Carbon–Hydrogen Bond and Carbon–Carbon Bond Activation of Alkanes with Rhodium Porphyrins

CHAN, Yun Wai

A Thesis Submitted

in Partial Fulfilment of the Requirements for the Degree of

Doctor of Philosophy

in

Chemistry

The Chinese University of Hong Kong

August 2010

UMI Number: 3483858

UMI®

Dissertation Publishing

ProQuest®

<u>Thesis/Assessment Committee</u>

Professor MAK, Thomas Chung Wai (Chair)

Professor CHAN, Kin Shing (Thesis Supervisor)

Professor CHOW, Hak Fun (Committee Member)

Professor LAU, Tai-Chu (External Examiner)

Table of Contents

Acknowledgement

Abbreviations

δ	: chemical Shift	m	: multiplet (NMR)
		M^+	: molecular ion
Anal	: analytical	M	: molarity
Ar	: Aryl	Me	: methyl
Bn	: benzyl	mg	: milligram (s)
BDE.	: bond dissociation energy	min	: minute (s)
br	: broad singlet (NMR)	mL	: milliliter (s)
^{t}Bu	: *tert*-butyl	mmol	: milimole (s)
Bz	: benzyl	MS	: mass spectrometry
Calcd.	: calculated	NBS	: *N*-bromosuccinimide
CCA	: carbon carbon bond activation	nm	: nanometer
CHA	: carbon hydrogen bond activation	NMR	: nuclear magnetic resonance
COD	: 1,5-cyclooctadiene	OAc	: acetate anion
Cp	: cyclopentadienyl	Por	: porphyrin dianion
d	: day (s)	ppm	: part per million
d	: doublet (NMR)	Ph	: phenyl
DMF	: *N,N*-dimethylformamide	PhCN	: benzonitrile
e.e.	: enantiomeric excess	^{i}Pr	: isopropyl
E	: enthalpy	Py	: pyridine
Et	: ethyl	q	: quartet (NMR)
FABMS	: fast atom bombardment mass spectrometry	qu	: quintet (NMR)
ESI	: Electrospray ionization	R	: alkyl group
g	: gram (s)	r.t.	: room temperature
G	: Gibbs free energy	s	: second (s)
h	: hour (s)	s	: singlet (NMR)
HRMS	: highest resolution mass spectrometry	S	: entropy
Hz	: Hertz	TEMPO	: tetramethylpiperidinoxy
IR	: infrared	THF	: tetrahydrofuran
J	: coupling constant		
K	: equilibrium constant	t	: triplet (NMR)
		TLC	: thin-layer chromatography
		TMS	: tetramethylsilane

Structural Abbreviations for Porphyrins
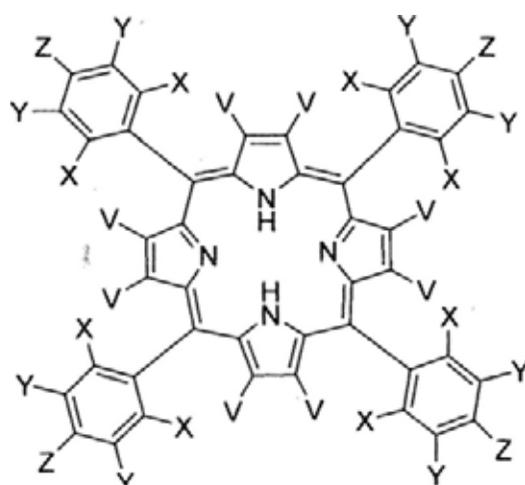
Nomenclature of Porphyrins

Abbreviations	Porphyrin	Substituents			
		V	X	Y	Z
H$_2$(ttp)	5,10,15-20-tetratolylporphyrin	H	H	H	Me
H$_2$(tpp)	5,10,15-20-tetraphenylporphyrin	H	H	H	H
H$_2$(btpp)	5,10,15-20-tetrakis(p-t-butyl-phenyl)porphyrin	H	H	H	^{t}Bu
H$_2$(bocp)	2,3,7,8,12,13,17,18-Octachloro-5,10,15-20-tetrakis(p-t-butyl-phenyl)porphyrin	Cl	H	H	^{t}Bu
H$_2$(oep)	2,3,7,8,12,13,17,18-octaethylporphyrin	Et	H	H	H
H$_2$(tmp)	5,10,15-20-tetramesitylporphyrinato	H	Me	H	Me

Abstract

The objectives of this research focus on the investigation of carbon–hydrogen bond activation (CHA) and carbon–carbon bond activation (CCA) of alkanes by rhodium porphyrin complexes as well as the mechanistic understanding.

$$Rh(ttp)X + R-H \xrightarrow[\substack{120\ ^{\circ}C,\ N_2 \\ \text{dark, 6-24 h}}]{K_2CO_3\ (10\ equiv)} Rh(ttp)-R$$

X = Cl, H, Rh(ttp)   29-76%

R = *n*-pentyl, *n*-hexyl,
   n-heptyl, *c*-pentyl,
   c-hexyl
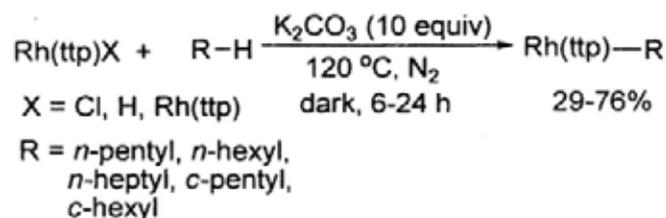
Base-promoted CHA of unstrained alkanes with 5,10,15,20-tetratolylporphyrinatorhodium complexes, Rh(ttp)X (X = Cl, H, Rh(ttp)), has been achieved. Rh(ttp)Cl, reacted with *n*-pentane, *n*-hexane, *n*-heptane, *c*-pentane and *c*-hexane in the presence of potassium carbonate at 120 °C in 6 to 24 h to give rhodium porphyrin alkyls, Rh(ttp)R, in 29-76% yields. Mechanistic investigations suggested that $Rh_2(ttp)_2$ and Rh(ttp)H are key intermediates for the parallel CHA step. The roles of base are (i) to facilitate the formation of Rh(ttp)Y ($Y^- = OH^-$, KCO_3^-), (ii) to enhance the CHA rate with alkane and generate Rh(ttp)H by a Rh(ttp)Y species which is more reactive than Rh(ttp)Cl, and (iii) to provide a parallel CHA pathway by $Rh_2(ttp)_2$.

$$Rh(ttp)X + \bigcirc \xrightarrow[120\ ^{\circ}C,\ 6\ h,\ N_2,\ dark]{K_2CO_3\ (10\ equiv)} Rh(ttp)(c\text{-heptyl}) + Rh(ttp)Bn + Rh(ttp)H \quad \text{Total Yield}$$

X = Cl, H, Rh(ttp)   30-76%   0-25%   0-30%   73-85%
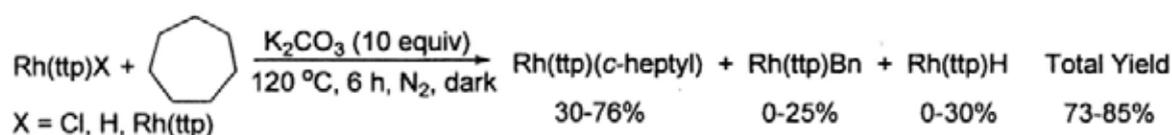
K_2CO_3-promoted CHA of the ring-strained cycloheptane with Rh(ttp)Cl at 120 °C in 6 h gave the CHA product Rh(ttp)(*c*-heptyl) and together with, unexpectedly, the CCA product Rh(ttp)Bn, in 30% and 24% yields, respectively. Mechanistic studies revealed that Rh(ttp)(*c*-heptyl) undergoes β-hydride elimination in neutral condition or β-proton elimination in basic condition followed by reprotonation to give rhodium(III) porphyrin hydride, Rh(ttp)H, and *c*-heptene. Successive base-promoted CHA of *c*-heptene with Rh(ttp)H, followed by β-proton elimination, generates cycloheptatriene. The CHA of cycloheptatriene with Rh(ttp)H formed

Rh(ttp)(c-heptatrienyl), which underwent rearrangement with carbon–carbon cleavage at 120 °C in 16 d to yield Rh(ttp)Bn in 96% yield.

Rh(ttp)X + [octagon] $\xrightarrow[\substack{120\ °C,\ N_2,\ dark \\ 7.5\text{-}15\ h}]{\text{w/o } K_2CO_3\ (10\ equiv)}$ Rh(ttp)(c-octyl) + Rh(ttp)(n-octyl) + Rh(ttp)H   Total Yield

X = Cl, H, Rh(ttp)   0-60%   4-73%   0-73%   73-97%
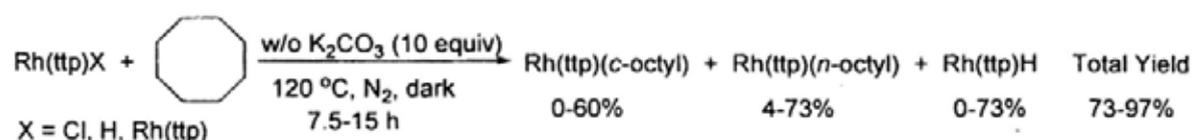
c-Octane reacted with Rh(ttp)Cl at 120 °C in 7.5 h in the presence of K_2CO_3 to yield Rh(ttp)(n-octyl) and Rh(ttp)H in 33% and 58% yields, respectively. Mechanistic investigations indicate that the CCA product is generated from the Rh^{II}(ttp)-catalyzed 1,2-addition of c-octane with Rh(ttp)H. Reaction of c-octane and Rh(ttp)H/Rh$_2$(ttp)$_2$ (10:1) selectively yielded Rh(ttp)(n-octyl) in 73% at 120 °C in 15 h. The catalyst Rh^{II}(ttp) radical cleaves the C–C bond of c-octane to form to a Rh(ttp)–alkyl radical, which then abstracts a hydrogen atom from Rh(ttp)H to generate the Rh(ttp)(n-octyl), and subsequently leading to regeneration of the Rh^{II}(ttp) radical.

摘要

本論文主要研究了銠卟啉絡合物與烷烴進行碳-氫鍵和碳-碳鍵的活化反應，同時對反應過程的機理進行了探討。

在鹼的促進作用下，銠卟啉絡合物，Rh(ttp)X (X = Cl, H, Rh(ttp))，可與無張力的烷烴進行碳氫鍵活化反應。在 120 °C，添加碳酸鉀的條件下，Rh(ttp)X 可以與正戊烷，正己烷，正庚烷，環戊烷以及環己烷進行反應，經過 6-24 h 得到相應的銠卟啉烷基絡合物，Rh(ttp)R，其產率為 29-76%。機理研究表明，$Rh_2(ttp)_2$ 及 Rh(ttp)H 可以分別與烷烴進行碳氫鍵活化反應，因此它們都是關鍵的碳氫鍵活化的中間體。鹼的作用在於：(i) 促進 Rh(ttp)Y (Y⁻ = OH⁻, KCO_3^-)的形成；(ii) 與 Rh(ttp)Cl 相比，Rh(ttp)Y 具有更高的反應活性，從而促進 Rh(ttp)H 的產生，提高烷烴碳氫鍵活化的速度；(iii) 促進 $Rh_2(ttp)_2$的形成，為碳氫鍵活化反應提供一個平行過程。

碳酸鉀可以促進 Rh(ttp)Cl 與具有環張力的環庚烷進行碳氫鍵活化反應，在 120 °C 條件下，經過 6 h，得到碳氫鍵活化產物，Rh(ttp)(c-heptyl)，其產率為 30%；同時意外得到了碳碳鍵活化的產物 Rh(ttp)Bn，其產率為 24%。機理研究顯示 Rh(ttp)(c-heptyl)在中性條件下可進行 β-氫消除，或者在鹼性條件下進行 β-質子消除，隨後通過質子化作用，從而產生三價銠卟啉氫化物，Rh(ttp)H, 以及環庚烯。在鹼的促進作用下，Rh(ttp)H 與環庚烯進行連續的碳氫鍵活化反應，隨後進行 β-質子消除，產生環庚三烯。Rh(ttp)H 與環庚三烯進行碳氫鍵活化反應，形成 Rh(ttp)(c-heptatrienyl)。在 120 °C 條件下，Rh(ttp)(c-heptatrienyl)通過重排作用，發生碳碳鍵斷裂反應，經過 16 d，得到 Rh(ttp)Bn，其產率為 96%。

在 120 °C，添加碳酸鉀的條件下，環辛烷與 Rh(ttp)Cl 反應，經過 7.5 h，得到 Rh(ttp)(n-octyl)以及 Rh(ttp)H，其產率分別為 33%及 58%。機理研究表明，Rh(ttp)H 與環辛烷在 Rh^{II}(ttp)的催化作用下可以進行 1，2-加成反應，從而得到碳碳鍵活化的產物。在 120 °C 條件下，環辛烷與 Rh(ttp)H/$Rh_2(ttp)_2$ (10:1) 進行反應，經過 15 h，選擇性的得到了 Rh(ttp)(n-octyl)，其產率為 73%。環辛烷的碳碳鍵在催化劑 Rh^{II}(ttp)游離基的作用下斷裂，從而形成銠卟啉烷基游離基。然後銠卟啉烷基游離基從 Rh(ttp)H 上得到一個氫原子，形成 Rh(ttp)(n-octyl)，並再次產生銠卟啉游離基。

Chapter 1   General Introduction

1.1   General Introduction to Alkanes

1.1.1   Bond Strength

Alkanes are non-polar saturated hydrocarbons which are made of either strong C–H or C–C single bonds with bond dissociation energy over 80 kcal mol^{-1} (Tables 1.1 and 1.2).[1,2] As a result, they are usually chemically inert.

Table 1.1 C–H Bond Dissociation Energies (BDE) of Some Alkane Molecules[2]

C–H bond of Alkane	BDE (kcal mol^{-1})	C–H bond of Alkane	BDE (kcal mol^{-1})
CH_3–H	105.0	c-C_3H_5–H	106
CH_3CH_2–H	100.5	c-C_4H_7–H	96.8
n-C_3H_7–H	100.9	c-C_5H_9–H	95.6
n-C_4H_9–H	100.7	c-C_6H_{11}–H	99.5
n-C_5H_{11}–H	100.2	c-C_7H_{13}–H	94.0
n-C_6H_{13}–H	99.0	c-C_8H_{15}–H	95.7
n-C_7H_{15}–H	98.0		

Table 1.2 C–C Bond Dissociation Energies of Some Alkane Molecules[2]

C–C bond of Alkane	BDE (kcal mol^{-1})	C–C bond of Alkane	BDE (kcal mol^{-1})
CH_3–CH_3	90.2	C_2H_5–C_2H_5	86.8
CH_3–C_2H_5	88.5	C_2H_5–C_3H_7	87.3
CH_3–n-C_3H_7	88.9	C_2H_5–n-C_4H_9	86.9
CH_3–n-C_4H_9	88.8	n-C_3H_7–n-C_3H_7	87.5

1.1.2 Steric Strain

Due to the non-bonding repulsions between adjacent atoms or like charges as well as also bond-angle strain, the structure of a molecule may be forced in a particular arrangement and lead to a sharp increase in the energy of the system. This is called strain energy. Unlike straight chain alkane which is relatively strain-free, the strain energy of cycloalkane is usually the driving force of reactions. There are three important sources of steric strain: (i) Prelog strain, which is caused by the intramlecular van der Waals repulsive forces of large atoms or groups crowding together; (ii) Baeyer strain, which is originated from bond-angle distortion; (iii) Pitzer strain, is caused from torsional deformation by σ-bond rotation from the most stable conformation. Table 1.3 lists the strain energy and the C–C BDE of some cycloalkanes.[3]

Table 1.3 Ring Strain and C–C BDE of Cycloalkanes[3]

Cycloalkane	Strain energy (kcal mol^{-1})[3a]	BDE of C–C bond (kcal mol^{-1})[3b,c]
Cyclopentane	6.5	86.9[d]
Cyclohexane	0	87.3
Cycloheptane	6.3	86.6
Cyclooctane	9.6	79.6

1.2 Activation and Functionalization of Alkanes by Transition Metals

Carbon–hydrogen activation (CHA) and carbon–carbon activation (CCA) of alkanes by transition metals involves the cleavage of the strong and inert alkyl C–H and C–C bonds, respectively and the subsequent formation of M–H or M–C bonds (eqs 1.1-1.4).[1,4] The ultimate goal in alkane activation is the catalytic conversion of hydrocarbons into more functionalized and potentially more useful chemicals. The initial C–H and C–C activations of

alkanes by metal-containing species can be viewed as the first step towards the conversion of alkanes into commodity chemicals.

$$\text{C-H} + M \longrightarrow \text{C-M-H} \quad (1.1)$$

$$\text{C-H} + 2M \longrightarrow \text{C-M} + \text{M-H} \quad (1.2)$$

$$\text{C-C} + M \longrightarrow \text{C-M-C} \quad (1.3)$$

$$\text{C-C} + 2M \longrightarrow 2 \, \text{C-M} \quad (1.4)$$
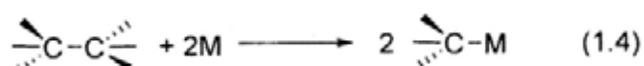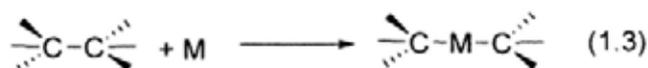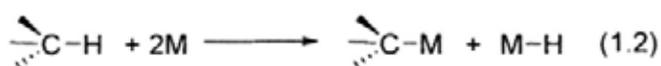
The functionalization of alkanes by transition metals consists of two essential steps: (1) activation of alkanes, and (2) conversion of the M–C bond to a functional group, for example C–O, C–N and C=C bonds.

1.2.1 Importance of Alkane Activation

CHA and CCA of alkane are potentially broadly applicable in the industrial synthesis of bulk chemical like methanol via syn-gas synthesis (Scheme 1.1),[5a] Transition metal complexes were also found to catalyze the transformation of natural product via alkyl CHA (Scheme 1.2).[5b,c]
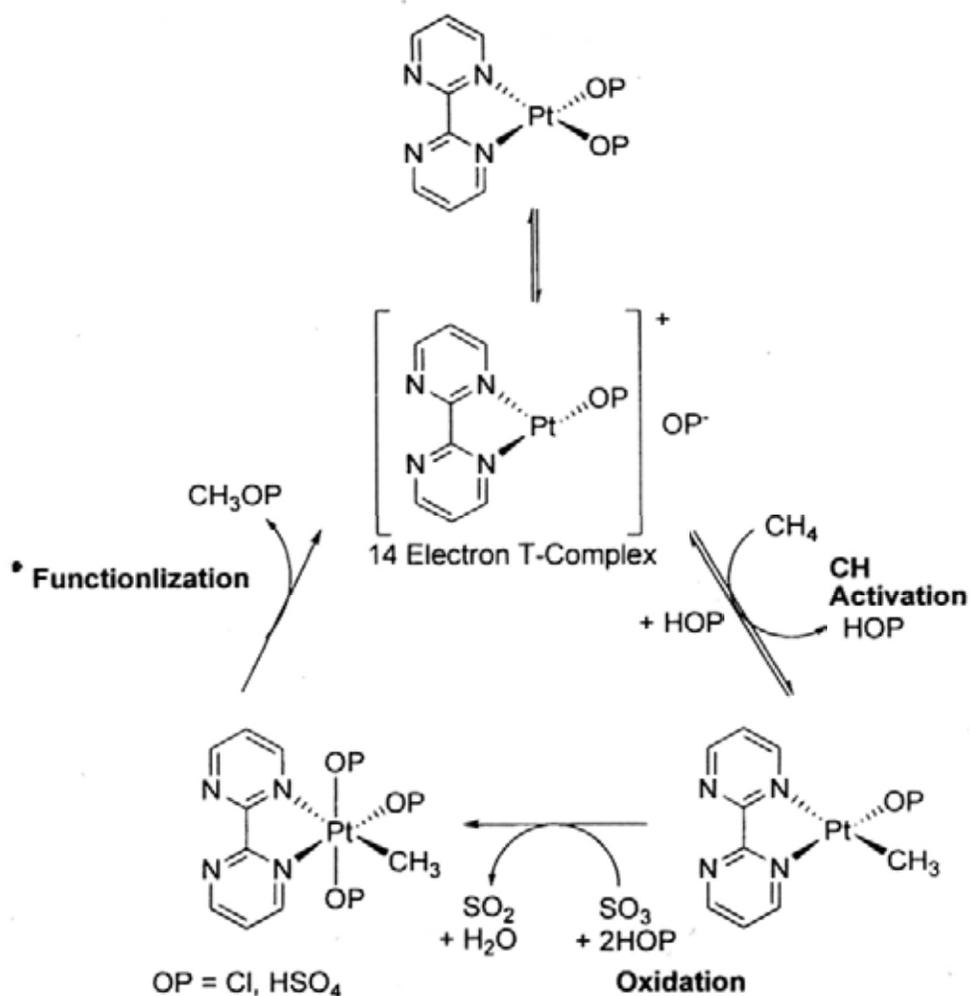
Scheme 1.1 Catalytic Oxidation of Methane Potentially Applicable in Industry
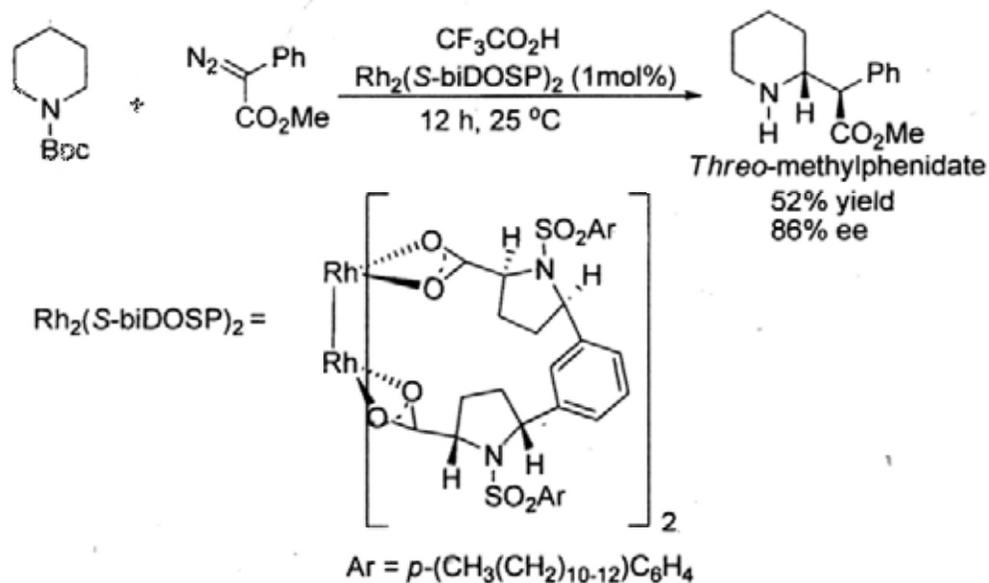
Scheme 1.2 Synthesis of *Threo*-methylphenidate by Rh$_2$(*S*-biDOSP)$_2$

1.2.2 Challenges of CHA and CCA

In the course of alkane functionalization, the bond activation step is usually the most challenging step due to the inertness of alkane. Both alkyl CHA and CCA are difficult, it is commonly accounted by their high bond dissociation energies. Indeed, CHA and CCA encounter difficulties in different aspects.

1.2.2.1 Difficulties of Alkane CHA

Generally, the CHA of alkanes faces challenges in the following aspects:

(1) Chemoselectivity: Vigorous reaction conditions and reactive reagents are usually employed for alkane functionalization as they are inert. The product of an alkane functionalization reaction is very likely more reactive than the starting material and so reacts faster with the functionalizing reagent.[1] It is called over-functionalization and can be a severe problem. For example, it is very difficult to stop the air oxidation of methane at the methanol stage. The methanol formed is more reactive than methane so that it preferentially reacts with the oxidizing agent. Many of the reactions in this section can only be run to give low or very low conversion in order to obtain a satisfactory selectivity.

(2) Regioselectivity: When there are more than one type of C–H bonds in an alkane molecule, an important selectivity issues arises (primary, secondary and tertiary C–H bonds). Tertiary radicals and carbonium ions are more stable than their secondary or primary analogs. Therefore, if carbon-centered radicals or carbonium ions are involved in the functionalization steps, an intrinsic selectivity pattern: tertiary > secondary > primary would happen. However, for very bulky reagents or in reactions in which the C–H bond to be broken is brought side-on to the functional group, for example S_N2, primary position is favored due to steric effects.[1]

(3) Alkane dehydrogenation as well as carbonylation are classic examples of CHA, however, both transformation are not favorable at ambient conditions (eqs 1.5 and 1.6). However, dehydrogenation is favorable at high reaction temperature as hydrogen gas is

generated. Due to the decrease of entropy after transformation, the addition of a C–H bond across an olefin is endogonic at high reaction temperature (eq 1.7).[6]

		At ambient conditions	At high temperature
$H_2C=CH_2$ + H_2 (1.5)		$\Delta H = + 10$ kcal mol^{-1} $\Delta G = \quad 0$ kcal mol^{-1}	$\Delta G < 0$
+ CO → (1.6)		$\Delta H = + \;\; 5$ kcal mol^{-1} $\Delta G = + 15$ kcal mol^{-1}	$\Delta G > 0$
CH_3–H + → (1.7)		$\Delta H = - 10$ kcal mol^{-1} $\Delta G = \quad 0$ kcal mol^{-1}	$\Delta G > 0$
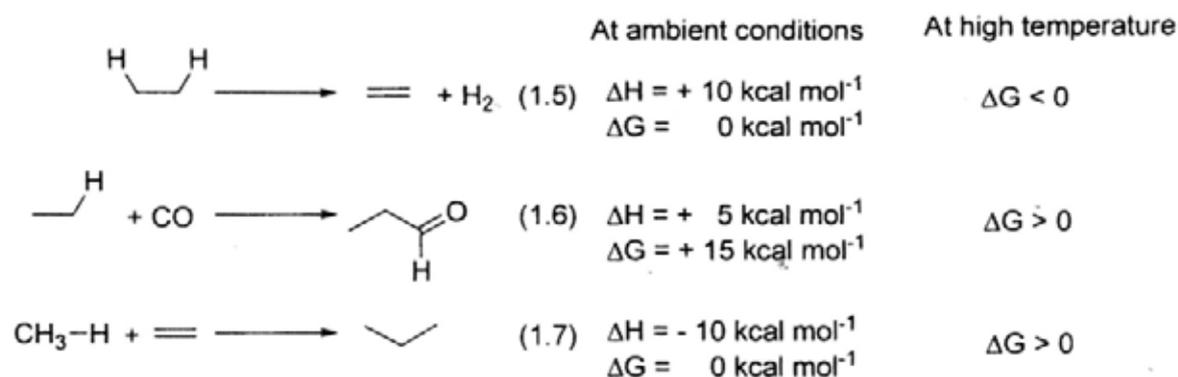
1.2.2.2 Difficulties of Alkane CCA

Carbon–carbon bond activation of alkanes with transition metal complexes are more challenging than much carbon–hydrogen bond activation.[7] This is mainly accounted by two reasons: (i) kinetically inaccessibility of the C–C bonds of alkanes due to the surrounding C–H bonds (Figure 1.1), and (ii) steric repulsion between the ligands surrounding the metal and the alkyl group bound to it.[8] As a result, CCA is much more difficult and less reported than CHA.
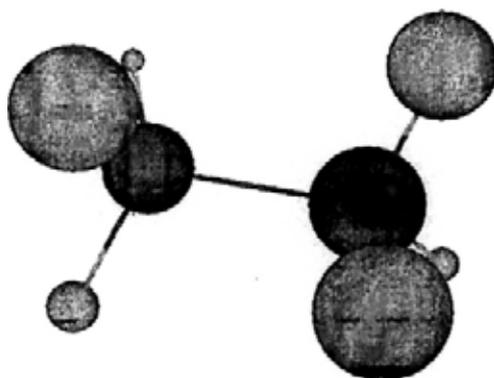
Figure 1.1 Structure of an Ethane Molecule (Ball and Stick Model)

1.3   Carbon–Hydrogen Activation of Alkanes by Transition Metal Complexes

1.3.1   Stoichiometric CHA of Alkane by Transition Metal Complexes

CHA by transition metal complexes are generally divided into five categories: (A) electrophilic activation, (B) oxidation addition, (C) σ-bond metathesis, (D) homolytic cleavage and (E) reversible addition of C–H bond across M=X.

1.3.1.1 Electrophilic Activation

In 1972, Shilov et al. published a remarkable stoichiometric "electrophilic" CHA of methane with $PtCl_6^{2-}$ to give methanol and methyl chloride (eq 1.8).[4] The reaction is catalytic in Pt(II), but unfortunately stoichiometric in Pt(IV). Shilov proposed a reasonable mechanism not long after his discovery (Scheme 1.3).[4] Methane is first activated by Pt(II) to form a methylplatinium(II) intermediate, which is then oxidized to an electrophilic methylplatinium(IV) intermediate. Functionalized products, methanol or methyl chloride come from either (i) reductive elimination of Pt(IV) methyl group and coordinated H_2O or Cl^- or (ii) nucleophilic attack at the carbon center by an external nucleophile (H_2O or Cl^-), accompanying with the reduction of Pt(IV) to Pt(II).

$$CH_4 + PtCl_6^{2-} + H_2O \;(Cl^-) \xrightarrow[\;H_2O,\;120\ ^\circ C\;]{PtCl_4^{2-}} CH_3OH\;(CH_3Cl) + PtCl_4^{2-} + 2HCl \quad (1.8)$$

Scheme 1.3 Proposed Mechanism for Shilov's Methane Oxidation

1.3.1.2 Oxidative Addition

In oxidative addition, a metal complex, with vacant-sites and a relatively low oxidation state, is oxidized by the metal insertion of C–H bond. Both the formal oxidation state of the metal and the electron count of the metal complex increase by two. As oxidative addition is a bimolecular process, it follows the second order rate law (rate = k [M][Sub]).[9]

In the late 1980s, Bergman demonstrated the intermolecular CHA of neopentane with iridium dihydride complex via oxidation addition of the iridium(I) intermediate to give hydridoalkyl iridium(III) complex (eq 1.9).[10]
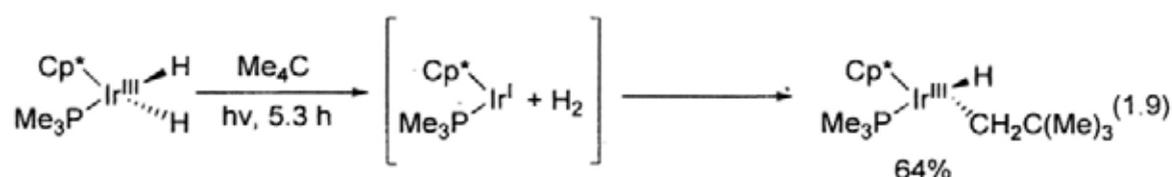
Stoichiometric alkyl CHA reactions were later found to be successful in other transition metal systems like Os (eq 1.10).[11]
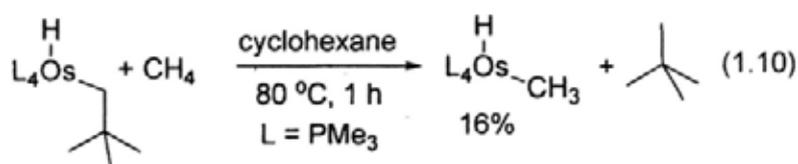
Some of the above examples laid down a good foundation for the development of catalytic functionalization of alkane. Photochemical carbonylation of n-pentane was catalyzed by Rh(PMe$_3$)$_2$(CO)Cl to give aldehydes (eq 1.11).[12] The first well-characterized catalytic dehydrogenation system was reported by Crabtree. However, such a system required either a sacrificial hydrogen acceptor or irradiation (eq 1.12).[13a] Acceptorless dehydrogenation was later reported to be successfully catalyzed by Ir pincer complex (eq 1.13).[13b] Borylation of alkane was also catalyzed by Cp*Re(CO)$_3$ and Cp*Rh(η^4-C$_6$Me$_6$) (eq 1.14 and 1.15).[14a,b] Indeed, catalytic borylation of aromatic C–H bonds was achieved by [IrCl(COD)] with 2,2'-bipyridine[14c] and Cp*IrH$_2$(BPin)$_2$ (where HBPin = pinacolborane).[14d]

$$\text{pentane} + CO \text{ (1 atm)} \xrightarrow[\text{hv, r.t., 16.5 h}]{\text{cat. Rh(PMe}_3)_2(CO)Cl} \quad \text{hexanal} \quad (2725\%/Rh) + \text{2-methylpentanal} \quad (<60\%/Rh) \quad (1.11)$$

$$\text{cyclohexane} + 2 \; t\text{-Bu-CH=CH}_2 \xrightarrow[\text{150 °C, 18 h}]{\text{cat. [IrH}_2Y_2L_2]A} \text{benzene} + 2 \; t\text{-Bu-CH}_2CH_3 \quad (1.12)$$
$$60\%$$

$$Y = Me_2CO, \; L = P(p\text{-FC}_6H_4)_3, \; A = SbF_6$$

$$\text{cyclodecane} \xrightarrow[\text{reflux}]{(^RPCP)IrH_2} \text{cyclodecene} + H_2 \quad (1.13)$$

$$\text{pentane} + B_2pin_2 \xrightarrow[\text{hv, CO, 25 °C, 56 h}]{[Cp^*Re(CO)_3] \; (2.4 \text{ mol\%})} \text{pentyl-Bpin} \; (95\%) + HBpin \; (32\%) \quad (1.14)$$

$$\text{octane} + H\text{-Bpin} \xrightarrow[\text{150 °C, 14 h}]{Cp^*Rh(\eta^4\text{-}C_6Me_6) \; (5 \text{ mol\%})} \text{octyl-Bpin} \; (65\%) + H_2 \quad (1.15)$$
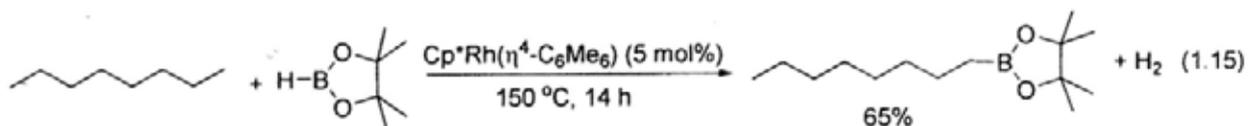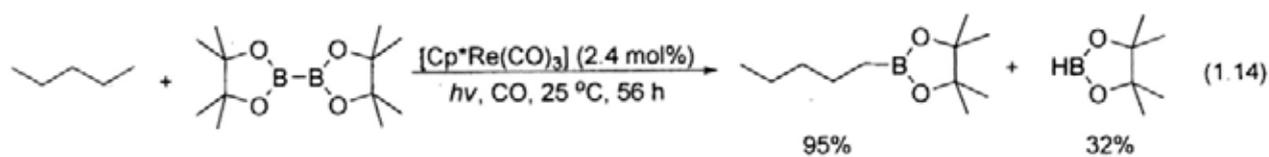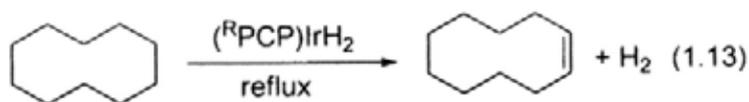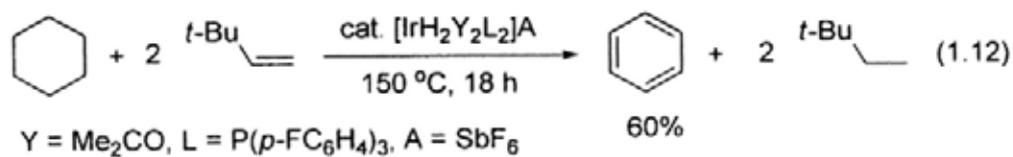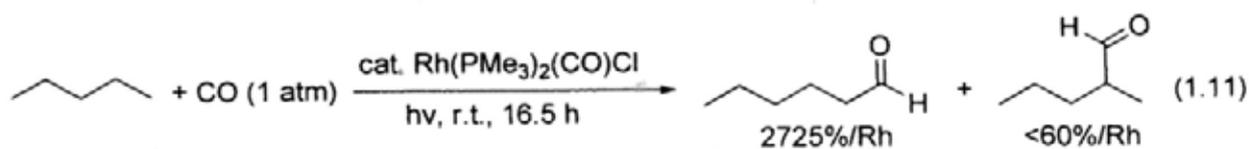
1.3.1.3 σ-Bond Metathesis

σ-Bond metathesis is also a bimolecular process. Different from oxidative addition, the oxidation state of the transition metal involved σ-bond metathesis remains unchanged. A number of examples were reported in which d^0 metal alkyls underwent σ-bond metathesis with alkanes. A four-centered transition state is generally accepted.

In 1983, Waston reported that Cp*$_2$LuMe underwent exchange with $^{13}CH_4$ to give Cp*$_2$Lu$^{13}CH_3$ at 70 °C in cyclohexane solvent (eq 1.16).[15] Bercaw also reported the methyl exchange reaction between Cp*ScMe and $^{13}CH_4$ (eq 1.17).[16]
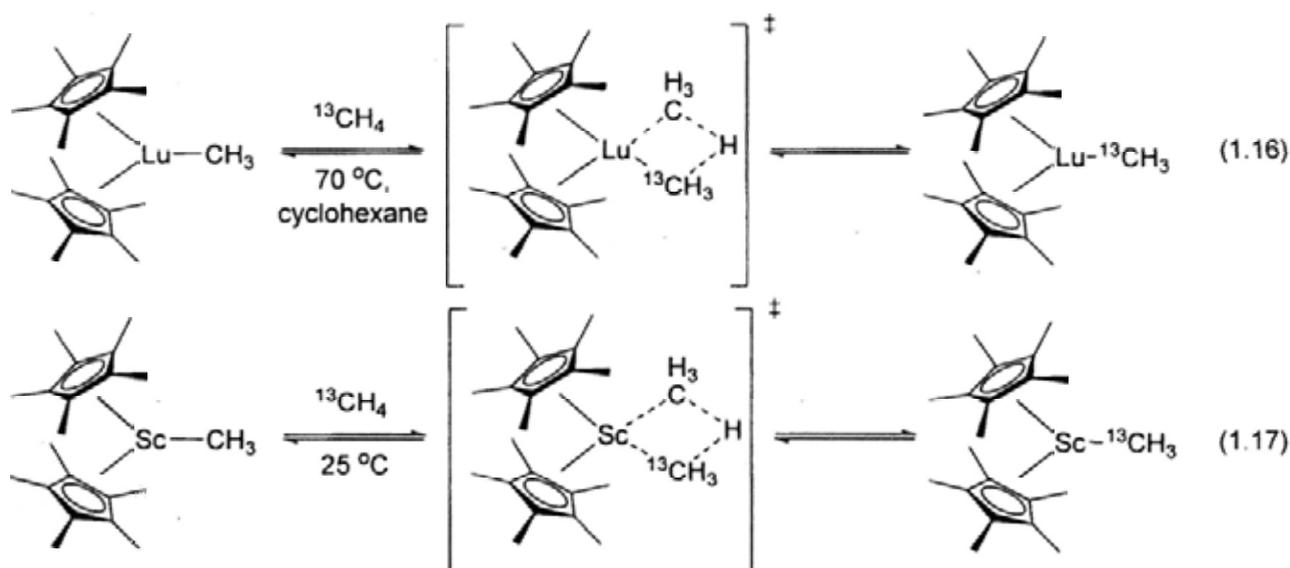
1.3.1.4 Homolytic Cleavage (Radical Pathway)

One of the most remarkable classes of organometallic CHA system is based on porphyrin complexes. Wayland et al. demonstrated the CHA of methane with metalloradical Rh^{II}(tmp) (tmp = tetramesitylporphyrinato dianion) to give Rh(tmp)Me and Rh(tmp)H (eq 1.18).[17a]

$$2Rh^{II}(tmp) + CH_4 \underset{K_1 = 7300}{\overset{353\ K}{\rightleftharpoons}} Rh(tmp)H + Rh(tmp)CH_3 \quad (1.18)$$
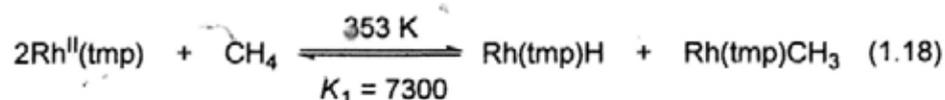
Further mechanistic studies suggested that the CHA reaction is first order in methane and second order in $Rh^{II}(tmp)$ which follow:

$$\text{Rate} = k\,[Rh^{II}(tmp)]^2\,[CH_4]$$

Temperature dependence of the forward rate constant k gives activation parameters for the methane CHA reaction ($\Delta H^\ddagger = 7.1 \pm 1.0$ kcal mol^{-1}; $\Delta S^\ddagger = -39 \pm 5$ cal mol^{-1} K^{-1}). The large deuterium isotopic effects of the reaction (k_H/k_D (298 K) = 8.6; (k_H/k_D (353K) = 5.1) implicate that the rate-determining step involves a linear C⋯H⋯Rh fragment. The small activation enthalpy ($\Delta H^\ddagger = 7.1 \pm 1.0$ kcal mol^{-1}) indicates that the cleavage of C⋯H bond in the transition state is accompanied by the formation of both Rh⋯C and Rh⋯H bonds. Therefore, the methane activation was proposed to go through a linear 4-centered transition state (Scheme 1.4).[17b]
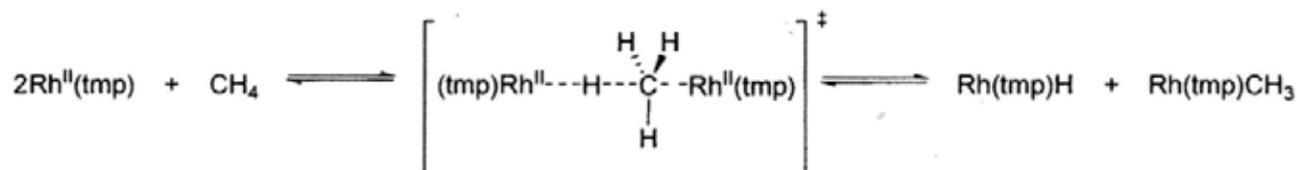
Scheme 1.4 Methane CHA via Termolecular Transition State

1.3.1.5 1,2-Addition of C–H bond across M=X

In 1988, Wolczanski[18] and Bergman[19] independently reported that Zr(IV) amido complexes could undergo 1,2-elimination of alkane to give the corresponding transient imido complexes. Wolczanski examined the reactivity of the newly-formed imido complex with methane and resulted in the formation of Zr-CH3 complex via the 1,2-addition of alkyl C–H bond across the Zr=N bond (eq 1.19).

L = NHSi^{t}Bu$_3$

11
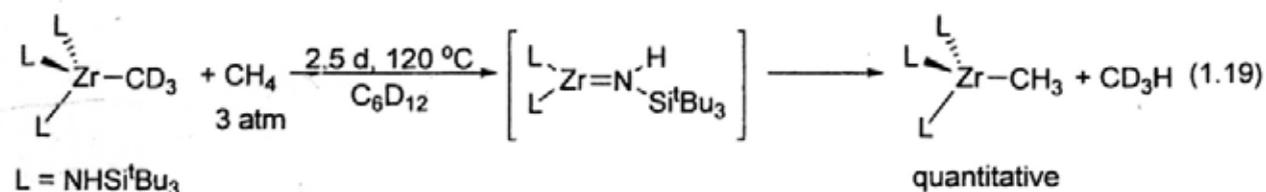
Legzdins reported a series of Mo and W systems which underwent CHA of hydrocarbons, including alkane, via the addition across the proposed M=C intermediates (Scheme 1.5).[20]
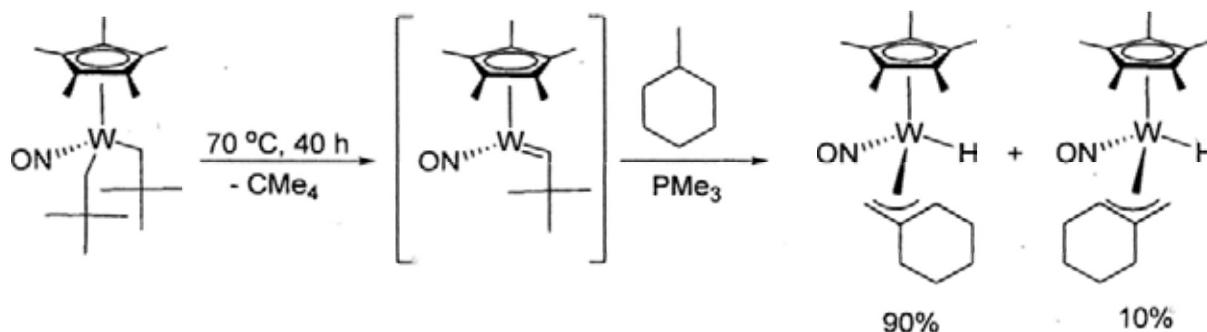
Scheme 1.5 Alkyl CHA by Cp*W complexes

1.3.2 Catalytic CHA of Alkane with Transition Metal Complexes

The detailed studies of stoichiometric reactions of alkyl CHA with different transition metal complexes provided a basic understanding of the reaction mechanism. Some of the stiochoimetric CHA had been developed into catalytic functionalization (Table 1.4).

Table 1.4 Selected Examples of Catalytic CHA with Transition Metal Complexes

Catalytic Reaction	Examples
Dehydrogenation 1999 Goldman et al.[21]	n-octane + 1-decene $\xrightarrow[\text{n-octane, 150 °C, 120 min}]{(t\text{-Bu}PCP)IrH_2 \ (1.0 \ mM)}$ 1-octene + decane (1.20) (0.5 M) — 97% $t\text{-Bu}$PCP = 2,6-bis[di(t-butyl)phosphinomethyl]phenyl
H–D Exchange 1982 Schwartz et al.[22]	n-butane-d_0 + D_2 $\xrightarrow[\text{100 °C, 2 d}]{[Si]-ORh, \ H \ (4 \ mol\%)}$ mixture of n-butane-d_{1-9} (1.21) recovered 20% yield — 79%
Carbonylation 1991 Crabtree et al.[23]	cyclohexane + CO $\xrightarrow[\text{1-5 h}]{Hg^* \ (254 \ nm)}$ cyclohexane-CHO + dicyclohexyl ketone (1.22) total yield 10-70%
Methane Oxidation 1998 Periana et al.[5]	$CH_4 + 2H_2SO_4 \xrightarrow[\text{220 °C, 2.5 h}]{cat. \ (bypm)PtCl_2} CH_3OSO_3H + 2H_2O + SO_2$ (1.23) 72% bypm = 2,2'-bipyrimidine
Amination 2008 Perez et al.[24]	cyclohexane + PhI=NTs $\xrightarrow[\text{80 °C, 4 h}]{5 \ mol\% \ Tp^{*,Br}Ag}$ cyclohexyl-N(H)-Ts (1.24) 90 % ($Tp^{*,Br}$ = hydrotris(3,4,5-tribromo)pyrazolylborate ligand)
Chlorination 1984 Schwartz et al. 25	$CH_4 + Cl_2 \xrightarrow[\text{100 °C, 11 h}]{[Si]-ORh, \ Cl \ H \ (2 \ mol\%)} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4$ (1.25) recovered yield 86.3% — 12.6% — 1.1% — trace — trace
Isomerization 1979 Arata et al.[26]	n-butane $\xrightarrow[\text{150 °C, <1 min}]{cat. \ H_2SO_4\text{-}SbF_5/ZrO_2}$ isobutane (1.26) 80% — 20%
Boronation 2000 Hartwig et al.[27]	Cp*W(CO)$_3$[Bcat(Me)$_2$] + pentene $\xrightarrow[\text{>6 h}]{Hg \ lamp}$ hexyl-Bcat(Me)$_2$ (1.27) 85% {[Bcat(Me)$_2$] = B-1, 2-O$_2$C$_6$H$_2$-3, 5-Me$_2$}

1.4 Carbon–Carbon Activation by Transition Metal Complexes

Carbon–carbon bond activation of alkanes with transition metal complexes are much less reported than carbon–hydrogen activation.[7] Several strategies have been commonly employed to realize CCA, including ring strain relief,[28] the aromaticity driven CCA from pre-aromatic system,[29] chelation assisted CCA,[30] intermolecular CCA of imine[31] and carbonyl,[32,33] intramolecular β-carbon-carbon bond cleavage[34-37] and alkane metathesis.[38] They will be discussed one by one in the following section.

1.4.1 Ring Strain Relief

Early CCA examples with transition metal complexes were focused on ring strained molecules as the cleavage of the highly strained system provided extra driving force for the reaction (eqs 1.28-1.30).[28]
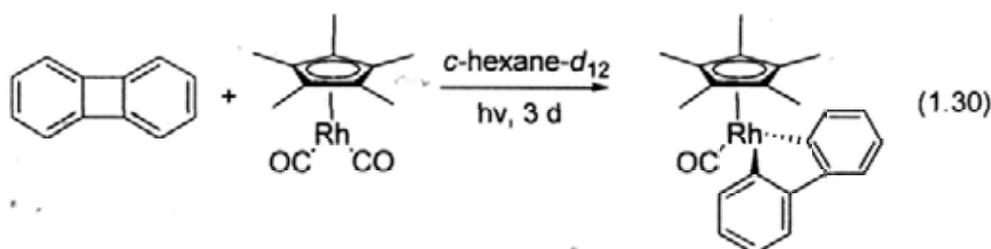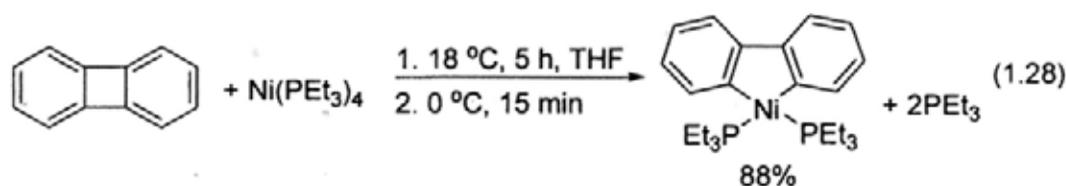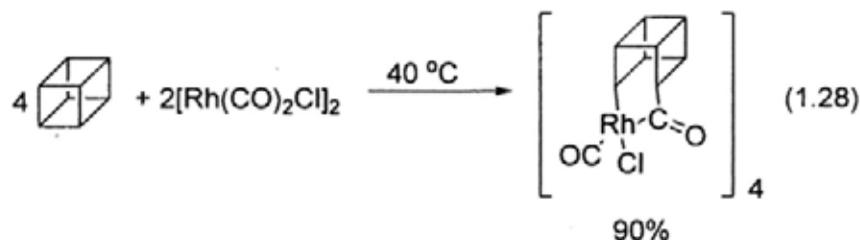
The above examples demonstrate the cleavage of ring strained C–C bond and meanwhile with the formation of M–C bond. Since M–C bond is relatively weak (30 to 70 kcal mol^{-1}),[2] the organometallic compounds formed are easily further transformed to complete the functionalization (eq 1.31).[28c]

$$\text{(biphenylene)} + \underset{\text{(500 Torr)}}{CO} \xrightarrow[\text{160 °C, 6 d}]{\substack{Cp^*Rh(CO)_2 \\ c\text{-hexane-}d_{12}}} \text{(fluorenone)} \quad (1.31)$$

97%
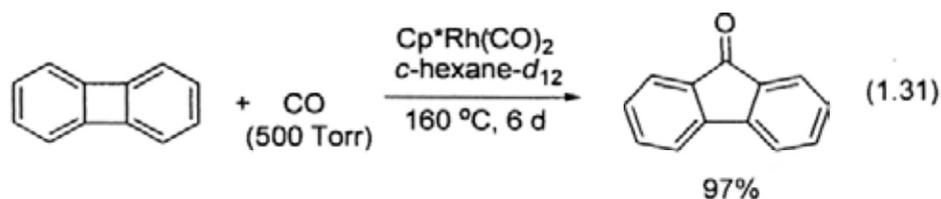
1.4.2 Aromaticity Driven CCA

The transformation of an aromatic compound from the corresponding pre-aromatic one provides an extra driving force. Crabtree et al. reported that the carbon-carbon bond of 1,1-dimethylcyclopentadiene was cleaved by Ir complexes to give the corresponding η^5-methylcyclcopentadienyl(methyl)iridium (eq 1.32).[29a] Hughes also found that $Mn_2(CO)_{10}$ reacted with neat pentamethylcyclopentadiene to afford a mixture of CHA product, $Mn(\eta^5\text{-}C_5Me_5)(CO)_3$ and CCA product, $Mn(\eta^5\text{-}C_5Me_4H)(CO)_3$ (eq 1.33).[29b]

$$\left[\text{Me Me cyclopentadiene-}\ddot{i}\text{-Ir}[P(p\text{-F-C}_6H_4)_3]_2\right]^+ \xrightarrow{145\ ^\circ\text{C, 18 h}} \left[\text{Me Me-Ir}[P(p\text{-F-C}_6H_4)_3]_2\right]^+ \quad (1.32)$$

quantitative

$$Mn_2(CO)_{10} + \text{(tetramethylcyclopentadiene)} \xrightarrow[\substack{2.\ 155 \to 205\ ^\circ\text{C, 3 h} \\ 3.\ 205\ ^\circ\text{C, 0.5 h}}]{1.\ 155\ ^\circ\text{C, 0.5 h}} \underset{\substack{OC^{-}\overset{|}{\underset{CO}{Mn}}{}^{-}CO \\ 77}}{} + \underset{\substack{OC^{-}\overset{|}{\underset{CO}{Mn}}{}^{-}CO \\ 23}}{} \quad (1.33)$$

$$77 \quad : \quad 23$$

> 70%
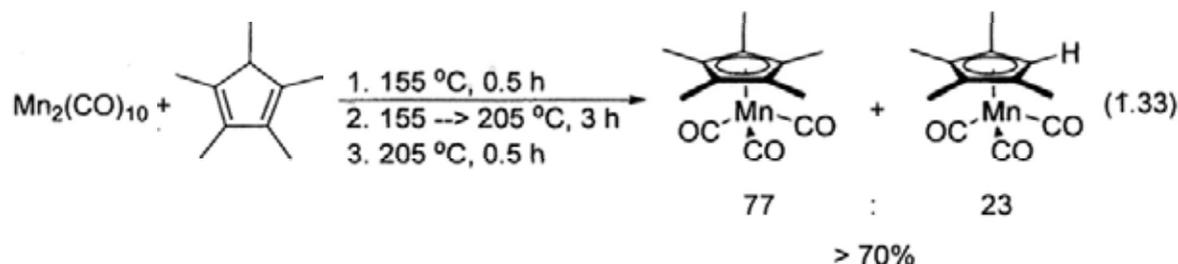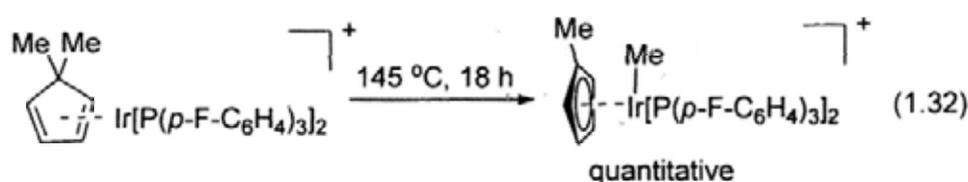
1.4.3 Intramolecular CCA in Pincer-Type System

Chelation assisted CCA makes use of a strategy in which the targeted carbon-carbon bond is brought close to the metal center by ligand coordination of the substrate so as to lower the activation barrier. Intramolecular sp^2-sp^3 CCA in pincer type (PCP) system by Milstein et al. gave the best illustration (eq 1.34).[30]

$$\text{(PCP ligand with -P}^t\text{Bu}_2\text{, -Me, -P}^t\text{Bu}_2) + [Rh(CH_2=CH_2)_2Cl]_2 \xrightarrow[\text{rt, 24h}]{\text{benzene}} \text{(Rh pincer complex -PH}^t\text{Bu}_2\text{, Me, Rh-Cl, -P}^t\text{Bu}_2) \quad (1.34)$$

98%
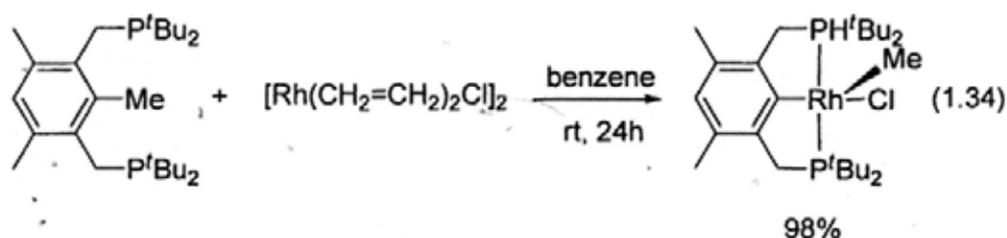
The coordinating P ligands in the target molecule brings the Rh center into close proximity, and subsequently inserts into the aryl-Me bond. Mechanistic investigation of the CCA reaction revealed that the initial coordination of the diphosphine ligand to the rhodium olefin complex is the rate-determining step.[30b] The operating mechanism involves parallel benzylic CHA and aromatic CCA, the CHA product eventually converts to the thermodynamically favored CCA product (Scheme 1.6).
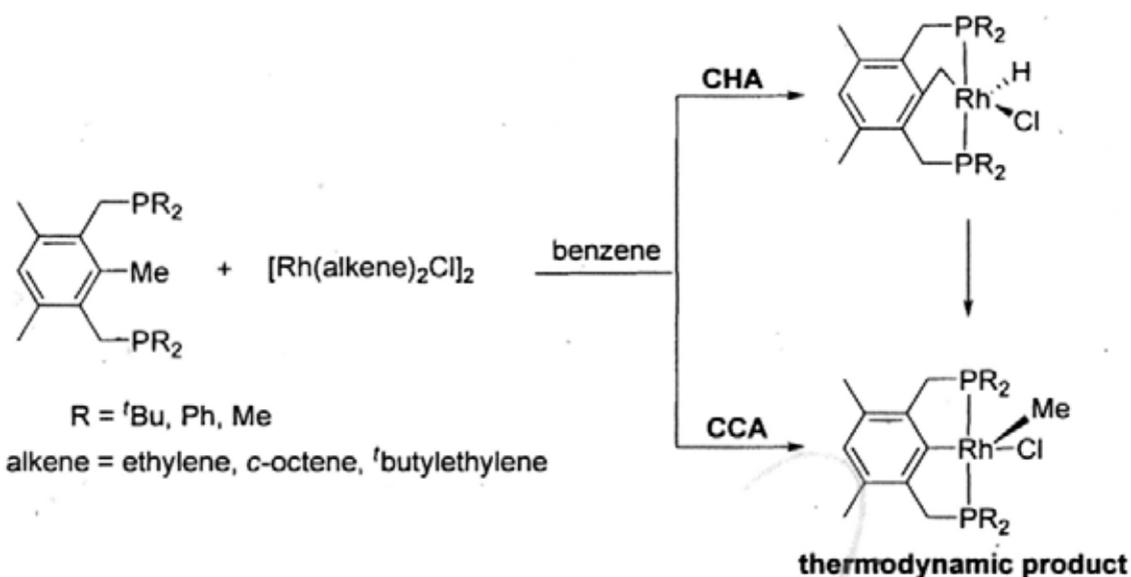
Scheme 1.6 Proposed Mechanism of Parallel CHA and CCA in PCP System

When less bulky dimethylphosphines was employed in the PCP ligand, the more stable CCA product formed. However, when less basic diphenylphosphine was used, CHA product became more stable and formed preferretially.[30]

1.4.4 Chelation-Assisted Intermolecular CCA of Imine

Jun et al. discovered that by using 2-amino-3-picoline, a temporary chelating auxiliary which reacted with ketone to form ketimine, $Rh^ICl(PPh_3)_3$ facilitated the CCA of unstrained ketone (Scheme 1.7).
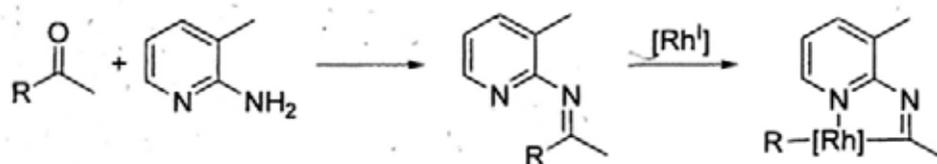
Scheme 1.7 Chelation Assisted CCA of Imine

16

The C_α-C_β bond of the newly formed ketimine is cleaved by Rh(PPh$_3$)$_3$Cl with the generation of (iminoacyl)rhodium alkyl.[31]

The nitrogen atom on the pyridine ring directed the rhodium center to the C_α–C_β bond of the imine via a chelation-assisted strategy. This approach has also been applied to the C–C activation of primary amines,[31c] alkyne,[31d-f] cycloalkanone imine (eq 1.35)[31g] and catalytic CCA of unstrained ketone (eq 1.36).[31h]
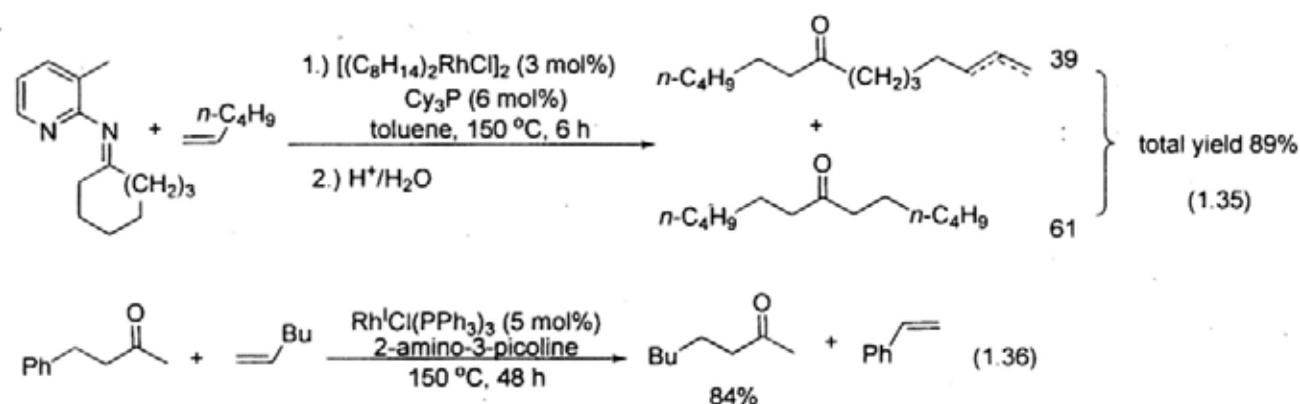
1.4.5 Intermolecular CCA of Carbonyl

The C–C bond adjacent to a carbonyl group is more potent to be cleaved due to two reasons: (1) the C–C bond is weaker than alkyl C–C bond by around 5 kcal mol^{-1} in general;[2] (2) the carbonyl group serves as a directing group to the metal center and brings the targeted C–C bond in close proximity. Suggs found that [Rh(C$_2$H$_4$)$_2$]$_2$ cleaved the β-keto C–C bond of 8-quinolinyl alkyl ketones (eq 1.37).[32] Ito reported that [Rh(cod)]BF$_4$ catalyzed the transformation of substituted cyclobutanone to give the lactones via CCA (Scheme 1.8).[33a,b]

R = Me, Et, Bn, CD$_2$Ph   quantitative
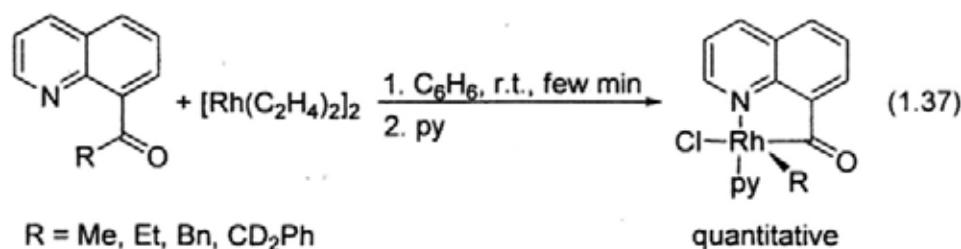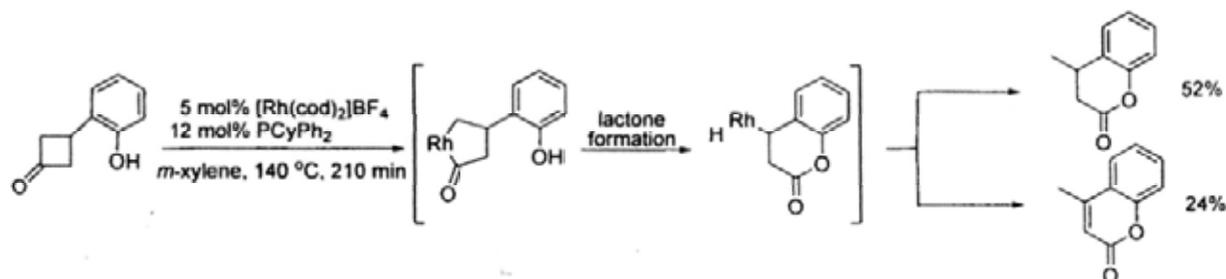
Scheme 1.8 Lactone formation catalyzed by Rh^I complex via CCA

More recently, Douglas et al. facilitated the intramolecular carbo-acylation with catalyst [RhCl(C$_2$H$_4$)$_2$] (1.38).[33c]
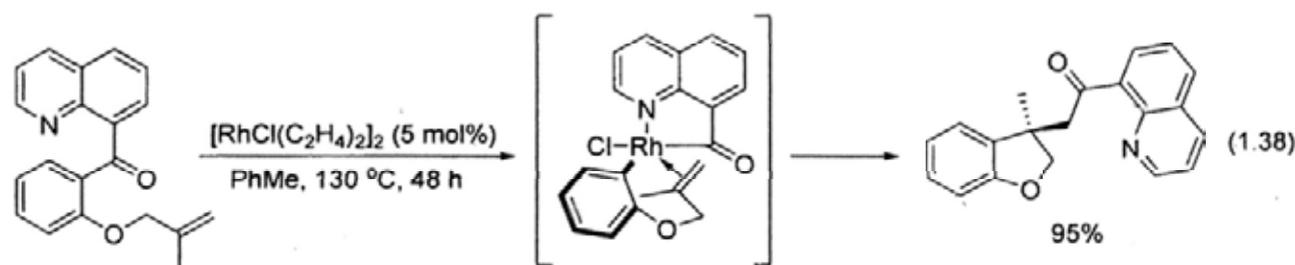
1.4.6 Intramolecular β-Alkyl Elimination

Intramolecular β-alkyl elimination of transition metal complexes like metal alkyl, alkoxide and amido complexes are mostly reported with highly Lewis acidic transition metals. The C$_\alpha$-C$_\beta$ bonds of the metal complexes are cleaved to give metal alkyl and the corresponding olefin, carbonyl or imine (Scheme 1.9).

M = transition metal
X = C, O or NH
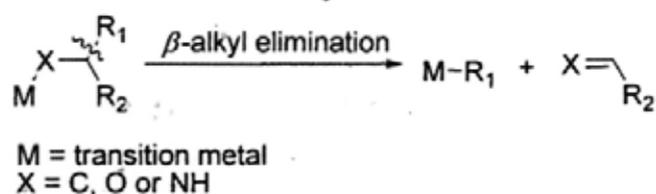
Scheme 1.9 General Expression of Intramolecular β-Alkyl Elimination

1.4.6.1 Intramolecular β-Alkyl Elimination of Metal Alkyl

The first example of β-alkyl elimination of metal alkyl was demonstrated by the thermal decomposition of coordinatively unsaturated lutetium isobutyl complex to yield lutetium methyl complex and propene via β-methyl elimination (eq 1.39).[34a] Bercaw later

also reported that scandocene isobutyl complex underwent β-methyl elimination to give scandocene methyl complex and propene (eq 1.40).[34b]

$$\text{Cp*}_2\text{Lu} \xrightarrow[\text{22 °C, 12 h}]{\text{cyclohexane-}d_{12}} \text{Cp*}_2\text{Lu–Me} + \diagup \quad (1.39)$$
$$20\text{-}40\%$$

$$\xrightarrow[\text{25 °C, 20 min}]{\text{cyclohexane-}d_{12}}$$

quantitative

1.4.6.2 Intramolecular β-Alkyl Elimination of Metal Alkoxide

Bergman et al. carried out detailed reactivity study of ruthenium metallacycles which gave metallacyclic enolate via β-methyl elimination (eq 1.41).[35] By applying β-alkyl elimination in its catalytic cycle, Uemura et al. reported various Pd[II]-catalyzed dealkylation of alcohols (eqs 1.42-1.43).[36]

$$\xrightarrow{\text{45 °C, 8h}}$$

L = PMe$_3$

$$+ \text{CH}_4 \quad (1.41)$$

51%

Pd(OAc)$_2$ (10 mol%)
pyridine, MS3A
toluene, 16 h, 80 °C, O$_2$

(1.42)

97%

Ph—≡—, OH + ⟍CO$_2$Et

Pd(OAc)$_2$ (10 mol%)
pyridine, MS3A
toluene, 48 h, 80 °C, O$_2$

Ph—≡—⟍⟍—CO$_2$Et (1.43)

57%

1.4.6.3 Intramolecular β-Alkyl Elimination of Metal Amido

Uemura et al. utilized β-alkyl elimination in palladium catalysis for other organic transformation and constructed a new Pd(0) catalytic system using cyclobutanone O-

acyloximes to afford unsaturated nitriles (eq 1.44).[37a] Later, Ir complex was used to yield saturated nitriles where CCA occurred at the sterically less hindered site (eq 1.45).[37b]

Ph—⬡=N–OCOMe $\xrightarrow[\text{THF, reflux, 24 h}]{\substack{\text{Pd(0) (5 mol\%)} \\ \text{(R)-(+)-BINAP (7.5 mol\%)} \\ \text{K}_2\text{CO}_3 \text{ (1 equiv)}}}$ Ph⤒CN + Ph⤒CN (1.44)

6%   76%

[structure]–N–OBz $\xrightarrow[\substack{\text{dihydroanthracene} \\ \text{K}_2\text{CO}_3, \text{DMF}, 50\ ^\circ\text{C}, 24\ h}]{\substack{\text{[Ir(cod)Cl]2 (2.5 mol\%)} \\ \text{BnBPA (5 mol\%)}}}$ [structure]–CN (1.45)

80%
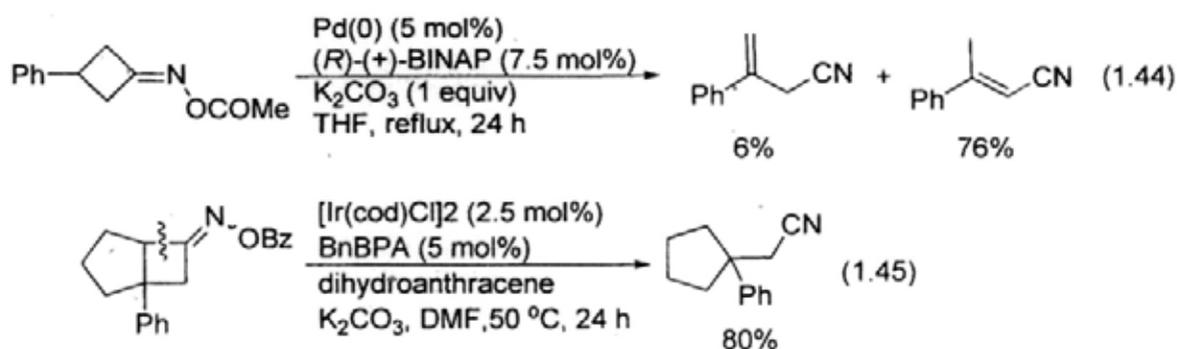
1.4.7 CCA by Alkane Metathesis

Basset et al. developed a silica-supported tantalum hydride complex, ($\equiv$Si–O–Si$\equiv$)($\equiv$Si–O–)$_2$Ta–H which catalyzed the transformation of linear or branched alkanes into the next higher and lower alkanes at 25 to 200 °C.[38] The Ta–H complex facilitated the conversion of propane to give a mixture of methane, ethane, n-butane, isobutene and n-pentane in 15.7%, 37.4%, 27.2%, 6.7% and 6.5% yields, respectively at 150 °C in 80 hours (eq 1.46).

$$C_3H_8 \xrightarrow[\text{150 °C, 80 h}]{\text{cat. [Ta]}-\text{H}} CH_4 + C_2H_6 + \textit{n-}C_4H_{10} + \textit{i-}C_4H_{10} + \textit{n-}C_5H_{12} \quad (1.46)$$

15.7%   37.4%   27.2%   6.7%   6.5%

[Ta]$-$H = ($\equiv$Si$-$O$-$Si$\equiv$)($\equiv$Si$-$O$-$)$_2$Ta$-$H
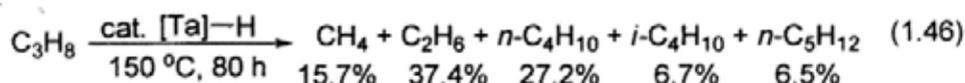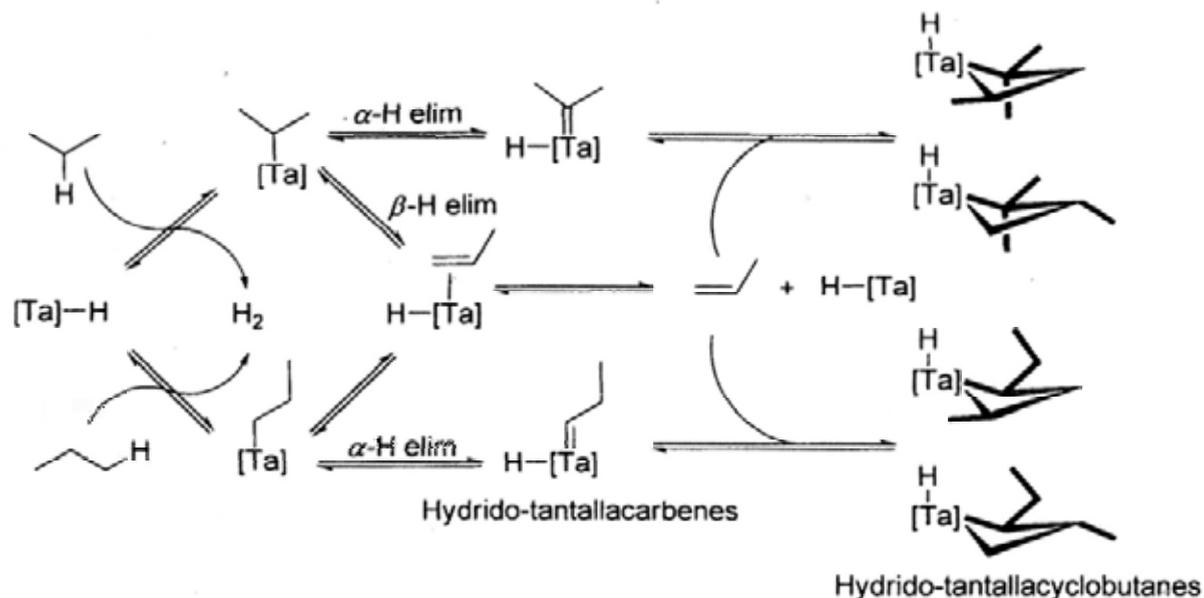
Scheme 1.10a Mechanistic Scheme of the Formatiom of Hydrido-tantallacyclobutanes from

[Ta]–H and Propane
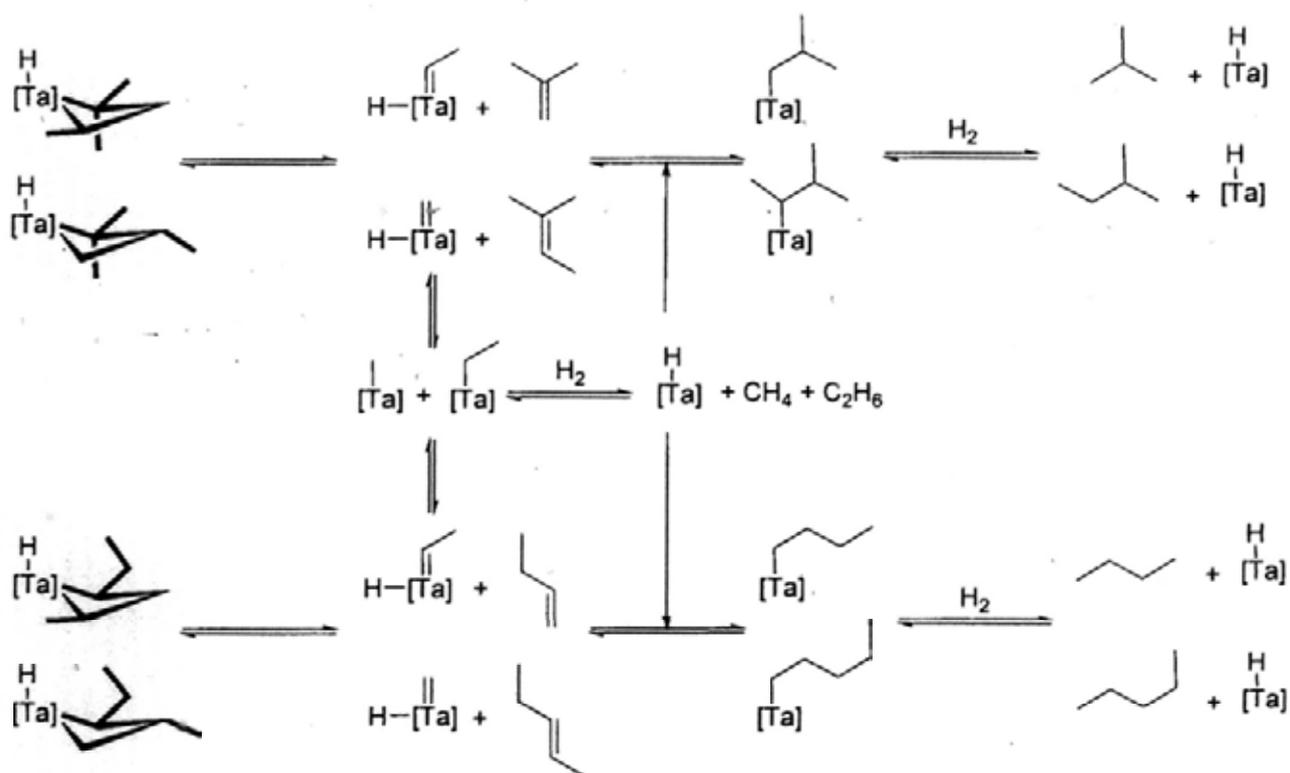
Scheme 1.10b Transformation of Hydrido-tantallacyclobutanes to [Ta]–H and

Various Alkanes via Hydrogenlysis

Basset et al. proposed a mechanism in which propane first reacts with Ta–H via CHA

to give Ta–propyls and hydrogen. Ta–propyls then undergo α–H elimination to give hydrido-

tantallacarbenes or β–H elimination to give Ta–H and propene via four possible tantallacyclobutanes (Scheme 1.10a). Subsequently, the tantallacyclobutanes transform to Ta–alkyls which further react with hydrogen to generate a mixture of alkane and regenerate [Ta]–H catalyst (Scheme 1.10b).

One of the major disadvantages of this type of CCA is poor selectivity problem. Even though propane has only one chemically equivalent C–C bond, the CCA of propane gave a mixture of methane, ethane, *n*-butane, *i*-butane, 2-methylbutane and *n*-pentane.[38]

1.4.8 CCA by Nucleophilic Attack

Ogoshi et al. reported that the C–C bond of cyclopropane was also cleaved by the nucleophilic attack of rhodium(I) porphyrin to the carbon center under mild conditions (eq 1.47).[39] An acyl or ester group on the cyclopropane ring facilitated the aliphatic CCA.

$$\left[(oep)Rh^{I}\right]^{\ominus} + \triangleright\!\!-R \xrightarrow[\text{35 °C, 1.5 h}]{\text{ethanol}} (oep)Rh^{III}CH_2CH_2CH_2R \quad (1.47)$$

oep = octaethylporphyrinato dianion

R = COCH$_3$, 77%
R = CO$_2$C$_2$H$_5$, 12%
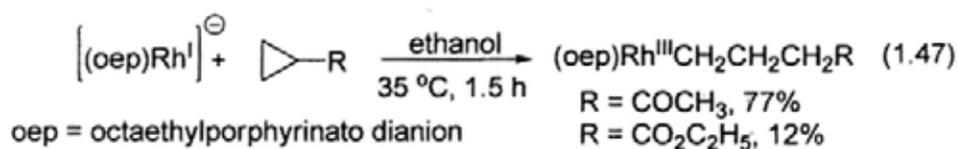
1.4.9 Catalytic CCA of Alkane with Transition Metal Complexes

Based on the above fundamental investigation of CCA, a few strategies have been applied to catalytic functionalization. The following table lists the selected examples (Table 1.5).

Table 1.5 Selected Examples of Transition Metal Catalyzed CCA

Catalytic Reaction	Examples
Carbonylation 1997 Jones et al.[28c]	(1.31)
Intrmolecular Carbo-Acylation 2009 Douglas et al.[33c]	(1.38)
Dealkylation of Alcohol and Imine 2003 Uemura et al.[36] and 2005 Uemura et al.[37]	(1.42) (1.45)
Alkane Metathesis 1997 Basset et al.[38]	$C_2H_6 \xrightarrow[150\ ^\circ C,\ 80\ h]{cat.\ [Ta]-H} CH_4 + C_3H_8 + n\text{-}C_4H_{10} + i\text{-}C_4H_{10}$ (1.46) 53% 44% 2.6% 0.4%
Lactones Formation 2000 Ito et al.[33]	(1.48)
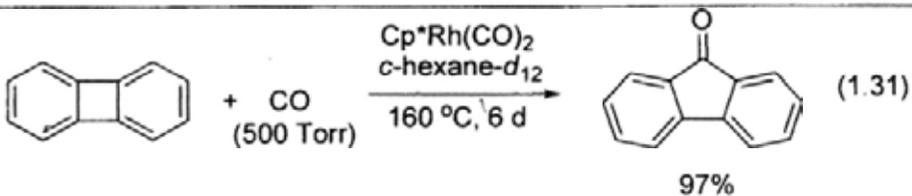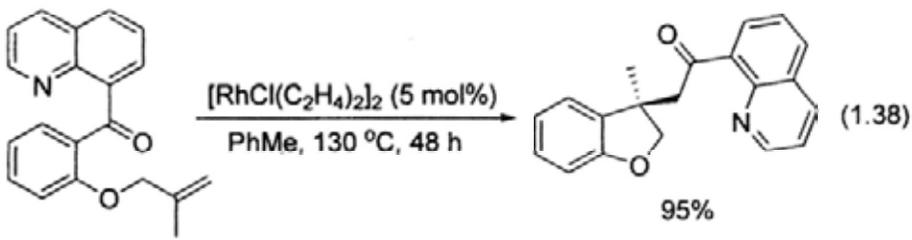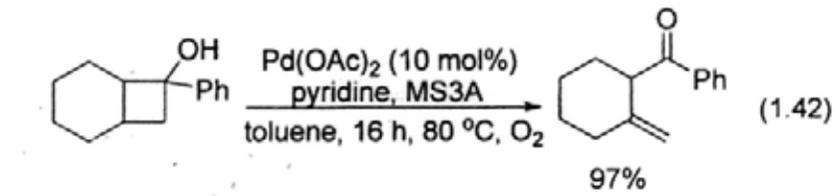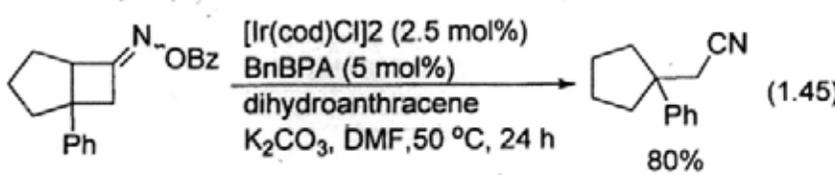
23
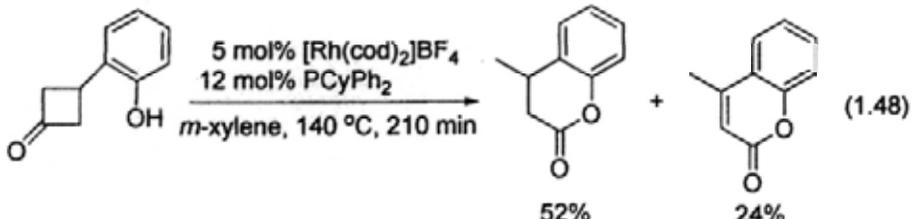
1.5 Porphyrins and Metalloporphyrins

1.5.1 Porphyrin Ligands

Porphyrins are heterocyclic macrocycles which consist of four pyrrole subunits interconnected at their α carbon atoms by methine bridges. They contain 22 π electrons, with 18 π electrons in the 16-membered ring conjugated system (Figure 1.3).[40,41] Porphyrins obey the Huckel's rule and therefore the macromolecules are aromatic and highly conjugated systems. Consequently, they have very intense absorption in the visible region. The diagonal radii of the cavity (C_t-N = 2.098 Å) allow the coordination of various metal centers in the plane of the four nitrogen atoms.[41] When incorporated with metals, porphyrins serve as planar tetradentate, dianionic macrocyclic ligands to form stable complexes. ^{1}H NMR spectroscopy confirms the aromaticity with a shielding effect on a nucleus which resides out of the porphyrin plane.[41]

porphyrin   metalloporphyrin
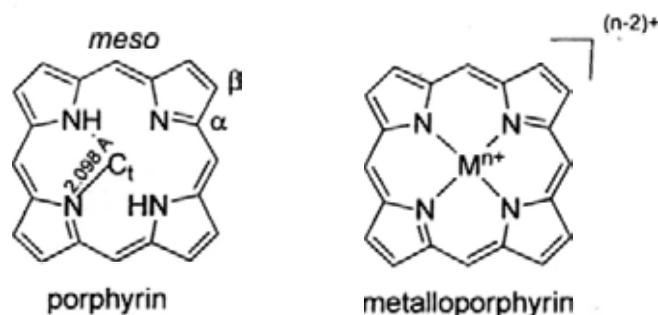
Figure 1.3   Structures of Porphyrin and Metalloporphyrin

A wide variety of porphyrin ligands can be easily synthesized by substitution of the peripheral positions of the porphyrin (*meso*- and *β*-). Substitution of the four *meso*-hydrogens with aryl groups gives *meso*-tetraarylporphyrins. The aryl groups are essentially orthogonal to the plane of the 18 π aromatic porphyrin macrocycle. They are much easier to synthesize than the *β*-substituted ones and easily modified with a variety of functional groups.[42]

1.5.2 Metalloporphyrins

Metalloporphyrins, with the insertion of metal atoms/ions in the center cavity of porphyrins, are commonly found in nature. Iron porphyrin is one of the best known examples as it is found in the core of hemoglobin for oxygen carriers (Figure 1.4a).[43] Four Nobel Prizes were awarded to the scientists who studied the chemistry of coenzymes B_{12} (Table 1.6),[43b] a substituted cobalt porphyrin working as rearrangement catalysts (Figure 1.4b).[43] They are important model compounds for understanding the chemical reactivities and relationships of several biologically important macromolecules.[44]
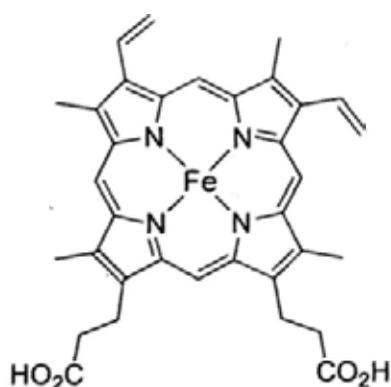
Heme group working as oxygen carriers

Figure 1.4a Structure of Heme
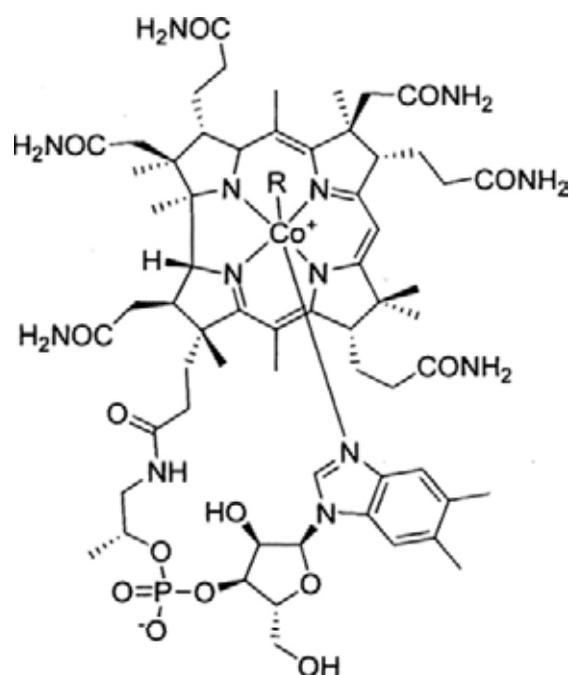
R = 5'-deoxyadenosyl, Me, OH, CN

Figure 1.4b Structure of Vitamin B_{12}

Table 1.6 Nobel laureates and their work with vitamin B_{12}

Year	Nobel Laureates	Contribution
1934	Whipple, G. H.	Discovery of vitamin B_{12}
	Murphy, W. P.	
	Dam. H. C. P.	
1957	Lord Todd, A. R.	Structure determination of vitamin B_{12}
1964	Hodgkin, D. C.	Structure determination of vitamin B_{12} (X-ray crystallography)
1965	Woodward, R. B.	Synthesis of vitamin B_{12}

Replacing the two inner pyrrole protons by metal ions, porphyrins can serve as very stable tetradentate ligands to give metalloporphyrins (eq 1.49).

$$M^{n+} + \text{porphyrin} \underset{\text{demetalation}}{\overset{\text{metalation}}{\rightleftharpoons}} \text{metalloporphyrin}^{(n-2)+} + 2H^+ \quad (1.49)$$
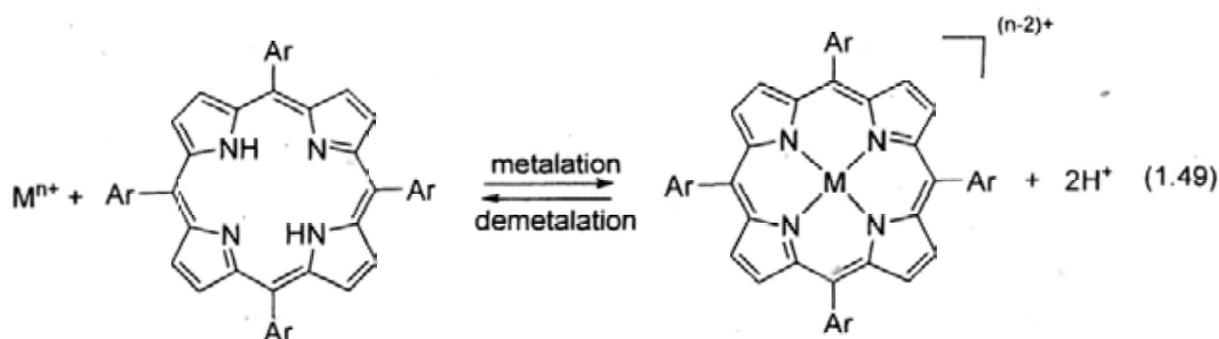
Porphyrin ligands are selective towards coordination in term of the size of metal ions. Due to the size of the central cavity of porphyrins, metals with ionic radii 60 – 70 pm, are optimally fit into the central cavity in planar coordination to give square-planar complexes.[40b,45] Therefore, the 1st row transition metal ions usually fit into the cavity. However, the 2nd and 3rd row transition metal ions have larger ionic radii and therefore form complexes with slightly out of plane structures upon coordination of porphyrins (Table 1.7, Figure 1.5). Metalloporphyrins are characterized with their intense colour (Soret band at 400 nm) and exhibit unique reactivities.[46]

in-plane coordination
(side view)

out-of-plane coordination
(side view)
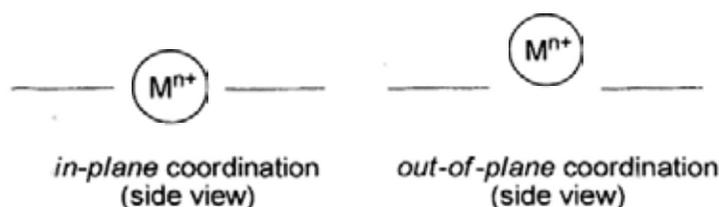
Figure 1.5 *In-plane* and *out-of-plane* coordination of metal ions with porphyrins

Table 1.7 Suitability of Various Transition Metal Ions with Porphyrin Coordination[45]

Metal ion	Ionic radius (pm)	Suitability of metal ion in complexes
Co^{2+}	82	Relatively large (out of plane)
Co^{3+}	64	Proper size
Rh^{2+}	86	Too large, out of plane
Rh^{3+}	75	Relatively large (out of plane)
Ir^{2+}	89	Too large, out of plane
Ir^{3+}	75	Relatively large (out of plane)

1.5.3 Structural Features of Metalloporphyrins

Porphyrins are aromatic tetradentate ligands which prefer a planar or nearly planar arrangement, but it has also been found to be highly flexible. Introducing steric crowding of substituents at the *meso*- and β-positions of porphyrin would result in the deformation of porphyrin in either ruffle or saddle deformation or a mixture of these two deformations (Figure 1.6).[47] The deformation of porphyrin are known to cause significant changes in the chemical and spectroscopic properties including axial ligand affinities, redox potentials, transition dipoles and red shift.[48] The enantioselectivity of catalytic epoxidation can be fine-tuned by nonplanar deformations.[48c]
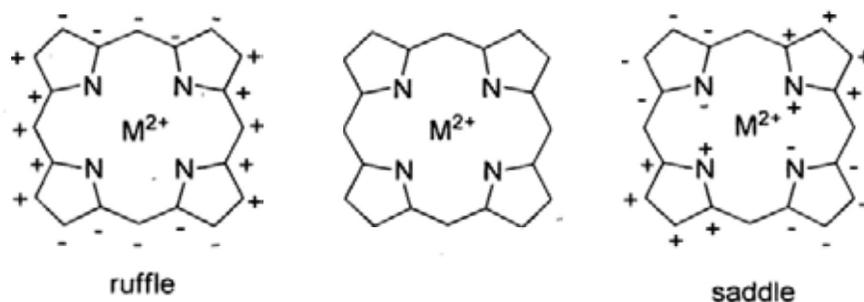
ruffle   saddle

Figure 1.6 Schematic Depiction of Ruffled and Saddled Confirmations. (The + and − indicate

displacements on opposite sides of the mean plane of the porphyrin)

1.5.4 Vacant Coordination Sites of Metalloporphyrins

As a tetradentate ligand, a porphyrin occupies the four equatorial coordination sites of

a metal center, the two axial coordination sites of metalloporphyrin are available for further

ligand coordination to form an octahedral complex. For a controlled stoichiometric or

catalytic activation of substrates there is indeed a need for two such open coordination sites:

one for substrate binding and another for the regulation of catalytic activity (e.g. using the

trans-effect).[46,49] As cis- and trans- effects on axial coordination at the metal centre affect

ligand reactivity, extensive efforts have been spent on this area.[50,51]

1.5.5 Chemistry of Metalloporphyrins

Chemists have been interested in efficient and highly selective chemical

transformations which are easily achieved in enzymatic reactions but almost impossible by

conventional synthetic methods. Learning from nature, biomimic approach, is one of the most

exciting fields in organometallic chemistry.[45,52]

Since metalloporphyrins reversibly bind to small molecules, they are promising

catalysts.[52] Metalloporphyrins have shown remarkable reactivity in various catalytic reactions,

such as amidation of alkanes (eq 1.50),[53] N-H insertion of amine (eq 1.51),[54]

28

cyclopropanation of alkenes (eq 1.52),[55] epoxidation (eqs 1.53),[56] hydroxylation (eq 1.54)[57] and oxidation of alkenes (eq 1.55).[58]

Amidation of Alkanes

$$\text{Adamantane} \xrightarrow[\substack{\text{PhI=NTs} \\ \text{CH}_2\text{Cl}_2,\ 40\ ^\circ\text{C},\ 2\ \text{h}}]{\text{Ru(tpfpp)CO (0.01 mol\%)}} \text{Adamantane-NHTs} \quad (1.50)$$

98%

Amine N-H Insertion

$$\text{Et}_2\text{NH} + \text{N}_2\text{CHCO}_2\text{Et} \xrightarrow[\substack{25\ ^\circ\text{C},\ 10\ \text{min},\ \text{CH}_2\text{Cl}_2}]{\text{Fe(tpp)Cl (1 mol\%)}} \text{Et-N(Et)-CH}_2\text{-C(O)-O-Et} \quad (1.51)$$

86%

Cyclopropanation

$$\text{Ph} + \text{N}_2\text{=C(CO}_2\text{Et)(NO}_2) \xrightarrow[\substack{-20\ ^\circ\text{C},\ 24\ \text{h},\ \text{N}_2 \\ \text{C}_2\text{H}_4\text{Cl}_2}]{\text{Co(P1) (5 mol\%)}} \text{Ph-cyclopropane-CO}_2\text{Et, NO}_2 \quad (1.52)$$

P1 = 3,5-Di-*t*-Bu-ChenPhyrin   98%, Z:E = 92:8, 92% *ee*

Epoxidation

$$\text{cyclohexene} \xrightarrow[\substack{\text{H}_2\text{O}_2,\ \text{CH}_3\text{CN/CH}_3\text{OH} \\ \text{r.t.},\ 15\ \text{min}}]{\text{Fe}^{III}(\text{tppf}_{20})\ (0.1\ \text{mM})} \text{cyclohexene oxide} \quad (1.53)$$

98%
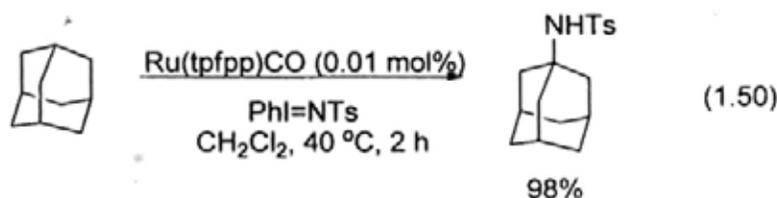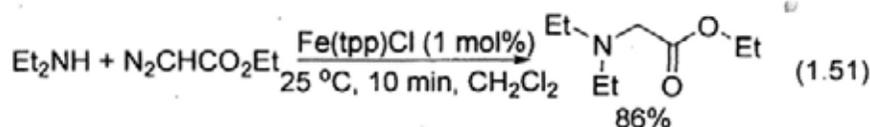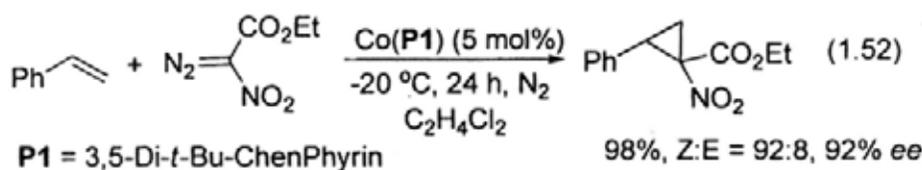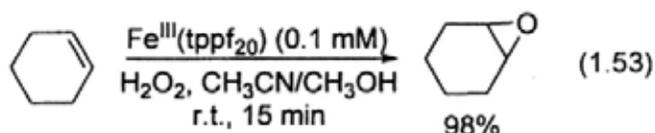
Fe^{III}(tppf$_{20}$) = 5,10,15,20-tetrakis-(2,3,4,5,6-pentafluorophenyl)porphyrinato iron(III)

Hydroxylation of Alkanes

$$\text{norbornane} \xrightarrow[\substack{\text{PFIB, CH}_2\text{Cl}_2,\ \text{rt},\ 2\ \text{min}}]{\text{Fe(tdcpBr}_8)\text{Cl (0.01 mol\%)}} \text{norbornane-OH} + \text{norbornane-OH} \quad (1.54)$$

82% (exo:endo = 6.7:1)

Oxidation of Alkene

$$\text{styrene} \xrightarrow[\substack{\text{NaIO}_4,\ \text{imidazole}, \\ 80\ ^\circ\text{C},\ 24\ \text{h}}]{\text{MnCl-(tpp)-(PEO}_{750})_4\ (0.001\text{M})} \text{benzaldehyde} \quad (1.55)$$

97%
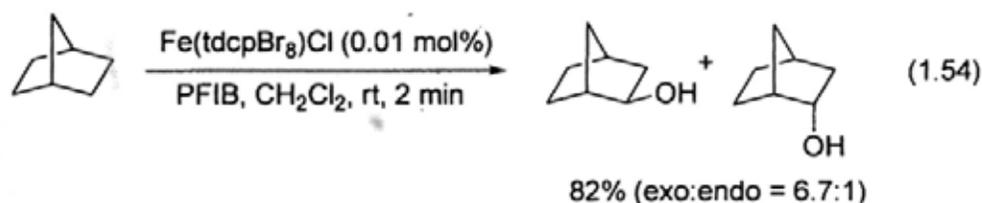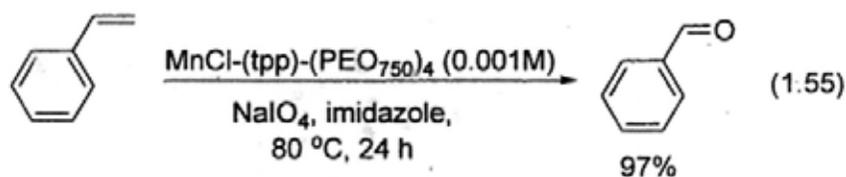
PEO$_{750}$ = CH$_3$(OCH$_2$CH$_2$)$_{16}$O- group

1.6 Chemistry of Rhodium Porphyrin Complexes

Rhodium can be easily incorporated into the porphyrin cavities by refluxing free porphyrins with rhodium(III) halides in PhCN (eq 1.56).[59,60] The most common oxidation states of rhodium are +1 and +3 while +2 is less common.[40b] Figure 1.7 shows the energy level diagrams for $Rh^I(por)$, $Rh^{II}(por)$ and $Rh^{III}(por)$ and they exhibit the reactivities of nucleophile, radical and electrophile, respectively.

$$RhCl_3 + H_2(ttp) \xrightarrow[\text{air, 3 h}]{\text{PhCN, reflux}} Rh(ttp)Cl \quad (1.56)$$
$$70\%$$
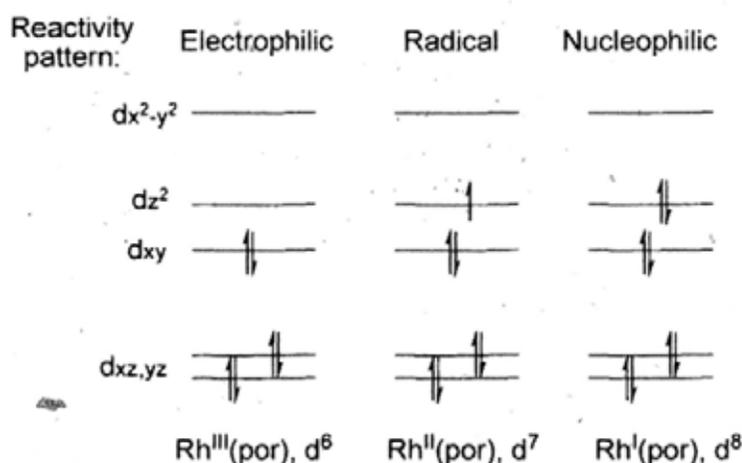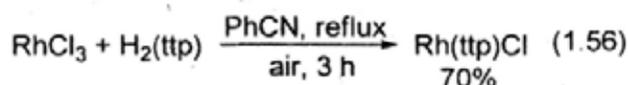
Figure 1.7 Energy Level Diagrams for Rh(por) at Various Oxidation States

1.6.1 Rh^I(por) Chemistry

$Rh^I(por)$ complexes are generally prepared by reduction of $Rh^{III}(por)$ chloride. The anionic complexes contain a pair of electron in the dz^2 orbital and therefore, react like strong nucleophiles. $Rh^I(por)$ are well known for addition reactions[60] and nucleophilic substitution.[61] Rh(por) alkyl complexes are generally prepared by the nucleophilic substitution of alkyl halides with $Rh^I(por)$ complexes (eq 1.57).[61]

$$[Rh^I(oep)]^\ominus + CH_3I \xrightarrow[\text{10 min, r.t.}]{\text{benzene}} Rh^{III}(oep)CH_3 \quad (1.57)$$
$$46\%$$
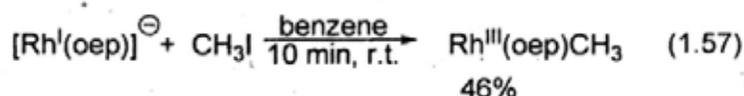
1.6.2 Rh^{II}(por) Chemistry

Rh^{II}(por) complexes have a half-filled dz^2 orbital which make them react like organic radicals and manifest unusually diverse reactions in chemistry.[40b] For less bulky porphyrins (such as ttp and oep), monomeric Rh^{II}(por) complexes equilibrate to give Rh–Rh bonded complexes since (por)Rh–Rh(por) bonds range from 12-16 kcal mol^{-1}.[17b,62] More bulky Rh^{II}(por) complexes such as tmp hardly dimerize and essentially remain monomeric form.

Wayland et al. reported the preparation of a metalloformyl porphyrin complex Rh(oep)CHO from the insertion of CO into Rh(oep)H (eq 1.58).[63] At that time, there was a lack of precedence for the insertion of CO into metal-hydride bond.[63]

$$(oep)RhH \ + \ CO \ \xrightarrow{\text{benzene}} \ (oep)RhCHO \qquad (1.58)$$
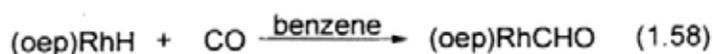
Mechanistic investigation of the CO insertion into Rh(oep)H was later carried out by Haplern et al..[64] A radical chain mechanism was proposed (Scheme 1.11). Rh$_2$(oep)$_2$, which forms from Rh(oep)H in equilibrium amount, gives Rh^{II}(oep) radical as the Rh–Rh bond is weak. Rh^{II}(oep) radical then attacks CO to generate a C–centered acyl rhodium radical and subsequent hydrogen atom abstraction from Rh(oep)H gives Rh(oep)CHO and regenerate Rh(oep) radical.

$$(oep)RhH \ \rightleftharpoons \ [Rh(oep)]_2 \ + \ H_2$$

initiation/termination : $[Rh(oep)]_2 \ \rightleftharpoons \ 2\,(oep)Rh\cdot$

propagation : $(oep)Rh\cdot \ + \ CO \ \rightleftharpoons \ (oep)Rh\dot{C}O$

$(oep)Rh\dot{C}O \ + \ (oep)RhH \ \longrightarrow \ (oep)RhCHO \ + \ (oep)Rh\cdot$
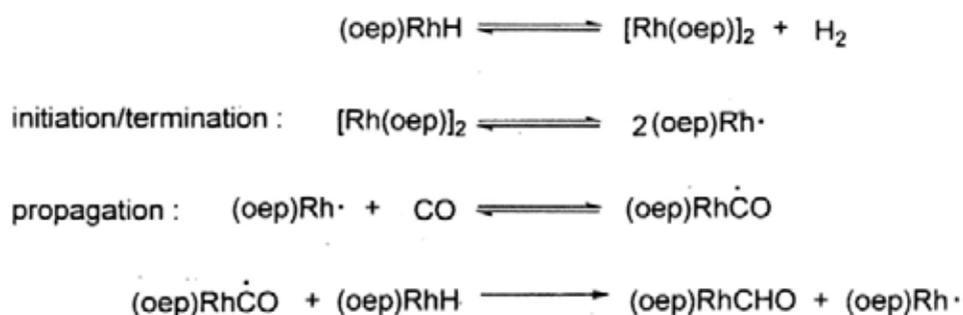
Scheme 1.11 Proposed Mechanism for CO insertion into Rh(oep)H

Monomeric Rh^{II}(por) complexes are odd electron complexes and act like radicals in various reactions. A series of Rh^{II}(por) chemistry has been reported by Wayland et al. and Chan et al.. Various chemical transformations of Rh^{II}(por) are summarized by eqs 1.59-1.71,

including Rh-Rh homolysis/dimerization (eq 1.59),[64] activation of CO (eqs 1.60 and 1.61),[65] methane activation (eq 1.62),[17b] C–H activation of toluene (eq 1.63),[17b] isocyanide activation (eq 1.64),[66] silyl cyanide oxidation addition (eq 1.65),[67] H_2 activation (eq 1.66),[68] aliphatic C–C activation (eq 1.67),[69a,b] reaction with diazo compound (eq 1.68),[69c] reductive coupling of CO (eq 1.69),[70] alkene coupling (eq 1.70)[71a] and ligand induced disproportionation (eq 1.71).[71b]

Rh-Rh Homolysis/Dimerization

$$Rh_2(oep)_2 \xrightleftharpoons{30\ ^\circ C} 2(oep)Rh \cdot \quad (1.59)$$

Activation of CO

$$Rh_2(oep)_2 + H_2 + 2CO \xrightleftharpoons{C_6D_6,\ 25\ ^\circ C} \underset{\text{quantitative}}{2Rh(oep)CHO} \quad (1.60)$$

Activation of CO

$$Rh_2(oep)_2 + H_2O + 3CO \xrightleftharpoons{C_6D_6,\ 25\ ^\circ C} \underset{\text{quantitative}}{2Rh(oep)CHO + CO_2} \quad (1.61)$$

Methane Activation

$$2(tmp)Rh \cdot + CH_4 \underset{k = 0.83\ L^2\ mol^{-2}\ s^{-1}}{\overset{353\ K,\ K = 7300}{\xrightleftharpoons{\hspace{2cm}}}} (tmp)RhH + (tmp)RhCH_3 \quad (1.62)$$

Toluene CHA

$$2(tmp)Rh \cdot + PhCH_3 \overset{353\ K}{\underset{k = 6.12 \times 10^{-2}\ L^2\ mol^{-2}\ s^{-1}}{\xrightleftharpoons{\hspace{2cm}}}} (tmp)RhH + (tmp)RhCH_2Ph \quad (1.63)$$

CNA of Isocynaides

$$Rh_2(oep)_2 + 2CNCH_3 \xrightleftharpoons{C_6D_6,\ 1\ h,\ 295\ K} (oep)Rh\text{-}CH_3 + (oep)Rh(CN)(CH_3NC) \quad (1.64)$$
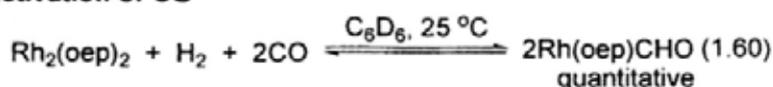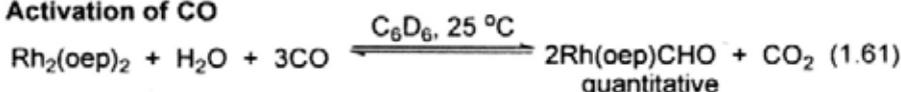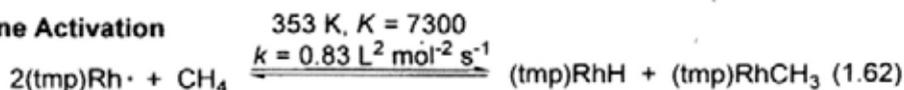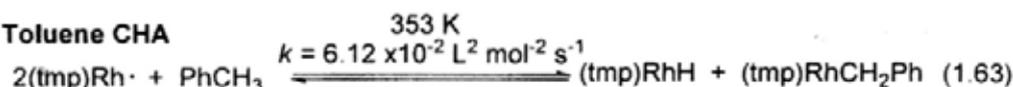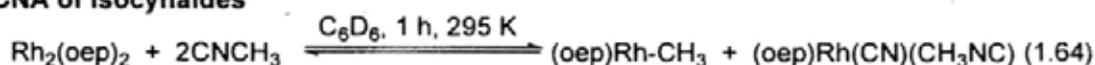
Oxidative Addition of Silyl Cyanide

$$2Rh(tmp) \cdot + Me_3SiCN + py \xrightarrow[110\ ^\circ C,\ 1h]{benzene,\ N_2} \underset{88\%}{Rh(tmp)SiMe_3} + \underset{81\%}{pyRh(tmp)CN} \quad (1.65)$$

H$_2$ Activation

$$2(tmp)Rh \cdot + H_2 \xrightarrow[k = 1.6\ L^2\ mol^{-2}\ s^{-1}]{296\ K} 2(tmp)RhH \quad (1.66)$$

Aliphatic CCA

$$(tmp)Rh \cdot + R\text{...} \xrightarrow[70\text{-}110\ ^\circ C]{C_6H_6,\ N_2} \underset{40\text{-}86\%}{(tmp)RhR} \quad (1.67)$$
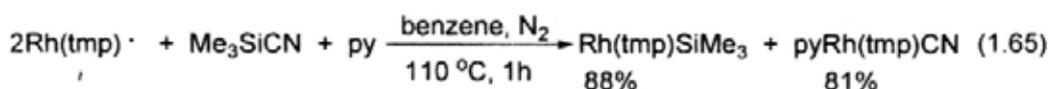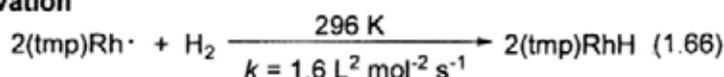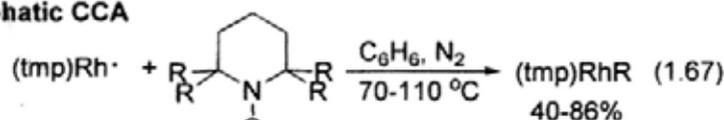
R = Me, CD$_3$, Et, Bn

Reaction with diazo complexes
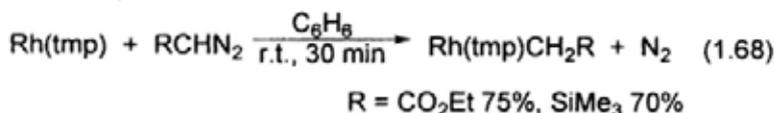
$$Rh(tmp) + RCHN_2 \xrightarrow[r.t.,\ 30\ min]{C_6H_6} Rh(tmp)CH_2R + N_2 \quad (1.68)$$

R = CO$_2$Et 75%, SiMe$_3$ 70%

Reductive Coupling of CO

$$2(tmp)Rh \cdot + 2CO \xrightarrow{25\ ^\circ C} \underset{\text{quantitative}}{Rh(pmt)\text{-}C(O)\text{-}C(O)\text{-}Rh(tmp)} \quad (1.69)$$

Alkene Coupling

$$Rh_2(oep)_2 + CH_2=CH(CO_2X) \xrightleftharpoons{2\ d,\ 300\ ^\circ C} \underset{\text{quantitative}}{(oep)RhCH_2CH(CO_2X)Rh(oep)} \quad (1.70)$$

X = H, CH$_3$, CH$_3$CH$_2$

Ligand Induced Disproportionation

$$Rh_2(oep)_2 + 2py \xrightleftharpoons{298\ K,\ K = 129} (oep)Rh(py)_2^+ + (oep)Rh^- \quad (1.71)$$

33
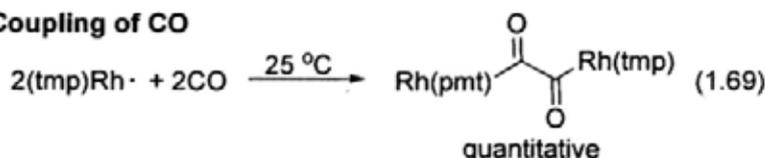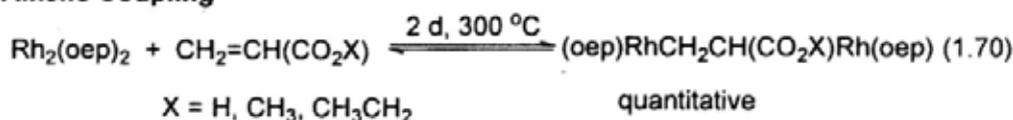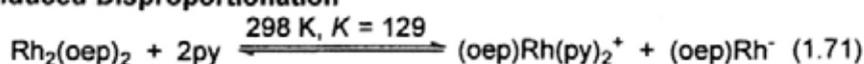
1.6.3 Rh^{III}(por) Chemistry

Rh^{III}(por) complexes have full-filled d$_{xy}$ orbital at the outermost energy level and are diamagnetic. They are usually kinetically inert and air stable. This makes Rh^{III}(por) complexes such as Rh(por) halides and alkyls serve as starting materials.

The chemistry of Rh^{III}(por) is very fruitful and various examples are summarized in eqs 1.72-1.78 including thermal decomposition (eq 1.72),[72] oxidation (eq 1.73),[72] intermolecular reductive elimination (eq 1.74),[73] alkyl 1,2-rearrangement (eq 1.75),[74] aldehydic CHA (eq 1.76),[75] base-promoted BnCCA of toluene (eq 1.77)[76] and CCA of ether (eq 1.78).[77]

Thermal decomposition
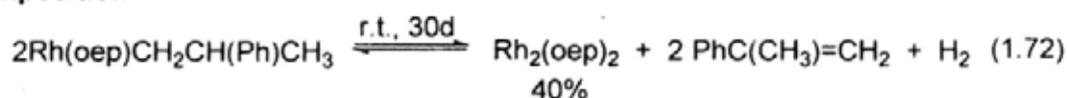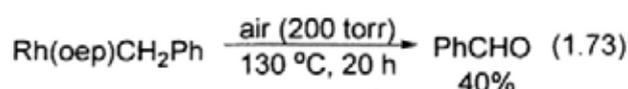
$$2Rh(oep)CH_2CH(Ph)CH_3 \xrightarrow{\text{r.t., 30d}} Rh_2(oep)_2 + 2\ PhC(CH_3)=CH_2 + H_2 \quad (1.72)$$
$$40\%$$

Oxidation

$$Rh(oep)CH_2Ph \xrightarrow[130\ °C,\ 20\ h]{\text{air (200 torr)}} PhCHO \quad (1.73)$$
$$40\%$$

Intermolecular reductive elimination

$$(oep)RhCH_2OH + (oep)RhH \xrightarrow{80\ °C,\ 8\ h} Rh_2(oep)_2 + CH_3OH \quad (1.74)$$
$$\text{quantitative} \quad \text{quantitative}$$

Alkyl 1,2-rearrangement

$$Rh(bocp)CH_2CH_2Ph \xrightarrow[80\ °C,\ 10\ h]{\text{benzene-}d_6,} Rh(bocp)CH(CH_3)Ph \quad (1.75)$$
$$87\%$$

Aldehydic CHA

$$Rh(ttp)Cl + \underset{H}{\overset{O}{\parallel}}\!\!\!-Ph \xrightarrow[1\ d]{200\ °C} (ttp)Rh\!\!-\!\!\underset{}{\overset{O}{\parallel}}\!\!\!-Ph \quad (1.76)$$
$$79\%$$

Base-promoted BnCHA

$$Rh(ttp)Cl + PhCH_3 \xrightarrow[120\ °C,\ 30\ min]{K_2CO_3\ (10\ equiv)} Rh(ttp)CH_2Ph \quad (1.77)$$
$$97\%$$
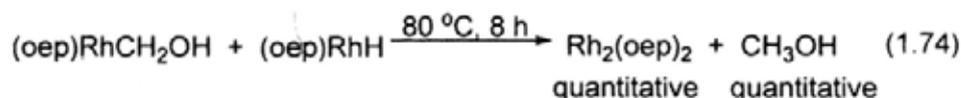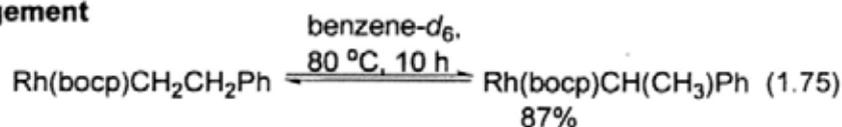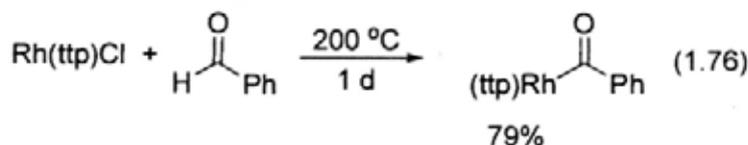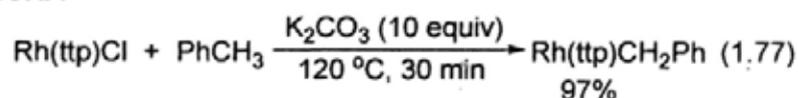
Base-Promoted CCA of Ether

$$Rh(tmp)X + (PrCH_2)_2O \xrightarrow[80\ °C.\ 1\ d,\ N_2]{KOH\ (10\ equiv)} Rh(tmp)Pr \quad (1.78)$$
$$X = I\ 53\%$$
$$= Cl\ 23\%$$
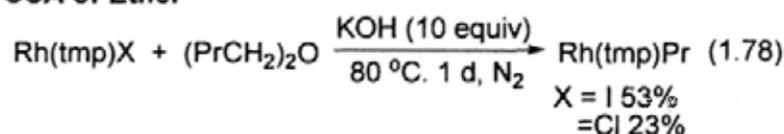
Since $Rh^{III}(por)$ has a empty dz^2 and electron deficient, four coordinated cationic $Rh^{III}(por)$ reacts like a Lewis acid or electrophile to undergo electrophilic aromatic substitution with arene (eqs 1.79 and 1.80),[78,79] electrophilic addition to alkene (eq 1.81)[80] and α-metalation of ketone (eq 1.82).[80] Besides, $Rh^{III}(por)$ are well known for catalytic cyclopropanation of alkenes (eq 1.83)[81] and catalytic Aldol condensation (eq 1.84).[80]

Electrophilic Aromatic Substitution
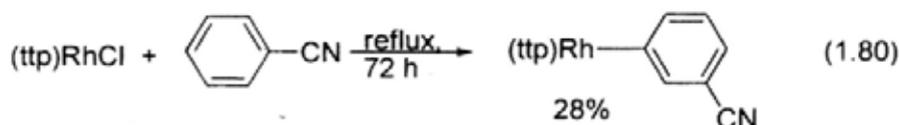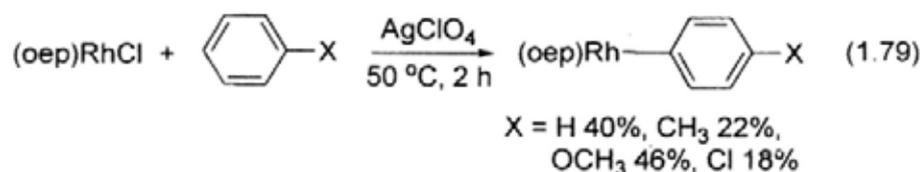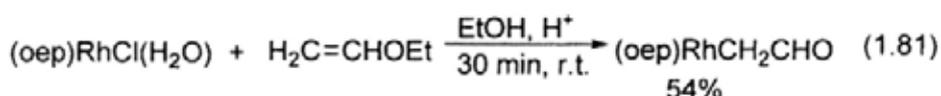
$$(oep)RhCl + \text{(arene)}-X \xrightarrow[50\,°C,\ 2\,h]{AgClO_4} (oep)Rh-\text{(arene)}-X \quad (1.79)$$

X = H 40%, CH₃ 22%,
OCH₃ 46%, Cl 18%

$$(ttp)RhCl + \text{(arene)}-CN \xrightarrow[72\,h]{reflux} (ttp)Rh-\text{(arene)}-CN \quad (1.80)$$

28%

Electrophilic Addition

$$(oep)RhCl(H_2O) + H_2C=CHOEt \xrightarrow[30\,min,\ r.t.]{EtOH,\ H^+} (oep)RhCH_2CHO \quad (1.81)$$

54%

α-Metalation of Ketone

$$(oep)RhCl + \text{ketone} \xrightarrow[50\,°C,\ N_2]{AgClO_4} (oep)Rh\text{-ketone} \quad (1.82)$$

R = H 50%, COCH₃, 70%, CO₂CH₂CH₃ 65%

Catalytic Cyclopropanation of Alkene

$$\text{(cyclohexene)} + N_2CHCO_2Et \xrightarrow[pentane,\ 20\,°C,\ 12\,h]{Rh(tmp)I\ (0.01\ mol\%)} \text{products} \quad (1.83)$$

83% (syn/anti = 1.17)

Catalytic Aldol Condensation

$$2\ \text{(cyclohexanone)} \xrightarrow[50\,°C,\ time,\ N_2]{Rh(oep)ClO_4\ (0.01\ mol\%)} \text{product} + H_2O \quad (1.84)$$

~90%
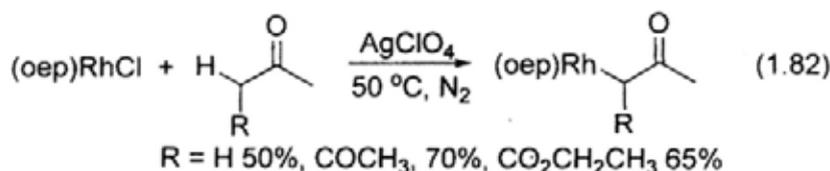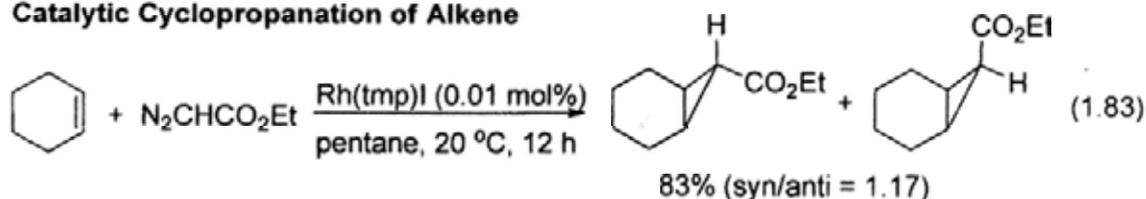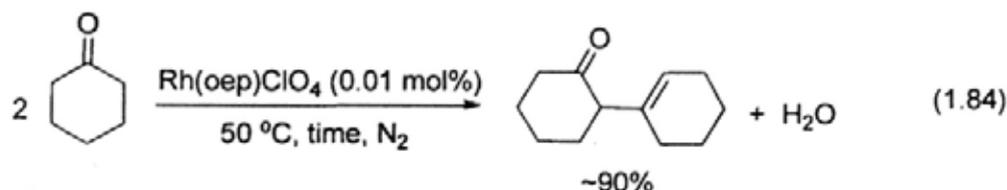
1.7 Scope of Thesis

The objectives of the research focus on the studies of the C–H and C–C activation of alkanes with rhodium porphyrin complexes. The thesis is outlined in the following sections:

(i)   base-promoted C–H activation of aliphatic alkanes and non-strained cycloalkanes with rhodium(III) porphyrin complexes

(ii)   metalloradical-promoted functionalization of cycloheptane to rhodium(III) porphyrin benzyl via C–H and C–C activations

(iii) metalloradical-promoted aliphatic C–C activation of cyclooctane

(iv)   summary of C–H and C–C activations of alkanes

Reference

(1) (a) *Comprehensive organic synthesis: selectivity, strategy & efficiency in modern organic chemistry*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York 1991. (b) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245-269. (c) Crabtree, R. H. *Dalton Trans.* **2001**, *17*, 2437-2450.

(2) Luo, Y. R. *Comprehensive Handbook of Chemical Bond Energies*, CRC Press, Boca Raton, FL, 2007.

(3) (a) Isaacs, N. S. *Physical Organic Chemistry*; Longman: Essex, 1987. (b) The BDE of C–C bonds are calculated based on the $\Delta H_{formation}$, see Stull, D. R.; Westrum, E. F. Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; John Wiley & Sons: New York 1969. (c) Exner, K.; Schleyer, P. V. R. *J. Phys. Chem. A* **2001**, *105*, 3407-3416. (d) The C–C BDE of *c*-hexane is calculated to be 82.7 kcal mol^{-1} and the literature reported value is 87.3 kcal mol^{-1}. The C–C BDE of *c*-pentane is calculated to be 82.9 kcal mol^{-1}. So, the C–C BDE of *c*-pentane is corrected by 4 kcal mol^{-1} to 86.9 kcal mol^{-1}.

(4) Goldberg, K. I.; Goldman, A. S., Eds. *Activation and Functionalization of C–H Bonds*; ACS Symposium Series 885; American Chemical Society: Washington, DC, 2004.

(5) (a) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H. *Science* **1998**, *280*, 560-564. (b) Davies, H. M. L.; Manning, J. R. *Nature* **2008**, *451*, 417-424. (c) Davies, H. M. L.; Hansen, T.; Hopper, D. W.; Panaro, S. A. *J. Am. Chem. Soc.* **1999**, *121*, 6509-6510.

(6) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507-514.

(7) (a) Jones, W. D. *Nature* **1993**, *364*, 676-677. (b) Murakami, M.; Ito, Y. *In Topics in Organometallic Chemistry, Vol. 3, Activation of Unreactive Bonds and Organic Synthesis*, Murai, S. Ed., Springer-Verlag: Berlin Heidelberg, 1999, 97-129.

(8) Sen, A. *Acc. Chem. Res.* **1998**, *31*, 550-557.

(9) Thayer, J. S. *Organometallic Chemistry. An Overview*, New York, N. Y., Weinheim: VCH Publishers, 1987.

(10) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352-354.

(11) (a) Harper, T. G. P.; Shinomoto, R. S.; Deming, M. A.; Flood, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 7915-7916.

(12) Sakakura, T.; Tanaka, M. *Chem. Lett.* **1987**, 249. Sakakura, T.; Tanaka, M. *J. Chem. Soc., Chem. Commun.*, **1987**, 758-759.

(13) (a) Burk, M. J.; Crabtree, R. H.; Parnell, C. P.; Uriarte, R. J. *Organometallics* **1984**, *3*, 816-817. Burk, M. J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 8025-8032.(b) Xu, W.; Rosini, G. P.; Gupta, M.; Jensen, C. M.; Kaska, W. C.; Krogh-Jespersen, K.; K.; Goldman, A. S. *Chem. Coumm.* **1997**, 2273-2274.

(14) (a) Chen, H.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 3391-3393. (b) Chen, H.; Schlecht, S.; Semple, T. C.; Hartwig, J. F. *Science* **2000**, *287*, 1995-1997. (c) Boller, T. M.; Murphy, J. M.; Hapke, M.; Ishiyama, T.; Miyaura, N.; Hartwig, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 14263-14278. (d) Cho, J. Y.; Tse, M. K.; Holmes, D.; Maleczka, R. E.; Smith, M. R. *Science* **2002**, *295*, 305-308.

(15) Waston, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491-6493.

(16) Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* **1984**, *56*, 1-10.

(17) (a) Wayland, B. B.; Sherry, A. E. *J. Am. Chem. Soc.* **1990**, *112*, 1259-1261. (b) Wayland, B. B.; Ba, S.; Sherry, A. E. *J. Am. Chem. Soc.* **1991**, *113*, 5305-5311.

(18) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731-8733.

(19) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729-8731.

(20) Wada, K.; Pamplin, C. B.; Legzdins, P.; Patrick, B. O.; Tsyba, I.; Bau, R. A. *J. Am. Chem. Soc.* **2003**, *125*, 7035-7048.

(21) Liu, F.; Pak, E. B.; Singh, B.; Jensen, C. M.; Goldman, A. S. *J. Am. Chem. Soc.* **1999**, *121*, 4086-4087.

(22) Ward, M. D.; Schwartz, J. *Organometallics* **1982**, *1*, 1030-1032.

(23) Ferguson, R. R.; Crabtree, R. H. *J. Org. Chem.* **1991**, *56*, 5503-5510.

(24) Gomez-Emeterio, B. P.; Urbano, J.; Diaz-Requejo, M. M.; Perez, P. J. *Organometallics* **2008**, *27*, 4126-4130.

(25) Kitajima, N.; Schwartz, J. *J. Am. Chem. Soc.* **1984**, *106*, 2220-2222.

(26) Hino, M.; Kobayashi, S.; Arata, K. *J. Am. Chem. Soc.* **1979**, *101*, 6439-6441.

(27) Waltz, K. M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2000**, *122*, 11358-11369.

(28) (a) Cassar, L.; Eaton, P. E.; Halpern, J. *J. Am. Chem. Soc.* **1970**, *92*, 3515-3518. (b) Eisch, J. J.; Piotrowski, A. M.; Han, K. I.; Kruger, C.; Tsay, T. H. *Organometallics* **1985**, *4*, 224-231. (c) Perthuisot, C.; Edelbach, B. L.; Zubris, D. L.; Jones, W. D. *Organometallics* **1997**, *16*, 2016-2023.

(29) (a) Crabtree, R. H.; Dion, R. P.; Gibboni, D. J.; McGrath, D. V.; Holt, E. M. *J. Am. Chem. Soc.* **1986**, *108*, 7222-7227. (b) Hemond, R. C.; Hughes, R. P.; Locker, H. B. *J. Am. Chem. Soc.* **1986**, *5*, 2391-2392.

(30) (a) Gozin, M.; Weisman, A.; Ben-David, Y.; Mistein, D. *Nature* **1993**, *364*, 699-670. (b) Rybtchinski, B.; Vigalok, A.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **1996**, *118*, 12406-12415. (c) van der Boom, M. E.; Liou, S. Y.; Ben-David, Y.; Gozin, M.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 13415-13421. (d) Rybtchinski, B.; Milstein, D. *Angrew. Chem. Int. Ed.* **1999**, *38*, 870-883. (e) van der Boom, M. E.; Liou, S. Y.; Ben-David, Y.; Gozin, M.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 13415-13421. (f) Rybtchinski, B.; Milstein, D.; *J. Am. Chem. Soc.* **1999**, *121*, 4528-4529.

(31) (a) Jun, C. -H. *Chem. Soc. Rev.* **2004**, *33*, 610 –618. (b) Jun, C. -H.; Moon, C. W.; Lee, D. -Y. *Chem. Eur. J.* **2002**, *8*, 2420-2428. (c) Jun, C.-H.; Chung, K.-Y.; Hong, J.-B. *Org. Lett.* **2001**, *3*, 785-787. (d) Lim, S.-G.; Lee, J. H.; Moon, C. W.; Hong, J.-B.; Jun, C.-H. *Org. Lett.* **2003**, *5*, 2759-2761. (e) Park, Y. J.; Kwon, B.-I.; Ahn, J.-A.; Lee, H.; Jun, C.-H. *J. Am. Chem. Soc.* **2004**, *126*, 13892-13893. (f) Jun, C.-H.; Lee, H.; Moon, C. W.; Hong, H.-S. *J. Am. Chem. Soc.* **2001**, *123*, 8600-8601. (g) Jun, C.-H.; Lee, H.; Lim, S.-G. *J. Am. Chem. Soc.* **2001**, *123*, 751-752. (h) Jun, C.-H.; Lee, H. *J. Am. Chem. Soc.* **1999**, *121*, 880-881.

(32) (a) Suggs, J. W.; Jun, C. H. *J. Am. Chem. Soc.* **1984**, *106*, 3054-3056. (b) Suggs, J. W.; Jun, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 4679-4681.

(33) (a) Murakami, M.; Amii, H.; Ito, Y. *Nature* **1994**, *370*, 541-542. (b) Murakami, M.; Tsuruta, T.; Ito, Y. *Angew. Chem. Int. Ed.* **2000**, *39*, 2484-2486. (c) Dreis, A. M.; Douglas, C. J. *J. Am. Chem. Soc.* **2009**, *131*, 412-413.

(34) (a) Waston, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471-6473. (b) Hajela, S.; Bercaw, J. E. *Organometallics* **1994**, *13*, 1147-1154.

(35) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *Organometallics* **1991**, *10*, 3344-3362.

(36) (a) Nishimura, T.; Ohe, K.; Uemura, S. *J. Am. Chem. Soc.* **1999**, *121*, 2645-2646. (b) Nishimura, T.; Araki, H.; Maeda, Y.; Uemura, S. *Org. Lett.* **2003**, *5*, 2997-2999.

(37) (a) Nishimura, T.; Uemura, S. *J. Am. Chem. Soc.* **2000**, *122*, 12049-12050. (b) Nishimura, T.; Yoshinaka, T.; Nishiguchi, Y.; Maeda,Y.; Uemura, S. *Org. Lett.* **2005**, *7*, 2425-2427.

(38) (a) Vidal, V.; Theolier, A.; Thivolle-Cazat, J.; Basset, J. M. *Science* **1997**, *276*, 99-102. (b) Basset, J. M.; Coperet, C.; Lefort, L.; Maunders, B. M.; Maury, O.; Le Roux, E.; Saggio, G.; Soignier, S.; Soulivong, D.; Sunley, G. J.; Taoufik, M.; Thivolle-Cazat, J. *J. Am. Chem. Soc.* **2005**, *127*, 8604-8605.

(39) Ogoshi, H.; Setsune, J. I.; Yoshida, Z. I. *J. Organomet. Chem.* **1980**, *185*, 95-104.

(40) (a) Fleischer, E. B. *Acc. Chem. Res.* **1970**, *3*, 105-112. (b) *The Porphyrin Handbook Volume 3*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: Boston, 2000. (c) *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier Scintific Pub. Co.: Mew York, 1975. (d) Ogoshi, H. Mizutani, A. *Acc. Chem. Res.* **1998**, *31*, 81-89.

(41) *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier Scientific Pub. Co.: Mew York, 1975.

(42) Shanumgathasan, S.; Edwards, C.; Boyle, R. W. *Tetrahedron* **2000**, *56*, 1025-1046.

(43) (a) *Chemistry and Biochemistry of B_{12}*; Banerjee, R., Ed.; John Wiley: New York, 1999. (b) Hodgkin, D. C.; Kamper, J.; Mackay, M.; Pickworth, J. *Nature* **1956**, *178*, 64-66. (c) *http://nobelprize.org/nobel_prizes/medicine/articles/carpenter/table.html*, Accessed on 13th March, 2010.

(44) (a) Schrauzer, G. N. *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 414-426. (b) Schrauzer, G. N. *Acc. Chem. Res.* **1968**, *1*, 97-103. *B_{12}*; Dolphin, D. Ed.; Wiley-Interscience: New York, 1982.

(45) (a) *Bioinorganic Chemistry: Inorganic Elements In The Chemistry of Life: An Introduction and Guide*; Kaim, W.; Schwederski, B., Eds.; John Wiley: New York, 1994. (b) Emsley, J. *The Elements* 3rd Ed., Clarendon Press: Oxford, 1998.

(46) (a) *The Porphyrins*; Dolphin, D., Ed.; Academic press: New York, 1979. (b) Dolphin, D.; Felton, R. H. *Acc. Chem. Res.* **1974**, *7*, 26-32.

(47) (a) Haddad, R. E.; Gazeau, S.; Pecaut, J.; Marchon, J. C.; Medforth, C. J.; Shelnutt, J. A. *J. Am. Chem. Soc.* **2003**, *125*, 1253-1268. (b) Ryeng, H.; Ghosh, A. *J. Am. Chem. Soc.* **2002**, *124*, 8099-8103.

(48) (a) Shelnutt, J. A.; Song, X.-Z.; Ma, J.-G.; Jia, S.-L.; Jentzen, W.; Medforth, C. J. *Chem. Soc. Rev.* **1998**, *27*, 31-41. (b) Ogura, H.; Yatsunyk, L.; Medforth, C. J.; Smith, K. M.;

Barkigia, K. M.; Renner, M. W.; Melamed, D.; Walker, F. A. *J. Am. Chem. Soc.* **2001**, *123*, 6564-6578. (c) Gazeau, S.; Pecaut, J.; Haddad, R. E.; Shelnutt, J. A.; Marchon, J.-C. *Eur. J. Inorg. Chem.* **2002**, 2956-2960.

(49) (a) *Chemistry and Biochemistry of B_{12}*; Banerjee, R., Ed.; John Wiley: New York, 1999.

    (b) Hodgkin, D. C.; Kamper, J.; Mackay, M.; Pickworth, J. *Nature* **1956**, *178*, 64-66.

(50) Gassman, P. G.; Ghosh, A.; Almlo, J. *J. Am. Chem. Soc.* **1992**, *114*, 9990-10000.

(51) (a) Collman, J. P.; Brauman, J. I.; Doxsee, K. M.; Sessler, J. L.; Morris, R. M.; Gibson, Q. H. *Inorg. Chem.* **1983**, *22*, 1427-1432. (b) Collman, J. P.; Boulatov, R. *J. Am. Chem. Soc.* **2000**, *122*, 11812-11821.

(52) *The Porphyrin Handbook Volume 6*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: Boston, 2000.

(53) Liang, J. L.; Yuan, S. X.; Huang, J. S.; Yu, W. Y.; Che, C. M. *Angew. Chem. Int. Ed.* **2002**, *41*, 3468-3468.

(54) Baumann, K. L.; Mbuvi, H. M.; Du, G.; Woo, L. K. *Organometallics* **2007**, *26*, 3995-4002.

(55) Zhu, S.; Perman, J. A.; Zhang, X. P. *Angew. Chem., Int. Ed.* **2008**, *47*, 8460-8463.

(56) Smeureanu, G.; Aggarwal, A.; Soll, C. E.; Arijeloye, J.; Malave, E.; Drain, C. M. *Chem. Eur. J.* **2009**, *15*, 12133-12140.

(57) Traylor, T. G.; Hill, K. W.; Fann, W.-P.; Tsuchiya, S.; Bunlap, B. E. *J. Am. Chem. Soc.* **1992**, *114*, 1308-1312.

(58) Liu, S. -T.; Reddy, V.; Lai, R. -Y. *Tetrahedron* **2007**, *63*, 1821-1825.

(59) (a) Zhou, X.; Li, Q.; Mak, T. C. W.; Chan, K. S. *Inorg. Chim. Acta* **1998**, *270*, 551-554. (b) Zhou, X.; Tse, M. K.; Wu, D.-D.; Mak, T. C. W.; Chan, K. S. *J. Organomet. Chem.* **2000**, *598*, 80-86. (c) Mak, K. W.; Yeung, S. K.; Chan, K. S. *Organometallics* **2002**, *21*, 2362-2364.

(60) Ogoshi, H.; Setsune, J.; Omura, T.; Yoshida, Z. *J. Am. Chem. Soc.* **1975**, *97*, 6461-6466.

(61) Ogoshi, H.; Omura, T.; Yoshida, Z. *J. Am. Chem. Soc.* **1973**, *95*, 1666-1668.

(62) (a) Wayland, B. B.; Coffin, V. L.; Farnos, M. D. *Inorg. Chem.* **1988**, *27*, 2745-2747. (b) Wayland, B. B. *Polyhedron* **1988**, *7*, 1545-1555.

(63) Wayland. B. B.: Woods, B. A. *J. Chem. Soc., Chem. Commun.* **1981**, 700-701.

(64) Paonessa, R. S.; Thomas, N. C.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *107*, 4333-4335.

(65) Wayland, B. B.; Woods, B. A.; Pierce, R. *J. Am. Chem. Soc.* **1982**, *104*, 302-303.

(66) Poszmik, G.; Carroll, P. J.; Wayland, B. B. *Organometallics* **1993**, *12*, 3410-3417.

(67) Chan, K. S.; Zhang, L. R.; Fung, C. W. *Organometallics* **2004**, *23*, 6097-6098.

(68) Wayland, B. B.; Ba, S.; Sherry, A. E. *Inorg. Chem.* **1992**, *31*, 148-150.

(69) (a) Tse, M. K.; Chan, K. S. *J. Chem. Soc., Dalton Trans.* **2001**, 510-511. (b) Chan, K. S.; Li, X. Z.; Dzik, W. I.; de Bruin, B. *J. Am. Chem. Soc.* **2008**, *130*, 2051-2061. (c) Zhang, L. R.; Chan, K. S. *Organometallics* **2007**, *26*, 679-684.

(70) Wayland, B. B.; Sherry, A. E.; Poszmik, G.; Bunn, A. G. *J. Am. Chem. Soc.* **1992**, *114*, 1673-1681.

(71) (a) Wayland, B. B.; Poszmik, G. *Organometallics* **1992**, *11*, 3534-3542. (b) Wayland, B. B.; Balkus, K. J., Jr.; Farnos, M. D. *Organometallics* **1989**, *8*, 950-955.

(72) De Rossi, K. J.; Wayland, B. B. *J. Am. Chem. Soc.* **1985**, *107*, 7941-7944.

(73) Van Voorhees, S. L.; Wayland, B. B. *Organometallics* **1985**, *4*, 1887-1888.

(74) Mak, K. W.; Chan, K. S. *J. Am. Chem. Soc.* **1998**, *120*, 9689-9687.

(75) Chan, K. S.; Lau, C. M. *Organometallics* **2006**, *25*, 260-265.

(76) Chan, K. S.; Chiu, P. F.; Choi, K. S. *Organometallics* **2007**, *26*, 1117-1119.

(77) Lai, T. H.; Chan, K. S. *Organometallics* **2009**, *28*, 6845-6846.

(78) Aoyama, Y.; Yoshida, T.; Sakurai, K.; Ogoshi, H. *Organometallics* **1986**. *5*, 168-173.

(79) (a) Zhou, X.; Li, Q.; Mak, T. C. W.; Chan, K. S. *Inorg. Chim. Acta* **1998**, *270*, 551-554.

(b) Zhou, X.; Tse, M. K.; Wu, D.-D.; Mak, T. C. W.; Chan, K. S. *J. Organomet. Chem.* **2000**, *598*, 80-86.

(80) Aoyama, Y.; Tanaka, Y.; Yoshida, T.; Toi, H.; Ogoshi, H. *J. Organomet. Chem.* **1987**, *329*, 251-266.

(81) (a) Callot, H. J.; Piechocki, C. *Tetrahedron Lett.* **1980**, *21*, 3489-3492. (b) Callot, H. J.; Metz, F.; Piechocki, C. *Tetrahedron* **1982**, *38*, 2365-2369.

Chapter 2   Base-promoted Carbon–Hydrogen Bond Activation of Alkanes with

Rhodium(III) Porphyrin Complexes

2.1   Carbon–Hydrogen Bond Activation by Rhodium(III) Porphyrins

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

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

The Chan group have been interested in the CHA by rhodium(III) porphyrin complexes. Rhodium porphyrin chloride can activate the *meta* C–H bond of benzonitrile to give (*m*-cyanophenyl) rhodium porphyrin complexes selectively via an S_EAr mechanism.[6] Aryl and alkyl aldehydes also undergo selective aldehydic CHA to give rhodium porphyrin

aryl and alkyl acyls.[7] Recently, Chan et al. have reported the selective benzylic CHA of toluenes promoted by base.[8] These types of CHA are mechanistically puzzling, though a heterolytic or σ-bond methathesis pathway was suggested.

2.2 Objectives of the Work

The objectives of this work are to (i) broaden the synthetic scope and (ii) to gain further mechanistic understanding of the alkyl CHA with rhodium porphyrin complexes.

2.3 Preparation of Starting Materials

2.3.1 Preparation of Porphyrins[9]

Tetraphenylporphyrin (H$_2$tpp),[9a-c] tetratolylporphyrin (H$_2$ttp)[9b,9d] and tetra-(4-*tert*-butylphenyl)porphyrin (H$_2$(btpp))[9c] were directly synthesized from the co-tetramerization of the corresponding aldehydes and pyrrole in refluxing propanoic acid for 30 min in 16%, 18% and 13% yields, respectively according to the literatures (eq 2.1).[9]

$$R = H, 16\%$$
$$R = CH_3, 18\%$$
$$R = {}^tBu, 13\%$$

(2.1)
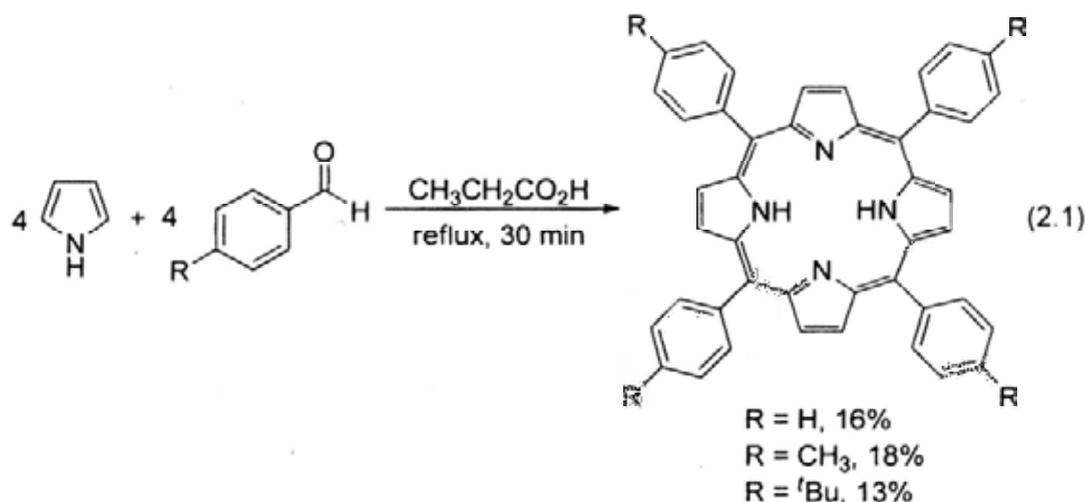
An electron-deficient porphyrin, H$_2$bocp, which bears eight chlorine atoms at the β-positions, was synthesized in three steps from H$_2$(btpp) (Scheme 2.1).[9d,10]
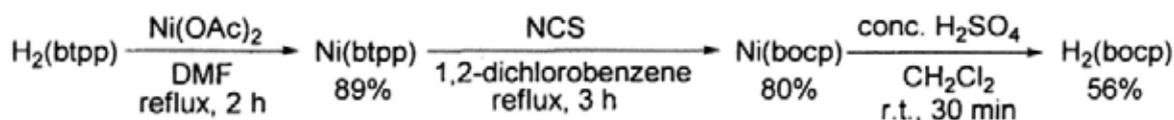
Scheme 2.1 Synthetic Procedures of H$_2$(bocp)

2.3.2 Preparation of Rhodium Porphyrin Complexes

2.3.2.1 Synthesis of Rh(ttp)Cl, Rh(tpp)Cl and Rh(bocp)Cl

Rhodium porphyrin chlorides complexes $Rh^{III}(ttp)Cl$, $Rh^{III}(tpp)Cl$ and $Rh^{III}(bocp)Cl$ were synthesized by the metallation of corresponding free porphyrin with $RhCl_3 \cdot xH_2O$ in refluxing PhCN (eq 2.2).[11]

$$RhCl_3 \cdot xH_2O + H_2(por) \xrightarrow[\text{reflux, 3 h}]{\text{PhCN}} Rh(por)Cl \quad (2.3)$$

por = ttp **1a**, 72%
por = tpp **1b**, 73%
por = bocp **1c**, 82%
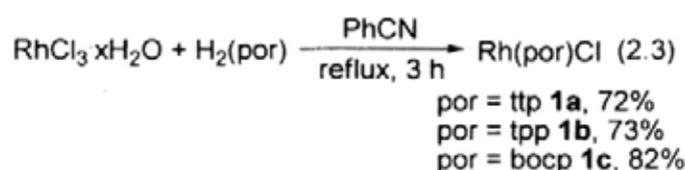
2.3.2.2 Synthesis of Rh(ttp)H

Rh(ttp)H **1d** was synthesized according to the literature method.[12] Rh(ttp)Cl **1a** was first reduced by $NaBH_4$ and then the reaction mixture was protonated by diluted HCl to give Rh(ttp)H in 80% yield (eq 2.4).

$$Rh(ttp)Cl \xrightarrow[\text{2. HCl (0.1 M)}]{\substack{\text{1. } NaBH_4/NaOH_{(aq),} \\ 50\ ^{\circ}C,\ 1\ h}} Rh(ttp)H \quad (2.4)$$
80%
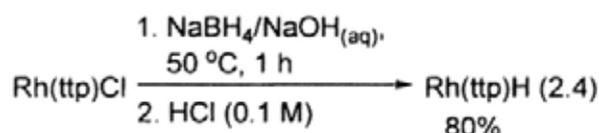
2.3.2.3 Synthesis of Rh$_2$(ttp)$_2$

Rh$_2$(ttp)$_2$ **1e** was synthesized according to the literature method.[12] Rh(ttp)H **1d** was added into degassed benzene and the red solution was irradiated at $\lambda > 445$ nm at 6-11 $^{\circ}$C for 10 hours to give Rh$_2$(ttp)$_2$ **1e** in quantitative yield and presumably hydrogen (eq 2.5).

$$Rh(ttp)H \xrightarrow[\substack{\lambda > 445\ nm \\ 6\text{-}11\ ^{\circ}C,\ 10\ h}]{\text{benzene}} Rh_2(ttp)_2 + H_2 \quad (2.5)$$
quantitative
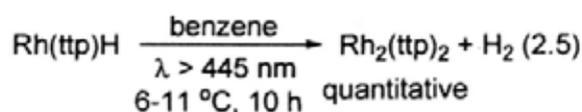
2.3.2.4 Synthesis of Rh(ttp)⁻Na⁺

Rh(ttp)⁻Na⁺ **1e** was synthesized according to the literature method.[13] Rh(ttp)Cl **1a** was dissolved in degassed benzene and then Na/Hg was added (eq 2.6). The reaction mixture was stirred at room temperature for 15 min. The resultant deep reddish brown solution was transferred via cannular under nitrogen atmosphere for subsequent reaction.

$$\text{Rh(ttp)Cl} \xrightarrow[\substack{\text{Na/Hg} \\ 25\ ^\circ\text{C, 15 min}}]{\text{benzene}} \text{Rh(ttp)}^-\text{Na}^+ \quad (2.6)$$
quantitative
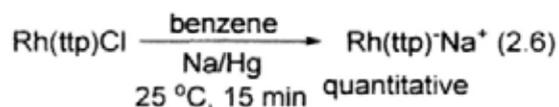
2.4   Optimization of Reaction Conditions

2.4.1   Temperature Effect

Initially, rhodium(III) tetrakis-(4-tolylporphyrin) chloride (Rh(ttp)Cl; **1a**) reacted with c-hexane at 80 °C and 100 °C for 24 hours to give a trace amount of Rh(ttp)(c-hexyl) (eq 2.7, Table 2.1, entries 1 and 2). At 120 °C for 24 hours, successful CHA of c-hexane occurred and Rh(ttp)(c-hexyl) **2a** was obtained in 31% yield (Table 2.1, entry 3). When the temperature was further increased to 150 °C or 200 °C, Rh(ttp)(c-hexyl) **2a** was obtained in lower yields of Rh(ttp)(c-hexyl) **2a** were obtained in 16% and 18%, respectively (Table 2.1, entries 4 and 5). Likely, Rh(ttp)(c-hexyl) **2a** is thermally unstable. Indeed, when Rh(ttp)(c-hexyl) **2a** was heated in c-hexane at 120 °C and 150 °C for 1 day, the recovery yields were 80% and 41%, respectively. Therefore, the optimal reaction temperature was selected to be 120 °C.

Table 2.1 Effect of Temperature on CHA of c-Hexane

$$\text{Rh(ttp)Cl} + \bighexagon \xrightarrow{\text{temp, 24 h, N}_2} \text{Rh(ttp)}\!-\!\bighexagon \quad (2.7)$$
1a   **2a**
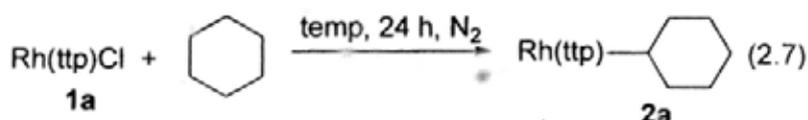
Entry	Temp (°C)	Yield (%)
1	80	Trace
2	100	3
3	120	31
4	150	16
5	200	18

2.4.2   Base Effect

With the reported based-promoted benzylic CHA of toluenes by $Rh^{III}(ttp)Cl$[8] and other examples of base promoted CHA by transition-metal complexes,[14] we sought to examine the promoting effect of various base. Table 2.2 and eq 2.8 list the results of the screenings. The ligand, PPh$_3$, only gave coordination complex **3**, without any CHA product (Table 2.2, entry 2). On the other hand, non-coordinating bases of 2,2'-bipyridine, 2,6-di-*tert*-butylpyridine, and 2,6-diphenylpyridine gave higher yield of over 50% of Rh(ttp)(*c*-hexyl) in 1 day (eq 2.8, Table 2.2, entries 3-5). However, a shorter reaction time of 6 hours resulted in much lower yield of 23% (Table 2.2, entry 6).

Table 2.2 Base Effect in CHA

$$Rh(ttp)Cl + \bigcirc \xrightarrow[120\,^{\circ}C,\ time,\ N_2]{base\ (10\ equiv)} Rh(ttp)-\hspace{-4pt}\langle\bigcirc\rangle \quad (2.8)$$

1a   **2a**
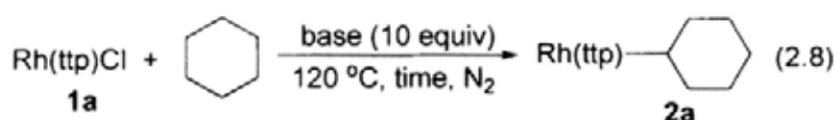
Entry	Base	Time (h)	Yield (%)
1	Nil	24	31
2	PPh$_3$	24	0[a]
3	2,2'-bpy[b]	48	50
4	2,6-dbpy[c]	24	50
5	2,6-dppy[d]	24	58
6	2,6-dppy[d]	6	23
7	NaOH	6	47
8	NaOAc	6	51
9	K$_2$CO$_3$	6	59
10	K$_2$CO$_3$	24	40

[a] Rh(ttp)Cl(PPh$_3$) **3** was obtained in 83%

[b] 2,2'-bpy = 2,2'-bipyridine; [c] 2,6-dbpy = 2,6-di-*tert*-butylpyridine; [d] 2,6-dppy = 2,6-diphenylpyridine

To our delight, nucleophilic inorganic bases were found to promote both the yields and rates of CHA (Table 2.2, entries 7-9). When NaOH was added, the reaction only took 6 hours and the yield of **2a** was 47%. NaOAc gave a slightly higher yield of 51%, and K$_2$CO$_3$

gave the highest yield of 59%. These nucleophilic bases required just 6 hours for the reaction to complete. Prolonged heating to 1 day with K_2CO_3 resulted in a lower yield of 40% (Table 2.2, entry 10). From these results, the optimal reaction conditions were found to require K_2CO_3 in 6 hours.

Table 2.3 Effect of K_2CO_3 Loading in CHA of c-Hexane

$$Rh(ttp)Cl + \bigcirc \xrightarrow[120\ ^{\circ}C,\ N_2]{K_2CO_3} Rh(ttp)-\bigcirc \quad (2.9)$$
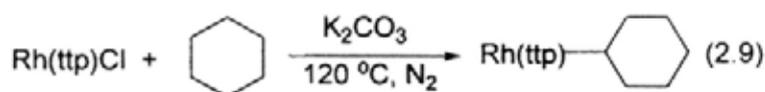
Entry	K_2CO_3 equiv	Time (h)	Yield (%)
1	Nil	24	31
2	5	24	35
3	10	6	59
4	20	6	56

The loading of base was further optimized (eq 2.9, Table 2.3). Five equivalents of K_2CO_3 increased the reaction yield slightly, but the reaction rate was not faster (Table 2.3, entry 2 vs 1). A higher loading of 10 equivalents of K_2CO_3 increased both the reaction yield and rate (Table 2.3, entry 3). However, a further increase to 20 equivalents of K_2CO_3 did not result in any further enhancement in yield (Table 2.3, entry 4). Therefore, the optimized reaction conditions were found to require 10 equiv of K_2CO_3 at 120 °C. Visual inspection of the reaction mixture showed that even 5 equiv of K_2CO_3 did not dissolve completely at 120 °C; therefore, the reaction mixture was heterogeneous.

2.4.3 Ligand Effect

The structures of porphyrin in the rhodium porphyrin chlorides affect the rates and yields of the CHA of c-hexane. The electronic effects of CHA were examined by three Rh(por)Cl species, including Rh(ttp)Cl **1a**, Rh(tpp)Cl **1b** (tpp = 5,10,15,20-tetraphenylporphyrinato dianion) and Rh(bocp)Cl **1c** (bocp = 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(p-tert-butylphenyl)porphyrinato dianion) (Table 2.4, eq 2.10). The

reaction rates followed the order of electron-deficient Rh(por)Cl: Rh(bocp)Cl > Rh(tpp)Cl > Rh(ttp)Cl (Table 2.4, entries 1-3).

Table 2.4 CHA of c-Hexane with Rh(por)Cl

$$\text{Rh(por)Cl} + \bigcirc \xrightarrow[\substack{\text{120 °C, N}_2}]{\substack{\text{K}_2\text{CO}_3 \text{ (10 equiv)}}} \text{Rh(por)}\!-\!\bigcirc \quad (2.10)$$
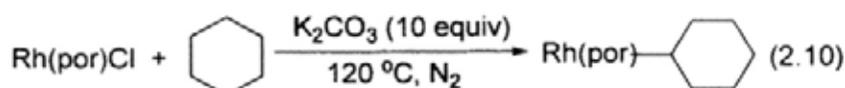
Entry	por	Time (h)	Yield (%)
1	ttp	6	2a (59)
2	tpp	5	4a (52)
3	bocp	1	4b (61)

2.5   Base-promoted CHA of Alkanes

The optimized K_2CO_3-promoted reaction conditions were successfully applied to other alkanes. c-Pentane and c-hexane gave the c-pentyl and c-hexyl complexes, in 76% and 59% yields, respectively in 6 hours (eq 2.11, Table 2.5, entries 1-2). The straight-chain alkanes reacted with Rh(ttp)Cl **1a** more slowly than c-hexane (Table 2.5, entries 3-5 vs 2). A longer time of 24 hours was required. The yields of Rh(ttp) alkyls increased with the chain length, presumably due to the observed increasing solubility of Rh(ttp)Cl **1a** in longer-chain hydrocarbons. Selective terminal CHA took place to give only the primary Rh(ttp) alkyls. While the thermal isomerization of Rh(ttp)CH$_2$CH$_2$CH$_3$ into Rh(ttp)CH(CH$_3$)$_2$ has been reported, the time to establish equilibrium requires 10 days.[15] Therefore, the isomerization of these Rh(ttp) alkyls did not occur in 24 hours.

Table 2.5 Activation of Alkanes with Rh(ttp)Cl

$$\text{Rh(ttp)Cl} + \text{R-H} \xrightarrow[\text{120 °C, time, N}_2]{\text{K}_2\text{CO}_3 \text{ (10 equiv)}} \text{Rh(ttp)-R} \quad (2.11)$$
$$\textbf{1a} \qquad\qquad\qquad\qquad\qquad\qquad \textbf{2a-e}$$
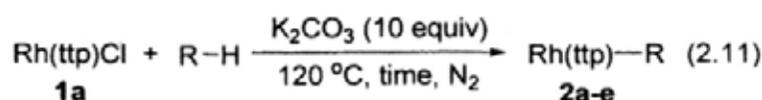
Entry	Substrate	Time (h)	Yield (%)
1	c-pentane	6	Rh(ttp)(c-hexyl) **2b** (76)
2	c-hexane	6	Rh(ttp)(c-pentyl) **2a** (59)
3	n-pentane	24	Rh(ttp)(n-pentyl) **2c** (29)
4	n-hexane	24	Rh(ttp)(n-hexyl) **2d** (40)
5	n-heptane	24	Rh(ttp)(n-heptyl) **2e** (58)

We were not able to detect any c-hexanol, c-hexyl chloride, c-hexene or c-hexanone by GC-MS analysis of the crude reaction mixture. It may be that the concentration of these species, if formed, was low in the presence of 1000 times more c-hexane.

2.6 Stability of Rh(ttp)Alkyls

In order to understand the lower yield of Rh(ttp) alkyl with longer reaction time (Table 2.3, entries 9 and 10), the thermal stability of Rh(ttp) alkyls in the presence of K_2CO_3 at 120 °C was examined and monitored by ^{1}H NMR spectroscopy.

2.6.1 Stability of Rh(ttp)(c-pentyl) with Base

Rh(ttp)(c-pentyl) **2b** and K_2CO_3 (10 equiv) were added into benzene-d_6 and the reaction mixture was heated at 120 °C for 5 days (eq 2.12, Table 2.6, Figures 2.1 and 2.2).

$$2 \text{ Rh(ttp)} \xrightarrow[\text{120 °C, 5d}]{\begin{array}{c}\text{benzene-}d_6 \\ \text{K}_2\text{CO}_3 \text{ (10 equiv)}\end{array}} \text{Rh(ttp)}^-\text{K}^+ + \text{K}^+ \quad (2.12)$$

Remaining 16%   43%   6%
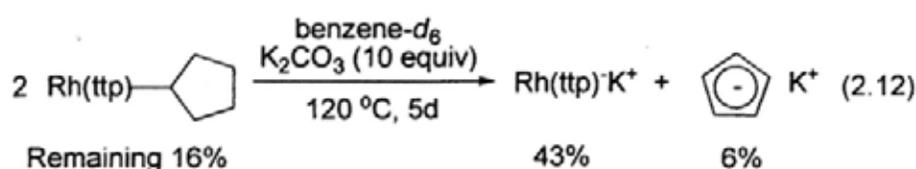
After 30 minutes of heating, the pyrrole signal of Rh(ttp)(c-pentyl) **2b** shifted up from δ 8.99 to δ 8.59 ppm and was assigned to Rh(ttp)⁻. Rh(ttp)⁻ and Rh(ttp)H were formed in 34% and

8% yields, respectively. Then after 13 hours, a small amount of cyclopentadienyl anion ^{1}H NMR signal appeared (δ 5.69 ppm). [11] After 5 days, its yield increased to 6%. When dilute aqueous HCl was added into the reaction mixture, Rh(ttp)H **1d** (δ (β-pyrrole) = δ 9.03 ppm) was observed, further supporting the formation of Rh(ttp)˙.
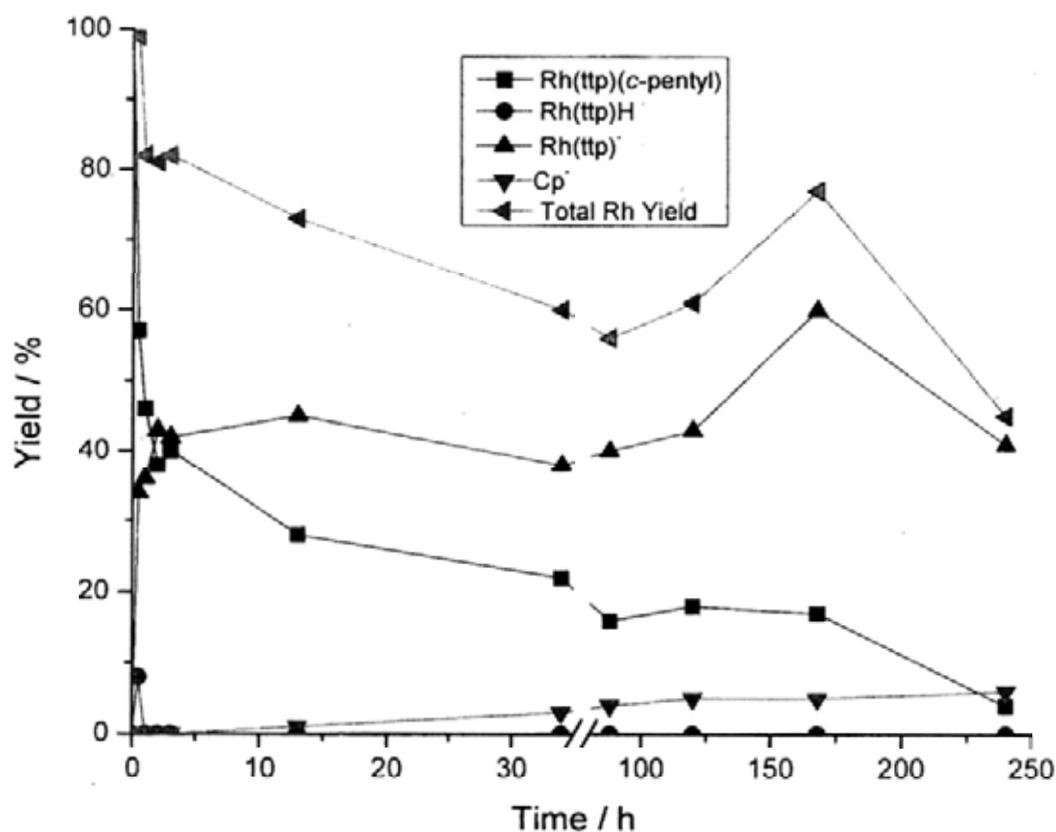
Figure 2.1 Reaction Time Profile of Decomposition of Rh(ttp)(c-pentyl) **2b**

53

Table 2.6 Reaction Time Profile of the Decomposition of Rh(ttp)(c-pentyl)

Entry	Time / h	Yield / %				
		Rh(ttp)(c-pentyl)	Rh(ttp)H	Rh(ttp)⁻	Cp⁻	Total Rh
1	0	100	0	0	0	100
2	0.5	57	8	34	0	99
3	1	46	0	36	0	82
4	2	38	0	43	0	81
5	3	40	0	42	0	82
6	13	28	0	45	1	73
7	34	22	0	38	3	60
8	88	16	0	40	4	56
9	120	18	0	43	5	61
10	168	17	0	60	5	77
11	240	4	0	41	6	45

Rh(ttp)⁻

Rh(ttp)(c-pentyl)

t = 120 h

t = 0.5 h

t = 0 h
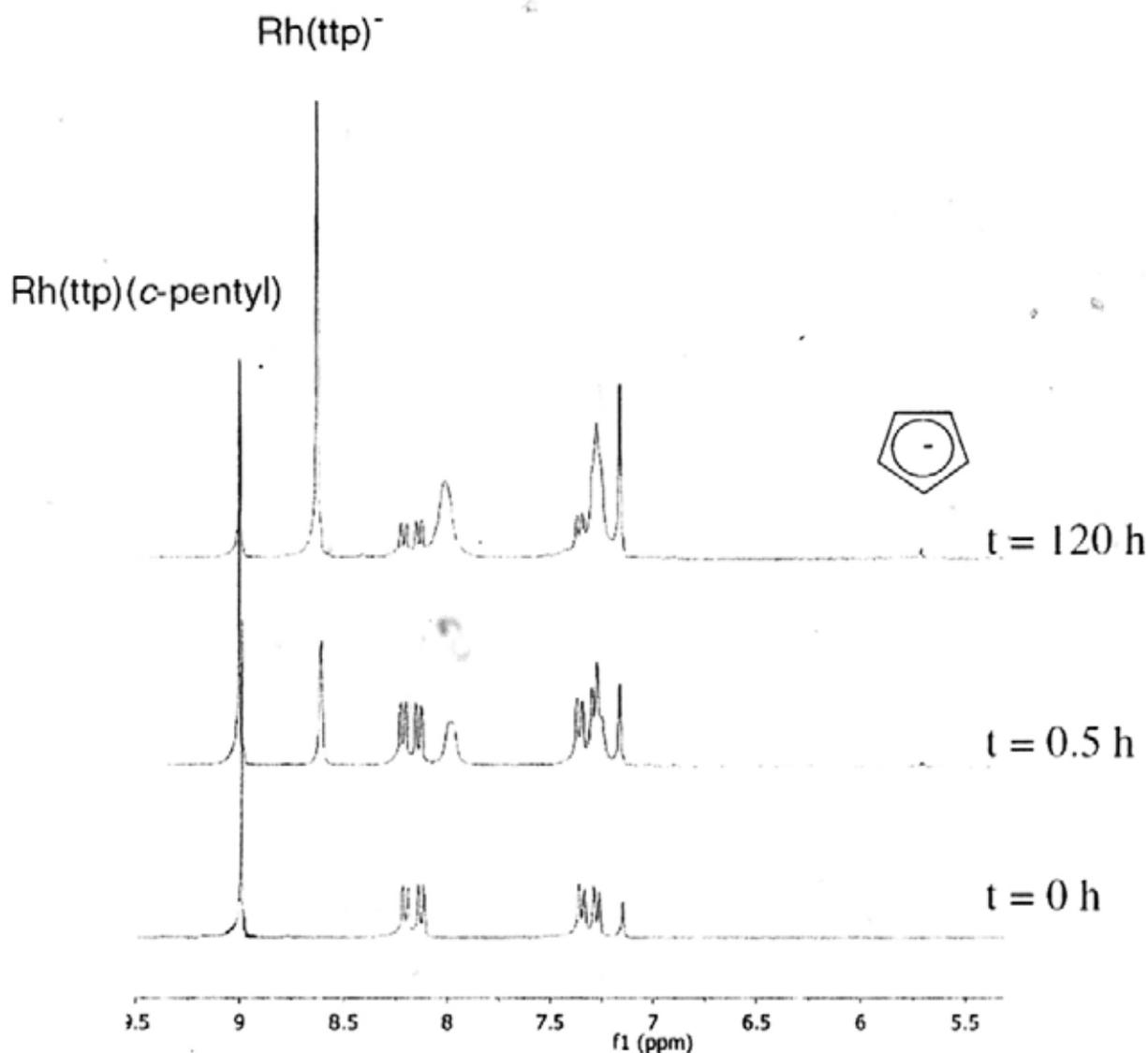
Figure 2.2 ^{1}H NMR Spectra of the Reaction Rh(ttp)(c-pentyl) with K_2CO_3 in Benzene-d_6
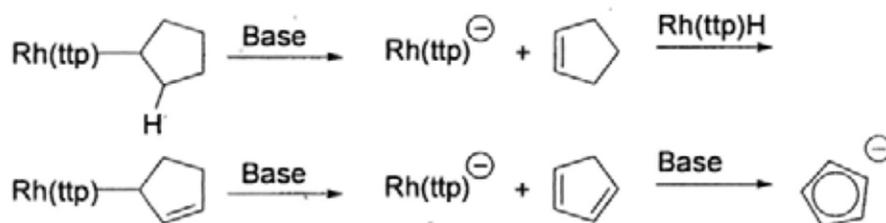
Scheme 2.2 Proposed Decomposition Pathway of Rh(ttp)(c-pentyl) **2b**

It is rationalized that K_2CO_3 abstracts the β-alkyl proton of Rh(ttp)(c-pentyl) **2b** by an

E_2 elimination to give Rh(ttp)⁻ **1e** and c-pentene (Scheme 2.2). As Rh(ttp)H **1d** is a

moderately strong acid with pK_a about 11,[16] Rh(ttp)⁻ **1e** is therefore a good leaving group.

Similar base-induced β-elimination has also been reported.[17] Then c-pentene can further undergo CHA at the allylic position and subsequent β-proton elimination to give cyclopentadiene which mostly either dimerizes or polymerizes but still yields small amount of cyclopentadienyl anion upon reaction with base.

2.6.2 Stability of Rh(ttp)(c-hexyl) with Base

Rh(ttp)(c-hexyl) **2a** was more stable than Rh(ttp)(c-pentyl) **2b** under the same basic, thermal conditions (eq 2.13). After 5 days, 27% of Rh(ttp)(c-hexyl) **2a** remained and Rh(ttp)H **1d** formed in 44% yield, presumably from the protonation of Rh(ttp)⁻ **1e** intermediate with some residual water present in solvent or K_2CO_3.

$$\text{Rh(ttp)} \underset{27\%}{-\bigcirc} \xrightarrow[\substack{120\ ^{\circ}\text{C, 5 d}}]{\substack{\text{benzene-}d_6 \\ K_2CO_3\ (10\ \text{equiv})}} \text{Rh(ttp)H} \underset{44\%}{\quad} \quad (2.13)$$

Indeed, heating Rh(ttp)(c-hexyl) **2a** with K_2CO_3 (10 equiv) in c-hexane-d_{12} at 120 °C for 5 days gave a mixture of Rh(ttp)(c-hexyl) **2a** and Rh(ttp)(c-hexyl-d_{11}) **2a**-d_{11} in 95% yield (with k_H/k_D = 22.8). Also 4% yield of benzene (with respect to Rh yield) was observed by ¹H NMR spectroscopy (eq 2.14, Figure 2.3).

$$\text{Rh(ttp)} -\bigcirc \xrightarrow[\substack{120\ ^{\circ}\text{C, 5 d}}]{\substack{c\text{-hexane-}d_{12} \\ K_2CO_3\ (10\ \text{equiv})}} \text{Rh(ttp)} -\bigcirc \Big/ -\bigcirc{}^{d_{11}} + \bigcirc \quad (2.14)$$

95%, k_H/k_D = 22.8   4%

Figure 2.3 ^{1}H NMR Spectra of the Reaction Rh(ttp)(c-hexyl) with K_2CO_3 in c-Hexane-d_{12}

The higher stability of Rh(ttp)(c-hexyl) **2a** is likely due to the smaller dihedral angle of Rh–C_α–C_β–H_β in disfavoring the <u>anti-periplanar</u> transition state of an E_2 elimination.[18] (Dihedral angles of Rh–C_α–C_β–H_β of Rh(ttp)(c-pentyl) **2b** Rh(ttp)(c-hexyl) **2a** are $131°$ and $122°$, respectively. See X-ray crystallography section 2.7.)

2.6.3 Stability of Rh(ttp)(n-hexyl) with Base

Rh(ttp)(n-hexyl) **2d** is more stable than Rh(ttp)(c-pentyl) **2b** and Rh(ttp)(c-hexyl) **2a**. Rh(ttp)(n-hexyl) **2d** underwent slower reaction to give Rh(ttp)H **1d** and n-hexene in 33% and 6% yields, respectively as well as the 1,2-rearrangement product **2d'** in 2% yield under the same reaction conditions (eq 2.15).[9d,10]
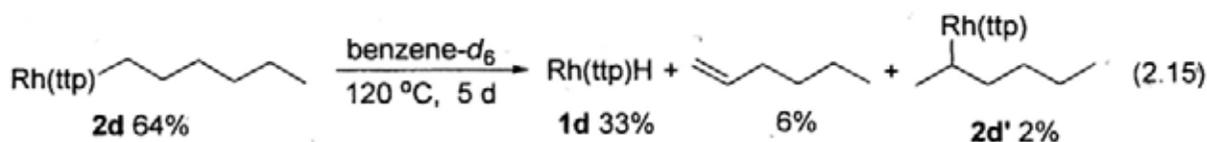
These CHA reactions further provide a facile, convenient synthesis of Rh(por) alkyls. For comparison, a previous synthesis of rhodium porphyrin alkyl was achieved by a two-step process via reductive alkylation (NaBH₄/RBr) with yields from 48-97%.[19] This synthetic route can access a variety of rhodium porphyrin alkyls directly from alkanes in one step.

2.7 X-ray Structure Determination

Table 2.7 Selected Bond lengths (Å) and Angles (deg) for Rh(por)R

Entry	Rh(ttp)R	Rh-C length (Å)	Dihedral angle between phenyl group and the mean plane (deg)	Max. deviation from 24-least sq plane (Å)	Rh-N$_{average}$ (Å)
1	Rh(ttp)(c-hexyl) **2a**	2.126(7)	80.79 (7)	0.465(4)	2.019
2	Rh(ttp)(c-pentyl) **2b**	2.073(7)	80.98 (3)	0.452(7)	2.017
3	Rh(ttp)(n-heptyl) **2e**	2.048(3)	82.25(5)	0.552(3)	2.019
4	Rh(oep)CH₃[16]	1.970(4)	----	----	2.027

Table 2.7 lists selected bond lengths and angles for complexes **2a,b,e**. Figures 2.4-2.6 show the molecular structures of **2a,b,e,** respectively (30% thermal ellipoids). The Rh–C bond lengths of **2a,b,e** range from 2.07 to 2.13 Å (Table 2.7, entries 1-3) and are similar to the reported Rh–C bond lengths of Rh(oep)Me (oep = 2,3,7,8,12,13,17,18-

octaethylporphyrinato dianion) (1.97 Å)[20] (Table 2.7, entries 4). The Rh-N_{avg} bond lengths do not vary significantly (2.017 Å - 2.019 Å). The Rh–C bond lengths appear to follow the steric size of alkyls in the order: c-hexyl > c-pentyl > n-heptyl (Table 2.7, entries 1-3). The various alkyls do not cause large distortion of the mean porphyrin plane from planarity in these complexes **2a** (0.465 Å), **2b** (0.452 Å), and **2e** (0.552 Å). The porphyrin structures of Rh(ttp)(c-hexyl) **2a**, Rh(ttp)(c-pentyl) **2b** and Rh(ttp)(n-hexyl) **2e** are slightly distorted to adopt a saddle form (Figures 2.7-2.9).
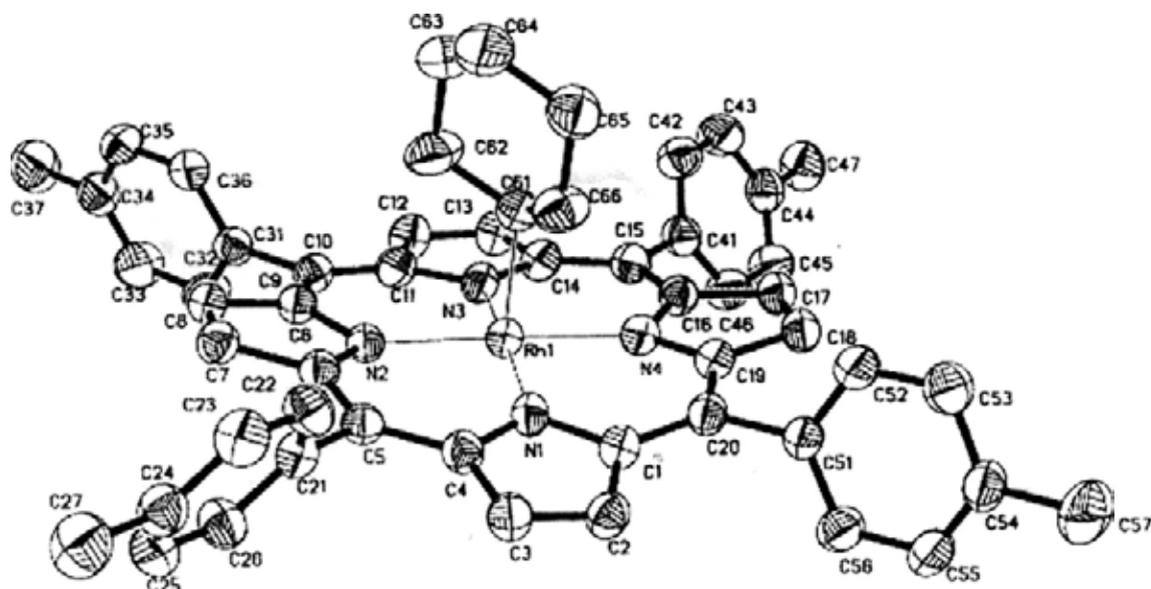
Figure 2.4 ORTEP Presentation of the Molecular Structure with Numbering Scheme for

Rh(ttp)(*c*-hexyl) **2a** (30% Probability Displacement Ellipsoids).
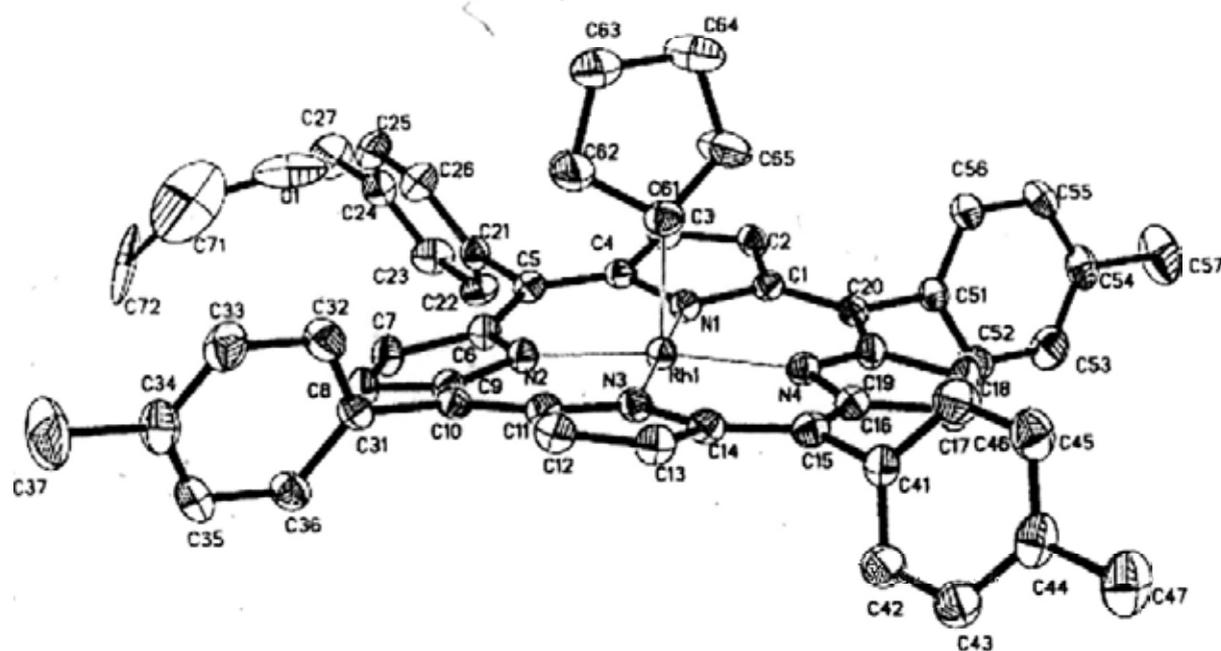
Figure 2.5 ORTEP Presentation of the Molecular structure with Numbering Scheme for

Rh(ttp)(*c*-pentyl) ·EtOH **2b** (EtOH omitted for clarity) (30% Probability Displacement
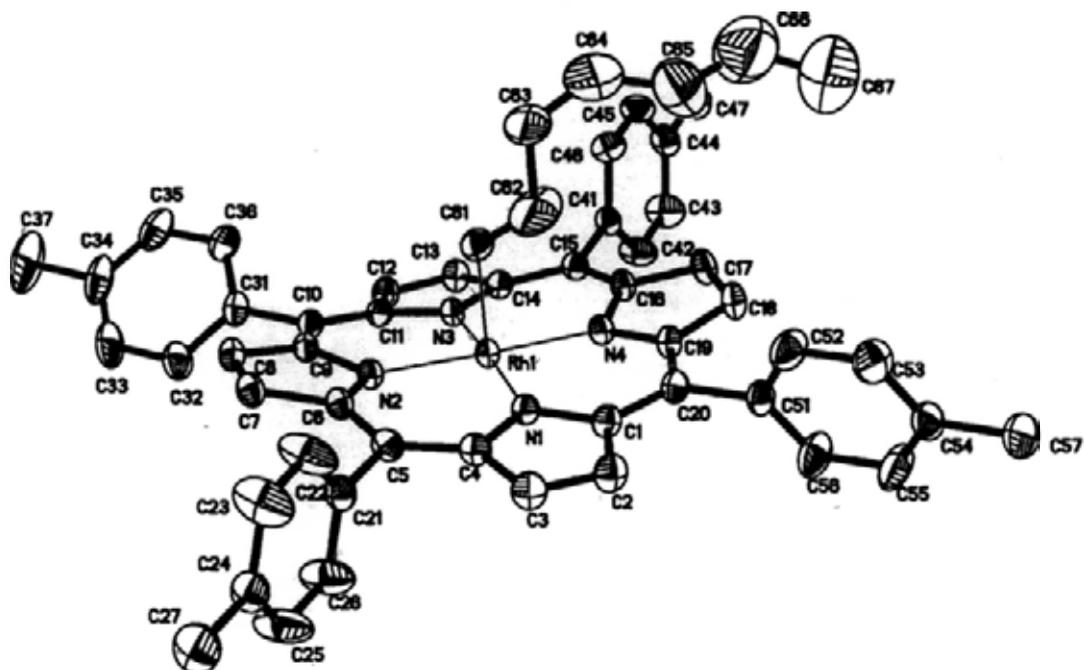
Ellipsoids).

Figure 2.6 ORTEP Presentation of the Molecular Structure with Numbering Scheme for Rh(ttp)(*n*-heptyl) **2e** (30% Probability Displacement Ellipsoids).

Figures 2.7-2.9 The conformations of porphyrins showing the displacement of the core atoms and of Rh from the 24-atom least squares plane of porphyrin core (in pm; negative values correspond to displacement towards the alkyl group). Absolute values of the angles between pyrrole rings and the least-squares plane, and angles between pyrrole rings and the least-squares plane, and angles between phenyl substituents and the least-squares plane, are shown in bold.
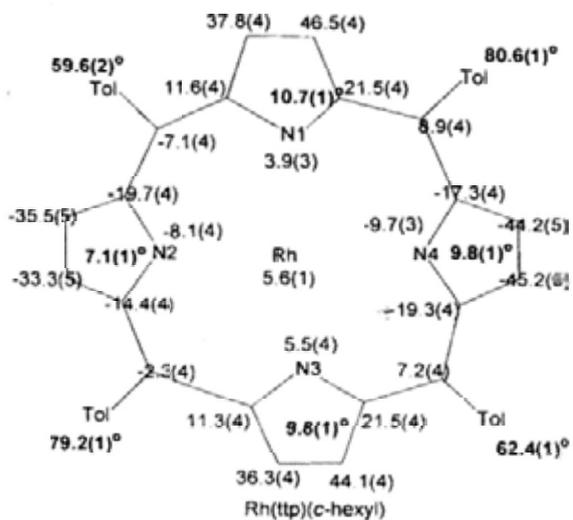
Figure 2.7a

Figure 2.7b

Rh(ttp)(c-hexyl)
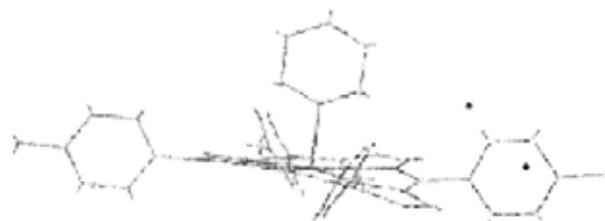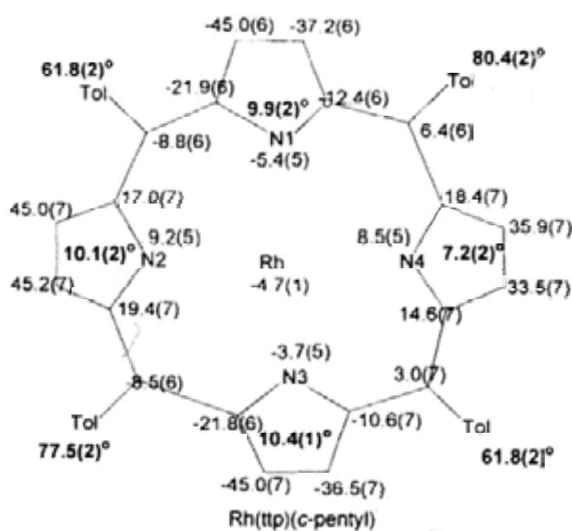
Figure 2.8a

Figure 2.8b

Rh(ttp)(c-pentyl)
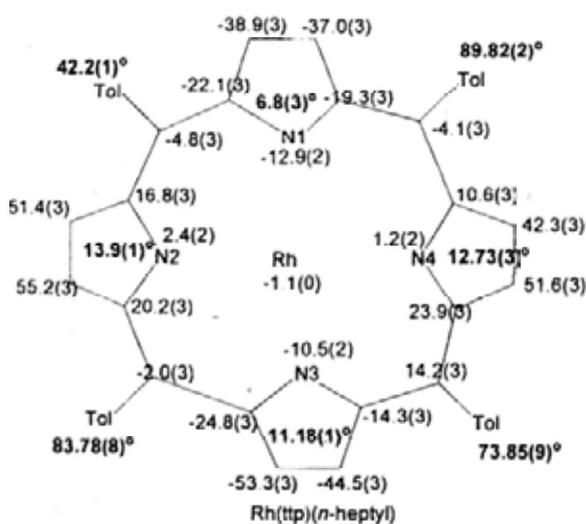
Figure 2.9a

Figure 2.9b

Rh(ttp)(n-heptyl)

2.8 Mechanistic Studies

2.8.1 Proposed Mechanism for CHA

Since Rh(ttp)Cl reacted with alkane in the absence and presence of base, scheme 2.3 shows two possible pathways for the proposed mechanism of alkyl CHA with Rh(ttp)Cl **1a**.
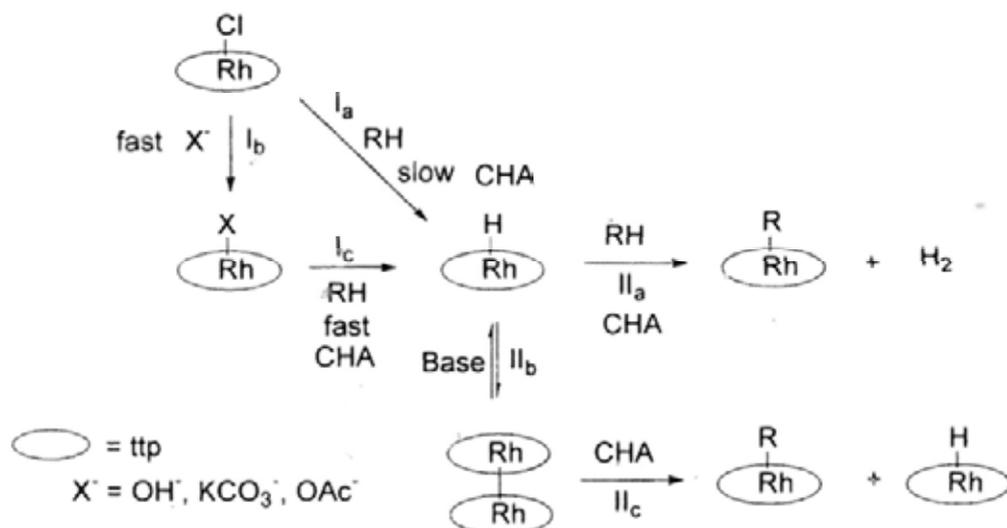
Scheme 2.3 Proposed Mechanism of Alkyl CHA with Rh(ttp)Cl

2.8.2 Alkyl CHA in the Absence of Base

Pathway I_a. In the absence of base, Rh(ttp)Cl **1a** initially undergoes heterolysis to form Rh(ttp) cation and chloride anion, most likely as an ion pair (Scheme 2.3).[6-8] An alkane then coordinates to the Rh metal center to form a C–H–Rh complex.[21] Finally, the alkyl C–H bond is cleaved to give Rh(ttp)H **1d**. The coordination of alkane to the Rh metal center is supported by the inhibition of CHA by PPh$_3$ (Table 2.2, entry 2). Upon addition of PPh$_3$, Rh(ttp)Cl **1a** did not react with c-hexane at 120 °C in 24 hours to give any Rh(ttp)(c-hexyl) **2a** (eq 2.16).

$$\text{Rh(ttp)Cl} + \text{PPh}_3 + \bigcirc \xrightarrow{\text{120 °C, 24 h}} \text{Rh(ttp)Cl(PPh}_3) \quad (2.16)$$
$$\text{quantitative}$$

When the reaction of Rh(ttp)Cl **1a** with c-hexane (50 equiv) in benzene-d_6 in a sealed NMR tube at 120 °C was traced by ^{1}H NMR spectroscopy over the course of 12 hours, no

intermediate was observed. Only Rh(ttp)H **1d** and Rh(ttp)(*c*-hexyl) **2a** were formed in 68 and

4%, respectively (eq 2.17). No stable, long-lived intermediate likely formed, suggesting

Rh(por)Cl ion pair or C–H–Rh complex is highly reactive. Furthermore, the major product is

Rh(ttp)H **1d** in benzene solvent rather than Rh(ttp)(*c*-hexyl) **2a** in *c*-hexane solvent. Probably,

the reaction of Rh(ttp)H **1d** with a slight excess of *c*-hexane is slow.

$$\text{Rh(ttp)Cl} + \underset{\text{50 equiv}}{\bigcirc} \xrightarrow[\text{120 °C, 24 h}]{\text{benzene-}d_6} \underset{68\%}{\text{Rh(ttp)H}} + \underset{4\%}{\text{Rh(ttp)}}\!\!-\!\!\bigcirc \qquad (2.17)$$

2.8.3 Base-promoted Alkyl CHA

Pathway $\mathbf{I_b}$. In the base-promoted reaction, Rh(ttp)Cl **1a** initially undergoes ligand

substitution with MX to give Rh(ttp)X (MX = NaOH, or NaOAc, or K$_2$CO$_3$). Recently,

iridium(III) hydroxide,[22a] iridium(III) alkoxide,[22b] rhodium(III) hydroxide,[22c] ruthenium(II)

hydroxide[22d] and rhodium(III) alkoxide[22e] have been reported and these ruthenium and

iridium complexes can undergo C–H activation.[22a,22b,22d] Rh(ttp)X is then rapidly reduced by

an alkane to form Rh(ttp)H **1d** which then yields the metal–metal bonded Rh$_2$(ttp)$_2$ **1e** quickly

in basic media.[23]

When the reaction mixture with K$_2$CO$_3$ in benzene-d_6 was followed by ^{1}H NMR

spectroscopy, no Rh(ttp)H **1d** but only Rh$_2$(ttp)$_2$ **1e** were observed after 30 minutes (eq 2.18,

Figure 2.10, Table 2.8). Likely, Rh(ttp)H **1d** was converted rapidly to Rh$_2$(ttp)$_2$ **1e** in a basic

medium. After 3 hours, Rh(ttp)(*c*-hexyl) **2a** slowly grew in to about 15% yield and Rh(ttp)H

1d formed quickly in up to 50% yield. The composition of the reaction mixture remained

more or less the same up to 12 hours with a major amount of Rh(ttp)H **1d** and small amounts

of Rh$_2$(ttp)$_2$ **1e** and Rh(ttp)(*c*-hexyl) **2a** present. It is likely that with a slight excess of *c*-

hexane in benzene instead of *c*-hexane as the solvent, the base promoted E$_2$ elimination of

Rh(ttp)(*c*-hexyl) **2a** becomes competitive to re-form Rh(ttp)⁻ **1e** or Rh(ttp)H **1d** after

protonation from the small amount of water present as well as forming the coproduct c-hexene. c-Hexene can also further undergo multiple CHA and E$_2$ elimination to give benzene analogous to c-pentene.

$$Rh(ttp)Cl \ + \ \bigcirc \xrightarrow[120\,°C,\ 3h]{\substack{K_2CO_3\ (10\ equiv) \\ \text{benzene-}d_6\ (1000\ equiv)}} Rh(ttp)\!-\!\!\bigcirc \ + \ Rh(ttp)H \quad (2.18)$$
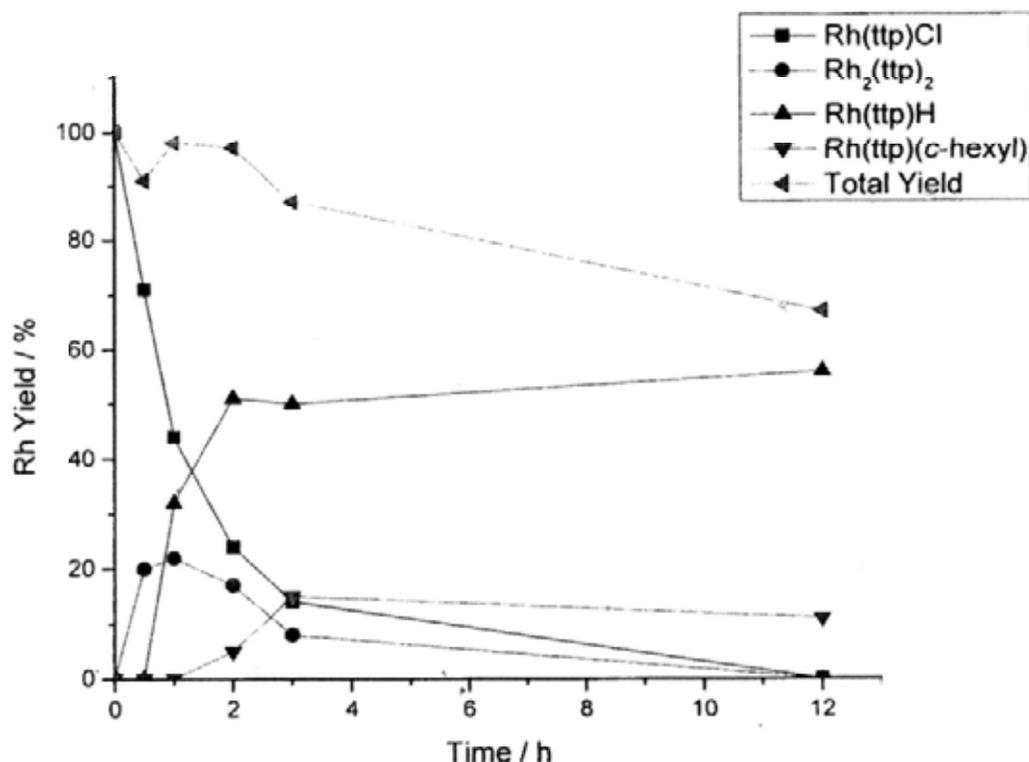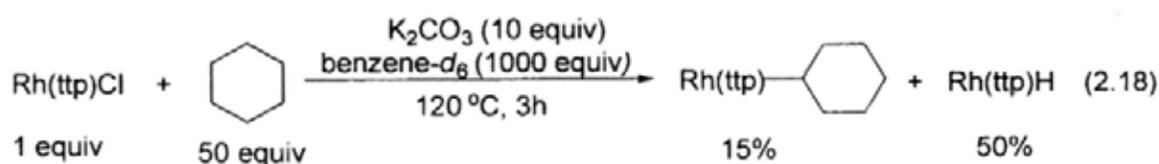
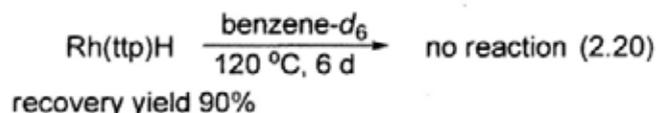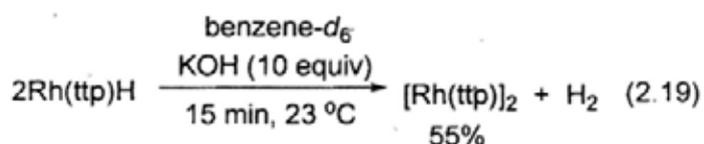1 equiv   50 equiv   15%   50%

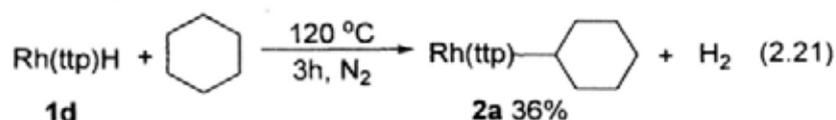Figure 2.10 Time Profile of Reaction Rh(ttp)Cl and c-Hexane with K$_2$CO$_3$.

Table 2.8 Reaction Time Profile of Rh(ttp)Cl and c-hexane with K_2CO_3

Entry	Time (h)	Yield (%)				
		Rh(ttp)Cl	$Rh_2(ttp)_2$	Rh(ttp)H	Rh(ttp)(c-hexyl)	Total
1	0	100	0	0	0	100
2	0.5	71	20	0	0	91
3	1	44	22	32	0	98
4	2	24	17	51	5	97
5	3	14	8	50	15	87
6	12	0	0	56	11	67
7	36	0	0	53	8	61
8	96	0	0	52	9	61

Independent experiment showed that $Rh_2(ttp)_2$ **1e** and presumably H_2 were formed quickly over 15 minutes at room temperature from Rh(ttp)H **1d** added with base (eq 2.19). However, Rh(ttp)H **1d** was thermally stable in the absence of base, even upon heating at 120 °C for 6 days with 90% recovery (eq 2.20). Therefore, both $Rh_2(ttp)_2$ **1e** and Rh(ttp)H **1d** can activate R–H to give Rh(ttp)R in pathways **II$_a$**, **II$_b$** and **II$_c$** (Scheme 2.3).

$$2Rh(ttp)H \xrightarrow[\substack{15\ min,\ 23\ °C}]{\substack{benzene\text{-}d_6 \\ KOH\ (10\ equiv)}} \underset{55\%}{[Rh(ttp)]_2} + H_2 \quad (2.19)$$

$$\underset{\text{recovery yield 90\%}}{Rh(ttp)H} \xrightarrow[\substack{120\ °C,\ 6\ d}]{\substack{benzene\text{-}d_6}} \text{no reaction} \quad (2.20)$$

To further understand why Rh(ttp)H **1d** did not react completely with slight excess c-hexane in benzene solvent, the thermal CHA reaction of Rh(ttp)H **1d** with c-hexane at 120 °C in 3 hours was carried out. Indeed, Rh(ttp)(c-hexyl) **2a** was formed in 36% yield and supported the intermediancy of Rh(ttp)H **1d** (eq 2.21). The low yield of Rh(ttp)(c-hexyl) **2a** in a slight excess of c-hexane is probably due to unfavorable equilibrium with limited c-hexane as well as the base-promoted or thermal β-H elimination of Rh(ttp)(c-hexyl) **2a**.

$$\text{Rh(ttp)H} + \bighexagon \xrightarrow[\text{3h, N}_2]{120\ ^\circ\text{C}} \text{Rh(ttp)}-\bigpentagon + \text{H}_2 \quad (2.21)$$

1d   **2a** 36%

2.8.4   Kinetic Isotope Effect of Alkyl CHA

To gain further information about the nature of the transition state and the possible Rh species involved (pathway I_c and II_{a-c}), the kinetic isotope effects of the CHA reaction were measured by a series of competition experiments. Rh(ttp)Cl **1a** was reacted with an equimolar mixture of c-hexane and c-hexane-d_{12} in the presence of 10 equivalents of K_2CO_3 at 120 °C in 6 hours. The ratio of Rh(ttp)(c-hexyl) **2a** to Rh(ttp)(c-hexyl)-d_{11} were determined to be 9.1:1.0 by ^{1}H NMR spectroscopy. The large kinetic isotope effect (KIE) supported the C–H cleavage step to give Rh(ttp)(c-hexyl) **2a** is involved in the rate limiting step. The observed KIE is truly a kinetic value as Rh(ttp)(c-hexyl) **2a** did not exchange with c-hexane-d_{12} under the same conditions. Likewise, the KIEs of the CHA with Rh(ttp)H **1d** and Rh$_2$(ttp)$_2$ **1e** with or without K_2CO_3 were measured to be about 9.0. (eq 2.22, Table 2.9). Rh(ttp)H was also found to be more reactive than Rh$_2$(ttp)$_2$ **1e**.

Table 2.9 KIE Values of Reactions of Rh(ttp)X with c-Hexane

$$\text{Rh(ttp)X} + \bighexagon / \bighexagon^{d_{12}} \xrightarrow[\substack{120\ ^\circ\text{C,} \\ \text{N}_2,\ \text{time}}]{\text{Base}} \text{Rh(ttp)}-\bighexagon / -\bighexagon^{d_{11}} \quad (2.22)$$

1.00   :   1.00
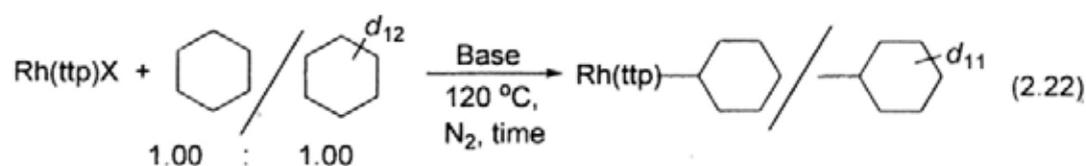
Entry	Rh(ttp)X	Base	Time (h)	KIE by ^{1}H NMR	Yield (%)
1	Rh(ttp)Cl	K_2CO_3 (10 equiv)	6	9.1±0.3[a]	32
2	Rh(ttp)H	Nil	3	8.9±0.3	54
3	Rh(ttp)H	K_2CO_3 (10 equiv)	3	8.5±0.4	59
4	Rh$_2$(ttp)$_2$	Nil	6	8.7±0.3	38
5	Rh$_2$(ttp)$_2$	K_2CO_3 (10 equiv)	6	9.0±0.3	42

[a]KIE determined by MS was 9.7(±0.2)

2.8.5 Reactivity Studies of Proposed Intermediates

To gain further support that $Rh_2(ttp)_2$ **1e** is an intermediate, the reaction of $Rh_2(ttp)_2$ **1e** with c-hexane in benzene-d_6 in a sealed NMR tube was monitored by ^1H NMR spectroscopy (eq 2.23). After 8 hours, both Rh(ttp)(c-hexyl) **2a** and Rh(ttp)H **1d** were obtained in 12 and 82% yield, respectively (eq 2.23). The much higher yield of Rh(ttp)H **1d** suggests that, even under thermal conditions, Rh(ttp)(c-hexyl) **2a** still can generate Rh(ttp)H **1d** by β-H elimination, as ascertained by the independent thermal experiment shown in eq 2.24. Therefore, $Rh_2(ttp)_2$ **1e** is confirmed to be a viable intermediate in the CHA reaction in both neutral and basic conditions. The expected coproduct, c-hexene, was not observed, and was rationalized by further rapid dehydrogenation of c-hexene to yield benzene.

Since the large values of KIEs of the CHA of CH_4 (8.6, 25 °C and 5.1, 80 °C) and of toluene (6.5, 80 °C) with Rh^{II}(tmp) (tmp = 5,10,15,20-tetramesitylporphyrinato dianion) are supportive of a bimetalloradical linear, termolecular transition state,[23] the similar magnitude of KIEs in the reaction of c-hexane with Rh(ttp) complexes suggest that Rh^{II}(ttp) also undergo similar bimetalloradical activation with c-hexane. However, the conversion of Rh(ttp)H **1d** to $Rh_2(ttp)_2$ **1e** in the absence of base is very slow; therefore, we tend to favor that both Rh(ttp)H **1d** and $Rh_2(ttp)_2$ **1e** are parallel reacting species under both neutral and basic conditions. However, we could not fully understand the high KIE value of 8.9 measured for the thermal reaction with Rh(ttp)H **1d** (Table 2.9, entry 2). The larger value of KIE can have two possible explanations, (1) the tunneling contribution and (2) the parallel reaction of Rh(ttp)H and $Rh_2(ttp)_2$ in CHA.[23]

Scheme 2.4 Branching Reaction of Carbocation

Thibblin et. al has reported that heterolysis of C–Cl bond of 1,1-diphenylethyl chloride, which is almost rate-limiting, generates a diphenylmethylcarbocation and chloride anion(Scheme 2.4). The diphenylmethylcarbocation is a common intermediate for the subsequent branching conversion of alcohol/ether via solvolysis and olefin via elimination. The expression for the isotope effects are the following:

$k_s^H/k_s^D = (k_1^H/k_1^D)(k_2^H/k_2^D)(k_{-1}^D+k_2^D+k_3^D)/(k_{-1}^H+k_2^H+k_3^H)$, where k_s is the rate of solvolysis of 1,1-diphenylethyl chloride;

$k_e^H/k_e^D = (k_1^H/k_1^D)(k_3^H/k_3^D)(k_{-1}^D+k_2^D+k_3^D)/(k_{-1}^H+k_2^H+k_3^H)$, where k_e is the rate of elimination of 1,1-diphenylethyl chloride;

As the heterolysis does not involve a C–H cleavage, the isotope effect k_1^H/k_1^D is assumed to be a secondary isotope effect and therefore has a value of $1.16 < k_1^H/k_1^D < 1.52$.[23c] Also, k_2^H/k_2^D is a secondary isotope effect since no C–H cleavage is involved. The primary isotope effect k_3^H/k_3^D should have a substantial value. Detailed mechanistic investigation suggests that fast backward heterolysis ($k_{-1} \gg k_2, k_3$) would result in enlarged kinetic isotope effect.[23b] This is because when ($k_{-1} \gg k_2, k_3$), k_e^H/k_e^D is close to $(k_1^H/k_1^D)(k_3^H/k_3^D)$, where k_1^H/k_1^D is

larger than unity. In the case of alkyl CHA, the branching reaction of $Rh_2(ttp)_2$ with c-hexane is from the common intermediate of Rh(ttp)H **1d**.

As Rh(ttp)H was shown to be a viable intermediate of the CHA reaction (eq 2.21), two detailed mechanistic possibilities, oxidative addition and σ-bond metathesis, could exist (Scheme 2.5). For the oxidative addition, a seven-coordinated Rh(V) complex (A) formed at first with three ligands R, H, and H on the same face of the porphyrin, which then undergoes reductive elimination to give Rh(ttp)R and H_2. Though Rh(V) organometallic complexes are uncommon, they can be stabilized by strongly σ-donating ligand as silyl[24] and hydride. The two *cis*-dihydrides e.g. $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiMe_3)_2]$ and $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiEt_3)_2]$[24] are not sterically demanding enough to rule out the oxidative addition pathway. Alternatively, a concerted σ-bond metathesis or its variants like σ-complex (B) assisted metathesis[25] could be a viable pathway.
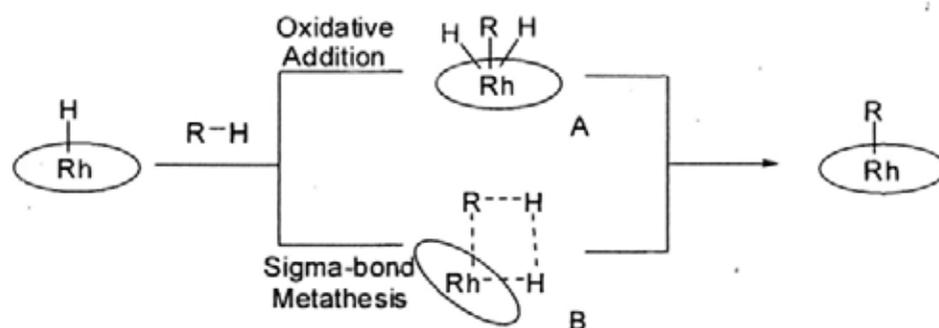
Scheme 2.5 Proposed Pathways of Alkyl CHA with Rh(ttp)H

The large KIE values of c-hexane CHA with Rh(ttp)Cl (9.1) and with Rh(ttp)H (8.9) are not typical of "normal" σ-bond metathesis process,[26] but they are similar to the KIE values of other CHA reactions involving methane-eliminating σ-bond metathetical events (8.7-9.1).[27a,b] As Rh(ttp)H **1d** reacts with c-hexane to give Rh(ttp)(c-hexyl) **2a**, it may undergo σ-bond metathesis with H_2-elimination. Such σ-bond metathesis with H_2 elimination was also be proposed in the alkane metathesis catalyzed by silica-supported tantalum hydride.[27c]

2.8.6 Recent Finding in Rh(ttp)OH

Recently, Mr Kwong Shing Choi in Chan's laboratory has discovered the base-promoted conversion of Rh(ttp)Cl to $Rh_2(ttp)_2$ via the formation of Rh(ttp)OH (Scheme2.6).[28]
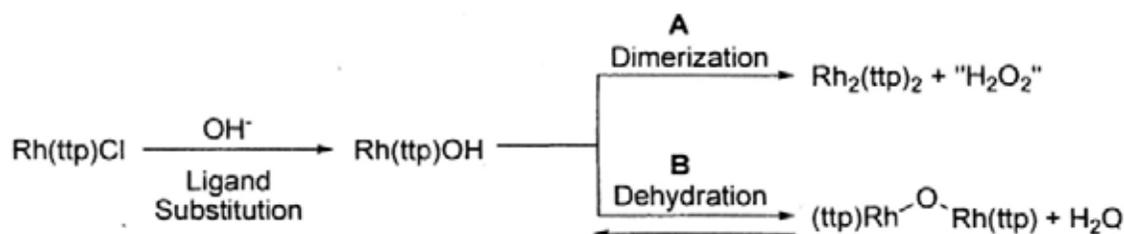
Scheme 2.6 Base-promoted reduction of Rh(ttp)Cl to $Rh_2(ttp)_2$

In the view of this finding, a new mechanism proposal is added for the elimination of $Rh_2(ttp)_2$. Rh(ttp)Cl first undergoes rapid ligand substitution with OH^- to give Rh(ttp)OH. The highly reactive Rh(ttp)OH then dimerizes via parallel pathways **A** and **B**. In pathway **A**, Rh(ttp)OH dimerizes to give $Rh_2(ttp)_2$ and H_2O_2 which disproportionates quickly to generate water and oxygen molecule. At the same time, a μ-oxo dirhodium complex is formed from intermolecular dehydration in pathway **B**. The μ-oxo dirhodium complex probably undergoes backward reaction in the presence of H_2O/OH^- and eventually gives $Rh_2(ttp)_2$.

2.9   Conclusion

Base-promoted aliphatic CHA of alkanes were achieved with rhodium(III) porphyrin complexes to give rhodium(III) porphyrin alkyls. Mechanistic investigations suggested both Rh(ttp)H **1d** and $Rh_2(ttp)_2$ **1e** are key intermediates for the parallel CHA step. The roles of base are (i) to facilitate the formation of Rh(ttp)OH; (ii) to enhance the CHA rate with alkane and generate Rh(ttp)H by more reactive Rh(ttp)X than Rh(ttp)Cl; (iii) to provide a parallel CHA pathway by $Rh_2(ttp)_2$.

References

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

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

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

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

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

(6) (a) Zhou, X.; Li, Q.; Mak, T. C. W.; Chan, K. S. *Inorg. Chim. Acta* **1998**, *270*, 551-554. (b) Zhou, X.; Wang, R-J.; Xue, F.; Mak, T. C. W.; Chan, K. S. *J. Organomet. Chem.* **1999**, *580*, 22-25. (c) Zhou, X.; Tse, M. K.; Wu, D.-D.; Mak, T. C. W.; Chan, K.S. *J. Organomet. Chem.* **2000**, *598*, 80-86.

(7) Chan, K. S.; Lau, C. M. *Organometallics* **2006**, *25*, 260-265.

(8) Chan, K. S.; Chiu, P. F.; Choi, K. S, *Organometallics* **2007**, *26*, 1117-1119.

(9) (a) Wagner, R. W.; Lawrence, D. S.; Lindsey, J. S. *Tetrahedron Lett.* **1987**, *28*, 3069-3070. (b) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476-477. (c) Alder, A. D.; Longo, F. R.; Shergalis, W. *J. Am. Chem. Soc.* **1964**, *86*, 3145-3149. (d) Mak, K. W.; Chan, K. S. *J. Am. Chem. Soc.* **1998**, *120*, 9686-9687. (e) Chan, K. S.; Mak, K. W.; Tse, M. K.; Yeung, S. K.; Li, B. Z.; Chan, Y. W. *J. Orgomet. Chem.* **2008**, *693*, 399-407.

(10) Mak, K. W.; Xue, F.; Mak, T. C. W.; Chan, K. S. *J. Chem. Soc., Dalton Trans.* **1999**, *19*, 3333-3334.

(11) Buchler, J. W.; Dreher, C.; Kunzel, F. M. *In Metal Complexes with Tetrapyrrole Ligands III: Structure and Bonding, vol. 84*; Buchler, J. W.; Ed.; Springer-Verlag: Berlin Heideelberg, 1995.

(12) Wayland, B. B.; Van Voorhees, S. L. Wilker, C. *Inorg. Chem.* **1986**, *25*, 4039-4042.

(13) (a) Tse, A. K.S.; Wu, B. M.; Mak, T. C. W.; Chan, K. S. *J. Organomet. Chem.* **1998**, *568*, 257-261. (b) Dolphin, D.; Halko, D. J.; Johnson, E. *Inorg. Chem.* **1981**, *20*, 4348-4351.

(14) (a) Liang, L. C.; Lin, J. M.; Lee, W. Y. *Chem. Comm.* **2005**, *19*, 2462-2464. (b) Harkins, S. B.; Peters, J. C. *Organometallics* **2002**, *21*, 1753-1755. (c) Wang, C.; Ziller, J. W.; Flood, T. C. *J. Am. Chem. Soc.* **1995**, *117*, 1647-1648.

(15) Mak, K. W.; Xue, F.; Mak, T. C. W.; Chan, K. S. *J. Chem. Soc., Dalton Trans.* **1999**, *19*, 3333-3334.

(16) Nelson, A. P.; Dimagno, S. G. *J. Am. Chem. Soc.* **2000**, *122*, 8569-8570.

(17) Sanford, M. S.; Groves, J. T. *Angew. Chem. Int. Ed.* **2004**, *43*, 588-590.

(18) March, J. *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, 3rd Edition, Wiley: New York, **1985**.

(19) (a) Brothers, P. J.; Collman, J. P. *Acc. Chem. Res.* **1986**, *19*, 209-215. (b) Lexa, D.; Mispelter, J.; Saveant, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 6806-6812. (c) Perree-Fauvent, M.; Gaudemer, A.; Boucly, P.; Devynck, J. *J. Organomet. Chem.* **1976**, *120*, 439-451. (d) Chan, K. S.; Mak, K. W.; Tse, M. K.; Yeung, S. K.; Li, B. Z.; Chan, Y. W. *J. Organomet. Chem.* **2008**, *693*, 399-407.

(20) Whang, D. M.; Kim, K. M. *Acta Cryst. C* **1991**, *47*, 2547-2550.

(21) Bengali, A. A.; Schultz, H.; Moore, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 9369-9377.

(22) (a) Tenn, W. J.; Young, K. J. H.; Oxgaard, J.; Nielsen, R. J.; Goddard, W. A.; Periana, R. A. *Organometallics* **2006**, *25*, 5173-5175. (b) Oxgaard, J.; Tenn, W. J.; Nielson, R. J.; Periana, R. A.; Goddard, W. A. *Organometallics* **2007**, *26*, 1565-1567. (c) Fu, X. F.; Wayland, B. B. *J. Am. Chem. Soc.* **2004**, *126*, 2623-2631. (d) Feng, Y.; Lail, M.; Barakat, K. A.; Cundari, T. R.; Gunnoe, T. B.; Peterson, J. L. *J. Am. Chem. Soc.* **2005**, *127*, 14174-14175. (e) Collman, J. P.; Boulatov, R. *Inorg. Chem.* **2001**, *40*, 560-563.

(23) (a) Wayland, B. B.; Ba, S.; Sherry, A. E. *J. Am. Chem. Soc.* **1991**, *113*, 5305-5311. (b) Thibblin, A.; Sidhu, H. *J. Am. Chem. Soc.* **1992**, *114*, 7403-7407. (c) Values of $1.10\pm0.05/\beta$-D have been reported; Westaway, K. C. *Isotopes in Organic Chemistry*; Buncel, E.; Lee, C. C., Eds.; Elsevier: Amsterdam 1987.(d) Kwart, H. *Acc. Chem. Res.* **1982**, *15*, 401-408.

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

(25) Perutz, R. N.; Sabo-Etienne, S. *Angew. Chem. Int. Ed.* **2007**, *46*, 2578-2592.

(26) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203-219.

(27) (a) Zhang, S.; Piers, W. E.; Gao, X.; Parvez, M. *J. Am. Chem. Soc.* **2000**, *122*, 5499-5509. (b) Conroy, K. D.; Hayes, P. G.; Piers, W. E.; Parvez, M. *Organometallics* **2007**, *26*, 4464-4470. (c) Basset, J. M.; Coperet, C. ; Lefort, L. ; Maunders, B. M.; Maury, O.; Le Roux, E.; Saggio, S.; Soulivong, D.; Sunley, G. J. ; Taoufik, M.; Thivolle-Cazat, J. *J. Am. Chem. Soc.* **2005**, *127*, 8604-8605.

(28) Kwong Shing Choi's unpublished results, 2010.

Chapter 3   Metalloradical-promoted Functionalization of Cycloheptane to Rhodium Porphyrin Benzyl via C–H and C–C Bond Activation

3.1   Introduction

3.1.1   Properties of Cycloheptane

c-Heptane is a colourless combustible liquid at ambient conditions. It is readily miscible with ethanol and ether but insoluble in water.[1a] The lowest-energy conformational isomer is a twisted chair form, which is very fluxional (fluxional energy = 8.2 kcal mol^{-1}) (Figure 3.1).[1b] Some other properties concerning the reactivity of *c*-heptane are summarized in Table 3.1.
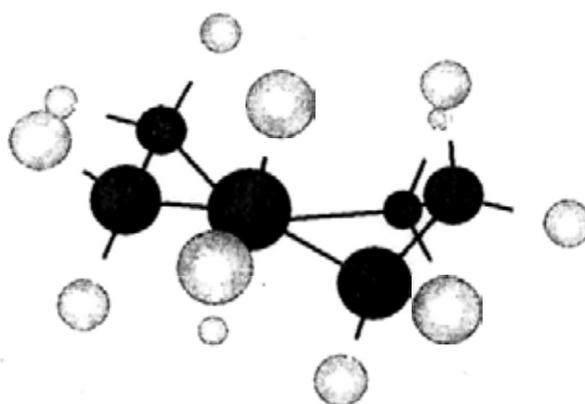
Figure 3.1 Ball and Stick Model of *c*-Heptane (twisted chair form)

Table 3.1 Properties Concerning the Reactivity of *c*-Heptane[2-4]

Properties	Corresponding Value
BDE of C–H	94.0 kcal mol^{-1}
BDE of C–C	86.6 kcal mol^{-1}
Ring Strain	6.3 kcal mol^{-1}
Diamagnetic Susceptibility	-73.9 x 10^{-6} cm^3 mol^{-1}
Dielectric Constant	2.0784 at 20.0 °C

3.1.2 CHA of Cycloheptane

c-Heptane is well known to undergo transition-metal catalyzed CHA including amination,[5] C–C formation,[6] dehydrogenation[7] and oxidation (eqs 3.1-3.4).[8]
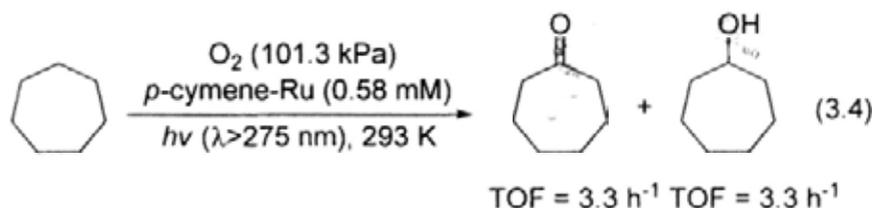
Amination

(S)-nta = (S)-N-1,8-naphthoylalanine

$$Rh_2\{(S)\text{-nta}\}_4 \text{ (3 mol\%)}$$
$$PhI(OCOtBu)_2 \text{ (1.4 equiv)}$$
$$(Cl_2CH)_2/MeOH: 3/1$$
$$-35\ ^\circ C,\ 3\ d$$

96%

(3.1)

C-C Formation

2 (7.4 mmol) + (0.5 mmol)

Sc(OTf)$_3$ (0.025 mmol)
tBuOOtBu (1.0 mmol)
135 $^\circ$C, 16 h, air

71%

(3.2)

Dehydrogenation

RhCl(CO)(PMe$_3$)$_2$ (0.4 mM)
H$_2$ (1000 psi)
60 $^\circ$C, 100 min

TON = 53   TON = 230

(3.3)

Oxidation

O$_2$ (101.3 kPa)
p-cymene-Ru (0.58 mM)
hv (λ>275 nm), 293 K

TOF = 3.3 h^{-1} TOF = 3.3 h^{-1}

(3.4)
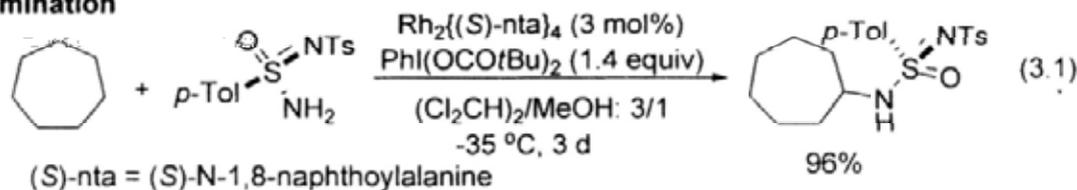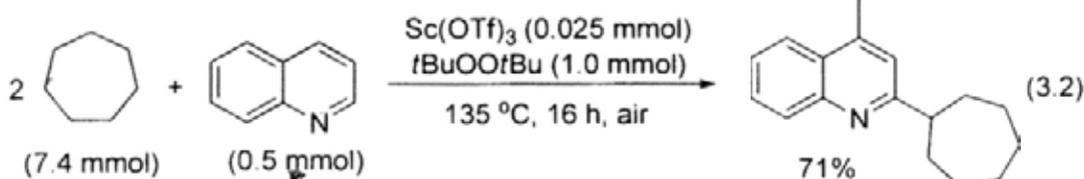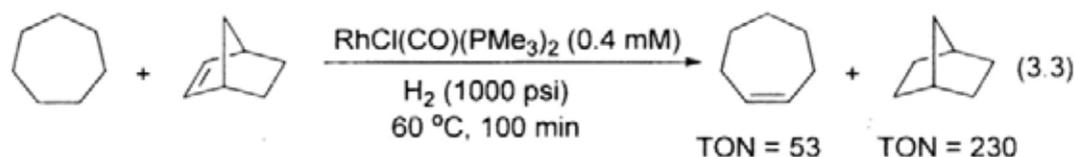
3.1.3 CCA of Cycloheptane

By contrast, the C–C bond of c-heptane is more reluctant to cleave by transition-metal complexes and consequently, there are very limited CCA examples. Aliphatic C–C bond of c-heptane is weaker than C–H bonds by around 8 kcal mol^{-1}.[2] However, the aliphatic C–C bond is shielded by C–H bonds and this makes the transition-metal complex difficult to access the C–C bond.[9] Recently, Basset et al. reported the hydrogenolysis of c-heptane catalyzed by tantalum hydride complex supported on silica to give a mixture of acyclic alkanes and cyclic alkanes (eq 3.5).[10]

$$\text{c-heptane} + H_2 \xrightarrow[160\ ^\circ C,\ 50\ h]{\text{cat. } [(\equiv SiO)_2 Ta-H]} CH_4 + C_2H_6 + C_3H_8 + \text{c-hexane} + \text{methylcyclohexane} + \text{others} \quad (3.5)$$

CH$_4$	C$_2$H$_6$	C$_3$H$_8$		
45%	20%	5%	20%	5%

The hydrogenolysis of c-heptane possibly undergoes a series of alkane metathesis via the formation of hydrido-tantallacarbenes.[11] The major drawback of the reaction system is the poor selectivity which leads to the formation of many products.

3.2 Objectives of the Work

The objectives of this work are to (i) broaden the synthetic scope and (ii) to gain further mechanistic understanding of the alkyl CHA and CCA with rhodium porphyrin complexes.

3.3 Discovery of CCA of c-Heptane

After the investigation of base-promoted CHA of alkane with c-pentane and c-hexane, the substrate was extended to c-heptane. Initially, c-heptane was found to react with Rh(ttp)Cl **1a** to give Rh(ttp)(c-heptyl) **5a** in 18% yield as the sole CHA product while 70% yield of Rh(ttp)Cl was recovered (eq 3.6). However, when K$_2$CO$_3$ was added, Rh(ttp)(c-heptyl) **5a**, the CCA product, Rh(ttp)Bn **5b**, and Rh(ttp)H **1d** were formed in 30%, 25% and 30% yields, respectively.

$$\text{Rh(ttp)Cl} + \text{c-heptane} \xrightarrow[120\ ^\circ C,\ N_2]{\text{additives}} \text{Rh(ttp)(c-heptyl)} + \text{Rh(ttp)Bn} + \text{Rh(ttp)H} \quad (3.6)$$

1a recovered			5a	5b	1d	Total Yield
70%	no base	24 h	18%	0%	0%	88%
0%	K$_2$CO$_3$ (10 equiv)	6 h	30%	25%	30%	85%

Since the thermal conversion of c-heptane to toluene takes place slowly at 360 $^\circ$C (eq 3.7),[12] the formation of Rh(ttp)Bn **5b** likely comes from Rh(ttp)(c-heptyl) **5a**.

$$\text{(3.7)}$$

3.4 Mechanistic Investigation

3.4.1 Reaction Time Profile

To gain further mechanistic understanding, the reaction of Rh(ttp)Cl and c-heptane at 120 °C in benzene-d_6 in the presence of K_2CO_3 was monitored by ^{1}H NMR spectroscopy in a NMR tube (eq 3.8, Figure 3.2, Table 3.2).

$$\text{(3.8)}$$

5a 17%   **5b** 14%   **1d** 62%   42% (w.r.t. Rh(ttp)Cl)

Figure 3.2 Time Profile of Reaction of Rh(ttp)Cl with c-Heptane in the Presence of K_2CO_3

79

Table 3.2 Time Profile of Reaction of Rh(ttp)Cl with c-Heptane in the Presence of K_2CO_3

Time/h	Rh(ttp)Cl 1a	Rh(ttp)(c-heptyl) 5a	Rh(ttp)Bn 5b	Rh(ttp)H 1d	$Rh_2(ttp)_2$ 1e	c-heptene	Total Rh pdt	Total Org pdt
								Yield %
0	100	0	0	0	0	0	100	0
0.5	72	0	9	16	3	0	100	9
1	37	0	13	43	6	25	99	38
2	15	0	13	64	7	43	98	56
16	0	18	14	62	0	42	94	74
72	0	20	14	62	0	42	96	77
96	0	23	14	59	0	41	96	79
264	0	23	15	58	0	43	97	82

After 2 hours of reaction, only 15% yield of Rh(ttp)Cl 1a remained while Rh(ttp)Bn 5b, $Rh_2(ttp)_2$ 1e and Rh(ttp)H 1d were formed in 12%, 7% and 64% yields, respectively. After 16 hours, Rh(ttp)Cl 1a and $Rh_2(ttp)_2$ 1e completely reacted; the yield of Rh(ttp)H 1d still remained at 62%. At the same time, the yield of Rh(ttp)Bn 5b did not increase while Rh(ttp)(c-heptyl) 5a formed in 17% yield. c-Heptene was observed in 42% yield. Since the complete consumption of $Rh_2(ttp)_2$ 1e significantly slowed down further conversion of Rh(ttp)(c-heptyl) 5a to Rh(ttp)Bn 5b, $Rh_2(ttp)_2$ 1e likely has a promoting role in the transformation. Therefore, both $Rh_2(ttp)_2$ and Rh(ttp)H are possible intermediates.

3.4.2 Reactivity of Rh$_2$(ttp)$_2$ and Rh(ttp)H with c-Heptane

Rh$_2$(ttp)$_2$ and Rh(ttp)H were then reacted with c-heptane separately. Indeed, both Rh$_2$(ttp)$_2$ and Rh(ttp)H gave Rh(ttp)(c-heptyl) only in 76% and 73% yields, respectively (eq 3.9). Therefore, they are intermediates for CHA only.

$$
\text{Rh(ttp)X} \quad + \quad \bigcirc \quad \xrightarrow[\text{120 °C, N}_2]{} \quad \text{Rh(ttp)}\!-\!\bigcirc \qquad (3.9)
$$

		5a
X = Rh(ttp)	5 min	76%
X = H	15 min	73%
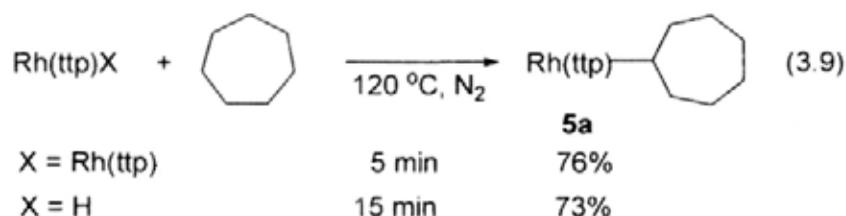
3.4.3 Conversion of Rh(ttp)(c-heptyl) to Rh(ttp)Bn

As neither Rh$_2$(ttp)$_2$ nor Rh(ttp)H reacted with c-heptane to give Rh(ttp)Bn, Rh(ttp)(c-heptyl) likely undergoes further reaction via CCA in order to account for the formation of Rh(ttp)Bn. To find out whether the CHA product is an intermediate for CCA, Rh(ttp)(c-heptyl) was heated in neutral and basic conditions separately (eq 3.10 and 3.11). In neutral conditions, Rh(ttp)(c-heptyl) **5a** yielded only Rh(ttp)H **1d** and c-heptene in 24% and 17% yield, respectively after 6 days (eq 3.10, Figure 3.3, Table 3.3). Rh(ttp)H and c-heptene likely form from the β-hydride elimination of Rh(ttp)(c-heptyl).

$$
\text{Rh(ttp)}\!-\!\bigcirc \quad \underset{\text{120 °C, 6 d}}{\overset{\text{benzene-}d_6}{\rightleftharpoons}} \quad \text{Rh(ttp)H} \quad + \quad \bigcirc \qquad (3.10)
$$

5a 63% (recovered)   **1d** 24%   17%
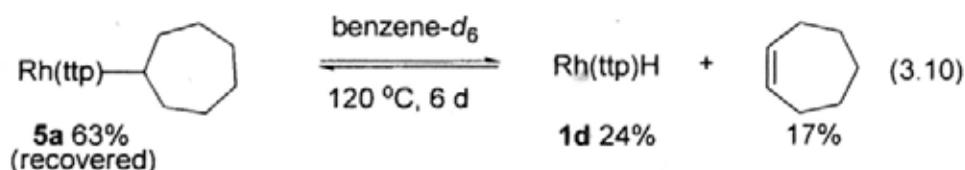
In fact, the β-hydride elimination of metal alkyl was well-known to give metal hydride and olefin.[13] Once the metal hydride and olefin forms, reverse 1,2-addition proceeds to give metal alkyl (Scheme 3.1)

81
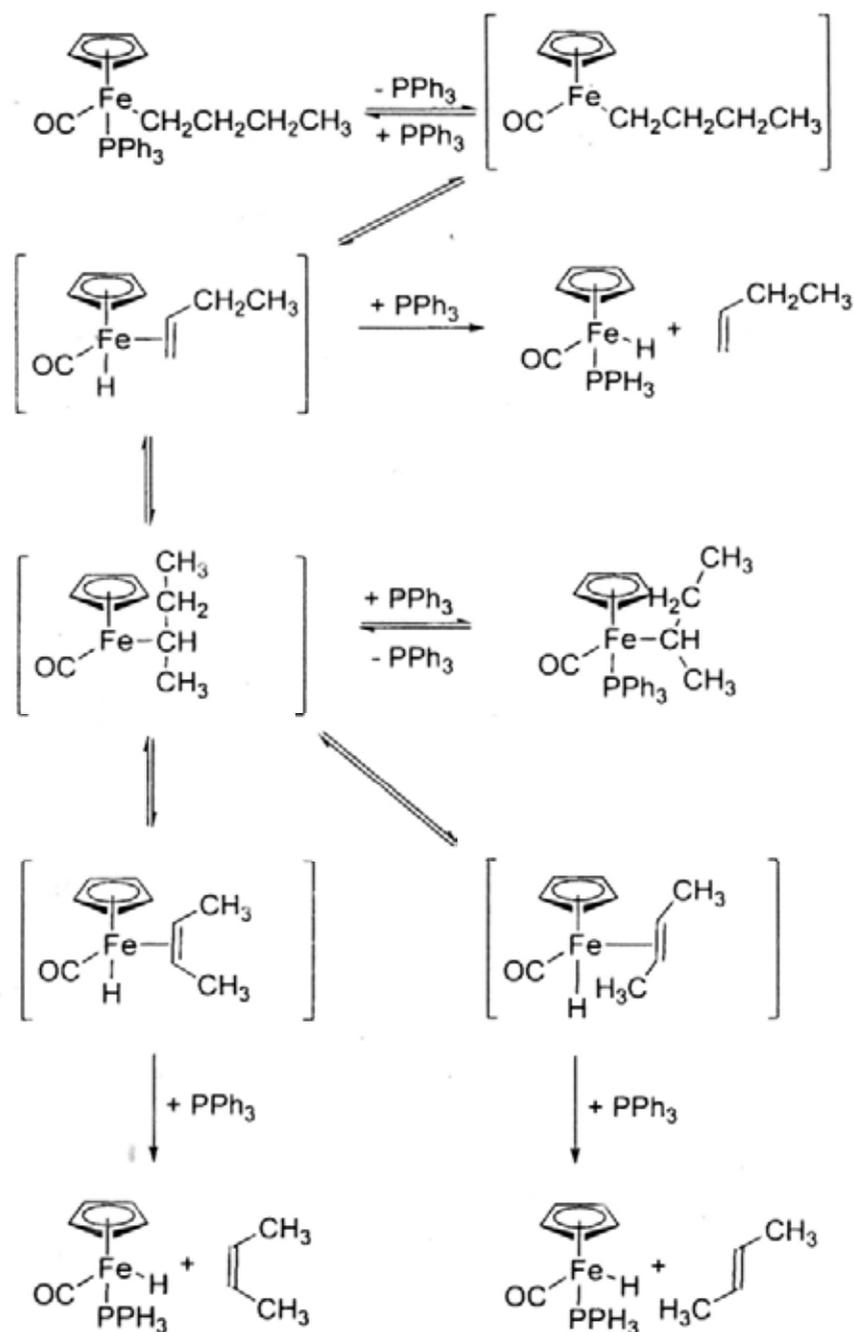
Scheme 3.1 β-Hydride Elimination of Metal Alkyl and Olefin Metal Hydride Insertion

The 1,2-rearrangemet of rhodium porphyrin alkyls were reported by Chan et al..[14] Several β-substituted ethylrhodium complexes underwent 1,2-alkyl rearrangement at 120 °C in benzene-d_6. The mechanism of the reaction is likely to proceed via a β-hydride elimination with an olefin formed as the intermediate (Scheme 3.2). The secondary alkylrhdoium complexes yielded the primary alkylrhodium complexes. With either primary or secondary

complexes as the starting materials, similar tautomeric ratios were obtained. Therefore, the reversibility of the rearrangement was established.
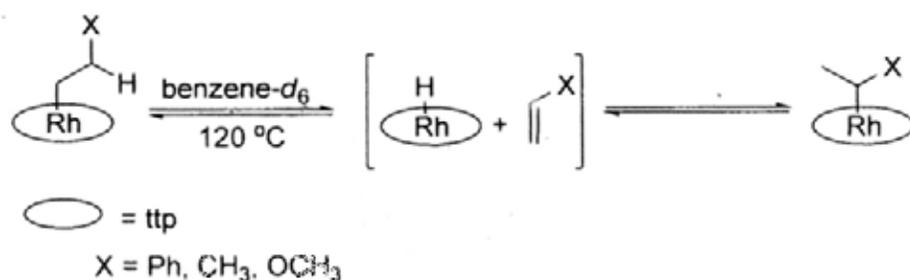
Scheme 3.2 Reversible 1,2-Alkyl Rearrangement of Rhodium Porphyrin Alkyl
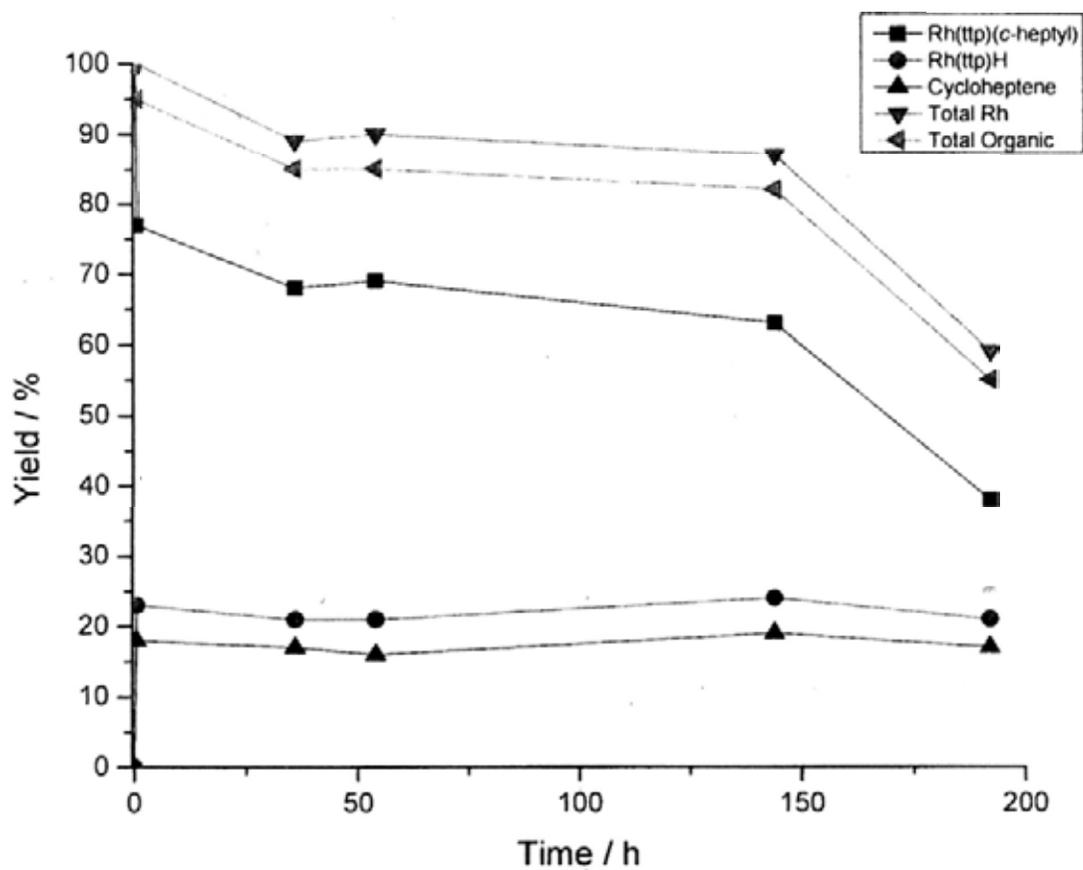
Figure 3.3 Time Profile of Thermal Reaction of Rh(ttp)(c-heptyl)

83

Table 3.3 Time Profile of Thermal Reaction of Rh(ttp)(c-heptyl) **5a**

			Yield %		
Time/h	**5a**	**1d**	c-heptene	Total Rh pdt	Total Org pdt
0	100	0	0	100	100
0.5	77	23	18	100	95
36	68	21	17	89	85
54	69	21	16	90	85
144	63	24	19	87	82
192	38	21	17	59	55

While in basic conditions, Rh(ttp)Bn **5b** was observed in 6% yield in 6 days, together with 28% yield of Rh(ttp)H and 20% yield of c-heptene (eq 3.11, Figure 3.4, Table 3.4).

$$\text{Rh(ttp)}\text{--} \bigcirc \xrightarrow[\text{K}_2\text{CO}_3 \text{ (10 equiv)}]{\text{benzene-}d_6} \text{Rh(ttp)Bn} + \text{"H}_2\text{"} + \text{Rh(ttp)H} + \bigcirc \quad (3.11)$$

5a 64%   120 °C, 6 d   **5b** 6%   **1d** 28%   20%
(recovered)
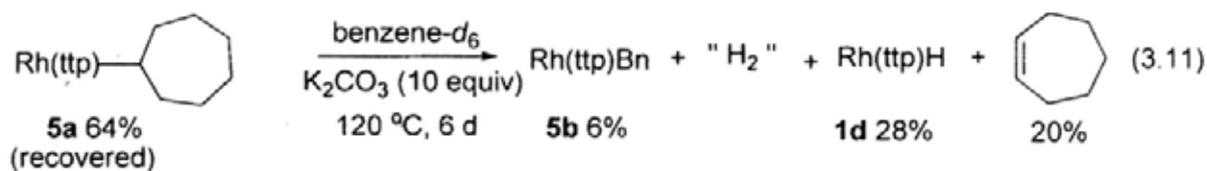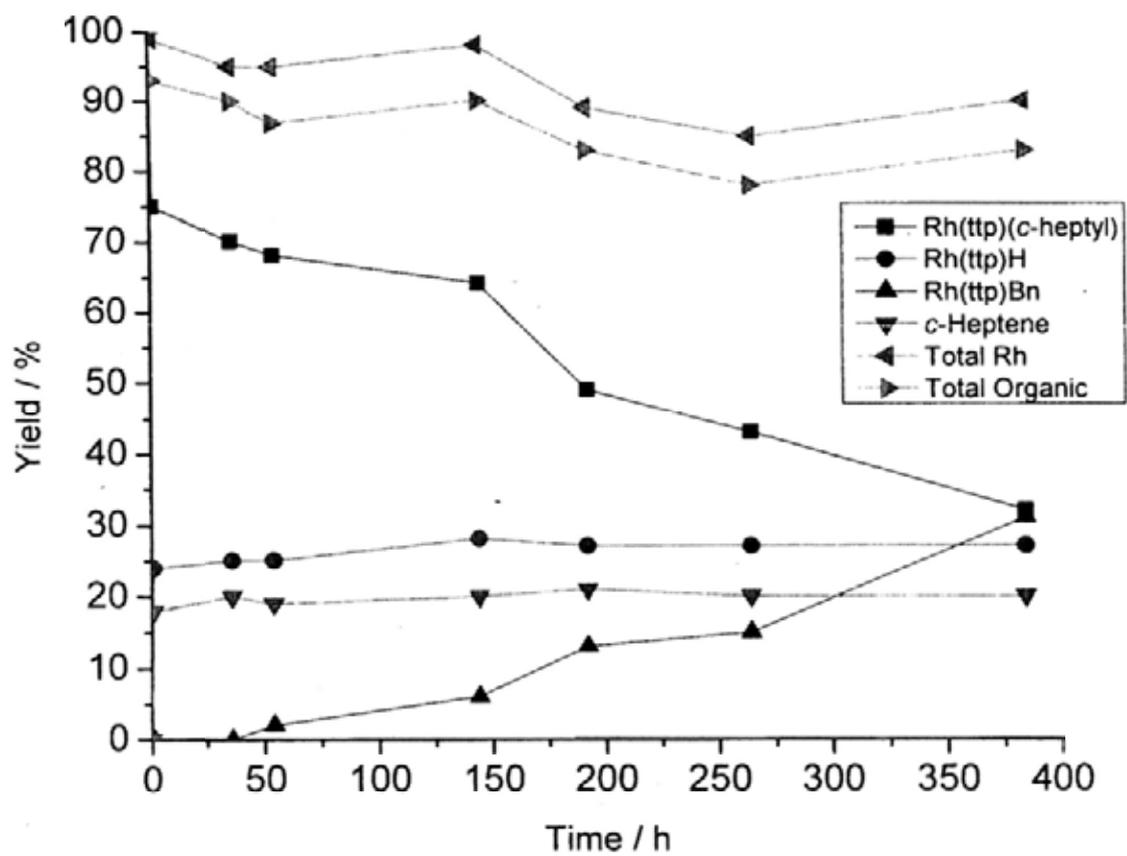
Figure 3.4 Time Profile of Thermal Reaction of Rh(ttp)(c-heptyl) with K_2CO_3

Table 3.4 Time Profile of Thermal Reaction of Rh(ttp)(c-heptyl) with K_2CO_3

Time/h	5a	5b	1d	c-heptene	Total Rh pdt	Total Org pdt
				Yield %		
0	100	0	0	0	100	100
1	75	24	0	18	99	93
36	70	25	0	20	95	90
54	68	25	2	19	95	87
144	64	6	28	20	98	90
192	49	13	27	21	89	83
264	43	15	27	20	85	78
384	32	31	27	20	90	83

The conversion of Rh(ttp)(c-heptyl) **5a** to Rh(ttp)Bn **5b** likely undergoes a β-hydride elimination[14] to give Rh(ttp)H **1d** and c-heptene. However, a base is required for further reaction to give Rh(ttp)Bn **5b**. Therefore, the CHA product is an intermediate for CCA product only in the presence of K_2CO_3.

As Rh^{II}(por) dimer (por = porphyrin) can form by the thermal[15] or base-promoted[16] dehydrogenative dimerization of Rh^{III}(por)H (eqs 3.12-3.13), the possible promoting role of $Rh_2(ttp)_2$ in converting Rh(ttp)(c-heptyl) to Rh(ttp)Bn was examined (eq 3.14, Figure 3.5, Table 3.5). To our delight, Rh(ttp)(c-heptyl) added with $Rh_2(ttp)_2$ (1 mol%) gave Rh(ttp)Bn, and the rate promoting rate effect of $Rh_2(ttp)_2$ (1 mol%) was about 6 times than that of K_2CO_3 (10 equiv).

$$2\,\text{Rh(tpp)H} \;\underset{\text{80 °C, <0.5 h}}{\overset{\text{benzene-}d_6}{\rightleftharpoons}}\; \text{Rh}_2(\text{tpp})_2 + \text{H}_2 \quad (3.12)$$

$$\underset{\text{91% recovered}}{2\,\text{Rh(ttp)H}} \;\xrightarrow[\text{120 °C, 1 d}]{\text{benzene-}d_6}\; \text{Rh}_2(\text{ttp})_2 + \underset{6\%}{\text{"H}_2\text{"}} \quad (3.13)$$

Rh(ttp)⬡ $\xrightarrow[\substack{\text{Rh}_2(\text{ttp})_2\ (1\ \text{mol\%})\\ \text{120 °C, 22 h}}]{\text{benzene-}d_6}$ Rh(ttp)Bn + Rh(ttp)H + ⬡ (3.14)

5a 28%   **5b** 6%   **1d** 61%   38%
(recovered)
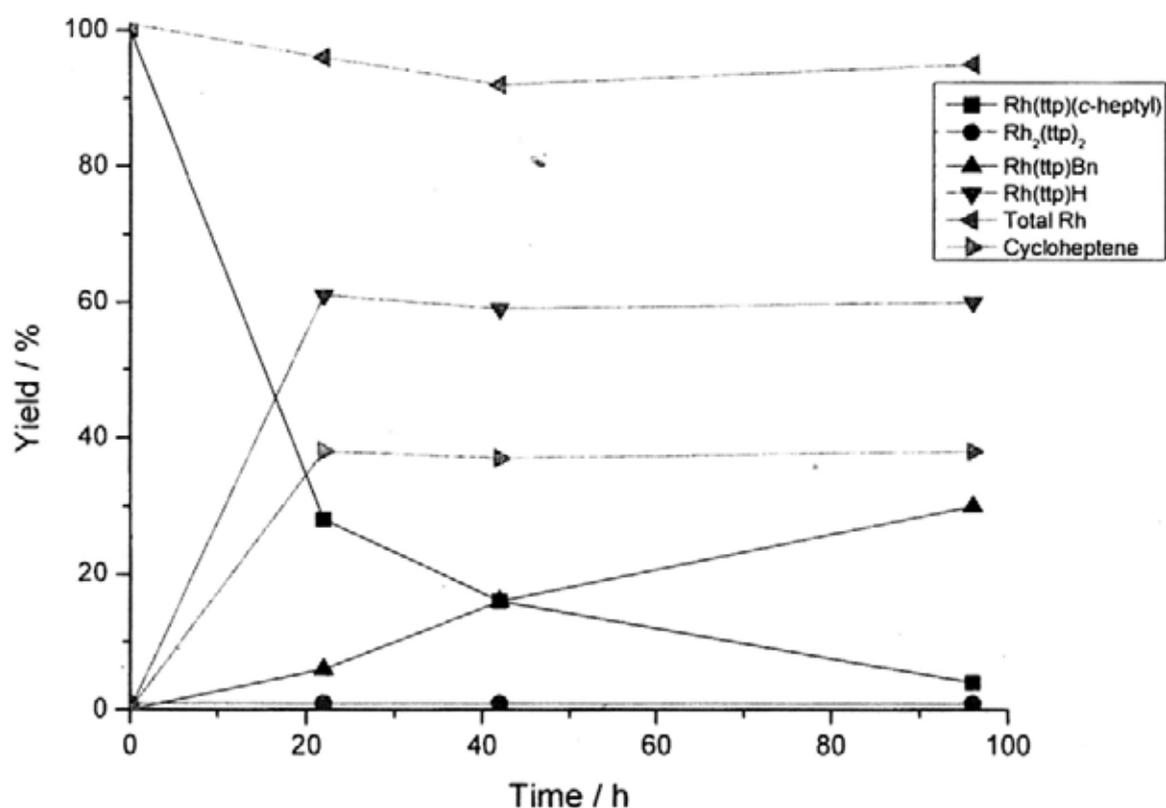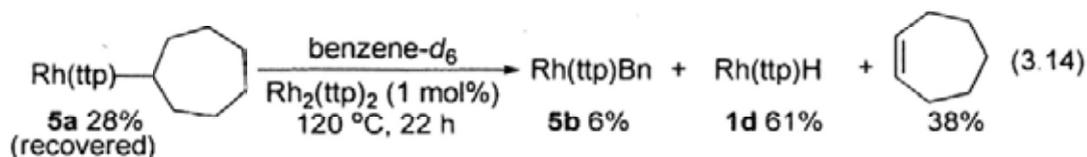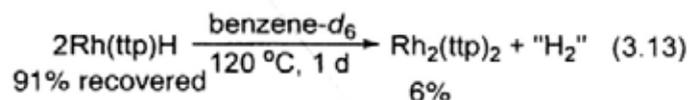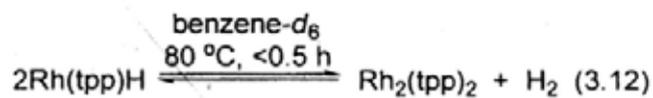
Figure 3.5 Time Profile of Conversion of Rh(ttp)(c-heptyl) to Rh(ttp)Bn with 1 mol% Rh$_2$(ttp)$_2$

Table 3.5 Time Profile of Conversion of Rh(ttp)(c-heptyl) to Rh(ttp)Bn with 1 mol%
$Rh_2(ttp)_2$

			Yield %			
Time/h	**5a**	**5b**	**1d**	c-heptene	Total Rh pdt	Total Org pdt
0	100	0	0	0	100	100
22	28	6	61	38	95	62
42	16	16	59	37	91	69
96	4	30	60	38	94	72

3.5 Proposed Mechanistic Pathways

As Rh(ttp)(c-heptyl) **5a** was converted to Rh(ttp)Bn **5b** in the presence of K_2CO_3, the direct transformation is very unlikely and therefore stepwise conversions are more reasonable. Scheme 3.3 shows three proposed mechanistic pathways and their corresponding key intermediates. Each one was examined to elucidate the mechanism of Rh(ttp)Bn formation.
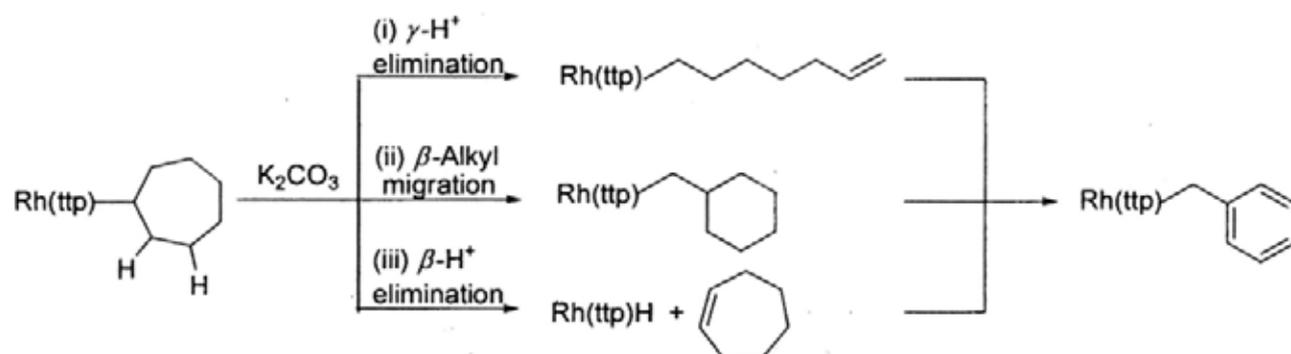
Scheme 3.3 Proposed Mechanistic Pathways for the Conversion of Rh(ttp)(c-heptyl) to Rh(ttp)Bn with K_2CO_3

3.5.1 Conversion of Rh(ttp)(c-heptyl) to Rh(ttp)Bn via γ-H$^+$ Elimination

In pathway (i), Rh(ttp)(c-heptyl) **5a** undergoes a γ-H$^+$ elimination to give $Rh(ttp)(CH_2)_5(CH=CH_2)$ **6a** and the subsequent dehydrogenation and rearrangement lead to

the formation of Rh(ttp)Bn **5b** (Scheme 3.4). In fact, (*c*-heptyl)tantalum complex was proposed to undergo γ-H elimination to generate $Ta(CH_2)_5(CH=CH_2)$ for further reaction.[17a]
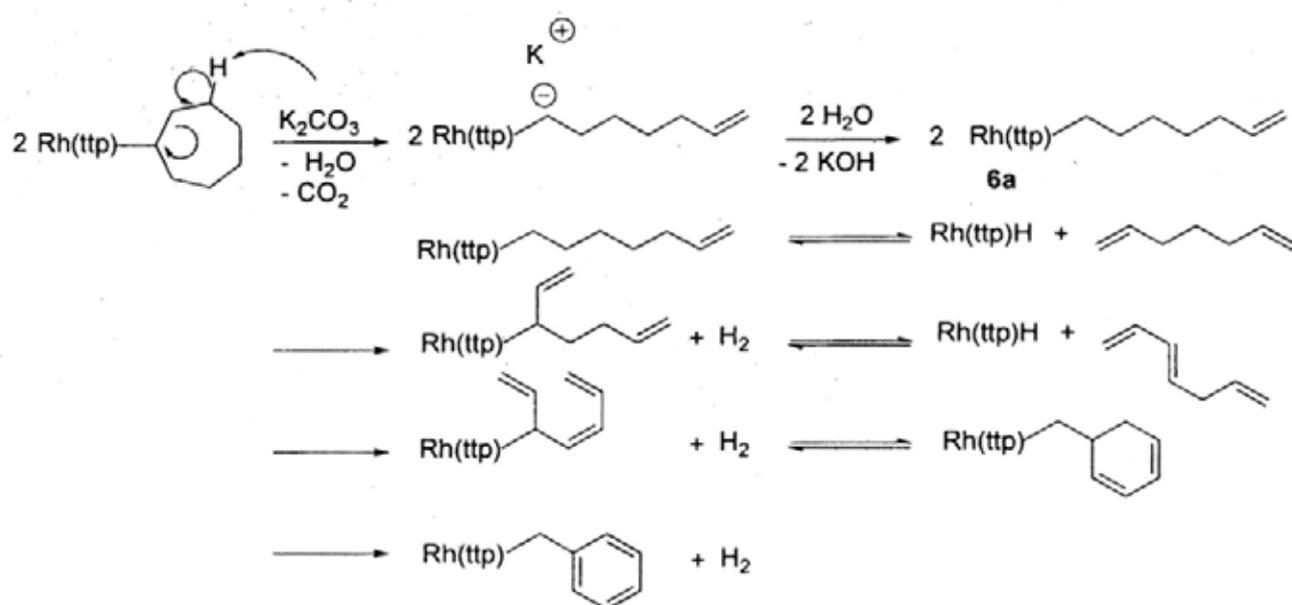
Scheme 3.4 Proposed Mechanism of γ-H$^+$ Elimination of Rh(ttp)(*c*-heptyl)

$Rh(ttp)(CH_2)_5(CH=CH_2)$ **6a** was independently synthesized by reductive alkylation (eq 3.15).[18] $Rh(ttp)(CH_2)_5(CH=CH_2)$ **6a** was then heated at 120 °C in the presence of K_2CO_3 for 14 days and only gave 28% yield of the 1,2-rearrangement[14] product, $Rh(ttp)(CH(CH_3)CH_2CH_2CH_2CH=CH_2)$ **6b** while 70% yield of $Rh(ttp)(CH_2)_5(CH=CH_2)$ **6a** was recovered (eq 3.16). No Rh(ttp)Bn **5b** was observed. Pathway (i) is ruled out.
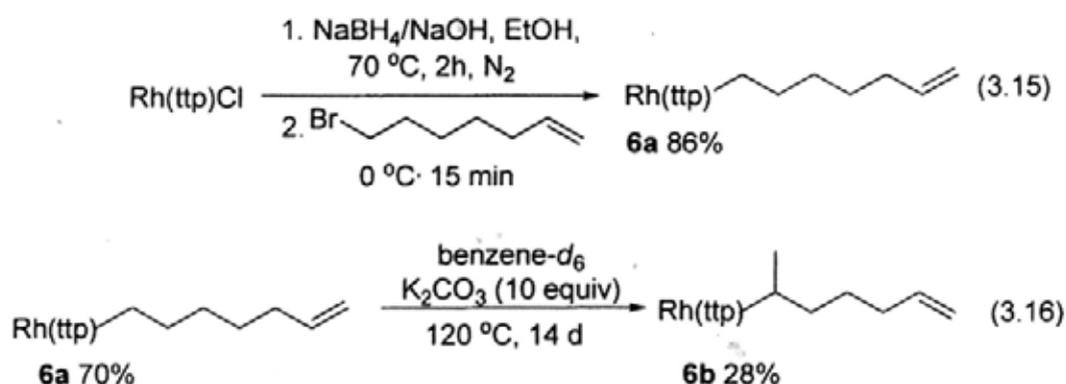
3.5.2 Conversion of Rh(ttp)(c-heptyl) to Rh(ttp)Bn via β-Alkyl Migration

In pathway (ii), Rh(ttp)(c-heptyl) **5a** undergoes a β-alkyl migration to form ((c-hexyl)methyl)rhodium **6c** complex which gives Rh(ttp)Bn **5b** upon further dehydrogenation. In fact, the conversion of c-heptane to methylcyclohexane was achieved by a Ta–H catalyst (eq 3.17).[10] Besides, the WO$_2$-catalyzed dehydrogenation of methylcyclohexane was well-documented (eq 3.18).[17b]
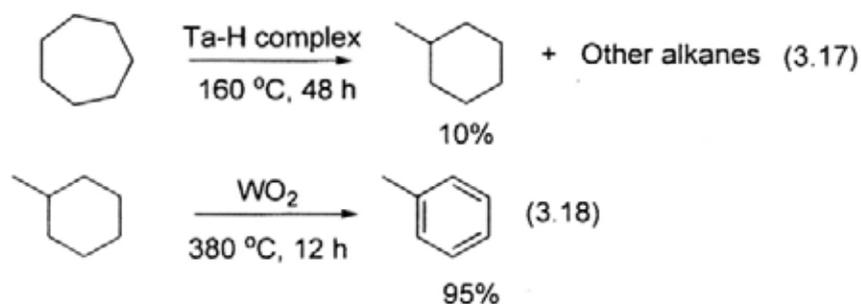
Therefore, ((c-hexyl)methyl)rhodium **6c** was independently synthesized by reductive alkylation (eq 3.19).[18] However, when ((c-hexyl)methyl)rhodium **6c** was heated at 120 °C for 5 days in the presence of K$_2$CO$_3$, only 5% yield of Rh(ttp)Bn **5b** and 60% yield of Rh(ttp)H **1d** were observed (eq 3.20). Therefore, pathway (ii) is only a minor pathway based on the yield and very slow rate.
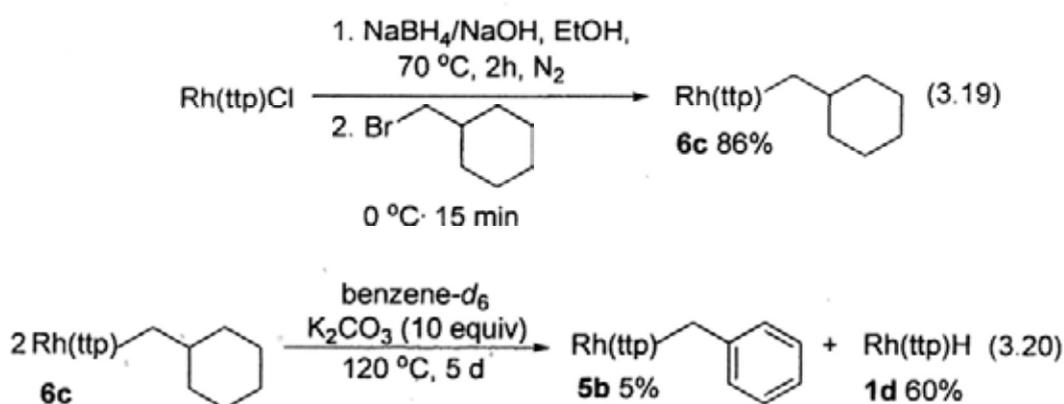
3.5.3 Conversion of Rh(ttp)(c-heptyl) to Rh(ttp)Bn via β-H⁺ Elimination

As Rh(ttp)(c-heptyl) **5a** gave Rh(ttp)H **1d** and c-heptene via β-H and β-H⁺ elimination in the absence and presence of K$_2$CO$_3$ (eqs 3.10 and 3.11),[16] c-heptene formed

can be dehydrogenated further to give cycloheptatriene (CHT) which can then produce Rh(ttp)Bn **5b**. Scheme 3.5 illustrates the detailed proposed mechanism of the $Rh_2(ttp)_2$-catalyzed dehydrogenation of *c*-heptane to give cycloheptatriene. **5a** initially undergoes the reversible β-H elimination/addition[14] to give Rh(ttp)H **1d** and *c*-heptene which is then rapidly trapped by $Rh_2(ttp)_2$ **1e** to yield **7a**.[19] Successive β-H elimination and addition reactions of **7a** with $Rh_2(ttp)_2$ **1e** finally gives CHT. Rh(ttp)H **1d** or $Rh_2(ttp)_2$ **1e** then reacts with CHT to give Rh(ttp)(cycloheptatrienyl) **8**.
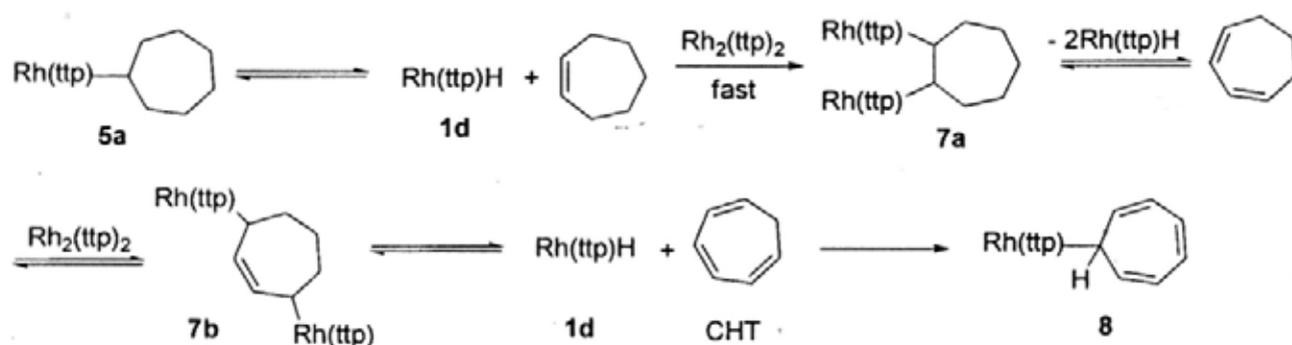
Scheme 3.5 Proposed Mechanism of *c*-Heptane Dehydrogenation

Supporting lines of evidence came the following experiments. $Rh_2(ttp)_2$ **1e** reacted at room temperature with *c*-heptene rapidly to give the 1,2-addition product **7** quantitatively (eq 3.21).
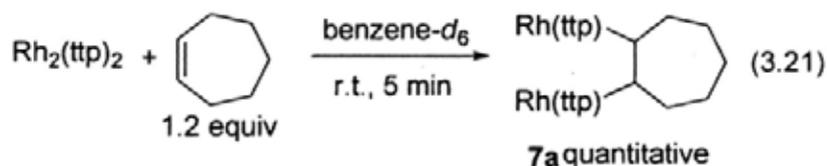
7a was also found to be reactive and thermally unstable even at ambient conditions (Figure 3.6). The freshly prepared **7a** (t = 0 h) gave a clean ^{1}H NMR spectrum. After standing at ambient conditions for 12 hours, **7a** decomposed to give $Rh_2(ttp)_2$ **1e**, *c*-heptene and Rh(ttp)(*c*-heptyl) **5a** in 5%, 2% and 42% yields, respectively, while 48% of **7a** remained (eq 3.22).
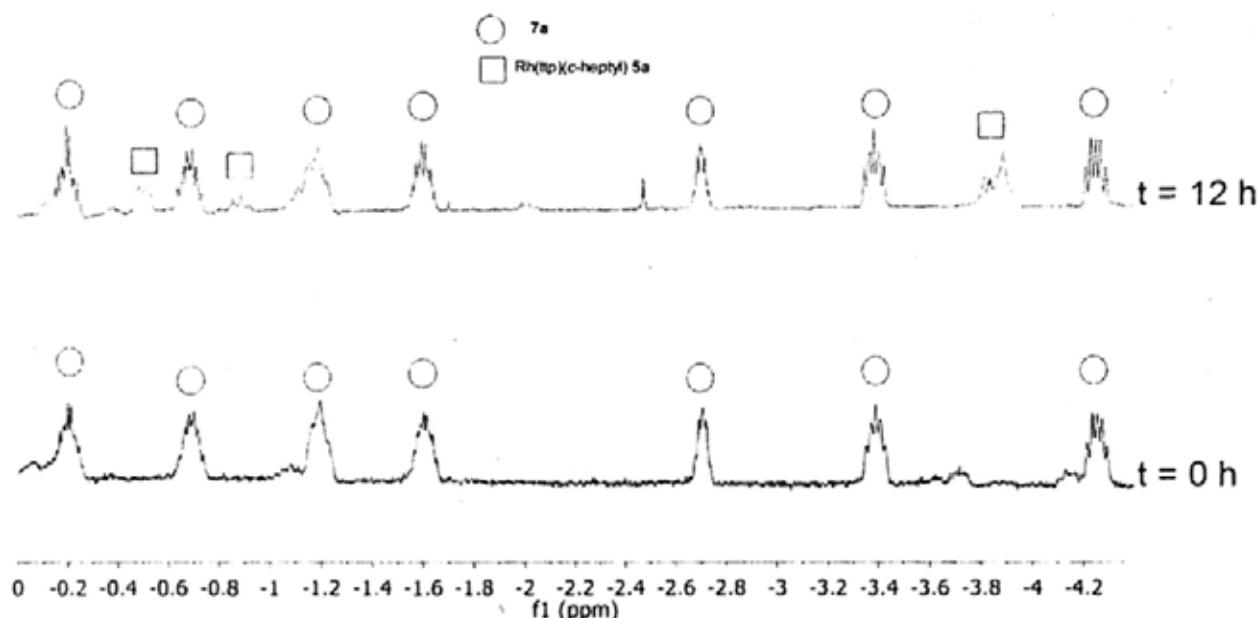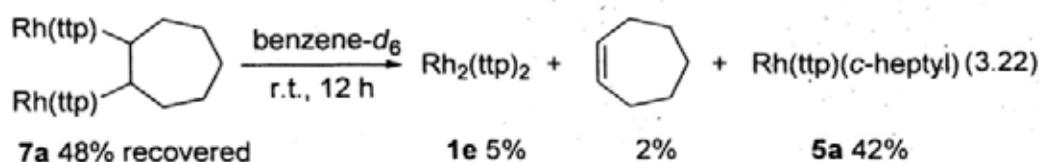
Figure 3.6 ^{1}H NMR Spectra of **7a** at 0 h and 12 h at Ambient Conditions (Upfield Region)

Thus, the freshly prepared **7a** was heated at 120 °C for 21 hours to give Rh(ttp)H **1d**, Rh(ttp)(*c*-heptyl) **5a** and Rh(ttp)Bn **5b** in 20%, 58% and 19% yields, respectively (eq 3.23, Figure 3.7, Table 3.6).[20] Therefore, **7a** is a viable intermediate for the formation of Rh(ttp)Bn.
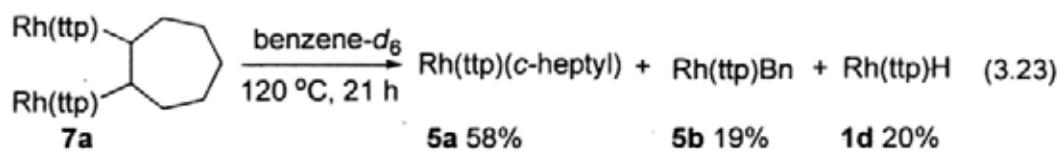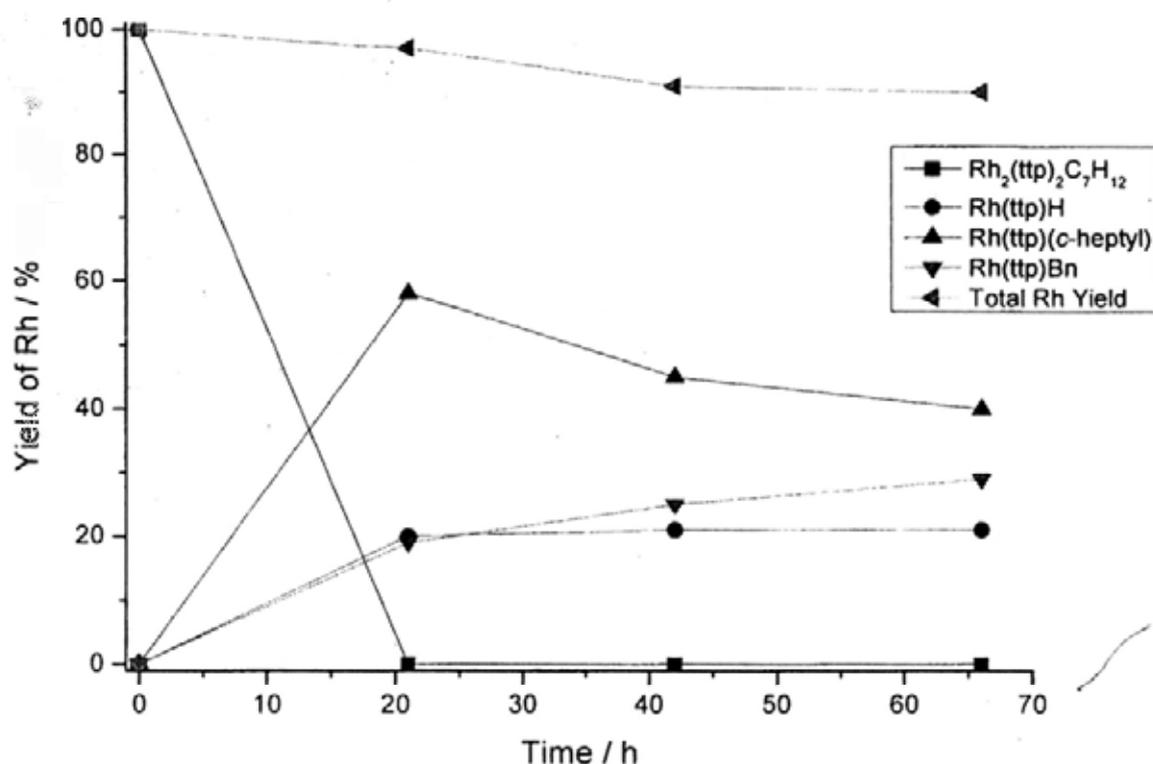
Figure 3.7 Time Profile of Conversion from **7a**

Table 3.6 Time profile of conversion from **7a**

Time/h	7a	5a	5b	1d	Total Rh pdt
			Yield %		
0	100	0	0	0	100
21	0	58	19	20	97
42	0	45	25	21	91
66	0	40	29	21	90

As Rh(ttp)(cycloheptatrienyl) **8a** is proposed to be formed from the CHA of CHT with $Rh_2(ttp)_2$ or Rh(ttp)H (Scheme 3.6), the reactivity of $Rh_2(ttp)_2$ and Rh(ttp)H towards CHT were examined separately. Indeed, both $Rh_2(ttp)_2$ and Rh(ttp)H reacted with CHT

quickly at room temperature to give Rh(ttp)(cycloheptatrienyl) **8** quantitatively (eq 3.24).[21]

The structure of Rh(ttp)(cycloheptatrienyl) **8** was eluciated by X-ray crystallography (Figure 3.8).
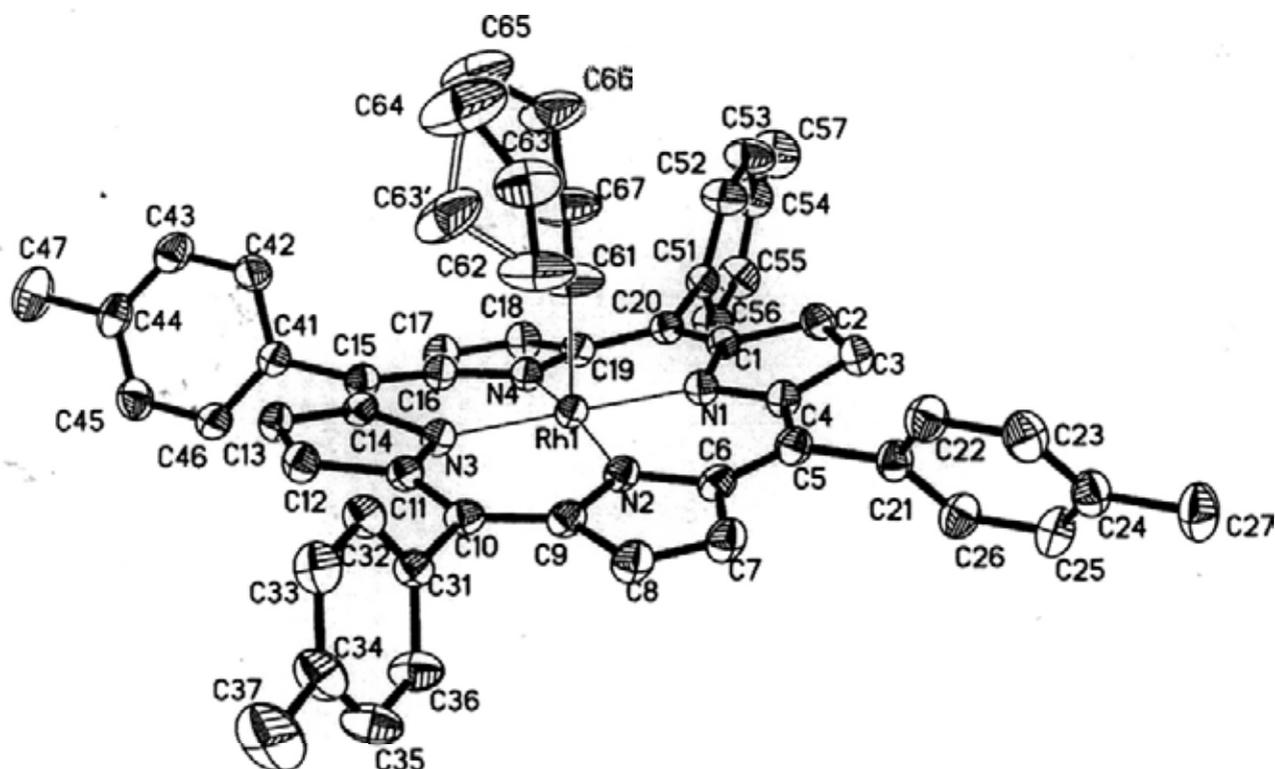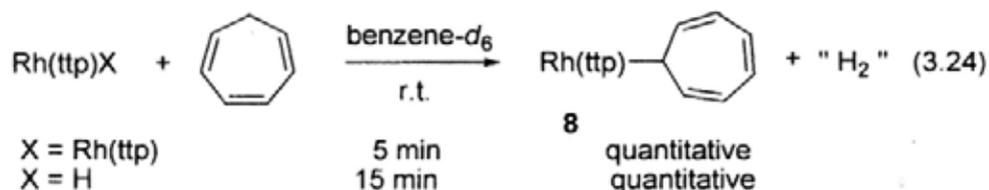
Figure 3.8 ORTEP Presentation of Rh(ttp)(cyclpheptatrienyl) **8** (30% Probability Displacement Ellipsoids). Rh–C = 2.10 Å, R = 0.0364

Therefore, $Rh_2(ttp)_2$ is shown to promote the formation of Rh(ttp)(cycloheptatrienyl) **8** by rapidly trapping *c*-heptene, *c*-hepta-1,3-diene and CHT from the β-hydride elimination of **5a**, **7a** and **7b**.

To account for the formation of Rh(ttp)Bn **5b**, scheme 3.6 shows the proposed mechanism of the Rh^{II}-catalyzed transformation of **8** to **5b**. Rh^{II}(ttp), dissociated from

$Rh_2(ttp)_2$ through its weak Rh–Rh bond (16 kcal mol^{-1}),[2,15] reacts with **8** to give the carbon center radical **9a** which then isomerizes to give a cyclopropylmethyl radical **9b** and subsequently upon ring opening produces **9c** (Scheme 3.7).[22] **9c** can undergo a β-H elimination to give the Rh-substituted benzyl radical **9d**. Hydrogen atom transfer from Rh(ttp)H to **9d** yields Rh(ttp)Bn **5b** and regenerates Rh^{II}(ttp).
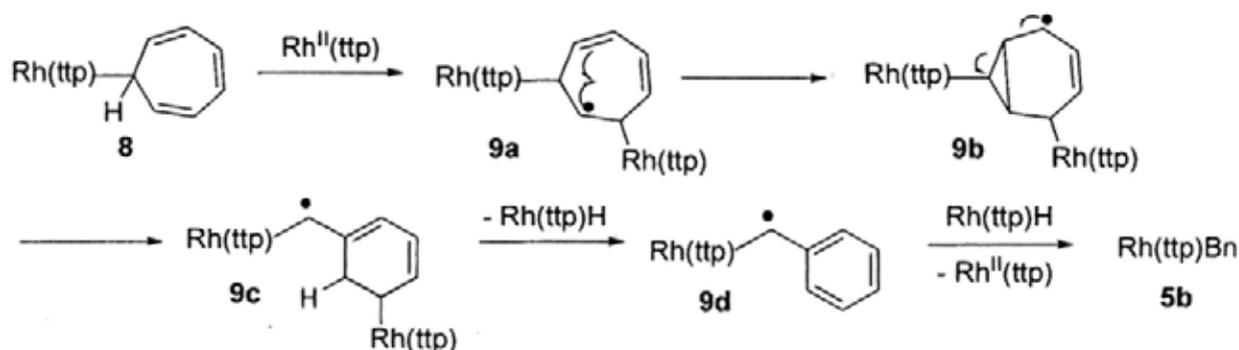
Scheme 3.6 Proposed Mechanism for Rh^{II} Catalyzed CCA
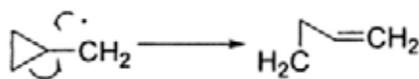
Scheme 3.7 Conversion of Cyclopropylmethyl Radical to 3-Butenyl Radical

3.6 Mechanistic Studies of Conversion of Rh(ttp)(cycloheptatrienyl) to Rh(ttp)Bn

3.6.1 ^{1}H NMR Kinetics

In order to gain a deeper mechanistic understanding of the conversion of Rh(ttp)(cycloheptatrienyl) **8** to Rh(ttp)Bn **5b**, the kinetics of the conversion of **8** to **5b** were monitored by ^{1}H NMR spectroscopy (eq 3.25). The kinetic runs were monitored with the disappearance of Rh(ttp)(cycloheptatrienyl) **8** for at least three half-lives by ^{1}H NMR spectroscopy. The NMR tube was thermostatted in a GC-oven within ± 0.2 °C.
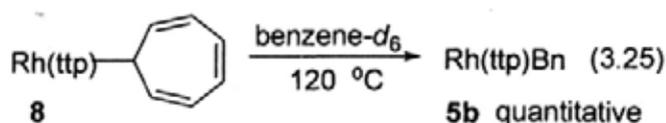
The kinetic data taken were then fitted by first-order exponential decay with the software OriginPro 7.5.

3.6.2 Determination of Reaction Order and Rate Constant

The rate equation can be expressed as eq 3.26, where k_{obs} was the observed rate constant of the reaction.

$$\text{Rate} = k_{obs} [8]^m \qquad (3.26)$$

Firstly, the value of m was evaluated. Typical conditions were $[8]_0 = 6.95 \times 10^{-3}$ M to 13.90×10^{-3} M and T = 120 °C. The results were fitted well by a first-order exponential decay function (Figures 3.9 and 3.10). The kinetic order of **8** is therefore one.
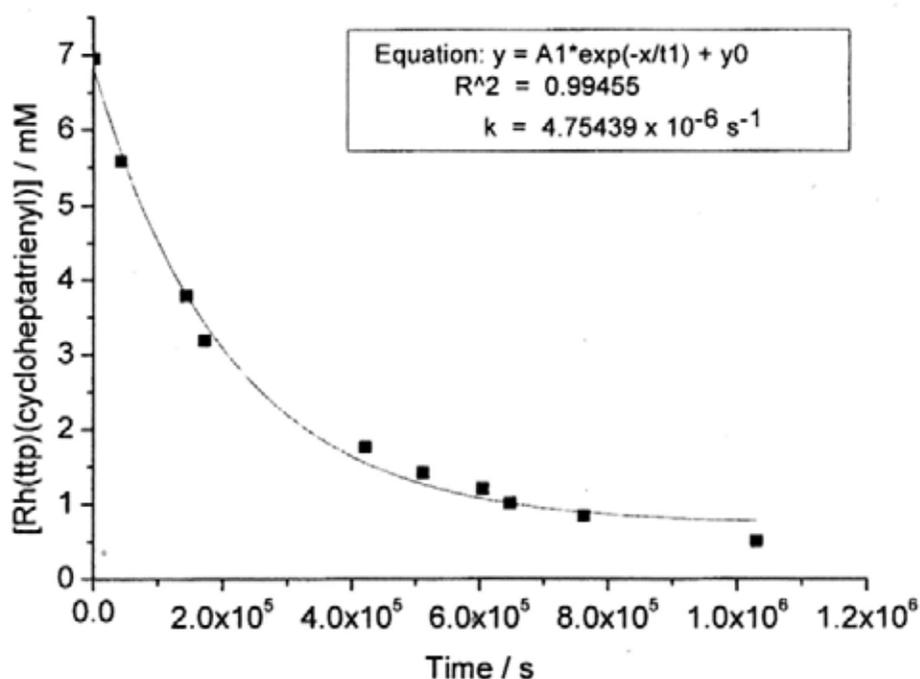
Figure 3.9 Time Profile of Rh(ttp)(cycloheptatrienyl) (6.95 mM) at 120 °C
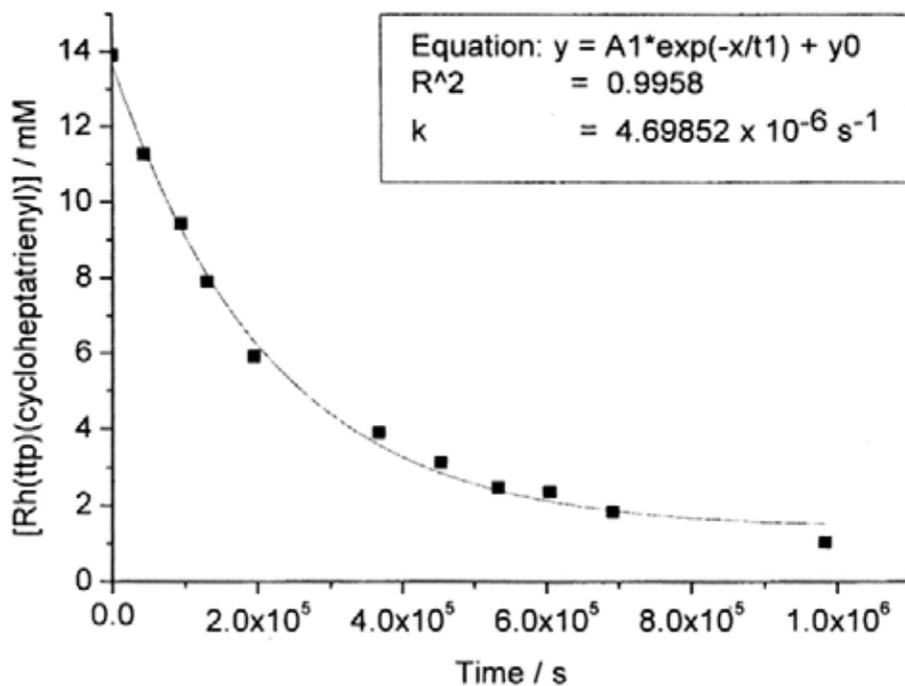
Figure 3.10 Time Profile of Rh(ttp)(cycloheptatrienyl) (13.90 mM) at 120 °C

Table 3.7 (entries 1 and 2) show that k_{obs} did not change with the initial concentration of Rh(ttp)(cycloheptatrienyl) **8**. The kinetic order of Rh(ttp)(cycloheptatrienyl) **8** was confirmed to be one. According to the above results, the rate law can be expressed as rate = k [**8**], where $k = 4.75 \times 10^{-6} \text{ s}^{-1}$ at 120 °C. The conversion of **8** to **5b** was a first order reaction.

Table 3.7 k_{obs} at different conditions

Entry	$[8]_0 \times 10^3$ /M	Temp / °C	$1/T$ ($\times 10^3$ K^{-1})	$k_{obs} \times 10^6$ /s^{-1}	Error $\times 10^7$ /s^{-1}	$k \times 10^4$ / L^{-1} mol^{-1} s^{-1}
1	6.95	120	2.545	4.75439	3.97540	6.84892
2	13.90	120	2.545	4.69852	3.45935	6.76046
3	6.95	130	2.481	8.76127	8.45695	12.6043
4	6.95	140	2.421	15.4640	34.0559	22.3022
5	6.95	150	2.364	41.0845	57.0695	59.1367

The thermal conversion of CHT to toluene has been reported by Gaynor et al. (eq 3.27).

$$800\text{-}1130\ \text{K} \qquad (3.27)$$
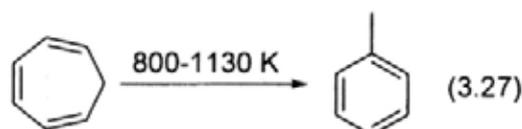
According to the data obtained from literature,[23] log (A_∞/s^{-1}) was 13.6 and E_∞ was 217.7 kJ mol^{-1}. The thermal conversion rate of CHT to toluene at 120 °C is extrapolated by applying Arrhenius equation.

$$\ln k = -E_a/RT + \ln A$$

At 120 °C, $\ln k = -217.7 \times 1000 / (8.314 \times 393) + \ln (10^{13.6})$

$$\ln k = -35.3$$

$$k = 4.61 \times 10^{-16}\ \text{s}^{-1}$$

The rate of the thermal conversion of CHT to toluene at 120 °C is evaluated to be 4.61 $\times 10^{-16}$ s^{-1}.[23] Therefore, the conversion of 8 to 5b is 10^{10} faster than the organic transformation.

3.6.3 Activation Parameters

The rates were measured at different temperatures. Typical experimental conditions were [Rh(ttp)(cycloheptatrienyl] = 6.95 x 10^{-3} M, T = 120 °C – 150 °C (eq 3.28). The results are shown in Table 3.7 (entries 1, 3-5) and Figures 3.8, 3.11-3.13. These data were used in the estimation of activation parameters.
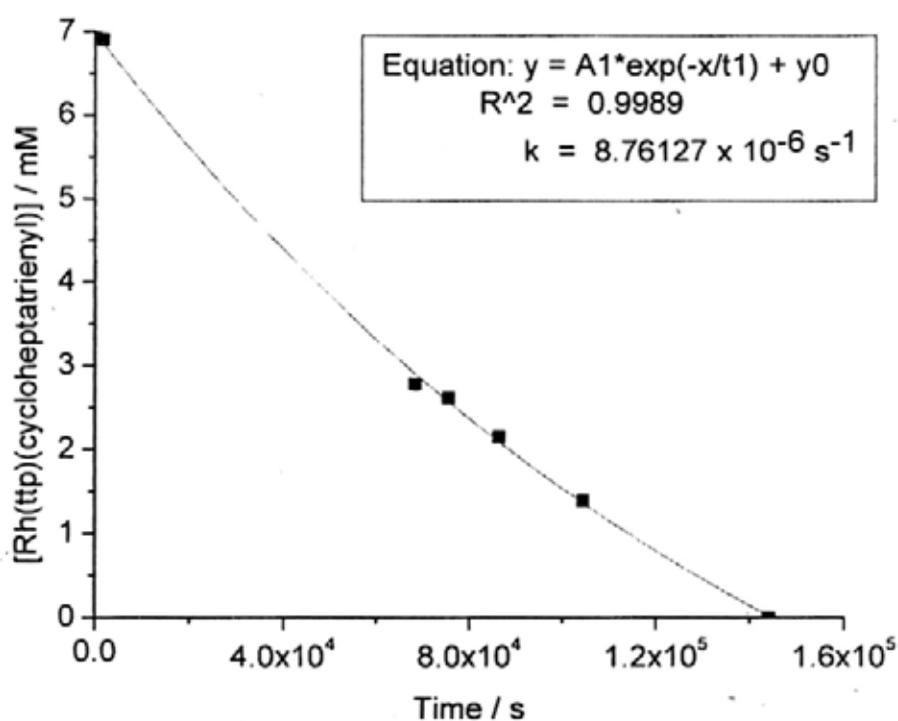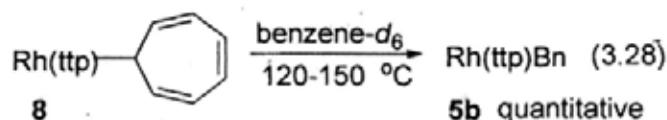
$$\text{Rh(ttp)} \overbrace{\hspace{2cm}} \xrightarrow[\text{120-150 °C}]{\text{benzene-}d_6} \text{Rh(ttp)Bn} \quad (3.28)$$

8   **5b** quantitative

Equation: y = A1*exp(-x/t1) + y0
R^2 = 0.9989
k = 8.76127 x 10^{-6} s^{-1}

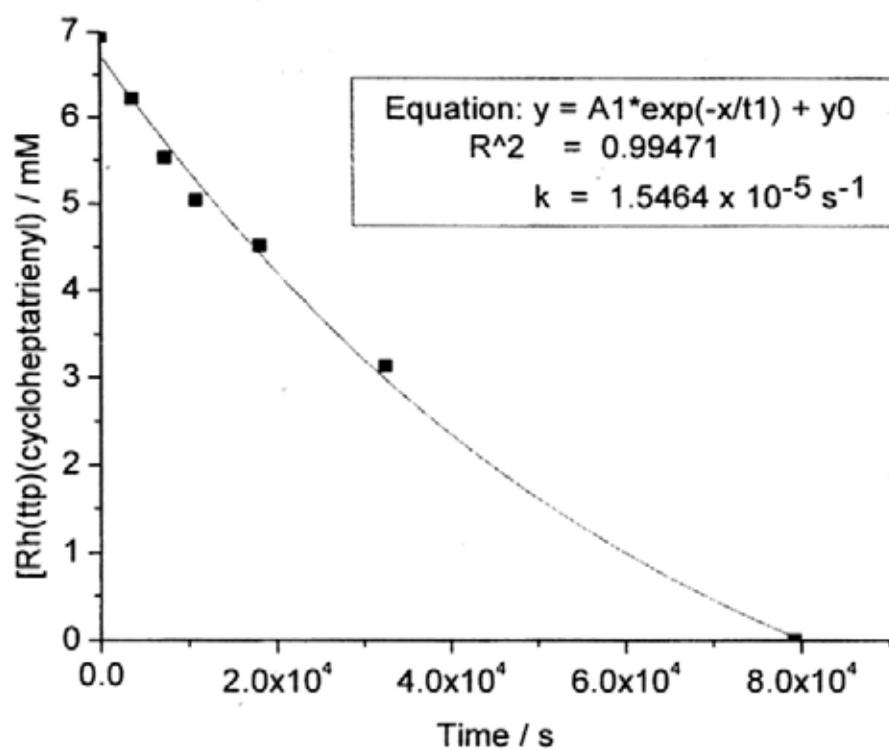Figure 3.11 Time Profile of Rh(ttp)(cycloheptatrienyl) (6.95 mM) at 130 °C

Figure 3.12 Time Profile of Rh(ttp)(cycloheptatrienyl) (6.95 mM) at 140 ^{o}C
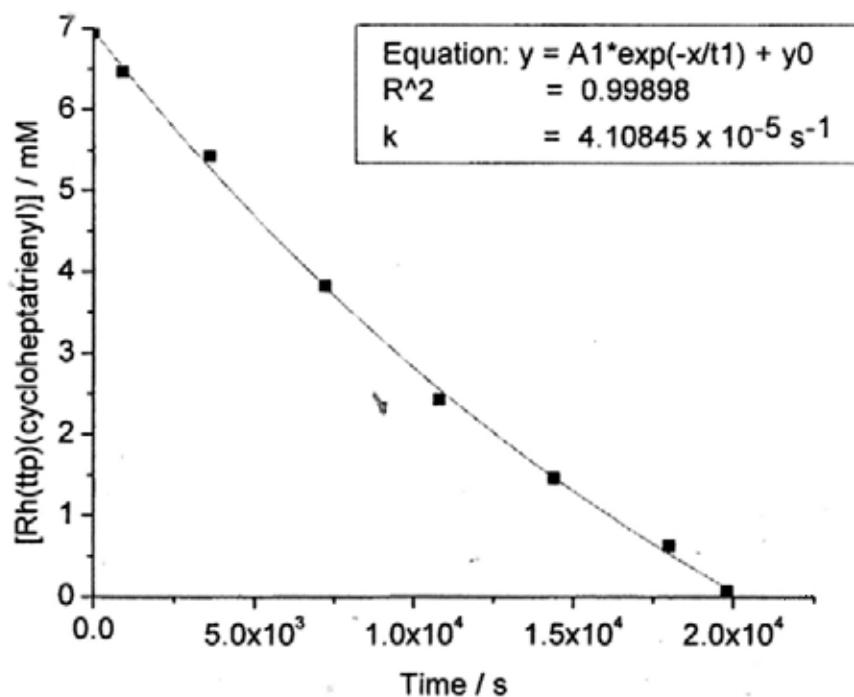

Figure 3.13 Time Profile of Rh(ttp)(cycloheptatrienyl) (6.95 mM) at 150 ^{o}C

The Eyring equation describes the temperature dependence of reaction rate (eq 3.29).[3a]

$$\ln(k/T) = -\Delta H^{\ddagger}/(RT) + \ln(\kappa/h) + \Delta S^{\ddagger}/R \quad (3.29)$$

(κ is the Boltzmann constant, R is the ideal gas constant and h is the Planck's constant.)

Therefore, a plot of $\ln(k/T)$ against $1/T$ gives a linear Eyring plot with a slope of $-\Delta H^{\ddagger}/R$ and a y-intercept of $\ln(\kappa/h) + \Delta S^{\ddagger}/R$ (Figure 3.13, Table 3.8).[3a]

Table 3.8 $\ln(k_{obs}/T)$ at different $(1/T)$

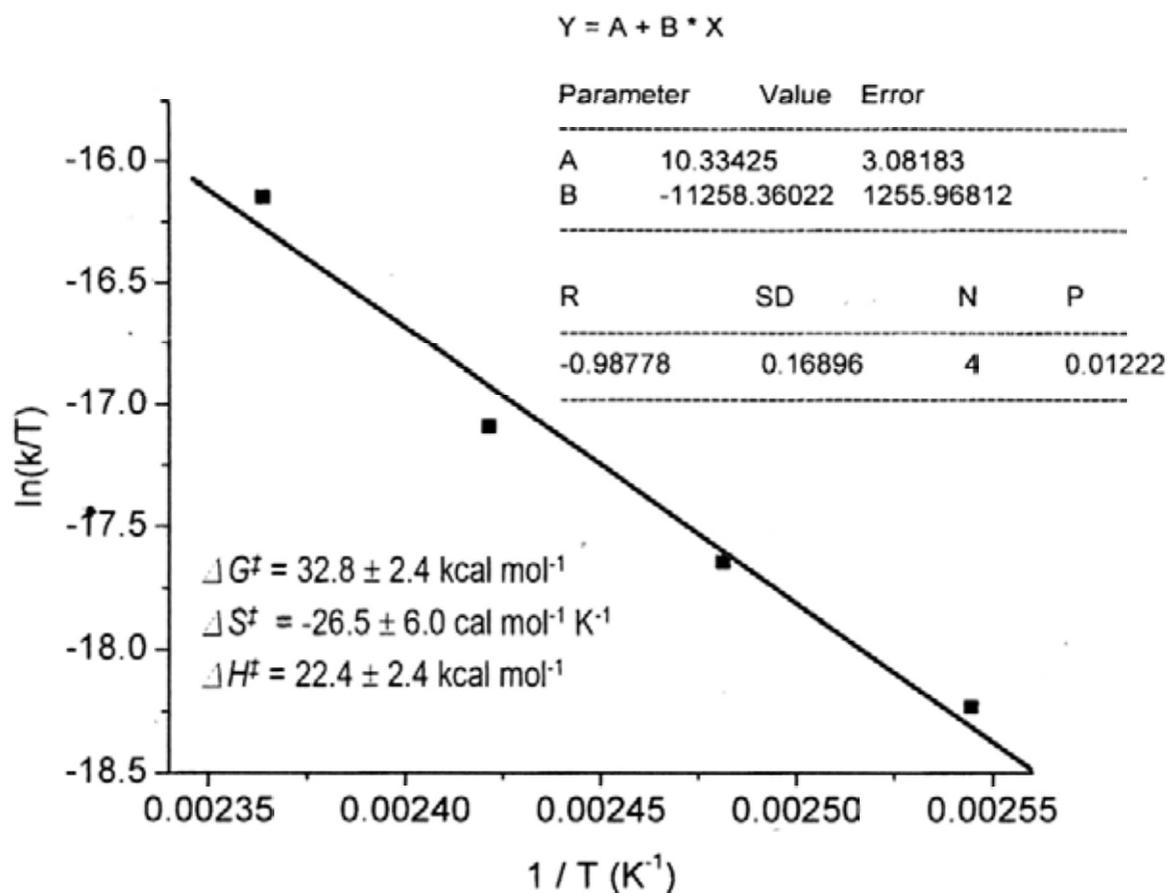| Entry	Temp / °C	$1/T$ (x 10^{-3} K^{-1})	k_{obs} x10^6 /s^{-1}	Error x10^7 /s^{-1}	$\ln(k_{obs}/T)$
1	120	2.545	4.75439	3.97540	-18.2303
2	130	2.481	8.76127	8.45695	-17.6441
3	140	2.421	15.4640	34.0559	-17.1004
4	150	2.364	41.0845	57.0695	-16.1473

Y = A + B * X

Parameter	Value	Error
A	10.33425	3.08183
B	-11258.36022	1255.96812

R	SD	N	P
-0.98778	0.16896	4	0.01222

$\Delta G^{\ddagger} = 32.8 \pm 2.4$ kcal mol^{-1}

$\Delta S^{\ddagger} = -26.5 \pm 6.0$ cal mol^{-1} K^{-1}

$\Delta H^{\ddagger} = 22.4 \pm 2.4$ kcal mol^{-1}

Figure 3.14 Eyring Plot of the Conversion of **8** to **5b** over the Temperature Range 120-150 °C

Since y-intercept $=$ $\ln(\kappa/h) + \Delta S^{\ddagger}/R$

10.39025 $=$ $\ln(1.3807 \times 10^{-23}/6.6261 \times 10^{-34}) + \Delta S^{\ddagger}/1.9859$

$\Delta S^{\ddagger}$ $=$ -26.5 ± 6.0 cal mol^{-1} K^{-1}

And slope $=$ $-\Delta H^{\ddagger}/R$

-11280 $=$ $-\Delta H^{\ddagger}/1.9859$

$\Delta H^{\ddagger}$ $=$ 22.4 ± 2.4 kcal mol^{-1}

Then $\Delta G^{\ddagger}$ $=$ $\Delta H^{\ddagger} - T \Delta S^{\ddagger}$

$\Delta G^{\ddagger}$ $=$ 32.8 ± 2.4 kcal mol^{-1}

The Eyring plot of conversion of **8** to **5b** over the temperature range $120^{\circ}C - 150\ ^{\circ}C$ (Figure 3.14, Table 3.8) yielded $\Delta H^{\ddagger} = 22.4 \pm 2.4$ kcal mol^{-1}, $\Delta S^{\ddagger} = -26.5 \pm 6.0$ cal mol^{-1} K^{-1}, and $\Delta G^{\ddagger} = 32.8 \pm 2.4$ kcal mol^{-1} (Figure 3.15).
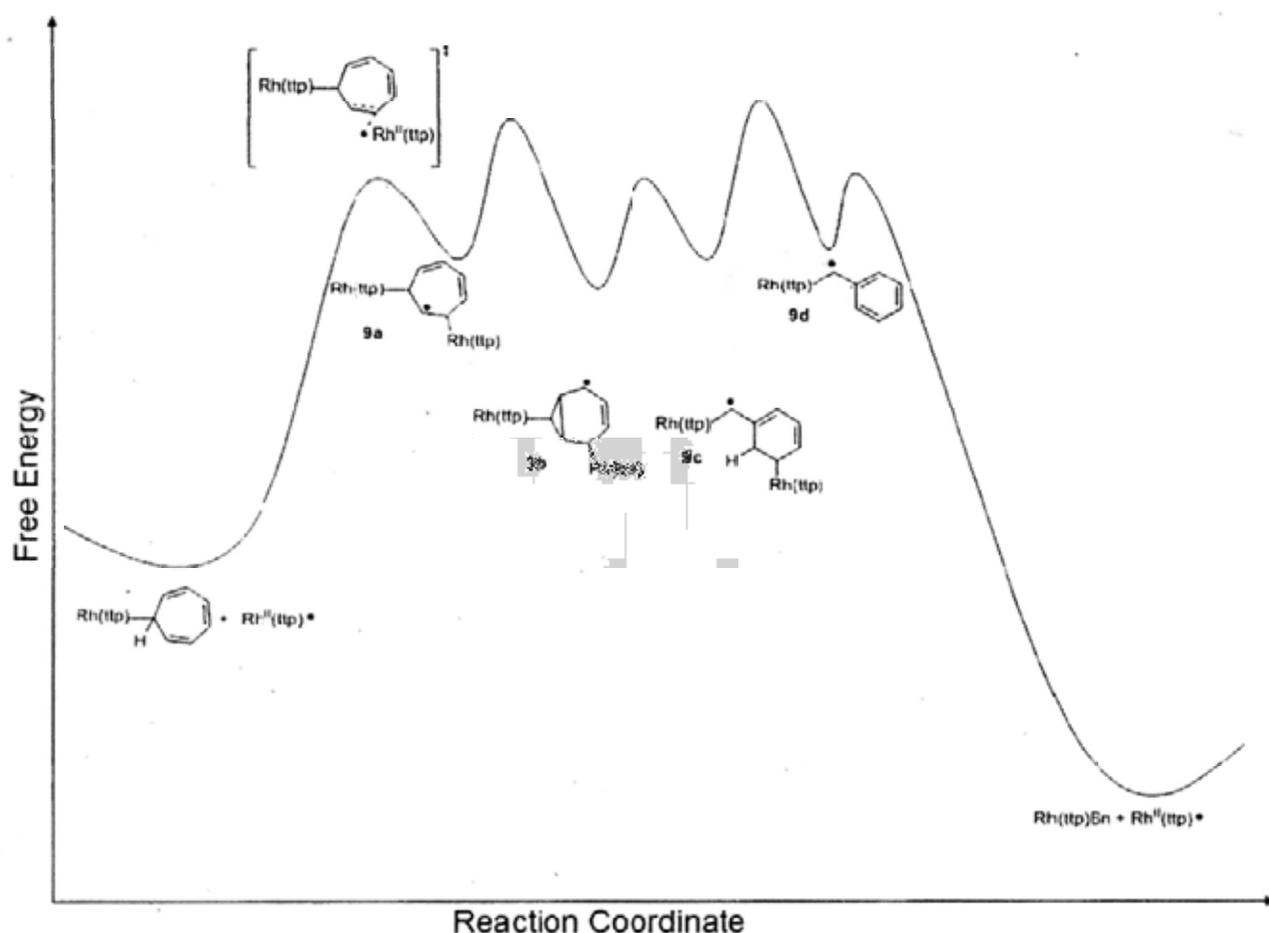

Figure 3.15 Energy Level Diagram of the Conversion of Rh(ttp)(cycloheptatrienyl) to Rh(ttp)Bn

3.6.4 Promoting Effects of Additives

Since K_2CO_3 (10 equiv) promoted the reaction of Rh(ttp)Cl and *c*-heptane to give Rh(ttp)Bn via the promoted generation of Rh$_2$(ttp)$_2$ from Rh(ttp)H co-product (eq 3.6), the promoting effects of both K_2CO_3 and Rh$_2$(ttp)$_2$ were examined separately (eq 3.30, Figures 3.16-3.18).
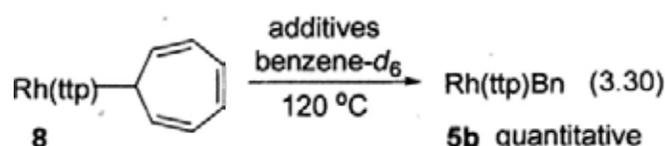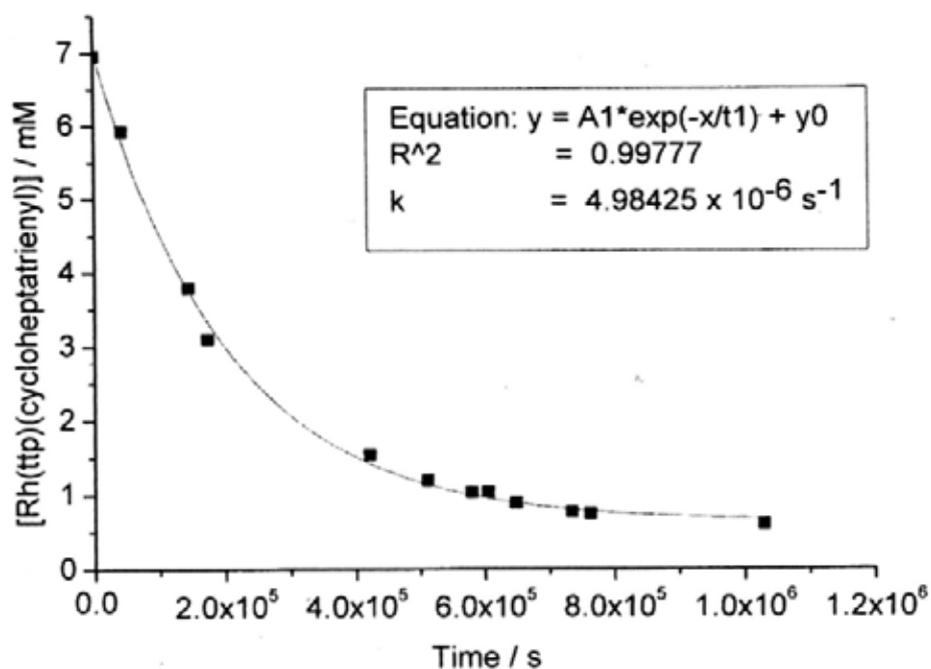
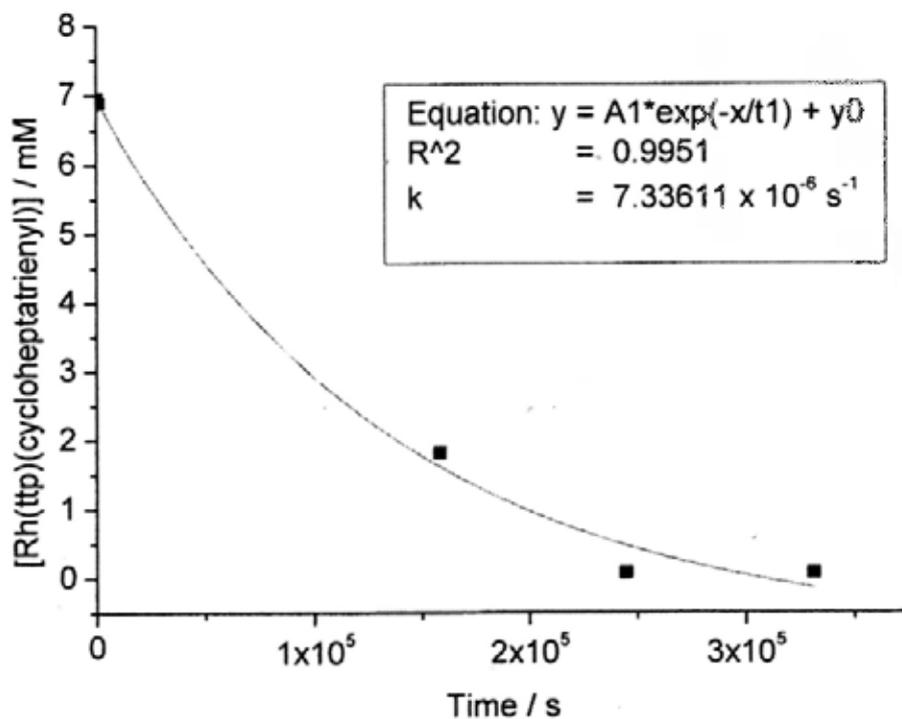Figure 3.16 Time profile of Rh(ttp)(cycloheptatrienyl) (6.95 mM) with K$_2$CO$_3$ at 120 $^{\circ}$C

Figure 3.17 Time profile of Rh(ttp)(cycloheptatrienyl) (6.95 mM) with Rh$_2$(ttp)$_2$ (3.48 x 10^{-5}

M, 1 mol%)

Equation: $y = A1 \cdot \exp(-x/t1) + y0$
$R^2 = 0.99939$
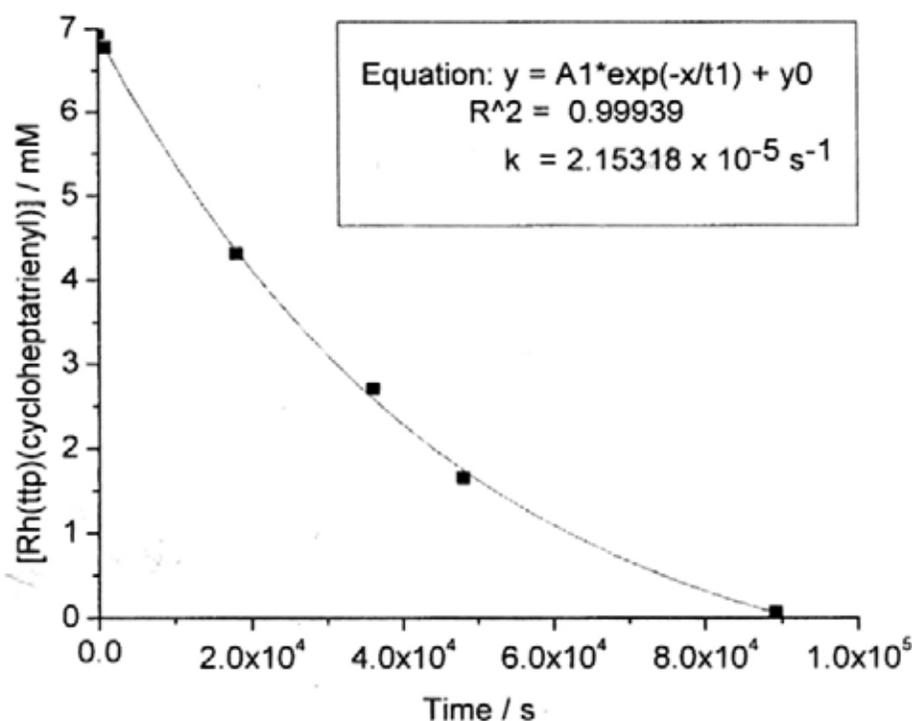$k = 2.15318 \times 10^{-5}\ s^{-1}$

Figure 3.18 Time profile of Rh(ttp)(cycloheptatrienyl) (6.95 mM) with Rh$_2$(ttp)$_2$ (3.48×10^{-4} M, 10 mol%)

Table 3.9 k_{obs} with different additive conditions (120 °C)

Entry	$[8]_0 \times 10^3$ /M	Additive	$k_{obs} \times 10^6$ /s^{-1}	Error $\times 10^7$ /s^{-1}
1	6.95	---	4.75439	3.97540
2	6.95	K$_2$CO$_3$ (10 equiv)	4.98425	2.36672
3	6.95	Rh$_2$(ttp)$_2$ (3.48×10^{-5} M)[a]	7.33611	2.04693
4	6.95	Rh$_2$(ttp)$_2$ (3.48×10^{-4} M)[b]	21.5318	12.6614

[a] 1 mol%; [b] 10 mol%

With or without the addition of K$_2$CO$_3$, the reaction rates of the transformation of **8** to **5b** are identical within experimental errors (Table 3.9, entries 1 and 2). Therefore, the conversion of **8** to **5b** is independent of K$_2$CO$_3$.

On the other hand, a small amount of $Rh_2(ttp)_2$ (1 mol%, 6.49 x 10^{-5} M) significantly enhanced the conversion rate from 4.75 x 10^{-6} s^{-1} to 7.34 x 10^{-6} s^{-1} (Table 3.9, entry 3 vs 1). A further increase in the amount of $Rh_2(ttp)_2$ to 10 mol% enhanced the rate by 3 times to 2.15 x 10^{-5} s^{-1} (Table 3.9, entry 4 vs 3).

The equilibrium concentration of $Rh^{II}(ttp)$ catalyst in solution is governed by the equilibrium constant K (eq 3.31). The equilibrium constant K is approximated according to eqs 3.32-3.33.[14] The bond dissociation energy of (ttp)Rh–Rh(ttp) bond is reported to be around 16 kcal mol^{-1}.[2] As two more molar of $\dot{R}h^{II}(ttp)$ radicals are generated from one molar of $Rh_2(ttp)_2$, the estimated $-T\Delta S_{298K}$ term is -10 kcal mol^{-1}.[3a,24] Therefore, the equilibrium constant K at 298 K is 3.95 x 10^{-5}.

$$Rh_2(ttp)_2 \xrightleftharpoons{K} 2Rh(ttp)\bullet \quad (3.31)$$
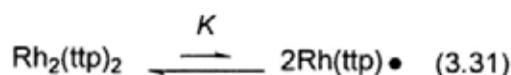
$$-\Delta G = RTlnK \quad\quad (3.32)$$

$$\Delta G = \Delta H - T\Delta S \quad\quad (3.33)$$

Therefore,

$$-(\Delta H - T\Delta S) = RTlnK$$

$$-(16 \text{ kcal mol}^{-1} - 10 \text{ kcal mol}^{-1}) = 1.9859 \times 10^{-3} \text{ kcal mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} \times lnK$$
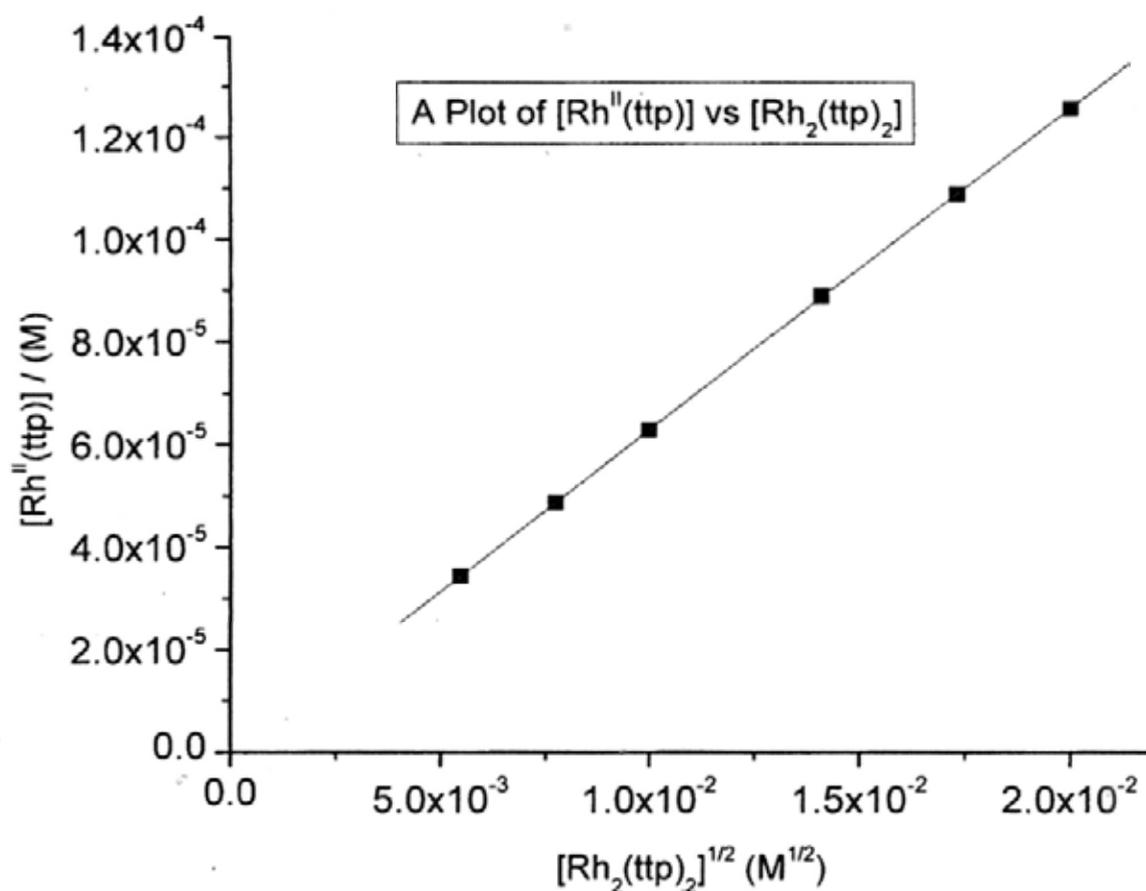
$$K = 3.95 \times 10^{-5}$$

Figure 3.19 A Plot of $[Rh^{II}(ttp)]$ at Various $[Rh_2(ttp)_2]^{1/2}$

Table 3.10 $[Rh^{II}(ttp)]$ at Various $[Rh_2(ttp)_2]^{1/2}$ Base on Calculation

Entry	$[Rh_2(ttp)_2]$ / M	$[Rh_2(ttp)_2]^{1/2}$ / $M^{1/2}$	$[Rh^{II}(ttp)]$ / M
1	3.0000×10^{-5}	5.4772×10^{-3}	3.4424×10^{-5}
2	6.0000×10^{-5}	7.7460×10^{-3}	4.8683×10^{-5}
3	1.0000×10^{-4}	1.0000×10^{-2}	6.2849×10^{-5}
4	2.0000×10^{-4}	1.4142×10^{-2}	8.8882×10^{-5}
5	3.0000×10^{-4}	1.7321×10^{-2}	1.0886×10^{-4}
6	4.0000×10^{-4}	2.0000×10^{-2}	1.2570×10^{-4}

At 298 K, the $[Rh^{II}(ttp)]$ at $Rh_2(ttp)_2$ added in 1 mol% (3.48×10^{-5} M) and 10 mol% (3.48×10^{-4} M) are estimated to be 4.16×10^{-5} M and 1.17×10^{-4} M, respectively. Therefore, even 10-fold change of $[Rh_2(ttp)_2]$ results in a 3.3-fold change of $[Rh^{II}(ttp)]$ (Table 3.10 entry 4 vs 3, Figure 3.19). The k_{obs} increased from 7.34×10^{-6} s^{-1} with 3.48×10^{-5} M of $Rh_2(ttp)_2$ added (entry 3) to 2.15×10^{-5} s^{-1} with 3.48×10^{-4} M of $Rh_2(ttp)_2$ added (entry 4). The rate equation of $Rh^{II}(ttp)$-catalyzed conversion of **8** to **5b** is therefore 1st order in $[Rh^{II}(ttp)]$. So, rate = k [**8**][$Rh^{II}(ttp)$].

3.7 Overall Proposed Mechanism

Scheme 3.8 summarizes the overall proposed mechanism for the transformation of Rh(ttp)(c-heptyl) **5a** to Rh(ttp)Bn **5b**.
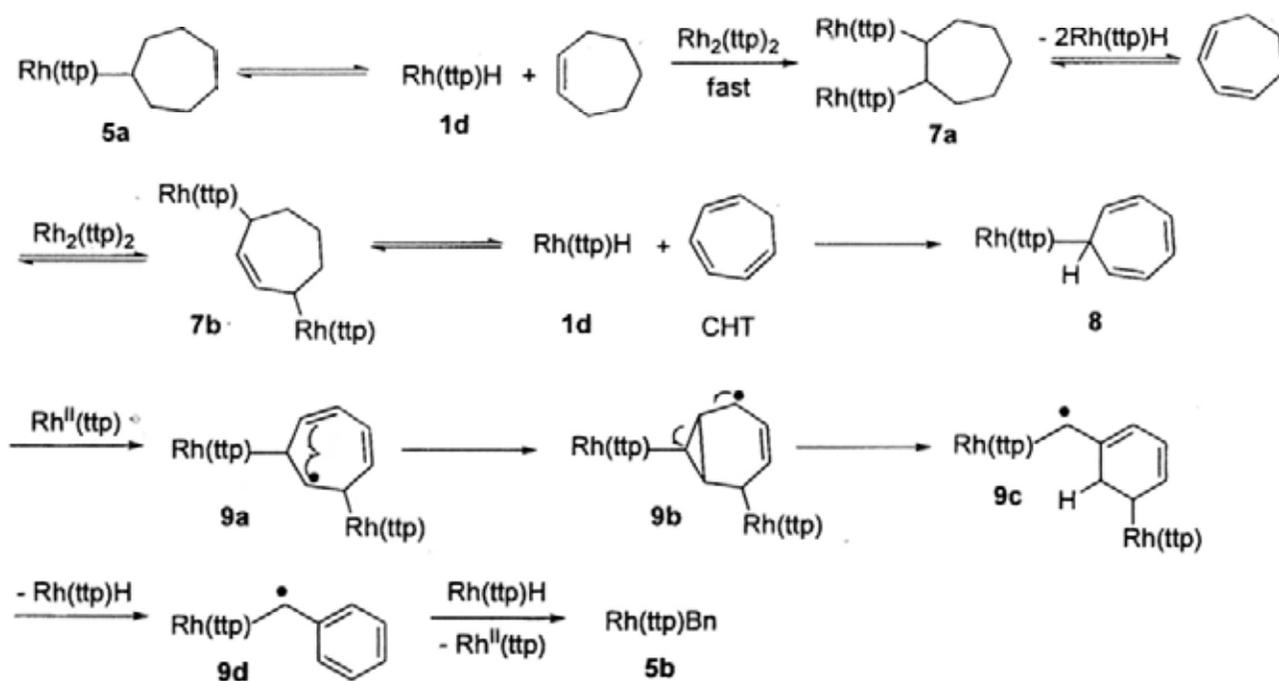
Scheme 3.8 Overall Proposed Mechanism for the Conversion of **5a** to **5b**

3.8 Conclusion

The mild, selective conversion of *c*-heptane to rhodium porphyrin benzyl via CHA and CCA has been reported. Rh(ttp)(*c*-heptyl) which formed from the base-promoted CHA of Rh(ttp)Cl and *c*-heptane is the intermediate leading to the CCA product Rh(ttp)Bn. Rh$_2$(ttp)$_2$ is generated from base-promoted dehydrogenative dimerization of Rh(ttp)H and facilitates the functionalization as follow: i) undergoing a facile CHA process; ii) trapping the alkene intermediate formed for further dehydrogenation and iii) catalyzing the rearrangement of Rh(ttp)(cycloheptatrienyl) **8** to Rh(ttp)Bn **5b**.

References

(1) (a) Mackay, D.; Shiu, W. Y.; Ma, K. C.; Lee, S. C. *Physical-Chemical Properties and Environmental Fate for Organic Chemicals 2nd Ed, Volume. 1*, CRC Press, Boca raton, FL, 2006. (b) Bocian, D. F.; Pickett, H. M.; Rounds, T. C.; Strauss, H. L. *J. Am. Chem. Soc.* **1975**, *97*, 687-695.

(2) Luo, Y. R. *Comprehensive Handbook of Chemical Bond Energies*, CRC Press, Boca Raton, FL, 2007.

(3) (a) Isaacs, N. S. *Physical Organic Chemistry*; Longman: Essex, 1987. (b) The BDE of C–C bonds are calculated based on the $\Delta H_{formation}$, see Stull, D. R.; Westrum, E. F. Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; John Wiley & Sons: New York 1969.

(4) *CRC Handbook of Chemistry & Physics 84th Ed.*, Lide, D. R. Ed. 2004.

(5) Liang, C. G.; Collet, F.; Robert-Peillard, F.; Muller, P.; Dodd, R. H.; Dauban, P. *J. Am. Chem. Soc.* **2008**, *130*, 343-350.

(6) Deng, G. J.; Li, C. J. *Org. Lett.* **2009**, *11*, 1171-1174.

(7) Maguire, J. A.; Goldman, A. S. *J. Am. Chem. Soc.* **1991**, *113*, 6706-6708.

(8) Tada, M.; Akatsuka, Y.; Yang, Y.; Sasaki, T.; Kinoshita, M.; Motokura, K.; Iwasawa, Y. *Angew. Chem. Int. Ed.* **2008**, *47*, 9252-9255.

(9) (a) Jun, C.-H. *Chem. Soc. Rev.* **2004**, *33*, 610-618. (b) Murakami, M; Amii, H.; Ito, Y. *Nature* **1994**, *370*, 540-541.

(10) Rataboul, F.; Chabanas, M.; de Mallmann, A.; Coperet, C.; Thivolle-Cazat, J.; Basset, J. M.; *Chem. Eur. J.* **2003**, *9*, 1426-1434.

(11) Basset, J. M.; Coperet, C.; Lefort, L.; Maunders, B. M.; Maury, O.; Le Roux, E.; Saggio, G.; Soignier, S.; Soulivong, D.; Sunley, G. J.; Taoufik, M.; Thivolle-Cazat, J. *J. Am. Chem. Soc.* **2005**, *127*, 8604-8605.

(12) Ruzicka, L. Seidel, C. F. *Helv. Chim. Acta* **1936**, *19*, 424-433.

(13) (a) Reger, D. L.; Culbertson, E. C. *Inorg. Chem.* **1977**, *16*, 3104-3107. (b) Reger, D. L.; Culbertson, E. C. *J. Am. Chem. Soc.* **1976**, *98*, 2789-2794.

(14) (a) Mak, K. W.; Chan, K. S. *J. Am. Chem. Soc.* **1998**, *120*, 9686-9687. (b) Mak, K. W.; Xue, F.; Mak, T. C. W.; Chan, K. S. *J. Chem. Soc., Dalton Trans.* **1999**, *19*, 3333-3334.

(15) Wayland, B. B.; van Voorhees, S. L.; Wilker, C. *Inorg. Chem.* **1986**, *25*, 4039-4042.

(16) Chan, Y. W.; Chan, K. S. *Organometallics* **2008**, *27*, 4625-4635.

(17) (a) Rataboul, F.; Chabanas, M.; de Mallmann, A.; Coperet, C.; Thivolle-Cazat, J.; Basset, J. M. *Chem. Eur. J.* **2003,** *9,* 1426-1434. (b) B elatel, H. Al-Kandari, H.; Al-Kharafi, F.; Garin, F.; Katrib, A. *Appl. Catal. A* **2007**, *318*, 227-233.

(18) Chan, K. S.; Mak, K. W.; Tse, M. K.; Yeung, S. K.; Li, B. Z.; Chan, Y. W. *J. Organomet. Chem.* **2008**, *693*, 399-407.

(19) Paonessa, R.S.; Thomas, N C.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *107*, 4333-4335.

(20) Rh(ttp)(*c*-heptyl) **1** is a formal monohydrogenated product from **5**. **5** likely gives Rh(ttp)(*c*-heptyl) radical via homolysis which then abstracts a hydrogen atom from Rh(ttp)H to give **1**.

(21) Rh$_2$(ttp)$_2$ reacted faster with CHT and Rh(ttp)H was formed as the intermediate co-product.

(22) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry. Part A: Structure and Mechanisms*, Plenum Press, New York, 1977, 504-510.

(23) (a) Woods, W. G. *J. Org. Chem.* **1958**, *23*, 110-112. (b) Gaynor, B. J.; Gilbert, R. G. *Int. J. Chem. Kinet.* **1976**, *8*, 695-707.

(24) Wayland, B. B.; Ba, S; Sherry, A. E. *J. Am. Chem. Soc.* **1991**, *113*, 5305-5311.

Chapter 4 Metalloradical-Catalyzed Aliphatic Carbon–Carbon Bond Activation of Cyclooctane

4.1 Introduction

4.1.1 Properties of Cyclooctane

c-Octane is a colourless combustible liquid at ambient conditions. It is readily miscible with ethanol and ether but insoluble in water.[1a] c-Octane is the conformationally most complex cycloalkane as it has so many forms of comparable energy. Computational studies suggest that the boat-chair conformation is the most stable one while the crown form is slightly less stable (fluxional energy = 7-8 kcal mol^{-1}) (Figure 4.1).[1b] Some other properties concerning the reactivity of c-octane are summarized in Table 4.1.

Crown Form   Boat-Chair Form

Figure 4.1 Crown Form and Boat-Chair Form of c-Octane (Hydrogen Hidden)

Table 4.1 Properties Concerning the Reactivity of c-Octane[2-4]

Properties	Corresponding Value
BDE of C–H	95.7 kcal mol^{-1}
BDE of C–C	79.6 kcal mol^{-1}
Ring Strain	9.6 kcal mol^{-1}
Diamagnetic Susceptibility	-85.3 x 10^{-6} cm^3 mol^{-1}
Dielectric Constant	2.116 at 20.0 $^\circ$C

4.1.2 CHA of c-Octane

Alkane functionalization in a homogenous medium is an important and challenging process which involves either carbon–hydrogen bond activation (CHA)[5] or carbon–carbon bond activation (CCA)[6] with organic, inorganic and organometallics reagents. Although aliphatic C–C bonds are weaker than aliphatic C–H bonds, CCA of alkanes is much less reported due to the steric hindrance of the C–C bond by the attack of a transition metal complex.[7]
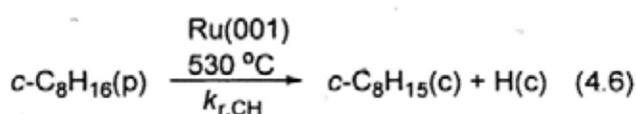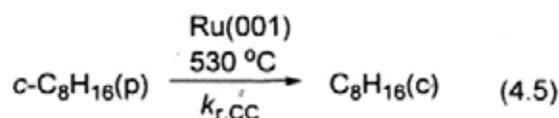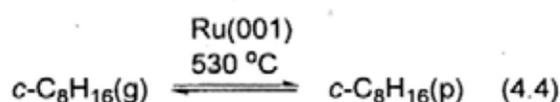
c-Octane is a relatively unstrained cycloalkane and therefore serves as a commonly investigated substrate in alkane functionalization, mostly involving CHA. Some examples of CHA of c-octane are the iridium(I) pincer dihydride-catalyzed dehydrogenation to c-octene (eq 4.1),[8a] the FeCl$_3$-catalyzed aerobic oxidation to c-octanol and c-octanone (eq 4.2),[8b] as well as the MnO$_2$-catalyzed bromination to c-octyl bromide (eq 4.3).[8c]

$$\text{TOF} = 0.0094 \text{ min}^{-1} \quad (4.1)$$

$$(4.2)$$

$$(4.3)$$
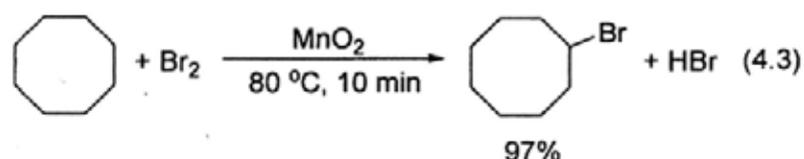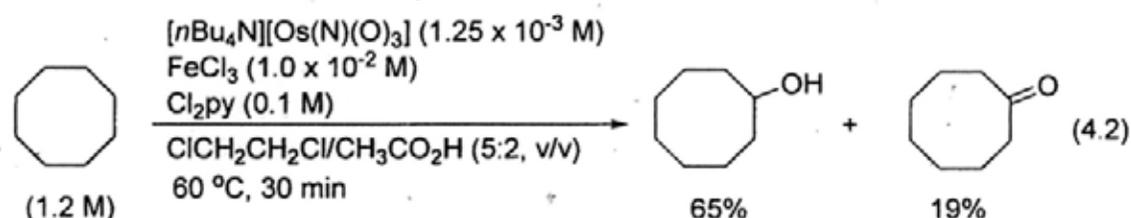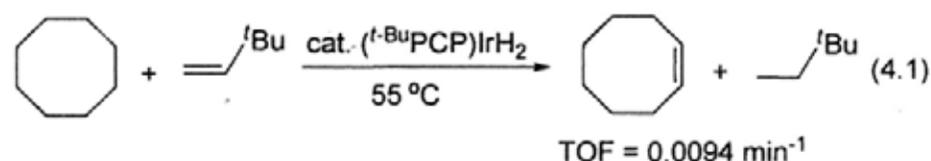
4.1.3 CCA of c-Octane

Examples of CCA of c-octane are rarely reported. A CCA of c-octane in a heterogenous medium requires a very high reaction temperature of 530 °C and consequently results in both CHA and CCA (eqs 4.4-4.6).[7a] An oxidative CCA of c-octane catalyzed by N-
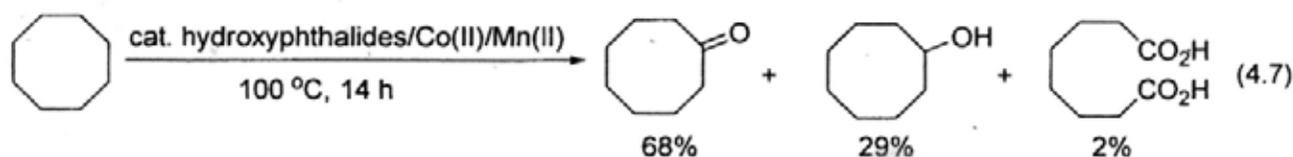
113

hydroxyphthalides/Co(II)/Mn(II) at 100 °C in 14 h gives ω-dicarboxylic acids in 2% yield only (eq 4.7).[7b]

$$c\text{-}C_8H_{16}(g) \; \underset{}{\overset{\substack{Ru(001) \\ 530\ ^\circ C}}{\rightleftharpoons}} \; c\text{-}C_8H_{16}(p) \quad (4.4)$$

$$c\text{-}C_8H_{16}(p) \; \xrightarrow[k_{r,CC}]{\substack{Ru(001) \\ 530\ ^\circ C}} \; C_8H_{16}(c) \quad (4.5)$$

$$c\text{-}C_8H_{16}(p) \; \xrightarrow[k_{r,CH}]{\substack{Ru(001) \\ 530\ ^\circ C}} \; c\text{-}C_8H_{15}(c) + H(c) \quad (4.6)$$

(g) : gaseous state;

(p) : physically adsorbed state;

(c) : chemisorbed product

$$\text{(4.7)}$$

$$68\% \qquad 29\% \qquad 2\%$$

4.2   Objectives of the Work

The objectives of this work are to (i) broaden the synthetic scope; (ii) to gain further mechanistic understanding of the aliphatic CCA of *c*-octane with rhodium porphyrin complexes and (iii) identifying the unique role of Rh(II) porphyrin (Scheme 4.1).

$$M-H \; \xrightarrow[\text{cat. M·}]{\substack{CCA \\ c\text{-octane}}} \; \underset{\text{selective}}{M-(n\text{-octyl})}$$
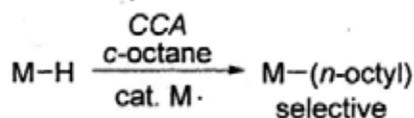
Scheme 4.1. CCA Pathway of *c*-Octane with MH

4.3   Discovery of CCA of *c*-Octane

Initially, *c*-octane was found to react poorly with Rh(ttp)Cl **1a** to give Rh(ttp)(*c*-octyl) **10a** and Rh(ttp)(*n*-octyl) **10b** in 5% and 8% yields, respectively (eq 4.8, Table 4.2, entry 1). A 72% yield of Rh(ttp)Cl **1a** was recovered, and a trace amount of Rh(ttp)H **1d** was observed.

Both CHA and CCA products formed but the reaction was inefficient. The addition of KOH (10 equiv) to the reaction mixture, Rh(ttp)(c-octyl), Rh(ttp)(n-octyl) and Rh(ttp)H were obtained in 6%, 25% and 62% yields, respectively in 7.5 h (Table 4.2, entry 2). When K_2CO_3 (10 equiv) was added,[9] Rh(ttp)Cl was consumed in 7.5 h and Rh(ttp)(n-octyl) **10b** and Rh(ttp)H **1d** were obtained in 33% and 58% yields, respectively (Table 4.2, entry 3). The CCA product **10b** is the formal 1,2-addition product of Rh(ttp)H **1d** into c-octane. The substrate c-octane was found to be free of n-octane and 1-octene by GC-MS analysis (Appendix). Therefore, Rh(ttp)(n-octyl) was indeed the CCA product of c-octane. The structures of **10a** and **10b** were confirmed by independent syntheses (eq 4.9).[10] **10b** was further characterized by X-ray crystallography (Figure 4.2).
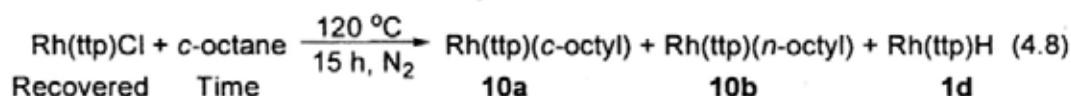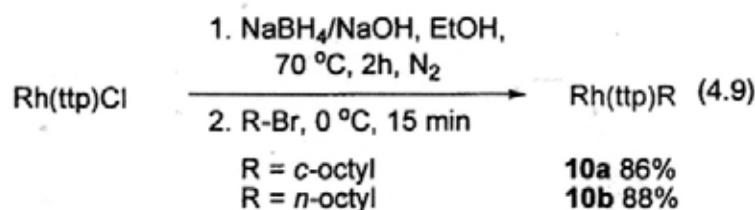
$$Rh(ttp)Cl + c\text{-octane} \xrightarrow[15\text{ h, N}_2]{120\ ^\circ C} Rh(ttp)(c\text{-octyl}) + Rh(ttp)(n\text{-octyl}) + Rh(ttp)H \quad (4.8)$$

Recovered   Time   **10a**   **10b**   **1d**

Table 4.2 Reaction of c-Octane with Rh(ttp)Cl in the Absence and Presence of Base

Entry	Additive[a]	Time	Yield (%)				
			Rh(ttp)Cl recovered	Rh(ttp)(c-octyl)	Rh(ttp)(n-octyl)	Rh(ttp)H	Total
1	-----	2 d	72	5	8	0	85
2	KOH	7.5 h	0	6	25	62	93
3	K_2CO_3	7.5 h	0	0	33	58	91

[a] 10 equiv

$$Rh(ttp)Cl \xrightarrow[\text{2. R-Br, 0 }^\circ C, 15\text{ min}]{\substack{\text{1. NaBH}_4/\text{NaOH, EtOH,} \\ 70\ ^\circ C, 2h, N_2}} Rh(ttp)R \quad (4.9)$$

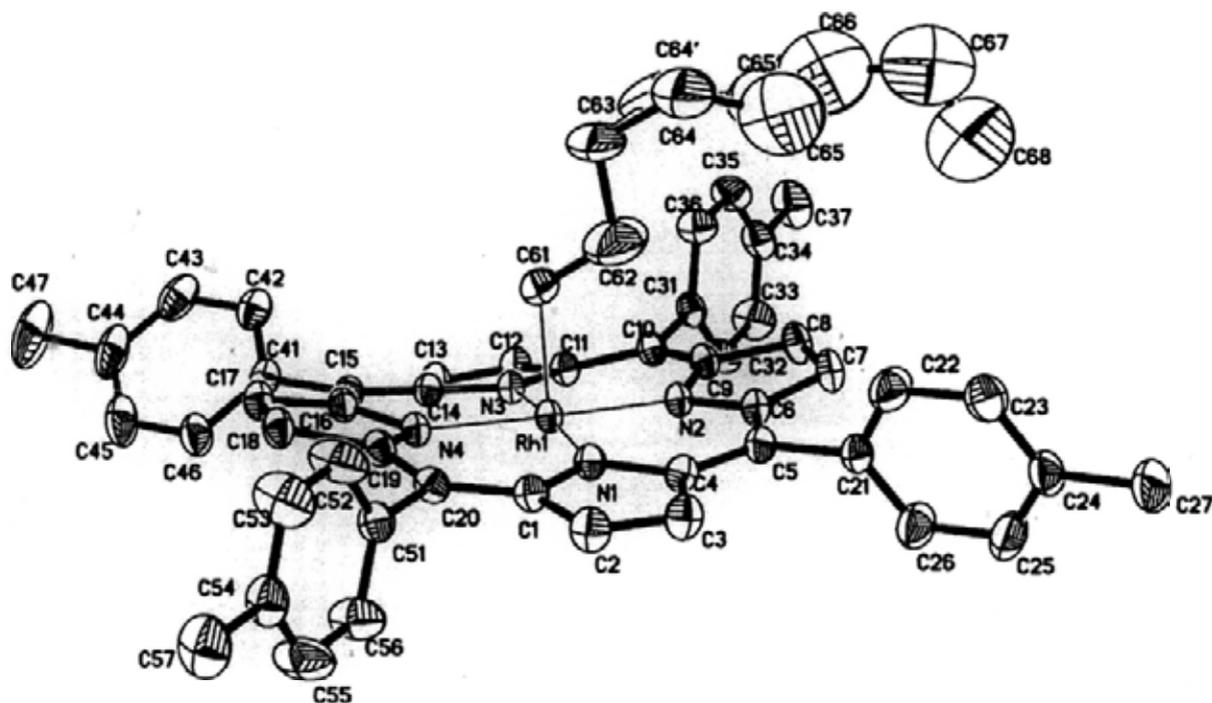R = c-octyl   **10a** 86%
R = n-octyl   **10b** 88%

Figure 4.2 ORTEP Presentation of Rh(ttp)(*n*-octyl) **10b** (30% Probability Displacement Ellipsoids). Rh-C = 2.03 Å, R = 0.0522

4.4   Mechanistic Investigation

4.4.1   Conversion of CHA Product Rh(ttp)(*c*-octyl) to CCA Product Rh(ttp)(*n*-octyl)

In some CCA of hydrocarbons, transition metal complexes reacted with hydrocarbons to give CHA and CCA products in parallel and consecutive pathways.[11] Milstein et al. discovered that diphosphine 1,3-bis[(di-*tert*-butylphosphino)methyl]-2,4,6-trimethylbenzene reacted with [Rh(alkene)Cl]$_2$ with parallel CHA and CCA pathways (Scheme 4.2).[11a] The CHA product was eventually converted to the thermodynamically favorable CCA product in prolonged reaction.
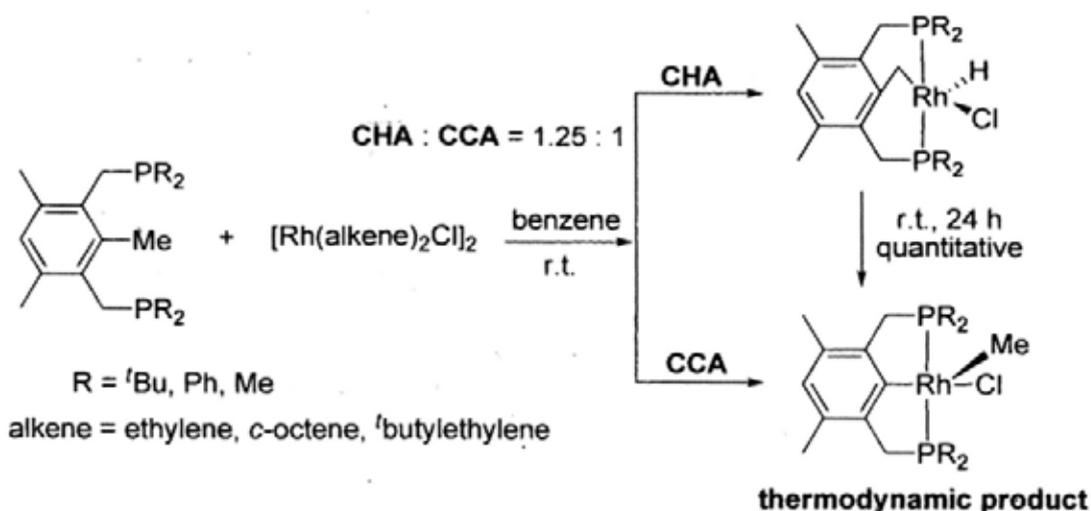
Scheme 4.2 Proposed Mechanism of Parallel CHA and CCA in PCP System

Jones and co-workers discovered that $Cp^*Rh(PMe_3)(Ph)(H)$ activated the aromatic C–H bond of biphenylene to give Rh–aryl complex.[11b] The Rh–aryl complex was found to be an intermediate to the final CCA product (Scheme 4.3).
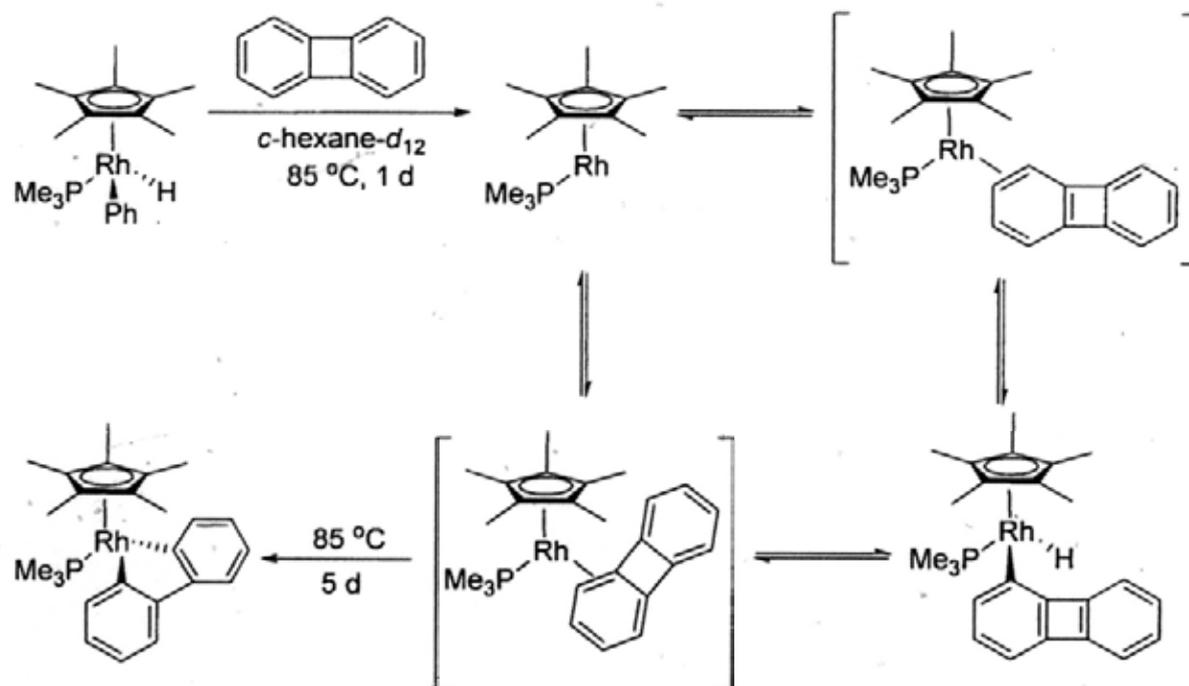
Scheme 4.3 Proposed Mechanism of the CCA of Biphenylene with $Cp^*Rh(PMe_3)(Ph)(H)$ via CHA Intermediate

To investigate whether the CHA product is an intermediate for CCA,[11] Rh(ttp)(c-octyl) **10a** was heated in benzene-d_6 in both neutral and basic conditions separately. Without K_2CO_3, Rh(ttp)(c-octyl) **10a** gave Rh(ttp)(n-octyl) **10b**, Rh(ttp)H **1d** and c-octene in 10%, 76%, and 36% yields, respectively after 21 h (eq 4.10, Figure 4.3, Table 4.3).
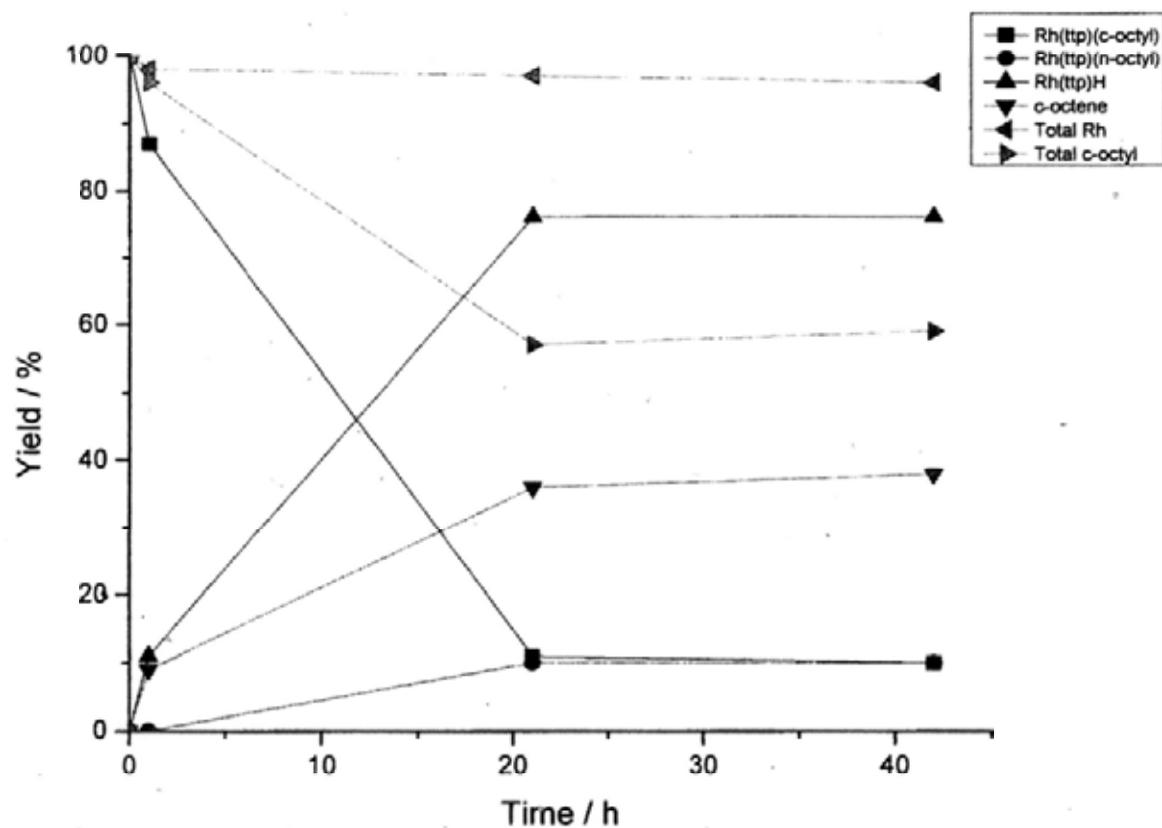
$$\text{Rh(ttp)(c-octyl)} \xrightarrow[\text{120 °C, 21 h}]{\text{benzene-}d_6} \text{Rh(ttp)(n-octyl)} + \text{Rh(ttp)H} + c\text{-octene} \quad (4.10)$$

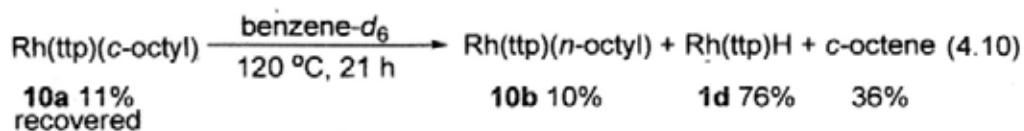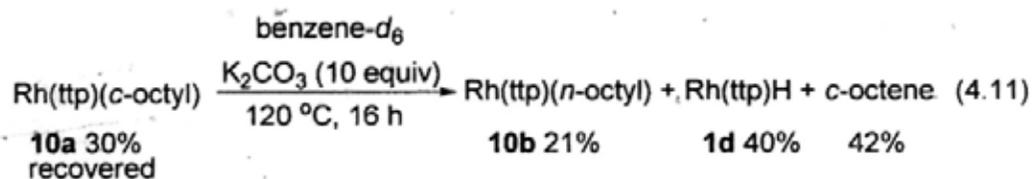**10a** 11% recovered   **10b** 10%   **1d** 76%   36%

Figure 4.3 Time Profile of Thermal Reaction of Rh(ttp)(c-octyl) **10a**

Table 4.3 Time Profile of Thermal Reaction of Rh(ttp)(c-octyl) **10a**

	Yield %					
Time/h	Rh(ttp)(c-octyl)	Rh(ttp)(n-octyl)	Rh(ttp)H	c-octene	Total Rh pdt	Total Org pdt
0	100	0	0	0	100	0
1	87	0	11	9	98	96
21	11	10	76	36	97	57
42	10	10	76	38	96	59

In the presence of K_2CO_3 (10 equiv), Rh(ttp)(n-octyl) **10b** was isolated in a higher yield of 21% in 16 h (eq 4.11, Figure 4.4, Table 4.4). However, both reactions were low yielding and incomplete. Therefore, the CHA product is not a major intermediate leading to the CCA product.

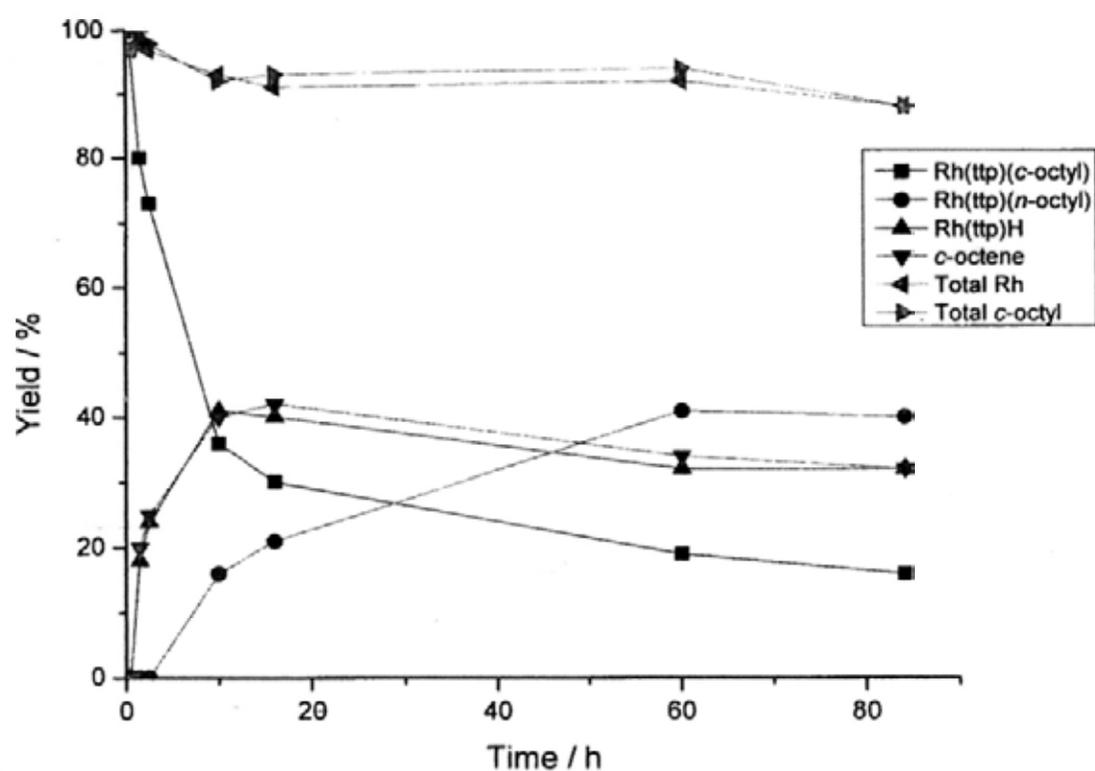$$\text{Rh(ttp)(c-octyl)} \xrightarrow[\substack{K_2CO_3 \ (10 \ equiv) \\ 120 \ ^\circ C, \ 16 \ h}]{\text{benzene-}d_6} \text{Rh(ttp)(n-octyl)} + \text{Rh(ttp)H} + \text{c-octene} \quad (4.11)$$

10a 30% recovered   **10b** 21%   **1d** 40%   42%

Figure 4.4 Time Profile of Basic Reaction of Rh(ttp)(c-octyl) **10a**

Table 4.4 Time Profile of Basic Reaction of Rh(ttp)(c-octyl) **10a**

	Yield %					
Time/h	Rh(ttp)(c-octyl)	Rh(ttp)(n-octyl)	Rh(ttp)H	c-octene	Total Rh pdt	Total Org pdt
0	100	0	0	0	100	100
0.5	97	00	0	0	97	97
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
60	19	41	32	34	92	94
84	16	40	32	32	88	88

4.4.2 Reaction Time Profile

To enhance the CCA reaction of Rh(ttp)Cl **1a** with *c*-octane based on mechanistic understandings, the reaction was monitored by ^{1}H NMR spectroscopy in a sealed NMR tube (eq 4.12, Figure 4.5, Table 4.5).

$$\text{Rh(ttp)Cl} + c\text{-octane} \xrightarrow[\substack{120\ ^\circ\text{C, 62 h}}]{\substack{\text{benzene-}d_6 \\ \text{K}_2\text{CO}_3\ (10\ \text{equiv})}} \text{Rh(ttp)(}n\text{-octyl)} + \text{Rh(ttp)H} + c\text{-octene} \quad (4.12)$$

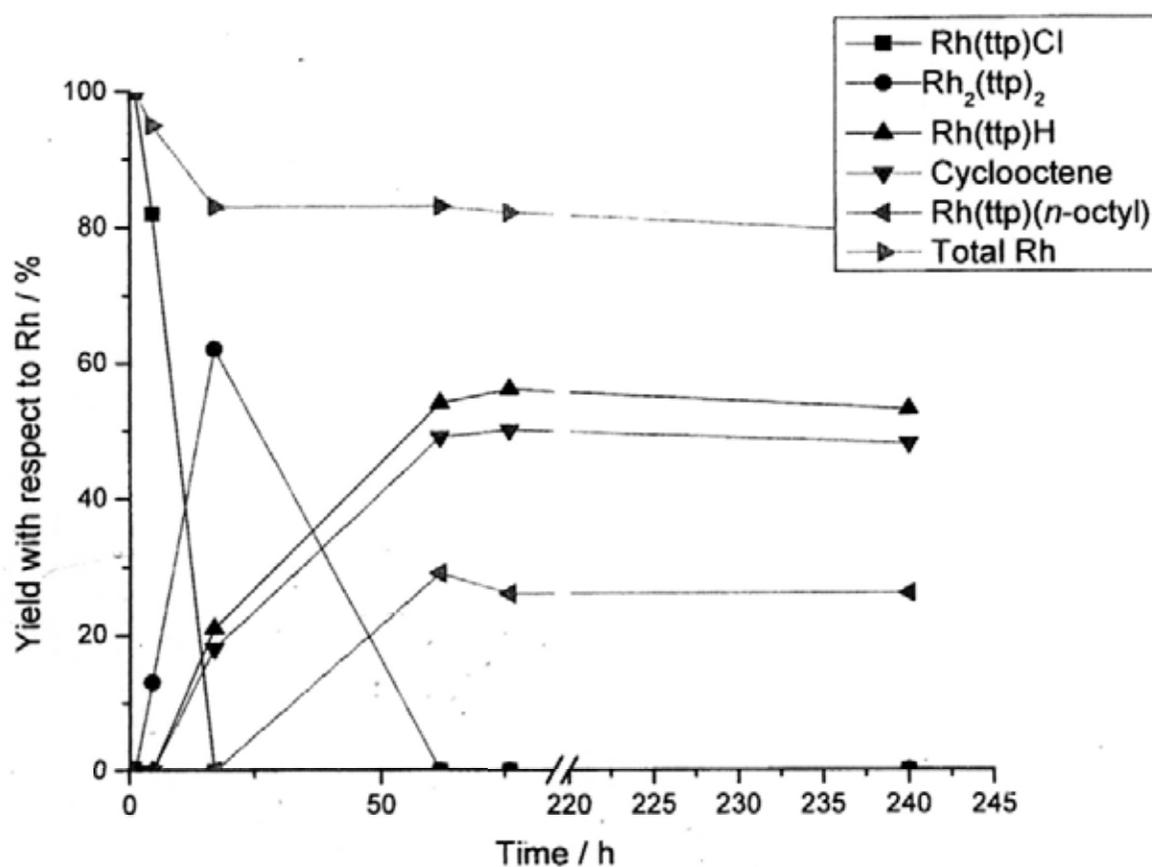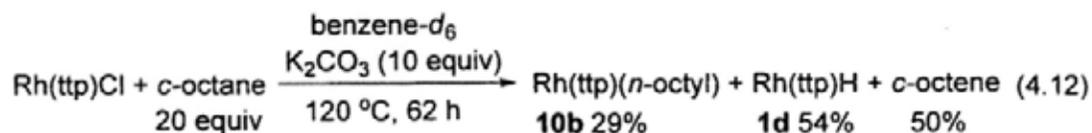20 equiv   **10b** 29%   **1d** 54%   50%

Figure 4.5 Time Profile of Reaction of Rh(ttp)Cl with *c*-Octane in the Presence of Potassium Carbonate

Table 4.5 Time Profile of Reaction of Rh(ttp)Cl with c-Octane in the Presence of Potassium Carbonate

Time/h	Rh(ttp)Cl	Rh(ttp)(n-octyl)	Rh(ttp)H	c-octene	Rh$_2$(ttp)$_2$	Total Rh	Total Org
0	100	0	0	0	0	100	0
0.5	100	0	0	0	0	100	0
1	100	0	0	0	0	100	0
4.5	82	0	0	0	13	95	0
17	0	0	21	18	62	83	18
62	0	29	54	50	0	83	79
76	0	26	56	52	0	82	78
240	0	26	53	48	0	79	74

Initially, Rh(ttp)Cl was first converted to Rh$_2$(ttp)$_2$ **1e** in the presence of K$_2$CO$_3$.[12] At 4.5 h, 82% yield of Rh(ttp)Cl remained while Rh$_2$(ttp)$_2$ **1e** was formed in 13% yield. After 17 h, Rh(ttp)Cl completely reacted. Rh$_2$(ttp)$_2$ **1e**, Rh(ttp)H **1d** and c-octene were formed in 62%, 21% and 18% yields, respectively. After 62 h, Rh$_2$(ttp)$_2$ **1e** completely reacted. The yields of Rh(ttp)H **1d** and c-octene increased to 54% and 50%, respectively and only 29% yield of Rh(ttp)(n-octyl) **10b**, the CCA product, was obtained. Finally, Rh(ttp)(n-octyl) was generated in prolonged heating and still, Rh(ttp)H was consumed slowly and mostly remained unreacted even after 10 days. Therefore, both Rh$_2$(ttp)$_2$ and Rh(ttp)H are possible intermediates. The observed ^{1}H NMR upfield signals at δ = -5 to 1 ppm (Figure 4.6) were assigned to Rh(ttp)–incorporated c-octene oligomers (about 15% NMR yield), which indicate the occurrence of Rh^{II}(ttp)–initiated oligomerization of c-octene.[13]
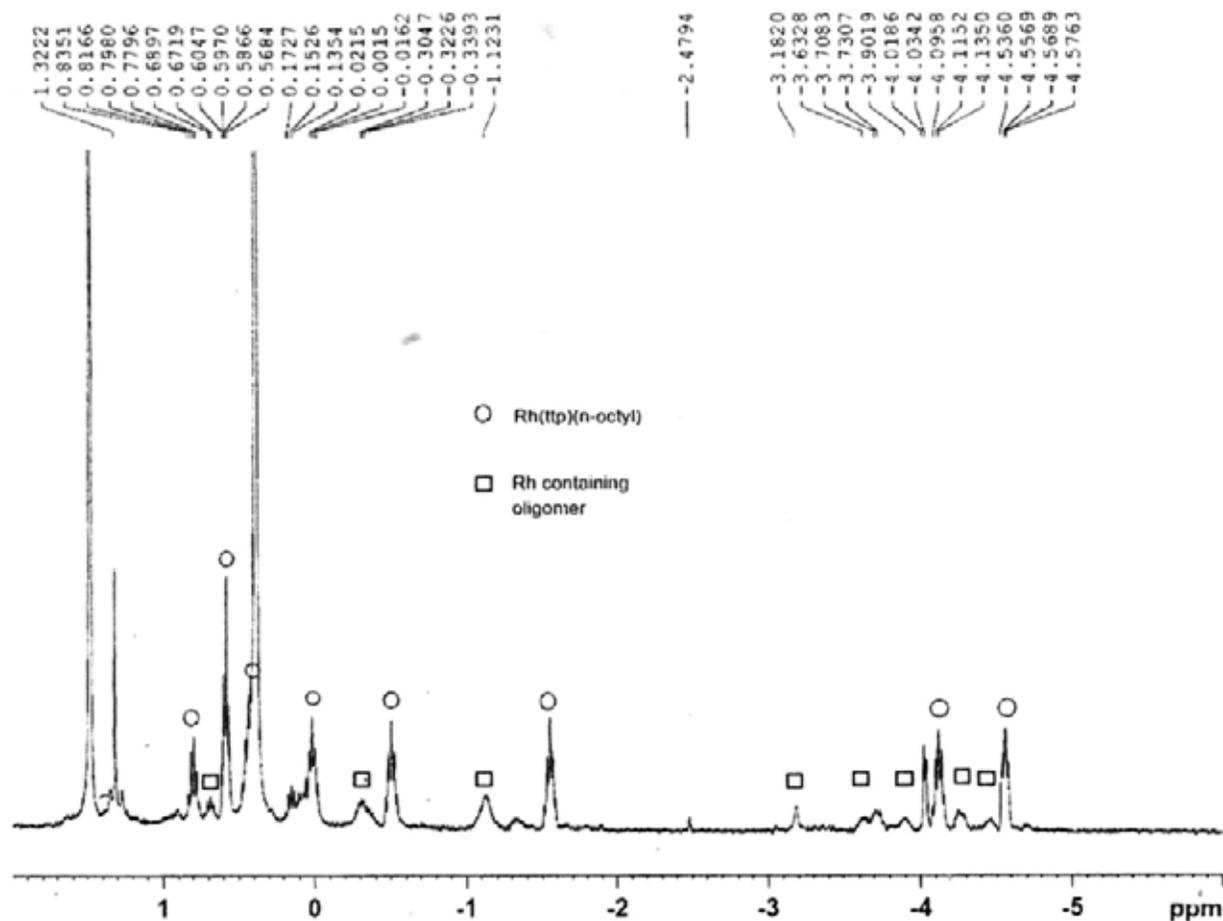
Figure 4.6 ^{1}H NMR Spectrum of Rh(ttp)(*n*-octyl) and Suspected Oligomer in Benzene-d_6

Olefin is well known to undergo polymerization.[13] For example, ethene polymerized readily in the presence of BzO–OBz, which produces BzO• radical by homolysis (eq 4.13, scheme 4.4).[13c] *c*-Octene underwent polymerization to produce a vinyl polymer in the presence of appropriate transition metal catalyst (eq 4.14).[13d]

$$n \ H_2C{=}CH_2 \xrightarrow[\text{100-250 °C}]{\text{cat. BzO-OBz}} {-}{\Big[}CH_2{-}CH_2{\Big]}_n \quad \text{(eq 4.13)}$$
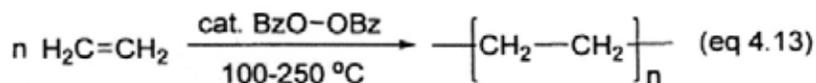
Free Radical Chain Mechanism

Initiation

$$BzO{-}OBz \longrightarrow 2\,BzO\cdot$$

Propagation

$$BzO\cdot + {=\!\!=} \longrightarrow BzO{-}CH_2{-}\overset{\cdot}{C}H_2$$

$$BzO{-}CH_2{-}\overset{\cdot}{C}H_2 + n\,{=\!\!=} \longrightarrow BzO{\Big[}CH_2{-}CH_2{\Big]}_n CH_2{-}\overset{\cdot}{C}H_2$$

Termination

$$2\,BzO{\Big[}CH_2{-}CH_2{\Big]}_n CH_2{-}\overset{\cdot}{C}H_2 \longrightarrow BzO{\Big[}CH_2{-}CH_2{\Big]}_{2n+2}{-}OBz$$

Scheme 4.4 Free Radical Chain Mechanism of Ethylene

$$\text{(eq 4.14)}$$

73%
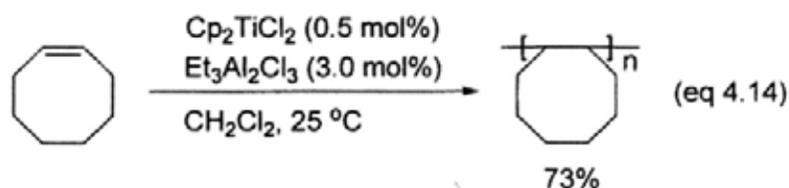
The formation of *c*-octene, which forms from the β-H elimination of Rh(ttp)(*c*-octyl) **10a**, indicated the CHA of *c*-octane. When *c*-octene accumulates, it serves as a trap for Rh₂(ttp)₂ and therefore stops the CCA (Scheme 4.5).
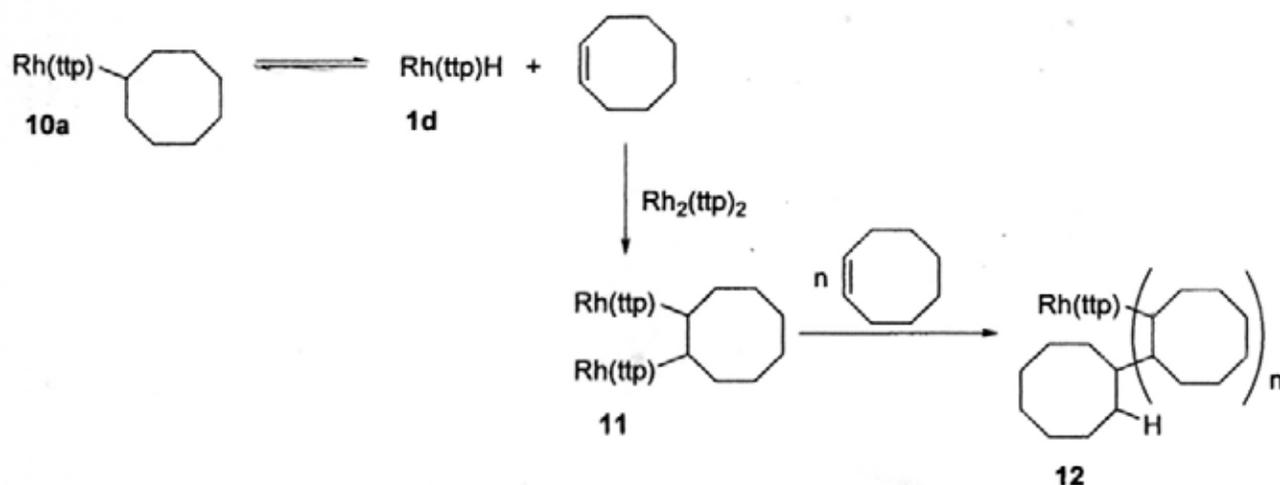
Scheme 4.5 Formation of *c*-Octene and Trap for Rh₂(ttp)₂

In fact, in the reaction of eq 4.12, a small piece of gum-like substance was observed in the red reaction mixture which was more viscous than c-octane solution. $Rh^{II}(ttp)$ radical likely polymerizes the c-octene formed in the reaction mixture as shown in scheme 4.6.

Chain initiation

$$Rh_2(ttp)_2 \rightleftharpoons 2Rh(ttp)\cdot$$

Chain propagation
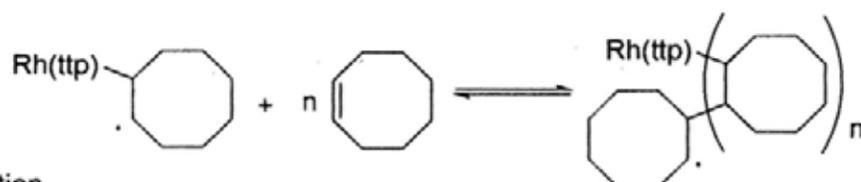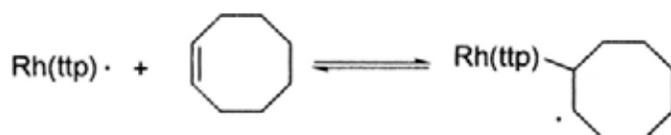
Chain termination

12
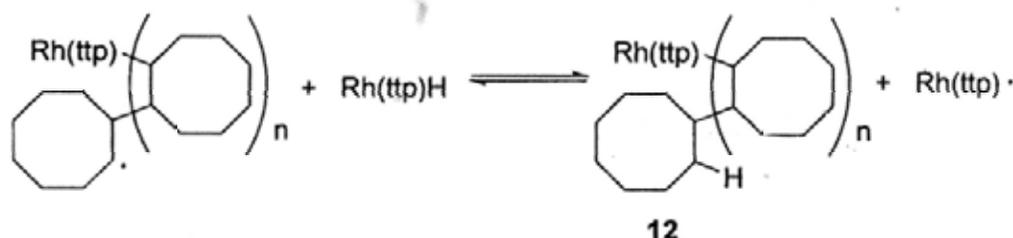
Scheme 4:6 $Rh^{II}(ttp)$–Initiated Oligomerization of c-Octene

Indeed, $Rh_2(ttp)_2$ reacted with c-octene to give a suspected di-rhodium alkyl **11** ($\delta = 4.70$ ppm) (eq 4.15). However, **11** was thermally unstable even at room temperature and decomposed possibly via Rh–C homolysis.[14] The Rh–alkyl radical then reacts with excess c-octene to give **12**.

$$(4.15)$$

4.4.3 Reactivity of Intermediates Rh(ttp)H and Rh$_2$(ttp)$_2$ towards *c*-Octane

To investigate the intermediacy of Rh(ttp)H and Rh$_2$(ttp)$_2$, Rh(ttp)H **1d** and Rh$_2$(ttp)$_2$

1e were then separately reacted with *c*-octane. Rh(ttp)H **1d** indeed reacted with *c*-octane at

120 °C in 15 h to give Rh(ttp)(*n*-octyl) **10b** selectively, though in only 21% yield, and was

also recovered in 73% yield (eq 4.16). Prolonged heating of Rh(ttp)H in *c*-octane to 12 d

yielded Rh(ttp)(*n*-octyl) and Rh$_2$(ttp)$_2$ in 94% and 2% yields, respectively (eq 4.17). As

Rh(ttp)H underwent slow dehydrogenative dimerization to give 6% yield of Rh$_2$(ttp)$_2$ at 120

°C in 1 day (eq 4.18), similar to the report by Wayland and co-workers (eq 4.19),[15] the small

amount of Rh$_2$(ttp)$_2$ formed in eq 4.16 likely facilitates the 1,2-addition of Rh(ttp)H into *c*-
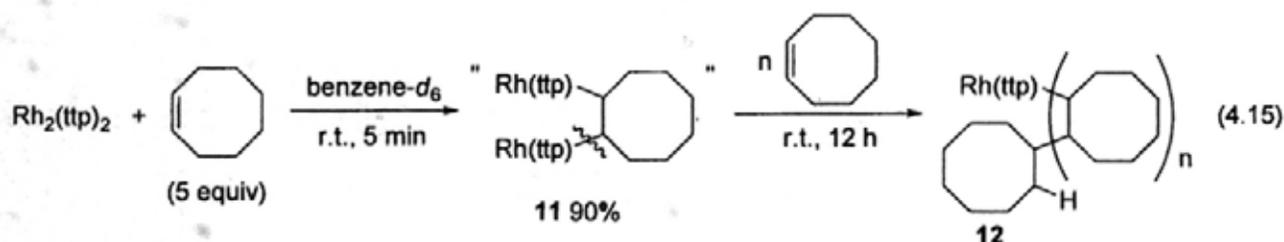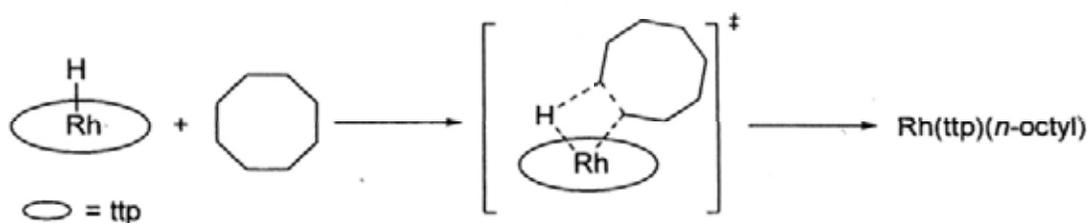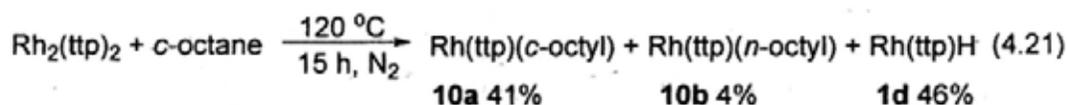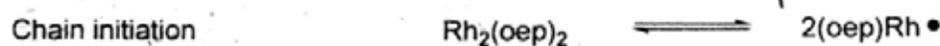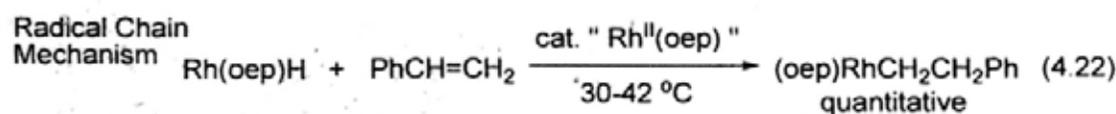
octane.[16]

$$\text{Rh(ttp)H} + c\text{-octane} \xrightarrow[\text{15 h, N}_2]{120\ ^\circ\text{C}} \text{Rh(ttp)(}n\text{-octyl)} \qquad (4.16)$$
$$\text{73\% recovered} \qquad\qquad\qquad \textbf{10b}\ 21\%$$

$$\text{Rh(ttp)H} + c\text{-octane} \xrightarrow[\text{12 d, N}_2]{120\ ^\circ\text{C}} \text{Rh(ttp)(}n\text{-octyl)} + \text{Rh}_2\text{(ttp)}_2 \quad (4.17)$$
$$\textbf{10b}\ 94\% \qquad\qquad 2\%$$

$$2\text{Rh(ttp)H} \xrightarrow[\text{120 }^\circ\text{C, 1 d}]{\text{benzene-}d_6} \text{Rh}_2\text{(ttp)}_2 + \text{"H}_2\text{"} \qquad (4.18)$$
$$\text{91\% recovered} \qquad\qquad 6\%$$

$$2\text{Rh(tpp)H} \xrightarrow[\text{80 }^\circ\text{C, <0.5 h}]{\text{benzene-}d_6} \text{Rh}_2\text{(tpp)}_2 + \text{"H}_2\text{"} \qquad (4.19)$$

The alternative σ-bond metathesis is possible but less favored based on the discussion

in below: (i) The addition of PPh$_3$ to Rh(ttp)H gave quantitative Rh(ttp)H(PPh$_3$) (eq 4.20).

Rh(ttp)H(PPh$_3$) does not undergo further dimerization to give Rh$_2$(ttp)$_2$(PPh$_3$) and therefore

no CCA occurs.

$$\text{Rh(ttp)H} + \text{PPh}_3 + c\text{-octane} \xrightarrow[\text{1.5 d, N}_2]{120\ ^\circ\text{C}} \text{Rh(ttp)H(PPh}_3)\ (4.20)$$
$$\text{quantitative}$$

(ii) In order to form Rh(ttp)(*n*-octyl) via σ-bond metathesis, the Rh(ttp)–H and the C–

C bonds of *c*-octane are required to force on the same side of a porphyrin plane to form a

very crowded 4-centered transition state (Scheme 4.7).[17]

Scheme 4.7 4-Centered Transition State via σ-Bond Metathesis

The other possible intermediate $Rh_2(ttp)_2$ **1e** was also reacted with c-octane. Rh(ttp)(c-octyl) **10a**, Rh(ttp)(n-octyl) **10b** and Rh(ttp)H **1d** were formed in 41%, 4% and 46% yields, respectively (eq 4.21) with a very low yield of CCA product.[18] Therefore, both Rh(ttp)H **1d** and $Rh_2(ttp)_2$ **1e** gave low yielding reactions and are likely only minor reaction intermediates by themselves.

$$Rh_2(ttp)_2 + c\text{-octane} \xrightarrow[\text{15 h, } N_2]{120\ °C} Rh(ttp)(c\text{-octyl}) + Rh(ttp)(n\text{-octyl}) + Rh(ttp)H \quad (4.21)$$

$$\textbf{10a } 41\% \qquad\qquad \textbf{10b } 4\% \qquad\qquad \textbf{1d } 46\%$$
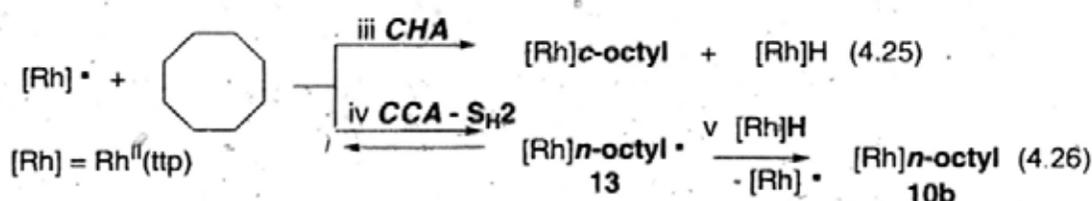
4.5 Proposed Mechanism of Rh^{II}(ttp)-Catalyzed CCA of c-Octane

Even though both Rh(ttp)H and $Rh_2(ttp)_2$ are intermediates, independent experiments showed that they separately reacted with c-octane to give poor CCA yields. Therefore, Rh^{II}(ttp)/$Rh_2(ttp)_2$ may act as a catalyst to facilitate the 1,2-addition of c-octane with Rh(ttp)H. Indeed, a Rh^{II}(oep)–catalyzed (oep = octylethylporphyrin dianion) 1,2-addition of styrene was reported by Haplern et al..[16] Styrene underwent facile 1,2-addition reaction with Rh(oep)H to give Rh(oep)CH_2CH_2Ph (eq 4.22).[16] Rh^{II}(oep), which forms from homolysis of $Rh_2(oep)_2$, inserts into the C=C bond to give a Rh–alkyl radical (Scheme 4.8). The Rh–alkyl radical formed then abstracts a hydrogen atom from Rh(oep)H to yield the 1,2-addition product Rh(oep)CH_2CH_2Ph and regenerates Rh^{II}(oep).

Radical Chain Mechanism

$$Rh(oep)H \ + \ PhCH=CH_2 \ \xrightarrow[\text{30-42 °C}]{\text{cat. " Rh}^{II}\text{(oep) "}} \ (oep)RhCH_2CH_2Ph \quad (4.22)$$
quantitative

Chain initiation $\qquad Rh_2(oep)_2 \ \rightleftharpoons \ 2(oep)Rh\bullet$

Chain propagation $\ (oep)Rh\bullet \ + \ PhCH=CH_2 \ \rightleftharpoons \ (oep)RhCH_2\overset{\bullet}{C}HPh$

$(oep)RhCH_2\overset{\bullet}{C}HPh \ + \ Rh(oep)H \ \longrightarrow \ (oep)RhCH_2CH_2Ph \ + \ Rh(oep)\bullet$

Scheme 4.8 Proposed Radical Chain Mechanism of Rh^{II}(oep)-catalyzed 1,2-addition of Styrene with Rh(oep)H
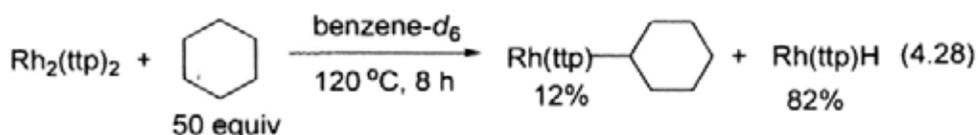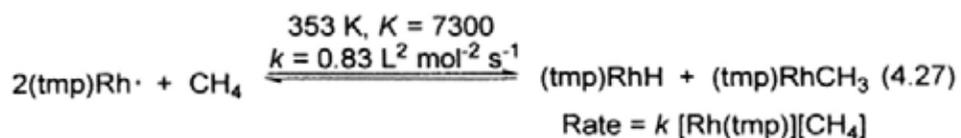
Based on the mechanism of the Rh^{II}-catalyzed insertion of Rh(oep)H into styrene reported by Halpern et al.,[16] the CCA of c-octane, being a 1,2-addition reaction, is proposed to be catalyzed by Rh^{II} (Scheme 4.9).

CCA catalyzed by [Rh^{II}]

$$2[Rh]\!-\!H \ \rightleftharpoons \ [Rh]_2 \ + \ H_2 \quad (4.23)$$

$$[Rh]_2 \ \xrightarrow{\ ii\ } \ 2[Rh] \quad (4.24)$$

$[Rh]\bullet \ +$ (octagon)

iii **CHA** $\quad [Rh]c\text{-octyl} \ + \ [Rh]H \quad (4.25)$

iv **CCA - S_H2** $\quad [Rh]n\text{-octyl}\bullet \ \xrightarrow[-\ [Rh]\bullet]{v\ [Rh]H} \ [Rh]n\text{-octyl} \quad (4.26)$
$\qquad\qquad\qquad\qquad\quad$ **13** $\qquad\qquad\qquad\qquad$ **10b**

$[Rh] = Rh^{II}(ttp)$

Scheme 4.9 Proposed Mechanism of Rh^{II}-Catalyzed 1,2-Addition of c-Octane with RhH

$Rh_2(ttp)_2$ **1e** formed from thermolysis of Rh(ttp)H, initially undergoes homolysis to give Rh^{II}(ttp) (eqs 4.23 and 4.24).[15] Rh^{II}(ttp) then reacts with c-octane in parallel CHA (pathway iii, eq 4.25) and CCA (pathway iv, eq 4.26). Rh^{II}(por) has been shown to undergo CHA with alkane to give Rh(por)R and Rh(por)H with a termolecular rate law (eqs 4.27-4.28).[12,19]

$$2(tmp)Rh\cdot + CH_4 \xrightleftharpoons[k = 0.83\ L^2\ mol^{-2}\ s^{-1}]{353\ K,\ K = 7300} (tmp)RhH + (tmp)RhCH_3 \quad (4.27)$$

$$Rate = k\ [Rh(tmp)][CH_4]$$

$$Rh_2(ttp)_2 + \underset{\text{50 equiv}}{\bigcirc} \xrightarrow[120\ ^\circ C,\ 8\ h]{\text{benzene-}d_6} \underset{12\%}{Rh(ttp)\!-\!\bigcirc} + \underset{82\%}{Rh(ttp)H} \quad (4.28)$$

For the CCA pathway, $Rh^{II}(ttp)$ can cleave the C–C bond of c-octane to generate the alkyl radical **13** (pathway iv, eq 4.26) which can also reverse back rapidly (Figure 4.7).[20] **13** can then abstract a hydrogen atom from the weak (ttp)Rh–H bond (~60 kcal mol^{-1})[21a] to form a strong alkyl C–H bond,[21b] providing the driving force of the reaction (pathway v).
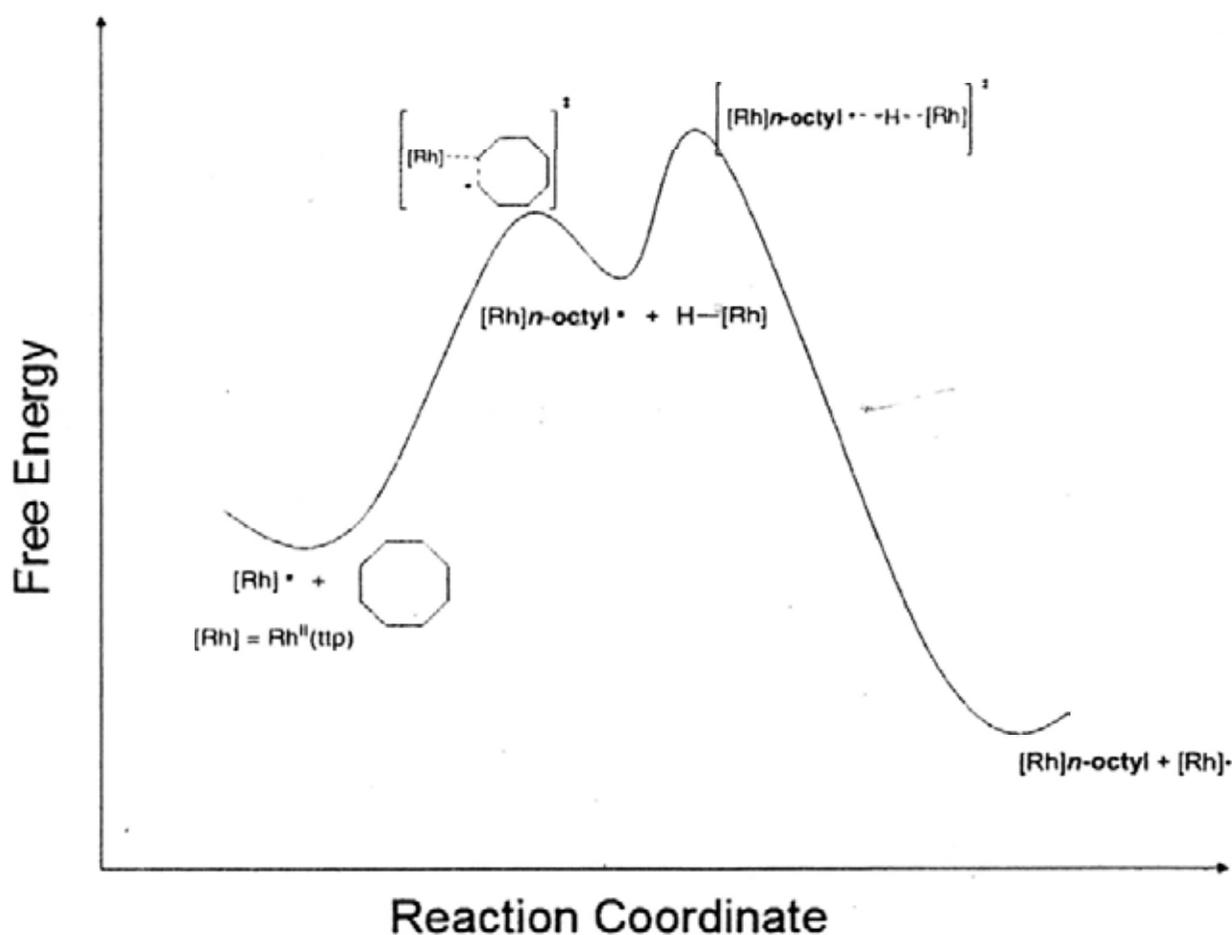
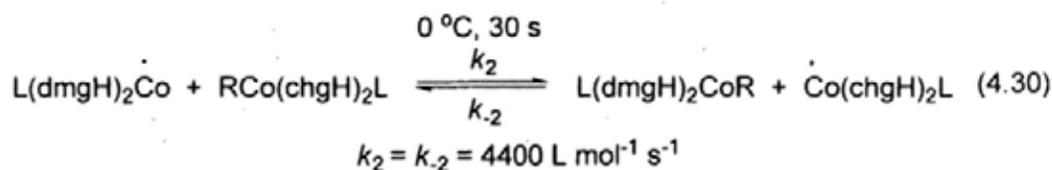Figure 4.7 Energy Profile of Rh^{II}(ttp)-Catalyzed 1,2-Addition of Rh(ttp)H with c-octane (eq 4.26)

Indeed, the cleavage of C–C bond via bimolecular homolytic substitution (S_H2) has been reported (eq 4.29).[20a] Scheme 4.10 shows a ring opening reaction of cyclopropane via S_H2. The Cl atom formed from photolysis of Cl_2 attacks the α-carbon to give an alkyl radical. Finally, the chlorine-substituted alkyl radical abstracts a Cl atom from Cl_2 to yield the product.

Reaction

$$\text{cyclopropane(Cl)(Cl)} + Cl_2 \xrightarrow[\text{0-5 °C, 35 min}]{hv, CCl_4} ClCH_2CH_2CCl_3 + Cl_2CHCH_2CCl_3 \quad (4.29)$$

36%   45%

Mechanism

$$Cl_2 \xrightarrow[\text{0 °C, CCl}_4]{hv} 2Cl\cdot$$

$$Cl + \text{cyclopropane(Cl)(Cl)} \longrightarrow ClCH_2CH_2\overset{\cdot}{C}Cl_2$$

$$ClCH_2CH_2\overset{\cdot}{C}Cl_2 + Cl_2 \longrightarrow ClCH_2CH_2CCl_3 + Cl\cdot$$

$$ClCH_2CH_2CCl_3 + Cl_2 \longrightarrow Cl_2CHCH_2CCl_3 + HCl$$
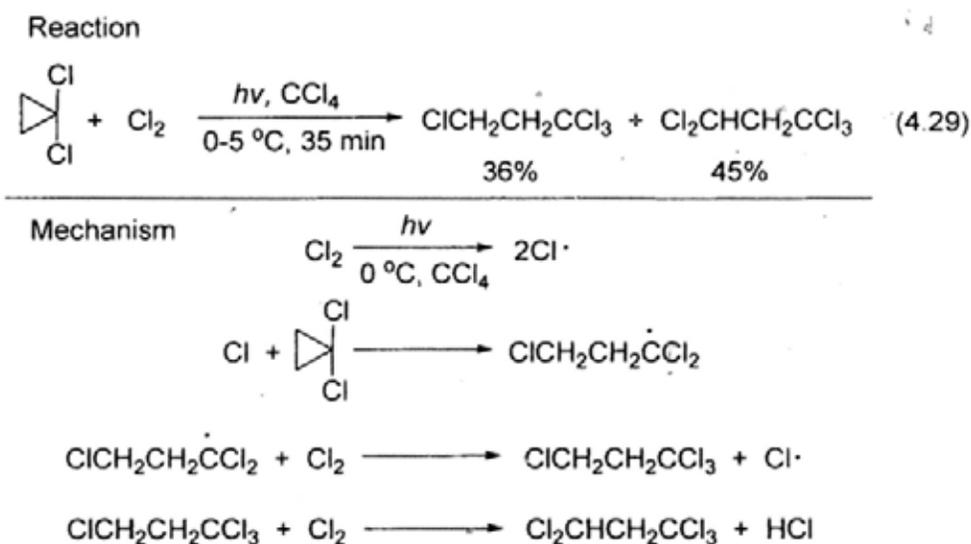
Scheme 4.10 CCA of Cyclopropane with Chlorine Radical via S_H2

Furthermore, Co^{II} radical was reported to attack an sp^3 carbon to give Co–alkyl complex via S_H2 (eq 4.30).[20b] Therefore, the C–C bond of c-octane is proposed to be cleaved by Rh^{II}(ttp) radical via S_H2.

$$L(dmgH)_2\overset{\cdot}{C}o + RCo(chgH)_2L \underset{k_{-2}}{\overset{\overset{\text{0 °C, 30 s}}{k_2}}{\rightleftharpoons}} L(dmgH)_2CoR + \overset{\cdot}{C}o(chgH)_2L \quad (4.30)$$

$$k_2 = k_{-2} = 4400 \text{ L mol}^{-1} \text{ s}^{-1}$$

R = Me; L = py; dmgH = dimethylglyoximato ligand
chgH = conjugate base of cyclohexanedione dioxime

4.5.1 Synergetic Effect of Rh(ttp)H/Rh₂(ttp)₂ in CCA of c-Octane

Therefore, the proposed mechanism can be validated qualitatively by increasing the ratio of Rh(ttp)H/Rh₂(ttp)₂ for more efficient trapping of **11** to **10b** (eq 4.31, Table 4.6).
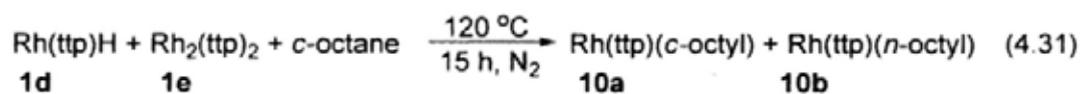
$$\text{Rh(ttp)H} + \text{Rh}_2\text{(ttp)}_2 + c\text{-octane} \xrightarrow[\text{15 h, N}_2]{120\ ^\circ\text{C}} \text{Rh(ttp)(}c\text{-octyl)} + \text{Rh(ttp)(}n\text{-octyl)} \quad (4.31)$$

$$\quad\quad \textbf{1d} \quad\quad\quad\quad \textbf{1e} \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \textbf{10a} \quad\quad\quad\quad \textbf{10b}$$

Table 4.6 Rh^{II}(ttp)-Catalyzed CCA of c-Octane wih Rh(ttp)H

Entry[a]	Rh(ttp)H:Rh₂(ttp)₂	Yield **10a** (%)	Yield **10b** (%)	Total yield (%)
1[b]	1:0	0	21	21
2	2:1	60	18	78
3	5:1	53	26	79
4	10:1	0	73	73

[a] The results are the average of at least duplicate. [b] 73% Rh(ttp)H recovered

Indeed, mixtures of Rh(ttp)H and Rh₂(ttp)₂ were more efficient reagents and enhanced the total yields up to 79% (Table 4.6, entries 2-4 vs 1). The selectivity towards 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) and Rh(ttp)(n-octyl) in 60% and 18% yields, respectively (Table 4.6, entry 2). When the Rh(ttp)H/Rh₂(ttp)₂ ratio increased to 5:1, the yield of Rh(ttp)(n-octyl) increased to 26% yield but that of Rh(ttp)(c-octyl) decreased to 53% yield (entry 3). Rh(ttp)(n-octyl) was selectively obtained in 73% yield from the reaction with the 10:1 ratio of Rh(ttp)H:Rh₂(ttp)₂ (entry 4). The aliphatic CCA of c-octane was thus achieved successfully with the Rh^{II}-catalyzed 1,2-addition of Rh(ttp)H.

4.5.2 Steric of Porphyrin

The sterically more hindered Rh(tmp) was not effective for CCA (tmp = 5,10,15,20-tetramesitylporphyrinato dianion) (Scheme 4.11). When the mixture of Rh(tmp)H **14a** and Rh^{II}(tmp) **14b** (10:1) was reacted with c-octane at 120 °C for 15 h, no reaction occurred and 90% yield of Rh(tmp)H **14a** was recovered (eq 4.32). Rh^{II}(tmp) **14b** only underwent CHA with c-octane to give Rh(tmp)H **14a** and c-octene in 86% and 40% yields, respectively (eq 4.33).
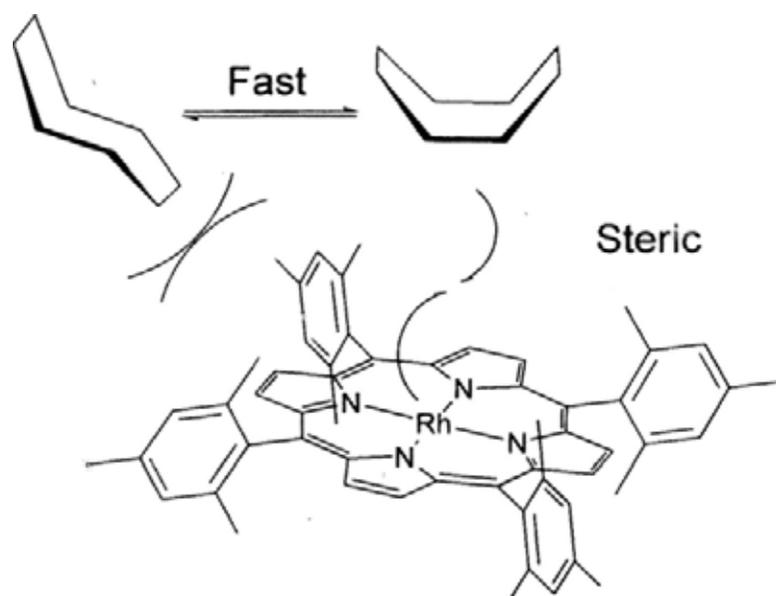
Scheme 4.11 Sterically Hindered Transition State for Rh^{II}(tmp)

$$\text{Rh(tmp)H + Rh}^{II}\text{(tmp) + }c\text{-octane} \xrightarrow[\text{15 h, N}_2]{120\,^{\circ}\text{C}} \text{Rh(tmp)H} \qquad (4.32)$$
$$\quad\; 10 \quad : \quad\; 1 \qquad\qquad\qquad\qquad\qquad\quad 90\%$$

$$\text{Rh}^{II}\text{(tmp) + }c\text{-octane} \xrightarrow[\text{15 h, N}_2]{120\,^{\circ}\text{C}} \text{Rh(tmp)H + }c\text{-octene} \quad (4.33)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad 86\% \qquad\quad 40\%$$
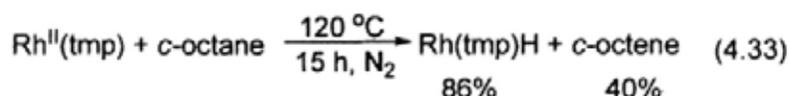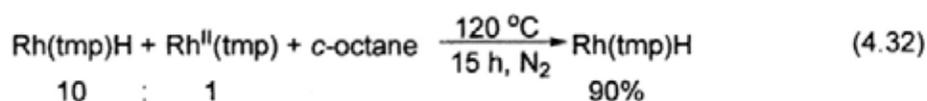
The formation of c-octene likely results from the CHA product Rh(tmp)(c-octyl) **14c** which rapidly undergoes facile β-hydride elimination to give c-octene and Rh(tmp)H (Scheme 4.12). Indeed, the attempted synthesis of Rh(tmp)(c-octyl) **14c** by reductive alkylation (NaBH$_4$/c-octyl bromide) gave Rh(tmp)H **14a** and c-octene in 89 and 77% yields, respectively.

$$\text{Rh}^{II}(\text{tmp}) \xrightarrow{\ c\text{-octane}\ } \text{Rh(tmp)}(c\text{-octyl}) + \text{Rh(tmp)H}$$

14b   **14c**   **14a**

$- c$-octene

Scheme 4.12 Formation of Rh(tmp)H from CHA of Rh^{II}(tmp) and c-Octane

4.6   Conclusion

The CCA of c-octane was achieved by Rh(ttp)Cl in the presence of K$_2$CO$_3$ to give Rh(ttp)(n-octyl). Even though Rh(ttp)H and Rh$_2$(ttp)$_2$ were found to be intermediates, they gave poor CCA yields when reacted with c-octane separately and therefore are minor CCA pathways. The 1,2-addition of Rh(ttp)H into the C–C bond of c-octane was significantly improved by catalytic amount of Rh$_2$(ttp)$_2$. Mechanistic investigation suggested that Rh^{II}(ttp) radical which forms from homolysis of Rh$_2$(ttp)$_2$ cleaves the C–C bond of c-octane and generates a Rh–alkyl radical **13** possibly via S$_H$2. The Rh–alkyl radical **13** then abstracts a hydrogen atom from Rh(ttp)H to give Rh(ttp)(n-octyl). The steric of porphyrin inhibited the CCA of c-octane.

References

(1) (a) Mackay, D.; Shiu, W. Y.; Ma, K. C.; Lee, S. C. *Physical-Chemical Properties and Environmental Fate for Organic Chemicals 2nd Ed, Volume. 1*, CRC Press, Boca raton, FL, 2006. (b) Pakes, P. W.; Rounds, T. C.; Strauss, H. L. *J. Phys. Chem.* **1981**, *85*, 2469-2475.

(2) Luo, Y. R. *Comprehensive Handbook of Chemical Bond Energies*, CRC Press, Boca Raton, FL, 2007.

(3) (a) Isaacs, N. S. *Physical Organic Chemistry*; Longman: Essex, 1987. (b) The BDE of C–C bonds are calculated based on the $\Delta H_{formation}$, see Stull, D. R.; Westrum, E. F. Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; John Wiley & Sons: New York 1969.

(4) *CRC Handbook of Chemistry & Physics 84th Ed.*, Lide, D. R. Ed. 2004.

(5) (a) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879-2932. (b) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245-269.

(6) (a) Jun, C. H. *Chem. Soc. Rev.* **2004**, *33*, 610-618. (b) Murakami, M; Amii, H.; Ito, Y. *Nature* **1994**, *370*, 540-541. (c) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759-1792. (d) Goldman, A. S. *Nature* **2010**, *463*, 435-436.

(7) (a) For a heterogeneous medium: see Hagedom, C. J.; Weiss, M. J.; Kim, T. W.; Weinberg, W. H. *J. Am. Chem. Soc.* **2001**, *123*, 929-940. (b) Sawatari, N.; Yokota, T.; Sakaguchi, S.; Ishii, Y. *J. Org. Chem.* **2001**, *66*, 7889-7891.

(8) (a) For a leading reference: see Renkema, K. B.; Kissin, Y. V.; Goldman, A. S. *J. Am. Chem. Soc.* **2003**, *125*, 7770-7771. (b) Yiu, S. M.; Wu, Z. B.; Lau, T. C. *J. Am. Chem. Soc.* **2004**, *126*, 14921-14929. (c) Jiang, X. F.; Shen, M. H.; Tang, Y.; Li, C. Z. *Tetrahedron Lett.* **2005**, *46*, 487-489.

(9) Rh(ttp)Cl reacted with alkane in basic medium to give $Rh_2(ttp)_2$ and Rh(ttp)H as intermediates. See ref 12.

(10) **10a** and **10b** were fully characterized. The chemical shifts of ^{13}C NMR of Rh–C of **10a** and **10b** were δ = 40.62 (d, $^1J_{Rh-C}$ = 26.4 Hz) and 15.69 (d, $^1J_{Rh-C}$ = 26.8 Hz), respectively.

(11) (a) Rybtchinski, B.; Vigalok, A.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **1996**, *118*, 12406-12415. (b) Perthuisot, C.; Jones, W. D. *J. Am. Chem. Soc.* **1994**, *116*, 3647-3648.

(12) Chan, Y. W.; Chan, K. S. *Organometallics* **2008**, *27*, 4625-4635.

(13) (a) Cho, I. *Prog. Polym. Sci.* **2000**, *25*, 1043-1087. (b) Stohandl, J.; Vozka, P.; Varekova, I.; Karafiat, M.; Ondr J, J.; Mejzlik, J.; Balcar, H.; Stepanek, K.; Heller, G.; Lederer, J. U.S. Patent 5 455 318, 1995. (c) Motherwell, W. B.; Crich, D. *Free Radical Chain Reaction in Organic Synthesis*, Academic Press, London, 1992. (d) Dragutan, V.; Streck, R. C *atalytic Polymerization of Cycloolefins: Ionic, Ziegler-Natta and Ring-Opening Metathesis Polymerization 1st Ed.*, Elsevier, Amsterdam, 2000

(14) Homolytic cleavage Rh–C of di-rhodium alkyl complex likely occurs. A similar case of **7a** was reported in Chapter 3, see eq 3.20 and reference 20 of Chapter 3.

(15) Wayland, B. B.; van Voorhees, S. L.; Wilker, C. *Inorg. Chem.* **1986**, *25*, 4039-4042.

(16) Paonessa, R.S.; Thomas, N C.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *107*, 4333-4335.

(17) For 4 centered transition state, see (a) Mak, K. W.; Chan, K. S. *J. Am. Chem. Soc.* **1998**, *120*, 9686-9687. (b) Mak, K. W.; Xue, F.; Mak, T. C. W.; Chan, K. S. *J. Chem. Soc., Dalton Trans.* **1999**, *19*, 3333-3334.

(18) Wayland, B. B.; Ba, S.; Sherry, A. E. *J. Am. Chem. Soc.* **1991**, *113*, 5305-5311.

(19) (a) Davies, A. G.; Roberts, B. P. *Acc. Chem. Res.* **1972**, *5*, 387-392. (b) Johnson, M. D. *Acc. Chem. Res.* **1983**, *16*, 343-349. (c) Incremona, J. H.; Upton, C. J. *J. Am. Chem. Soc.* **1972**, *94*, 301-303.

(20) (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.

Chapter 5   Comparison of CHA and CCA of Various Cycloalkanes

The reactivity patterns of cycloalkanes with rhodium porphyrin complexes are analyzed by the C–H and C–C bond strengths as well as the ring closing rate of cycloalkanes. The previous findings in Chapters 2, 3 and 4 show that c-pentane and c-hexane reacted with rhodium porphyrin complexes via CHA to yield only the corresponding CHA products while c-heptane and c-octane gave the corresponding CHA and CCA products. c-Octane underwent the $Rh^{II}(ttp)$-catalyzed 1,2-addition with Rh(ttp)H to give Rh(ttp)(n-octyl) selectively. To account for the different reactivity of cycloalkanes with rhodium porphyrin complexes, the C–H and C–C bond dissociation energies, ring strains and ring closure rates of various cycloalkanes listed in Table 5.1 are used as the physical base.

Table 5.1 Bond Dissociation Energies and Ring Strains of Various Cycloalkanes[1-2]

| Alkane | BDE | | ΔBDE^{a} | Ring Strain |
| | C–H | C–C | | |
	(kcal mol^{-1})	(kcal mol^{-1})	(kcal mol^{-1})	(kcal mol^{-1})
n-pentane	100.2	88.8	11.4	Not Applicable
n-hexane	99.0	88.1	10.9	Not Applicable
n-heptane	98.0	88.0	10.0	Not Applicable
c-pentane	95.6	86.9[2d]	12.7	6.5
c-hexane	99.5	87.3	16.8	0
c-heptane	94.0	86.6	7.4	6.3
c-octane	95.7	79.6	16.1	9.6

^{a} ΔBDE is the BDE difference of C–H and C–C.

5.1   Thermodynamics Consideration of CHA and CCA of Cycloalkanes

The estimation of the thermodynamics of CHA and CCA with Rh(ttp)H allows the quantitative understandings of these processes. Scheme 5.1 outlines the computation of the thermodynamics of CHA and CCA of c-pentane as a general example.
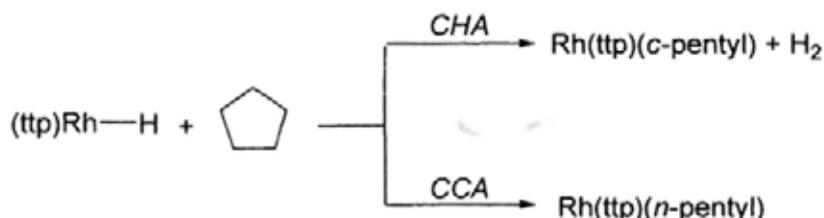
Scheme 5.1 CHA and CCA of c-Pentane with Rh(ttp)H

The BDEs of Rh–H, Rh–C and H–H are taken to be 60 kcal mol^{-1}, 48 kcal mol^{-1} and 105 kcal mol^{-1}, respectively.[1]

For CHA,

$\Delta H_{(CHA, 298)}$ =   BDE of (Rh–H + C–H of c-pentane) – BDE of (Rh–C + H–H)

                = $(60 + 95.6) - (48 + 105)$ kcal mol^{-1}

                =   2.6 kcal mol^{-1}

Assuming the molar entropies of Rh(ttp)H ~ Rh(ttp)(c-pentyl), the molar entropy of H$_2$ and c-pentane at 298 K are 31.0 and 48.9 cal mol^{-1} K^{-1}, respectively.[2a,2c]

$\Delta S_{(CHA,298)}$ = $-(48.9) + (31.0)$ cal mol^{-1} K^{-1}

                = -17.9 cal mol^{-1} K^{-1}

$\Delta G_{(CHA, 298)}$ = $\Delta H_{(CHA, 298)} - T\Delta S_{(CHA, 298)}$

                = $(2.6) - 298(-17.9/1000)$ kcal mol^{-1}

                = $2.6 + 5.3$ cal mol^{-1} K^{-1}

                =   7.9 kcal mol^{-1}

For CCA,

$$\Delta H_{(CCA, 298)} = \text{BDE of (Rh–H + C–C of } c\text{-pentane)} - \text{BDE of (Rh–C + C–H of } n\text{-pentyl)}$$
$$- \text{ring strain}$$
$$= (60 + 86.9) - (48 + 100) - (6.5) \text{ kcal mol}^{-1}$$
$$= -7.6 \text{ kcal mol}^{-1}$$

The molar entropies of Rh(ttp)H is assumed to be similar to that of Rh(ttp)(n-pentyl). The molar entropy of H_2 and c-pentane at 298 K are 31.0 and 48.9 cal mol^{-1} K^{-1}, respectively.[2a,2c]

$$\Delta S_{(CCA, 298)} = -48.88 \text{ cal mol}^{-1} \text{ K}^{-1}$$
$$\Delta G_{(CCA, 298)} = \Delta H_{(CHA, 298)} - T\Delta S_{(CHA, 298)}$$
$$= (-7.6) - 298(-48.88/1000) \text{ kcal mol}^{-1}$$
$$= (-7.6) - (-14.56) \text{ kcal mol}^{-1}$$
$$= 7.0 \text{ kcal mol}^{-1}$$

The estimated ΔH, ΔS and ΔG of CHA and CCA of various cycloalkanes and Rh(ttp)H are listed (Table 5.2).

Table 5.2 ΔH, ΔS and ΔG of CHA and CCA of Various Cycloalkanes and Rh(ttp)H

	kcal mol^{-1}					
	$\Delta H_{(CHA,298)}$	$T\Delta S_{(CHA,298)}$	$\Delta G_{(CHA,298)}$	$\Delta H_{(CCA,298)}$	$T\Delta S_{(CCA,298)}$	$\Delta G_{(CCA,298)}$
c-pentane	2.6	-5.3	7.9	-7.6	-14.6	7.0
c-hexane	6.5	-5.3	11.8	-4.3	-14.6	10.3
c-heptane	1.0	-5.3	6.3	-5.7	-14.6	5.9
c-octane	2.7	-5.3	8.0	-16.0	-14.6	-1.4

Based on the above estimation, the CHA of c-pentane, c-hexane, c-heptane and c-octane with Rh(ttp)H are slightly unfavorable at 298 K (Table 5.2). However, at 393 K (120 °C), the formation of co-product, gaseous hydrogen ($\Delta S_{393} = 33.1978$ cal mol^{-1} K^{-1}),[3] provides the extra driving force to make the CHA spontaneous (Table 5.3).

Table 5.3 Entropy of H$_2$ in Different Temperature[a]

Temp (K)	ΔS (cal mol^{-1} K^{-1})	$T\Delta S$ (kcal mol^{-1})
298	31.2679	9.3178
393	33.1938	13.0452
433	33.8780	14.6692
453	34.1962	15.4909

[a] $\Delta S(T_2, G) = \Delta S(298 \text{ K}, G) + (C_{pm})(\ln(T_2/298))$, where T_2 is the temperature interested, $C_{pm}(H_2)$ at 298 K is 6.88038 cal mol^{-1} K^{-1}, $S_{(298)}$ of H$_2$ is 31.2679 cal mol^{-1} K^{-1}. See ref 3.

The CCA of c-pentane, c-hexane, c-heptane and c-octane with Rh(ttp)H are thermodynamically more favorable than the CHA (Table 5.2). The CCA of c-octane is thermodynamically favorable ($\Delta G < 0$) while c-pentane, c-hexane and c-heptane are slightly unfavorable ($\Delta G > 0$). Therefore, the ring opening product was only observed in c-octane case. As $\Delta H_{(CCA)}$ is negative and $-T\Delta S_{(CCA)}$ is positive, the CCA of cycloalkane is more probable at lower temperature.

5.2   Kinetic Consideration of CHA and CCA of Cycloalkanes

As the CCA of *c*-octane is shown to be Rh^{II}-catalyzed, the kinetics of the key

Rh^{II}(ttp)-catalyzed 1,2-addition of cycloalkane with Rh(ttp)H is considered (Scheme 5.2).
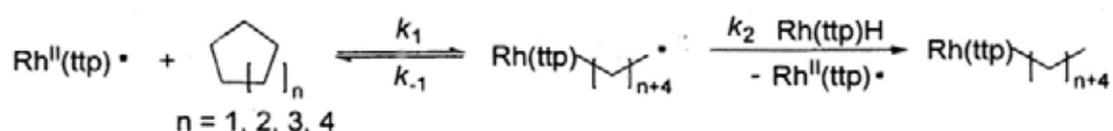
Scheme 5.2 Mechanistic Scheme of Rh^{II}(ttp)-Catalyzed 1,2-Addition of Cycloalkane with

Rh(ttp)H

$$\text{Rate of CCA} = k_1[Rh^{II}(ttp)][\text{cycloalkane}]$$

$$\text{Rate of Backward CCA} = k_{-1}[Rh(ttp)\text{alkyl}\bullet]$$

$$\text{Rate of H Abstraction} = k_2[Rh(ttp)\text{alkyl}\bullet][Rh(ttp)H]$$

At steady state, $d[Rh(ttp)\text{alkyl}\bullet]/dt = 0$,

$$k_1[Rh^{II}(ttp)][\text{cycloalkane}] = k_{-1}[Rh(ttp)\text{alkyl}\bullet] + k_2[Rh(ttp)\text{alkyl}\bullet][Rh(ttp)H]$$

In order to achieve a successful CCA, the ring closure rate of cycloalkane should be

slow enough so that the Rh–alkyl radical has sufficient time to abstract the H atom from

Rh(ttp)H (k_{-1} is comparable to $k_2[Rh(ttp)H]$). Since the ring closure rates of bi-alkyl radical

are not reported, the ring closure rate of olefin radical cyclization (Scheme 5.3)[4a-c] and

anionic cyclization of (ϖ-brom-oalkyl)malonates (Scheme 5.4)[4d] are listed for reference

(Table 5.4).

Table 5.4 Ring Closing Rates of Various Cycloalkane[4]

| Ring Size | Olefin Radical Cyclization[a] | | Anionic Cyclization[b] |
	exo rate (s^{-1})	endo rate (s^{-1})	Rate (s^{-1})
5	2.7×10^5	$\sim 4 \times 10^6$	6.0×10^2
6	5.4×10^3	4.0×10^3	7.2×10^{-1}
7	1.2×10^2	9.0×10^2	6.3×10^{-3}
8	0	1.2×10^2	1.1×10^{-4}

[a] at 25 °C, see ref 4a-c. [b] at 25 °C, see ref 4d

exo   n = 1 $k_{exo} = 2.7 \times 10^5 \ s^{-1}$ c-pentylmethyl radical

n = 2 $k_{exo} = 5.4 \times 10^3 \ s^{-1}$ c-hexylmethyl radical

n = 3 $k_{exo} = 1.2 \times 10^2 \ s^{-1}$ c-heptylmethyl radical

n = 4   dos not cyclized   c-octylmethyl radical

endo   n = 0 $k_{endo} \sim 4 \times 10^6 \ s^{-1}$ c-pentyl radical

n = 1 $k_{endo} = 4.0 \times 10^3 \ s^{-1}$ c-hexyl radical

n = 2 $k_{endo} = 9.0 \times 10^2 \ s^{-1}$ c-heptyl radical

n = 3 $k_{endo} = 1.2 \times 10^2 \ s^{-1}$ c-octyl radical
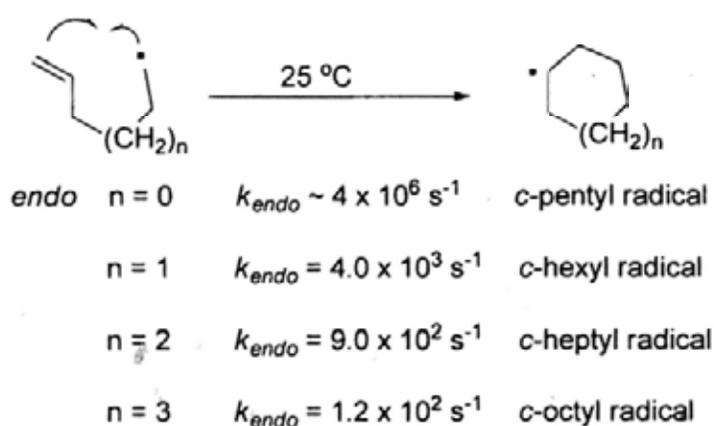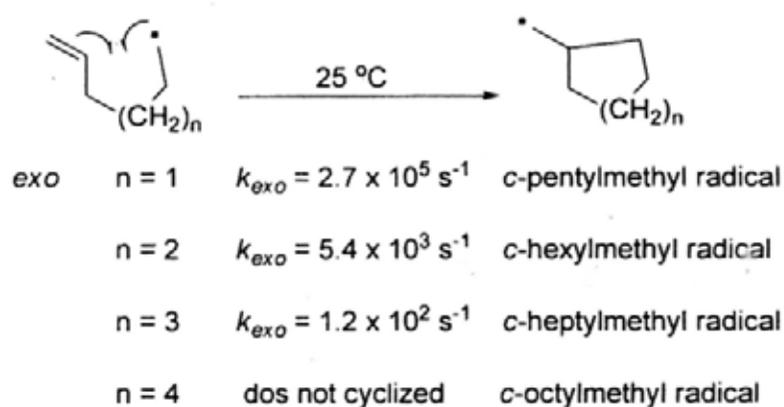
Scheme 5.3 Olefin Radical Cyclization

$$\text{Br(CH}_2)_n-\overset{\displaystyle CO_2Et}{\underset{\displaystyle CO_2Et}{CH}} \quad \underset{\longleftarrow}{\overset{\text{base}}{\rightleftharpoons}} \quad \text{Br(CH}_2)_n-\overset{\displaystyle CO_2Et}{\underset{\displaystyle CO_2Et}{\overset{\ominus}{C}}} \quad \xrightarrow[-\,Br^{\ominus}]{k_{intra}} \quad (CH_2)_n\,\overset{\displaystyle CO_2Et}{\underset{\displaystyle CO_2Et}{\overset{\ominus}{C}}}$$
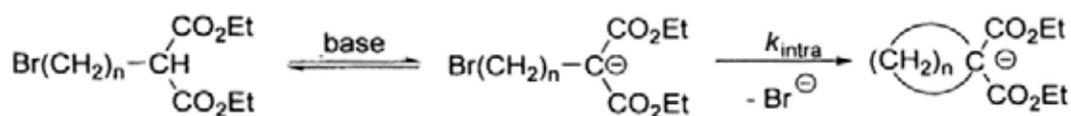
Scheme 5.4 Cyclization of (ϖ-brom-oalkyl)malonates

The rate closure rates of various cycloalkanes follow the order:

$$c\text{-octane} < c\text{-heptane} \ll c\text{-hexane} \ll c\text{-pentane}$$

As c-octane has the slowest ring closure rate among the four cycloalkanes, the CCA product Rh(ttp)(n-octyl) was obtained. Furthermore, the higher ring strain of c-octane (9.6 kcal mol^{-1}) favors the ring opening and disfavors the ring closure.[2a] The ring closure rate of c-pentane, c-hexane and c-heptane are much faster and their ring strains are smaller. So, no corresponding Rh(ttp)(n-alkyl) was obtained. Therefore, the ring opening CCA of c-octane is favored by both thermodynamic and kinetic factors.

On the other side, the rate closure rates of c-pentane and c-hexane are very fast. So even the corresponding Rh–alkyl radicals form, the lifetimes of the Rh–alkyl radicals are too short to abstract H atom from Rh(ttp)H due to rapid ring closure. Therefore, the CCA of c-pentane, c-hexane and c-heptane with Rh(ttp)H are both thermodynamically and kinetically less unfavorable.

5.3 Consideration of Rh(ttp)Bn Formation

For c-heptane, the formation of Rh(ttp)Bn is a consequence of Rh^{II}-catalyzed successive dehydrogenation of c-heptane, c-heptene and c-hepta-1,3-diene which then gives cycloheptatriene. Cycloheptatriene further reacted with Rh(ttp)H/Rh$_2$(ttp)$_2$ to generate Rh(ttp)(cycloheptatrienyl) and eventually form Rh(ttp)Bn via Rh^{II}-catalyzed CCA.

Therefore, the thermodynamic of Rh(ttp)Bn formation is considered below (Scheme 5.5).
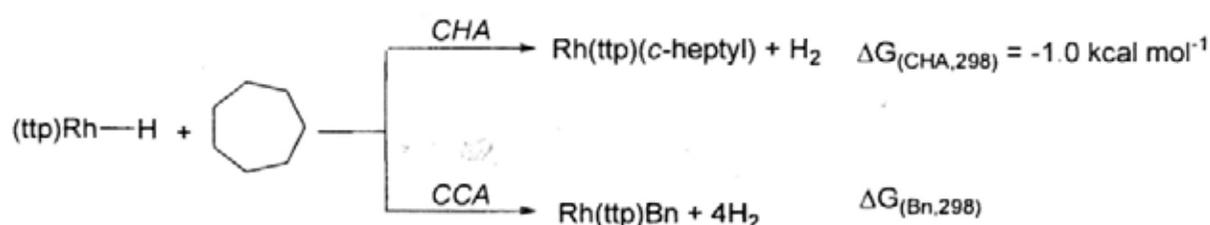
Scheme 5.5 CHA and CCA of c-Heptane with Rh(ttp)H

The difference of ΔG_f^o of c-heptane and toluene is estimated to be the same as the difference of $\Delta G_{(CHA,298)}$ and $\Delta G_{(Bn,298)}$ (Scheme 5.6).
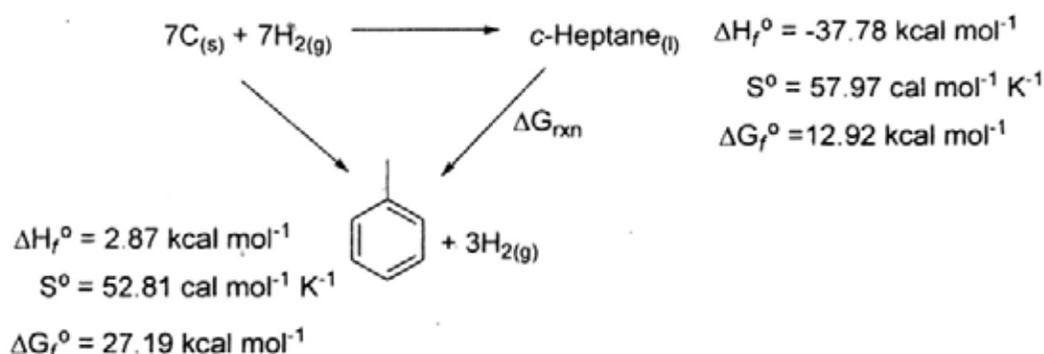
Scheme 5.6 Conversion of c-Heptane to Toluene[5]

$$\Delta G_{rxn} = (27.19 - 12.92) \text{ kcal mol}^{-1}$$

$$= 14.27 \text{ kcal mol}^{-1}$$

Therefore, $\Delta G_{(Bn,298)}$ is estimated to be 13.3 kcal mol^{-1}. Since 3 moles of H$_2$ are generated from the conversion of Rh(ttp)(c-heptyl) to Rh(ttp)Bn, they are likely to provide the driving force of the reaction at 120 °C. The $\Delta G_{(Bn,393)}$ is estimated as below.

$$\Delta G_{(Bn,393)} = \Delta G_{(Bn,298)} - T(\Delta\Delta S)$$

$$\Delta\Delta S = \Delta S_{393} - \Delta S_{298}$$

$$= 3 \times (1.3875 \times 10^2 - 1.3070 \times 10^2)$$

$$= 24.15 \text{ J mol}^{-1} \text{ K}^{-1} \text{ or } 5.78 \text{ cal mol}^{-1} \text{ K}^{-1}$$

So,

$$\Delta G_{(Bn,393)} = \Delta G_{(Bn,298)} - T\Delta\Delta S$$

$$= 13.3 - 393(5.78/1000) \text{ kcal mol}^{-1}$$

$$= 11.0 \text{ kcal mol}^{-1}$$

5.4   Thermodynamic Consideration of CHA and CCA of *n*-Alkanes

The extension of the above analysis raises an interesting question whether a straight chain alkane can undergo CCA. The thermodynamics of CHA and CCA of *n*-pentane are estimated as an example (Scheme 5.7).
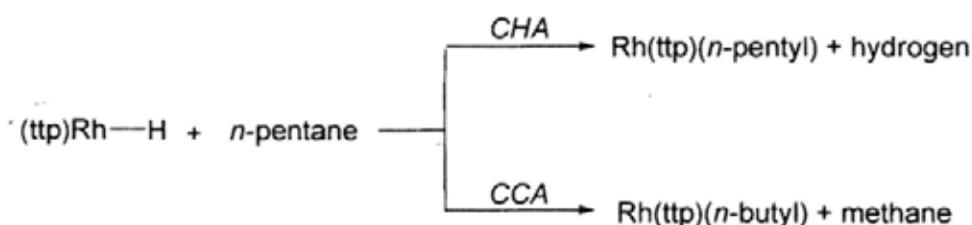
Scheme 5.7 CHA and CCA of *n*-Pentane with Rh(ttp)H

For CHA,

$$\Delta H_{(CHA, 298)} = \text{BDE of (Rh–H + C–H of } n\text{-pentane)} - \text{BDE of (Rh–C + H–H)}$$

$$= (60 + 100.2) - (50 + 105) \text{ kcal mol}^{-1}$$

$$= 5.2 \text{ kcal mol}^{-1}$$

145

Assuming the molar entropies of Rh(ttp)H ~ Rh(ttp)(n-pentyl), the molar entropies of H_2, CH_4 and n-pentane at 298 K are 31.0 cal mol^{-1} K^{-1}, 44.5 cal mol^{-1} K^{-1} and 62.5 cal mol^{-1} K^{-1}, respectively.[2a,2c]

$$\Delta S_{(CHA, 298)} = \text{-(S of } n\text{-pentane)} + \text{(S of } H_2\text{)}$$

$$= \text{-(62.5)} + (31.0) \text{ cal mol}^{-1} \text{ K}^{-1}$$

$$= \text{-31.5 cal mol}^{-1} \text{ K}^{-1}$$

$$\Delta G_{(CHA, 298)} = \Delta H_{(CHA, 298)} - T\Delta S_{(CHA, 298)}$$

$$= (5.2) - 298(-31.5/1000) \text{ kcal mol}^{-1}$$

$$= (5.2) + (9.4) \text{ kcal mol}^{-1}$$

$$= 14.6 \text{ kcal mol}^{-1}$$

For CCA,

$$\Delta H_{(CCA, 298)} = \text{BDE of (Rh–H + C–C of } n\text{-pentane)} - \text{BDE of (Rh–C + C–H of } methane\text{)}$$

$$= (60 + 88.8) - (50 + 105) \text{ kcal mol}^{-1}$$

$$= \text{-6.2 kcal mol}^{-1}$$

$$\Delta S_{(CCA, 298)} = \text{-(Molar entropy of } n\text{-pentane)} + \text{(Molar entropy of methane)}$$

$$= \text{-(62.5)} + (44.5) \text{ cal mol}^{-1} \text{ K}^{-1}$$

$$= \text{-18.0 cal mol}^{-1} \text{ K}^{-1}$$

$$\Delta G_{(CCA, 298)} = \Delta H_{(CCA, 298)} - T\Delta S_{(CCA, 298)}$$

$$= (-6.2) - 298(-18.0/1000) \text{ kcal mol}^{-1}$$

$$= -(6.2) - (-5.4) \text{ kcal mol}^{-1}$$

$$= \text{-0.8 kcal mol}^{-1}$$

The above analysis show that the CCA of n-pentane with Rh(ttp)H is thermodynamically more favorable than the CHA. However, n-pentane only undergoes CHA.

The kinetic barrier of a Rh^{II}(por) attack at the carbon center is sterically more hindered to allow this reaction channel. Moreover, the C–H bonds of n-pentane are kinetically more accessible than C–C bonds.[6]

5.5   Kinetic Consideration of CHA and CCA of n-Alkanes

Since ethane is the simplest molecule with only one C–C bond, the kinetics of CHA and CCA consideration of ethane are estimated as well (Scheme 5.8). Rh^{II}(ttp) may either react with ethane to give Rh(ttp)Me and a methyl radical via CHA or generate Rh(ttp)Et and Rh(ttp)H via CHA.

$$\underset{CHA}{Rh(ttp)-CH_2CH_3 + Rh(ttp)H} \underset{}{\overset{k_2}{\rightleftharpoons}} Rh^{II}(ttp) + \underset{CCA}{H_3C-CH_3} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Rh(ttp)-CH_3 + \overset{\cdot}{C}H_3$$
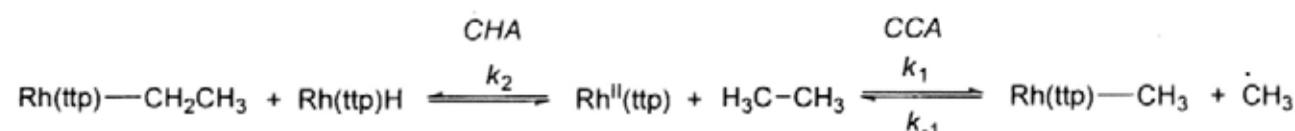
Scheme 5.8 Proposed Mechanistic Scheme of Rh^{II}(ttp)-Catalyzed CCA of n-Alkane with Rh(ttp)H

For the CCA, Rh^{II}(ttp) likely cleaves the C–C bond of ethane via S_H2.[6] However, as shown in scheme 5.8, the methyl radical can undergo reverse reaction with Rh(ttp)Me to regenerate the Rh^{II}(ttp) and C_2H_6. Neither the forward reaction rate (k_1) nor the backward reaction rate (k_{-1}) are reported. Therefore, the rate of S_H2 can only be estimated from other S_H2 examples. The rate of alkyl exchange of $(chgH)_2Co–Me$ to $(dmgH)_2Co–Me$ via S_H2 was reported to be 4400 M^{-1} s^{-1} (eq 5.1).[6]

$$L(dmgH)_2\overset{\cdot}{Co} + MeCo(chgH)_2L \underset{k_{-3}}{\overset{\overset{0\ ^\circ C,\ 30\ s}{k_3}}{\rightleftharpoons}} L(dmgH)_2CoMe + \overset{\cdot}{Co}(chgH)_2L \quad (5.1)$$
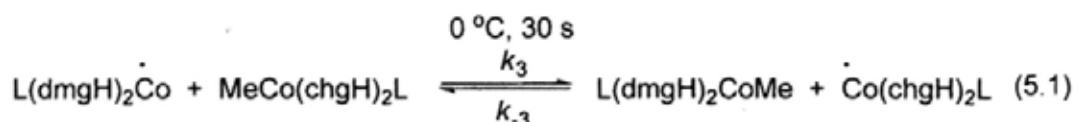
$$k_2 = k_{-2} = 4400\ L\ mol^{-1}\ s^{-1}$$

L = py; dmgH = dimethylglyoximato ligand
chgH = conjugate base of cyclohexanedione dioxime

For the CHA channel, Rh^{II}(ttp) reacts with ethane to give Rh(ttp)Et and Rh(ttp)H. In fact, Wayland et al. reported that Rh_2(DPB) (DPB = 1,8-bis[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrinyl)]biphenylene) reacted with ethane to give the CHA product exclusively (eq 5.2).[7a]

$$C_2H_6 + \quad \begin{array}{c} \boxed{Rh^{II}} \\ \\ \boxed{Rh^{II}} \end{array} \quad \xrightarrow{\text{296 K}} \quad \begin{array}{c} \boxed{Rh} \\ | \\ H \\ | \\ Et \\ | \\ \boxed{Rh} \end{array} \qquad (5.2)$$

quantitative
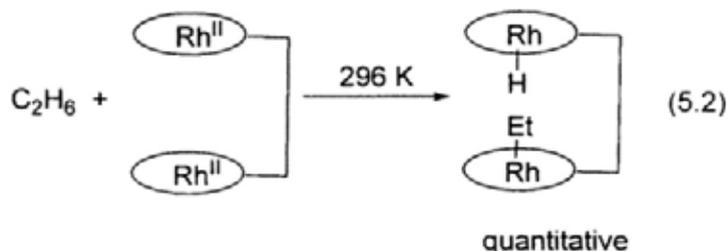
Even the CCA is thermodynamically more favorable than the CHA by 10 kcal mol^{-1}, no CCA occurs. Therefore, Wayland et al. proposed that the absence of observed C–C cleavage is kinetic in origin. The interaction of Rh^{II} center with the C–H unit is kinetically more favorable for the near concerted cleavage than the C–C bond (Figures 5.1a and 5.1b). The rate of reaction follows: rate = k $[Rh^{II}(tmp)]^2$ $[C_2H_6]$. Indeed, Wayland reported that the CHA of methane with Rh^{II}(tmp) with rate = k $[Rh^{II}(tmp)]^2$ $[CH_4]$, where $k_{(296\ K)}$ = 0.132 M^{-2} s^{-2} [7b]

CHA

kinetically more favorable
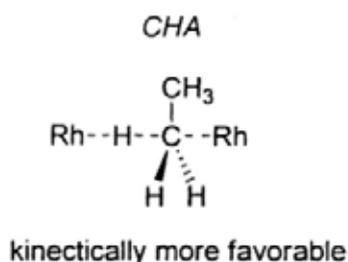
Figure 5.1a 4-Centered Transition State of CHA

CCA

kinetically less favorable
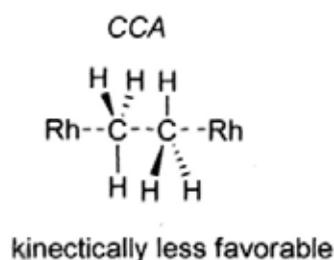
Figure 5.1b 4-Centered Transition State of CCA

$$\text{Rate of CCA} = k_1[Rh^{II}(ttp)][C_2H_6]$$

$$\text{Rate of backward CCA} = k_{-1}[Rh^{II}(ttp)Me][\cdot CH_3]$$

$$\text{Rate of CHA} = k_2[Rh^{II}(ttp)]^2[C_2H_6]$$

So, the CCA of ethane is possible when $k_1[Rh^{II}(ttp)][C_2H_6] > k_{-1}[Rh^{II}(ttp)Me][\cdot CH_3]$ and $k_2[Rh^{II}(ttp)]^2[C_2H_6]$ (Scheme 5.8).

5.6 Conclusion

The thermodynamics and kinetics of the CHA and CCA of alkanes with Rh(ttp)H were considered. The CHA of cycloalkane is usually thermodynamically less favorable but kinetically more favorable while the CCA is thermodynamically more favorable but kinetically less favorable. The CCA of c-octane is spontaneous ($\Delta G_{(CCA,298)} < 0$). The ring opening CCA of c-octane is accounted by the relatively slow ring closure rate. The CCA of n-alkane with Rh(ttp)H is spontaneous, but is not observed, possibly due to kinetic reasons.

References

(1) Luo, Y. R. *Comprehensive Handbook of Chemical Bond Energies*, CRC Press, Boca Raton, FL, 2007.

(2) (a) Isaacs, N. S. *Physical Organic Chemistry*; Longman: Essex, 1987. (b) The BDE of C–C bonds are calculated based on the $\Delta H_{formation}$, see Stull, D. R.; Westrum, E. F. Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; John Wiley & Sons: New York 1969. (c) *CRC Handbook of Chemistry & Physics 84th Ed.*, Lide, D. R. Ed. 2004. (d) The C–C BDE of *c*-hexane is calculated to be 82.7 kcal mol^{-1} and the literature reported value is 87.3 kcal mol^{-1}. The C–C BDE of *c*-pentane is calculated to be 82.9 kcal mol^{-1}. So, the C–C BDE of *c*-pentane is corrected by 4 kcal mol^{-1} to 86.9 kcal mol^{-1}.

(3) Yaws, C. L. *Chemical Properties Handbook: Physical, Thermodynamic, Environmental, Transport, Safety, and Health Related Properties for Organic and Inorganic Chemicals*; McGraw-Hill: New York, 1999.

(4) For exo- and endo-cyclization, see (a) Li, A.; Shtarev, A. B.; Smart, B. E.; Yang, Z. Y.; Lusztyk, J. Ingold, K. U.; Bravo, A.; Dolbier, W. R. Jr. *J. Org. Chem.* **1999**, *64*, 5993-5999. For exo-cyclization, see (b) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151-1176. (c) Walton, J. C. *Topics in Current Chemistry: Radicals in Synthesis II, Chapter Unusual Radical Cyclisations*; Springer Berlin: Heidelberg 2006. For anioinc cyclization, see (d) Casadei, M. A.; Galli, C.; Mandolini, L. *J. Am. Chem. Soc.* **1984**, *106*, 1051-1056.

(5) Stull, D. R.; Westrum, E. F. Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; John Wiley & Sons: New York 1969.

(6) Johnson, M. D. *Acc. Chem. Res.* **1983**, *16*, 343-349.

(7) (a) Zhang, X. X.; Wayland, B. B. *J. Am. Chem. Soc.* **1994**, *116*, 7897-7898. (b) Wayland, B. B.; Ba, S.; Sherry, A. E. *J. Am. Chem. Soc.* **1991**, *113*, 5305-5311.

Chapter 6   Experimental Section

6.1   General Procedure

All materials were obtained from commercial suppliers and used without further purification unless otherwise specified. Benzene was distilled from sodium. Benzene-d_6 was vacuum distilled from sodium, degrassed thrice by freeze-thaw-pump cycle and store in a Teflon scrawhead stoppered flask. Hexanes for chromatography were distilled from anhydrous calcium chloride. N,N-Dimethylformamide (DMF) was distilled from magnesium sulfate under reduced pressure. Tetrahyrofuran (THF) was distilled from sodium benzophenone ketyl prior to use. Ethers were distilled from sodium. Benzonitrile was distilled from anhydrous P_2O_5. Thin layer chromatography was performed on Merck pre-coated silica gel 60 F_{254} plates. Silica gel (Merck, 70-230 and 230-400 mesh) was used for column chromatography.

6.2   Experimental Instrumentation

^{1}H NMR spectra were recorded on a Bruker DPX 300 (300 MHz) spectrometer and a Bruker AvanceIII 400 (400 MHz). Spectra were referenced internally to the residual proton resonance in C_6D_6 (δ 7.15 ppm) or $CDCl_3$ (δ 7.26 ppm) or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ) are reported in parts per million (ppm). ^{13}C NMR spectra were recorded on a Bruker DPX 300 (75 MHz) and a Bruker AvanceIII 400 (100 MHz).spectrometer and referenced to $CDCl_3$ (δ 77.10 ppm) spectra. Coupling constants (J) are reported in hertz (Hz). Mass spectra (HRMS) were performed on a Thermofinnigan MAT 95 XL instrument (FABMS).

GC-MS analysis was conducted on a GCMS-QP2010 Plus system using a Rtx-5MS column (30 m x 0.25 mm). The details of GC program are as follow:

The column oven temperature and injection temperature are 50.0 and 250.0 °C. Helium is used as carrier gas. Flow control mode is chosen as linear velocity (36.3 cm s^{-1}) with pressure 53.5 kPa. The total flow, column flow and purge flow are 24.0, 1.0 and 3.0 mL min^{-1}, respectively. Split mode injection with split ratio 20.0 is applied. After injection, the column oven temperature is kept at 50 °C for 5 minutes and then temperature is elevated at a rate of 20 °C min^{-1} for 10 minutes until 250 °C. The temperature of 250 °C is kept for 5 minutes.

6.3 Experimental Procedure

Chapter 2

Preparation of 5,10,15,20-Tetratolylporphyrin [H$_2$ttp][1,2] Pyrrole (24 mL, 340 mmol) was added dropwise to a refluxing solution of tolylaldehyde (35 mL, 340 mmol) in propionic acid (1.25 L). The resulting mixture was refluxed in air for 30 minutes. The resulting black solution was cooled to room temperature, and MeOH (1.5 L) was added to obtain the solid purple porphyrin. The mixture was filtered and washed with MeOH. Purple powder (10.3 g, 15 mmol, 18 %) were obtained. R$_f$ = 0.87 (CH$_2$Cl$_2$). ^{1}H NMR (CDCl$_3$, 300 MHz) δ -2.78 (s, 2 H), 2.71 (s, 12 H), 7.54 (d, 8 H, J = 8.0 Hz), 8.08 (d, 8 H, J = 8.0 Hz), 8.85 (s, 8 H).

Preparation of 5,10,15,20-Tetraphenylporphyrin [H$_2$tpp][1,2] Pyrrole (24 mL, 340 mmol) was added dropwise to a refluxing solution of benzaldehyde (35 mL, 344 mmol) in propionic acid (1.25 L). The resulting mixture was refluxed in air for 30 minutes. The resulting black solution was cooled to room temperature, and MeOH (1.5 L) was added to obtain the solid purple porphyrin. The mixture was filtered and washed with MeOH. Purple powder (8.3 g, 14 mmol, 16 %) were obtained. R$_f$ = 0.87 (CH$_2$Cl$_2$). ^{1}H NMR (CDCl$_3$, 400 MHz) δ -2.77 (s, 2 H), 7.74 (d, 12 H, J = 8.0 Hz), 8.23 (d, 8 H, J = 8.0 Hz), 8.85 (s, 8 H).

Preparation of 5,10,15,20-Tetra(4-*tert*-butylphenyl)porphyrin [H$_2$(btpp)][2] Pyrrole (24 mL, 340 mmol) was added dropwise to a refluxing solution of 4-*tert*-benzaldehyde (55 g, 340

mmol) in propionic acid (1.25 L). The resulting mixture was refluxed in air for 30 minutes. The resulting black solution was cooled to room temperature, and MeOH (1.5 L) was added to obtain the solid purple porphyrin. The mixture was filtered and washed with MeOH. Purple powder (9.6 g, 11 mmol, 13 %) were obtained. R_f = 0.71 (hexane/CH_2Cl_2 = 1:1). ^{1}H NMR (CDCl$_3$, 300 MHz) δ -2.76 (s, 2 H), 1.60 (s, 36 H), 7.75 (d, 8 H, J = 8.2 Hz), 8.14 (d, 8 H, J = 8.2 Hz), 8.86 (s, 8 H).

Preparation of 2,3,7,8,12,13,17,18-Octachloro-5,10,15,20-tetrakis-(p-tert-butylphenyl)porphyrin [H$_2$bocp][2] A suspension of H$_2$(btpp) (2.00 g, 2.39 mmol) and Ni(OAc)$_2$·4H$_2$O (2.41 g, 4.80 mmol) in DMF (200 mL) was refluxed for 1.5 h. The color of the suspension changed from purple to reddish purple. The reaction mixture was cooled to room temperature and was worked up by extraction with CHCl$_3$/H$_2$O. The combined organic extract was rotary evaporated and the reddish purple residue obtained was purified by recrystallization with CHCl$_3$/MeOH to give reddish purple crystalline solids of 5,10,15,20-tetrakis(p-tert-butylphenyl)porphyrinato nickel(II) Ni(btpp) (1.91 g, 2.11 mmol, 89 %).

Ni(btpp) (1.91 g, 2.11 mmol) and NCS (2.88 g, 21.6 mmol) were dissolved in o-dichlorobenzene (200 mL) and the mixture was heated at 140 °C for 3 h to give a red mixture. The solvent was then removed under high vacuum. The dark red residue was purified by flash column chromatography over neutral alumina using CHCl$_3$ as the eluent. The second major red band was collected. Ni(bocp) (1.96 g, 1.68 mmol, 80 %) was obtained after removal of solvent by rotary evaporation.

Concentrated sulfuric acid (200 mL) was then added to a solution of Ni(bocp) (1.96 g, 1.68 mmol) in CH$_2$Cl$_2$ (300 mL). The mixture was stirred at room temperature for 30 min. The resulting green suspension was then poured onto ice cubes and the mixture was extracted with CH$_2$Cl$_2$/H$_2$O. The combined green organic extract was neutralized with Na$_2$CO$_3$, washed with saturated NaCl solution, dried with MgSO$_4$, and filtered. The solvent was then removed

by rotary evaporation. The greenish blue crude product obtained was purified by column chromatography over silica gel using a solvent mixture of hexane/CH_2Cl_2 (2:1) as the eluent. The fast moving brown fraction was discarded. The column was then eluted with CH_2Cl_2 and the major green band was collected. After removal of solvent by rotary evaporation, greenish blue solids (1.02 g, 0.94 mmol, 56 %) were obtained. R_f = 0.26 (hexane/CH_2Cl_2 = 2:1). ^{1}H NMR (CDCl$_3$, 300 MHz) δ 1.52 (s, 36 H), 7.74 (d, 8 H, J = 7.8 Hz), 8.06 (d, 8 H, J = 7.8 Hz).

Preparation of 5,10,15,20-Tetratolyporphyrinatorhodium(III) Chloride, Rh(ttp)Cl.[2]

H$_2$ttp (350 mg, 0.51 mmol) and RhCl$_3$·xH$_2$O (206 mg, 1.00 mmol) were refluxed in PhCN (30 mL) in air for 3 h. The solvent was then removed under high vacuum and the crude product was purified by column chromatography over silica gel (70-230 mesh) eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1) then by pure CH_2Cl_2. The major red band was collected. After removal of solvent by rotary evaporation, red solids (373 mg, 0.39 mmol, 72 %) were obtained and were further purified by recrystallization from CH_2Cl_2/CH_3OH. R_f = 0.30 (CH_2Cl_2). ^{1}H NMR (CDCl$_3$, 300 MHz) δ 2.70 (s, 12 H), 7.50-7.56 (m, 8 H), 8.07 (d, 4 H, J = 7.5 Hz), 8.20 (d, 4 H, J = 7.5 Hz) 8.94 (s, 8 H).

Preparation of 5,10,15,20-Tetraphenylporphyrinatorhodium(III) Chloride, Rh(tpp)Cl.[2]

H$_2$tpp (350 mg, 0.51 mmol) and RhCl$_3$·xH$_2$O (206 mg, 1.00 mmol) were refluxed in PhCN (30 mL) in air for 3 h. The solvent was then removed under high vacuum and the crude product was purified by column chromatography over silica gel (70-230 mesh) eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1) then by pure CH_2Cl_2. The major red band was collected. After removal of solvent by rotary evaporation, red solids (373 mg, 0.39 mmol, 72 %) were obtained and were further purified by recrystallization from CH_2Cl_2/CH_3OH. R_f = 0.30 (CH_2Cl_2). ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.75 (m, 12 H), 8.22 (d, 4 H, J = 7.5 Hz), 8.28 (d, 4 H, J = 7.5 Hz) 8.94 (s, 8 H).

Preparation of 2,3,7,8,12,13,17,18-Octachloro-5,10,15,20-tetrakis- (p-tert-butylphenyl)porphyrinato](benzonitrile) rhodium(III) Chloride [Rh(bocp)Cl].[2]

Rh(bocp)Cl was synthesized from H_2bocp (500 mg, 0.45 mmol) and $RhCl_3 \cdot xH_2O$ (142 mg, 0.54 mmol) by the same procedure as described for **1a**. The crude product was purified by column chromatography over silica gel using a solvent mixture of hexane/CH_2Cl_2 (2:3) as the eluent. The fast moving green fraction was discarded and the major red fraction that eluted off with CH_2Cl_2 was collected. After rotary evaporated to dryness, reddish brown solids (460 mg, 0.37 mmol, 82 %) were obtained. R_f = 0.62 (hexane/CH_2Cl_2 = 2:3); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.55 (s, 36 H), 5.69 (d, 2 H, J = 7.7 Hz), 6.77 - 6.83 (m, 2 H), 7.12 (t, 1 H, J = 7.3 Hz), 7.61 - 7.76 (m, 8 H), 8.01 (m, 8 H).

Preparation of 5, 10, 15, 20-Tetratolylporphyrinatorhodium(III) Hydride [Rh(ttp)H] (1d).[3,4] A suspension of Rh(ttp)Cl **3a** (100 mg, 0.11 mmol) in MeOH (50 mL) and a solution of $NaBH_4$ (17 mg, 0.45 mmol) in aq. NaOH (0.1 M, 2 mL) were purged with N_2 for 15 min separately. The solution of $NaBH_4$ was added slowly to the suspension of Rh(ttp)Cl via a cannula. The mixture was heated at 50 °C under N_2 for 1 h to give a brown solution. The solution was then cooled to 0 °C under N_2 and degassed 0.1 M HCl (40 mL) was added via a cannula. A brick red suspension was formed. After stirred at room temperature for another 15 min under N_2, the brick red precipitate was collected after filtration and washing with water (2 x 10 mL) under N_2. The brick red residues (80 mg, 0.10 mmol, 92 %) were obtained after vacuum dried. ^{1}H NMR (C_6D_6, 300 MHz) δ -40.12 (d, 1 H, J_{Rh-H} = 43.5 Hz), 2.42 (s, 12 H), 7.16 (d, 4 H, J = 8.2 Hz), 7.35 (d, 4 H, J = 8.2 Hz), 7.95 (d, 4 H, J = 8.1 Hz), 8.22 (d, 4 H, J = 8.1 Hz), 9.03 (s, 8 H).

Preparation of $Rh_2(ttp)_2$[4] Rh(ttp)H (10.0 mg, 0.013 mmol) was dissolved in degassed benzene (4.0 mL). The reaction mixture was then degassed by three freeze-pump-thaw method and refilled with N_2. The solution was irradiated under a 400 W Hg-lamp at 6-11 °C

until all the starting material was consumed as indicated by TLC analysis (~10 h) to give Rh$_2$(ttp)$_2$ in quantitative yield.

Preparation of Rh (ttp)⁻Na⁺⁵ Rh(ttp)Ca (10.0 mg, 0.013 mmol) was dissolved in degassed benzene (4.0 mL). The reaction mixture was then degassed by three freeze-pump-thaw method and refilled with N$_2$. Na/Hg was added into the reaction mixture. The reaction mixture was stirred at room temperature for 15 min. The resultant deep reddish brown solution was transferred via cannular under nitrogen atmosphere for subsequent reaction. Rh(ttp)⁻Na⁺ was formed quantitatively.

Reaction of Alkanes with Rh(ttp)Cl (1a).

(5, 10, 15, 20-Tetratolyporphyrinato)(cyclohexyl) rhodium(III), [Rh(ttp)(c-hexyl)] (2a). Rh(ttp)Cl (1a) (20.1 mg, 0.025 mmol) was added into c-hexane (3.0 mL). The red suspension was degassed for three freeze-thaw-pump cycles and was then heated at 120 °C under N$_2$ in the dark for 24 hours. After 24 hours, the mixture turned into dark red. Excess c-hexane was removed by vacuum distillation. The dark red residue was then purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH$_2$Cl$_2$ (4:1) to give Rh(ttp)(c-hexyl) (2a) as a red solid (6.6 mg, 0.007 mmol, 31%) which was further recrystallized from CH$_2$Cl$_2$/MeOH. R$_f$ = 0.84 (hexane/CH$_2$Cl$_2$ = 1:1). ^{1}H NMR (CDCl$_3$, 300 MHz) δ -4.25 (m, 5 H, H$_a$, H$_b$ and H$_b$'), -1.23 (q, 2 H, J = 12.3 Hz, H$_c$'), -0.95 (tq, 1 H, J = 3.3, 12.9 Hz, H$_d$), −0.58 (d, 2 H, J = 12.6 Hz, H$_c$), -0.08 (d, 1 H, J = 12.6 Hz, H$_d$'), 2.69 (s, 12 H, p-methyl), 7.52 (d, 8 H, J = 7.5 Hz, m-phenyl), 8.01 (d, 4 H, J = 8.4 Hz, o'-phenyl), 8.06 (d, 4 H, J = 7.8 Hz, o-phenyl), 8.68 (s, 8 H, pyrrole). ^{13}C NMR (CDCl$_3$, 75 MHz) δ 21.69, 25.17, 26.95, 33.36, 39.37 (d, $^1J_{Rh-C}$ = 27.6 Hz), 122.81, 127.40, 127.55, 130.88, 131.52, 131.71, 134.25, 137.23, 139.53, 143.40. Calcd. for (C$_{54}$H$_{46}$N$_4$Rh)$^+$: m/z 854.2850. Found: m/z 854.2859. Anal. Calcd. for C$_{54}$H$_{46}$N$_4$Rh: C, 75.87; H, 5.54; N, 6.55. Found C, 75.41; H, 5.57; N, 6.50. Single crystal for X-ray diffraction analysis was grown from CH$_2$Cl$_2$/methanol.

(ttp)Rh — with cyclohexane structure labeled H_b, H_d, H_b', H_a, H_c', H_c, H_d'
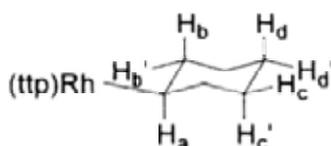
Reaction of Rh(ttp)Cl with *c*-Hexane at 80 °C. Rh(ttp)Cl (**1a**) (20.2 mg, 0.025 mmol) was added into *c*-hexane (3.0 mL). The red suspension was degassed for three freeze-thaw-pump cycles and was then heated at 80 °C under N_2 in the dark for 24 hours. After 24 hours, the mixture turned into dark red. Excess *c*-hexane was removed by vacuum distillation. The dark red residue was then purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (4:1) to give Rh(ttp)(*c*-hexyl) (**2a**) as a red solid (0.2 mg, 0.00023 mmol, 1%).

Reaction of Rh(ttp)Cl with *c*-Hexane at 100 °C. Rh(ttp)Cl (**1a**) (19.9 mg, 0.025 mmol) was added into *c*-hexane (3.0 mL). The red suspension was degassed for three freeze-thaw-pump cycles and was then heated at 100 °C under N_2 in the dark for 24 hours. After 24 hours, the mixture turned into dark red. Excess *c*-hexane was removed by vacuum distillation. The dark red residue was then purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (4:1) to give Rh(ttp)(*c*-hexyl) (**2a**) as a red solid (0.6 mg, 0.00070 mmol, 3%).

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

Reaction of Rh(ttp)Cl with *c*-Hexane at 200 °C. Rh(ttp)Cl (**1a**) (20.0 mg, 0.025 mmol) was added into *c*-hexane (3.0 mL). The red suspension was degassed for three freeze-thaw-pump

cycles and was then heated at 200 °C under N_2 in the dark for 24 hours. After 24 hours, the mixture turned into dark red. Excess c-hexane was removed by vacuum distillation. The dark red residue was then purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (4:1) to give Rh(ttp)(c-hexyl) (**2a**) as a red solid (3.8 mg, 0.0045 mmol, 18%).

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

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

Reaction of Rh(ttp)Cl and c-Hexane with K_2CO_3. Rh(ttp)Cl (**1a**) (20.4 mg, 0.025 mmol) and anhydrous potassium carbonate (34.9 mg, 0.252 mmol) were added in c-hexane (3.0 mL). The red reaction mixture was degassed for three freeze-thaw-pump cycles and was heated at 120 °C under N_2 for 6 hours. Excess c-hexane was removed by vacuum distillation, the dark red crude product was extracted with CH_2Cl_2/H_2O. The organic layer was collected, dried and evaporated to dryness and the residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (4:1). Red solid, Rh(ttp)(c-hexyl) (**2a**) (12.7 mg, 0.015 mmol, 59%) was collected.

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

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

Reaction of Rh(ttp)Cl and *c*-Hexane with NaOAc. Rh(ttp)Cl (**1a**) (20.1 mg, 0.025 mmol) and sodium acetate (20.4 mg, 0.249 mmol) were added in *c*-hexane (3.0 mL). The red reaction mixture was degassed for three freeze-thaw-pump cycles and was heated at 120 °C under N_2 for 6 hours. Excess *c*-hexane was removed by vacuum distillation, the dark red crude product was extracted with CH_2Cl_2/H_2O. The organic layer was collected, dried and evaporated to dryness and the residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (4:1) to give the red solid Rh(ttp)(*c*-hexyl) (**2a**) (10.9 mg, 0.013 mmol, 51%).

Reaction of Rh(ttp)Cl and *c*-Hexane with 2,2'-Bipyridine. Rh(ttp)Cl (**1a**) (20.6 mg, 0.026 mmol) and 2,2'-bipyridine (39.9 mg, 0.255 mmol) were added in *c*-hexane (3.0 mL). The red reaction mixture was degassed for three freeze-thaw-pump cycles and was heated at 120 °C under N_2 for 48 hours. Excess *c*-hexane was removed by vacuum distillation, the residue was

purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (4:1) to give the red solid, Rh(ttp)(c-hexyl) (**2a**) (11.0 mg, 0.013 mmol, 50%).

Reaction of Rh(ttp)Cl and c-Hexane with 2,6-Diphenylpyridine. Rh(ttp)Cl (**1a**) (19.8 mg, 0.025 mmol) and 2,6-diphenylpyridine (57.2 mg, 0.245 mmol) were added in c-hexane (3.0 mL). The red reaction mixture was degassed for three freeze-thaw-pump cycles and was heated at 120 °C under N_2 for 24 hours. Excess c-hexane was removed by vacuum distillation, the residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (4:1) to give the red solid, Rh(ttp)(c-hexyl) (**2a**) (12.2 mg, 0.014 mmol, 58%).

Reaction of Rh(ttp)Cl and c-Hexane with 2,6-di-tert-Butylpyridine. Rh(ttp)Cl (**1a**) (19.7 mg, 0.024 mmol) and 2,6-di-tert-butylpyridine (46.4 mg, 54.5 μL, 0.243 mmol) were added in c-hexane (3.0 mL). The red reaction mixture was degassed for three freeze-thaw-pump cycles and was heated at 120 °C under N_2 for 24 hours after excess c-hexane was removed by vacuum distillation, the residue was then purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (4:1) to give the red solid, Rh(ttp)(c-hexyl) (**2a**) (10.3 mg, 0.012 mmol, 50%).

**Reaction of Rh(ttp)Cl and c-Hexane with K_2CO_3 for 24 h.** Rh(ttp)Cl (**1a**) (20.1 mg, 0.025 mmol) and anhydrous potassium carbonate (34.7 mg, 0.252 mmol) were added in c-hexane (3.0 mL). The red reaction mixture was degassed for three freeze-thaw-pump cycles and was heated at 120 °C under N_2 for 24 hours. Excess c-hexane was removed by vacuum distillation, the dark red crude product was extracted with CH_2Cl_2/H_2O. The organic layer was collected, dried and evaporated to dryness and the residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (4:1). Red solid, Rh(ttp)(c-hexyl) (**2a**) (8.6 mg, 0.010 mmol, 40%) was collected

Reaction of Rh(ttp)Cl and *c*-Hexane with 2,6-di-tert-Butylpyridine for 6 h. Rh(ttp)Cl (**1a**) (20.3 mg, 0.025 mmol) and 2,6-diphenylpyridine (57.0 mg, 0.245 mmol) were added in *c*-hexane (3.0 mL). The red reaction mixture was degassed for three freeze-thaw-pump cycles and was heated at 120 °C under N_2 for 6 hours. Excess *c*-hexane was removed by vacuum distillation, the residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (4:1) to give the red solid, Rh(ttp)(*c*-hexyl) (**2a**) (4.9 mg, 0.0057 mmol, 23%).

Chloro(5, 10, 15, 20-Tetratolyporphyrinato)(triphenylphosphine)rhodium(III), [Rh(ttp)Cl(PPh₃)] (2f). Rh(ttp)Cl (**1a**) (19.9 mg, 0.025 mmol) and triphenylphosphine (64.7 mg, 0.247 mmol) were added in *c*-hexane (3.0 mL). The red reaction mixture was degassed for three freeze-thaw-pump cycles and was heated at 120 °C under N_2 for 24 hours. Excess *c*-hexane was removed by vacuum distillation, the residue was purified by column chromatography on silica gel eluting with ethyl acetate to give Rh(ttp)Cl(PPh₃) (**2f**) (21.9 mg, 0.021 mmol, 83%). R_f = 0.65 (ethyl acetate). ^{1}H NMR (CDCl₃, 300 MHz) δ 2.68 (s, 12 H, *p*-methyl), 3.84 (dd, 6 H, *J* = 7.6, 10.7 Hz, *m*-phenyl of PPh₃), 6.51 (td, 6 H, *J* = 2.2, 7.8 Hz, *o*-phenyl of PPh₃), 6.90 (td, 3 H, *J* = 5.3, 11.2 Hz, *p*-phenyl of PPh₃), 7.49 (d, 8 H, *J* = 8.0 Hz, *m*-phenyl), 7.66 (d, 4 H, *J* = 7.6 Hz, *o'*-phenyl), 8.04 (d, 4 H, *J* = 7.49 Hz, *o*-phenyl), 8.72 (s, 8 H, pyrrole). ^{13}C NMR (CDCl₃, 75 MHz) δ 21.63, 121.63, 126.79, 126.92, 127.00, 127.66, 129.36, 131.02, 131.14, 132.15, 132.65, 134.16, 135.05, 137.05, 139.31, 142.75. Calcd. for $(C_{66}H_{51}N_4PRh)^+$: m/z 1033.2901. Found: m/z 1033.2885.

**Investigation of Base Loading in CHA of *c*-Hexane (5 equiv of K₂CO₃).** Rh(ttp)Cl (**1a**) (20.3 mg, 0.025 mmol) and anhydrous potassium carbonate (34.9 mg, 0.126 mmol) were added in *c*-hexane (3.0 mL). The red reaction mixture was degassed for three freeze-thaw-pump cycles and was heated at 120 °C under N_2 for 24 hours. Excess *c*-hexane was removed by vacuum distillation, the dark red crude product was extracted with CH_2Cl_2/H_2O. The

organic layer was collected, dried and evaporated to dryness and the residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (4:1). Red solid, Rh(ttp)(c-hexyl) (**2a**) (7.5 mg, 0.0088 mmol, 35%) was collected.

Investigation of Base Loading in CHA of *c*-Hexane (20 equiv of K_2CO_3). Rh(ttp)Cl (**1a**) (20.1 mg, 0.025 mmol) and anhydrous potassium carbonate (68.8 mg, 0.498 mmol) were added in *c*-hexane (3.0 mL). The red reaction mixture was degassed for three freeze-thaw-pump cycles and was heated at 120 °C under N_2 for 6 hours. Excess *c*-hexane was removed by vacuum distillation, the dark red crude product was extracted with CH_2Cl_2/H_2O. The organic layer was collected, dried and evaporated to dryness and the residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (4:1). Red solid, Rh(ttp)(c-hexyl) (**2a**) (11.9 mg, 0.014 mmol, 56%) was collected.

(5, 10, 15, 20-Tetraphenylporphyrinato)(cyclohexyl)rhodium(III), [Rh(tpp)(*c*-hexyl)] (4a). Rh(tpp)Cl (**1b**) [25,26] (20.2 mg, 0.027 mmol) and anhydrous potassium carbonate (37.2 mg, 0.269 mmol) were added in *c*-hexane (3.0 mL) and formed a bright red reaction mixture. The bright red reaction mixture was degassed for three freeze-thaw-pump cycles and was heated at 120 °C under N_2 in the dark for 5 hours. After 5 hours, the mixture turned into dark red. Excess *c*-hexane was removed by vacuum distillation. The dark red residue was extracted with CH_2Cl_2/H_2O. The organic layer was collected, dried and evaporated to dryness and then purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (4:1). Rh(tpp)(c-hexyl) (**4a**) was collected as a red solid was collected (11.2 mg, 0.014 mmol, 52%), R_f = 0.83 (hexane/CH_2Cl_2 = 1:1). ^1H NMR (CDCl$_3$, 300 MHz) δ -4.26 (m, 5 H, H$_a$, H$_b$ and H$_b$'), -1.21 (q, 2 H, J = 12.3 Hz, H$_c$'), -0.94 (tq, 1 H, J = 3.3, 12.9 Hz, H$_d$), –0.56 (d, 2 H, J = 11.4 Hz, H$_c$), -0.07 (d, 1 H, J = 12.9 Hz, H$_d$'), 7.50 (m, 8 H, *m*-phenyl), 8.13 (d, 4 H, J = 4.5 Hz, *o*'-phenyl), 8.19 (d, 4 H, J = 6.6 Hz, *o*-phenyl), 8.67 (s, 8 H, pyrrole). ^{13}C NMR (CDCl$_3$, 75 MHz) δ 25.14, 26.95, 33.39, 39.65 (d, $^1J_{Rh-C}$ = 29.5 Hz),

122.87, 126.70, 126.84, 127.69, 131.61, 133.78, 134.34, 142.39, 143.30. Calcd. for $(C_{50}H_{39}N_4Rh)^+$: m/z 798.2224 Found: m/z 798.2171. Anal. Calcd. for $C_{50}H_{39}N_4Rh$: C, 75.18; H, 4.92; N, 7.01; Found C, 74.68; H, 4.89; N, 6.70.
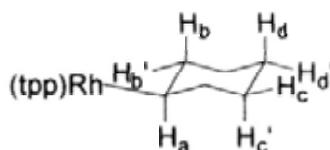
[2,3,7,8,12,13,17,18-Octachloro-5,10,15,20-tetrakis(p-tert-butylphenyl)porphyrinato] (cyclohexyl)rhodium(III), Rh(bocp)(c-hexyl) (4b). Rh(bocp)Cl (1c) [25,26] (21.7 mg, 0.017 mmol) and anhydrous potassium carbonate (24.0 mg, 0.174 mmol) were added in c-hexane (3.0 mL) and formed a bright red reaction mixture. The bright red reaction mixture was degassed for three freeze-thaw-pump cycles and was heated at 120 °C under N_2 in the dark for 1 hour. After 1 hour, the mixture turned into dark red. Excess c-hexane was removed by vacuum distillation. The dark red residue was extracted with CH_2Cl_2/H_2O. The organic layer was collected, dried and evaporated to dryness and then purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (4:1) to give the red solid, Rh(bocp)(c-hexyl) (4b) (13.8 mg, 0.011 mmol, 61%). R_f = 0.86 (hexane/CH_2Cl_2 = 1:1). ^{1}H NMR (CDCl$_3$, 300 MHz) δ -3.63 (q, 2 H, J = 9.6 Hz, H$_b$), -3.46 (q, 2 H, J = 9.3 Hz, H$_b$'), -3.17 (td, 1 H, J = 3.0, 9.0 Hz, H$_a$), -0.85 (q, 2 H, J = 12.3 Hz, H$_c$'), -0.71 (t, 1 H, J = 12.9 Hz, H$_d$), -0.25 (d, 2 H, J = 12.0 Hz, H$_c$), 1.36 (d, 1 H, J = 12.0 Hz, H$_d$'), 1.55 (s, 36 H, ^{t}Bu), 7.70 (d, 8 H, J = 8.7 Hz, m-phenyl), 8.54 (d, 4 H, J = 7.2 Hz, o'-phenyl), 7.95 (d, 4 H, J = 7.2 Hz, o-phenyl). ^{13}C NMR (CDCl$_3$, 75 MHz) δ 25.18, 27.61, 29.86, 31.85, 35.11, 35.78, 122.56, 124.71, 133.02, 134.05, 134.73, 138.11, 152.76. Calcd. for $(C_{66}H_{63}N_4Cl_8Rh)^+$: m/z 1298.1551 Found: m/z 1298.1519. Anal. Calcd. for $C_{66}H_{63}N_4Cl_8Rh$: C, 61.04; H, 4.89; N, 4.31; Found C, 61.11; H, 5.05; N, 4.19.
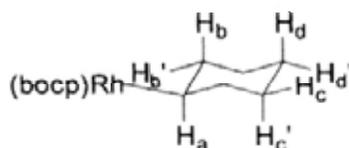
(5, 10, 15, 20-Tetratolyporphyrinato)(cyclopentyl)rhodium(III), [Rh(ttp)(*c*-pentyl)] (2b).
Rh(ttp)Cl (**1a**) (20.0 mg, 0.025 mmol) and anhydrous potassium carbonate (34.2 mg, 0.248 mmol) were added in *c*-pentane (3.0 mL). The red reaction mixture was degassed for three freeze-thaw-pump cycles and was heated at 120 °C under N_2 in the dark for 6 hours. Excess *c*-pentane was removed by vacuum distillation. The dark red crude product was extracted with CH_2Cl_2/H_2O. The organic layer was collected, dried and evaporated to dryness and then residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (4:1). The red solid of Rh(ttp)(*c*-pentyl) (**2b**) was collected (16.0 mg, 0.017 mmol, 75%). R_f = 0.85 (hexane/CH_2Cl_2 = 1:1). ^{1}H NMR (CDCl$_3$, 300 MHz) δ -4.90 (m, 2 H, H_b), -4.37 (m, 1 H, H_a), –3.46 (m, 2 H, H_b'), -1.03 (m, 4 H, H_c), 2.69 (s, 12 H, *p*-methyl), 7.52 (t, 8 H, *J* = 6.2 Hz, *m*-phenyl), 8.00 (d, 4 H, *J* = 8.5 Hz, *o*'-phenyl), 8.09 (d, 4 H, *J* = 8.6 Hz, *o*-phenyl), 8.69 (s, 8 H, pyrrole). ^{13}C NMR (CDCl$_3$, 75 MHz) δ 18.87, 22.14, 29.52, 34.53, 123.20, 127.86, 127.92, 131.91, 134.19, 134.61, 137.69, 139.94, 143.93. Calcd. for $(C_{53}H_{45}N_4Rh)^+$: m/z 840.2694. Found: m/z 840.2694. Anal. Calcd. for $C_{53}H_{45}N_4Rh$: C, 75.71; H, 5.39; N, 6.66. Found C, 75.29; H, 5.37; N, 6.53. Single crystal for X-ray diffraction analysis was grown from CH_2Cl_2/ethanol.
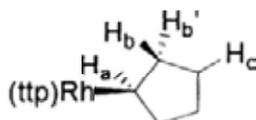
(5, 10, 15, 20-Tetratolyporphyrinato)(*n*-pentyl)rhodium(III), [Rh(ttp)(*n*-pentyl)] (2c).
Rh(ttp)Cl (**1a**) (20.4 mg, 0.025 mmol) and anhydrous potassium carbonate (34.9 mg, 0.252 mmol) were added in *n*-pentane (3.0 mL) and formed a bright red reaction mixture. The bright red reaction mixture was degassed for three freeze-thaw-pump cycles and was heated

at 120 °C under N_2 in the dark for 24 hours. After 24 hours, the mixture turned into dark red. Excess *n*-pentane was removed by vacuum distillation. The dark red residue was extracted with CH_2Cl_2/H_2O. The organic layer was collected, dried and evaporated to dryness and then purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (4:1). Rh(ttp)(*n*-pentyl) (**2c**) was collected as the major product. Red solid, Rh(ttp)(*n*-pentyl) (**2c**), was collected (6.5 mg, 0.008 mmol, 31%). $R_f = 0.78$ (hexane/CH_2Cl_2 = 1:1). ^1H NMR (CDCl$_3$, 300 MHz) δ -4.97 (td, 2 H, $J = 2.4$, 7.5 Hz, H$_a$), -4.50 (qu, 2 H, $J = 7.2$ Hz, H$_b$), -1.59 (qu, 2 H, $J = 2.1$ Hz, H$_c$), −0.49 (q, 2 H, $J = 6.9$ Hz, H$_d$), -0.25 (t, 3 H, $J = 7.2$ Hz, H$_e$), 2.69 (s, 12 H, *p*-methyl), 7.53 (t, 8 H, $J = 6.0$ Hz, *m*-phenyl), 7.98 (d, 4 H, $J = 8.6$ Hz, *o*'-phenyl), 8.08 (d, 4 H, $J = 8.3$ Hz, *o*-phenyl), 8.70 (s, 8 H, pyrrole) ^{13}C NMR (CDCl$_3$, 75 MHz) δ 12.81, 15.66 (d, $^1J_{Rh-C} = 27.2$ Hz), 20.72, 21.69, 26.86, 28.50, 122.51, 127.47, 127.52, 131.49, 133.81, 134.10, 137.25, 139.50, 143.37 Calcd. for $(C_{53}H_{47}N_4Rh)^+$: m/z 840.2694. Found: m/z 840.2682. Anal. Calcd. for $C_{53}H_{47}N_4Rh$: C, 75.52; H, 5.62; N, 6.64; Found C, 75.43; H, 5.67; N, 6.36. (qu = quintet)
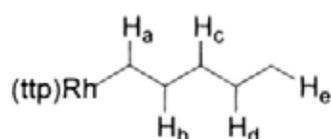
(**5, 10, 15, 20-Tetratolyporphyrinato)(*n*-hexyl)rhodium(III), [Rh(ttp)(*n*-hexyl)] (2d).** Rh(ttp)Cl (**1a**) (20.6 mg, 0.026 mmol) and anhydrous potassium carbonate (35.3 mg, 0.255 mmol) were added in *n*-hexane (3.0 mL) and formed a bright red reaction mixture. The bright red reaction mixture was degassed for three freeze-thaw-pump cycles and was heated at 120 °C under N_2 in the dark for 24 hours. After 24 hours, the mixture turned into dark red. Excess *n*-hexane was removed by vacuum distillation. The dark red residue was extracted with CH_2Cl_2/H_2O. The organic layer was collected, dried and evaporated to dryness and then purified by column chromatography on silica gel with a solvent mixture of hexane/CH_2Cl_2

(4:1). Rh(ttp)(*n*-hexyl) (**2d**) was collected as the major product. The red solid of Rh(ttp)(*n*-hexyl) (**2d**), was collected (10.6 mg, 0.012 mmol, 49%). R_f = 0.84 (hexane/CH$_2$Cl$_2$ = 1:1). ^{1}H NMR (CDCl$_3$, 300 MHz) δ -4.96 (td, 2 H, J = 3.0, 9.0 Hz, H$_a$), -4.51 (qu, 2 H, J = 7.8 Hz, H$_b$), -1.58 (qu, 2 H, J = 7.5 Hz, H$_c$), -0.57 (qu, 2 H, J = 7.5 Hz, H$_d$), 0.10 (m, 2 H, H$_e$), 0.17 (t, 3 H, J = 7.2 Hz, H$_f$), 2.68 (s, 12 H, *p*-methyl), 7.52 (d, 4 H, J = 5.7 Hz, *m'*-phenyl), 7.54 (d, 4 H, J = 5.7 Hz, *m*-phenyl), 7.97 (d, 4 H, J = 7.2 Hz, *o'*-phenyl), 8.06 (d, 4 H, J = 8.3 Hz, *o*-phenyl), 8.69 (s, 8 H, pyrrole) ^{13}C NMR (CDCl$_3$, 75 MHz) δ 13.53, 15.69 (d, $^1J_{Rh-C}$ = 27.2 Hz), 21.40, 21.69, 26.06, 27.13, 29.84, 122.53, 127.47, 130.89, 131.51, 131.85, 133.83, 134.11, 137.25, 139.52, 143.39 Calcd. for (C$_{54}$H$_{49}$N$_4$Rh)$^+$: m/z 856.3007. Found: m/z 856.3017. Anal. Calcd. for C$_{54}$H$_{49}$N$_4$Rh: C, 75.69; H, 5.76; N, 6.54; Found C, 75.61; H, 5.72; N, 6.53.
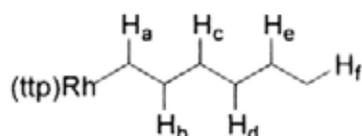
(5, 10, 15, 20-Tetratolyporphyrinato)(*n*-heptyl)rhodium(III), [Rh(ttp)(*n*-heptyl)] (2e). Rh(ttp)Cl (**1a**) (20.9 mg, 0.026 mmol) and anhydrous potassium carbonate (35.3 mg, 0.255 mmol) were added in *n*-heptane (3.0 mL) and formed a bright red reaction mixture. The bright red reaction mixture was degassed for three freeze-thaw-pump cycles and was heated at 120 °C under N$_2$ in the dark for 24 hours. After 24 hours, the mixture turned into dark red. Excess *n*-heptane was removed by vacuum distillation. The dark red residue was extracted with CH$_2$Cl$_2$/H$_2$O. The organic layer was collected, dried and evaporated to dryness and then purified by column chromatography on silica gel with a solvent mixture of hexane/CH$_2$Cl$_2$ (4:1). Rh(ttp)(*n*-heptyl) (**2e**) was collected as the major product. Red solid, Rh(ttp)(*n*-heptyl) (**2e**), was collected (13.2 mg, 0.015 mmol, 59%). R_f = 0.83 (hexane/CH$_2$Cl$_2$ = 1:1). ^{1}H NMR (CDCl$_3$, 300 MHz) δ -4.97 (td, 2 H, J = 3.0, 8.7 Hz, H$_a$), -4.53 (qu, 2 H, J = 7.2Hz, H$_b$), -1.63

(qu, 2 H, J = 7.2 Hz, H$_c$), -0.55 (qu, 2 H, J = 7.2 Hz, H$_d$), -0.04 (d, 2 H, J = 9.0 Hz, H$_e$), 0.45 (q, 3 H, J = 6.0 Hz, H$_g$), 0.52 (qu, 2 H, J = 7.2 Hz, H$_f$), 2.69 (s, 12 H, p-methyl), 7.51 (d, 4 H, J = 6.6 Hz, m'-phenyl), 7.53 (d, 4 H, J = 6.3 Hz, m-phenyl), 7.98 (d, 4 H, J = 6.9 Hz, o'-phenyl), 8.08 (d, 4 H, J = 7.2 Hz, o-phenyl), 8.70 (s, 8 H, pyrrole) ^{13}C NMR (CDCl$_3$, 75 MHz) δ 13.89, 15.71 (d, $^1J_{Rh-C}$ = 27.5 Hz), 21.69, 22.10, 26.25, 27.06, 27.24, 30.57, 122.52, 126.22, 127.45, 127.52, 131.49, 133.80, 134.11, 137.23, 139.51, 143.38 Calcd. for (C$_{55}$H$_{51}$N$_4$Rh)$^+$: m/z 870.3163 Found: m/z 870.3167. Anal. Calcd. for C$_{55}$H$_{51}$N$_4$Rh: C, 75.85; H, 5.90; N, 6.43; Found C, 75.77; H, 5.96; N, 6.31. Single crystal for X-ray diffraction analysis was grown from CH$_2$Cl$_2$/methanol.
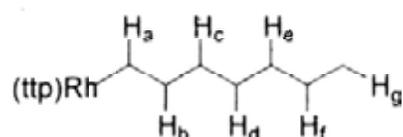
Decomposition of Rh(ttp)(c-pentyl) (2b) with K$_2$CO$_3$ in Benzene-d_6. Rh(ttp)(c-pentyl) (6.7 mg, 0.0080 mmol) and potassium carbonate (11.0 mg, 0.080 mmol) were added into benzene-d_6 (520 μL) in a NMR tube. The red reaction mixture was degassed for three freeze-thaw-pump cycles and the NMR tube was sealed under vacuum. It was heated to 120 ^{o}C and the reaction mixture was monitored with ^{1}H NMR spectroscopy and NMR yields were taken.

For the observation of Rh(ttp)H, dilute HCl solution was added into the NMR tube with shaking. It was brought to take a ^{1}H NMR spectrum immediately after the addition of dilute HCl.

Decomposition of Rh(ttp)(c-hexyl) (2a) with K$_2$CO$_3$ in Benzene-d_6. Rh(ttp)(c-hexyl) (6.9 mg, 0.0081 mmol) and potassium carbonate (11.0 mg, 0.080 mmol) were added into benzene-d_6 (520 μL) in a NMR tube. The red reaction mixture was degassed for three freeze-thaw-pump cycles and the NMR tube was sealed under vacuum. It was heated to 120 ^{o}C and the reaction mixture was monitored with ^{1}H NMR spectroscopy and NMR yields were taken.

Decomposition of Rh(ttp)(*n*-hexyl) (2d) with K$_2$CO$_3$ in Benzene-*d$_6$*. Rh(ttp)(*n*-hexyl) (6.9 mg, 0.0081 mmol) and potassium carbonate (11.0 mg, 0.080 mmol) were added into benzene-*d$_6$* (520 μL) in a NMR tube. The red reaction mixture was degassed for three freeze-thaw-pump cycles and the NMR tube was sealed under vacuum. It was heated to 120 °C and the reaction mixture was monitored with ^{1}H NMR spectroscopy and NMR yields were taken.

Sealed NMR Tube Experiment of Rh(ttp)Cl and *c*-hexane in Benzene-*d$_6$*. Rh(ttp)Cl (**1a**) (5.1 mg, 0.0066 mmol) and *c*-hexane (34 μL, 0.316 mmol) were added into benzene-*d$_6$* (520 μL) in a NMR tube. The red mixture was degassed for three freeze-thaw-pump cycles and the NMR tube was sealed under vacuum. It was heated at 120 °C in the dark. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

Sealed NMR Tube Experiment of Rh(ttp)Cl and *c*-hexane with K$_2$CO$_3$ in Benzene-*d$_6$*. Rh(ttp)Cl (**1a**) (5.1 mg, 0.0066 mmol), *c*-hexane (34 μL, 0.316 mmol) and K$_2$CO$_3$ (8.7 mg, 0.063 mmol) were added into benzene-*d$_6$* (520 μL) in a NMR tube. The red mixture was degassed for three freeze-thaw-pump cycles and the NMR tube was sealed under vacuum. It was heated at 120 °C in the dark. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

Reaction of Rh(ttp)H with KOH. Rh(ttp)H (**1d**) (8.0 mg, 0.010 mmol) and potassium hydroxide (14.3 mg, 0.104 mmol) were added into degassed benzene-*d$_6$* (520 μL) in NMR tube. The reaction mixture was degassed for three freeze-thaw-pump cycles and the NMR tube was sealed under vacuum. The reaction mixture was then warmed to 23 °C in a water bath for 15 minutes. It was brought to ^{1}H NMR spectroscopy. Rh$_2$(ttp)$_2$ was obtained (55% NMR yield).

Thermal Stability of Rh(ttp)H. Rh(ttp)H (**1d**) (7.9 mg, 0.010 mmol) and was added into degassed benzene-*d$_6$* (520 μL) in NMR tube. The reaction mixture was degassed for three freeze-thaw-pump cycles and the NMR tube was sealed under vacuum. The reaction mixture

was then heated to 120 °C for 6 days. It was brought to ^{1}H NMR spectroscopy. The NMR yield of Rh(ttp)H was found to be 90%.

Reaction of Alkanes with Rh(ttp)H (1d). Rh(ttp)H (1d) (10.0 mg, 0.013 mmol) was added into c-hexane (3.0 mL). The red suspension was degassed for three freeze-thaw-pump cycles and was then heated at 120 °C under N_2 in the dark for 3 hours. After 3 hours, the mixture turned into red. Excess c-hexane was removed by vacuum distillation. The dark red residue was then purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (4:1) to give Rh(ttp)(c-hexyl) (2a) as a red solid (4.0 mg, 0.0047 mmol, 36%).

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

The product ratio was calculated as follow:

(i) ^{1}H NMR

Integration of alkyl proton of Rh(ttp)(c-hexyl) at δ = -4.26 (observed = 5.193) and integration of alkyl proton of the Rh(ttp)(c-hexyl)/Rh(ttp)(c-hexyl)-d_{11} δ = -4.26 (observed = 4.680) were

used to calculated the ratio with the integration of pyrrole signal of **2a** (δ = 8.63) was taken as 8. Let the integration of that alkyl deuterium to be Y. Y is equal to the integration of that alkyl proton without deuterium incorporation (5.193) minus the observed integration of that alkyl proton with deuterium incorpation (4.680). k_H/k_D is equal to the integration of alkyl proton (4.680) over the integration of alkyl deuterium (5.193-4.680). The calculated k_H/k_D is 9.1($\pm$0.3).

(ii) MS method:

The product ratio is calculated to be the molecular peak intensity of Rh(ttp)(c-hexyl) (observed to be 60.0) over the molecular peak intensity of Rh(ttp)(c-hexyl)-d_{11} (observed to be 6.1). The product ratio is calculated to be 9.7($\pm$0.2).

Alkyl exchange of Rh(ttp)(*c*-hexyl) (2a) with *c*-hexane-*d*$_{12}$ at 120 °C. Rh(ttp)(c-hexyl) (2a) (5.4 mg, 0.0063 mmol) was added with cyclohexane-d_{12} (0.5 mL) in a Telfon screw capped NMR tube. The red solution was degassed for three freeze-thaw-pump cycles. The NMR tube was sealed under vacuum. It was heated at 120 °C in the dark and the reaction was monitored by ^{1}H NMR. The product ratio was calculated as follow:

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

For the case of 42 hours, k_H/k_D is equal to the integration of alkyl proton (5.191) over the integration of alkyl deuterium (5.370-5.191). The calculated k_H/k_D is 22.9.

Competition Reaction of *c*-hexane and *c*-hexane-*d*$_{12}$ with Rh(ttp)H (1d). Rh(ttp)H (1d) (10.1 mg, 0.013 mmol) was added into mixture of c-hexane (1.50 ml, 14.000 mmol) and c-

hexane-d_{12} (1.49 ml, 14.000 mmol). The red mixture was degassed for three freeze-thaw-pump cycles and was heated at 120 °C under N_2 in the dark for 3 hours. Then excess c-hexane/c-hexane-d_{12} mixture was removed by vacuum distillation. Dark red residue was brought to ^1H NMR spectroscopy. It was then purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (4:1). The red fraction was collected. After rotary evaporation, product mixture of Rh(ttp)(c-hexyl) (**2a**) and Rh(ttp)(c-hexyl)-d_{11} was obtained as a red solid (6.0 mg, 0.0070 mmol, 54%). Integration of alkyl proton of the Rh(ttp)(c-hexyl)/Rh(ttp)(c-hexyl)-d_{11} δ = -4.26 was found to be 4.668. The calculated k_H/k_D was 8.9(±0.3).

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

Competition Reaction of c-hexane and c-hexane-d_{12} with $Rh_2(ttp)_2$ (1e). $Rh_2(ttp)_2$ (**1e**) (10.3 mg, 0.0067 mmol) was added into mixture of c-hexane (1.50 ml, 14.000 mmol) and c-hexane-d_{12} (1.49 ml, 14.000 mmol). The red mixture was degassed for three freeze-thaw-pump cycles and was heated at 120 °C under N_2 in the dark for 6 hours. Then excess c-

hexane/c-hexane-d_{12} mixture was removed by vacuum distillation. Dark red residue was brought to ^{1}H NMR spectroscopy. It was then purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH$_2$Cl$_2$ (4:1). The red fraction was collected. After rotary evaporation, product mixture of Rh(ttp)(c-hexyl) (**2a**) and Rh(ttp)(c-hexyl)-d_{11} was obtained as a red solid (4.3 mg, 0.0050 mmol, 38%). Integration of alkyl proton of the Rh(ttp)(c-hexyl)/Rh(ttp)(c-hexyl)-d_{11} δ = -4.26 was found to be 4.659. The calculated k_H/k_D was 8.7($\pm$0.3).

Competition Reaction of c-hexane and c-hexane-d_{12} with Rh$_2$(ttp)$_2$ (1e) with K$_2$CO$_3$. Rh$_2$(ttp)$_2$ (**1e**) (10.1 mg, 0.0065 mmol) and potassium carbonate (9.0 mg, 0.065 mmol) were added into mixture of c-hexane (1.50 ml, 14.000 mmol) and c-hexane-d_{12} (1.49 ml, 14.000 mmol). The red mixture was degassed for three freeze-thaw-pump cycles and was heated at 120 °C under N$_2$ in the dark for 6 hours. Then excess c-hexane/c-hexane-d_{12} mixture was removed by vacuum distillation. Dark red residue was brought to ^{1}H NMR spectroscopy. It was then purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH$_2$Cl$_2$ (4:1). The red fraction was collected. After rotary evaporation, product mixture of Rh(ttp)(c-hexyl) (**2a**) and Rh(ttp)(c-hexyl)-d_{11} was obtained as a red solid (4.7 mg, 0.0055 mmol, 42%). Integration of alkyl proton of the Rh(ttp)(c-hexyl)/Rh(ttp)(c-hexyl)-d_{11} δ = -4.26 was found to be 4.673. The calculated k_H/k_D was 9.0($\pm$0.3).

Sealed NMR Tube Experiment of Rh$_2$(ttp)$_2$ (1e) and c-hexane in Benzene-d_6. Rh$_2$(ttp)$_2$ (**1e**) (5.1 mg, 0.0033 mmol) and c-hexane (34 μL, 0.316 mmol) were added into benzene-d_6 (520 μL) in a NMR tube. The red mixture was degassed for three freeze-thaw-pump cycles and the NMR tube was sealed under vacuum. It was heated at 120 °C in the dark. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

β-Hydride Elimination of Rh(ttp)(c-hexyl) (2a). Rh(ttp)(c-hexyl) (6.8 mg, 0.0081 mmol) was added into benzene-d_6 (520 μL) in a NMR tube. The red reaction mixture was degassed for three freeze-thaw-pump cycles and the NMR tube was sealed under vacuum. It was heated to 120 °C and the reaction mixture was monitored with ^{1}H NMR spectroscopy and NMR yields were taken.

Chapter 3

Reaction of Cycloheptane with Rh(ttp)Cl.

(5, 10, 15, 20-Tetratolyporphyrinato)(cycloheptyl) rhodium(III), [Rh(ttp)(c-heptyl)] (5a). Rh(ttp)Cl[1] (20.4 mg, 0.025 mmol) was added in c-heptane (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 24 hours. Excess c-heptane was removed by vacuum distillation. The residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1). Red solid, Rh(ttp)(c-heptyl) (5a) (4.0 mg, 0.0046 mmol, 18%) was collected and was further recrystallized from CH_2Cl_2/MeOH. R_f = 0.84 (hexane/CH_2Cl_2 = 1:1). ^{1}H NMR (CDCl$_3$, 300 MHz) δ -4.53 (m, 2), -4.05 (m, 3 H), -1.26 (m, 4 H), -0.22 (m, 2 H), -0.06 (m, 2 H), 2.69 (s, 12 H, p-methyl), 7.54 (d, 8 H, J = 5.4 Hz, m-phenyl), 8.00 (d, 4 H, J = 7.5 Hz, o'-phenyl), 8.08 (d, 4 H, J = 7.8 Hz, o-phenyl), 8.69 (s, 8 H, pyrrole). ^{13}C NMR (CDCl$_3$, 75 MHz) δ 21.69, 22.09, 27.85, 33.24, 39.37 (d, $^1J_{Rh-C}$ = 27.6 Hz), 122.87, 127.42, 127.55, 131.52, 133.63, 134.25, 137.23, 137.23, 139.53, 143.50. Calcd. for $(C_{55}H_{49}N_4Rh)^+$: m/z 868.3007. Found: m/z 868.3016. Single crystal for X-ray diffraction analysis was grown from CH_2Cl_2/methanol.

Reaction of Cycloheptane and Rh(ttp)Cl with Potassium Carbonate. Rh(ttp)Cl (20.4 mg, 0.025 mmol) and anhydrous potassium carbonate (34.9 mg, 0.252 mmol) was added in c-heptane (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 6 hours. Excess c-heptane was removed by vacuum distillation. The dark red crude product was extracted with CH_2Cl_2/H_2O. The organic layer was collected, dried and evaporated to dryness and the residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1). Red solids, Rh(ttp)(c-heptyl) (5a) (6.6 mg, 0.0076 mmol, 30%) and Rh(ttp)Bn (5b) (5.5 mg, 0.0064 mmol, 25%) were collected.

Sealed NMR Tube Experiment of Rh(ttp)Cl and Cycloheptane with Potassium Carbonate in Benzene-d_6. Rh(ttp)Cl (3.5 mg, 0.0043 mmol), cycloheptane (11 µL, 0.091 mmol) and potassium carbonate (5.9 mg, 0.0427 mmol) were added into benzene-d_6 (500 µL) in a NMR tube. The red mixture was degassed for three freeze-thaw-pump cycles and the NMR tube was flame-sealed under vacuum. It was heated 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 Cycloheptane with $Rh_2(ttp)_2$. $Rh_2(ttp)_2$ (9.5 mg, 0.0062 mmol) was added in c-heptane (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 5 minutes. Excess c-heptane was removed by vacuum distillation. The residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1). Red solid, Rh(ttp)(c-heptyl) (1) (8.2 mg, 0.0093 mmol, 76%) was collected and was further recrystallized from CH_2Cl_2/MeOH.

Reaction of Cycloheptane with Rh(ttp)H. Rh(ttp)H (9.5 mg, 0.012 mmol) was added in c-heptane (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 15 minutes. Excess c-heptane was removed by vacuum distillation. The residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1). Red solid, Rh(ttp)(c-heptyl) (5a) (7.8 mg, 0.090 mmol, 73%) was collected and was further recrystallized from CH_2Cl_2/MeOH.

Sealed NMR Tube Experiment of Rh(ttp)(c-heptyl) in Benzene-d_6. Rh(ttp)(c-heptyl) (**5a**) (3.8 mg, 0.0044 mmol) was added into benzene-d_6 (500 μL) in a NMR tube. The red solution was degassed for three freeze-thaw-pump cycles and the NMR tube was flame-sealed under vacuum. It was heated at 120 °C in the dark. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

Sealed NMR Tube Experiment of Rh(ttp)(c-heptyl) with Potassium Carbonate in Benzene-d_6. Rh(ttp)(c-heptyl) (**5a**) (3.8 mg, 0.0044 mmol) and potassium carbonate (6.0 mg, 0.044 mmol) were added into benzene-d_6 (500 μL) in a NMR tube. The red solution was degassed for three freeze-thaw-pump cycles and the NMR tube was flame-sealed under vacuum. It was heated at 120 °C in the dark. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

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

Independent Synthesis of Rh(ttp)(n-heptyl).[6] A suspension of Rh(ttp)Cl (100 mg, 0.11 mmol) in EtOH (50 mL) and a solution of NaBH$_4$ (17 mg, 0.45 mmol) in aq. NaOH (0.1 M, 2 mL) were purged with N$_2$ for 15 minutes separately. The solution of NaBH$_4$ was added slowly to the suspension of Rh(ttp)Cl via a cannula. The mixture was heated at 50 °C under N$_2$ for 1 hour. The solution was then cooled to 30 °C under N$_2$ and 7-heptenyl bromide (23 mg, 1.20 mmol) was added. A reddish orange suspension was formed. After stirred at room temperature for another 15 minutes under N$_2$, the reaction mixture was worked up by

extraction with CH_2Cl_2/H_2O. The combined organic extract was dried ($MgSO_4$), filtered and rotatory evaporated. The reddish orange residue was purified by column chromatography over silica gel (250 - 400 mesh) using a solvent mixture of hexane/CH_2Cl_2 (1:1) as the eluent. The major orange fraction was collected and gave a reddish orange solid of Rh(ttp)($CH_2)_5$($CH=CH_2$) **6a** (96.0 mg, 0.11 mmol, 86%) as the product after rotary evaporation.

Sealed NMR Tube Experiment of Rh(ttp)($CH_2)_5$($CH=CH_2$) 6a with Potassium Carbonate in Benzene-d_6. Rh(ttp)($CH_2)_5$($CH=CH_2$) **6a** (3.8 mg, 0.0044 mmol) and potassium carbonate (6.0 mg, 0.044 mmol) were added into benzene-d_6 (500 μL) in a NMR tube. The red solution was degassed for three freeze-thaw-pump cycles and the NMR tube was flame-sealed under vacuum. It was heated at 120 °C in the dark. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

Independent Synthesis of Rh(ttp)(cyclohexylmethyl).[6] A suspension of Rh(ttp)Cl (100 mg, 0.11 mmol) in EtOH (50 mL) and a solution of $NaBH_4$ (17 mg, 0.45 mmol) in aq. NaOH (0.1 M, 2 mL) were purged with N_2 for 15 minutes separately. The solution of $NaBH_4$ was added slowly to the suspension of Rh(ttp)Cl via a cannula. The mixture was heated at 50 °C under N_2 for 1 hour. The solution was then cooled to 30 °C under N_2 and c-hexylmethyl bromide (23 mg, 1.20 mmol) was added. A reddish orange suspension was formed. After stirred at room temperature for another 15 minutes under N_2, the reaction mixture was worked up by extraction with CH_2Cl_2/H_2O. The combined organic extract was dried ($MgSO_4$), filtered and rotatory evaporated. The reddish orange residue was purified by column chromatography over silica gel (250 - 400 mesh) using a solvent mixture of hexane/CH_2Cl_2 (1:1) as the eluent. The major orange fraction was collected and gave a reddish orange solid of Rh(ttp)CH_2(c-C_6H_{11}) **6c** (92.5 mg, 0.11 mmol, 86%) as the product after rotary evaporation.

Sealed NMR Tube Experiment of Rh(ttp)CH$_2$(c-C$_6$H$_{11}$) 6c with Potassium Carbonate in Benzene-d_6. Rh(ttp)CH$_2$(c-C$_6$H$_{11}$) 6c (3.8 mg, 0.0044 mmol) and potassium carbonate (6.0 mg, 0.044 mmol) were added into benzene-d_6 (500 μL) in a NMR tube. The red solution was degassed for three freeze-thaw-pump cycles and the NMR tube was flame-sealed under vacuum. It was heated at 120 °C in the dark. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

Sealed NMR Tube Experiment of Rh$_2$(ttp)$_2$ and Cycloheptene in Benzene-d_6. c-Heptene (2 μL, 0.021 mmol) was added into a solution of Rh$_2$(ttp)$_2$ (3.4 mg, 0.0022 mmol) in 500 μL degassed benzene in a NMR tube. The solvent was removed by vacuum distillation after 5 minutes. 500 μL degassed benzene-d_6 was then added. The red solution was degassed for three freeze-thaw-pump cycles and the NMR tube was flame-sealed under vacuum. It was brought to ^{1}H NMR analysis after sealed. The ^{1}H NMR signal of Rh$_2$(ttp)$_2$ was not observed. Instead, a clean NMR spectrum was obtained. The newly formed Rh(ttp) compound was proposed to be the 1,2-addition product 5. ^{1}H NMR (C$_6$D$_6$, 400 MHz) δ -4.24 (m, 1), -3.39 (m, 1 H), -2.70 (m, 1 H), -1.60 (m, 1 H), -1.20 (m, 1 H), -0.68 (m, 1 H), -0.18 (m, 1 H), 0.13 (m, 2 H), 2.41 (s, 24 H, p-methyl), 4.01 (m, 2 H), 7.30 (d, 8 H, J = 6.4 Hz, m-phenyl), 7.33 (d, 8 H, J = 8.0 Hz, m'-phenyl), 8.13 (d, 8 H, J = 7.6 Hz, o'-phenyl), 8.19 (d, 8 H, J = 7.5 Hz, o-phenyl), 8.97 (s, 16 H, pyrrole).

Sealed NMR Tube Experiment of Rh$_2$(ttp)$_2$ and Cycloheptene Benzene-d_6 at 120 °C. c-Heptene (2 μL, 0.021 mmol) was added into a solution of Rh$_2$(ttp)$_2$ (3.4 mg, 0.0022 mmol) in 500 μL degassed benzene in a NMR tube. The solvent was removed by vacuum distillation after 5 minutes. 500 μL degassed benzene-d_6 was then added. The red solution was degassed for three freeze-thaw-pump cycles and the NMR tube was flame-sealed under vacuum. It was brought to ^{1}H NMR analysis after sealed. The ^{1}H NMR signal of Rh$_2$(ttp)$_2$ was not observed. Instead, a clean NMR spectrum was obtained. The newly formed Rh(ttp) compound

proposed to be the 1,2-addition product **5**. The reaction tube was heated to 120 °C. It was monitored with ^1H NMR spectroscopy at particular time intervals and the NMR yields were taken.

Sealed NMR Tube Experiment of Rh$_2$(ttp)$_2$ and Cycloheptatriene in Benzene-d_6. Rh$_2$(ttp)$_2$ (3.6 mg, 0.0047 mmol), cycloheptatriene (5 μL) and degassed benzene-d_6 (500 μL) were added 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 kept at room temperature, monitored with ^1H NMR spectroscopy at particular time intervals and the NMR yields were taken. **8** was obtained quantitatively. ^1H NMR (C$_6$D$_6$, 400 MHz) δ 2.44 (s, 19), 7.32 (d, 8 H, J = 7.4 Hz, m-phenyl), 7.35 (d, 4 H, J = 7.8 Hz, o-phenyl), 8.13 (d, 4 H, J = 5.4 Hz, m'-phenyl), 8.14 (d, 4 H, J = 5.4 Hz, o'-phenyl), 8.93 (s, 8 H, pyrrole). ^{13}C NMR (C$_6$D$_6$, 100 MHz) δ 21.50, 123.47, 131.82, 132.80, 134.22, 134.28, 134.92, 137.11, 140.43, 144.24. Calcd. for (C$_{55}$H$_{43}$N$_4$Rh)$^+$: m/z 862.2537. Found: m/z 862.2549.

Sealed NMR Tube Experiment of Rh(ttp)H and Cycloheptatriene in Benzene-d_6. Rh(ttp)H (3.6 mg, 0.0047 mmol), cycloheptatriene (5 μL) and degassed benzene-d_6 (500 μL) were added 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 kept at room temperature, monitored with ^1H NMR spectroscopy at particular time intervals and the NMR yields were taken.

Synthesis of Rh(ttp)(cycloheptatrienyl) 8. Rh(ttp)H (3.6 mg, 0.0047 mmol) and cycloheptatriene (5 μL) were added into degassed benzene (500 μL). The red solution was degassed for three freeze-thaw-pump cycles, purged with N$_2$ and put into a water bath at 25 °C for 15 minutes. Excess solvent was removed by vacuum distillation. 500 μL degassed benzene-d_6 was then added. The product was found to be air-sensitive and decomposed

during column chromatography. As the ^{1}H NMR spectrum was clean, no further purification step was required.

Rearrangement reaction of Rh(ttp)(cycloheptatrienyl) at 6.95 mM. Rh(ttp)(cycloheptatrienyl) (3.0 mg, 0.0035 mmol) was added into degassed benzene-d_6 (500 μL) in a NMR tube. The red solution was degassed for three freeze-thaw-pump cycles and the NMR tube was flame-sealed under vacuum. It was heated at 120 °C in the dark. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. For this and the following reactions, the collected kinetic data were fitted by first-order exponential decay using OriginPro 7.5 sofware.

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

Rearrangement reaction of Rh(ttp)(cycloheptatrienyl) at 6.95 mM at 130 °C. Rh(ttp)(cycloheptatrienyl) (3.0 mg, 0.0035 mmol) was added into degassed benzene-d_6 (500 μL) in a NMR tube. The red solution was degassed for three freeze-thaw-pump cycles and the NMR tube was flame-sealed under vacuum. It was heated at 130 °C in the dark. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

Rearrangement reaction of Rh(ttp)(cycloheptatrienyl) at 6.95 mM at 140 °C. Rh(ttp)(cycloheptatrienyl) (3.0 mg, 0.0035 mmol) was added into degassed benzene-d_6 (500 μL) in a NMR tube. The red solution was degassed for three freeze-thaw-pump cycles and the NMR tube was flame-sealed under vacuum. It was heated at 140 °C in the dark. It was

monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

Rearrangement reaction of Rh(ttp)(cycloheptatrienyl) at 6.95 mM at 150 °C.
Rh(ttp)(cycloheptatrienyl) (3.0 mg, 0.0035 mmol) was added into degassed benzene-d_6 (500 µL) in a NMR tube. The red solution was degassed for three freeze-thaw-pump cycles and the NMR tube was flame-sealed under vacuum. It was heated at 150 °C in the dark. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

Rate extrapolation of CHT to toluene at 120 °C. Accoding to the data obtained from literature,[5] log ($\underline{A}_a$/s^{-1}) was 13.6 and $\underline{E}_a$ was 217.7 kJmol^{-1}. By Arrhenius equation,

$\ln k = -E_a/RT + \ln A$

At 120 °C, $\ln k = -217.7 \times 1000 / (8.314 \times 393) + \ln (10^{13.6})$

$\ln k = -35.3$

$k = 4.61 \times 10^{-16}$ s^{-1}

Rearrangement reaction of Rh(ttp)(cycloheptatrienyl) at 6.95 mM with Potassium Carbonate. Rh(ttp)(cycloheptatrienyl) (3.0 mg, 0.0035 mmol) and potassium carbonate (4.8 mg, 0.035 mmol) were added into degassed benzene-d_6 (500 µL) in a NMR tube. 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 ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

Rearrangement reaction of Rh(ttp)(cycloheptatrienyl) at 6.95 mM with 1 mol% Rh$_2$(ttp)$_2$. Rh(ttp)(cycloheptatrienyl) (3.0 mg, 0.0035 mmol) and 1 mol% Rh$_2$(ttp)$_2$ (0.027 mg, 1.7 × 10^{-5} mmol) were added into degassed benzene-d_6 (500 µL) in a NMR tube. 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 ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

Rearrangement reaction of Rh(ttp)(cycloheptatrienyl) at 6.95 mM with 10 mol% Rh₂(ttp)₂. Rh(ttp)(cycloheptatrienyl) (3.0 mg, 0.0035 mmol) and 10 mol% Rh₂(ttp)₂ (0.27 mg, 1.7 x 10^{-4} mmol) were added into degassed benzene-d_6 (500 µL) in a NMR tube. 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 ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

Chapter 4
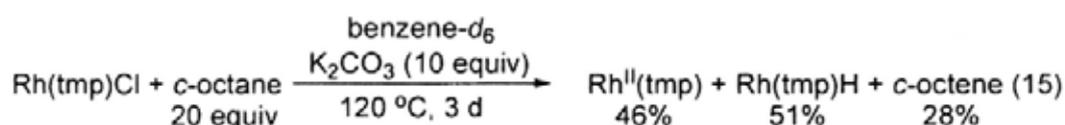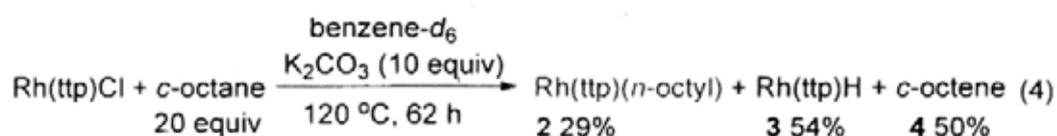
Reaction of *c*-octane with Rh(ttp)Cl. Rh(ttp)Cl (20.6 mg, 0.026 mmol) was added in *c*-octane (3.0 mL). The red reaction mixture was degassed for three freeze-thaw-pump cycles, purged with N₂ and heated at 120 °C under N₂ for 48 hours. Excess *c*-octane was removed by vacuum distillation. The residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH₂Cl₂ (1:1). Red solid, Rh(ttp)(*c*-octyl) **10a** (1.0 mg, 0.0011 mmol, 5%) and Rh(ttp)(*n*-octyl) **10b** (1.9 mg, 0.0021 mmol, 8%) were collected, and further recrystallized from CH₂Cl₂/MeOH. The product ratio was calculated by ^{1}H NMR integration. Rh(ttp)Cl was recovered (14.8 mg) after column chromatography. Characterization of Rh(ttp)(*c*-octyl) **1**: R_f = 0.84 (hexane/CH₂Cl₂ = 1:1). ^{1}H NMR (C₆D₆, 400 MHz) δ -4.25 (m, 2), -3.66 (m, 3 H), -1.13 (m, 4 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). ^{13}C NMR (CDCl₃, 75 MHz) δ 21.70, 22.54, 25.23, 25.85, 30.40, 40.62 (d, $^1J_{Rh\text{-}C}$ = 26.4 Hz), 122.86, 127.42, 127.54, 131.48, 133.62, 134.25, 137.22, 139.52, 143.52. HRMS: calcd. for (C₅₆H₅₁N₄Rh+H)$^+$: m/z 883.3242. Found: m/z 883.3214. Characterization of Rh(ttp)(*n*-octyl) **2**: R_f = 0.84 (hexane/CH₂Cl₂ =

1:1). ^{1}H NMR (C$_6$D$_6$, 400 MHz) δ -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 (t, 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) δ 14.00, 15.69 (d, $^1J_{Rh-C}$ = 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, 137.23, 139.48, 143.35. HRMS: calcd. for (C$_{56}$H$_{53}$N$_4$Rh)$^+$: m/z 884.3320. Found: m/z 884.3336. Single crystal for X-ray diffraction analysis was grown from CH$_2$Cl$_2$/CH$_3$OH.

Reaction of c-Octane and Rh(ttp)Cl with Potassium Hydroxide. Rh(ttp)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 N$_2$ and heated at 120 °C under N$_2$ for 7.5 hours. Excess c-octane was removed by vacuum distillation. The red residue was added with benzene-d$_6$ (500 μL) under N$_2$ for ^{1}H NMR spectroscopy and the NMR yield of Rh(ttp)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/CH$_2$Cl$_2$ (1:1). Red solids, Rh(ttp)(c-octyl) **10a** (1.3 mg, 0.0015 mmol, 6%)and Rh(ttp)(n-octyl) **10b** (5.6 mg, 0.0063 mmol, 25%) were collected.

Reaction of c-Octane and Rh(ttp)Cl with Potassium Carbonate. Rh(ttp)Cl (20.4 mg, 0.025 mmol) and anhydrous potassium carbonate (34.9 mg, 0.252 mmol) 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 7.5 hours. Excess c-octane was removed by

vacuum distillation. The red residue was added with benzene-d_6 (500 μL) under N_2 for ^{1}H NMR spectroscopy and the NMR yield of Rh(ttp)H (58%) was estimated. The crude mixture was then extracted with CH_2Cl_2/H_2O. The organic layer was collected, dried and evaporated to dryness and the residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1). Red solids, Rh(ttp)(*n*-octyl) **10b** (7.5 mg, 0.0085 mmol, 33%) were collected.

Independent Synthesis of Rh(ttp)(*c*-octyl).[6] A suspension of Rh(ttp)Cl (100 mg, 0.11 mmol) in EtOH (50 mL) and a solution of NaBH$_4$ (17 mg, 0.45 mmol) in aq. NaOH (0.1 M, 2 mL) were purged with N_2 for 15 minutes separately. The solution of NaBH$_4$ was added slowly to the suspension of Rh(ttp)Cl via a cannula. The mixture was heated at 50 °C under N_2 for 1 hour. The solution was then cooled to 30 °C under N_2 and *c*-octyl bromide (23 mg, 1.20 mmol) was added. A reddish orange suspension was formed. After stirred at room temperature for another 15 minutes under N_2, the reaction mixture was worked up by extraction with CH_2Cl_2/H_2O. The combined organic extract was dried (MgSO$_4$), filtered and rotatory evaporated. The reddish orange residue was purified by column chromatography over silica gel (250 - 400 mesh) using a solvent mixture of hexane/CH_2Cl_2 (1:1) as the eluent. The major orange fraction was collected and gave a reddish orange solid of Rh(ttp)(*c*-octyl) **10a** (94.1 mg, 0.11 mmol, 86%) as the product after rotary evaporation.

Independent Synthesis of Rh(ttp)(*n*-octyl).[6] A suspension of Rh(ttp)Cl (100 mg, 0.11 mmol) in EtOH (50 mL) and a solution of NaBH$_4$ (17 mg, 0.45 mmol) in aq. NaOH (0.1 M, 2 mL) were purged with N_2 for 15 minutes separately. The solution of NaBH$_4$ was added slowly to the suspension of Rh(ttp)Cl via a cannula. The mixture was heated at 50 °C under N_2 for 1 hour. The solution was then cooled to 30 °C under N_2 and *n*-octyl bromide (23 mg, 1.20 mmol) was added. A reddish orange suspension was formed. After stirred at room temperature for another 15 minutes under N_2, the reaction mixture was worked up by

extraction with CH_2Cl_2/H_2O. The combined organic extract was dried ($MgSO_4$), filtered and rotatory evaporated. The reddish orange residue was purified by column chromatography over silica gel (250 - 400 mesh) using a solvent mixture of hexane/CH_2Cl_2 (1:1) as the eluent. The major orange fraction was collected and gave a reddish orange solid of Rh(ttp)(n-octyl) **10b** (96.5 mg, 0.11 mmol, 88%) as the product after rotary evaporation.

$$\text{Rh(ttp)Cl} \xrightarrow[\text{2. R-Br, 0 °C, 15 min}]{\substack{\text{1. NaBH}_4\text{/NaOH, EtOH,} \\ \text{70 °C, 2h, N}_2}} \text{Rh(ttp)R}$$

R = c-octyl   **10a** 86%
R = n-octyl   **10b** 88%
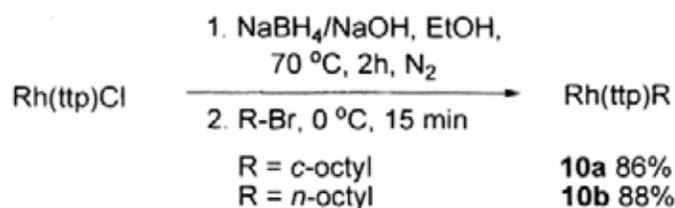
Thermal Stability of Rh(ttp)(c-octyl) in Benzene-d_6. Rh(ttp)(c-octyl) **10a** (3.9 mg, 0.0044 mmol) was added into benzene-d_6 (500 µL) in a NMR tube. The red solution was degassed for three freeze-thaw-pump cycles and the NMR tube was flame-sealed under vacuum. It was heated at 120 °C in the dark. It was monitored with ^1H NMR spectroscopy at particular time intervals and the NMR yields were taken.

Stability of Rh(ttp)(c-octyl) with Potassium Carbonate in Benzene-d_6. Rh(ttp)(c-octyl) **10a** (3.9 mg, 0.0044 mmol) and potassium carbonate (6.0 mg, 0.044 mmol) were added into benzene-d_6 (500 µL) in a NMR tube. The red solution was degassed for three freeze-thaw-pump cycles and the NMR tube was flame-sealed under vacuum. 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(ttp)Cl and c-Octane with Potassium Carbonate in Benzene-d_6. Rh(ttp)Cl (3.5 mg, 0.0043 mmol), c-octane (11 µL, 0.087 mmol) and potassium carbonate (5.9 mg, 0.0427 mmol) were added into benzene-d_6 (500 µL) in a NMR tube. The red mixture was degassed for three freeze-thaw-pump cycles and the NMR tube was flame-sealed under vacuum. It was heated at 120 °C in the dark. It was monitored with ^1H NMR spectroscopy at particular time intervals and the NMR yields were taken.

Sealed NMR Tube Experiment of Rh$_2$(ttp)$_2$ and Cyclooctene Benzene-d_6 at Room Temperature. c-Octene (2 μL, 0.021 mmol) was added into a solution of Rh$_2$(ttp)$_2$ (3.4 mg, 0.0022 mmol) in 500 μL degassed benzene in a NMR tube. The solvent was removed by vacuum distillation after 5 minutes. 500 μL degassed benzene-d_6 was then added. The red solution was degassed for three freeze-thaw-pump cycles and the NMR tube was flame-sealed under vacuum. It was brought to ^{1}H NMR analysis after sealed. The ^{1}H NMR signal of Rh$_2$(ttp)$_2$ was not observed. Instead, a clean NMR spectrum was obtained. The newly formed Rh(ttp) compound was proposed to be the 1,2-addition product. The reaction tube was kept at room temperature. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

Reaction of c-Octane with Rh(ttp)H. Rh(ttp)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 N$_2$ and heated at 120 °C under N$_2$ for 15 hours. Excess c-octane was removed by vacuum distillation. The residue was added with benzene-d_6 (500 μL) under N$_2$ protection for ^{1}H NMR spectroscopy and the recovered yield of Rh(ttp)H (73%) was estimated. 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(ttp)(n-octyl) **10b** (2.3 mg, 0.0026 mmol, 21%) was collected and was further recrystallized from CH$_2$Cl$_2$/MeOH.

Reaction of c-Octane with Rh(ttp)H and PPh$_3$. 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 N$_2$ and heated at 120 °C under N$_2$ for 15 hours. Excess c-octane was removed by vacuum distillation. The residue was added with benzene-d_6 (500 μL) under N$_2$ protection for ^{1}H NMR spectroscopy. Rh(ttp)H(PPh$_3$) was obtained in quantitative NMR yield. ^{1}H NMR (C$_6$D$_6$, 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* = 2.4, 7.6 Hz, *m*-phenyl), 6.52 (t, 1 H, *J* = 6.8 Hz), 7.35 (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(ttp)H. Rh(ttp)H (3.2 mg, 0.0041 mmol) was added in benzene-d_6 (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 ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

Reaction of *c*-Octane with Rh$_2$(ttp)$_2$. Rh$_2$(ttp)$_2$ (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 N$_2$ and heated at 120 °C under N$_2$ for 15 hours. Excess *c*-octane was removed by vacuum distillation. The red residue was added with benzene-d_6 (500 μL) under N$_2$ protection for ^{1}H NMR spectroscopy and the yield of Rh(ttp)H (46%) was estimated. The residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH$_2$Cl$_2$ (1:1). Red solids, Rh(ttp)(*c*-octyl) **10a** (4.5 mg, 0.0051 mmol, 41%) and Rh(ttp)(*n*-octyl) **10b** (0.4 mg, 0.00045 mmol, 4%) were collected and the product ratio was calculated by ^{1}H NMR integration.

Reaction of *c*-Octane with 2:1 Mixture of Rh(ttp)H and Rh$_2$(ttp)$_2$. Rh(ttp)H (9.6 mg, 0.012 mmol) and Rh$_2$(ttp)$_2$ (4.8 mg, 0.0031 mmol) were added in *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 15 hours. 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(ttp)(*c*-octyl) **10a** (9.8 mg, 0.011 mmol, 60%) and Rh(ttp)(*n*-octyl) **10b** (3.0 mg, 0.0034 mmol, 18%) were collected and the product ratio was calculated by ^{1}H NMR integration.

Reaction of *c*-Octane with 5:1 Mixture of Rh(ttp)H and Rh₂(ttp)₂. Rh(ttp)H (9.6 mg, 0.012 mmol) and $Rh_2(ttp)_2$ (1.9 mg, 0.0012 mmol) were added in *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 15 hours. 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_2Cl_2 (1:1). Red solid, Rh(ttp)(*c*-octyl) **10a** (6.9 mg, 0.0078 mmol, 53%) and Rh(ttp)(*n*-octyl) **10b** (3.4 mg, 0.0038 mmol, 26%) were collected and the product ratio was calculated by ^{1}H NMR integration.

Reaction of *c*-Octane with 10:1 Mixture of Rh(ttp)H and Rh₂(ttp)₂. Rh(ttp)H (9.6 mg, 0.012 mmol) and $Rh_2(ttp)_2$ (1.0 mg, 0.00065 mmol) were added in *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 15 hours. 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_2Cl_2 (1:1). Red solid Rh(ttp)(*n*-octyl) **10b** (8.9 mg, 0.010 mmol, 73%) was collected and was further recrystallized from CH_2Cl_2/MeOH.

Reaction of *c*-Octane with 10:1 Mixture of Rh(tmp)H and Rh^{II}(tmp). Rh(tmp)H[7] (10.6 mg, 0.012 mmol) and Rh^{II}(tmp)[8] (1.1 mg, 0.0012 mmol) were added in *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 hours. Excess *c*-octane was removed by vacuum distillation. The colourless 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 N_2 for ^{1}H NMR spectroscopy. Red solution of Rh(tmp)H (90% yield, estimated by ^{1}H NMR spectroscopy) was obtained.

Reaction of *c*-octane with Rh^{II}(tmp). Rh^{II}(tmp) (10.6 mg, 0.0012 mmol) were added in *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 hours. Excess c-octane was removed by vacuum distillation. The colourless 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 N_2 for ^{1}H NMR spectroscopy. Red solution of Rh(tmp)H (86% yield, estimated by ^{1}H NMR spectroscopy) was obtained.

Attempt Synthesis of Rh(tmp)(c-octyl). 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 purged with N_2 for 15 minutes separately. The solution of $NaBH_4$ was added slowly to the suspension of Rh(tmp)Cl via a cannula. The mixture was heated at 50 °C under N_2 for 1 hour. The solution was then cooled to 30 °C under N_2 and c-octyl bromide was added. A reddish orange suspension was formed. After stirred at room temperature for another 15 minutes under N_2, the reaction mixture was vacuum-distillated and the distillate was brought to ^{1}H NMR spectroscopy after extraction with C_6D_6/H_2O. c-Octene (77% yield, estimated by ^{1}H NMR) was observed. The reddish orange residue was washed with degassed H_2O (2 x 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 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.

Rh(tmp)Cl $\xrightarrow[\text{2. c-octyl-Br, 0 °C, 15 min}]{\substack{\text{1. NaBH}_4\text{/NaOH, EtOH,} \\ \text{70 °C, 2h, N}_2}}$ "Rh(tmp)(c-octyl)" $\longrightarrow$ Rh(tmp)H + c-octene
                                                                                                        89%   77%

Rh(ttp)Cl $\xrightarrow[\text{2. c-octyl-Br, 0 °C, 15 min}]{\substack{\text{1. NaBH}_4\text{/NaOH, EtOH,} \\ \text{70 °C, 2h, N}_2}}$ Rh(ttp)(c-octyl)
                                                                                                        86%

The sterically less hindered Rh(ttp)Cl gave 86% yield of Rh(ttp)(c-octyl) via reductive alkylation while more hindered Rh(tmp)Cl resulted in 89% yield of Rh(tmp)H but not Rh(tmp)(c-octyl).

Reaction of Rh(tmp)Cl and c-Octane with Potassium Carbonate in Benzene-d_6.
Rh(tmp)Cl[9] (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-d_6 (500 μL) in a NMR tube. The red mixture was degassed for three freeze-thaw-pump cycles and the NMR tube was flame-sealed under vacuum. It was heated at 120 °C in the dark. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

$$\text{Rh(ttp)Cl} + \underset{\text{20 equiv}}{c\text{-octane}} \xrightarrow[\substack{\text{120 °C, 62 h}}]{\substack{\text{benzene-}d_6 \\ \text{K}_2\text{CO}_3 \text{ (10 equiv)}}} \underset{\textbf{2}\ 29\%}{\text{Rh(ttp)}(n\text{-octyl})} + \underset{\textbf{3}\ 54\%}{\text{Rh(ttp)H}} + \underset{\textbf{4}\ 50\%}{c\text{-octene}} \quad (4)$$

$$\text{Rh(tmp)Cl} + \underset{\text{20 equiv}}{c\text{-octane}} \xrightarrow[\substack{\text{120 °C, 3 d}}]{\substack{\text{benzene-}d_6 \\ \text{K}_2\text{CO}_3 \text{ (10 equiv)}}} \underset{46\%}{\text{Rh}^{II}\text{(tmp)}} + \underset{51\%}{\text{Rh(tmp)H}} + \underset{28\%}{c\text{-octene}} \quad (15)$$

Rh(tmp)Cl reacted with c-octane in benzene-d_6 in the presence of K_2CO_3 and gave Rh^{II}(tmp), Rh(tmp)H and c-octene in 46%, 51% and 50% yields, respectively at 120 °C in 3 days. Compared to Rh(ttp)Cl, Rh(tmp)Cl is likely too bulky to react with the C-C bond of c-octane to give Rh(tmp)(n-octyl).

References

1. (a) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476. (b) Alder, A. D.; Longo, F. R.; Shergalis, W. *J. Am. Chem. Soc.* **1964**, *86*, 3145-3149.

2. (a) Mak, K. W. *PhD. Thesis*, The Chinese University of Hong Kong, 1998. (b) Mak, K. W.; Chan, K. S. *J. Am. Chem. Soc.* **1998**, *120*, 9686-9687.

3. Mak, K. W.; Xue, F.; Mak, T. C. W.; Chan, K. S. *J. Chem. Soc., Dalton Trans.* **1999**, *19*, 3333-3334.

4. (a) Wayland, B. B.; Van Voorhees, S. L. Wilker, C. *Inorg. Chem.* **1986**, *25*, 4039-4042. (b) Ogoshi, H.; Setsune, J.; Omura, T.; Yoshida, Z. *J. Am. Chem. Soc.* **1975**, *97*, 6461-6466.

5. (a) Tse, A. K.S.; Wu, B. M.; Mak, T. C. W.; Chan, K. S. *J. Organomet. Chem.* **1998**, *568*, 257-261. (b) Dolphin, D.; Halko, D. J.; Johnson, E. *Inorg. Chem.* **1981**, *20*, 4348-4351.

6. (a) Ogoshi, H.; Setsune, J.; Omura, T.; Yoshida, Z. *J. Am. Chem. Soc.* **1975**, *97*, 6461-6466. (b) Chan, K. S.; Mak, K. W.; Tse, M. K.; Yeung, S. K.; Li, B. Z.; Chan, Y. W. *J. Organomet. Chem.* **2008**, *693*, 399-407.

7. Wayland, B. B.; Ba, S.; Sherry, A. E. *J. Am. Chem. Soc.* **1991**, *113*, 5305-5311.

8. (a) Wayland, B. B.; Sherry, A. E.; Poszmik, G.; Bunn, A. G. *J. Am. Chem. Soc.* **1992**, *114*, 1673-1681. (b) Li, G.; Zhang, F. F.; Pi, N.; Chen, H. L.; Zhang, S. Y.; Chan, K. S. *Chem. Lett.* **2001**, 284-285.

Table 1. Crystal Data and Structure Refinement Parameters for 2a, 2b, 2e, 5a and 10b

	Rh(ttp)(c-hexyl) 2a	Rh(ttp)(c-pentyl) 2b	Rh(ttp)(n-heptyl) 2e	Rh(ttp)(c-heptyl) 5a	Rh(ttp)(cycloheptatrienyl) 8	Rh(ttp)(n-octyl) 10b
Color, shape	Purple Prism	Purple Prism	Purple Prism	Purple Prism	Purple Prism	Purple Prism
empirical formula	$C_{54}H_{47}N_4Rh \cdot CH_2Cl_2$	$C_{53}H_{45}N_4Rh \cdot CH_3OH$	$C_{56}H_{51}N_4Rh$	$C_{55}H_{48}N_4Rh \cdot CH_2Cl_2$	$C_{55}H_{42}N_4Rh$	$C_{56}H_{53}N_4Rh$
formula wt	939.79	886.91	882.92	952.81	861.84	884.93
Temp (K)	293 (2)	293 (2)	293 (2)	293 (2)	296(2)	293 (2)
wavelength(Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/n$	P1	$P2_1/n$	$P2_1/n$	P-1
unit cell dimens						
a (Å)	15.509 (2)	15.579 (2)	10.578 (2)	15.510 (4)	15.486 (1)	10.578 (2)
b (Å)	18.651 (2)	18.482 (2)	14.575 (3)	18.697 (5)	18.711 (1)	14.574 (3)
c (Å)	16.266 (2)	16.155 (2)	16.226 (4)	16.441 (4)	16.421 (1)	16.226 (4)
α (deg)	90	90	65.745 (4)	90	90	65.745 (4)
β (deg)	106.993 (2)	107.516 (2)	77.764 (4)	106.569 (2)	106.763 (1)	77.764 (4)
γ (deg)	90	90	82.348 (4)	90	90	82.348 (4)
Volumn (Å³)	4499.6 (9)	4436.1 (10)	2225.8 (9)	4570 (2)	4555.9 (2)	2225.8 (9)
Z	4	4	2	4	4	2
Calcd density (g cm⁻³)	1.387	1.328	1.317	1.385	1.256	1.320
abs coeff (mm⁻¹)	0.541	0.430	0.426	0.534	0.415	0.426
F(000)	1944	1848	920	1972	1780	924

cryst size (mm)	0.40 x 0.30 x 0.20	0.50 x 0.30 x 0.20	0.50 x 0.40 x 0.30	0.40 x 0.30 x 0.20	0.50 x 0.40 x 0.30	0.50 x 0.40 x 0.30
θ range for data collection (deg)	1.60 to 28.04	1.72 to 25.00	1.53 to 28.08	1.59 to 25.00	1.59 to 25.25	1.53 to 25.00
Limiting indices	-20 = h = 18 -24 = k = 24 -21 = l = 20	-18 = h = 18 -21 = k = 19 -19 = l = 19	-13 = h = 13 -19 = k = 18 -21 = l = 12	-17 <= h <= 18 -22 <= k <= 15 -19 <= l <=19	-18 <= h <= 16 -22 <= h <= 22 -19 <= h <= 19	-12 <= h <= 12 -17 <= k <= 16 -19 <= l <=11
no. of rflns collected/ unique	30232/10856 [(R (int) = 0.0414)	23310/7800 [R (int) = 0.0479)	15187/10539 [R (int) = 0.0239]	24091/8037 [(R (int) = 0.0679)	42092/8244 [R(int) = 0.0468]	12098/7803 [(R (int) = 0.0230)
Completeness to θ = 28	99.6	99.8	97.3	99.7	100.0	99.5
Absorp corr	SADABS	SADABS	SADABS	SADABS	Multi-scan	SADABS
max. and min. transmn	1.0000 and 0.836682	1.0000 and 0.660829	1.0000 and 0.616130	1.0000 and 0.351677	0.7456 and 0.6264	1.0000 and 0.616130
Refinement method	Full-matrix least squares on F²	Full-matrix least squares on F²	Full-matrix least squares on F²	Full-matrix least squares on F²	Full-matrix least squares on F²	Full-matrix least squares on F²
no. of data/ restraints / params	10856 / 2 / 559	7800 / 14 / 550	10539 / 10 / 568	8037 / 20 / 568	8244 / 17 / 550	7803 / 40 / 568
GOF	1.025	1.069	1.036	1.058	1.061	1.054
final R indices [$I>2s(I)$]	$R_1 = 0.0572$	$R_1 = 0.0677$	$R_1 = 0.0449$	$R_1 = 0.0920$	$R_1 = 0.0364$	$R_1 = 0.0424$
	$_wR_2 = 0.1511$	$_wR_2 = 0.1861$	$_wR_2 = 0.1124$	$_wR_2 = 0.2530$	$_wR_2 = 0.1030$	$_wR_2 = 0.1119$

R indices (all data)	$R_1 = 0.0945$	$R_1 = 0.1032$	$R_1 = 0.0616$	$R_1 = 0.1513$	$R_1 = 0.0435$	$R_1 = 0.0522$
	$_wR_2 = 0.1784$	$_wR_2 = 0.2249$	$_wR_2 = 0.1245$	$_wR_2 = 0.3138$	$_wR_2 = 0.1081$	$_wR_2 = 0.1208$
Largest diff peak and hole (e Å^3)	1.597 and -1.788	2.976 and -0.711	0.774 and -0.421	1.509 and -1.136	0.750 and -0.336	0.868 and -0.536

[a] $R_1 = \sum(||F_0|-|F_c||)/\sum|F_0|$. [b] $_wR_2 = \left\{\sum[_w(F_0{}^2 - F_c{}^2)^2]/\sum[_w(F_0{}^2)^2]\right\}^{1/2}$. [c] Weighting scheme $w^{-1} = \sigma^2(F_0{}^2) + (w_1 P)^2 + w_2 P$ where $P = (F_0{}^2 + 2F_c{}^2)/3$.
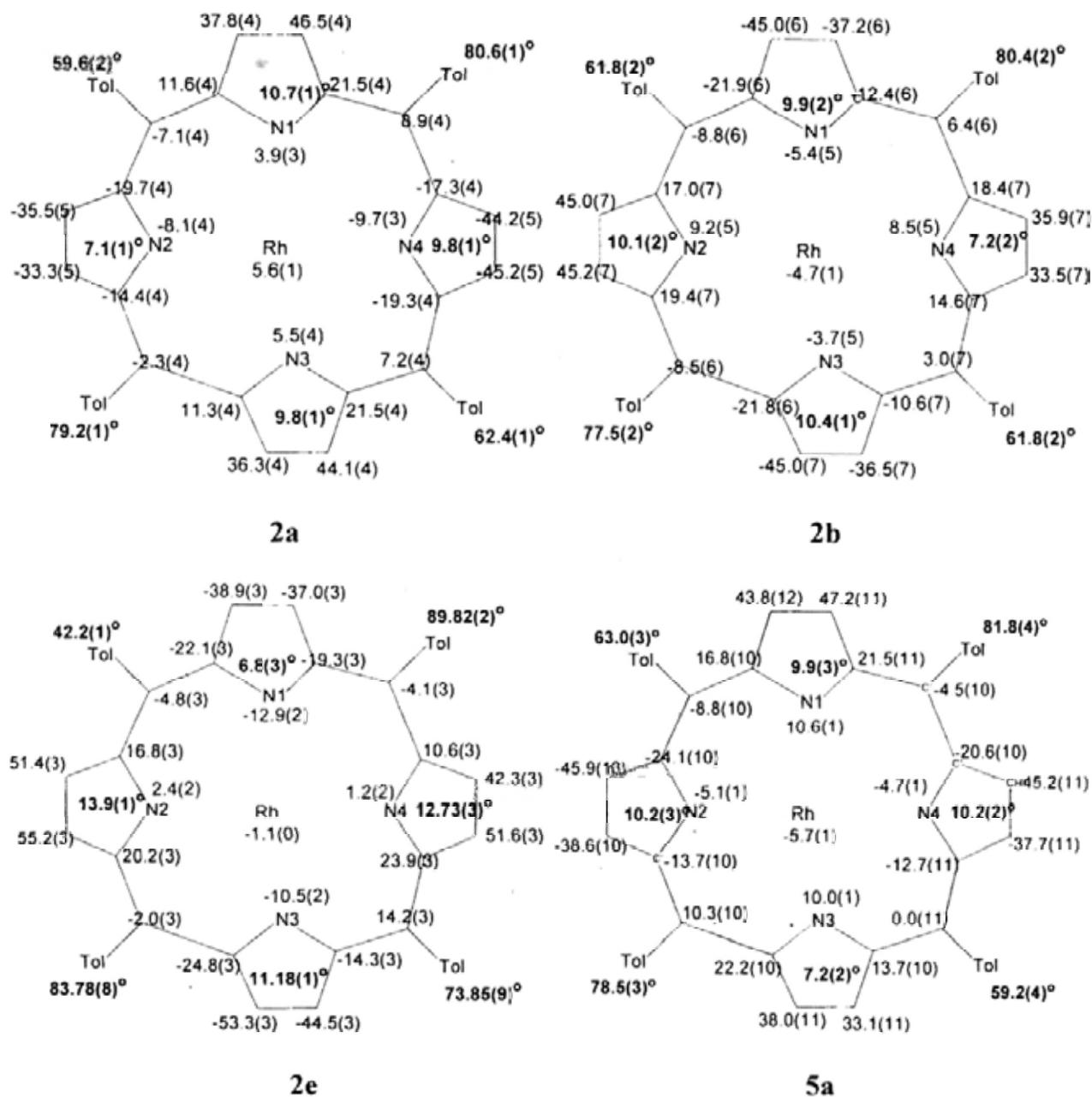
Figure 1. The conformations of porphyrins showing the displacement of the core atoms and of Rh from the 24-atom least squares plane of porphyrin core (in pm; negative values correspond to displacement towards the alkyl group). Absolute values of the angles between pyrrole rings and the least-squares plane, and angles between pyrrole rings and the least-squares plane, and angles between phenyl substituents and the least-squares plane, are shown in bold.

2a

2b

2e

5a
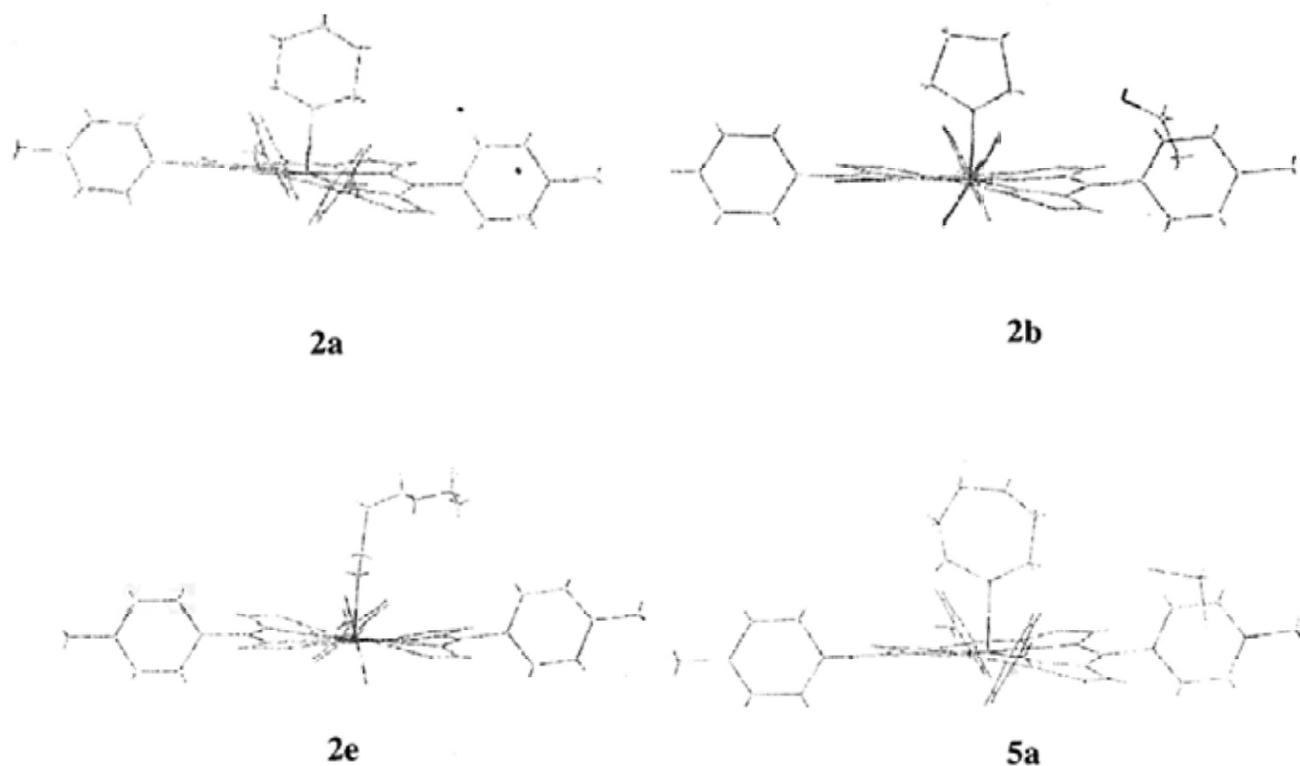
Figure 2. Wireframe presentation of the molecular structures for **2a, 2b, 2e and 5a,** respectively.

8

10b
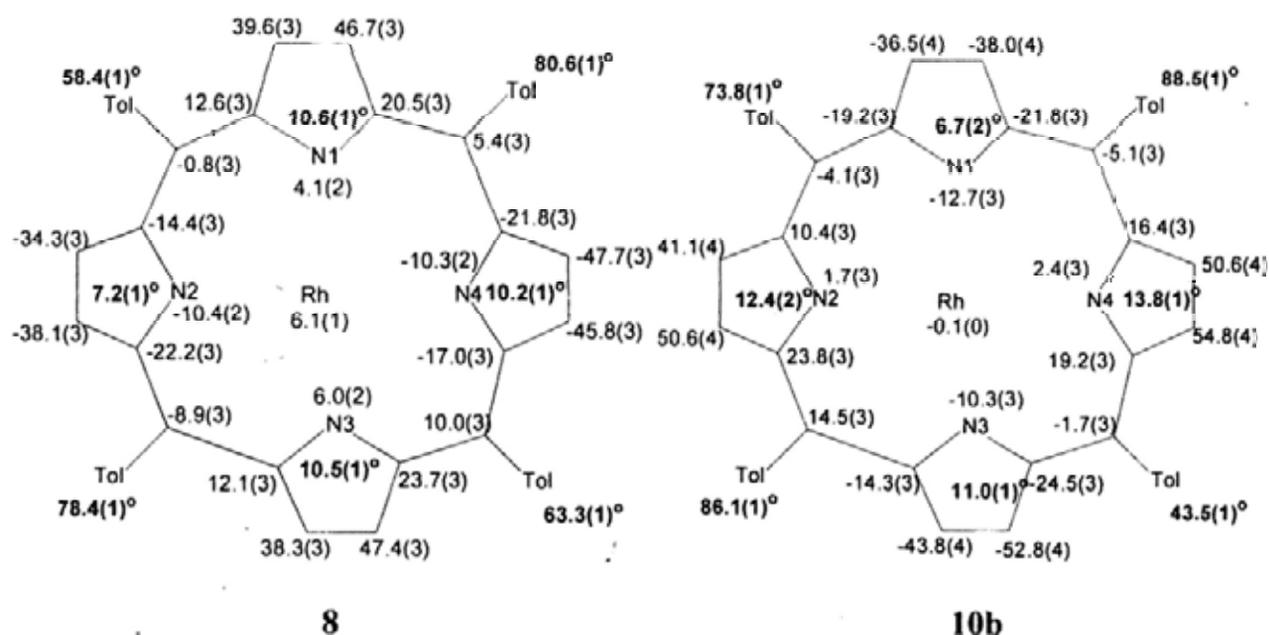
Figure 3. The conformations of porphyrins in **10b** showing the displacement of the core atoms and of Rh from the 24-atom least squares plane of porphyrin core (in pm; positive values correspond to displacement towards the alkyl group). Absolute values of the angles

between pyrrole rings and the least-squares plane, and angles between pyrrole rings and the least-squares plane, and angles between phenyl substituents and the least-squares plane, are shown in bold.

8   10b
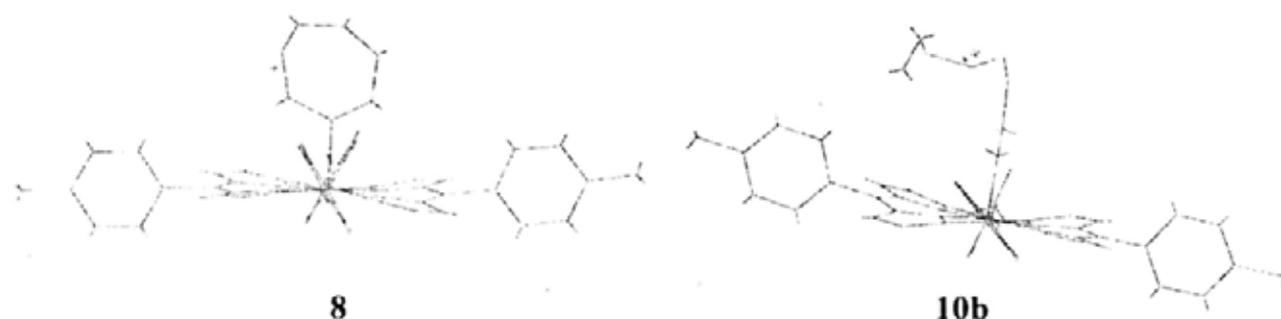
Figure 4. Wireframe presentation of the molecular structures for 8 and 10b.

Table 2. Bond lengths [Å] and angles [deg] for Rh(ttp)(c-hexyl) 2a.

Rh(1)-N(2)	2.012(3)	C(12)-C(13)	1.345(7)
Rh(1)-N(4)	2.016(3)	C(13)-C(14)	1.442(6)
Rh(1)-N(1)	2.021(3)	C(14)-C(15)	1.390(6)
Rh(1)-N(3)	2.026(3)	C(15)-C(16)	1.393(6)
Rh(1)-C(61)	2.093(5)	C(15)-C(41)	1.506(6)
N(1)-C(1)	1.376(5)	C(16)-C(17)	1.431(6)
N(1)-C(4)	1.381(5)	C(17)-C(18)	1.346(6)
N(2)-C(6)	1.380(5)	C(18)-C(19)	1.434(6)
N(2)-C(9)	1.383(5)	C(19)-C(20)	1.401(6)
N(3)-C(11)	1.377(5)	C(20)-C(51)	1.493(6)
N(3)-C(14)	1.378(5)	C(21)-C(22)	1.376(6)
N(4)-C(19)	1.371(5)	C(21)-C(26)	1.381(7)
N(4)-C(16)	1.388(5)	C(22)-C(23)	1.387(7)
C(1)-C(20)	1.404(6)	C(23)-C(24)	1.368(8)
C(1)-C(2)	1.433(6)	C(24)-C(25)	1.370(9)
C(2)-C(3)	1.336(6)	C(24)-C(27)	1.523(7)
C(3)-C(4)	1.436(6)	C(25)-C(26)	1.387(7)
C(4)-C(5)	1.395(6)	C(31)-C(36)	1.379(7)
C(5)-C(6)	1.390(6)	C(31)-C(32)	1.389(7)
C(5)-C(21)	1.496(6)	C(32)-C(33)	1.382(7)
C(6)-C(7)	1.445(6)	C(33)-C(34)	1.371(8)
C(7)-C(8)	1.333(7)	C(34)-C(35)	1.381(8)
C(8)-C(9)	1.445(6)	C(34)-C(37)	1.520(7)
C(9)-C(10)	1.389(6)	C(35)-C(36)	1.377(7)
C(10)-C(11)	1.392(6)	C(41)-C(42)	1.365(6)
C(10)-C(31)	1.507(6)	C(41)-C(46)	1.381(6)
C(11)-C(12)	1.447(6)	C(42)-C(43)	1.383(6)

C(43)-C(44)	1.363(7)	C(6)-C(5)-C(4)	124.2(4)
C(44)-C(45)	1.390(8)	C(6)-C(5)-C(21)	117.5(4)
C(44)-C(47)	1.509(7)	C(4)-C(5)-C(21)	118.3(4)
C(45)-C(46)	1.384(7)	N(2)-C(6)-C(5)	125.9(4)
C(51)-C(56)	1.371(6)	N(2)-C(6)-C(7)	109.2(4)
C(51)-C(52)	1.385(6)	C(5)-C(6)-C(7)	124.7(4)
C(52)-C(53)	1.378(6)	C(8)-C(7)-C(6)	107.3(4)
C(53)-C(54)	1.382(7)	C(7)-C(8)-C(9)	108.3(4)
C(54)-C(55)	1.371(8)	N(2)-C(9)-C(10)	125.9(4)
C(54)-C(57)	1.515(7)	N(2)-C(9)-C(8)	108.5(4)
C(55)-C(56)	1.406(7)	C(10)-C(9)-C(8)	125.6(4)
C(61)-C(62)	1.466(7)	C(9)-C(10)-C(11)	124.8(4)
C(61)-C(66)	1.479(8)	C(9)-C(10)-C(31)	117.3(4)
C(62)-C(63)	1.528(8)	C(11)-C(10)-C(31)	117.9(4)
C(63)-C(64)	1.489(9)	N(3)-C(11)-C(10)	125.7(4)
C(64)-C(65)	1.462(10)	N(3)-C(11)-C(12)	109.0(4)
C(65)-C(66)	1.531(8)	C(10)-C(11)-C(12)	125.3(4)
Cl(1)-C(71)	1.776(8)	C(13)-C(12)-C(11)	107.2(4)
Cl(2)-C(71)	1.713(9)	C(12)-C(13)-C(14)	107.8(4)
		N(3)-C(14)-C(15)	125.1(4)
N(2)-Rh(1)-N(4)	171.59(14)	N(3)-C(14)-C(13)	108.8(4)
N(2)-Rh(1)-N(1)	89.93(14)	C(15)-C(14)-C(13)	125.8(4)
N(4)-Rh(1)-N(1)	90.00(14)	C(14)-C(15)-C(16)	125.0(4)
N(2)-Rh(1)-N(3)	90.33(14)	C(14)-C(15)-C(41)	117.4(4)
N(4)-Rh(1)-N(3)	89.64(14)	C(16)-C(15)-C(41)	117.5(4)
N(1)-Rh(1)-N(3)	179.25(14)	N(4)-C(16)-C(15)	124.3(4)
N(2)-Rh(1)-C(61)	91.63(18)	N(4)-C(16)-C(17)	108.9(4)
N(4)-Rh(1)-C(61)	96.77(18)	C(15)-C(16)-C(17)	126.5(4)
N(1)-Rh(1)-C(61)	92.14(17)	C(18)-C(17)-C(16)	107.5(4)
N(3)-Rh(1)-C(61)	88.56(18)	C(17)-C(18)-C(19)	107.6(4)
C(1)-N(1)-C(4)	106.5(3)	N(4)-C(19)-C(20)	125.5(4)
C(1)-N(1)-Rh(1)	126.0(3)	N(4)-C(19)-C(18)	109.3(4)
C(4)-N(1)-Rh(1)	126.3(3)	C(20)-C(19)-C(18)	125.0(4)
C(6)-N(2)-C(9)	106.7(4)	C(19)-C(20)-C(1)	124.0(4)
C(6)-N(2)-Rh(1)	126.8(3)	C(19)-C(20)-C(51)	118.4(4)
C(9)-N(2)-Rh(1)	126.5(3)	C(1)-C(20)-C(51)	117.6(4)
C(11)-N(3)-C(14)	107.0(3)	C(22)-C(21)-C(26)	117.9(4)
C(11)-N(3)-Rh(1)	126.1(3)	C(22)-C(21)-C(5)	121.5(4)
C(14)-N(3)-Rh(1)	126.1(3)	C(26)-C(21)-C(5)	120.5(4)
C(19)-N(4)-C(16)	106.4(3)	C(21)-C(22)-C(23)	121.0(5)
C(19)-N(4)-Rh(1)	126.5(3)	C(24)-C(23)-C(22)	121.2(5)
C(16)-N(4)-Rh(1)	127.0(3)	C(23)-C(24)-C(25)	117.9(5)
N(1)-C(1)-C(20)	125.0(4)	C(23)-C(24)-C(27)	121.0(6)
N(1)-C(1)-C(2)	109.3(4)	C(25)-C(24)-C(27)	121.1(6)
C(20)-C(1)-C(2)	125.6(4)	C(24)-C(25)-C(26)	121.6(6)
C(3)-C(2)-C(1)	107.5(4)	C(21)-C(26)-C(25)	120.4(5)
C(2)-C(3)-C(4)	107.9(4)	C(36)-C(31)-C(32)	117.5(5)
N(1)-C(4)-C(5)	125.4(4)	C(36)-C(31)-C(10)	121.4(4)
N(1)-C(4)-C(3)	108.7(4)	C(32)-C(31)-C(10)	121.0(4)
C(5)-C(4)-C(3)	125.8(4)	C(33)-C(32)-C(31)	120.7(5)

C(34)-C(33)-C(32)	121.7(5)	C(52)-C(51)-C(20)	120.1(4)
C(33)-C(34)-C(35)	117.5(5)	C(53)-C(52)-C(51)	120.8(5)
C(33)-C(34)-C(37)	122.1(5)	C(52)-C(53)-C(54)	121.5(5)
C(35)-C(34)-C(37)	120.4(5)	C(55)-C(54)-C(53)	117.5(5)
C(36)-C(35)-C(34)	121.4(5)	C(55)-C(54)-C(57)	121.1(5)
C(35)-C(36)-C(31)	121.1(5)	C(53)-C(54)-C(57)	121.4(5)
C(42)-C(41)-C(46)	117.5(4)	C(54)-C(55)-C(56)	121.6(5)
C(42)-C(41)-C(15)	121.9(4)	C(51)-C(56)-C(55)	120.0(5)
C(46)-C(41)-C(15)	120.5(4)	C(62)-C(61)-C(66)	114.6(5)
C(41)-C(42)-C(43)	121.3(5)	C(62)-C(61)-Rh(1)	114.5(4)
C(44)-C(43)-C(42)	121.7(5)	C(66)-C(61)-Rh(1)	114.5(4)
C(43)-C(44)-C(45)	117.2(4)	C(61)-C(62)-C(63)	113.3(5)
C(43)-C(44)-C(47)	121.7(5)	C(64)-C(63)-C(62)	114.2(5)
C(45)-C(44)-C(47)	121.1(5)	C(65)-C(64)-C(63)	112.1(6)
C(46)-C(45)-C(44)	120.9(5)	C(64)-C(65)-C(66)	114.3(6)
C(41)-C(46)-C(45)	121.0(5)	C(61)-C(66)-C(65)	112.5(5)
C(56)-C(51)-C(52)	118.5(4)	Cl(2)-C(71)-Cl(1)	114.9(6)
C(56)-C(51)-C(20)	121.4(4)		

Table 3. Bond lengths [A] and angles [deg] for Rh(ttp)(c-pentyl) **2b**.

Rh(1)-N(4)	2.014(6)	C(9)-C(10)	1.395(9)
Rh(1)-N(1)	2.015(5)	C(10)-C(11)	1.393(9)
Rh(1)-N(3)	2.018(5)	C(10)-C(31)	1.502(9)
Rh(1)-N(2)	2.019(5)	C(11)-C(12)	1.442(9)
Rh(1)-C(61)	2.073(7)	C(12)-C(13)	1.325(10)
N(1)-C(1)	1.388(8)	C(13)-C(14)	1.446(10)
N(1)-C(4)	1.394(8)	C(14)-C(15)	1.401(10)
N(2)-C(6)	1.364(8)	C(15)-C(16)	1.392(10)
N(2)-C(9)	1.376(8)	C(15)-C(41)	1.503(10)
N(3)-C(11)	1.375(8)	C(16)-C(17)	1.453(10)
N(3)-C(14)	1.384(8)	C(17)-C(18)	1.347(11)
N(4)-C(16)	1.366(9)	C(18)-C(19)	1.426(10)
N(4)-C(19)	1.380(9)	C(19)-C(20)	1.402(10)
C(1)-C(20)	1.386(9)	C(20)-C(51)	1.491(9)
C(1)-C(2)	1.438(9)	C(21)-C(22)	1.372(10)
C(2)-C(3)	1.351(10)	C(21)-C(26)	1.397(10)
C(3)-C(4)	1.435(9)	C(22)-C(23)	1.397(11)
C(4)-C(5)	1.385(9)	C(23)-C(24)	1.394(12)
C(5)-C(6)	1.405(10)	C(24)-C(25)	1.377(11)
C(5)-C(21)	1.488(9)	C(24)-C(27)	1.517(10)
C(6)-C(7)	1.432(10)	C(25)-C(26)	1.376(10)
C(7)-C(8)	1.344(10)	C(31)-C(32)	1.372(10)
C(8)-C(9)	1.435(9)	C(31)-C(36)	1.385(10)

C(32)-C(33)	1.405(11)	C(20)-C(1)-C(2)	125.8(6)
C(33)-C(34)	1.362(13)	N(1)-C(1)-C(2)	109.5(6)
C(34)-C(35)	1.366(12)	C(3)-C(2)-C(1)	107.2(6)
C(34)-C(37)	1.529(12)	C(2)-C(3)-C(4)	108.3(6)
C(35)-C(36)	1.382(11)	C(5)-C(4)-N(1)	125.2(6)
C(41)-C(42)	1.373(11)	C(5)-C(4)-C(3)	126.0(6)
C(41)-C(46)	1.384(11)	N(1)-C(4)-C(3)	108.7(6)
C(42)-C(43)	1.370(11)	C(4)-C(5)-C(6)	124.4(6)
C(43)-C(44)	1.372(12)	C(4)-C(5)-C(21)	117.5(6)
C(44)-C(45)	1.387(13)	C(6)-C(5)-C(21)	118.1(6)
C(44)-C(47)	1.514(11)	N(2)-C(6)-C(5)	125.5(6)
C(45)-C(46)	1.368(11)	N(2)-C(6)-C(7)	109.4(6)
C(51)-C(52)	1.371(11)	C(5)-C(6)-C(7)	125.0(6)
C(51)-C(56)	1.382(10)	C(8)-C(7)-C(6)	107.2(6)
C(52)-C(53)	1.425(12)	C(7)-C(8)-C(9)	107.5(6)
C(53)-C(54)	1.362(13)	N(2)-C(9)-C(10)	124.8(6)
C(54)-C(55)	1.381(12)	N(2)-C(9)-C(8)	108.7(6)
C(54)-C(57)	1.515(11)	C(10)-C(9)-C(8)	126.0(6)
C(55)-C(56)	1.383(10)	C(11)-C(10)-C(9)	124.3(6)
C(61)-C(62)	1.453(12)	C(11)-C(10)-C(31)	117.4(6)
C(61)-C(65)	1.479(12)	C(9)-C(10)-C(31)	118.3(6)
C(62)-C(63)	1.512(13)	N(3)-C(11)-C(10)	125.2(6)
C(63)-C(64)	1.518(14)	N(3)-C(11)-C(12)	109.1(6)
C(64)-C(65)	1.533(13)	C(10)-C(11)-C(12)	125.6(6)
O(1)-C(71)	1.481(9)	C(13)-C(12)-C(11)	108.0(6)
C(71)-C(72)	1.587(9)	C(12)-C(13)-C(14)	107.7(6)
		N(3)-C(14)-C(15)	125.2(6)
N(4)-Rh(1)-N(1)	89.8(2)	N(3)-C(14)-C(13)	108.8(6)
N(4)-Rh(1)-N(3)	90.3(2)	C(15)-C(14)-C(13)	126.1(6)
N(1)-Rh(1)-N(3)	179.8(2)	C(16)-C(15)-C(14)	124.2(7)
N(4)-Rh(1)-N(2)	172.2(2)	C(16)-C(15)-C(41)	118.6(6)
N(1)-Rh(1)-N(2)	90.3(2)	C(14)-C(15)-C(41)	117.2(6)
N(3)-Rh(1)-N(2)	89.6(2)	N(4)-C(16)-C(15)	126.6(7)
N(4)-Rh(1)-C(61)	91.6(3)	N(4)-C(16)-C(17)	109.3(6)
N(1)-Rh(1)-C(61)	92.5(3)	C(15)-C(16)-C(17)	124.1(7)
N(3)-Rh(1)-C(61)	87.7(3)	C(18)-C(17)-C(16)	106.7(6)
N(2)-Rh(1)-C(61)	96.1(3)	C(17)-C(18)-C(19)	107.8(7)
C(1)-N(1)-C(4)	106.3(5)	N(4)-C(19)-C(20)	125.6(6)
C(1)-N(1)-Rh(1)	127.2(4)	N(4)-C(19)-C(18)	109.6(6)
C(4)-N(1)-Rh(1)	125.6(4)	C(20)-C(19)-C(18)	124.8(7)
C(6)-N(2)-C(9)	106.9(5)	C(1)-C(20)-C(19)	124.6(6)
C(6)-N(2)-Rh(1)	126.3(4)	C(1)-C(20)-C(51)	118.5(6)
C(9)-N(2)-Rh(1)	126.7(4)	C(19)-C(20)-C(51)	116.9(6)
C(11)-N(3)-C(14)	106.4(5)	C(22)-C(21)-C(26)	117.8(7)
C(11)-N(3)-Rh(1)	126.1(4)	C(22)-C(21)-C(5)	121.7(6)
C(14)-N(3)-Rh(1)	126.4(5)	C(26)-C(21)-C(5)	120.5(6)
C(16)-N(4)-C(19)	106.6(6)	C(21)-C(22)-C(23)	120.9(7)
C(16)-N(4)-Rh(1)	126.5(5)	C(24)-C(23)-C(22)	121.0(8)
C(19)-N(4)-Rh(1)	126.9(5)	C(25)-C(24)-C(23)	117.6(7)
C(20)-C(1)-N(1)	124.7(6)	C(25)-C(24)-C(27)	121.5(8)

C(23)-C(24)-C(27)	120.9(8)	C(46)-C(45)-C(44)	120.8(8)
C(26)-C(25)-C(24)	121.4(8)	C(45)-C(46)-C(41)	121.7(8)
C(25)-C(26)-C(21)	121.3(7)	C(52)-C(51)-C(56)	118.4(7)
C(32)-C(31)-C(36)	117.3(7)	C(52)-C(51)-C(20)	120.4(7)
C(32)-C(31)-C(10)	121.0(6)	C(56)-C(51)-C(20)	121.2(6)
C(36)-C(31)-C(10)	121.7(6)	C(51)-C(52)-C(53)	120.2(8)
C(31)-C(32)-C(33)	120.9(7)		
C(34)-C(33)-C(32)	120.9(8)	C(54)-C(53)-C(52)	120.9(8)
C(33)-C(34)-C(35)	118.5(8)	C(53)-C(54)-C(55)	118.3(7)
C(33)-C(34)-C(37)	120.4(9)	C(53)-C(54)-C(57)	119.8(9)
C(35)-C(34)-C(37)	121.2(9)	C(55)-C(54)-C(57)	121.8(9)
C(34)-C(35)-C(36)	121.1(8)	C(54)-C(55)-C(56)	121.3(8)
C(35)-C(36)-C(31)	121.4(7)	C(51)-C(56)-C(55)	121.0(7)
C(42)-C(41)-C(46)	117.1(7)	C(62)-C(61)-C(65)	104.9(8)
C(42)-C(41)-C(15)	122.0(7)	C(62)-C(61)-Rh(1)	117.5(6)
C(46)-C(41)-C(15)	120.8(7)	C(65)-C(61)-Rh(1)	118.1(6)
C(43)-C(42)-C(41)	121.4(8)	C(61)-C(62)-C(63)	105.5(8)
C(42)-C(43)-C(44)	121.7(8)	C(62)-C(63)-C(64)	104.7(8)
C(43)-C(44)-C(45)	117.4(7)	C(63)-C(64)-C(65)	105.9(8)
C(43)-C(44)-C(47)	122.0(9)	C(61)-C(65)-C(64)	104.3(8)
C(45)-C(44)-C(47)	120.6(9)	O(1)-C(71)-C(72)	144.7(14)

Table 4. Bond lengths [A] and angles [deg] for Rh(ttp)(*n*-heptyl) **2e**.

Rh(1)-N(3)	2.013(2)	C(10)-C(11)	1.394(4)
Rh(1)-N(1)	2.015(2)	C(10)-C(31)	1.503(4)
Rh(1)-N(4)	2.021(2)	C(11)-C(12)	1.432(4)
Rh(1)-N(2)	2.026(2)	C(12)-C(13)	1.340(4)
Rh(1)-C(61)	2.048(3)	C(13)-C(14)	1.435(4)
N(1)-C(1)	1.371(3)	C(14)-C(15)	1.393(4)
N(1)-C(4)	1.381(3)	C(15)-C(16)	1.393(4)
N(2)-C(6)	1.377(3)	C(15)-C(41)	1.503(4)
N(2)-C(9)	1.377(3)	C(16)-C(17)	1.431(4)
N(3)-C(14)	1.378(3)	C(17)-C(18)	1.341(4)
N(3)-C(11)	1.380(3)	C(18)-C(19)	1.433(4)
N(4)-C(19)	1.374(3)	C(19)-C(20)	1.388(4)
N(4)-C(16)	1.379(3)	C(20)-C(51)	1.505(4)
C(1)-C(20)	1.393(4)	C(21)-C(26)	1.346(5)
C(1)-C(2)	1.439(4)	C(21)-C(22)	1.353(5)
C(2)-C(3)	1.340(4)	C(22)-C(23)	1.389(5)
C(3)-C(4)	1.437(4)	C(23)-C(24)	1.358(6)
C(4)-C(5)	1.388(4)	C(24)-C(25)	1.329(5)
C(5)-C(6)	1.399(4)	C(24)-C(27)	1.514(4)
C(5)-C(21)	1.506(4)	C(25)-C(26)	1.399(5)
C(6)-C(7)	1.432(4)	C(31)-C(36)	1.383(5)
C(7)-C(8)	1.341(4)	C(31)-C(32)	1.384(4)
C(8)-C(9)	1.440(4)	C(32)-C(33)	1.387(5)
C(9)-C(10)	1.400(4)	C(33)-C(34)	1.364(7)

C(34)-C(35)	1.375(6)	C(2)-C(3)-C(4)	108.2(3)
C(34)-C(37)	1.526(5)	N(1)-C(4)-C(5)	125.6(2)
C(35)-C(36)	1.393(5)	N(1)-C(4)-C(3)	108.5(2)
C(41)-C(42)	1.365(4)	C(5)-C(4)-C(3)	125.6(3)
C(41)-C(46)	1.379(4)	C(4)-C(5)-C(6)	125.0(2)
C(42)-C(43)	1.393(4)	C(4)-C(5)-C(21)	116.7(3)
C(43)-C(44)	1.373(5)	C(6)-C(5)-C(21)	118.3(2)
C(44)-C(45)	1.357(5)	N(2)-C(6)-C(5)	124.9(2)
C(44)-C(47)	1.518(4)	N(2)-C(6)-C(7)	108.9(2)
C(45)-C(46)	1.387(4)	C(5)-C(6)-C(7)	126.2(3)
C(51)-C(56)	1.355(5)	C(8)-C(7)-C(6)	107.8(2)
C(51)-C(52)	1.365(5)	C(7)-C(8)-C(9)	107.7(2)
C(52)-C(53)	1.390(5)	N(2)-C(9)-C(10)	125.1(2)
C(53)-C(54)	1.353(6)	N(2)-C(9)-C(8)	108.5(2)
C(54)-C(55)	1.352(5)	C(10)-C(9)-C(8)	126.2(2)
C(54)-C(57)	1.518(5)	C(11)-C(10)-C(9)	123.9(2)
C(55)-C(56)	1.388(5)	C(11)-C(10)-C(31)	118.2(2)
C(61)-C(62)	1.329(6)	C(9)-C(10)-C(31)	117.8(2)
C(62)-C(63)	1.519(6)	N(3)-C(11)-C(10)	124.9(2)
C(63)-C(64)	1.383(10)	N(3)-C(11)-C(12)	108.6(2)
C(64)-C(65)	1.396(10)	C(10)-C(11)-C(12)	126.2(2)
C(65)-C(66)	1.367(12)	C(13)-C(12)-C(11)	107.8(2)
C(66)-C(67)	1.384(11)	C(12)-C(13)-C(14)	107.7(2)
		N(3)-C(14)-C(15)	125.3(2)
N(3)-Rh(1)-N(1)	173.93(9)	N(3)-C(14)-C(13)	108.7(2)
N(3)-Rh(1)-N(4)	90.31(8)	C(15)-C(14)-C(13)	125.9(2)
N(1)-Rh(1)-N(4)	89.88(9)	C(16)-C(15)-C(14)	124.7(2)
N(3)-Rh(1)-N(2)	89.49(9)	C(16)-C(15)-C(41)	117.6(2)
N(1)-Rh(1)-N(2)	90.49(9)	C(14)-C(15)-C(41)	117.6(2)
N(4)-Rh(1)-N(2)	178.36(9)	N(4)-C(16)-C(15)	124.9(2)
N(3)-Rh(1)-C(61)	91.73(12)	N(4)-C(16)-C(17)	109.3(2)
N(1)-Rh(1)-C(61)	94.34(12)	C(15)-C(16)-C(17)	125.7(3)
N(4)-Rh(1)-C(61)	89.76(11)	C(18)-C(17)-C(16)	107.3(2)
N(2)-Rh(1)-C(61)	88.62(11)	C(17)-C(18)-C(19)	107.9(2)
C(1)-N(1)-C(4)	106.8(2)	N(4)-C(19)-C(20)	125.5(2)
C(1)-N(1)-Rh(1)	126.96(18)	N(4)-C(19)-C(18)	108.9(2)
C(4)-N(1)-Rh(1)	126.16(18)	C(20)-C(19)-C(18)	125.5(2)
C(6)-N(2)-C(9)	107.0(2)	C(19)-C(20)-C(1)	124.7(2)
C(6)-N(2)-Rh(1)	125.64(18)	C(19)-C(20)-C(51)	117.8(2)
C(9)-N(2)-Rh(1)	125.97(18)	C(1)-C(20)-C(51)	117.4(2)
C(14)-N(3)-C(11)	106.8(2)	C(26)-C(21)-C(22)	117.2(3)
C(14)-N(3)-Rh(1)	126.06(17)	C(26)-C(21)-C(5)	120.6(3)
C(11)-N(3)-Rh(1)	127.01(18)	C(22)-C(21)-C(5)	122.3(3)
C(19)-N(4)-C(16)	106.6(2)	C(21)-C(22)-C(23)	121.5(4)
C(19)-N(4)-Rh(1)	126.37(17)	C(24)-C(23)-C(22)	121.4(4)
C(16)-N(4)-Rh(1)	125.61(17)	C(25)-C(24)-C(23)	116.7(3)
N(1)-C(1)-C(20)	125.5(2)	C(25)-C(24)-C(27)	122.5(4)
N(1)-C(1)-C(2)	109.4(2)	C(23)-C(24)-C(27)	120.9(4)
C(20)-C(1)-C(2)	125.0(3)	C(24)-C(25)-C(26)	122.6(4)
C(3)-C(2)-C(1)	107.0(3)	C(21)-C(26)-C(25)	120.6(4)

C(36)-C(31)-C(32)	117.8(3)	C(44)-C(45)-C(46)	122.1(3)
C(36)-C(31)-C(10)	121.3(3)	C(41)-C(46)-C(45)	120.4(3)
C(32)-C(31)-C(10)	120.9(3)	C(56)-C(51)-C(52)	117.5(3)
C(31)-C(32)-C(33)	120.7(4)	C(56)-C(51)-C(20)	121.8(3)
C(34)-C(33)-C(32)	121.6(4)	C(52)-C(51)-C(20)	120.7(3)
C(33)-C(34)-C(35)	118.2(3)	C(51)-C(52)-C(53)	120.8(3)
C(33)-C(34)-C(37)	121.6(5)	C(54)-C(53)-C(52)	121.8(4)
C(35)-C(34)-C(37)	120.1(5)	C(55)-C(54)-C(53)	116.9(3)
C(34)-C(35)-C(36)	120.9(4)	C(55)-C(54)-C(57)	121.4(4)
C(31)-C(36)-C(35)	120.8(4)	C(53)-C(54)-C(57)	121.7(4)
C(42)-C(41)-C(46)	118.1(3)	C(54)-C(55)-C(56)	122.1(4)
C(42)-C(41)-C(15)	121.7(3)	C(51)-C(56)-C(55)	120.8(3)
C(46)-C(41)-C(15)	120.2(3)	C(62)-C(61)-Rh(1)	123.3(3)
C(41)-C(42)-C(43)	120.6(3)	C(61)-C(62)-C(63)	120.9(5)
C(44)-C(43)-C(42)	121.5(3)	C(64)-C(63)-C(62)	115.2(6)
C(45)-C(44)-C(43)	117.3(3)	C(63)-C(64)-C(65)	130.4(10)
C(45)-C(44)-C(47)	121.7(3)	C(66)-C(65)-C(64)	132.0(12)
C(43)-C(44)-C(47)	121.0(3)	C(65)-C(66)-C(67)	122.5(11)

Table 5. Bond lengths [A] and angles [deg] for Rh(ttp)(c-heptyl) **5a**.

Rh(1)-N(2)	2.021(8)	C(10)-C(11)	1.372(14)
Rh(1)-N(1)	2.023(8)	C(10)-C(31)	1.508(13)
Rh(1)-N(3)	2.029(8)	C(11)-C(12)	1.458(13)
Rh(1)-N(4)	2.032(8)	C(12)-C(13)	1.324(15)
Rh(1)-C(61)	2.125(14)	C(13)-C(14)	1.458(15)
N(1)-C(1)	1.376(12)	C(14)-C(15)	1.387(14)
N(1)-C(4)	1.406(12)	C(15)-C(16)	1.413(15)
N(2)-C(6)	1.377(12)	C(15)-C(41)	1.518(14)
N(2)-C(9)	1.403(12)	C(16)-C(17)	1.425(14)
N(3)-C(11)	1.361(12)	C(17)-C(18)	1.343(15)
N(3)-C(14)	1.379(12)	C(18)-C(19)	1.447(14)
N(4)-C(16)	1.370(13)	C(19)-C(20)	1.391(14)
N(4)-C(19)	1.377(13)	C(20)-C(51)	1.517(14)
C(1)-C(20)	1.392(14)	C(21)-C(22)	1.373(15)
C(1)-C(2)	1.431(14)	C(21)-C(26)	1.396(15)
C(2)-C(3)	1.308(14)	C(22)-C(23)	1.399(16)
C(3)-C(4)	1.413(14)	C(23)-C(24)	1.362(17)
C(4)-C(5)	1.378(14)	C(24)-C(25)	1.359(17)
C(5)-C(6)	1.411(14)	C(24)-C(27)	1.549(16)
C(5)-C(21)	1.479(13)	C(25)-C(26)	1.384(15)
C(6)-C(7)	1.427(13)	C(31)-C(36)	1.364(16)
C(7)-C(8)	1.335(14)	C(31)-C(32)	1.385(15)
C(8)-C(9)	1.415(13)	C(32)-C(33)	1.408(15)
C(9)-C(10)	1.402(13)	C(33)-C(34)	1.372(19)

C(34)-C(35)	1.34(2)	N(1)-C(1)-C(2)	108.3(9)
C(34)-C(37)	1.471(18)	C(20)-C(1)-C(2)	127.4(10)
C(35)-C(36)	1.446(17)	C(3)-C(2)-C(1)	107.8(9)
C(41)-C(42)	1.363(16)	C(2)-C(3)-C(4)	110.0(10)
C(41)-C(46)	1.368(16)	C(5)-C(4)-N(1)	124.9(9)
C(42)-C(43)	1.398(17)	C(5)-C(4)-C(3)	127.9(9)
C(43)-C(44)	1.381(19)	N(1)-C(4)-C(3)	107.0(8)
C(44)-C(45)	1.343(18)	C(4)-C(5)-C(6)	125.6(9)
C(44)-C(47)	1.513(16)	C(4)-C(5)-C(21)	117.8(9)
C(45)-C(46)	1.403(16)	C(6)-C(5)-C(21)	116.6(9)
C(51)-C(56)	1.354(15)	N(2)-C(6)-C(5)	123.8(9)
C(51)-C(52)	1.368(17)	N(2)-C(6)-C(7)	109.4(8)
C(52)-C(53)	1.373(19)	C(5)-C(6)-C(7)	126.4(9)
C(53)-C(54)	1.38(2)	C(8)-C(7)-C(6)	107.3(9)
C(54)-C(55)	1.342(19)	C(7)-C(8)-C(9)	109.0(9)
C(54)-C(57)	1.526(16)	C(10)-C(9)-N(2)	123.8(9)
C(55)-C(56)	1.385(16)	C(10)-C(9)-C(8)	127.8(9)
C(61)-C(67)	1.385(19)	N(2)-C(9)-C(8)	108.2(8)
C(61)-C(62)	1.459(19)	C(11)-C(10)-C(9)	125.3(9)
C(62)-C(63)	1.32(3)	C(11)-C(10)-C(31)	117.9(9)
C(63)-C(64)	1.32(3)	C(9)-C(10)-C(31)	116.8(9)
C(64)-C(65)	1.40(3)	N(3)-C(11)-C(10)	126.7(9)
C(65)-C(66)	1.42(2)	N(3)-C(11)-C(12)	108.0(9)
C(66)-C(67)	1.47(2)	C(10)-C(11)-C(12)	125.0(9)
Cl(1)-C(68)	1.784(10)	C(13)-C(12)-C(11)	108.4(9)
Cl(2)-C(68)	1.786(10)	C(12)-C(13)-C(14)	107.2(9)
		N(3)-C(14)-C(15)	126.8(9)
N(2)-Rh(1)-N(1)	90.0(3)	N(3)-C(14)-C(13)	108.2(9)
N(2)-Rh(1)-N(3)	90.1(3)	C(15)-C(14)-C(13)	125.0(9)
N(1)-Rh(1)-N(3)	171.0(3)	C(14)-C(15)-C(16)	124.7(9)
N(2)-Rh(1)-N(4)	179.4(4)	C(14)-C(15)-C(41)	117.9(9)
N(1)-Rh(1)-N(4)	89.6(3)	C(16)-C(15)-C(41)	117.4(9)
N(3)-Rh(1)-N(4)	90.2(3)	N(4)-C(16)-C(15)	124.8(9)
N(2)-Rh(1)-C(61)	91.6(5)	N(4)-C(16)-C(17)	109.3(9)
N(1)-Rh(1)-C(61)	96.0(5)	C(15)-C(16)-C(17)	125.9(9)
N(3)-Rh(1)-C(61)	93.0(5)	C(18)-C(17)-C(16)	108.1(9)
N(4)-Rh(1)-C(61)	88.8(5)	C(17)-C(18)-C(19)	106.8(9)
C(1)-N(1)-C(4)	106.5(8)	N(4)-C(19)-C(20)	125.6(9)
C(1)-N(1)-Rh(1)	127.4(7)	N(4)-C(19)-C(18)	108.7(9)
C(4)-N(1)-Rh(1)	126.0(6)	C(20)-C(19)-C(18)	125.5(9)
C(6)-N(2)-C(9)	106.0(8)	C(19)-C(20)-C(1)	125.2(9)
C(6)-N(2)-Rh(1)	126.8(6)	C(19)-C(20)-C(51)	118.3(9)
C(9)-N(2)-Rh(1)	126.0(7)	C(1)-C(20)-C(51)	116.4(9)
C(11)-N(3)-C(14)	108.1(8)	C(22)-C(21)-C(26)	117.2(10)
C(11)-N(3)-Rh(1)	126.2(6)	C(22)-C(21)-C(5)	122.8(10)
C(14)-N(3)-Rh(1)	125.7(7)	C(26)-C(21)-C(5)	120.0(10)
C(16)-N(4)-C(19)	106.9(9)	C(21)-C(22)-C(23)	120.5(11)
C(16)-N(4)-Rh(1)	126.9(7)	C(24)-C(23)-C(22)	121.3(11)
C(19)-N(4)-Rh(1)	125.3(7)	C(25)-C(24)-C(23)	118.9(11)
N(1)-C(1)-C(20)	123.9(10)	C(25)-C(24)-C(27)	120.8(12)

C(23)-C(24)-C(27)	120.3(12)	C(41)-C(46)-C(45)	120.3(12)
C(24)-C(25)-C(26)	120.6(12)	C(56)-C(51)-C(52)	116.1(11)
C(25)-C(26)-C(21)	121.4(11)	C(56)-C(51)-C(20)	122.4(10)
C(36)-C(31)-C(32)	118.7(10)	C(52)-C(51)-C(20)	121.4(10)
C(36)-C(31)-C(10)	119.7(10)	C(51)-C(52)-C(53)	121.4(14)
C(32)-C(31)-C(10)	121.6(9)	C(52)-C(53)-C(54)	121.4(15)
C(31)-C(32)-C(33)	120.3(11)	C(55)-C(54)-C(53)	116.6(12)
C(34)-C(33)-C(32)	121.8(12)	C(55)-C(54)-C(57)	122.1(14)
C(35)-C(34)-C(33)	117.5(11)	C(53)-C(54)-C(57)	121.3(15)
C(35)-C(34)-C(37)	121.5(15)	C(54)-C(55)-C(56)	121.1(12)
C(33)-C(34)-C(37)	121.0(15)	C(51)-C(56)-C(55)	122.4(12)
C(34)-C(35)-C(36)	122.7(13)	C(67)-C(61)-C(62)	124.0(14)
C(31)-C(36)-C(35)	118.9(13)	C(67)-C(61)-Rh(1)	116.5(10)
C(42)-C(41)-C(46)	119.1(11)	C(62)-C(61)-Rh(1)	115.4(9)
C(42)-C(41)-C(15)	119.6(11)	C(63)-C(62)-C(61)	124.6(17)
C(46)-C(41)-C(15)	121.3(11)	C(64)-C(63)-C(62)	140(3)
C(41)-C(42)-C(43)	119.6(13)	C(63)-C(64)-C(65)	121(2)
C(44)-C(43)-C(42)	121.9(13)	C(64)-C(65)-C(66)	117(2)
C(45)-C(44)-C(43)	117.4(12)	C(65)-C(66)-C(67)	123.8(16)
C(45)-C(44)-C(47)	122.9(14)	C(61)-C(67)-C(66)	123.8(14)
C(43)-C(44)-C(47)	119.7(14)	Cl(1)-C(68)-Cl(2)	111.2(14)
C(44)-C(45)-C(46)	121.8(13)		

Table 6. Bond lengths [A] and angles [deg] for Rh(ttp)(cycloheptatrienyl) **8**.

Rh(1)-N(2)	2.013(2)	C(6)-C(7)	1.448(4)
Rh(1)-N(4)	2.016(2)	C(7)-C(8)	1.343(4)
Rh(1)-N(3)	2.019(2)	C(8)-C(9)	1.436(4)
Rh(1)-N(1)	2.021(2)	C(9)-C(10)	1.396(4)
Rh(1)-C(61)	2.104(3)	C(10)-C(11)	1.399(4)
N(1)-C(1)	1.373(3)	C(10)-C(31)	1.500(4)
N(1)-C(4)	1.382(3)	C(11)-C(12)	1.432(4)
N(2)-C(6)	1.374(3)	C(12)-C(13)	1.342(4)
N(2)-C(9)	1.386(4)	C(13)-C(14)	1.435(4)
N(3)-C(11)	1.373(3)	C(14)-C(15)	1.394(4)
N(3)-C(14)	1.381(3)	C(15)-C(16)	1.396(4)
N(4)-C(16)	1.374(3)	C(15)-C(41)	1.496(3)
N(4)-C(19)	1.382(3)	C(16)-C(17)	1.439(4)
C(1)-C(20)	1.391(4)	C(17)-C(18)	1.342(4)
C(1)-C(2)	1.439(4)	C(18)-C(19)	1.433(4)
C(2)-C(3)	1.352(4)	C(19)-C(20)	1.401(4)
C(3)-C(4)	1.434(4)	C(20)-C(51)	1.502(3)
C(4)-C(5)	1.391(4)	C(21)-C(26)	1.372(4)
C(5)-C(6)	1.387(4)	C(21)-C(22)	1.385(4)
C(5)-C(21)	1.501(4)	C(22)-C(23)	1.387(4)

C(23)-C(24)	1.366(5)	C(9)-N(2)-Rh(1)	126.29(18)
C(24)-C(25)	1.375(5)	C(11)-N(3)-C(14)	106.5(2)
C(24)-C(27)	1.511(4)	C(11)-N(3)-Rh(1)	126.91(17)
C(25)-C(26)	1.389(4)	C(14)-N(3)-Rh(1)	125.72(16)
C(31)-C(36)	1.377(4)	C(16)-N(4)-C(19)	106.5(2)
C(31)-C(32)	1.380(4)	C(16)-N(4)-Rh(1)	126.56(17)
C(32)-C(33)	1.381(4)	C(19)-N(4)-Rh(1)	126.86(17)
C(33)-C(34)	1.366(5)	N(1)-C(1)-C(20)	125.6(2)
C(34)-C(35)	1.374(6)	N(1)-C(1)-C(2)	109.2(2)
C(34)-C(37)	1.517(5)	C(20)-C(1)-C(2)	125.1(2)
C(35)-C(36)	1.380(5)	C(3)-C(2)-C(1)	107.4(2)
C(41)-C(46)	1.363(4)	C(2)-C(3)-C(4)	107.3(2)
C(41)-C(42)	1.381(4)	N(1)-C(4)-C(5)	125.5(2)
C(42)-C(43)	1.391(4)	N(1)-C(4)-C(3)	109.2(2)
C(43)-C(44)	1.376(5)	C(5)-C(4)-C(3)	125.2(2)
C(44)-C(45)	1.374(5)	C(6)-C(5)-C(4)	124.3(2)
C(44)-C(47)	1.510(4)	C(6)-C(5)-C(21)	117.4(2)
C(45)-C(46)	1.397(4)	C(4)-C(5)-C(21)	118.2(2)
C(51)-C(56)	1.371(4)	N(2)-C(6)-C(5)	126.3(2)
C(51)-C(52)	1.381(4)	N(2)-C(6)-C(7)	108.8(2)
C(52)-C(53)	1.394(5)	C(5)-C(6)-C(7)	125.0(3)
C(53)-C(54)	1.381(5)	C(8)-C(7)-C(6)	107.6(3)
C(54)-C(55)	1.349(5)	C(7)-C(8)-C(9)	107.8(3)
C(54)-C(57)	1.522(4)	N(2)-C(9)-C(10)	125.9(2)
C(55)-C(56)	1.384(4)	N(2)-C(9)-C(8)	108.8(2)
C(61)-C(67)	1.444(4)	C(10)-C(9)-C(8)	125.0(3)
C(61)-C(62)	1.458(4)	C(9)-C(10)-C(11)	124.4(2)
C(62)-C(63)	1.425(6)	C(9)-C(10)-C(31)	117.3(2)
C(62)-C(63')	1.447(7)		
C(63)-C(64)	1.492(8)	C(11)-C(10)-C(31)	118.3(2)
C(63')-C(64)	1.533(8)	N(3)-C(11)-C(10)	125.0(2)
C(64)-C(65)	1.442(6)	N(3)-C(11)-C(12)	109.4(2)
C(65)-C(66)	1.459(6)	C(10)-C(11)-C(12)	125.6(2)
C(66)-C(67)	1.449(5)	C(13)-C(12)-C(11)	107.6(2)
		C(12)-C(13)-C(14)	107.5(2)
N(2)-Rh(1)-N(4)	170.62(9)	N(3)-C(14)-C(15)	125.2(2)
N(2)-Rh(1)-N(3)	90.18(9)	N(3)-C(14)-C(13)	109.0(2)
N(4)-Rh(1)-N(3)	90.05(8)	C(15)-C(14)-C(13)	125.6(2)
N(2)-Rh(1)-N(1)	89.94(9)	C(14)-C(15)-C(16)	124.4(2)
N(4)-Rh(1)-N(1)	89.74(9)	C(14)-C(15)-C(41)	118.0(2)
N(3)-Rh(1)-N(1)	179.39(9)	C(16)-C(15)-C(41)	117.6(2)
N(2)-Rh(1)-C(61)	92.42(12)	N(4)-C(16)-C(15)	125.2(2)
N(4)-Rh(1)-C(61)	96.94(12)	N(4)-C(16)-C(17)	108.9(2)
N(3)-Rh(1)-C(61)	91.85(15)	C(15)-C(16)-C(17)	125.6(2)
N(1)-Rh(1)-C(61)	88.75(15)	C(18)-C(17)-C(16)	107.6(2)
C(1)-N(1)-C(4)	106.8(2)	C(17)-C(18)-C(19)	107.5(2)
C(1)-N(1)-Rh(1)	125.87(17)	N(4)-C(19)-C(20)	124.4(2)
C(4)-N(1)-Rh(1)	126.26(17)	N(4)-C(19)-C(18)	109.1(2)
C(6)-N(2)-C(9)	107.0(2)	C(20)-C(19)-C(18)	126.0(2)
C(6)-N(2)-Rh(1)	126.70(18)	C(1)-C(20)-C(19)	124.3(2)

C(1)-C(20)-C(51)	117.7(2)	C(45)-C(44)-C(47)	120.4(3)
C(19)-C(20)-C(51)	117.9(2)	C(43)-C(44)-C(47)	121.7(3)
C(26)-C(21)-C(22)	118.0(3)	C(44)-C(45)-C(46)	120.9(3)
C(26)-C(21)-C(5)	121.4(3)	C(41)-C(46)-C(45)	121.2(3)
C(22)-C(21)-C(5)	120.5(3)	C(56)-C(51)-C(52)	118.2(3)
C(21)-C(22)-C(23)	120.1(3)	C(56)-C(51)-C(20)	121.6(3)
C(24)-C(23)-C(22)	122.1(3)	C(52)-C(51)-C(20)	120.2(3)
C(23)-C(24)-C(25)	117.4(3)	C(51)-C(52)-C(53)	119.7(3)
C(23)-C(24)-C(27)	120.9(3)	C(54)-C(53)-C(52)	121.7(3)
C(25)-C(24)-C(27)	121.7(3)	C(55)-C(54)-C(53)	117.1(3)
C(24)-C(25)-C(26)	121.3(3)	C(55)-C(54)-C(57)	121.4(4)
C(21)-C(26)-C(25)	121.0(3)	C(53)-C(54)-C(57)	121.4(4)
C(36)-C(31)-C(32)	118.1(3)	C(54)-C(55)-C(56)	122.2(3)
C(36)-C(31)-C(10)	119.9(3)	C(51)-C(56)-C(55)	120.7(3)
C(32)-C(31)-C(10)	122.0(2)	C(67)-C(61)-C(62)	123.8(3)
C(31)-C(32)-C(33)	120.7(3)	C(67)-C(61)-Rh(1)	115.0(2)
C(34)-C(33)-C(32)	121.5(3)	C(62)-C(61)-Rh(1)	116.6(2)
C(33)-C(34)-C(35)	117.6(3)	C(63)-C(62)-C(63')	52.1(6)
C(33)-C(34)-C(37)	121.4(4)	C(63)-C(62)-C(61)	126.5(5)
C(35)-C(34)-C(37)	121.0(4)	C(63')-C(62)-C(61)	118.9(6)
C(34)-C(35)-C(36)	121.8(3)	C(62)-C(63)-C(64)	118.5(6)
C(31)-C(36)-C(35)	120.4(3)	C(62)-C(63')-C(64)	114.5(6)
C(46)-C(41)-C(42)	118.1(3)	C(65)-C(64)-C(63)	122.2(6)
C(46)-C(41)-C(15)	121.9(2)	C(65)-C(64)-C(63')	114.1(6)
C(42)-C(41)-C(15)	120.0(2)	C(63)-C(64)-C(63')	49.3(6)
C(41)-C(42)-C(43)	120.9(3)	C(64)-C(65)-C(66)	120.9(5)
C(44)-C(43)-C(42)	121.0(3)	C(67)-C(66)-C(65)	124.7(4)
C(45)-C(44)-C(43)	117.9(3)	C(61)-C(67)-C(66)	123.8(4)

Table 7. Bond lengths [A] and angles [deg] for Rh(ttp)(*n*-octyl) **10b**.

Rh(1)-N(1)	2.017(3)	C(2)-C(3)	1.341(5)
Rh(1)-N(3)	2.019(3)	C(3)-C(4)	1.436(5)
Rh(1)-N(2)	2.024(3)	C(4)-C(5)	1.395(5)
Rh(1)-N(4)	2.030(3)	C(5)-C(6)	1.397(5)
Rh(1)-C(61)	2.031(4)	C(5)-C(21)	1.504(5)
N(1)-C(4)	1.373(4)	C(6)-C(7)	1.429(5)
N(1)-C(1)	1.383(4)	C(7)-C(8)	1.342(5)
N(2)-C(6)	1.374(4)	C(8)-C(9)	1.435(5)
N(2)-C(9)	1.382(4)	C(9)-C(10)	1.383(5)
N(3)-C(11)	1.377(4)	C(10)-C(11)	1.396(5)
N(3)-C(14)	1.383(4)	C(10)-C(31)	1.508(5)
N(4)-C(16)	1.378(4)	C(11)-C(12)	1.439(5)
N(4)-C(19)	1.382(4)	C(12)-C(13)	1.336(5)
C(1)-C(20)	1.388(5)	C(13)-C(14)	1.439(5)
C(1)-C(2)	1.433(5)	C(14)-C(15)	1.386(5)

C(15)-C(16)	1.403(5)	N(1)-Rh(1)-N(4)	90.42(11)
C(15)-C(41)	1.502(5)	N(3)-Rh(1)-N(4)	89.54(11)
C(16)-C(17)	1.443(5)	N(2)-Rh(1)-N(4)	178.47(11)
C(17)-C(18)	1.347(5)	N(1)-Rh(1)-C(61)	94.91(16)
C(18)-C(19)	1.435(5)	N(3)-Rh(1)-C(61)	91.25(16)
C(19)-C(20)	1.395(5)	N(2)-Rh(1)-C(61)	90.78(15)
C(20)-C(51)	1.502(5)	N(4)-Rh(1)-C(61)	87.71(15)
C(21)-C(22)	1.359(6)	C(4)-N(1)-C(1)	107.0(3)
C(21)-C(26)	1.367(6)	C(4)-N(1)-Rh(1)	126.8(2)
C(22)-C(23)	1.397(6)	C(1)-N(1)-Rh(1)	126.1(2)
C(23)-C(24)	1.359(7)	C(6)-N(2)-C(9)	106.6(3)
C(24)-C(25)	1.361(7)	C(6)-N(2)-Rh(1)	126.7(2)
C(24)-C(27)	1.523(6)	C(9)-N(2)-Rh(1)	125.4(2)
C(25)-C(26)	1.386(6)	C(11)-N(3)-C(14)	107.2(3)
C(31)-C(32)	1.369(5)	C(11)-N(3)-Rh(1)	125.9(2)
C(31)-C(36)	1.383(5)	C(14)-N(3)-Rh(1)	126.7(2)
C(32)-C(33)	1.401(6)	C(16)-N(4)-C(19)	107.2(3)
C(33)-C(34)	1.368(6)	C(16)-N(4)-Rh(1)	126.0(2)
C(34)-C(35)	1.368(6)	C(19)-N(4)-Rh(1)	125.5(2)
C(34)-C(37)	1.527(6)	N(1)-C(1)-C(20)	125.9(3)
C(35)-C(36)	1.385(6)	N(1)-C(1)-C(2)	108.4(3)
C(41)-C(42)	1.379(6)	C(20)-C(1)-C(2)	125.5(3)
C(41)-C(46)	1.381(6)	C(3)-C(2)-C(1)	108.1(3)
C(42)-C(43)	1.399(6)	C(2)-C(3)-C(4)	107.4(3)
C(43)-C(44)	1.373(8)	N(1)-C(4)-C(5)	125.6(3)
C(44)-C(45)	1.370(8)	N(1)-C(4)-C(3)	109.0(3)
C(44)-C(47)	1.529(7)	C(5)-C(4)-C(3)	125.3(3)
C(45)-C(46)	1.381(6)	C(4)-C(5)-C(6)	124.7(3)
C(51)-C(56)	1.356(6)	C(4)-C(5)-C(21)	117.5(3)
C(51)-C(52)	1.364(6)	C(6)-C(5)-C(21)	117.7(3)
C(52)-C(53)	1.398(6)	N(2)-C(6)-C(5)	125.2(3)
C(53)-C(54)	1.357(7)	N(2)-C(6)-C(7)	109.3(3)
C(54)-C(55)	1.345(7)	C(5)-C(6)-C(7)	125.5(3)
C(54)-C(57)	1.513(6)	C(8)-C(7)-C(6)	107.7(3)
C(55)-C(56)	1.405(6)	C(7)-C(8)-C(9)	107.6(3)
C(61)-C(62)	1.5272(11)	N(2)-C(9)-C(10)	125.4(3)
C(62)-C(63)	1.506(7)	N(2)-C(9)-C(8)	108.8(3)
C(63)-C(64)	1.498(10)	C(10)-C(9)-C(8)	125.7(3)
C(63)-C(64')	1.525(10)	C(9)-C(10)-C(11)	124.6(3)
C(64)-C(65)	1.526(10)	C(9)-C(10)-C(31)	117.6(3)
C(64')-C(65')	1.521(10)	C(11)-C(10)-C(31)	117.7(3)
C(64')-C(66)	2.03(3)	N(3)-C(11)-C(10)	125.3(3)
C(65)-C(66)	1.501(10)	N(3)-C(11)-C(12)	108.4(3)
C(65')-C(66)	1.514(10)	C(10)-C(11)-C(12)	126.2(3)
C(66)-C(67)	1.534(10)	C(13)-C(12)-C(11)	108.0(3)
C(67)-C(68)	1.490(9)	C(12)-C(13)-C(14)	107.8(3)
		N(3)-C(14)-C(15)	125.1(3)
N(1)-Rh(1)-N(3)	173.83(11)	N(3)-C(14)-C(13)	108.2(3)
N(1)-Rh(1)-N(2)	89.97(11)	C(15)-C(14)-C(13)	126.4(3)
N(3)-Rh(1)-N(2)	90.24(11)	C(14)-C(15)-C(16)	124.3(3)

C(14)-C(15)-C(41)	118.5(3)	C(53)-C(54)-C(57)	121.1(5)
C(16)-C(15)-C(41)	117.2(3)	C(54)-C(55)-C(56)	121.9(5)
N(4)-C(16)-C(15)	125.0(3)	C(51)-C(56)-C(55)	120.9(4)
N(4)-C(16)-C(17)	108.5(3)	C(62)-C(61)-Rh(1)	120.3(3)
C(15)-C(16)-C(17)	126.5(3)	C(63)-C(62)-C(61)	110.8(5)
C(18)-C(17)-C(16)	107.7(3)	C(64)-C(63)-C(62)	110.6(11)
C(17)-C(18)-C(19)	107.7(3)	C(64)-C(63)-C(64')	58.2(13)
N(4)-C(19)-C(20)	125.1(3)	C(62)-C(63)-C(64')	108.4(9)
N(4)-C(19)-C(18)	108.8(3)	C(63)-C(64)-C(65)	121.8(18)
C(20)-C(19)-C(18)	126.1(3)	C(65')-C(64')-C(63)	97.5(13)
C(1)-C(20)-C(19)	124.8(3)	C(65')-C(64')-C(66)	47.8(8)
C(1)-C(20)-C(51)	117.0(3)	C(63)-C(64')-C(66)	138.0(13)
C(19)-C(20)-C(51)	118.2(3)	C(66)-C(65)-C(64)	112(2)
C(22)-C(21)-C(26)	117.9(4)	C(66)-C(65')-C(64')	84.2(16)
C(22)-C(21)-C(5)	121.1(4)	C(65)-C(66)-C(65')	25.7(14)
C(26)-C(21)-C(5)	121.0(3)	C(65)-C(66)-C(67)	87.2(15)
C(21)-C(22)-C(23)	121.0(4)	C(65')-C(66)-C(67)	101.2(16)
C(24)-C(23)-C(22)	121.6(4)	C(65)-C(66)-C(64')	67.1(13)
C(23)-C(24)-C(25)	116.7(4)	C(65')-C(66)-C(64')	48.1(8)
C(23)-C(24)-C(27)	121.8(5)	C(67)-C(66)-C(64')	148.2(16)
C(25)-C(24)-C(27)	121.5(5)	C(68)-C(67)-C(66)	119.7(18)
C(24)-C(25)-C(26)	122.6(4)		
C(21)-C(26)-C(25)	120.3(4)		
C(32)-C(31)-C(36)	118.2(3)		
C(32)-C(31)-C(10)	121.6(3)		
C(36)-C(31)-C(10)	120.1(3)		
C(31)-C(32)-C(33)	120.5(4)		
C(34)-C(33)-C(32)	121.5(4)		
C(35)-C(34)-C(33)	117.3(4)		
C(35)-C(34)-C(37)	121.5(4)		
C(33)-C(34)-C(37)	121.2(4)		
C(34)-C(35)-C(36)	122.2(4)		
C(31)-C(36)-C(35)	120.3(4)		
C(42)-C(41)-C(46)	117.5(4)		
C(42)-C(41)-C(15)	121.4(4)		
C(46)-C(41)-C(15)	121.1(4)		
C(41)-C(42)-C(43)	120.7(5)		
C(44)-C(43)-C(42)	121.1(5)		
C(45)-C(44)-C(43)	117.9(4)		
C(45)-C(44)-C(47)	122.4(6)		
C(43)-C(44)-C(47)	119.7(7)		
C(44)-C(45)-C(46)	121.4(5)		
C(45)-C(46)-C(41)	121.3(5)		
C(56)-C(51)-C(52)	117.6(4)		
C(56)-C(51)-C(20)	120.5(3)		
C(52)-C(51)-C(20)	122.0(4)		
C(51)-C(52)-C(53)	120.6(4)		
C(54)-C(53)-C(52)	121.9(4)		
C(55)-C(54)-C(53)	117.0(4)		
C(55)-C(54)-C(57)	121.8(5)		

GC-MS Spectra

c-Octane and benzene-d_6 had been found to be free of *n*-octane and 1-octene.

The GC-MS reports are attached as follow:

i)   Sample *c*-octane spiked with *n*-octane and 1-octene

ii)   Sample *c*-octane

iii)   Solvent benzene-d_6

Details of Chemicals Used for GC-MS Analysis

Enrty	Chemical	Supplier	Grade
1	*c*-octane	Aldrich	99+%
2	*n*-octane	Fluka	>99%(GC)
3	1-octene	Fluka	99%
4	benzene-d_6	Cambridge Isotope	99.5%

i) GC-MS report of sample *c*-octane spiked with *n*-octane and 1-octene

Sample Cyclooctane spiked with 1-Octene & n-Octane

Chromatogram YWC_oct_spike C:\GCMSsolution\Data\Project1\YWC_oct_spike1.qgd
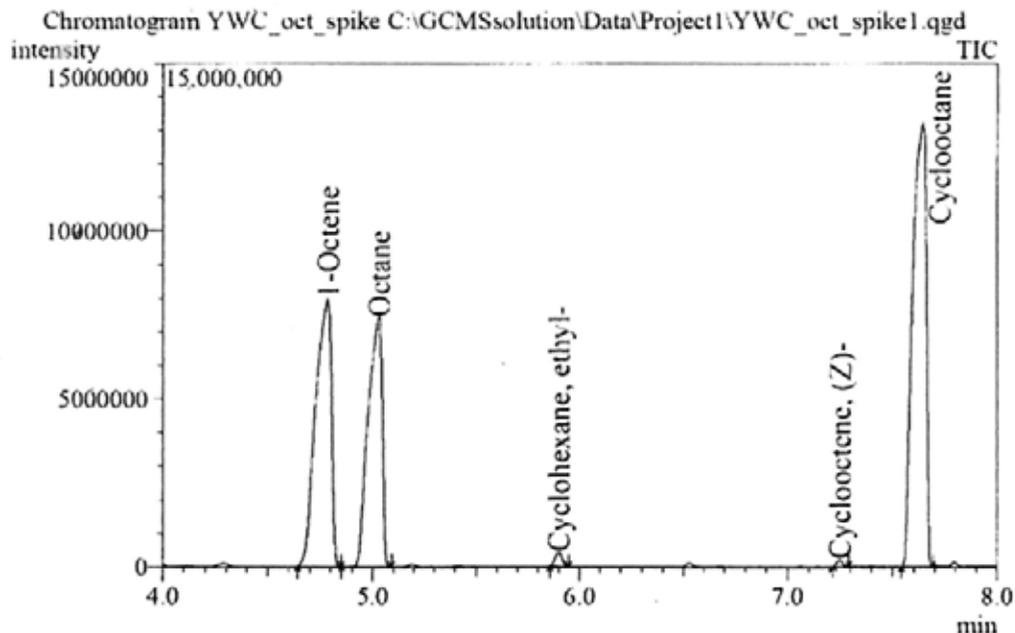
Quantitative Result Table

Name	R.Time	m/z	Area	Height
1-Octene	4.783	55.00	8351875	1543069
Octane	5.029	85.00	9302936	1952442
Cyclohexane, ethyl	5.900	83.00	312732	128068
Cyclooctene, (Z)-	7.248	67.00	96065	47529
Cyclooctane	7.644	56.00	8756382	1979570

ii) GC-MS report of sample *c*-octane

Sample Cyclooctane

Chromatogram YWC_oct_nonspike C:\GCMSsolution\Data\Project1\YWC_oct_nonspike.qgd
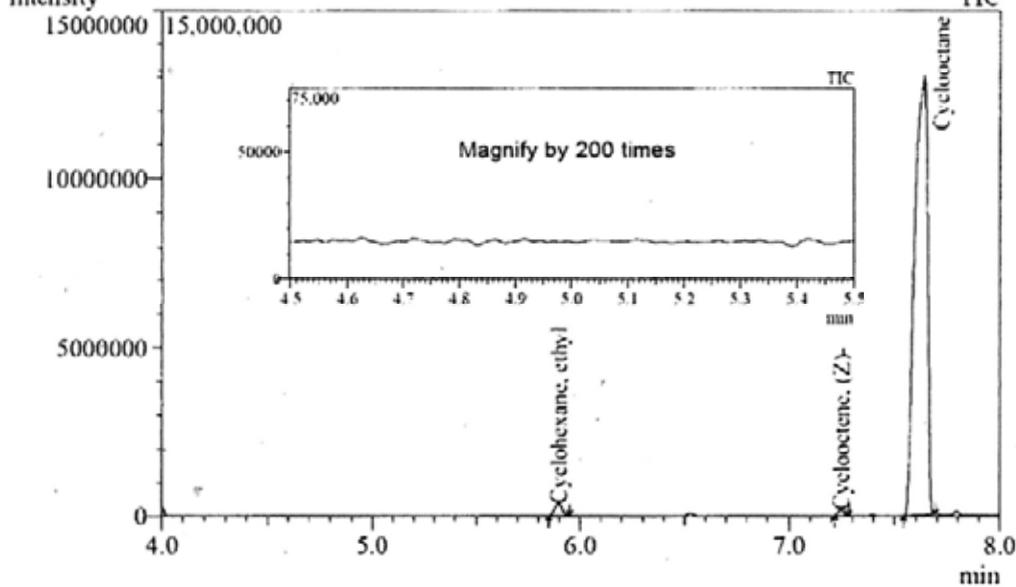
Quantitative Result Table

Name	R.Time	m/z	Area	Height
Cyclohexane, ethyl	5.896	83.00	279808	108316
Cyclooctene, (Z)-	7.246	67.00	85941	41119
Cyclooctane	7.639	56.00	8263485	1950977

iii) GC-MS report of solvent benzene-d_6

C6D6

Chromatogram YWC_C6D6_test C:\GCMSsolution\Data\Project1\YWC_C6D6_test.qgd

List of Spectra

Rh(ttp)(*c*-hexyl) (**2a**)

^{1}H NMR

^{13}C NMR

Rh(ttp)(*c*-pentyl) (**2b**)

^{1}H NMR

^{13}C NMR

Rh(ttp)(*n*-pentyl) (**2c**)

¹H NMR

¹³C NMR

Rh(ttp)(*n*-hexyl) (2d)

¹H NMR

¹³C NMR

Rh(ttp)(*n*-heptyl) (2e)

^{1}H NMR

^{13}C NMR

Rh(ttp)Cl(Ph₃) (2f)

¹H NMR

¹³C NMR

Rh(tpp)(*c*-hexyl) (**4a**)

¹H NMR

¹³C NMR

Rh(bocp)(*c*-hexyl) (4b)

¹H NMR

¹³C NMR

Rh(ttp)(*c*-heptyl) **5a** ^{1}NMR

YWC429.1 (H1)

Rh(ttp)(*c*-heptyl) **5a** ^{13}C NMR

C13

Rh₂(ttp)₂(C₇H₁₂) 7a ¹H NMR

YNC Rh2(ttp)2C7H12

Rh(ttp)(cycloheptatrienyl) 8 ¹H NMR

Rh(ttp)(cycloheptatrienyl) 8 ^{13}C NMR

YWC915(C13)

Rh(ttp)(c-octyl) 10a ^{1}NMR

YWC Rh(ttp)(c-octyl)(091125)

Rh(ttp)(*c*-octyl) **10a** ^{13}C NMR

Rh(ttp)(*n*-octyl) **10b** ^{1}H NMR

Rh(ttp)(*n*-octyl) **10b** ¹³C NMR