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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(tp)(tetratolylporphyrinato dianion) catalyzed 1,2-addition of Rh(tp)H to give Rh(tp)(n-octyl) (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(dimethylamino)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) or carbon–carbon bond activation (CCA) with organic, inorganic, and organometallic reagents followed by functionalization. Although aliphatic C–C bonds are weaker than aliphatic C–H bonds, CCA of alkanes by the attack of transition metal complexes 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.1

Cyclo-octane (c-octane) is a relatively unstrained cycloalkane with a strain energy of 9.6 kcal/mol1 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 dihydride-catalyzed dehydrogenation to c-octene,2a the FeCl3-catalyzed aerobic oxidation to c-octanol and c-octanone,2b as well as the MnO2-catalyzed bromination to c-octyl bromide.2c

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.3a Oxidative CCA of c-octane catalyzed by N-hydroxyphthalimides/Co(II)/Mn(II) at 100 °C in 14 h gives α,ω-dicarboxylic acids in 2% yield only following the major products being c-octanol and c-octanone.3b

We have recently discovered the base-promoted CHA of cyclic alkanes with Rh(III) porphyrins.4 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 dependency of the RhII(tp)(tmp = tetrakis(dimethylamino)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(tp) 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 RhII(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 1 was recovered, and a trace amount of Rh(tp)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(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

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Mechanistic Investigation: CHA as An Intermediate for CCA? In some CCAs of hydrocarbons with transition metal complexes, the CCA can be a parallel\textsuperscript{14a} and/or consecutive reaction channel\textsuperscript{14} with CHA. We thus investigated whether the CHA product is an intermediate for CCA. Rh(ttp)(c-octyl)\textsubscript{2} was heated in benzene-\textsubscript{d}\textsubscript{6} in both neutral and basic conditions separately. Without K\textsubscript{2}CO\textsubscript{3}, Rh(ttp)(c-octyl)\textsubscript{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 K\textsubscript{2}CO\textsubscript{3}, Rh(ttp)H indeed reacted with c-octane to give Rh(ttp) and the c-octene radical which gives Rh(ttp)\textsubscript{2} and c-octene 15% NMR yield), which indicate the occurrence of RhII(ttp)-c-octene-\textsubscript{d}\textsubscript{6} elimination of c-octane at 120 ppm to 1 ppm were examination of the detailed structures of these oligomers. The observed red gummy residue showing \textsuperscript{1}H NMR upfield signals at 5 = δ = -5 to 1 ppm were assigned to Rh(ttp)-incorporated c-octene oligomers (about 15\% NMR yield), which indicate the occurrence of Rh\textsuperscript{11}(ttp)-initiated oligomerization of c-octene.\textsuperscript{16,17} We did not pursue the examination of the detailed structures of these oligomers. The formation of c-octene, which forms from the \textsuperscript{1}H elimination of c-octane and K\textsubscript{2}CO\textsubscript{3} in benzene-\textsubscript{d}\textsubscript{6} (Table 4). Initially, Rh(ttp)Cl was first converted to Rh\textsubscript{2}(ttp)\textsubscript{2}, 6 in the presence of K\textsubscript{2}CO\textsubscript{3}.\textsuperscript{15} At 4.5 h, 82\% yield of Rh(ttp)Cl remained, while Rh\textsubscript{2}(ttp)\textsubscript{2} 6 was formed in 13\% yield. After 17 h, Rh(ttp)Cl was completely consumed. Rh\textsubscript{2}(ttp)\textsubscript{2}, 6, Rh(ttp)H 4, and c-octene 5 were formed in 62\%, 21\%, and 18\% yields, respectively. After 62 h, Rh\textsubscript{2}(ttp)\textsubscript{2} 6 completely reacted. The yields of Rh(ttp)H 4 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 Rh\textsubscript{2}(ttp)\textsubscript{2} and Rh(ttp)H are possible intermediates. The observed red gummy residue showing \textsuperscript{1}H 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\textsuperscript{11}(ttp)-initiated oligomerization of c-octene.\textsuperscript{16,17} We did not pursue the examination of the detailed structures of these oligomers. The formation of c-octene, which forms from the \textsuperscript{1}H elimination of Rh(ttp)(c-octyl)\textsubscript{2}, 2, indicates the occurrence of CHA of c-octene. When c-octene accumulates, it serves as a trap for Rh\textsubscript{2}(ttp)\textsubscript{2}, 6 and therefore stops the CCA.

### Reaction Profile with Rh(ttp)Cl

**Rh(ttp)Cl 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).

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

Prolonged heating of Rh(ttp)H in c-octane over 12 d yielded Rh(ttp)(n-octyl) and Rh(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).

\[
\text{Rh(ttp)H} + \text{c-octane} \rightarrow \text{Rh(ttp)(n-octyl) + Rh2(ttp)2 (3) 94% vs 3 2%}
\]

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 Rh2(ttp)2 was ligated to Rh2(ttp)2. No CCA of c-octane with Rh(ttp)H alone occurs at a fast enough rate.

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

**Scheme 2. 4-Centered Transition State via σ-Bond Metathesis Can Be Excluded**

**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/ Rh(ttp) 3 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 RhII(oep)CH2CH2Ph20 RhII(oep), which forms from homolysis of the weak Rh–Rh bond in RhII(oep)2,18 inserts into the C=C bond of styrene to give a RhII(oep)CH2C(H)Ph benzylic carbon-centered radical, which is also a reversible reaction. The RhII(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 the thermolysis of Rh(ttp)H (eq 7, Scheme 3), initially undergoes homolysis to give RhII(ttp)(eq 8 in ref 18). RhII(ttp) 7 then reacts with c-octane in parallel CHA (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 (S1,2)-like process22 (eq 10, Scheme 3) which can also reverse rapidly.20 Compound 8 can then abstract a hydrogen atom from the weak (tpp)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(oep) has been shown to undergo CHA with alkane to give RhII(oep)R and RhII(oep)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 RhII(ttp)H facilitates trapping of the carbon-centered radical 8 to give 3 and to regenerate RhII(ttp) 7. In this mechanism, RhII(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 up to 79% (Table 5, entries 2–4 vs 1). The selectivity toward CCA was further enhanced...
by an increase of the Rh(tpp)H/Rh₂(tpp)₂ ratio. The CCA of c-octane with the mixture of Rh(tpp)H/Rh₂(tpp)₂ in 2:1 ratio gave Rh(tpp)(c-octyl) 2 and Rh(tpp)(n-octyl) 3 in 60% and 18% yields, respectively (Table 5, entry 2). When the Rh(tpp)H/Rh₂(tpp)₂ ratio increased to 5:1, the yield of Rh(tpp)(n-octyl) 3 increased to 26% yield but that of Rh(tpp)(c-octyl) 2 decreased to 53% yield (entry 3). We were glad to observe that Rh(tpp)(n-octyl) 3 was selectively obtained in 73% yield from the reaction with the 10:1 ratio of Rh(tpp)H/Rh₂(tpp)₂ (entry 4). The elimination of the CHA channel (eq 9, Scheme 3) by a low concentration of Rh₂(tpp)₂ and efficient trapping of CHA by a higher concentration of Rh(tpp)H gave Rh(tpp)(c-octyl) 2 and Rh(tpp)(c-octyl) 3 in 73% yields (entry 5). The selective aliphatic CCA of c-octane was thus realized successfully, and the results confirm the proposed RhII(tpp)-catalyzed 1,2-addition of Rh(tpp)H over the C–C bond of c-octane.

**Influence of Porphyrin Sterics on CCA.** To further examine the reaction of c-octane with the analogous but sterically more hindered Rh(tmp) complexes (tmp = 5,10,15,20-tetramesitylporphyrinato dianion). Rh(tmp)Cl 10 reacted with c-octane (20 equiv) and K₂Co₃O₄ 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 allylic aliphatic CCA product (eq 11). 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). Indeed, the attempted synthesis of Rh(tmp)(c-octyl) 13 by the reductive alkylolation (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 metallocradical 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 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-c-octyl is formed directly from (por)Rh−H and the c-octene 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) C₆H₄⁻ diradical, thus producing (por)RhII and the 1-octyl radical C₆H₄⁻. Subsequent formation of (por)Rh-octyl is virtually barrierless and only requires a proper orientation of the RhII(por) and 1-octyl radical C₆H₄⁻ 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) metallocradical catalyzed reaction between (por)Rh−H and c-octene 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) metallocradical producing a
terminal octyl-radical species \((\text{por})\text{Rh-C}_8\text{H}_{16}^*\), which subsequently abstracts a hydrogen atom from \((\text{por})\text{Rh-H}\) to regenerate the \((\text{por})\text{Rh}^\text{II}\) 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 \(\text{c-octane}\) and the \(\text{Rh(tpp)}\) species. As such, we examined the hypothesized CCA reaction between \(\text{Rh}^\text{II}(\text{tpp})\) and \(\text{c-octane}\), followed by reaction of the \(\text{Rh(tpp)}\)octyl radical complex \(\text{III}\) with \(\text{Rh(tpp)(H)}\) to form \(\text{Rh(tpp)}\)octyl and \(\text{Rh}^\text{II}(\text{tpp})\) (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 \((\varepsilon = 2.27\) 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 \(\text{Rh(tpp)(H)}\) to form \(\text{Rh(tpp)}\)octyl and \(\text{Rh}^\text{II}(\text{tpp})\) 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 \(\text{SH}_2\)-type homolysis of one of the \(\text{C-C}\) bonds of \(\text{c-octane}\). In this CCA pathway, the \(\text{Rh}^\text{II}\) metallo-radical traps one of the two carbon radicals produced in this process in concert with \(\text{C-C}\) bond homolysis (Figure 1).

Despite stronger attractive dispersion (VdW) forces between \(\text{Rh(tpp)}\) and \(\text{c-octane}\), the \(\text{TS}_\text{C}\) 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
experimental barrier is also high (estimated at ~30–35 kcal mol\(^{-1}\)). The barrier (from II to TS\(_c\)) calculated at the BP86, def2-TZVP level (\(\Delta G^\ddagger = 36.8\) kcal mol\(^{-1}\); \(\Delta H^\ddagger = 35.8\) 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 Rh\(^{II}\)(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 Rh\(^{II}\)(tp) metallo-radical attacks the C–C bond of c-octane, likely via an S\(_4\)2 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 I (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 column chromatography. Characterization of Rh(tp)(c-octyl) 2: \(R_f = 0.84\) (hexane/CH\(_2\)Cl\(_2\) = 1:1). \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta = -4.25\) (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), 7.81 (d, 4 H, J = 7.7 Hz, o-phenyl), 8.97 (s, 8 H, pyrrole). \(^13\)C NMR (CDCl\(_3\), 75 MHz) \(\delta = 21.70, 22.54, 25.23, 25.85, 30.40, 40.62\) (\(J_{\text{C,H}} = -26.4\) Hz), 122.86, 127.42, 127.54, 131.48, 133.62, 134.25, 137.22, 139.52, 143.52. HRMS calc. for \(\text{C}_{14}\text{H}_{32}\text{N}_{11}\text{Rh}\) \(m/z = 883.3242\). Found: \(m/z = 883.3214\). 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 7.5 h. Excess c-octane was removed by vacuum distillation. The red residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH\(_2\)Cl\(_2\) (1:1). \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta = -4.55\) (td, 2 H, J = 2.8, 8.7 Hz), \(-4.11\) (qu, 2 H, J = 8.2 Hz), \(-1.55\) (qu, 2 H, J = 7.8 Hz), \(-0.50\) (qu, 2 H, J = 8.0 Hz). 0.02 (qu, 2 H, J = 7.5 Hz), 0.44 (qu, 2 H, J = 7.4 Hz), 0.59 (s, 3 H, J = 7.2 Hz), 0.80 (qu, 2 H, J = 7.6 Hz), 2.41 (s, 12 H, p-methyl), 7.27 (d, 4 H, J = 8.1 Hz, m-phenyl), 7.35 (d, 4 H, J = 6.4 Hz, m-phenyl), 8.12 (dd, 4 H, J = 1.7, 7.6 Hz, o-phenyl), 8.22 (dd, 4 H, J = 1.6, 7.6 Hz, o-phenyl), 8.99 (s, 8 H, pyrrole). \(^13\)C NMR (CDCl\(_3\), 100 MHz) \(\delta = 14.00, 15.69\) (\(J_{\text{C,H}} = 26.8\) Hz), 21.68, 22.41, 26.28, 27.04, 27.52, 27.96, 31.31, 122.49, 127.43, 127.51, 131.47, 133.78, 134.09, 135.23, 139.48, 143.35. HRMS calc. for \(\text{C}_{16}\text{H}_{34}\text{N}_{11}\text{Rh}\) \(m/z = 884.3320\). Found: \(m/z = 884.3336\). 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 7.5 h. Excess c-octane was removed by vacuum distillation. The red 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 (1.3 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 Hydroxide.** Rh(tp)Cl I (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 N\(_2\), and heated at 120 °C for 7.5 h. Excess c-octane was removed by vacuum distillation. The red residue was added with benzenedia (500 μL) under N\(_2\) for \(^1\)H NMR spectroscopy, and the NMR yield of Rh(tp)H (62%) was estimated. The crude mixture was then extracted with CH\(_2\)Cl\(_2\)/H\(_2\)O. 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 solids, Rh(tp)(n-octyl) 3 (7.5 mg, 0.0085 mmol, 33%), were collected.

**Independent Synthesis of Rh(tp)(c-octyl) 2.** A suspension of Rh(tp)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(tp)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 red 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 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 red orange solid of Rh(tp)(c-octyl) 2 (94.1 mg, 0.11 mmol, 86%) as the product after rotary evaporation.

**Independent Synthesis of Rh(tp)(n-octyl) 3.** A suspension of Rh(tp)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(tp)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 red 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 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 red orange solid of Rh(tp)(n-octyl) 3 (96.5 mg, 0.11 mmol, 88%) as the product after rotary evaporation.

**Thermal Stability of Rh(tp)(c-octyl) in Benzene-d₆.** Rh(tp)(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(tp)(c-octyl) with Potassium Carbonate in Benzene-d₆.** Rh(tp)(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(tp)Cl and c-Octane with Potassium Carbonate in Benzene-d₆.** Rh(tp)Cl (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(tp)H.** Rh(tp)H (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 residue was added with benzene-d₆ (500 µL) under N₂ protection for ¹H NMR spectroscopy. Rh(tp)(H/PPh₃)₃ was obtained in quantitative NMR yield. ¹H NMR (C₆D₆, 400 MHz) δ = 33.42 (b, 1 H), 2.39 (s, 12 H,CH₃), 1.58 (t, 2 H, J = 9.2 Hz), 6.28 (d, 2 H, J = 4.2, 7.6 Hz, m-phenyl), 6.52 (t, 1 H, J = 6.8 Hz), 7.55 (d, 4 H, J = 7.2 Hz, m-phenyl), 7.84 (d, 4 H, J = 7.6 Hz, o-phenyl), 7.89 (d, 4 H, J = 7.6 Hz, o-phenyl), 8.98 (s, 8 H, pyrrole).

**Thermal Dehydrogenative Dimerization of Rh(tp)H.** Rh(tp)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(tp) were taken. The H₂ concentration in solution was too low to be detected.

**Reaction of c-Octane with Rh₂(tp)H.** 6. Rh₂(tp)H (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 residue was added with benzene-d₆ (500 µL) under N₂ protection for ¹H NMR spectroscopy, and the yield of Rh₂(tp)(H/PPh₃)₃ 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(tp)(c-octyl) 2 (4.5 mg, 0.0051 mmol, 41%) and Rh₂(tp)(n-octyl) 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(tp)H and Rh₂(tp)H.** Rh(tp)H (9.6 mg, 0.012 mmol) and Rh₂(tp)H (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 purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH₂Cl₂ (1:1). Red solids, Rh₂(tp)(c-octyl) 2 (9.8 mg, 0.011 mmol, 60%) and Rh₂(tp)(n-octyl) 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(tp)H and Rh₂(tp)H.** Rh(tp)H (9.6 mg, 0.012 mmol) and Rh₂(tp)H (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 residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH₂Cl₂ (1:1). Red solids, Rh₂(tp)(c-octyl) 2 (6.9 mg, 0.0078 mmol, 53%) and Rh₂(tp)(n-octyl) 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(tp)H and Rh₂(tp)H.** Rh(tp)H (9.6 mg, 0.012 mmol) and Rh₂(tp)H (3.0 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 residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH₂Cl₂ (1:1). Red solid, Rh₂(tp)(n-octyl) 3 (8.9 mg, 0.010 mmol, 73%) was collected and was further recrystallized from CH₂Cl₂/MeOH.

**Reaction of Rh(tp)Cl 10 and c-Octane with Potassium Carbonate in Benzene-d₆.** Rh(tp)Cl (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 11 and Rh(tmp)H 12 (10.6 mg, 0.012 mmol) were added to 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 octane was removed by vacuum distillation. The colorless organic distillate was added with benzene-d 6 for 1H NMR spectroscopy, and octane was not observed. Degassed benzene-d 6 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 Rh(tmp)H 11 and Rh(tmp)H 12 (10.6 mg, 0.012 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-d 6 for 1H NMR spectroscopy, and c-octane (40% yield, estimated by 1H NMR) was observed. Degassed benzene-d 6 was added to N2 for 1H NMR spectroscopy. A red solution of Rh(tmp)H (86% yield, estimated by 1H NMR spectroscopy) was obtained.

**Computational Details.** Geometry optimizations were carried out with the Turbomole program package 28 coupled to the PQA Baker optimizer 26 via the BOPt package, 26 at the DFT/b-lyp 28a-d level (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 35) were taken into account based on single-point calculations, using the dielectric constant of benzene (ε = 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.

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(21) (a) The estimated bond dissociation energy (BDE) of (tp)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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