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Metalloradical-Catalyzed Selective 1,2-Rh-H Insertion into the Aliphatic Carbon–Carbon Bond of Cyclooctane

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Supporting Information

ABSTRACT: The selective aliphatic carbon–carbon activation of cyclo-octane (c-octane) was achieved via the RhII(ttp)-catalyzed 1,2-addition of Rh(ttp)H to give Rh(ttp)(n-octyl) (ttp = tetrahydrophyrinato dianion) in good yield under mild reaction conditions. This mechanism is further supported by DFT calculations. The reaction worked only with the sterically accessible Rh(ttp) porphyrin complex but not with the bulky Rh(tmp) system (tmp = tetrakismesitylporphyrinato dianion), thus showing the highly steric sensitivity of carbon–carbon bond activation by transition metal complexes.

INTRODUCTION

Alkane functionalization in a homogeneous medium is an important and challenging process which involves either carbon–hydrogen bond activation (CHA)1 or carbon–carbon bond activation (CCA)2 with organic, inorganic, and organometallics reagents followed by functionalization. Although aliphatic C–C bonds are weaker than aliphatic C–H bonds, CCA of alkanes by the attack of a transition metal complex is much less reported due to sterical hindrance of the carbon atoms which are shielded by peripheral C–H bonds as well as for statistical reasons associated with C–C bonds being typically less abundant than C–H bonds in organic compounds.3

Cyclo-octane (c-octane) is a relatively unstrained cycloalkane with a strain energy of 9.6 kcal/mol4 and therefore serves as a commonly studied substrate in alkane functionalization, mostly involving CHA. Some examples of CHA of c-octane are the iridium(I) pincer dihydrogenated dehydrogenation to c-octane,5a the FeCl3-catalyzed aerobic oxidation to c-iridium(I) pincer dihydride-catalyzed dehydrogenation to c-octanol and c-octanone,5b as well as the MnO2-catalyzed bromination to c-octyl bromide.5c

Reports of CCA of c-octane are rare. CCA of c-octane in a heterogeneous medium requires a very high reaction temperature of 530 °C and consequently results in both CHA and CCA.5a Oxidative CCA of c-octane catalyzed by N-hydroxyphthalides/Co(II)/Mn(II) at 100 °C in 14 h gives α- dicarboxylic acids in 2% yield only together with the major products being c-octanol and c-octanone.5b

We have recently discovered the base-promoted CHA of cyclic alkanes with Rh(III) porphyrins.6 In contrast to c-pentane6 and c-hexane,6 c-heptane7 undergoes both CHA and CCA to give Rh(III) porphyrin c-heptyl and benzyl.7 Both CHA and CCA have been proposed to involve Rh(II) porphyrin as a reagent or as a catalyst. These Rh(II) porphyrins are unique metalloradicals and exhibit rich chemistry in bond activations including CHA8,9 and CCA.10,11 The bimetalloradical CHA of methane and toluene, based on the second order dependence of the RhII(tmp) (tmp = tetrakis(3,5-dimethylphenyl)porphyrinato dianion) concentration in the rate laws, has been reported by Wayland et al.9 The CCA mechanism has been shown to be dependent on RhII(tmp) concentration, with a first order rate dependence in both the reaction with nitroxide,10 and in the reaction with 2-methyl substituted nitrile11 and second order dependence in the reaction with cyclophane.12 We have previously communicated the CCA of c-octane via the 1,2-addition of its carbon–carbon bond to Rh(ttp)H, catalyzed by the RhII(ttp) (ttp = tetrahydrophyrinato dianion) metalloradical to give Rh(ttp) (n-octyl)selectively13 (Scheme 1) and now report our full studies and theoretical calculations.

RESULTS AND DISCUSSION

Discovery and Optimization of CCA. Initially, c-octane was found to react poorly with Rh(ttp)(Cl) to give Rh(ttp)(c-octyl)2 and Rh(tpp)(n-octyl)3 in 5% and 8% yields, respectively (Table 1, entry 1). A 72% yield of Rh(ttp)(Cl)1 was recovered, and a trace amount of Rh(tpp)(H)4 was observed. Both CHA and CCA products formed but the reaction was inefficient. Upon addition of KOH (10 equiv) to the reaction mixture, Rh(ttp)(c-octyl), Rh(tpp)(n-octyl), and Rh(tpp)(H) were obtained in 6%, 25%, and 62% yields, respectively, in 7.5 h (Table 1, entry 2). When K2CO3 (10 equiv) was added,9 Rh(ttp)(Cl) was consumed in 7.5 h, and Rh(tpp)(n-octyl)3 and
Rh(ttp)H and 4 were obtained in 33% and 58% yields, respectively (Table 1, entry 3). The CCA product 3 is the formal 1,2-addition product of Rh(ttp)H 4 into the carbon–carbon bond of c-octane. The c-octane sample was pure and found to be free of n-octane and 1-octene by GC-MS analysis. Complexes 2 and 3 were independently synthesized by reductive alkylation with NaBH4/R-Br (eq 1). Therefore, Rh(ttp)(n-octyl)2 was obtained in 33% and 58% yields, respectively, after 21 h (Table 2). In the presence of K2CO3 (10 equiv), Rh(ttp)(n-octyl)3 was isolated in a higher yield of 21% in 16 h with 2 recovered in 30% yield together with 42% yield of c-octene (Table 3). However, both reactions were low yielding and incomplete. We propose that the small yields of Rh(ttp)(n-octyl)4 and c-octene 5 in 10%, 76%, and 36% yields, respectively, after 21 h (Table 2). In the presence of K2CO3, Rh(ttp)(n-octyl)3 was isolated in a higher yield of 21% in 16 h with 2 recovered in 30% yield together with 42% yield of c-octene (Table 3). However, both reactions were low yielding and incomplete. We propose that the small amounts of 3 is formed from a multistep pathway. The slow β-H elimination of 2 gives Rh(ttp)H 4 and c-octene. The slow homolysis of 2 gives Rh(ttp) and the n-octyl radical which undergoes disproportionation to give c-octane and 4. Rh(ttp)H and c-octane can then further react with Rh(ttp)H to Rh(ttp)(n-octyl)3 (see discussion below). Therefore, CHA product 2 is unlikely a major intermediate leading to CCA product 3 and is more reasonably a parallel reaction product.

**Mechanistic Investigation: CHA as An Intermediate for CCA?** In some CCA products of hydrocarbons with transition metal complexes, the CCA can be a parallel14- and/or consecutive reaction channel with CHA. We thus investigated whether the CHA product is an intermediate for CCA. Rh(ttp)(c-octyl)2 was heated in benzene-d6 in both neutral and basic conditions separately. Without K2CO3, Rh(ttp)(c-octyl)2 gave Rh(ttp)(n-octyl)3, Rh(ttp)H 4, and c-octene 5 in 10%, 76%, and 36% yields, respectively, after 21 h (Table 2). In the presence of K2CO3 in benzene-d6, the reaction was monitored by 1H NMR spectroscopy in a sealed NMR tube using CCA product Rh(ttp)(n-octyl)3 as an internal standard. The observed red gummy residue showing 1H NMR upfield signals at δ = −5 to 1 ppm were assigned to Rh(ttp)(n-octyl)3, which indicate the occurrence of Rh(ttp)-incorporated c-octene oligomers (about 15% NMR yield), which indicate the occurrence of CHA (Table 3). We did not pursue the examination of the detailed structures of these oligomers. The formation of c-octene, which forms from the β-H elimination of Rh(ttp)(c-octyl)2, indicates the occurrence of CHA of c-octene. The formation of c-octene, which forms from the β-H elimination of Rh(ttp)(c-octyl)2, indicates the occurrence of CHA of c-octene.

**Reaction Profile with Rh(ttp)Cl.** To gain further mechanistic understanding in order to enhance the CCA reaction of Rh(ttp)Cl 1 with c-octane, the reaction was monitored by 1H NMR spectroscopy in a sealed NMR tube using CCA product Rh(ttp)(n-octyl)3 as an internal standard. The observed red gummy residue showing 1H NMR upfield signals at δ = −5 to 1 ppm were assigned to Rh(ttp)(n-octyl)3, which indicate the occurrence of CHA (Table 3). We did not pursue the examination of the detailed structures of these oligomers. The formation of c-octene, which forms from the β-H elimination of Rh(ttp)(c-octyl)2, indicates the occurrence of CHA of c-octene.

**Rh(ttp)H as Intermediate in CCA?** To investigate whether Rh(ttp)H is the intermediate for CCA, Rh(ttp)H 4 was reacted with c-octane. Rh(ttp)H indeed reacted with c-octane at 120 °C.

---

**Table 1. Reaction of c-Octane with Rh(ttp)Cl**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additive</th>
<th>Time (h)</th>
<th>Rh(ttp)Cl + c-Octane</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>KOH</td>
<td>2 d</td>
<td>100</td>
<td>85</td>
</tr>
<tr>
<td>2</td>
<td>K2CO3</td>
<td>7.5 h</td>
<td>0</td>
<td>62</td>
</tr>
<tr>
<td>3</td>
<td>K2CO3</td>
<td>7.5 h</td>
<td>0</td>
<td>33</td>
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</tbody>
</table>

---

**Table 2. Reaction Progress of the Thermal Reaction of Rh(ttp)(c-octyl) 2**

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Benzene-d6</th>
<th>Rh(ttp)(c-octyl)</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

---

**Table 3. Reaction Progress of Rh(ttp)(n-octyl) 2 with K2CO3**

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Benzene-d6</th>
<th>Rh(ttp)(n-octyl)</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>97</td>
</tr>
<tr>
<td>1.5</td>
<td>0</td>
<td>0</td>
<td>98</td>
</tr>
<tr>
<td>2.5</td>
<td>0</td>
<td>0</td>
<td>97</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>0</td>
<td>93</td>
</tr>
<tr>
<td>16</td>
<td>0</td>
<td>0</td>
<td>91</td>
</tr>
</tbody>
</table>

---

**Table 4. Reaction Progress of Rh(ttp)Cl with c-Octane with K2CO3**

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Benzene-d6</th>
<th>Rh(ttp)ClH + c-Octane</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>97</td>
</tr>
<tr>
<td>1.5</td>
<td>0</td>
<td>0</td>
<td>98</td>
</tr>
<tr>
<td>2.5</td>
<td>0</td>
<td>0</td>
<td>97</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>0</td>
<td>93</td>
</tr>
<tr>
<td>16</td>
<td>0</td>
<td>0</td>
<td>91</td>
</tr>
</tbody>
</table>

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### References

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### Article

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**Rh(ttp)H as Intermediate in CCA?** To investigate whether Rh(ttp)H is the intermediate for CCA, Rh(ttp)H 4 was reacted with c-octane. Rh(ttp)H indeed reacted with c-octane at 120 °C.
in 15 h to give Rh(ttp)(n-octyl) 3 selectively, though in only 21% yield, and was also recovered in 73% yield (eq 2).

\[
\text{Rh(ttp)H + c-octane \rightarrow 120^\circ C \quad \text{Rh(ttp)(n-octyl) \ (2) \ 73\% \ recovered}}
\]

Prolonged heating of Rh(ttp)H in c-octane over 12 d yielded Rh(ttp)(n-octyl) and Rh2(ttp)2 in 94% and 2% yields, respectively (eq 3). As Rh(ttp)H underwent slow dehydrogenative dimerization to give 6% yield of Rh2(ttp)2 at 120 °C in 1 day (eq 4), similar to the report by Wayland and co-workers,18 the small amount of Rh2(ttp)2 formed may facilitate the 1,2-addition of Rh(ttp)H into c-octane (see the discussion below).

\[
\text{Rh(ttp)H + c-octane \rightarrow 120^\circ C \quad \text{Rh(ttp)(n-octyl) + Rh2(ttp)2 \ (3) \ 94\% \ 6\%}}
\]

It is intuitively tempting to suggest that Rh(ttp)H undergoes a 1,2-insertion into the CC bond of c-octane by σ-bond metathesis (Scheme 2).19 However, the requirement of a 12 d reaction time rules out the fact that Rh(ttp)H is a direct intermediate involved in the CC bond activation reaction. The fairly crowded 4-centered transition state in the same size of Rh porphyrin is geometrically not very attractive. Indeed, the reaction mixture of 1 equiv of PPh3, Rh(ttp)H, and c-octane upon heating at 120 °C for 1.5 d gave quantitative Rh(ttp)H(PPh3) but no Rh(ttp) n-octyl 3 (eq 5). Rh(ttp)H(PPh3) did not undergo any dimerization, and therefore no Ph3P was ligated to Rh2(ttp)2. No CCA of c-octane with Rh(ttp)H alone occurs at a fast enough rate.

\[
\text{Scheme 2. 4-Centered Transition State via σ-Bond Metathesis Can Be Excluded}
\]

\[
\begin{align*}
\text{H} & \quad \text{Rh} \\
\text{= ttp} & \quad \text{[\text{H}] } \\
\text{Rh(ttp)H + PPh3 + c-octane \rightarrow 120^\circ C \quad \text{Rh(ttp)(PPh3)) \ (5) \ quantitative}}
\end{align*}
\]

Rh2(ttp)2 as an Intermediate in CCA? We next examined whether Rh2(ttp)2 6 is a possible intermediate. Rh2(ttp)2 6 reacted with c-octane at 120 °C for 15 h to give Rh(ttp)(c-octyl) 2, Rh(ttp)(n-octyl) 3, and Rh(ttp)H 4 in 41%, 34%, and 46% yields, respectively (eq 6) with a very low yield of CCA

\[
\text{Rh2(ttp)2 + c-octane \rightarrow 120^\circ C \quad \text{Rh(ttp)(c-octyl) + Rh2(ttp)(n-octyl) + Rh(ttp)H \ (6) \ 41\% \ 34\% \ 46\%}}
\]

product 3 and is therefore not a major intermediate. Therefore, both Rh(ttp)H 4 and Rh2(ttp)2 6 separately gave low yielding reactions and are likely only minor reaction intermediates by themselves. We therefore investigated the synergistic effect of both Rh(ttp)H 4 and Rh2(ttp)2 6 to give Rh(ttp)(n-octyl) 3.

Proposed Mechanism of RhII(ttp)-Catalyzed 1,2-Insertion of Rh(ttp)H into the Carbon—Carbon Bond of c-Octane. We anticipated that the metalloradical RhII(ttp) 7/ RhII(ttp), may act as a catalyst to facilitate the 1,2-addition of c-octane with Rh(ttp). Indeed, Halpern reported in the elegant mechanistic studies that RhII(oep) catalyzes (oep = octylethylporphyrin dianion) the 1,2-addition of styrene to give Rh(oep)CH2CPh20 RhII(oep), which forms from homolysis of the weak Rh–Rh bond in RhII(oep)18 inserts into the C=C bond of styrene to give a Rh(oep)CH2CPh benzyl carbon-centered radical, which is also a reversible reaction. The Rh(oep)CH2CPh radical then abstracts a hydrogen atom from Rh(oep)H to yield the 1,2-addition product Rh(oep)-CH2CPh and regenerates RhII(oep). Thus, it is a RhII(ttp)-catalyzed 1,2-insertion of Rh(ttp)H into the carbon–carbon bond of styrene.

We thus recognized the similarity and anticipated that the CCA of c-octane, being a 1,2-addition reaction, can also be catalyzed by RhII(ttp) 7 (Scheme 3). RhII(ttp) 5 formed from the thermolysis of Rh(ttp)H (eq 7, Scheme 3), initially undergoes homolysis to give RhII(ttp) (eq 8 in ref 18) and RhII(oep) catalyzes (oep = octylethylporphyrin dianion) the 1,2-addition of styrene to give RhII(oep)-CH2CPh and regenerates RhII(oep). Thus, it is a RhII(ttp)-catalyzed 1,2-insertion of Rh(ttp)H into the carbon–carbon bond of styrene.

\[
\text{Scheme 3. Proposed Rh(ttp)-Catalyzed 1,2-Insertion of Rh(ttp)H into the Carbon—Carbon Bond of c-Octane}
\]

\[
\begin{align*}
2\text{[Rh]} & \rightarrow \text{Rh2 + H2} \ (7) \\
2\text{[Rh]} & \rightarrow \text{[Rh] (8)} \\
\text{[Rh]} + \text{c-Octyl} & \rightarrow \text{[Rh] (9)} \\
\text{[Rh] + c-Octyl} & \rightarrow \text{[Rh] (10)}
\end{align*}
\]
Table 5. RhII(ttp)-Catalyzed CCA of c-Octane with Rh(ttp)H

<table>
<thead>
<tr>
<th>Entry</th>
<th>Rh(ttp)H/Rh2(ttp)2 ratio (eq.)</th>
<th>Yield (%)</th>
<th>c-Octane yield (%)</th>
<th>Total yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0:1</td>
<td>00</td>
<td>21</td>
<td>21</td>
</tr>
<tr>
<td>2</td>
<td>0:2:1</td>
<td>60</td>
<td>18</td>
<td>78</td>
</tr>
<tr>
<td>3</td>
<td>0:5:1</td>
<td>53</td>
<td>26</td>
<td>79</td>
</tr>
<tr>
<td>4</td>
<td>10:1</td>
<td>73</td>
<td>73</td>
<td></td>
</tr>
</tbody>
</table>

“*The results are the average of at least duplicate measurements. rh(ttp)H recovered.

by an increase of the Rh(ttp)H/Rh2(ttp)2 ratio. The CCA of c-
orbit with the mixture of Rh(ttp)H/Rh2(ttp)2 in 2:1 ratio
gave Rh(ttp)(c-octyl) 2 and Rh(ttp)(n-octyl) 3 in 60% and
18% yields, respectively (Table 5, entry 2). When the
Rh(ttp)H/Rh2(ttp)2 ratio increased to 5:1, the yield of
Rh(ttp)(n-octyl) 3 increased to 26% yield but that of
Rh(ttp)(c-octyl) 2 decreased to 53% yield (entry 3). We
were glad to observe that Rh(ttp)(n-octyl) 3 was selectively
obtained in 73% yield from the reaction with the 10:1 ratio
of Rh(ttp)H/Rh2(ttp)2 (entry 4). The elimination of the
RH channel (eq 9, Scheme 3) by a low concentration of Rh2(ttp)6
and efficient trapping of 8 by a higher concentration of Rh(ttp)H
were achieved. The selective aliphatic CCA of c-octane was
thus realized successfully, and the results confirm the proposed
RhII(ttp)-catalyzed 1,2-addition of Rh(ttp)H over the C–C
bond of c-octane.

Influence of Porphyrin Sterics on CCA. To find out the
sensitivity of CCA toward porphyrin structure, we further
examined the reaction of c-octane with the analogous but
sterically more hindered Rh(tmp) complexes (tmp = 5,10,15,20-tetramesitylporphyrinato dianion).5 Rh(tmp)Cl 10
reacted with c-octane (20 equiv) and K2CO3 in benzene-d6
120 °C in 3d to give Rh(tmp)H, Rh(tmp), and c-octene in
51%, 46%, and 28%, respectively without any CCA product
(eq 11). When the mixture of Rh(tmp)H 11 and RhII(tmp) 12
(10:1) was reacted at 120 °C for 15 h, no reaction
occurred, and 90% yield of Rh(tmp)H 11 was recovered
(eq 12). RhII(tmp) 12 alone only underwent CHA with c-octane
to give Rh(tmp)H 11 and c-octene in 86% and 40% yields,
respectively (eq 13).

The formation of c-octene likely results from the
bimetalloradical CHA to give Rh(tmp)(c-octyl) 13, which
then rapidly undergoes facile β-hydride elimination to give
c-octene and Rh(tmp)H 7. The nearly 1:2 ratio of Rh(tmp)H to
c-octene further supports the occurrence of this process. The β-
hydride elimination of 13 is sterically enhanced by the
unfavorable steric interactions of the methyl groups at the 2,6
positions of mesityl groups in Rh(tmp) with the c-octyl group
resulting in a slight weakening of the Rh-c-octyl bond (Scheme
4).23 Indeed, the attempted synthesis of Rh(tmp)(c-octyl) 13
by the reductive alklylation (NaBH4/c-octyl bromide) at a lower
temperature of 50 °C gave Rh(tmp)H 9 and c-octene in 89 and
77% yields, respectively, showing the highly labile nature of
Rh(tmp)-c-octyl 13 compared to Rh(tmp)-c-octyl 2 (eq 1).

DFT Theoretical Calculations of the Proposed CCA
Step. To gain further understanding of the metalloradical CCA
step, DFT calculations were performed. Initial comparative
screening of different reaction pathways was performed at the
DFT-D3, b3-lyp, def2-TZVP levels using small atom Rh(por)
models of the actual Rh(tpp) species containing nonfunction-
alyzed porphyrin rings without meso-phenyl substituents.

All attempts to find a transition state corresponding to the σ-
bond metathesis 4-centered transition state described in
Scheme 2 were unsuccessful and led to the transition states
TSA or TSb corresponding to pathways A and B in Scheme 5.
These pathways correspond to hypothetical reactions in which
por(Rh)-c-octyl is formed directly from (por)Rh−H and the
c-octane reagent. In closed-shell singlet pathway A, simultaneous
hetolytic activation of the C–C bond of c-octane is accompanied
by proton transfer from the Rh-hydride moiety of (por)Rh–H to
the resulting negatively charged carbon atom formed from c-
octane in TSA. The transition state leads to subsequent proton
transfer from the beta-position of the “caticonic” carbon to
rhodium, producing 1-octene with regeneration of (por)Rh–H.
Subsequent insertion of 1-octene into the Rh–H bond of
(por)Rh–H could produce (por)Rh-ocyl, but the transition state
of this hypothetical step was not investigated in view of the
very high barrier of the preceding transition state TSA.
While interesting from a fundamental perspective, the high
transition state barrier of TSA makes pathway A rather
unrealistic. The same holds for pathway B, which proceeds at
the open-shell singlet (singlet biradical) surface employing the
broken-symmetry approach. This pathway involves C–C bond
homolysis of c-octane associated with simultaneous hydrogen-
atom transfer from (por)Rh−H to the (developing) −C,H5 ·
diradical, thus producing (por)RhII and the 1-octyl radical ·C8H17.
Subsequent formation of (por)Rh-ocyl is virtually barrierless and only requires a proper orientation of the
RhII(por) and 1-octyl radical ·C8H17 reagents to allow Rh–C
bond formation. Again, pathway B is fundamentally interesting but has a very high transition state barrier TSb, making this
pathway rather unrealistic in view of the experimental
observations.

In marked contrast to pathways A and B, the transition state
barrier TSb of pathway C involving a RhII(por) metalloradical
catalyzed reaction between (por)Rh–H and c-octane is much
lower, and hence, pathway C is a much more realistic scenario,
in good agreement with the experimental data (Scheme 5).
This pathway involves homolytic activation of the C–C bond
of c-octane by the RhII(por) metalloradical producing a
terminal octyl-radical species (por)Rh−C₈H₁₆⁺, which subsequently abstracts a hydrogen atom from (por)Rh−H to regenerate the (por)Rh⁺ metalloradical “catalyst” with the formation of the (por)Rh-octyl product.

Pathway C was further explored in more detail using the full atom Rh(tpp) models. We argued that the full atom models might lead to lower barriers in view of stronger (VdW) dispersion interactions between c-octane and the Rh(tpp) species. As such, we examined the hypothesized CCA reaction between RhII(tpp) and c-octane, followed by reaction of the Rh(tpp)octyl radical complex III with Rh(tpp)(H) to form Rh(tpp)octyl and RhII(tpp) (see Scheme 6). We employed both the BP86 and the b3-lyp functional to examine the details of pathway C. The def2-TZVP basis set and Grimme’s D3-DFT dispersion corrections were used in both cases. For the b3-lyp pathways, additional cosmo dielectric solvent corrections (ε = 2.27 corresponding to benzene) were included. The (free) energies associated with the reaction sequence depicted in Scheme 6 are listed in Table 6.

The DFT calculated pathway (Scheme 6) is in qualitative agreement with the proposed mechanism (Scheme 3). The first steps from I to III are endothermic and endergonic. This agrees with the experimental requirement to heat to drive the reaction. The subsequent reaction between the Rh(tpp)octyl radical complex III with Rh(tpp)(H) to form Rh(tpp)octyl and RhII(tpp) is exothermic and exergonic, and provides the driving force of the overall reaction. We were unable to find a transition state for this last step, likely because the barrier is too low with a flat reaction profile. The transition state of the first reaction step (from II via TS to III) involves a metallo-radical induced SH₂-type homolysis of one of the C−C bonds of c-octane. In this CCA pathway, the RhII metallo-radical traps one of the two carbon radicals produced in this process in concert with C−C bond homolysis (Figure 1).

Despite stronger attractive dispersion (VdW) forces between Rh(tpp) and c-octane, the TSₜ transition barrier is still sizable at the b3-lyp level (Table 1). However, it should be recalled at this point that the experimental reaction requires prolonged (15 h) heating to 120 °C to reach completion, and hence the
Scheme 6. DFT Calculated Metallo-Radical Catalyzed Reaction between c-Octane and (por)Rh-H (Pathway C) Including Selected Bond Lengths

```
DFT-D3, BP86, def2-TZVP, and DFT-D3, b3-lyp, def2-TZVP, and cosmo $\epsilon = 2.27$.
```

Table 6. DFT Calculated Energies Associated with the Computed Reaction Pathway Depicted in Scheme 6

<table>
<thead>
<tr>
<th></th>
<th>$\Delta E_{\text{BP86}}$ (kcal mol$^{-1}$)</th>
<th>$\Delta G_{\text{BP86}}^{c}$ (kcal mol$^{-1}$)</th>
<th>$\Delta H_{\text{BP86}}$ (kcal mol$^{-1}$)</th>
<th>$\Delta S_{\text{BP86}}$ (cal mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
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<td>0</td>
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</tr>
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<td>28.5</td>
<td>20.1</td>
<td>28.0</td>
</tr>
<tr>
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<td>+42.0</td>
<td>+34.9</td>
<td>-24.4</td>
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</tbody>
</table>

```
DFT-D3, BP86, def2-TZVP, and DFT-D3; b3-lyp, def2-TZVP, and cosmo $\epsilon = 2.27$.
```

Figure 1. Structure of transition state TS representing RhII-mediated S$_{2}$-type CCA of c-octane (b3-lyp, def2-TZVP).

Experimental barrier is also high (estimated at $\sim$30-35 kcal mol$^{-1}$). The barrier (from II to TS$_{c}$) calculated at the BP86, def2-TZVP level ($\Delta G^{z} = 36.8$ kcal mol$^{-1}$; $\Delta H^{z} = 35.8$ kcal mol$^{-1}$) is lower and in reasonable agreement with the experimental estimate. The barrier calculated at the b3-lyp, def2-TZVP seems to be overestimated by several kcal mol$^{-1}$ (which is not uncommon in DFT studies$^{24}$).

Conclusions. We have discovered the RhII(tp)-catalyzed 1,2-insertion of Rh(tp)H into the carbon–carbon bond of c-octane, which selectively produces Rh(tp)n-octyl in high yield. The RhII(tp) metallo-radical attacks the C–C bond of c-octane, likely via an S$_{2}$ process. DFT theoretical calculations support this mechanistic proposal. This represents a unique metallo-radical carbon–carbon activation process. Further studies are being continued to develop catalytic C–C bond functionalization.

Experimental and Computational Details

Reaction of c-Octane with Rh(tp)Cl. Rh(tp)Cl I (20.6 mg, 0.026 mmol) was added in c-octane (3.0 mL). The red reaction mixture was degassed for freeze–thaw–pump cycles, purged with N$_{2}$, and heated at 120 °C under N$_{2}$ for 48 h. Excess c-octane was removed by vacuum distillation. The residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH$_{2}$Cl$_{2}$ (1:1). Red solid, Rh(tp)(c-octyl) 2 (1.0 mg, 0.0011 mmol, 5%), and Rh(tp)(n-octyl) 3 (1.9 mg, 0.0021 mmol, 8%) were collected and further recrystallized from CH$_{2}$Cl$_{2}$/MeOH. The product ratio was calculated by $^1$H NMR integration. Rh(tp)Cl was recovered (14.8 mg) after chromatograph at (BP86 b3-lyp).

1. $\Delta E_{\text{BP86}}$, 2. $\Delta G_{\text{BP86}}^{c}$, 3. $\Delta H_{\text{BP86}}$, 4. $\Delta S_{\text{BP86}}$.

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Reaction of c-Octane with Rh(tp)Cl. Rh(tp)Cl 1 (20.6 mg, 0.026 mmol) was added in c-octane (3.0 mL). The red reaction mixture was degassed for three freeze–thaw–pump cycles, purged with N$_{2}$, and heated at 120 °C under N$_{2}$ for 48 h. Excess c-octane was removed by vacuum distillation. The residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH$_{2}$Cl$_{2}$ (1:1). Red solid, Rh(tp)(c-octyl) 2 (1.0 mg, 0.0011 mmol, 5%), and Rh(tp)(n-octyl) 3 (1.9 mg, 0.0021 mmol, 8%) were collected and further recrystallized from CH$_{2}$Cl$_{2}$/MeOH. The product ratio was calculated by $^1$H NMR integration. Rh(tp)Cl was recovered (14.8 mg) after chromatograph (BP86 b3-lyp).

Δ$E_{\text{BP86}}$, Δ$G_{\text{BP86}}^{c}$, Δ$H_{\text{BP86}}$, Δ$S_{\text{BP86}}$.

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was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH2Cl2 (1:1). Red solids, Rh2(tmp)Cl9 (9.6 mg, 0.012 mmol), was used as a starting material.

**Independent Synthesis of Rh(tmp)Cl (100 mg, 0.11 mmol) in ETOH (50 mL) and a solution of NaNbH4 (17 mg, 0.45 mmol) inaq. NaOH (0.1 M, 2 mL) were purged with N2 for 15 min separately. The solution of NaNbH4 was added slowly to the suspension of Rh2(tmp)Cl via a cannula. The mixture was heated at 50 °C under N2 for 1 h. The solution was then cooled to 30 °C under N2 and c-octyl bromide (23 mg, 1.20 mmol) was added. A reddish orange suspension was formed. After stirring at room temperature for another 15 min under N2, the reaction mixture was worked up by extraction with CH2Cl2/H2O. The combined organic extract was dried (MgSO4), filtered, and rotary evaporated. The redish orange residue was purified by column chromatography over silica gel (250-400 mesh) using a solvent mixture of hexane/CH2Cl2 (1:1) as the eluent. The major orange fraction was collected and gave a reddish orange solid of Rh(tmp)Cl (94.1 mg, 0.11 mmol, 86%) as the product after rotary evaporation.

**Independent Synthesis of Rh(tmp)(n-octyl) Cl (100 mg, 0.11 mmol) in ETOH (50 mL) and a solution of NaNbH4 (17 mg, 0.45 mmol) inaq. NaOH (0.1 M, 2 mL) were purged with N2 for 15 min separately. The solution of NaNbH4 was added slowly to the suspension of Rh(tmp)Cl via a cannula. The mixture was heated at 50 °C under N2 for 1 h. The solution was then cooled to 30 °C under N2 and n-octyl bromide (23 mg, 1.20 mmol) was added. A reddish orange suspension was formed. After stirring at room temperature for another 15 min under N2, the reaction mixture was worked up by extraction with CH2Cl2/H2O. The combined organic extract was dried (MgSO4), filtered, and rotary evaporated. The redish orange residue was purified by column chromatography over silica gel (250-400 mesh) using a solvent mixture of hexane/CH2Cl2 (1:1) as the eluent. The major orange fraction was collected and gave a reddish orange solid of Rh(tmp)(n-octyl)Cl (2, 3.9 mg, 0.0044 mmol) as the product after rotary evaporation.

**Thermal Stability of Rh(tmp)(c-octyl) in Benzene-d6.**

Rh(tmp)(c-octyl) 2 (3.9 mg, 0.0044 mmol) was added into benzene-d6 (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. It was heated at 120 °C in the dark. It was monitored with 1H NMR spectroscopy at particular time intervals, and the NMR yields were taken.

**Stability of Rh(tmp)(c-octyl) with Potassium Carbonate in Benzene-d6.**

Rh(tmp)(c-octyl) 2 (3.9 mg, 0.0044 mmol) and potassium carbonate (6.0 mg, 0.044 mmol) were added into benzene-d6 (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. It was heated at 120 °C in the dark. It was monitored with 1H NMR spectroscopy at particular time intervals, and the NMR yields were taken.

**Reaction of Rh(tmp)Cl and c-Octane with Potassium Carbonate in Benzene-d6.**

Rh(tmp)Cl 3 (3.5 mg, 0.0045 mmol), c-octane (11 μL, 0.087 mmol), and potassium carbonate (5.9 mg, 0.0427 mmol) were added into benzene-d6 (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 at 120 °C in the dark. It was monitored with 1H NMR spectroscopy at particular time intervals, and the NMR yields were taken.

**Reaction of c-Octane with Rh(tmp)H.**

Rh(tmp)H (9.6 mg, 0.012 mmol) was used as a starting material. The red reaction mixture was degassed for three freeze–thaw–pump cycles, purged with N2, and heated at 120 °C under N2 for 15 h. Excess c-octane was removed by vacuum distillation. The residue was added with benzene-d6 (500 μL) under N2 protection for 1H NMR spectroscopy. Rh(tmp)H(PPh3)2 was obtained in quantitative NMR yield. 1H NMR (CDCl3, 400 MHz) δ = 33.42 (b, 1 H), 2.39 (s, 12 H, p-methyl), 4.16 (t, 2 H, J = 9.2 Hz), 6.28 (td, 2 H, J = 4.2, 7.6 Hz, m-pyphenyl), 6.52 (t, 1 H, J = 6.8 Hz), 7.55 (d, 4 H, J = 7.2 Hz, m-pyphenyl), 7.84 (d, 4 H, J = 7.6 Hz, o-pyphenyl), 7.89 (d, 4 H, J = 7.6 Hz, o-pyphenyl), 8.98 (s, 8 H, pyrrole).

**Thermal Dehydrogenative Dimerization of Rh(tmp)H.**

Rh(tmp)H (3.2 mg, 0.0041 mmol) was added into benzene-d6 (500 μL). The red reaction mixture was degassed for three freeze–thaw–pump cycles, and the NMR tube was flame-sealed under vacuum. It was heated at 120 °C in the dark. It was monitored with 1H NMR spectroscopy at particular time intervals, and the NMR yields of Rh2(tmp), 6 were taken. The H3 concentration in solution was too low to be detected.

**Reaction of c-Octane with Rh2(tmp)Cl.** 6. Rh2(tmp)Cl (9.6 mg, 0.012 mmol) was added in c-octane (1.5 mL). The red reaction mixture was degassed for three freeze–thaw–pump cycles, purged with N2, and heated at 120 °C under N2 for 15 h. Excess c-octane was removed by vacuum distillation. The red solution was added with benzene-d6 (500 μL) under N2 protection for 1H NMR spectroscopy, and the yield of Rh2(tmp)(H) (46%) was estimated. The residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH2Cl2 (1:1). Red solids, Rh2(tmp)(c-octyl)Cl 2 (4.5 mg, 0.0051 mmol, 41%) and Rh2(tmp)(n-octyl)Cl 3 (0.4 mg, 0.00045 mmol, 4%), were collected, and the product ratio was calculated by 1H NMR integration.

**Reaction of c-Octane with a 2:1 Mixture of Rh(tmp)H and Rh2(tmp)Cl.**

Rh(tmp)H (9.6 mg, 0.012 mmol) and Rh2(tmp)Cl (4.8 mg, 0.0031 mmol) were added to c-octane (1.5 mL). The red reaction mixture was degassed for three freeze–thaw–pump cycles, purged with N2, and heated at 120 °C under N2 for 15 h. Excess c-octane was removed by vacuum distillation. The red solution was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH2Cl2 (1:1). Red solids, Rh2(tmp)(c-octyl)Cl 2 (9.8 mg, 0.011 mmol, 60%) and Rh(tmp)(n-octyl)Cl 3 (3.0 mg, 0.0034 mmol, 18%), were collected, and the product ratio was calculated by 1H NMR integration.

**Reaction of c-Octane with a 5:1 Mixture of Rh(tmp)H and Rh2(tmp)Cl.**

Rh(tmp)H (9.6 mg, 0.012 mmol) and Rh2(tmp)Cl (1.9 mg, 0.0012 mmol) were added to c-octane (1.5 mL). The red reaction mixture was degassed for three freeze–thaw–pump cycles, purged with N2, and heated at 120 °C under N2 for 15 h. Excess c-octane was removed by vacuum distillation. The red solution was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH2Cl2 (1:1). Red solids, Rh2(tmp)(c-octyl)Cl 2 (6.9 mg, 0.0078 mmol, 53%) and Rh(tmp)(n-octyl)Cl 3 (3.4 mg, 0.0038 mmol, 26%), were collected, and the product ratio was calculated by 1H NMR integration.

**Reaction of c-Octane with a 10:1 Mixture of Rh(tmp)H and Rh2(tmp)Cl.**

Rh(tmp)H (9.6 mg, 0.012 mmol) and Rh2(tmp)Cl (1.0 mg, 0.00065 mmol) were added to c-octane (1.5 mL). The red reaction mixture was degassed for three freeze–thaw–pump cycles, purged with N2, and heated at 120 °C under N2 for 15 h. Excess c-octane was removed by vacuum distillation. The red solution was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH2Cl2 (1:1). Red solid, Rh(tmp)(n-octyl)Cl 3 (8.9 mg, 0.010 mmol, 73%) was collected and was further recrystallized from CH2Cl2/MeOH.

**Reaction of Rh(tmp)Cl 10 and c-Octane with Potassium Carbonate in Benzene-d6.**

Rh(tmp)Cl 3 (4.0 mg, 0.0043 mmol), c-octane (11 μL, 0.087 mmol), and potassium carbonate (5.8 mg, 0.0420 mmol) were added into benzene-d6 (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 at...
120 °C in the dark. It was monitored with 1H NMR spectroscopy at particular time intervals, and the NMR yields were taken. Rh(tmp)H, RhII(tmp), and c-octene were in 51%, 46%, and 28% yields, respectively at 120 °C in 3 d.

**Reaction of c-Octane with a 1:1 Mixture of Rh(tmp)H 11 and RhII(tmp)H 12.** RhII(tmp)H (10.6 mg, 0.012 mmol) and Rh(tmp)H (1.1 mg, 0.0012 mmol) were added to c-octane (1.5 mL). The red reaction mixture was degassed for three freeze–thaw–pump cycles, purged with N2, and heated at 120 °C under N2 for 24 h. Excess c-octane was removed by vacuum distillation. The colorless organic distillate was added with benzene-d6 for 1H NMR spectroscopy, and c-octene was not observed. Degassed benzene-d6 was added to N2 for 1H NMR spectroscopy. A red solution of Rh(tmp)H (90% yield, estimated by 1H NMR spectroscopy) was obtained.

**Reaction of c-Octane with RhII(tmp)** 12. RhII(tmp) (10.6 mg, 0.0012 mmol) was added to c-octane (1.5 mL). The red reaction mixture was degassed for three freeze–thaw–pump cycles, purged with N2, and heated at 120 °C under N2 for 24 h. Excess c-octane was removed by vacuum distillation. The colorless organic distillate was added with benzene-d6 for 1H NMR spectroscopy, and c-octene (40% yield, estimated by 1H NMR) was observed. Degassed benzene-d6 was added to N2 for 1H NMR spectroscopy. A red solution of Rh(tmp)H (86% yield, estimated by 1H NMR spectroscopy) was obtained.

**Attempted Synthesis of Rh(tmp)(c-octyl) 13.** A suspension of Rh(tmp)Cl (20.0 mg, 0.022 mmol) in EtOH (5 mL) and a solution of NaBH4 (3 mg, 0.087 mmol) in aq. NaOH (0.1 M, 0.4 mL) were added with benzene-d6, degassed for 1 h. The solution was then cooled to 30 °C under N2 and benzene-d6 were added. A reddish orange suspension was formed. After stirring at room temperature for another 15 min under N2, the reaction mixture was vacuum-distilled, and the distillate went through 1H NMR spectroscopy after extraction with C6D6/H2O. c-Octene (77% yield, estimated by 1H NMR) was observed. The red reaction mixture was washed with degassed H2O (2 × 10 mL). The residue was dried with vacuum in the reaction tube, which was then protected with N2 and brought to analytical balance. Rh(tmp)H was obtained (17.1 mg, 0.19 mmol, 89%). Degassed benzene-d6 was added to the reddish orange residue for 1H NMR spectroscopy in a sealed NMR tube.

**Computational Details.** Geometry optimizations were carried out with the Turbomole program package26 coupled to the PQS Baker optimizer26 via the BOpt package,27 at the DFT/b3-lyp28a level (the reported structures in Scheme 6 and Table 6, using the full atom TPP models optimized at the b3-lyp level, additional dielectric constant corrections (cosmo35) were taken into account based on single point calculations, using the dielectric constant of benzene (ε = 2.27).

### ASSOCIATED CONTENT

5 Supporting Information

Reaction progress and computational data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00183.

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**Notes**

The authors declare no competing financial interest.

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### REFERENCES


(21) (a) The estimated bond dissociation energy (BDE) of (ttp)Rh-H is ~60 kcal mol⁻¹. See ref 19. (b) The BDE of n-octyl-H is ~100 kcal mol⁻¹; see Luo, Y. R. Handbook of Bond Dissociation Energies in Organic Compounds; CRC Press: Boca Raton, FL, 2003.


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