presence of K_2CO_3 and also occurs slowly.

As the Rh^{II}_2(por)$_2$ metal−metal-bonded dimer forms by the thermal[19,20] or much more rapid base-promoted[9b,12] dehydrogenative dimerization of Rh^{III}(por)H, the possible catalytic role of Rh_2(ttp)$_2$ in the conversion of Rh(ttp)(cycloheptyl) to Rh(ttp)Bn was examined (Table S3 and Figure S3 (Supporting Information)). To our delight, Rh(ttp)(cycloheptyl) added with Rh_2(ttp)$_2$ (1 mol %) gave Rh(ttp)Bn in 6% yield in 22 h (eq 4). Therefore, Rh_2(ttp)$_2$ catalyzes the conversion of **2** to **3**.



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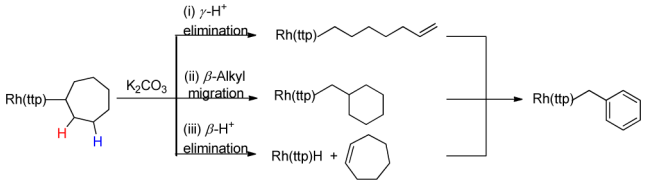
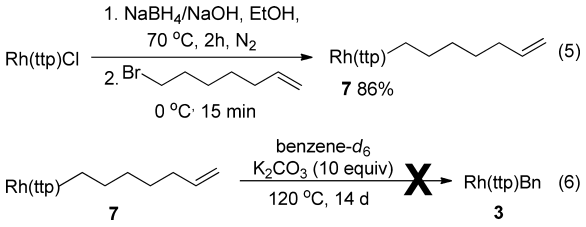
Proposed Mechanistic Pathways and Key Intermediates for 3. As Rh(ttp)(cycloheptyl) (**2**) was converted to Rh(ttp)Bn (**3**) in the presence of K_2CO_3 or a catalytic amount of $Rh_2(ttp)_2$, Scheme 3 shows three proposed mechanistic outlines and their corresponding key intermediates.

Scheme 3. Proposed Key Intermediates for CCA Product 3

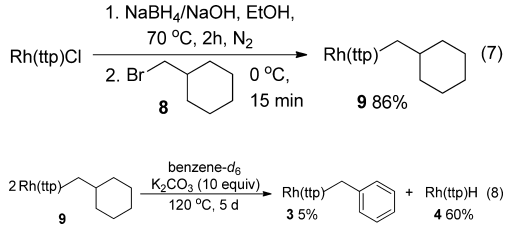


γ-H⁺ or H Elimination (Pathway i). Rh(ttp)(cycloheptyl) (**2**) undergoes the ionic process (i) via a γ-H^+ elimination with base, followed by C(α)−C(β) cleavage to give a Rh(ttp) olefinic α-carbon-centered carbanion and reprotonation to give Rh(ttp)($(CH_2)_5$(CH=CH_2)) (**7**) or the analogous radical process (2) via a γ-H abstraction with Rh^{II}(ttp), followed by C(α)−C(β) cleavage to give a Rh(ttp) olefinic α-carbon-centered radical and hydrogen atom abstraction to give **7**. **7** can undergo subsequent dehydrogenation and rearrangement, leading to the formation of Rh(ttp)Bn (**3**) (Scheme 3). In fact, a cycloheptyl tantalum complex has been proposed to undergo γ-H elimination to generate Ta($(CH_2)_5$(CH=CH_2).[21] Since Rh(ttp)(cycloheptyl) (**2**) did not undergo thermal conversion to Rh(ttp)Bn, only the base- or $Rh^{II}_2(ttp)_2$-catalyzed pathway is considered.

The suspected intermediate Rh(ttp)($(CH_2)_5$(CH=CH_2)) (**7**) was independently synthesized by the reductive alkylation of Rh(ttp)Cl with 7-bromo-1-heptene (eq 5).[22] Rh(ttp)-($(CH_2)_5$(CH=CH_2)) (**7**) was then heated to 120 °C for 14 days, and no Rh(ttp)Bn (**3**) was observed (eq 6). In view of the negative result, we did not conduct further Rh^{II}(ttp)-catalyzed reactions. Pathway i is ruled out.

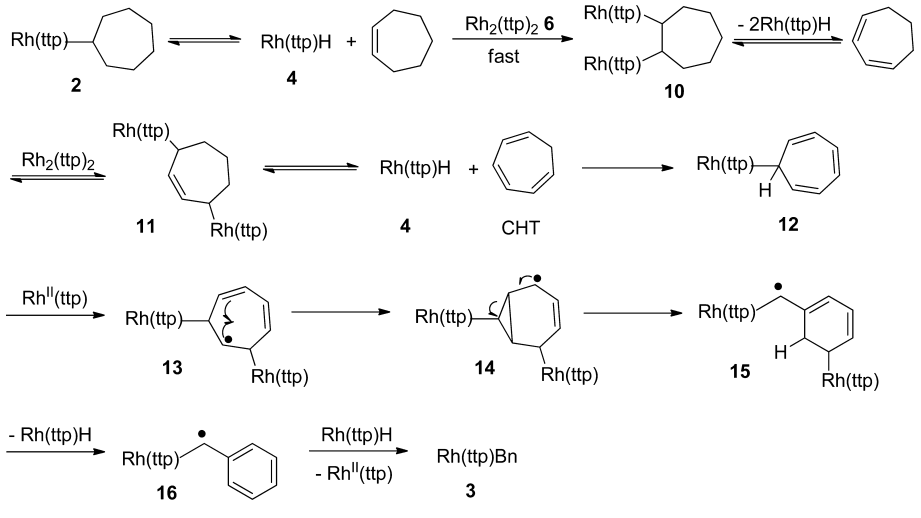


β-Alkyl Migration (Pathway ii). In pathway ii, Rh(ttp)-(cycloheptyl) (**2**) undergoes β-alkyl migration to form ((cyclohexyl)methyl)Rh(ttp) (**9**), which then gives Rh(ttp)Bn (**3**) upon further dehydrogenation, likely by a process discussed in more detail in pathway iii below. This pathway has literature precedence for a transition-metal-catalyzed process. The conversion of cycloheptane to methylcyclohexane is catalyzed by a Ta−H complex,[21] and the WO_2-catalyzed dehydrogenation of methylcyclohexane is well-documented.[23] Therefore, ((cyclohexyl)methyl)Rh(ttp) (**9**) was independently synthesized by reductive alkylation with **8** (eq 7).[22] However, when ((cyclohexyl)methyl)Rh(ttp) (**9**) was heated to 120 °C for 5 days in the presence of K_2CO_3, only a 5% yield of Rh(ttp)Bn (**3**) and 60% yield of Rh(ttp)H (**4**) were observed (eq 8). Therefore, pathway ii is at the most only a minor pathway on the basis of its low yield and very slow rate.



Conversion of Rh(ttp)(cycloheptyl) to Rh(ttp)-(cycloheptatrienyl) via β-H Elimination (Pathway iii). As Rh(ttp)(cycloheptyl) (**2**) gave Rh(ttp)H (**4**) and cycloheptene via β-H elimination in the absence and presence of K_2CO_3 (eqs 2 and 3), we reasoned that cycloheptene can be further dehydrogenated to give cycloheptatriene (CHT), which can then produce Rh(ttp)Bn (**3**) by a Rh^{II}(ttp)-catalyzed process. Scheme 4 illustrates the detailed proposed mechanism of the $Rh_2(ttp)_2$-catalyzed dehydrogenation of Rh(ttp)(cycloheptyl) (**2**) to give Rh(ttp)Bn (**3**). **2** initially undergoes reversible β-H elimination[18] to give Rh(ttp)H (**4**) and cycloheptene, which is then rapidly trapped by $Rh_2(ttp)_2$ (**6**) to yield the 1,2-addition product **10**.[20,24] Successive β-H elimination of **10** and a 1,4-addition reaction of cyclohepta-1,3-diene with $Rh_2(ttp)_2$ (**6**)

Scheme 4. Proposed Mechanism for Rh(ttp)-Catalyzed CCA



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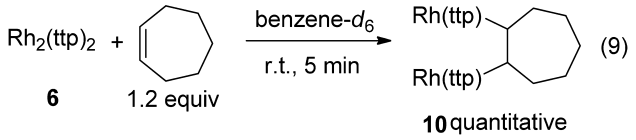
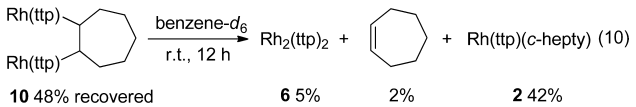
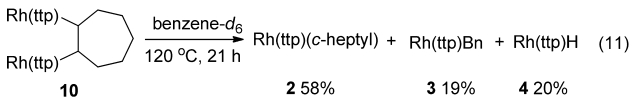
give **11**. Repeated β-H elimination of **11** gives Rh(ttp)H and CHT. Finally CHT reacts with Rh(ttp)H or $Rh_2(ttp)_2$ to give Rh(ttp)(cycloheptatrienyl) (**12**).

The conversion of **12** to **3** is a Rh^{II}(ttp)-catalyzed skeletal rearrangement. Initially, Rh^{II}(ttp) dissociates from $Rh_2(ttp)_2$ through the weak Rh−Rh bond (16.5 kcal mol^{-1})[25] and reacts with **12** to give the carbon center radical **13**, which then isomerizes to give the cyclopropylmethyl radical **14** and subsequently, upon ring opening and carbon−carbon bond cleavage, produce **15** (Scheme 4).[26] **15** undergoes a further β-H elimination to give the Rh-substituted benzyl radical **16**. Hydrogen atom transfer from Rh(ttp)H to **16** yields Rh(ttp)Bn (**3**) and regenerates Rh^{II}(ttp). Thus, the conversion of **12** to **3** is catalyzed by Rh^{II}(ttp).

Supporting lines of evidence came from the following experiments. $Rh_2(ttp)_2$ (**6**) reacted at room temperature with cycloheptene rapidly to give the 1,2-addition product **10** quantitatively (eq 9). **10** at room temperature in 12 h



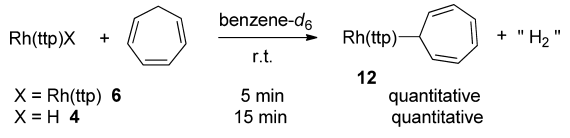




decomposed partially to give $Rh_2(ttp)_2$ (**6**), cycloheptene, and Rh(ttp)(cycloheptyl) (**2**) in 5, 2, and 42% yields, respectively (eq 10). Upon heating at 120 °C for 21 h, **10** gave Rh(ttp)H (**4**), Rh(ttp)(cycloheptyl) (**2**), and Rh(ttp)Bn (**3**) in 20, 58, and 19% yields, respectively (eq 11 and Table S1 and Figure S1 (Supporting Information)). Therefore, **10** is a viable intermediate for the formation of Rh(ttp)Bn.

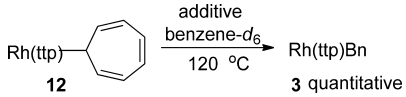
The proposed formation of Rh(ttp)(cycloheptatrienyl) (**12**) from the CHA of CHT with $Rh_2(ttp)_2$ or Rh(ttp)H (Scheme 4) was confirmed separately. Both $Rh_2(ttp)_2$ and Rh(ttp)H react with CHT quickly at room temperature to give **12** quantitatively (Scheme 5).

Scheme 5. CHA Reaction of CHT



In order to validate the Rh^{II}(ttp)-catalyzed skeletal isomerization of Rh(ttp)(c-heptatrienyl) (**12**) to Rh(ttp)Bn (**3**), the rates of the quantitative conversion of **12** to **3** at 120 °C with additives were monitored by ^{1}H NMR spectroscopy (Table 1). The disappearances of **12** followed a first-order decay, and the k_{obs} value does not change with the initial concentration of **12**, confirming the first-order kinetics (Table 1, entries 1 and 2, and Figure S5 (Supporting Information)). Added K_2CO_3 did not change the k_{obs} value (Table 1, entry 3) and therefore does not catalyze the reaction. However, the k_{obs} value increases with

Table 1. Additive Effect on the k_{obs} Value on Isomerization of 12 to 3



entry	$[12]_0/10^3$ M	additive	$k_{obs}/10^6$ s^{-1}	error/10^7 s^{-1}
1	6.95	none	4.75	4.0
2	13.90	none	4.70	3.5
3	6.95	K_2CO_3 (10 equiv)	4.98	2.34
4	6.95	$Rh_2(ttp)_2$ (3.48×10^{-5} M)	7.33	2.0
5	6.95	$Rh_2(ttp)_2$ (3.48×10^{-4} M)	21.53	12.7

higher concentration of added $Rh_2(ttp)_2$ (Table 1, entries 4 and 5) as reported.[14] A 10-fold increase of $[Rh_2(ttp)_2]$ produces a 3-fold enhancement of the rate, supporting a half-order dependence on $Rh_2(ttp)_2$ or first-order dependence on Rh(ttp), thus validating the Rh(ttp)-catalyzed isomerization. This supports the notion that K_2CO_3 only promotes the conversion of Rh(ttp)H into $Rh_2(ttp)_2$ but not that from **12** into **3**.[9b,12] It should be noted that this metalloradical-catalyzed isomerization[14] at 120 °C is much faster than the thermal isomerization of CHT to toluene, which only occurs at 800−1300 K at a sufficient rate.[27]

CONCLUSIONS

The mild conversion of cycloheptane to Rh(ttp)Bn via sequential CHA and CCA with Rh(ttp)Cl promoted by K_2CO_3 and Rh^{II}(ttp) has been observed. Rh(ttp)(cycloheptyl), which formed from the base-promoted CHA of Rh(ttp)Cl and cycloheptane, is the intermediate leading to the CCA product of Rh(ttp)Bn. Rh(ttp)(cycloheptyl) undergoes multiple β-H elimination to give Rh(ttp)H and CHT. CHT reacts with Rh(ttp)H or $Rh_2(ttp)_2$ either generated from the base-promoted dehydrogenative dimerization of Rh(ttp)H or added separately to produce **12**. The skeletal isomerization of Rh(ttp)(cycloheptatrienyl) (**12**) to Rh(ttp)Bn (**3**) operates via a metalloradical-catalyzed process.

EXPERIMENTAL SECTION

General Procedures. All materials were obtained from commercial suppliers and used without further purification unless otherwise specified. Benzene was distilled from sodium under nitrogen. Rhodium porphyrin complexes[9,12,24] were prepared according to the literature procedures, and they have been characterized. All solutions used were degassed three times by freeze−thaw−pump cycles and stored in a Teflon screwhead stoppered flask, which was wrapped with aluminum foil to protect it from light.

Yields from NMR sealed-tube experiments in benzene-d_6 were measured using the residual solvent proton as the internal standard. NMR kinetic data were analyzed with OriginPro 7.5 software from OriginLab Corp.

Experimental Procedures. *Reaction of Cycloheptane with Rh(ttp)Cl.* Rh(ttp)Cl[12] (**1**; 20.4 mg, 0.025 mmol) was added to cycloheptane (3.0 mL). The red reaction mixture was degassed for three freeze−thaw−pump cycles, purged with N_2, and heated to 120 °C under N_2 for 24 h. Excess cycloheptane was removed by vacuum distillation. The residue was purified by column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (1/1) as eluent to give a red solid. Rh(ttp)(cycloheptyl) (**2**; 4.0 mg, 0.0046 mmol, 18%) was collected and 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): δ −4.53 (m, 2), −4.05 (m, 3 H), −1.26 (m, 4 H), −0.22 (m, 2 H), −0.06 (m, 2

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H), 2.69 (s, 12 H, *p*-methyl), 7.54 (d, 8 H, J = 5.4 Hz, *m*-phenyl), 8.00 (d, 4 H, J = 7.5 Hz, *o*′-phenyl), 8.08 (d, 4 H, J = 7.8 Hz, *o*-phenyl), 8.69 (s, 8 H, pyrrole). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.69, 22.09, 27.85, 33.24, 39.37 (d, $^1J_{Rh-C}$ = 27.6 Hz), 122.87, 127.42, 127.55, 131.52, 133.63, 134.25, 137.23, 137.23, 139.53, 143.50. MS: calcd for $(C_{55}H_{49}N_4Rh)^+$ m/z 868.3007, found m/z 868.3016.

Reaction of Cycloheptane and Rh(ttp)Cl with Potassium Carbonate. Rh(ttp)Cl (20.4 mg, 0.025 mmol) and anhydrous potassium carbonate (34.9 mg, 0.252 mmol) were added to cycloheptane (3.0 mL). The red reaction mixture was degassed for three freeze−thaw−pump cycles, purged with N_2, and heated to 120 °C under N_2 for 6 h. Excess cycloheptane 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 (1/1) as eluent. The red solids Rh(ttp)(cycloheptyl) (**2**; 6.6 mg, 0.0076 mmol, 30%) and Rh(ttp)Bn (**3**; 5.5 mg, 0.0064 mmol, 25%) were collected.

Sealed NMR Tube Experiment of Rh(ttp)Cl and Cycloheptane with Potassium Carbonate in Benzene-d_6. Rh(ttp)Cl (3.5 mg, 0.0043 mmol), cycloheptane (11 μL, 0.091 mmol), and potassium carbonate (5.9 mg, 0.0427 mmol) were added to benzene-d_6 (500 μL) in a NMR tube. The red mixture was degassed for three freeze−thaw−pump cycles and the NMR tube was flame-sealed under vacuum. It was heated to 120 °C in the dark. The reaction was monitored with ^{1}H NMR spectroscopy.

Reaction of Cycloheptane with $Rh_2(ttp)_2$. $Rh_2(ttp)_2$ (9.5 mg, 0.0062 mmol) was added in cycloheptane (1.5 mL). The red reaction mixture was degassed for three freeze−thaw−pump cycles, purged with N_2 and heated to 120 °C under N_2 for 5 min. Excess cycloheptane was removed by vacuum distillation. The residue was purified by column chromatography on silica gel with a solvent mixture of hexane/CH_2Cl_2 (1:1). Red solid, Rh(ttp)(cycloheptyl) (**2**) (8.2 mg, 0.0093 mmol, 76%) was collected and was further recrystallized from CH_2Cl_2/MeOH.

Reaction of Cycloheptane with Rh(ttp)H. Rh(ttp)H (9.5 mg, 0.012 mmol) was added in cycloheptane (1.5 mL). The red reaction mixture was degassed for three freeze−thaw−pump cycles, purged with N_2, and heated to 120 °C under N_2 for 15 min. Excess cycloheptane was removed by vacuum distillation. The residue was purified by column chromatography on silica gel with a hexane/CH_2Cl_2 solvent mixture (1/1) as eluent. The red solid Rh(ttp)(cycloheptyl) (**2**; 7.8 mg, 0.090 mmol, 73%) was collected and was further recrystallized from CH_2Cl_2/MeOH.

Sealed NMR Tube Experiment of Rh(ttp)(cycloheptyl) in Benzene-d_6. Rh(ttp)(cycloheptyl) (**2**; 3.8 mg, 0.0044 mmol) was added to benzene-d_6 (500 μL) in a NMR tube. The red solution was degassed for three freeze−thaw−pump cycles, and the NMR tube was flame-sealed under vacuum. The solution was heated to 120 °C in the dark, and the reaction was monitored with ^{1}H NMR spectroscopy.

*Sealed NMR Tube Experiment of Rh(ttp)(cycloheptyl) (**2**) with Potassium Carbonate in Benzene-d_6.* Rh(ttp)(cycloheptyl) (**2**; 3.8 mg, 0.0044 mmol) and potassium carbonate (6.0 mg, 0.044 mmol) were added to benzene-d_6 (500 μL) in an NMR tube. The red solution was degassed for three freeze−thaw−pump cycles, and the NMR tube was flame-sealed under vacuum. The solution was heated to 120 °C in the dark. The reaction was monitored with ^{1}H NMR spectroscopy at particular time intervals, and the NMR yields were taken.

Sealed NMR Tube Experiment of Rh(ttp)(cycloheptyl) with 1 mol % of $Rh_2(ttp)_2$ in Benzene-d_6. Rh(ttp)(cycloheptyl) (**2**; 3.8 mg, 0.0044 mmol) and $Rh_2(ttp)_2$ (0.034 mg, 4.4×10^{-5} mmol) which was previously dissolved in 500 μL of degassed benzene-d_6 were added together in a NMR tube. The red solution was degassed for three freeze−thaw−pump cycles, and the NMR tube was flame-sealed under vacuum. The solution was heated to 120 °C in the dark. The reaction was monitored with ^{1}H NMR spectroscopy.

Independent Synthesis of Rh(ttp)(7-heptenyl).[12] A suspension of Rh(ttp)Cl (100 mg, 0.11 mmol) in EtOH (50 mL) and a solution of $NaBH_4$ (17 mg, 0.45 mmol) in aqueous NaOH (0.1 M, 2 mL) were purged with N_2 for 15 min separately. The solution of $NaBH_4$ was added slowly to the suspension of Rh(ttp)Cl via a cannula. The mixture was heated to 50 °C under N_2 for 1 h. The solution was then cooled to 0 °C under N_2, and 7-heptenyl bromide (23 mg, 1.20 mmol) was added. A reddish orange suspension was formed. After it was stirred at room temperature for another 15 min under N_2, the reaction mixture was worked up by extraction with CH_2Cl_2/H_2O. The combined organic extract was dried ($MgSO_4$), filtered, and rotary evaporated. The reddish orange residue was purified by column chromatography over silica gel (250−400 mesh) using a hexane/CH_2Cl_2 solvent mixture (1/1) as the eluent. The major orange fraction was collected and gave a reddish orange solid of Rh(ttp)-$((CH_2)_5(CH{=}CH_2))$ (**7**; 96.0 mg, 0.11 mmol, 86%) as the product after rotary evaporation. R_f = 0.84 (hexane/CH_2Cl_2 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ −4.96 (td, 2 H, J = 2.9, 9.0 Hz), −4.50 (qu, 2 H, J = 7.8 Hz), −1.56 (qu, 2 H, J = 7.4 Hz), −0.45 (qu, 2 H, J = 7.4 Hz), 0.80 (q, 2 H, J = 7.0 Hz), 2.69 (s, 12 H, *p*-methyl), 4.39 (dd, 1 H, J = 1.6, 17.0 Hz), 4.50 (dd, 1 H, J = 1.1, 11.0 Hz), 5.06 (m, 1 H), 7.53 (t, 8 H, J = 7.7 Hz), 7.98 (d, 4 H, J = 7.6 Hz), 8.07 (d, 4 H, J = 7.6 Hz), 8.70 (s, 8 H, pyrrole). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.69, 25.78, 26.84, 26.89, 32.54, 113.67, 122.50, 127.45, 127.52, 131.49, 133.79, 134.08, 137.25, 138.69, 139.44, 143.33. MS: calcd for $(C_{55}H_{49}N_4Rh)^+$ m/z 868.3007, found m/z 868.3011.

*Sealed NMR Tube Experiment of Rh(ttp)$((CH_2)_5(CH{=}CH_2))$ (**7**) with Potassium Carbonate in Benzene-d_6.* Rh(ttp)$((CH_2)_5(CH{=}CH_2))$ (**7**; 3.8 mg, 0.0044 mmol) and potassium carbonate (6.0 mg, 0.044 mmol) were added to benzene-d_6 (500 μL) in a NMR tube. The red solution was degassed for three freeze−thaw−pump cycles, and the NMR tube was flame-sealed under vacuum and was heated to 120 °C in the dark. The reaction was monitored with ^{1}H NMR spectroscopy.

*Independent Synthesis of Rh(ttp)(cyclohexylmethyl) (**9**).*[12] A suspension of Rh(ttp)Cl (100 mg, 0.11 mmol) in EtOH (50 mL) and a solution of $NaBH_4$ (17 mg, 0.45 mmol) in aqueous NaOH (0.1 M, 2 mL) were purged with N_2 for 15 min separately. The solution of $NaBH_4$ was added slowly to the suspension of Rh(ttp)Cl via a cannula. The mixture was heated to 50 °C under N_2 for 1 h. The solution was then cooled to 0 °C under N_2, and cyclohexylmethyl bromide (**8**; 23 mg, 1.20 mmol) was added. A reddish orange suspension was formed. After it was stirred at room temperature for another 15 min under N_2, the reaction mixture was worked up by extraction with CH_2Cl_2/H_2O. The combined organic extract was dried ($MgSO_4$), filtered, and rotary evaporated. The reddish orange residue was purified by column chromatography over silica gel (250−400 mesh) using a hexane/CH_2Cl_2 solvent mixture (1/1) as the eluent. The major orange fraction was collected and gave a reddish orange solid of Rh(ttp)CH_2(c-C_6H_{11}) (**9**; 92.5 mg, 0.11 mmol, 86%) as the product after rotary evaporation. R_f = 0.84 (hexane/CH_2Cl_2 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ −5.47 (s, 1 H), −5.08 (dd, 2 H, J = 3.4, 5.0 Hz), −2.42 (d, 2 H, J = 12.2 Hz), −2.11 (qd, 2 H, J = 2.8, 12.6 Hz), −0.45 (qt, 2 H, J = 3.3, 12.7 Hz), −0.25 (qt, 1 H, J = 3.6, 12.8 Hz), 0.36 (td, 2 H, J = 2.8, 12.8 Hz), 0.64 (d, 1 H, J =12.8 Hz), 2.69 (s, 12 H), 7.53 (t, 8 H, J = 7.8 Hz), 7.96 (d, 4 H, J = 7.7 Hz), 8.09 (d, 4 H, J =7.7 Hz), 8.70 (s, 8 H, pyrrole). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.69, 25.21, 25.56, 30.64, 36.31, 122.56, 127.47, 127.52, 131.48, 133.70, 134.10, 137.24, 139.45, 143.43. MS: calcd for $(C_{55}H_{49}N_4Rh)^+$ m/z 868.3007, found m/z 868.3015.

*Sealed NMR Tube Experiment of Rh(ttp)CH_2(cycloC_6H_{11}) (**9**) with Potassium Carbonate in Benzene-d_6.* Rh(ttp)CH_2(c-C_6H_{11}) (**9**; 3.8 mg, 0.0044 mmol) and potassium carbonate (6.0 mg, 0.044 mmol) were added to benzene-d_6 (500 μL) in an NMR tube. The red solution was degassed for three freeze−thaw−pump cycles, and the NMR tube was flame-sealed under vacuum. The tube was heated to 120 °C in the dark, and the reaction was monitored with ^{1}H NMR spectroscopy.

Sealed NMR Tube Experiment of $Rh_2(ttp)_2$ and Cycloheptene in Benzene-d_6. Cycloheptene (2 μL, 0.021 mmol) was added to a solution of $Rh_2(ttp)_2$ prepared from a stock solution with subsequent removal of solvent (3.4 mg, 0.0022 mmol) in 500 μL of degassed benzene in an NMR tube. The solvent was removed by vacuum distillation after 5 min. A 500 μL portion of degassed benzene-d_6 was then added. The red solution was degassed for three freeze−thaw−

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pump cycles, the NMR tube was flame-sealed under vacuum, and the solution was immediately analyzed by ^{1}H NMR. The ^{1}H NMR signal of $Rh_2(ttp)_2$ was not observed. Instead, a clean NMR spectrum of the newly formed 1,2-addition product **10** appeared. ^{1}H NMR (C_6D_6, 400 MHz): δ −4.24 (m, 2 H), −3.39 (m, 2 H), −2.70 (m, 2 H), −1.60 (m, 2 H), −1.20 (m, 2 H), −0.68 (m, 1 H), −0.18 (m, 1 H), 2.41 (s, 24 H, *p*-methyl), 7.30 (d, 8 H, J = 6.4 Hz, *m*-phenyl), 7.33 (d, 8 H, J = 8.0 Hz, *m*′-phenyl), 8.13 (d, 8 H, J = 7.6 Hz, *o*′-phenyl), 8.19 (d, 8 H, J = 7.5 Hz, *o*-phenyl), 8.97 (s, 16 H, pyrrole). Compound **10** is too unstable to allow a ^{13}C NMR spectrum to be taken.

Sealed NMR Tube Experiment of $Rh_2(ttp)_2$ and Cycloheptene in Benzene-d_6 at 120 °C. Cycloheptene (2 μL, 0.021 mmol) was added to a solution of $Rh_2(ttp)_2$ prepared from a stock solution with subsequent removal of solvent (3.4 mg, 0.0022 mmol) in 500 μL of degassed benzene in an NMR tube. The solvent was removed by vacuum distillation after 5 min. A 500 μL portion of degassed benzene-d_6 was then added. The red solution was degassed for three freeze−thaw−pump cycles, and the NMR tube was flame-sealed under vacuum. It was brought to ^{1}H NMR analysis after it was sealed. The 1,2-addition product Rh(ttp) complex **10** was formed cleanly. The reaction mixture was heated to 120 °C and was monitored with ^{1}H NMR spectroscopy.

Sealed NMR Tube Experiment of $Rh_2(ttp)_2$ and Cycloheptatriene in Benzene-d_6. $Rh_2(ttp)_2$ (3.6 mg, 0.0047 mmol) prepared from a stock solution with subsequent removal of solvent, cycloheptatriene (5 μL), and degassed benzene-d_6 (500 μL) were placed in an NMR tube. The red solution was degassed for three freeze−thaw−pump cycles, and the NMR tube was flame-sealed under vacuum. The reaction mixture was kept at room temperature and monitored with ^{1}H NMR spectroscopy at particular time intervals, and the NMR yields were taken. **12** was obtained quantitatively. ^{1}H NMR (C_6D_6, 400 MHz): δ 2.44 (s, 19), 7.32 (d, 8 H, J = 7.4 Hz, *m*-phenyl), 7.35 (d, 4 H, J = 7.8 Hz, *o*-phenyl), 8.13 (d, 4 H, J = 5.4 Hz, *m*′-phenyl), 8.14 (d, 4 H, J = 5.4 Hz, *o*′-phenyl), 8.93 (s, 8 H, pyrrole). ^{13}C NMR (C_6D_6, 100 MHz): δ 21.50, 123.47, 131.82, 132.80, 134.22, 134.28, 134.92, 137.11, 140.43, 144.24. MS: calcd for $(C_{55}H_{43}N_4Rh)^+$ m/z 862.2537, found m/z 862.2549.

Synthesis of Rh(ttp)(cycloheptatrienyl) (12). Rh(ttp)H (3.6 mg, 0.0047 mmol) and cycloheptatriene (5 μL) were added to degassed benzene (500 μL). The red solution was degassed for three freeze−thaw−pump cycles, purged with N_2, and put into a water bath at 25 °C for 15 min. Excess solvent was removed by vacuum distillation. A 500 μL portion of degassed benzene-d_6 was then added. The product **12** was found to be air-sensitive and decomposed during column chromatography. As the ^{1}H NMR spectrum was clean, no further purification step was required.

Rearrangement Reaction of Rh(ttp)(cycloheptatrienyl) at 6.95 mM. Rh(ttp)(cycloheptatrienyl) (**12**; 3.0 mg, 0.0035 mmol) was added to degassed benzene-d_6 (500 μL) in an NMR tube. The red solution was degassed for three freeze−thaw−pump cycles, and the NMR tube was flame-sealed under vacuum. The solution was heated to 120 °C in the dark. The reaction was monitored with ^{1}H NMR spectroscopy at particular time intervals, and the NMR yields were taken.

Rearrangement Reaction of Rh(ttp)(cycloheptatrienyl) (12) at 13.90 mM. Rh(ttp)(cycloheptatrienyl) (6.0 mg, 0.0070 mmol) was added to degassed benzene-d_6 (500 μL) in an NMR tube. The red solution was degassed for three freeze−thaw−pump cycles, and the NMR tube was flame-sealed under vacuum. The solution was heated to 120 °C in the dark. It was monitored with ^{1}H NMR spectroscopy, and the NMR yields were taken.

Rearrangement Reaction of Rh(ttp)(cycloheptatrienyl) (12) at 6.95 mM with Potassium Carbonate. Rh(ttp)(cycloheptatrienyl) (3.0 mg, 0.0035 mmol) and potassium carbonate (4.8 mg, 0.035 mmol) were added to degassed benzene-d_6 (500 μL) in an NMR tube. The red reaction mixture was degassed for three freeze−thaw−pump cycles, and the NMR tube was flame-sealed under vacuum. The solution was heated to 120 °C in the dark. The reaction was monitored with ^{1}H NMR spectroscopy, and the NMR yields were taken.

Rearrangement Reaction of Rh(ttp)(cycloheptatrienyl) (12) at 6.95 mM with 1 mol % of $Rh_2(ttp)_2$. Rh(ttp)(cycloheptatrienyl) (3.0 mg, 0.0035 mmol) and 1 mol % of $Rh_2(ttp)_2$ prepared from a stock solution (0.027 mg, 1.7×10^{-5} mmol) were added to degassed benzene-d_6 (500 μL) in an NMR tube. The red reaction mixture was degassed for three freeze−thaw−pump cycles, and the NMR tube was flame-sealed under vacuum. The solution was heated to 120 °C in the dark, the reaction was monitored with ^{1}H NMR spectroscopy, and the NMR yields were taken.

Rearrangement Reaction of Rh(ttp)(cycloheptatrienyl) (12) at 6.95 mM with 10 mol % of $Rh_2(ttp)_2$. Rh(ttp)(cycloheptatrienyl) (3.0 mg, 0.0035 mmol) and 10 mol % $Rh_2(ttp)_2$ (0.27 mg, 1.7×10^{-4} mmol) were added to degassed benzene-d_6 (500 μL) in an NMR tube. The red reaction mixture was degassed for three freeze−thaw−pump cycles, and the NMR tube was flame-sealed under vacuum. The solution was heated to 120 °C in the dark. The reaction was monitored with ^{1}H NMR spectroscopy, and the NMR yields were taken.

■ ASSOCIATED CONTENT

Supporting Information

Figures and tables giving the progress of reactions and spectroscopic data for compounds **2**, **7**, **9**, **10**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **2001**, *17*, 2437−2450. (b) Lersch, M.; Tilset, M. *Chem. Rev.* **2005**, *105*, 2471−2526.

(2) (a) Arndtsen, R. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154−162. (b) Sen, A. *Acc. Chem. Res.* **1998**, *31*, 550−557.

(3) Zulys, A.; Dochnahl, M.; Hollmann, D.; Lohnwitz, K.; Herrmann, J.-S.; Roesky, P. W.; Blechert, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 7794−7798.

(4) (a) Ward, M. D.; Schwartz, J. *Organometallics* **1982**, *1*, 1030−1032. (b) Kitajima, N.; Schwartz, J. *J. Am. Chem. Soc.* **1984**, *106*, 2220−2222. (c) Gottker-Schnetmann, I.; Brokkhart, M. *J. Am. Chem. Soc.* **2004**, *126*, 9330−9338. (d) Gottker-Schnetmann, I.; White, P. S.; Brookhart, M. *Organometallics* **2004**, *23*, 1766−1776. (e) Wong-Foy, A. G.; Bhalla, G.; Liu, X. Y.; Periana, R. A. *J. Am. Chem. Soc.* **2003**, *125*, 14292−14293. (f) Bhalla, G.; Periana, R. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 1540−1543. (g) Aoki, T.; Crabtree, R. H. *Organometallics* **1993**, *12*, 294−298. (h) Perutz, R. N.; Sabo-Etienne, S. . *Angew. Chem., Int. Ed.* **2007**, *464*, 2578−2592.

(5) (a) Gomez, M.; Robinson, D. J.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1983**, *15*, 825−826. (b) Monti, D.; Frachey, G.; Bassetti, M.; Haynes, A.; Sunley, G. J.; Maitlis, P. M.; Cantoni, A.; Bocelli, G. *Inorg. Chim. Acta* **1995**, *240*, 485−493. (c) Cho, J.-Y.; Tse, M. K.; Holmes, D.; Maleczka, R. E., Jr.; Smith, M. R. *Science* **2002**, *295*, 305−308.

(6) Anstey, M. R.; Yung, C. M.; Du, J.; Bergman, R. G. *J. Am. Chem. Soc.* **2007**, *129*, 776−777.

(7) (a) Zhou, X.; Li, Q.; Mak, T. C. W.; Chan, K. S. *Inorg. Chim. Acta* **1998**, *270*, 551−554. (b) Zhou, X.; Wang, R.-J.; Xue, F.; Mak, T. C. W.; Chan, K. S. *J. Organomet. Chem.* **1999**, *580*, 22−25. (c) Zhou, X.;

Tse, M. K.; Wu, D.-D.; Mak, T. C. W.; Chan, K. S. *J. Organomet. Chem.* **2000**, *598*, 80−86.
(8) (a) Chan, K. S.; Lau, C. M. *Organometallics* **2006**, *25*, 260−265. (b) Chan, K. S.; Lau, C. M. *Organometallics* **2006**, *25*, 260−265.
(9) (a) Chan, K. S.; Chiu, P. F.; Choi, K. S. *Organometallics* **2007**, *26*, 1117−1119. (b) Choi, K. S.; Chiu, P. F.; Chan, C. S.; Chan, K. S. *J. Chin. Chem. Soc.* **2013**, *60*, 779−793.
(10) Choi, K. S.; Lai, T. H.; Lee, S. Y.; Chan, K. S. *Organometallics* **2011**, *30*, 2633−2635.
(11) Wayland, B. B.; Ba, S.; Sherry, A. E. *J. Am. Chem. Soc.* **1991**, *113*, 5305−5311.
(12) Chan, Y. W.; Chan, K. S. *Organometallics* **2008**, *27*, 4625−4635.
(13) For an example of CCA of cyclcoctane, see: Chan, Y. W.; Chan, K. S. *J. Am. Chem. Soc.* **2010**, *132*, 6920−6922.
(14) Chan, Y. W.; Chan, K. S. *Chem. Commun.* **2011**, *47*, 4802−4804.
(15) For examples of base-promoted CHA, see: (a) Liang, L. C.; Lin, J. M.; Lee, W. Y. *Chem. Commun.* **2005**, *19*, 2462−2464. (b) Harkins, S. B.; Peters, J. C. *Organometallics* **2002**, *21*, 1753−1755. (c) Wang, C.; Ziller, J. W.; Flood, T. C. *J. Am. Chem. Soc.* **1995**, *117*, 1647−1648.
(16) Ruzicka, L.; Seidel, C. F. *Helv. Chim. Acta* **1936**, *19*, 424−433.
(17) (a) Reger, D. L.; Culbertson, E. C. *Inorg. Chem.* **1977**, *16*, 3104−3107. (b) Reger, D. L.; Culbertson, E. C. *J. Am. Chem. Soc.* **1976**, *98*, 2789−2794.
(18) (a) Mak, K. W.; Chan, K. S. *J. Am. Chem. Soc.* **1998**, *120*, 9686−9687. (b) Mak, K. W.; Xue, F.; Mak, T. C. W.; Chan, K. S. *J. Chem. Soc., Dalton Trans.* **1999**, *19*, 3333−3334.
(19) (a) Wayland, B. B.; van Voorhees, S. L.; Wilker, C. *Inorg. Chem.* **1986**, *25*, 4039−4042. (b) Wayland, B. B.; Ba, S.; Sherry, A. E. *Inorg. Chem.* **1992**, *31*, 148−150.
(20) Paonessa, R. S.; Thomas, N. C.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *107*, 4333−4335.
(21) Rataboul, F.; Chabanas, M.; de Mallmann, A.; Coperet, C.; Thivolle-Cazat, J.; Basset, J. M. *Chem. Eur. J.* **2003**, *9*, 1426−1434.
(22) Chan, K. S.; Mak, K. W.; Tse, M. K.; Yeung, S. K.; Li, B. Z.; Chan, Y. W. *J. Organomet. Chem.* **2008**, *693*, 399−407.
(23) Belatel, H.; Al-Kandari, H.; Al-Kharafi, F.; Garin, F.; Katrib, A. *Appl. Catal., A* **2007**, *318*, 227−233.695.
(24) Ogoshi, H.; Setsume, J.; Yoshida, Z. *J. Am. Chem. Soc.* **1977**, *99*, 3869−3870.
(25) Wayland, B. B.; Coffins, V. L.; Farnos, M. D. *Inorg. Chem.* **1988**, *27*, 2745−2747.
(26) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry Part A: Structure and Mechanisms*; Plenum Press: New York, 1977; pp 504−510.
(27) (a) Woods, W. G. *J. Org. Chem.* **1958**, *23*, 110−112. (b) Gaynor, B. J.; Gilbert, R. G. *Int. J. Chem. Kinet.* **1976**, *8*, 695−707.