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DOI
10.1021/acs.organomet.5b00183

Publication date
2015

Document Version
Final published version

Published in
Organometallics

License
Article 25fa Dutch Copyright Act

Citation for published version (APA):
Metalloradical-Catalyzed Selective 1,2-Rh-H Insertion into the Aliphatic Carbon–Carbon Bond of Cyclooctane

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ABSTRACT: The selective aliphatic carbon–carbon activation of cyclo-octane (c-octane) was achieved via the Rh(II)(tp)-catalyzed 1,2-addition of Rh(tp)H to give Rh(tp)(n-octyl)H (tp = tetratolylporphyrinato 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(tp) porphyrin complex but not with the bulky Rh(tmp) system (tmp = tetrakis(mesityl)porphyrinato 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 steric 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 dihydroxy-catalyzed dehydrogenation to c-octene,5a the FeCl3-catalyzed aerobic oxidation to c-octanol and c-octanone5b 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.6a Oxidative CCA of c-octane catalyzed by N-hydroxysyphthalides/Co(II)/Mn(II) at 100 °C in 14 h gives α,ω-dicarboxylic acids in 2% yield only along with the major products being c-octanol and c-octanone.6b

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-heptanyl 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 CHA6a,9 and CCA.10,11 The bimetalloradical CHA of methane and toluene, based on the second order dependence of the Rh(II)(tmp) (tmp = tetrakis(mesityl)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 Rh(II)(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(tp)H, catalyzed by the Rh(II)(tp) (tp = tetratolylporphyrinato dianion) metalloradical to give Rh(tp)(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(tp)Cl to give Rh(tp)(c-octyl)2 and Rh(tp)(n-octyl)3 in 5% and 8% yields, respectively (Table 1, entry 1). A 72% yield of Rh(tp)Cl was recovered, and a trace amount of Rh(tp)H was observed. Both CHA and CCA products formed but the reaction was inefficient. Upon addition of KOH (10 equiv) to the reaction mixture, Rh(tp)(c-octyl), Rh(tp)(n-octyl), and Rh(tp)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(tp)Cl was consumed in 7.5 h, and Rh(tp)(n-octyl)3 and...
Rh(ttp)H 

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

<table>
<thead>
<tr>
<th>entry</th>
<th>additive</th>
<th>time (h)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>total</th>
<th>yield (%)</th>
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<td>33</td>
<td>58</td>
<td>91</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

“10 equiv. aRecovery.

Mechanistic Investigation: CHA as An Intermediate for CCA? In some CCAs of hydrocarbons with transition metal complexes, the CCA can be a parallel14a and/or consecutive reaction channel14 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)H4, and c-octene5 in 10%, 76%, and 36% 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 amount of 3 is formed from a multistep pathway. The slow β-H elimination of 2 gives Rh(ttp)H4 and octene. The slow homolysis of 2 gives Rh(ttp) and the c-octyl radical which undergoes disproportionation to give c-octane and c-octene. 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.

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 with excess c-octane and K2CO3 in benzene-d6 (Table 4).

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

<table>
<thead>
<tr>
<th>time (h)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>total</th>
<th>yield (%)</th>
</tr>
</thead>
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<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<td>0</td>
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<td>0</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

0.5 2 | 100| 0 | 0 | 0 | 100   | 100       |
| 1.5 | 80| 100| 18| 20| 98    | 100       |
| 2.5 | 73| 100| 24| 25| 97    | 98        |
| 10  | 36| 16| 41| 40| 93    | 92        |
| 16  | 30| 21| 40| 42| 91    | 93        |

Initially, Rh(ttp)Cl was first converted to Rh2(ttp)2. 6 in the presence of K2CO3. At 4.5 h, 82% yield of Rh(ttp)Cl remained, while Rh2(ttp)2 6 was formed in 13% yield. After 17 h, Rh(ttp)Cl was completely consumed. Rh2(ttp)2, 6, Rh(ttp)H4, and c-octene5 were formed in 62%, 21%, and 18% yields, respectively. After 62 h, Rh2(ttp)2 completely reacted. The yields of Rh(ttp)H4 and c-octene increased to 54% and 50%, respectively, and only 29% yield of CCA product Rh(ttp)(n-octyl)3 was obtained. Finally, Rh(ttp)(n-octyl)3 was generated in prolonged heating of 62 h, and still, Rh(ttp)H was consumed slowly and mostly remained unreacted even after 10 days. Therefore, both Rh2(ttp)2 and Rh(ttp)H are possible intermediates. The observed red gummy residue showing 1H NMR upfield signals at δ = −5 to 1 ppm were assigned to Rh(ttp)-incorporated c-octene oligomers (about 15% NMR yield), which indicate the occurrence of Rh(ttp)-initiated oligomerization of c-octene.16,17 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-octane. When c-octene accumulates, it serves as a trap for Rh(ttp)H6 and therefore stops the CCA.

Rh(ttp)H as Intermediate in CCA? To investigate whether Rh(ttp)H is the intermediate for CCA, Rh(ttp)H4 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).

\[
\text{Rh(ttp)H + c-octane} \rightarrow \text{Rh(ttp)(n-octyl)} \quad (2)
\]

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 dehydrogen-
ative 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).

\[
\text{Rh(ttp)H + c-octane} \rightarrow \text{Rh(ttp)(n-octyl)} + \text{Rh2(ttp)2} \quad (3)
\]

It is intuitively tempting to suggest that Rh(ttp)H undergoes
a 1,2-insertion into the CC bond of c-octane by \( \sigma \)-bond
metathesis (Scheme 2). 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)(PPh3)n but no Rh(ttp) n-octyl 3 (eq 5). Rh(ttp)H-
PPh3) did not undergo any dimerization, and therefore no
PPh3 was ligated to Rh2(ttp)2. No CCA of c-octane with
Rh(ttp)H alone occurs at a fast enough rate.

\[
\text{Rh(ttp)H + PPh3 + c-octane} \rightarrow \text{Rh(ttp)(PPh3)₄} \quad (5)
\]

**Scheme 2.** 4-Centered Transition State via \( \sigma \)-Bond
Metathesis Can Be Excluded

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-
ocyl) 2, Rh(ttp)(n-octyl) 3, and Rh(ttp)H 4 in 41%, 4%,
and 46% yields, respectively (eq 6) with a very low yield of CCA

\[
\text{Rh2(ttp)2 + c-octane} \rightarrow \text{Rh(ttp)(c-octyl)} + \text{Rh(ttp)(n-octyl)} + \text{Rh(ttp)H} \quad (6)
\]

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-In-
sertion of Rh(ttp)H into the Carbon—Carbon Bond of c-
Octane. We anticipated that the metalloradical RhII(ttp) 7/
Rh(ttp)2 6 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 = octyle-
thylporphyrin dianion) the 1,2- addition of styrene to give
Rh(oep)CH2CH2Ph20 RhII(oep), which forms from homolysis
of the weak Rh–Rh bond in RhII(oep)2.14 inserts into the C=C
bond of styrene to give a Rh(oep)CH2C-HPh benzyl
centered radical, which is also a reversible reaction. The
Rh(oep)CH2CH2Ph radical then abstracts a hydrogen atom
from RhII(oep)H to yield the 1,2-addition product RhII(oep)-
CH2CH2Ph 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). Rh2(ttp)2 5 formed from

\[
\begin{cases}
\text{[RhII(oep)]} & \text{[RhII(oep)]} \\
\text{[RhII(oep)]} & \text{[RhII(oep)]}
\end{cases}
\]

the thermolysis of Rh(ttp)H (eq 7, Scheme 3), initially
undergoes homolysis to give RhIII(ttp) 8 (eq 8 in ref.19) RhII(ttp)
7 then reacts with c-octane in parallel CCA (eq 9, Scheme 3)
and CCA (eq 10, Scheme 3). For the CCA pathway, RhII(ttp)
can cleave the C=C bond of c-octane to generate the alkyl
radical 8 by a bimolecular homolytic substitution (S₅1₂-like
process22 (eq 10, Scheme 3) which can also reverse rapidly.20
Compound 8 can then abstract a hydrogen atom from the weak
(ttp)Rh·H bond (∼60 kcal mol⁻¹),21 serving as an alkyl radical
trap to form a strong alkyl C–H bond21b to provide the driving
force of the reaction (eq 10, Scheme 3).

The branching of CHA and CCA is reasoned to be strongly
dependent on the concentration of Rh2(ttp)2. RhII(por) has
been shown to undergo CHA with alkane to give Rh(por)R
and Rh(por)H with a termolecular rate law (eq 9, Scheme 3).8
The proposed CCA should, however, follow first order kinetics
in RhII(ttp) or half order kinetics in Rh2(ttp)2, thus requiring
much lower RhII(ttp) concentrations. At the same time, a large
excess concentration of Rh(ttp)H facilitates trapping of the
carbon-centered radical 8 to give 3 and to regenerate RhII(ttp)
7. In this mechanism, Rh2(ttp)2 is the precatalyst or more
precisely RhII(ttp) is the catalyst, but the reaction requires the
presence of Rh(ttp)H in excess. To validate this mechanism,
and to develop a selective CCA process, we conducted a series
of experiments for the reaction with c-octane by increasing the
concentration ratio of Rh(ttp)H/Rh2(ttp)2 for more efficient
trapping.

**Synergetic Effect of Rh(ttp)H/Rh2(ttp)2 in CCA of c-
Octane.** Indeed, mixtures of Rh(ttp)H and Rh2(ttp)2 were
much more efficient reagents, and the use of the combination
of both enhanced the total yields to up to 79% (Table 5, entries
2–4 vs 1). The selectivity toward CCA was further enhanced
by an increase of the Rh(ttp)H/Rh2(ttp)2 ratio. The CCA of c-octane 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 CHA channel (eq 9, Scheme 3) by a low concentration of Rh2(ttp)2 6 and efficient trapping of 8 by a higher concentration of Rh(ttp)H 2 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 steric 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 = 2,6-tetramethylporphyrinato dianion). Rh(tmp)Cl 10 reacted with c-octane (20 equiv) and K2CO3 in benzene-d6 at 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 with c-octane 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 alkylation (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(tmp) species containing nonfunctionalyzed 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-octyl is formed directly from (por)Rh–H and the c-octane reagent. In closed-shell singlet pathway A, simultaneous heterolysis 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 “cationic” 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-octyl, 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) C8H17 diradical, thus producing (por)RhII and the 1-octyl radical · C8H17. Subsequent formation of (por)Rh-octyl 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 TSC 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 \((\text{por})\text{Rh} - \text{C}_8\text{H}_{18}^*\), which subsequently abstracts a hydrogen atom from \((\text{por})\text{Rh} - \text{H}\) to regenerate the \((\text{por})\text{Rh}^{II}\) metalloradical “catalyst” with the formation of the \((\text{por})\text{Rh-octyl}\) product.

Pathway C was further explored in more detail using the full atom \(\text{Rh(tpp)}\) 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 \(\text{Rh(tpp)}\) species. As such, we examined the hypothesized CCA reaction between \(\text{Rh}^{II}(\text{tpp})\) and \(c\)-octane, followed by reaction of the \(\text{Rh(tpp)}\)octyl radical complex \(III\) with \(\text{Rh(tpp)}(\text{H})\) to form \(\text{Rh(tpp)}\)octyl and \(\text{Rh}^{II}(\text{tpp})\) (see Scheme 6). We employed both the BP86 and the \(b3\)-lyp functional to examine the details of pathway C. The \(\text{def}2\)-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 \((\epsilon = 2.27\) 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 \(\text{Rh(tpp)}\)octyl radical complex \(III\) with \(\text{Rh(tpp)}(\text{H})\) to form \(\text{Rh(tpp)}\)octyl and \(\text{Rh}^{II}(\text{tpp})\) 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 \(\text{C} - \text{C}\) bonds of \(\text{octane}\). In this CCA pathway, the \(\text{Rh}^{II}\) metallo-radical traps one of the two carbon radicals produced in this process in concert with \(\text{C} - \text{C}\) bond homolysis (Figure 1).

Despite stronger attractive dispersion (VdW) forces between \(\text{Rh(tpp)}\) and \(c\)-octane, the \(\text{TSc}\) 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

```
   + 1.538 A 1.535 A
   |   VNM adduct |
   |     (separated reagents) |
   | 1.532 A 1.528 A |
   |   |   |
   | II 1.279 A 2.308 A |
   |   |   |
   | TS 2.054 A 2.055 A |
   |   |   |
   | III 2.054 A 2.053 A |
   |   |   |
   | IV 2.054 A 2.055 A |
```

"DFT-D3, BP86, def2-TZVP, and DFT-D3, b3-lyp, def2-TZVP, and cosmo ε = 2.27.

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

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<th>∆E_{ZP} (kcal mol⁻¹)</th>
<th>∆G_{ZP} (kcal mol⁻¹)</th>
<th>∆H_{ZP} (kcal mol⁻¹)</th>
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"DFT-D3, BP86, def2-TZVP, and DFT-D3; b3-lyp, def2-TZVP, and cosmo ε = 2.27.

conclusion. We have discovered the Rh⁴⁺(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 Rh⁴⁺(tp) metallo-radical attacks the C–C bond of c-octane, likely via an S₈₂ process. DFT theoretical calculations support this mechanistic proposal. This represents a unique metalloradical 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 (2.06 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 N₂, and heated at 120 °C under N₂ 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/CH₂Cl₂ (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 CH₂Cl₂/MEOH. The product ratio was calculated by ¹H NMR integration. Rh(tp)Cl was recovered (14.8 mg) after column chromatography. Characterization of Rh(tp)(c-octyl): 2: Rf = 0.84 (hexane/CH₂Cl₂ = 1:1). ¹H NMR (CDCl₃, 400 MHz): δ = 4.25 (m, 2), -3.66 (m, 3 H), -0.32 (m, 2 H), 0.90 (m, 4 H), 2.41 (s, 12 H, p-methyl), 7.30 (d, 4 H, J = 7.3 Hz, m-phenyl), 7.33 (d, 4 H, J = 7.2 Hz, m'-phenyl), 8.18 (d, 4 H, J = 7.7 Hz, o'-phenyl), 8.97 (s, 8 H, pyrrole). ¹³C NMR (CDCl₃, 75 MHz) δ 21.70, 22.54, 25.23, 25.85, 30.40, 40.62 (d, J₇₋₈₋₋ = 6.4 Hz), 122.86, 127.42, 127.54, 131.48, 133.62, 134.25, 137.22, 139.52, 143.52. HRMS calcd. for (C₂₀H₈₄N₄RhH): m/z 883.3242. Found: m/z 883.3214.

**Reaction of c-Octane with Rh(tp)Cl with Potassium Hydroxide**: Rh(tp)Cl (20.4 mg, 0.025 mmol) and potassium hydroxide (14.2 mg, 0.254 mmol) was added in c-octane (3.0 mL). The red reaction mixture was degassed for three freeze–thaw–pump cycles, purged with N₂, and heated at 120 °C under N₂ for 7.5 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/CH₂Cl₂ (1:1). ¹H NMR spectrum, and the NMR yield of Rh(tp)H (62%) was estimated. The crude residue was removed by vacuum distillation. The organic layer was collected, dried, and evaporated to dryness, and the residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH₂Cl₂ (1:1). Red solid, Rh(tp)(c-octyl) 2 (1.3 mg, 0.0015 mmol, 6%), and Rh(tp)(n-octyl) 3 (5.6 mg, 0.0063 mmol, 25%) were collected.

**Reaction of c-Octane and Rh(tp)Cl with Potassium Carbonate**: Rh(tp)Cl (20.4 mg, 0.025 mmol) and anhydrous potassium carbonate (34.9 mg, 0.252 mmol) were added in c-octane (3.0 mL). The red reaction mixture was degassed for three freeze–thaw–pump cycles, purged with N₂, and heated at 120 °C under N₂ for 7.5 h. Excess c-octane was removed by vacuum distillation. The red residue was added with benzen-d₆ (500 µL) under N₂ for 1H NMR spectroscopy, and the NMR yield of Rh(tp)H (62%) was estimated. The crude mixture was then extracted with CH₂Cl₂/H₂O. The organic layer was collected, dried, and evaporated to dryness, and the residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH₂Cl₂ (1:1). Red solid, Rh(tp)(c-octyl) 2 (1.3 mg, 0.0015 mmol, 6%), and Rh(tp)(n-octyl) 3 (5.6 mg, 0.0063 mmol, 25%) were collected.

**Figure 1. Structure of transition state TS representing Rh⁴⁺-mediated S₈₂-type CCA of c-octane (b3-lyp, def2-TZVP).**
was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH₂Cl₂ (1:1). Red solids, Rh(ttp)(n-octyl) (7.5 mg, 0.0085 mmol, 33%), were collected.

**Independent Synthesis of Rh(ttp)(c-octyl) 2** A suspension of Rh(ttp)Cl (100 mg, 0.11 mmol) in EtOH (50 mL) and a solution of NaBH₄ (17 mg, 0.45 mmol) inaq. NaOH (0.1 M, 2 mL) were purged with N₂ for 15 min separately. The solution of NaBH₄ was added slowly to the suspension of Rh(ttp)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 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 to be detected.

**Thermal Stability of Rh(ttp)(c-octyl) in Benzene-d₆**. Rh(ttp)(c-octyl) (2.3 mg, 0.0026 mmol) was collected and was further recrystallized from CH₂Cl₂/MeOH.

**Reaction of c-Octane with Rh(ttp)H and PPh₃, Rh(ttp)H (9.6 mg, 0.012 mmol) and PPh₃ (3.2 mg, 0.012 mmol) were 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 residue was added with benzene-d₆ (500 μL) under N₂ protection for ¹H NMR spectroscopy. Rh(ttp)(H/PPh₃) was obtained in quantitative NMR yield. ¹H NMR (CD₂Cl₂, 400 MHz) δ = 7.34 (2H, J = 7.9 Hz, pyrrole), 7.26 (t, 1H, J = 7.6 Hz, m-phenyl), 7.19 (d, 4H, J = 7.9 Hz, o-phenyl), 7.17 (d, 4H, J = 8.0 Hz, p-phenyl).**

**Thermal Dehydrogenative Dimerization of Rh(ttp)H**. Rh(ttp)H (3.2 mg, 0.0041 mmol) was added in 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(ttp)₂ were taken. The N₂ concentration in solution was too low to be detected.

**Reaction of c-Octane with Rh₂(ttp)₂, 6.** Rh₂(ttp)₂ (9.6 mg, 0.012 mmol) and Rh₂(ttp)₂ (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 residue was added with benzene-d₆ (500 μL) under N₂ protection for ¹H NMR spectroscopy, and the yield of Rh₂(ttp)₂ (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(ttp)(c-octyl) (4.5 mg, 0.0051 mmol, 41%) and Rh₂(ttp)(n-octyl) (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(ttp)H and Rh₂(ttp)₂, 6.** Rh(ttp)H (9.6 mg, 0.012 mmol) and Rh₂(ttp)₂ (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 residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH₂Cl₂ (1:1). Red solids, Rh₂(ttp)(c-octyl) (9.8 mg, 0.011 mmol, 60%) and Rh₂(ttp)(n-octyl) (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(ttp)H and Rh₂(ttp)₂, 6.** Rh(ttp)H (9.6 mg, 0.012 mmol) and Rh₂(ttp)₂ (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 residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH₂Cl₂ (1:1). Red solids, Rh₂(ttp)(c-octyl) (2.3 mg, 0.0026 mmol, 21%) and Rh₂(ttp)(n-octyl) (3.2 mg, 0.0034 mmol, 21%), were collected, and was further recrystallized from CH₂Cl₂/MeOH.
120 °C in the dark. It was monitored with $^1$H NMR spectroscopy at particular time intervals, and the NMR yields were taken. Rh(tmp)H, Rh$^2$(tmp), and c-octene were in 51%, 46%, and 28% yields, respectively, at 120 °C in 3 d.

**Reaction of c-Octene with a 1:1 Mixture of Rh(tmp)H 11 and Rh$^2$(tmp)H 12**. Rh(tmp)H $^{10}$ (6.0 mg, 0.012 mmol) and Rh$^2$(tmp)H $^8$ (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 N$_2$, and heated at 120 °C under N$_2$ for 24 h. Excess c-octane was removed by vacuum distillation. The colorless organic distillate was added with benzene-d$_6$ for $^1$H NMR spectroscopy, and c-octene was not observed. Degassed benzene-d$_6$ was added to N$_2$ for $^1$H NMR spectroscopy. A red solution of Rh(tmp)H (90% yield, estimated by $^1$H NMR spectroscopy) was obtained.

**Reaction of c-Octene with Rh(tmp)H 12**. Rh(tmp)H (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 N$_2$, and heated at 120 °C under N$_2$ for 24 h. Excess c-octane was removed by vacuum distillation. The colorless organic distillate was added with benzene-d$_6$ for $^1$H NMR spectroscopy, and c-octene (40% yield, estimated by $^1$H NMR) was observed. Degassed benzene-d$_6$ was added to N$_2$ for $^1$H NMR spectroscopy. A red solution of Rh(tmp)H (86% yield, estimated by $^1$H 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 NaBH$_4$ (3 mg, 0.087 mmol) in aq. NaOH (0.1 M, 0.4 mL) were added with benzene-$d_8$. A reddish orange suspension was formed. After stirring at room temperature for another 15 min under N$_2$, the reaction mixture was vacuum-distilled, and the distillate went through $^1$H NMR spectroscopy after extraction with CD$_3$D$_3$/H$_2$O. c-Octene (77% yield, estimated by $^1$H NMR) was observed. The red reaction residue was washed with degassed H$_2$O (2 × 10 mL). The residue was dried by vacuum in the reaction tube, which was then protected with N$_2$ and brought to analytical balance. Rh(tmp)H$_2$ was obtained (17.1 mg, 0.19 mmol, 89%). Degassed benzene-d$_6$ was added to the reddish orange residue for $^1$H NMR spectroscopy in a sealed NMR tube. 

### Computational Details

Geometry optimizations were carried out with the Turbomole program package coupled to the P0S Baker optimizer via the BOPpt package. The def-TZVP basis set (small-core pseudopotentials on Rh) and Grimme’s D3 version dispersion corrections (disp3) for the geometry optimizations in all cases. All minima (no imaginary frequencies) and the transition state (one imaginary frequency) were characterized by calculating the Hessian matrix. ZPE and gas-phase thermal corrections (entropy and enthalpy, 298 K, 1 bar) from these analyses were calculated. The nature of the transition state was confirmed by IRC calculations. By calculation of the partition function of the molecules in the gas phase, the entropy of dissociation or coordination for reactions in solution is overestimated (overestimated enthalpy terms in the gas phase compared to solutions). For reactions in “solution,” we therefore corrected the Gibbs free energies for all steps involving a change in the number of species. Several methods have been proposed for corrections of gas phase to solution phase data. The minimal correction term is a correction for the condensed phase (CP) reference volume ($1 \text{ L mol}^{-1}$) compared to the gas phase (GP) reference volume ($24.5 \text{ L mol}^{-1}$). This leads to an entropy correction term (SCP = SGP + Rln(24.5)) for all species, affecting relative free energies (298 K) of all associative steps of $\Delta S^{\text{th}}$. Larger correction terms of $\Delta S^{\text{th}}$ have been suggested based on solid arguments, but they remain a bit debatable as to which entropy correction term is best to translate gas phase DFT data into free energies relevant for reactions in solution, in this article we adapted the suggested correction term of $\Delta S^{\text{th}} = 3.0 \text{ kcal mol}^{-1}$ for the reactions described in Scheme 6 and Table 6, using the full atom TPP models optimized at the b3-lyp level, additional dielectric constant corrections (cosmo$^3$) were taken into account based on single point calculations, using the dielectric constant of benzene ($\varepsilon = 2.27$).

### Associated Content

#### 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.

### Acknowledgments

We thank the General Research Fund of the Research Grants Council of Hong Kong (No: 400212), The Netherlands Organization for Scientific Research, Chemical Sciences (NWO-CW VICI project 016.122.613), and the NWO/RGC Joint Research Scheme sponsored by the Research Grants Council of Hong Kong and The Netherlands Organization for Scientific Research (D-HK002/11T) for financial support.

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