Catalytic Carbon-Carbon Bond Hydrogenation of Hydrocarbons with Water Catalyzed by Group 9 Metalloporphyrins

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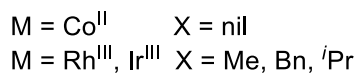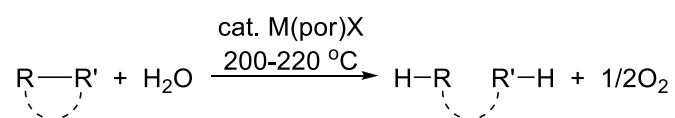
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Abstract

This thesis focuses on the mechanistic investigation of catalytic carbon-carbon σ-bond hydrogenation of hydrocarbons using water as the convenient hydrogen source under neutral conditions by group 9 metalloporphyrins M(por)X.

$$R\text{---}R' + H_2O \xrightarrow[\text{200-220 }^o\text{C}]{\text{cat. M(por)X}} H\text{---}R \quad R'\text{---}H + 1/2O_2$$

M = Co^{II} X = nil
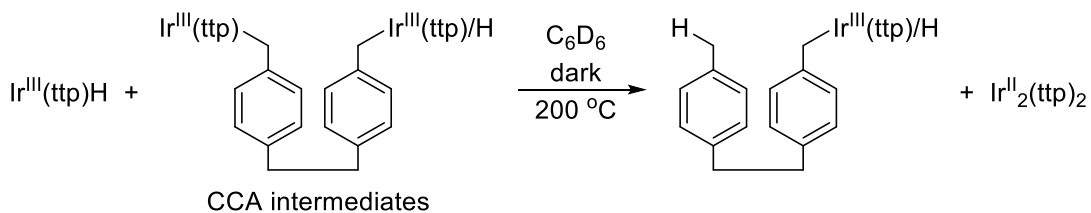M = Rh^{III}, Ir^{III} X = Me, Bn, ^{i}Pr

The benzylic carbon-carbon bond of [2.2]paracyclophane (PCP) was catalytically hydrogenated to give 4,4'-dimethylbibenzyl up to 98% yield using water with 10 mol% M(ttp)X pre-catalyst (ttp = 5,10,15,20-tetratolylporphyrinato dianion, M = Rh^{III} and Ir^{III}, X = Me, Bn and ^{i}Pr) at 200 ^{o}C in C$_6$D$_6$. Deuterium labeling experiments using D$_2$O supported water as the hydrogen source. Preliminary screening with Co^{II}(ttp) catalyst in polar DMF solvent at 220 ^{o}C also yielded the hydrogenation product selectively. The role of DMF is proposed to promote the hydrolysis of cobalt(III) porphyrin benzyl intermediates and increase the solubility of H$_2$O.

M = Co^{II} X = nil
M = Rh^{III}, Ir^{III} X = Me, Bn, ^{i}Pr
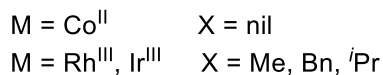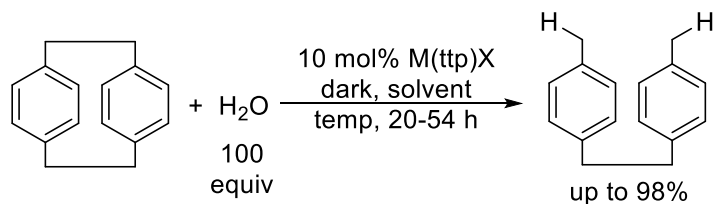
Kinetic studies on the stoichiometric benzylic CCA of PCP with $Rh^{II}(tmp)$ metalloradical (tmp = 5,10,15,20-tetramesitylporphyrinato dianion) gave the rate law as rate = $k[Rh^{II}(tmp)]^2[PCP]$. The 2nd order dependence on $Rh^{II}(tmp)$ radical suggests a bi-metalloradical CCA mechanism via a four-centered transition state.

bi-metalloradical CCA
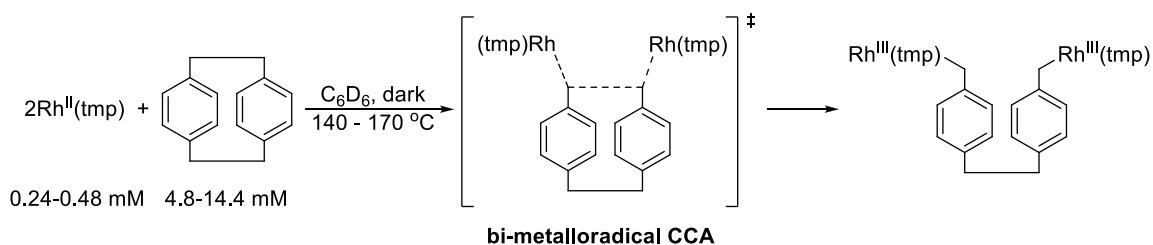
In the iridium catalyzed system, $Ir^{III}(ttp)H$ was found to have promoting role in the hydrogenation process. The bi-molecular reductive elimination between $Ir^{III}(ttp)H$ and the CCA intermediates speeded up the hydrogenation process. It is estimated that this process gave the hydrogenated alkyl fragment 3 times faster than hydrolysis of the CCA intermediates.

CCA intermediates

摘要

本論文主要探討在中性反應條件下，利用水作為一個方便的氫來源，以第 9 族金屬卟啉，M(por)X，催化碳氫化合物中的碳碳單鍵加氫反應的反應機制。

在 200 ℃ 及溶有 10 mol% M(ttp)X (M = Rh^{III} 和 Ir^{III}，X = Me，Bn 和 ^iPr) 預催化劑的氘代苯中，利用水把[2.2]二聚對二甲苯的苄基碳碳鍵進行催化加氫，生成高達 98%的 4,4'-二甲基聯苄 (下稱 PCP)。利用氘代水的氘標記實驗支持了氫的來源為水。另一方面，經過以 $Co^{II}(ttp)$催化劑進行了初步篩選後，能在 220 ℃ 及 DMF 極性溶濟中使加氫產物選擇性地生成。DMF 的作用被提議為促進鈷卟啉苄基的水解及增加了水的溶解度。

在進行了 $Rh^{II}(tmp)$與 PCP 的當量苄基碳碳鍵活化動力學實驗後，得出速率方程 rate = $k[Rh^{II}(tmp)]^2[PCP]$。$Rh^{II}(tmp)$的二級反應級數反映了一個經由四中心過渡態的雙金屬自由基碳碳鍵活化反應機制。

在由銥催化的系統中，發現了 $Ir^{III}(ttp)H$ 在加氫過程中的促進作用。$Ir^{III}(ttp)H$ 與碳碳鍵活化中間體的雙分子還原消除反應把加氫過程加快。根據估計，這個雙分子還原消除反應比碳碳鍵活化中間體的水解要快 3 倍。

Acknowledgement

I would like to take this opportunity to express my hearty gratitude and sincere thanks to Professor Kin Shing Chan for his continuous encouragement, valuable comments and providing me an excellent research environment since I joined the group in 2008. I have experienced exciting adventures to look for solutions to difficulties and challenges in chemical research. Prof. Chan enthusiastically shares his authoritative knowledge on my research work, as well as in various areas of chemistry. This greatly enriched my understanding on those topics.

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Finally, I am heavily indebted to my family members. Their care and understanding on me allow me to stay focus on the research work. I am very grateful to my family.

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Abbreviations

δ	: chemical Shift	J	: coupling constant
Anal	: analytical	K	: equilibrium constant
Ar	: Aryl	k	: rate constrant
OAc	: acetate	m	: multiplet (NMR)
Bn	: benzyl	M^+	: molecular ion
PhCN	: benzonitrile	M	: molarity
BDE	: bond dissociation energy	Me	: methyl
br	: broad singlet (NMR)	mg	: milligram (s)
^{t}Bu	: *tert*-butyl	min	: minute (s)
Bn	: benzyl	mL	: milliliter (s)
Calcd.	: calculated	mM	: milimolar (s)
CCA	: carbon carbon bond activation	mmol	: milimole (s)
CHA	: carbon hydrogen bond activation	nm	: nanometer
COD	: 1,5-cyclooctadiene	NMR	: nuclear magnetic resonance
Cp	: cyclopentadienyl	por	: porphyrin dianion
d	: day (s)	ppm	: part per million
ºC	: degree Celsius	Ph	: phenyl
K	: degree Kelvin	^{n}Pr	: *n*-propyl
d	: doublet (NMR)	^{i}Pr	: isopropyl
DMF	: *N,N*-dimethylformamide	py	: pyridine
H	: enthalpy	q	: quartet (NMR)
S	: entropy	quin	: quintet (NMR)
Et	: ethyl	R	: alkyl group
equiv	: equivalent (s)	R_f	: retention factor
ESI	: electrospray ionization	r.t.	: room temperature
FAB	: fast atom bombardment	s	: second (s)
g	: gram (s)	s	: singlet (NMR)
G	: Gibbs free energy	sept	: septet (NMR)
GC/MS	: gas chromatography/mass spectrometry	sext	: sextet (NMR)
h	: hour (s)	THF	: tetrahydrofuran
HRMS	: highest resolution mass spectrometry	t	: triplet (NMR)
Hz	: Hertz	TLC	: thin-layer chromatography
IR	: infrared	TMS	: tetramethylsilane

Structural Abbreviations for Porphyrins
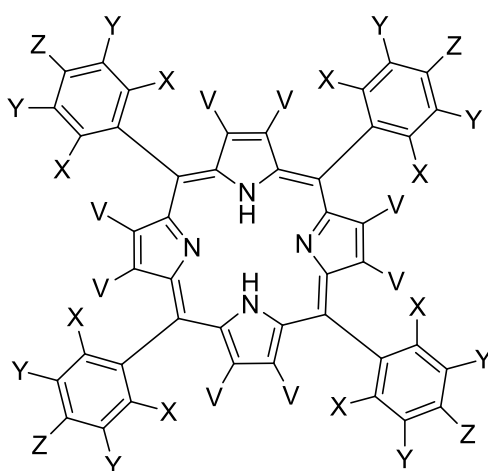
Nomenclature of Porphyrins

Abbreviation	Porphyrin	Substituent			
		V	X	Y	Z
H$_2$(tpp)	5,10,15,20-tetraphenylporphyrin	H	H	H	H
H$_2$(ttp)	5,10,15,20-tetratolylporphyrin	H	H	H	Me
H$_2$(tap)	5,10,15,20-tetraanisylporphyrin	H	H	H	OMe
H$_2$(t$_{p\text{-}CF3}$pp)	5,10,15,20-tetra(p-trifluoromethylphenyl)porphyrin	H	H	H	CF$_3$
H$_2$(t$_{p\text{-}Cl}$pp)	5,10,15,20-tetra(p-chlorophenyl)porphyrin	H	H	H	Cl
H$_2$(tmp)	5,10,15,20-tetramesitylporphyrin	H	Me	H	Me
H$_2$(ocp)	2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetraphenylporphyrin	Cl	H	H	H
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$_2$(tspp)	5,10,15,20-tetra(p-sulfonatophenyl)porphyrin	H	H	H	SO$_3^-$
H$_2$(oep)	2,3,7,8,12,13,17,18-octaethylporphyrin	Et	--	--	--

Chapter 1   General Introduction

1.1 General Introduction of Hydrocarbons

       Hydrocarbons are compounds made of carbon and hydrogen only, and the most basic class of organic compounds.[1] They are non-polar in nature. Hydrocarbons can generally be divided into 4 classes based on bonding structure: (1) alkane; (2) alkene; (3) alkyne; and (4) aromatics, which contain C-C, C=C, C≡C bonds and benzene ring in their carbon skeletons, respectively.

1.2 Hydrocarbons as Fuel

       Combustion of fuel is an exothermic reaction, where energy is released. Hydrocarbons are fossil fuels and exist in the form of coal, oil or natural gas with varying H:C ratio (Table 1.1).[1] Hydrocarbons with higher H:C ratio are considered as clean fuel as they tend to burn completely, or alternatively with more C-H bonds to be oxidized. Therefore, short chain hydrocarbons are ideal fuel, e.g. petrol. In petroleum industry, heavier hydrocarbons are converted to lower molecular weight fragments via hydrocracking process to increase their H:C ratio (eq 1.1).[2] This process involves the cleavage of aliphatic carbon-carbon bonds followed by hydrogenation.

Table 1.1 H:C Ratio of Different Hydrocarbon Sources.

Hydrocarbon Sources	Average H:C Ratio
Methane	4.0
Natural Gas	3.8
Petroleum Crude	1.8
Shale oil (raw)	1.5
Bituminous coal	0.8

acidic zeolite
> 400 °C
> 50 bar
20-70%
conversion

+ H_2
>100 equiv

(1.1)
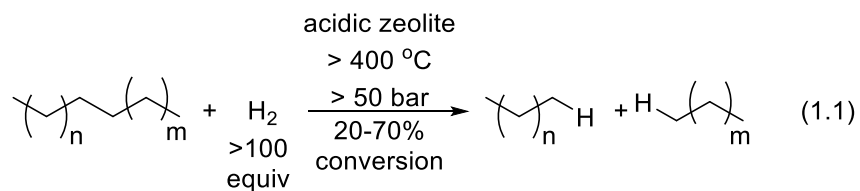
1.3 [2.2]Paracyclophane

1.3.1 General Introduction to Cyclophane

Cyclophanes are a type of hydrocarbon containing at least one aromatic ring bridged with carbon side chains of various lengths.[3] The aromatic ring, with benzene as the simplest form, is distorted into a boat form unless the side chain is sufficiently long. Table 1.2 summarizes the relationships between the bridge length n, distortion angle α and the theoretical heat of formation ΔH_f using [n]paracyclophane as the example.[3b] In general, the shorter the bridge length, the more distorted the aromatic ring, and therefore more strain.

Table 1.2 Relationships between bridge length, distortion angle and heat of formation in [n]paracyclophane.

	n	α (°)	ΔH_f (kcal/mol)[a]
$(CH_2)_n$ α [n]paracyclophane	9	9.6	-18.9
	8	13.4	-8.7
	7	16.4	5.1
	6	22.3	26.2
	5	28.6	53.8
	4	35.6	87.8
	3	79.4	117.8
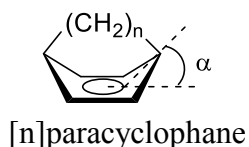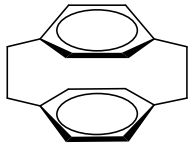
[a] Calculation at AM1 level.

1.3.2 Properties of [2.2]Paracyclophane

[2.2]Paracyclophane (PCP) contains two benzene rings bridged by two *para* -CH$_2$CH$_2$- groups. It is first prepared by Brown and Farthing in 1949 in the pyrolysis of *p*-xylene.[4] Table 1.3 summarizes some properties of PCP.

Table 1.3 Properties of [2.2]Paracyclophane.

	$\Delta H_f(gas)$[5]	57.7 kcal/mol
	Melting point[4]	285 °C
	CH$_2$-CH$_2$ length[6]	1.558 Å (93K), 1.630 Å (291K),
	Angle of bending of benzene[6]	14° (93 K and 291 K)
	Strain Energy[5]	31 kcal/mol
	1st oxidation potential[7]	1.52 V
	2nd oxidation potential[7]	1.80 V

1.3.3 Organic Examples of Carbon(sp^3)-Carbon(sp^3) Bond Cleavage of PCP

There are three types of C(sp^3)-C(sp^3) bond cleavage of PCP: (1) thermolysis; (2) photolysis; and (3) oxidative cleavage.

1.3.3.1 Thermolysis

Flash vacuum thermolysis of PCP at 600 °C resulted in cleavage of two bridging carbon-carbon bonds to give *p*-xylylene (eq 1.2).[8] Racemization of (-)-4-carbomethoxy[2.2]paracyclophane at 200 °C has been reported to go through a benzylic diradical intermediate (eq 1.3 and Scheme 1.1).[9] The diradical character was further supported by trapping using H atom donor solvent *p*-diisopropylbenzene. 4,4-Dimethylbibenzyl was formed in 21% yield when PCP was heated in *p*-diisopropylbenzene at 250 °C, together with oligomeric *p*-xylyl co-products (eq 1.4).[9]

$$\text{(1.2)}$$

(-)-(CO$_2$CH$_3$)PCP

$$\text{(1.3)}$$

R = CO$_2$CH$_3$
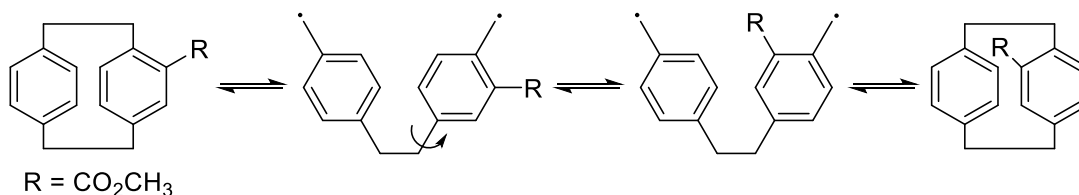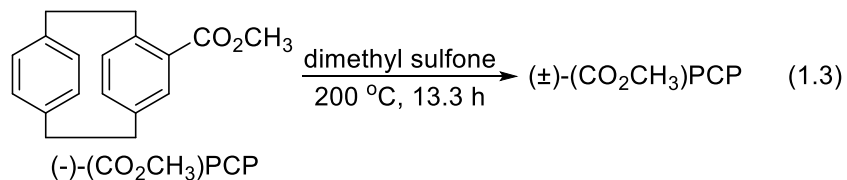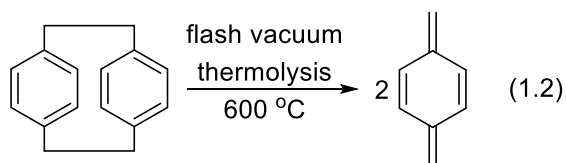
Scheme 1.1 Racemization of (-)-4-Carbomethoxy[2.2]paracyclophane via Diradical Intermediate

$$\text{(1.4)}$$

21%
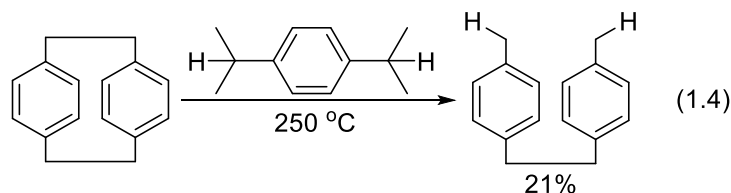
1.3.3.2 Photolysis

Kaupp has reported the CH$_2$-CH$_2$ bridge cleavage in PCP by photolysis. Irradiation of PCP in 2-methyltetrahydrofuran organic glass with 254 nm low pressure mercury arc lamp yielded the benzylic diradical at 77 K (eq 1.5).[10] At 83 K, *p*-xylylene was formed instead (eq 1.6).[10]

$$\text{(1.5)}$$

$$\text{(1.6)}$$
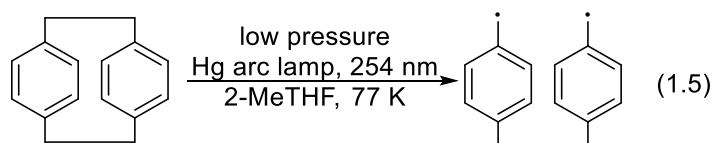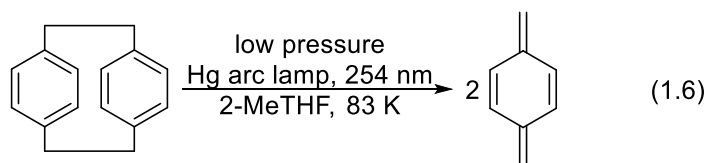
1.3.3.3 Oxidative Cleavage

The ethylene bridge is cleaved heterolytically in the presence of strong oxidizing agents. PCP undergwent ring opening under the action of cerium(IV) ammonium nitrate (CAN) in CHCl$_3$ to form the nitroxymethyl substituted product (eq 1.7).[11] NOBF$_4$ oxidized PCP successfully with ring cleavage to yield a mixture of aldehyde and oxime products (eq 1.8).[12]

$$\text{(1.7)}$$

% conversion = 23
% mass balance = 94

$$\text{(1.8)}$$
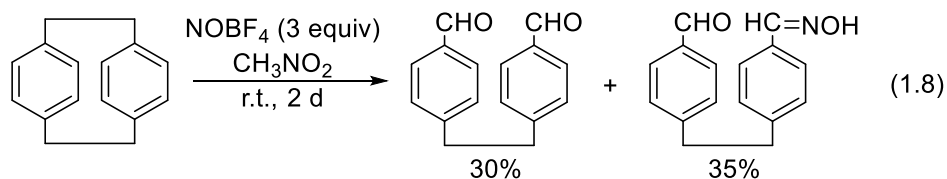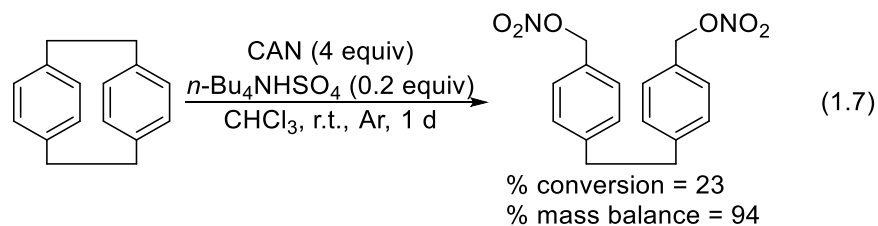
1.4 Carbon-Carbon Bond Activation by Transition Metal Complexes

Carbon-carbon bond activation (CCA) of hydrocarbons by transition metal complexes involves the cleavage of C-C bond followed by the formation of M-C bond (eqs 1.9 and 1.10).[13] In catalytic CCA, the M-C bond is further functionalized to give desired product (eq 1.11).

$$RH_2C-CH_2R' \ + \ M \ \longrightarrow \ RH_2C-M-CH_2R' \qquad \text{(1.9)}$$

$$RH_2C-CH_2R' \ + \ 2M \ \longrightarrow \ RH_2C-M \ + \ R'H_2C-M \qquad \text{(1.10)}$$

$$RH_2C-M \ + \ X\text{-}Y \ \longrightarrow \ RH_2C-X \ + \ M-Y \qquad \text{(1.11)}$$

5
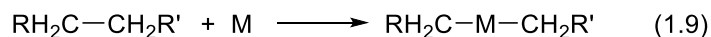
Homogeneous carbon-carbon bond activation of hydrocarbons with transition metal complexes is very challenging, mainly accounted by two reasons: (1) kinetically inaccessibility of the C-C bond due to the surrounding C-H bonds; and (2) competitive C-H bond activation because of forming stronger M-H bond than M-C bond.[14,15]

1.4.1 General Strategies

Several common strategies have been observed in the homogeneous CCA of organic substrates, including ring strain relief (eq 1.12),[16] chelation assistance (eq 1.13),[17] aromatization (eq 1.14),[18] β-alkyl elimination (eq 1.15)[19] and alkane metathesis (eq 1.16).[20] Since the scope of this thesis focus on CCA of hydrocarbons, the mechanistic details for functionalized substrates will not be discussed.

$$\text{(1.12)}$$

70%

$$\text{HRh(PPh}_3)_4 + \xrightarrow[\text{25 °C}]{\text{THF}} \xrightarrow[\text{90 °C}]{\text{H}_2 \text{ (80 psi)}} + \text{CH}_4 \quad \text{(1.13)}$$

quantitative

$$\text{L = P(p-FC}_6\text{H}_4)_3, \text{ S = acetone} \quad \text{(1.14)}$$

50%

6

Me$_2$Si$\diagdown$ ... Sc ... PMe$_3$ $\xrightarrow[\text{r.t., overnight}]{C_6D_{12}}$ Me$_2$Si$\diagdown$ ... Sc ... PMe$_3$, Me $+$ $\diagup\!\!\diagdown$ (1.15)

85%

$n\text{-}C_6H_{14}$ $\xrightarrow[\text{125 °C, 1 d}]{\substack{\text{Ir cat (0.14 mol\%)}\\\text{Mo cat (0.22 mol\%)}}}$ linear C$_2$ to C$_{15}$ (1.16)

135 TON
w.r.t. Ir

Ir cat = [aryl ring with O–P(^{t}Bu)$_2$ groups bound to Ir–(C$_2$H$_4$)]

Mo cat = [^{i}Pr, ^{i}Pr substituted aryl; N=Mo with Ph(H$_3$C)$_2$CHC=, OC(CF$_3$)$_2$(CH$_3$) ligands, OC(CF$_3$)$_2$(CH$_3$)]
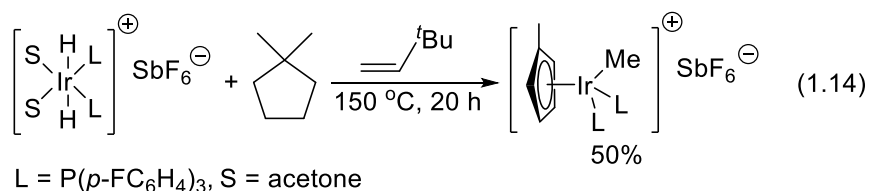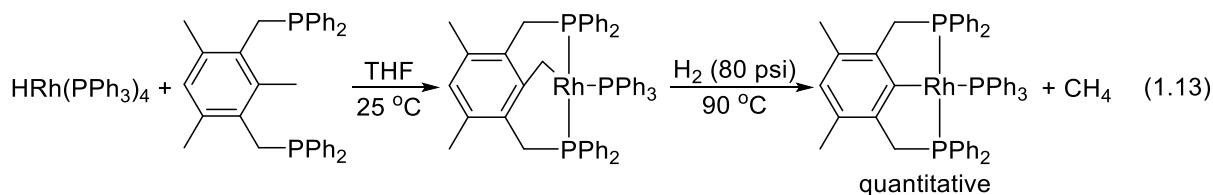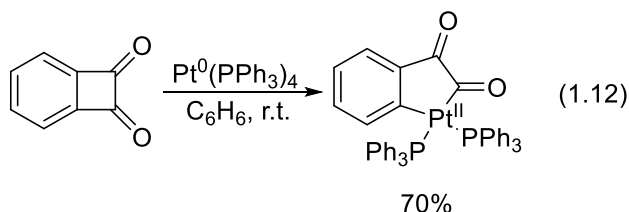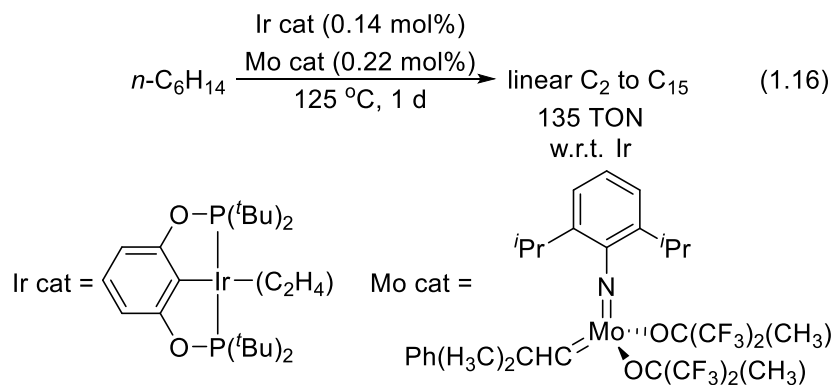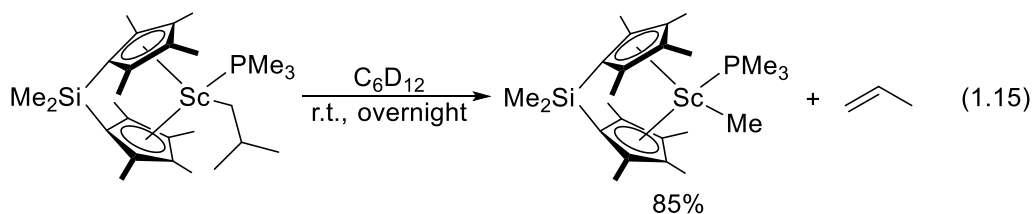
1.4.2 Carbon-Carbon Bond Activation of Hydrocarbons

Table 1.4 summarizes the stoichiometric and catalytic CCA of hydrocarbons with transition metal complexes in chronological order. Most of the examples reported are associated with ring strained hydrocarbons. From the table, the development of CCA of hydrocarbons can generally be divided into three eras: (1) 1972 and before; (2) 1974-1988; and (3) 1988 and after. They will be discussed one by one accompanied with representative examples in details.

1.4.2.1 1972 and Before

In 1955, Tipper reported the first CCA of hydrocarbon by reacting cyclopropane with PtCl$_2$ to yield the platinacyclobutane complex (eq 1.17).[21] It is proposed to go through an oxidative addition mechanism.

PtCl$_2$ + $\triangle$ $\xrightarrow[\text{r.t., overnight}]{\text{acetic anhydride}}$ $\left[\begin{array}{c} Cl\diagdown \\ Pt\diagup\!\!\diagdown \\ Cl\diagup \end{array} \right]_n$ (1.17)
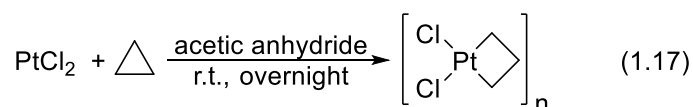
Most reports later on are restricted to the catalytic rearrangement of strained cyclopropyl and cyclobutyl ring systems. These rearrangements usually fall into either mechanism: (1) rearrangement by initial oxidative addition of metal to the C-C bond followed by retro-oxidative C-C coupling or (2) symmetry forbidden rearrangement catalyzed by metal with suitable d orbitals for interaction (Lewis acidic metal ion like Ag^+).

The oxidative addition mechanism is supported by the CO insertion in stoichiometric reactions investigated by Halpern. The low valent $[Rh(CO)_2Cl]_2$ inserts into the C-C bond of cubane at 40 ºC in $CHCl_3$ to yield 90% of the 6-membered metallocycle (eq 1.18).[28] The cyclopropane ring in quadricyclane reacted similarly with $[Rh(CO)_2Cl]_2$ to yield 80% of the 5-membered metallocycle (eq 1.19).[29]

$$(1.18)$$

$$(1.19)$$
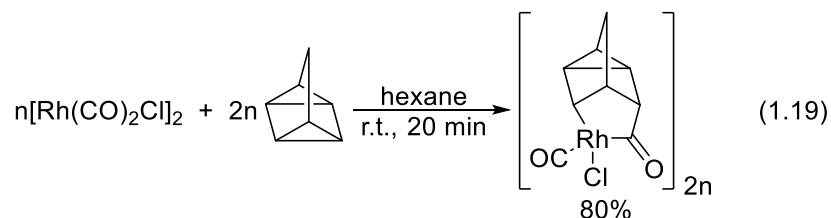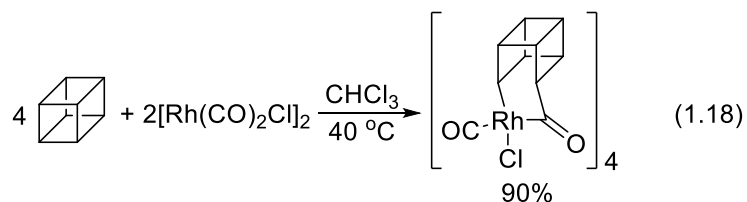
The metal catalyzed symmetry forbidden rearrangements are usually triggered by silver(I) complexes. It is suggested that the weak coordination of silver(I) to the strained C-C bond with partial π-bond character is involved in the first step, followed by intermediate formation with Ag-C bond and carbocation. For example, the rearrangement of tricyclohexane by $AgPF_6$ reported by Katz goes through the proposed mechanism depicted in Scheme 1.2.[35]
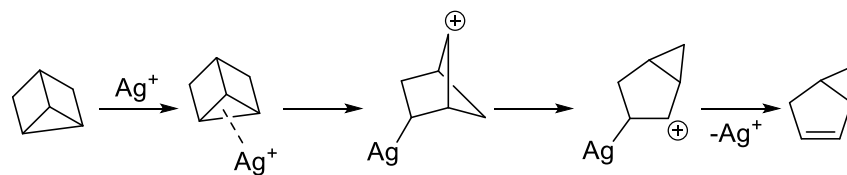
Scheme 1.2 Proposed Mechanism for the Ag$^+$ Catalyzed Rearrangement of Tricyclohexane

Interestingly, heterolytic cleavage of C-C bond to form M-C bond and carbocation intermediate in protic solvent by low valent [Rh(CO)$_2$Cl]$_2$ has also been proposed. In the [Rh(CO)$_2$Cl]$_2$ catalyzed rearrangement of tricycle[4.1.0.0]heptane carried out in MeOH, trapping products by the solvent were isolated (eq 1.20 and Scheme 1.3).[34] A carbocation intermediate is likely formed.
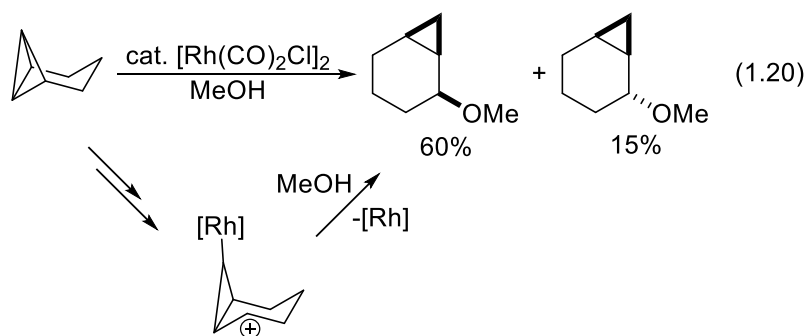
Scheme 1.3 [Rh(CO)$_2$Cl]$_2$ Catalyzed Rearrangement of Tricycle[4.1.0.0]heptane in MeOH.

1.4.2.2 1974-1988

In 1974-1988, the investigations on CCA are stoichiometric based with greatly broadened substrate scopes. There are successful reports on CCA of unstrained hydrocarbons.

Eilbracht reported the stoichiometric CCA of spiro[4.4]nona-1,3-diene with iron and molybdenum carbonyl complexes (eqs 1.21 and 1.22).[41] The relatively unstrained cyclopentane ring was cleaved driven by pre-coordination of metal to the diene moiety and subsequent aromatization.

$$\text{Fe}_2(\text{CO})_9 + \quad \xrightarrow[\text{reflux, 1.5 h}]{\text{C}_6\text{H}_6} \quad \text{(CO)}_2\text{Fe} \quad + \quad \text{Fe(CO)}_3 \qquad (1.21)$$

1 equiv   2%   42%

$$\text{Mo(CO)}_3(\text{diglyme}) + \quad \xrightarrow[\text{40 °C, 4 h}]{\text{hexane}} \quad \text{(CO)}_3\text{Mo} \qquad (1.22)$$

2 equiv   21%
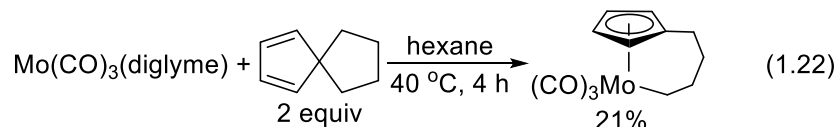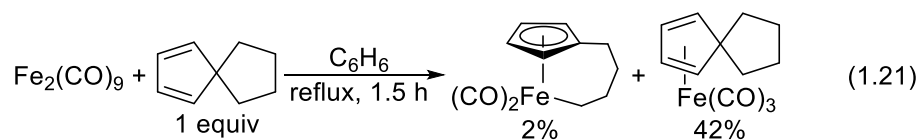
Crabtree in 1984 reported the CCA of 1,1-dimethylcyclopentane with iridium complex (Scheme 1.4).[18] The alkane first undergoes dehydrogenation with *t*-butylethylene as acceptor to form the iridium-diene π complex intermediate. Further heating results in methyl transfer and aromatization to give CCA product.

$$\left[\begin{array}{c} \text{S} \quad \text{H} \quad \text{L} \\ \text{Ir} \\ \text{S} \quad \text{H} \quad \text{L} \end{array}\right]^{\oplus} \text{SbF}_6{}^{\ominus} + \quad \xrightarrow[\text{150 °C, 8 h}]{^t\text{Bu}} \quad \text{---IrL}_2{}^+ \xrightarrow{\text{12 h}} \left[\begin{array}{c} \text{Me} \\ \text{Ir} \\ \text{L} \quad \text{L} \end{array}\right]^{\oplus} \text{SbF}_6{}^{\ominus}$$

50%

L = P(*p*-FC$_6$H$_4$)$_3$, S = acetone
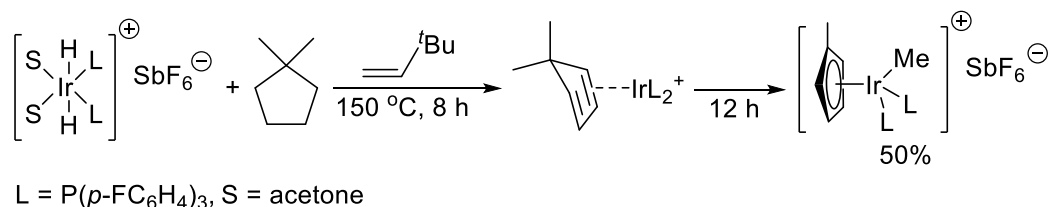
Scheme 1.4 Proposed Mechanism for the CCA of 1,1-Dimethylcyclopentane

Ogoshi reported an interesting finding on stoichiometric CCA by nucleophilic substitution. Rh^I(oep)$^-$ anion undergoes nucleophilic attack at the tri-bridged carbon in quadricyclane and [4.1.0.0]tricycloheptane followed by rapid protonation with solvent to give the corresponding Rh^{III}(oep)(alkyl) product in 23% and 24% yields, respectively (eqs 1.23 and 1.24).[40,44]

$$\text{Rh(oep)}^{\ominus} + \quad \xrightarrow[\text{50 °C, 10 h}]{\text{EtOH}} \quad \text{Rh(oep)} \qquad (1.23)$$

23%

$$Rh(oep)^{\ominus} + \quad \xrightarrow[50\ ^\circ C,\ 27\ h]{EtOH} \quad \underset{\underset{24\%}{Rh(oep)}}{} \qquad (1.24)$$
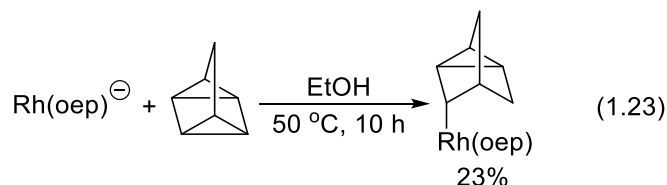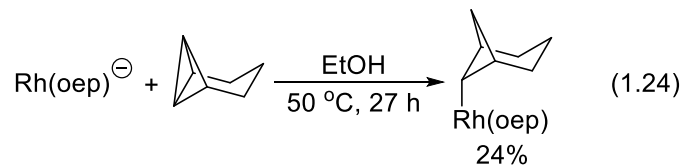
1.4.2.3 1988 and After

In 1988, Chatani reported the first catalytic CCA with insertion of another reagent to construct new carbon-carbon bond and carbon-heteroatom bond, which established the foundation of catalytic CCA development. In this report, Chatani described the palladium catalyzed ring opening of various substituted methylenecyclopropanes with Me_3SiCN to give β-(cyanomethyl)allylsilanes (eq 1.25).[48] Followed by this initial discovery, formation of new C-N,[67,80] C-O,[68,82,89] C-C(heteroaryl),[72,78] C-B[73] and C-Sn[84] bonds based on substituted methylenecyclopropane skeletons have been reported.

$$\underset{Ph}{\overset{Ph}{\diagdown}} + Me_3SiCN \xrightarrow[\underset{reflux,\ 20\ h}{toluene}]{\overset{PdCl_2\ (4\ mol\%)}{pyridine\ (8\ mol\%)}} \underset{Ph}{\overset{SiMe_3}{Ph}}\underset{56\%}{CN} \qquad (1.25)$$
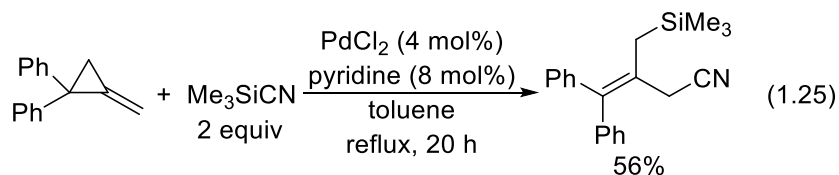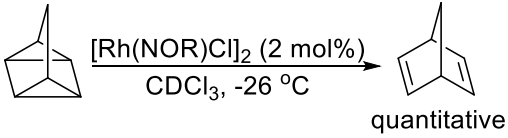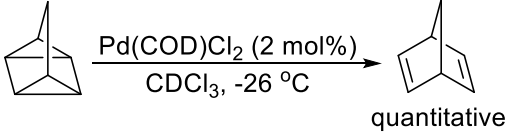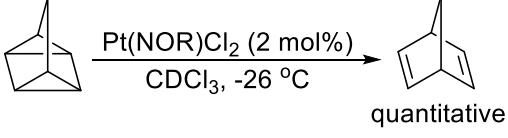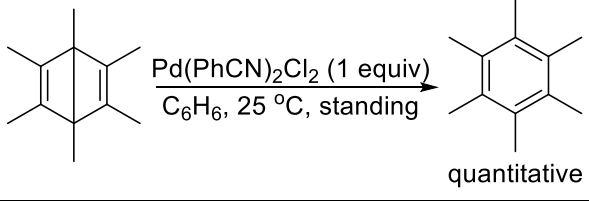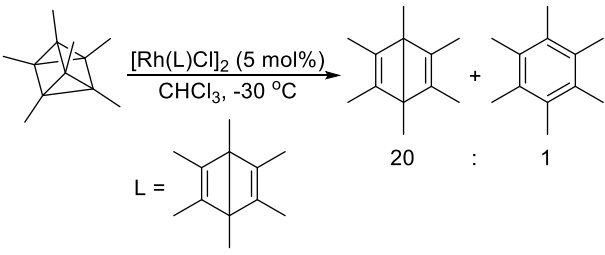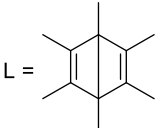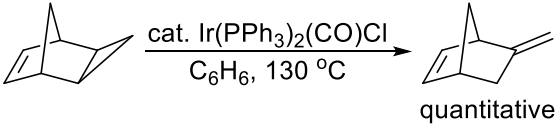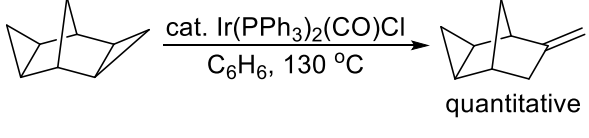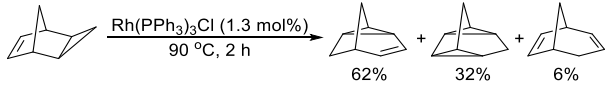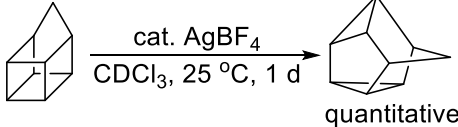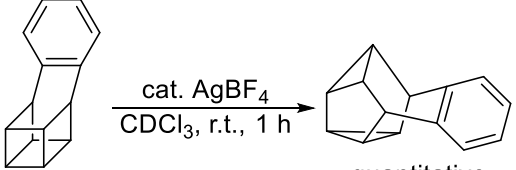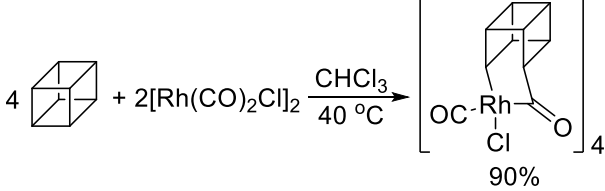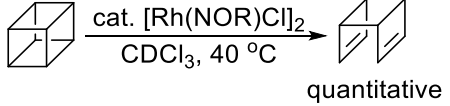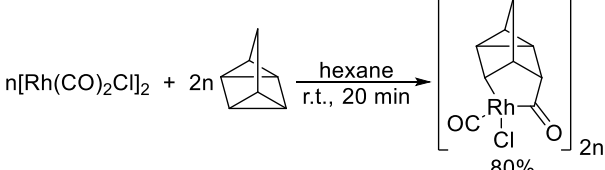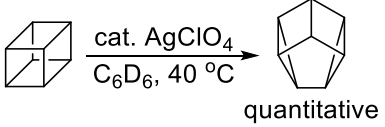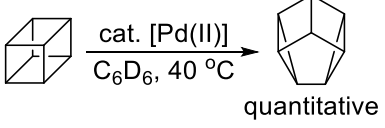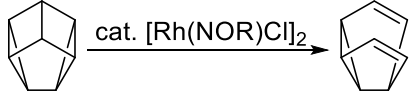
Goldman designed an elegant catalytic alkane metathesis which transformed *n*-hexane into a distribution of C_2 to C_{15} *n*-alkanes (eq 1.26).[20] The reaction is proposed to go through acceptorless dehydrogenation, isomerization, olefin metathesis and hydrogenation by the cooperation of hydrogenation/dehydrogenation catalyst and Schrock type metathesis catalyst (Scheme 1.5).

Ir cat (0.14 mol%)

$$n\text{-}C_6H_{14} \xrightarrow[\text{125 °C, 1 d}]{\text{Mo cat (0.22 mol%)}} \text{linear } C_2 \text{ to } C_{15} \qquad (1.26)$$

135 TON
w.r.t. Ir

Ir cat = (structure with O−P(^{t}Bu)$_2$, Ir−(C$_2$H$_4$), O−P(^{t}Bu)$_2$)

Mo cat = (structure with ^{i}Pr, ^{i}Pr, N, Mo, OC(CF$_3$)$_2$(CH$_3$), Ph(H$_3$C)$_2$CHC, OC(CF$_3$)$_2$(CH$_3$))

2 (hexane)

2[Ir]
2[Ir]H$_2$
dehydrogenation

2 (1-hexene)

[Mo]
metathesis

C$_3$H$_7$ —— C$_4$H$_9$ + ══

isomerization

isomerization

C$_3$H$_7$ —— C$_4$H$_9$ + ══

+

metathesis [Mo]

[Mo] *metathesis*

C$_3$H$_7$ —— + C$_5$H$_{11}$ ——

+

2[Ir]H$_2$

2[Ir]H$_2$

2[Ir]

2[Ir]

hydrogenation

hydrogenation

+

Scheme 1.5 Proposed Mechanism for the Catalytic Alkane Metathesis
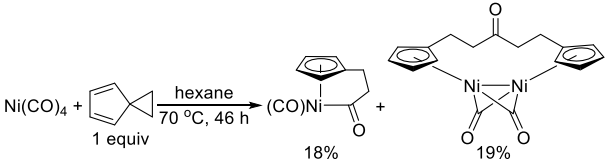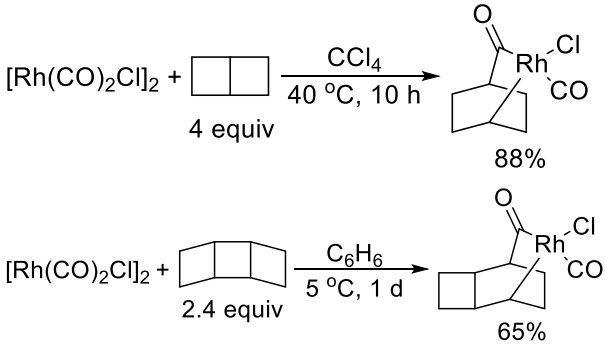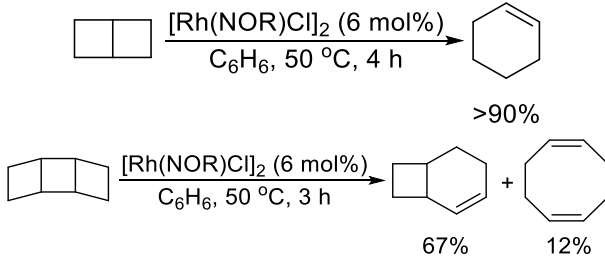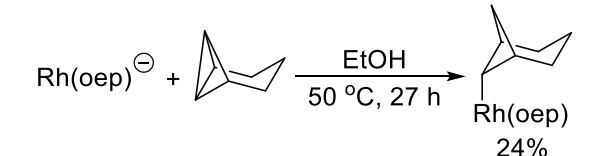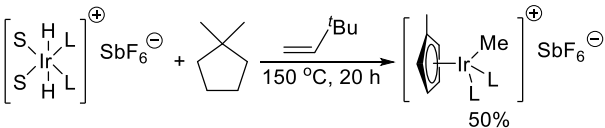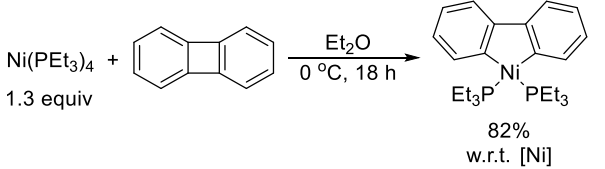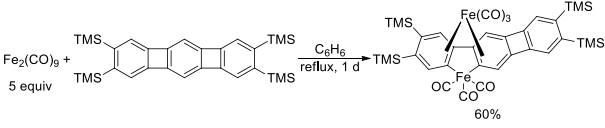
Table 1.4 Timeline of CCA of Hydrocarbons.
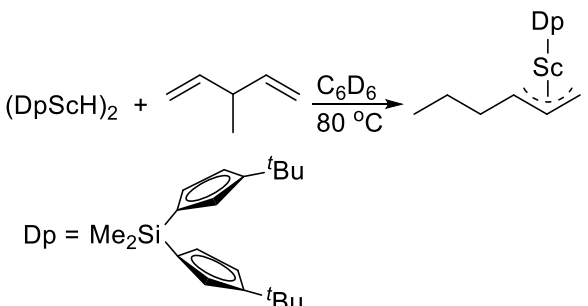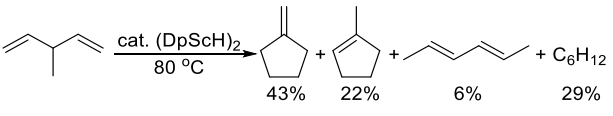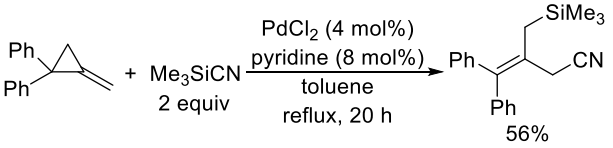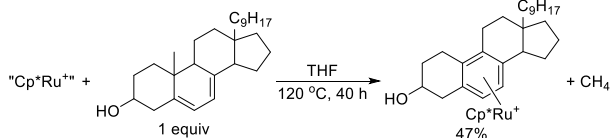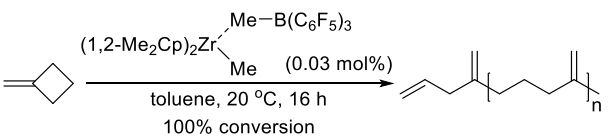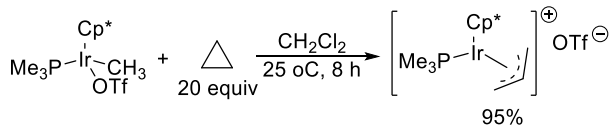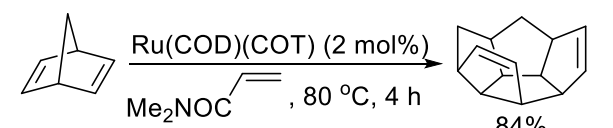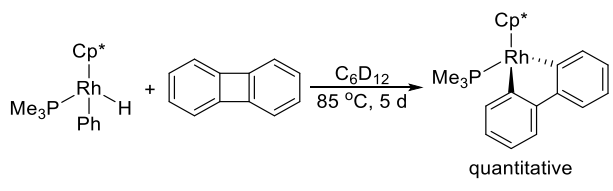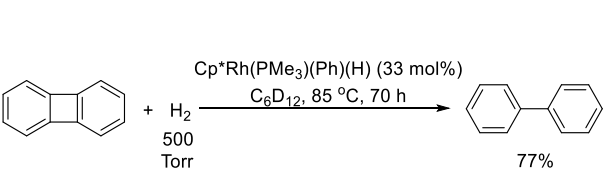
Stoichiometric	Catalytic
Tipper 1955[21] $PtCl_2$ + △ $\xrightarrow[\text{r.t., overnight}]{\text{acetic anhydride}}$ $\left[\begin{array}{c} Cl \\ Cl \end{array} Pt \diamond \right]_n$	
	Hogeveen 1967[22] $\xrightarrow[\text{CDCl}_3, -26\ ^oC]{\text{[Rh(NOR)Cl]}_2 \text{ (2 mol\%)}}$ quantitative $\xrightarrow[\text{CDCl}_3, -26\ ^oC]{\text{Pd(COD)Cl}_2 \text{ (2 mol\%)}}$ quantitative $\xrightarrow[\text{CDCl}_3, -26\ ^oC]{\text{Pt(NOR)Cl}_2 \text{ (2 mol\%)}}$ quantitative
	Maitlis 1967[23] $\xrightarrow[\text{C}_6\text{H}_6, 25\ ^oC, \text{ standing}]{\text{Pd(PhCN)}_2\text{Cl}_2 \text{ (1 equiv)}}$ quantitative
	Hogeveen 1967[24] $\xrightarrow[\text{CHCl}_3, -30\ ^oC]{\text{[Rh(L)Cl]}_2 \text{ (5 mol\%)}}$ + 20 : 1 L =
	Hogeveen 1969[25] $\xrightarrow[\text{C}_6\text{H}_6, 130\ ^oC]{\text{cat. Ir(PPh}_3)_2\text{(CO)Cl}}$ quantitative $\xrightarrow[\text{C}_6\text{H}_6, 130\ ^oC]{\text{cat. Ir(PPh}_3)_2\text{(CO)Cl}}$ quantitative

	Katz 1969[26]
	Rh(PPh₃)₃Cl (1.3 mol%), 90 °C, 2 h → 62% + 32% + 6%
	Paquette 1970[27]
	cat. AgBF₄, CDCl₃, 25 °C, 1 d → quantitative
	cat. AgBF₄, CDCl₃, r.t., 1 h → quantitative
Halpern 1970[28]	Halpern 1970[28]
4 + 2[Rh(CO)₂Cl]₂ →(CHCl₃, 40 °C) [OC–Rh(Cl)(O)]₄ 90%	cat. [Rh(NOR)Cl]₂, CDCl₃, 40 °C → quantitative
Halpern 1970[29]	
n[Rh(CO)₂Cl]₂ + 2n →(hexane, r.t., 20 min) [OC–Rh(Cl)(O)]₂ₙ 80%	
	Eaton 1970[30]
	cat. AgClO₄, C₆D₆, 40 °C → quantitative
	cat. [Pd(II)], C₆D₆, 40 °C → quantitative
	cat. [Rh(NOR)Cl]₂ →

Pettit 1970[31]	Pettit 1970[31]
$[Rh(CO)_2Cl]_2$ + (1 equiv) $\xrightarrow{CHCl_3}$ (Rh complex with Cl, CO, O) $[Rh(CO)_2Cl]_2$ + (1 equiv) $\xrightarrow{CHCl_3}$ (Rh complex with Cl, CO, OH)	(structure) $\xrightarrow[C_6H_6,\ 63\ ^oC,\ 3\ h]{[Rh(NOR)Cl]_2\ (10\ mol\%)}$ + + 70% 2% 28% (structure) $\xrightarrow[\substack{acetone \\ 56\ ^oC,\ 1\ min}]{AgBF_4\ (1\ equiv)}$ + + 18% 80% 2%

Gassman 1971[32]

(structure) $\xrightarrow[CH_3CN,\ r.t.,\ 15\ min]{[Rh(CO)_2Cl]_2\ (4\ mol\%)}$ (structure) 98%

(structure) $\xrightarrow[CH_3CN,\ 65\ ^oC,\ 2\ d]{trans\text{-}Rh(PPh_3)_2(CO)Cl\ (5\ mol\%)}$ +
 92% 5%

Masamune 1971[33]

(structure) $\xrightarrow[C_6H_6,\ r.t.]{AgClO_4\ (33\ mol\%)}$ > 90%

(structure) $\xrightarrow[C_6H_6,\ 26\ ^oC]{AgClO_4\ (33\ mol\%)}$ +
 69% 20%

(structure) $\xrightarrow[C_6H_6,\ 26\ ^oC]{AgClO_4\ (33\ mol\%)}$ +
 5% 94%

(structure) $\xrightarrow[C_6H_6,\ 26\ ^oC]{AgClO_4\ (33\ mol\%)}$ 97%

Gassman 1971[34]

(structure) $\xrightarrow[MeOH]{cat.\ [Rh(CO)_2Cl]_2}$ OMe + OMe
 60% 15%

Katz 1972[35]

(structure) $\xrightarrow[CH_2Cl_2,\ r.t.,\ 20\ h]{AgPF_6\ (30\ mol\%)}$ +
 67% 33%

(structure) $\xrightarrow[CCl_4,\ r.t.,\ 10\ min]{[Rh(CO)_2Cl]_2\ (10\ mol\%)}$ + + dimer
 10% 38% 38%

	Gassman 1972[36]
	Furukawa 1974[37]
	Miller 1974[38]
	Weissberger 1975[39]
Ogoshi 1975[40]	
Eilbracht 1976[41]	

Eilbracht 1976[42]	
Ni(CO)$_4$ + [structure] $\xrightarrow[\text{70 °C, 46 h}]{\text{hexane}}$ (CO)Ni [structure] + [Ni–Ni structure] 1 equiv 18% 19%	
Halpern 1979[43]	**Halpern 1979[43]**

[Rh(CO)$_2$Cl]$_2$ + [structure] $\xrightarrow[\text{40 °C, 10 h}]{\text{CCl}_4}$ [Rh structure]
4 equiv   88%
 	
[Rh(CO)$_2$Cl]$_2$ + [structure] $\xrightarrow[\text{5 °C, 1 d}]{\text{C}_6\text{H}_6}$ [Rh structure]
2.4 equiv   65%
	[structure] $\xrightarrow[\text{C}_6\text{H}_6\text{, 50 °C, 4 h}]{\text{[Rh(NOR)Cl]}_2\text{ (6 mol\%)}}$ [structure]
	           >90%
	
	[structure] $\xrightarrow[\text{C}_6\text{H}_6\text{, 50 °C, 3 h}]{\text{[Rh(NOR)Cl]}_2\text{ (6 mol\%)}}$ [structure] + [structure]
	      67% 12%

Ogoshi 1980[44]	

Rh(oep)$^\ominus$ + [structure] $\xrightarrow[\text{50 °C, 27 h}]{\text{EtOH}}$ [structure]
         Rh(oep)
         24%	

Crabtree 1984[18]	
[S,H,L Ir S,H,L]$^\oplus$ SbF$_6$$^\ominus$ + [structure] $\xrightarrow[\text{150 °C, 20 h}]{}$ [Ir structure]$^\oplus$ SbF$_6$$^\ominus$ 50% L = P(*p*-FC$_6$H$_4$)$_3$, S = acetone	
Eisch 1985[45]	

Ni(PEt$_3$)$_4$ + [structure] $\xrightarrow[\text{0 °C, 18 h}]{\text{Et}_2\text{O}}$ [Ni structure]
1.3 equiv   Et$_3$P   PEt$_3$
                 82%
              w.r.t. [Ni]	

Vollhardt 1985[46]	
Fe$_2$(CO)$_9$ + [TMS structure] $\xrightarrow[\text{reflux, 1 d}]{\text{C}_6\text{H}_6}$ [Fe(CO)$_3$ structure] 5 equiv 60%	

Bercaw 1988[47] (DpScH)$_2$ + $\xrightarrow[\text{80 °C}]{\text{C}_6\text{D}_6}$ Dp Sc Dp = Me$_2$Si with ^{t}Bu, ^{t}Bu substituents	Bercaw 1988[47] $\xrightarrow[\text{80 °C}]{\text{cat. (DpScH)}_2}$ + + + C$_6$H$_{12}$ 43% 22% 6% 29%
	Chatani 1988[48] Ph, Ph + Me$_3$SiCN (2 equiv) $\xrightarrow[\substack{\text{toluene}\\\text{reflux, 20 h}}]{\substack{\text{PdCl}_2\text{ (4 mol\%)}\\\text{pyridine (8 mol\%)}}}$ Ph, Ph SiMe$_3$ CN 56%
Chaudret 1993[49] "Cp*Ru$^+$" + (steroid, C$_9$H$_{17}$, HO) 1 equiv $\xrightarrow[\text{120 °C, 40 h}]{\text{THF}}$ (product, C$_9$H$_{17}$, HO, Cp*Ru$^+$) + CH$_4$ 47%	
	Marks 1993[50] $\xrightarrow[\substack{\text{toluene, 20 °C, 16 h}\\\text{100\% conversion}}]{(1,2\text{-Me}_2\text{Cp})_2\text{Zr}\text{, Me, Me–B(C}_6\text{F}_5)_3 \text{ (0.03 mol\%)}}$ (polymer)$_n$
Bergman 1993[51] Me$_3$P–Ir(Cp*)(CH$_3$)(OTf) + (20 equiv) $\xrightarrow[\text{25 °C, 8 h}]{\text{CH}_2\text{Cl}_2}$ [Me$_3$P–Ir(Cp*)]$^{\oplus}$ OTf$^{\ominus}$ 95%	
	Mitsudo, Watanabe 1994[52] $\xrightarrow[\text{Me}_2\text{NOC} \text{, 80 °C, 4 h}]{\text{Ru(COD)(COT) (2 mol\%)}}$ (product) 84%
Jones 1994[53] Me$_3$P–Rh(Cp*)(Ph)(H) + (biphenylene) $\xrightarrow[\text{85 °C, 5 d}]{\text{C}_6\text{D}_{12}}$ Me$_3$P–Rh(Cp*)(product) quantitative	Jones 1994[53] (biphenylene) + H$_2$ (500 Torr) $\xrightarrow[\text{C}_6\text{D}_{12}, 85 °C, 70 h]{\text{Cp*Rh(PMe}_3)(\text{Ph})(\text{H}) \text{ (33 mol\%)}}$ (biphenyl) 77%
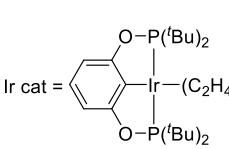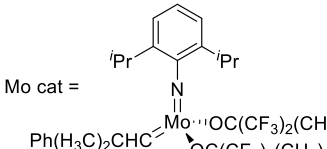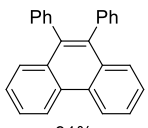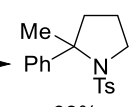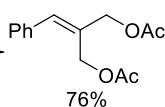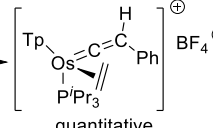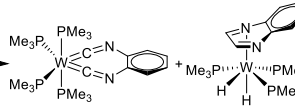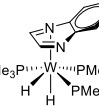
Rosenthal, Burlakov 1994[54]

Cp₂Zr(THF)(Me₃SiC₂SiMe₃) +
2 equiv

Me₃Si—≡—≡—SiMe₃ →(THF, r.t., 8 h)→ Cp₂Zr / ZrCp₂ product

45%

Suzuki 1994[55]

Cp—Ru(H)—Ru—Cp (trinuclear Ru hydride cluster with Cp* ligands)

+ cyclopentadiene (5 equiv) →(THF, r.t., 12 h)→ Ru₂ product

quantitative

Crabtree 1995[56]

[Ir(COD)Cl]₂ + biphenylene (1 equiv) →(CH₂Cl₂, 90 °C, 2 h)→ dimeric Ir complex

89 %

Casey, Hallenbeck 1995[57]

(Cp*₂YH)₂ + methylenecyclobutane (1 equiv) →(C₆D₁₁CD₃, -78 °C)→ *Cp—Y(Cp*) product

quantitative

Rubin 1996[58]

fullerene derivative →(CpCo(CO)₂, xylene, 135 °C)→ CpCo coordinated fullerene

25 %

Jones 1997[59]

Cp*Rh(CH₂=CH₂)₂ + biphenylene →(C₆H₁₂, 120 °C, 2.5 d)→ Cp*Rh—Rh Cp* product

2 equiv

83%

Jones 1997[59]

biphenylene + CO (500 Torr) →(Cp*Rh(CO)₂ (22 mol%), C₆D₁₂, 160 °C, 6 d)→ fluorenone

97%

biphenylene + CO (500 Torr) →(Cp*Co(CO)₂ (33 mol%), C₆D₁₂, 170 °C, 45 h)→ fluorenone

85%

Cp* OC—Rh—CO + [biphenylene] $\xrightarrow[h\nu,\ 3\ d]{C_6H_{12}}$ [Cp*Rh(CO) biphenyl product] 4 equiv yield not reported Cp* Co + [biphenylene] $\xrightarrow[90\ ^oC,\ 4\ d]{C_6D_{12}}$ [Cp*Co–Co Cp* product] 1 equiv 75%	
	Beletskaya 1997[60] [diphenylcyclopropane] + Et$_3$SiH $\xrightarrow[\text{toluene, 20 }^oC,\ 65\ h]{Rh(PPh_3)_3Cl\ (0.1\ mol\%)}$ [Ph,Ph product SiEt$_3$] 1 equiv 84%
	Yamamoto 1997[61] PhH$_2$CH$_2$C—[methylenecyclopropane] + H–C(Me)(CN)–CN $\xrightarrow[\text{THF, 100 }^oC,\ 2\text{-}3\ d]{Pd(PPh_3)_4\ (10\ mol\%)}$ PhH$_2$CH$_2$C—[product] CN CN Me 2 equiv 82%
Stanley, Rabideau 1998[62] Pt(PPh$_3$)$_2$(C$_2$H$_4$) + [corannulene-type PAH] $\xrightarrow[\begin{array}{c}1.\ r.t.,\ 15\ h\\2.\ reflux,\ 1\ h\end{array}]{\text{toluene}}$ [Pt(PPh$_3$)$_2$ inserted product] Ph$_3$P PPh$_3$ 5-10%	
Jones 1998[63] Pd(PEt$_3$)$_3$ + [biphenylene] $\xrightarrow[68\ ^oC,\ 14\ d]{C_6D_6}$ [dibenzmetallole Pd] 1.5 equiv Et$_3$P PEt$_3$ 98% Pt(PEt$_3$)$_3$ + [biphenylene] $\xrightarrow[80\ ^oC,\ 10\ d]{C_6D_6}$ [dibenzometallole Pt] Et$_3$P PEt$_3$ yield not reported	**Jones 1998**[63] [biphenylene] $\xrightarrow[C_6D_6,\ 120\ ^oC]{Pd(PEt_3)_3\ (10\ mol\%)}$ [tetraphenylene] 16 TON/d [biphenylene] $\xrightarrow[C_6D_6,\ 120\ ^oC]{Pt(PEt_3)_3\ (10\ mol\%)}$ [tetraphenylene] 0.135 TON/d

Yeh 1998[64]

$Fe_3(CO)_{12}$ + [biphenylene] → [diiron complex] **30%**

1 equiv, *n*-heptane reflux, 3 h

$Fe_2(CO)_9$ + [biphenylene] → [diiron complex] **36%**

1 equiv, *c*-hexane reflux, 5 h

$Ru_3(CO)_{12}$ + [biphenylene] → [diruthenium complex] **33%**

1 equiv, *n*-octane reflux, 4 h

$Os_3(CO)_{12}$ + [biphenylene] → [diosmium complex] **23%** + [triosmium cluster] **30%**

33% recovery, 6 equiv, *n*-decane, 200 °C, 15 h

Yamamoto 1998[65]

$Rh(PPh_3)_3Cl$ + [methylenecyclopropane with Ph] → [Rh complex] **95%**

5 equiv, toluene, 50 °C, 16 h

Jones 1998[66]

[biphenylene] + H_2 → [biphenyl] **16 TON/d**

$[Ni(dippe)H]_2$ (20 mol%), toluene-d_8, 50 °C, 0.92 atm

[biphenylene] + H_2 → [biphenyl] **2.2 TON/d**

$Pd(PEt_3)_3$ (20 mol%), toluene-d_8, 70 °C, 0.92 atm

[biphenylene] + H_2 → [biphenyl] **1 TON/12 d**

$Pt(PEt_3)_3$ (20 mol%), toluene-d_8, 120 °C, 0.92 atm

Yamamoto 1998[67]

[cyclopropylidene]-*c*-hex + Bn_2NH → *c*-hex-[allyl]-NBn_2 **72%**

2 equiv, $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (5 mol%), 12.5 mol% dppp, DME, 100 °C, 3 d

Yamamoto 1999[68]

[cyclopropylidene]-Hept + Ph-OH → Hept-[allyl]-O-Ph **69%**

1 equiv, $Pd(PPh_3)_4$ (5 mol%), $P(o\text{-tolyl})_3$ (10 mol%), toluene, 100 °C, 3 d

Jones 1999[69]

1.1 equiv · Ni(dippe)(PhC≡CPh) (10 mol%), O₂ (0.6 mol%), toluene-d_8, 70 °C · 3 TON/h

+ CO, 1 atm · Ni(dippe)(CO)₂ (20 mol%), THF-d_8, 100 °C · 2 TON/d

excess · Ni(dippe)(CN-2,6-xylyl)₂ (17 mol%), THF-d_8, 107 °C · 10 TON/d

Jones 1999[70]

1 equiv · Ni(dippe)(Me₃SiC≡CSiMe₃) (33 mol%), THF, 120 °C, 3 d · 41%

Sweigart 1999[71]

Pt(PPh₃)₂(C₂H₄) + [... Mn(CO)₃]⊕ BF₄⊖, 1 equiv · CH₂Cl₂, r.t., < 1 min · 98%

Yamamoto 2000[72]

5 equiv · Pd(PPh₃)₄ (5 mol%), O=PBu₃ (10 mol%), 120 °C, 28 h · 70%

Suginome, Ito 2000[73]

△=Ph + PhMe₂Si-Bpin, 2 equiv · Pt(PPh₃)₂(C₂H₄) (2 mol%), toluene, 110 °C, 8 h · 79% (E/Z = 83:17)

△=Ph + PhMe₂Si-Bpin, 1.5 equiv · Pd(OAc)₂ (2 mol%), ^{t}OcNC (15 mol%), toluene, 110 °C, 4 h · 78% (E/Z = 17:83)

Jones 2001[74]

+ BuO₂C, 1.3 equiv · Pd(PPh₃)₄ (5 mol%), p-cresol (1 equiv), C₆D₆, 120 °C, 6 d · 93%

+ B(OH)₂, 1 equiv · Pd(PPh₃)₄ (5 mol%), p-cresol (1 equiv), C₆D₆, 120 °C, 3 h · 91%

	Pd(PPh₃)₄ (5 mol%), p-cresol (10 mol%), C₆D₆, 120 °C, 7 h — 2 equiv — 84% Pd(PPh₃)₄ (5 mol%), p-cresol (10 mol%), C₆D₆, 120 °C, 1 d — 1 equiv — 85%
	Jones 2001[75] [Rh(dtbpm)Cl]₂ (10 mol%), C₆D₆, 85 °C, 18 h — 1 equiv — 96% Rh(dtbpm)(BP)Cl (10 mol%), C₆D₆/CD₂Cl₂, 125 °C, 13 h — n-Pr, 1 equiv — 61%
	Jones 2002[76] Ni(PN)(PhC≡CPh) (8 mol%), C₆D₆, 70 °C, 22.5 h — 1 equiv — 98%
	Chirik 2003[77] ⁿBu + H₂ (4 atm), Rh(PPh₃)₃Cl (2 mol%), toluene, 130 °C — ⁿBu, TOF = 0.25 ⁿBu, Rh(PPh₃)₃Cl (2 mol%), toluene, 130 °C — ⁿBu, TOF = 0.05
	Yamamoto 2004[78] Bu, Bu + pyridazine, Pd(PPh₃)₄ (5 mol%), 120 °C, 42-48 h — 5 equiv — Bu, Bu — 38%

	Goldman 2006[20]
	(dehydrogenation to olefin→metathesis→ hydrogenation)

Goldman 2006[20]

(dehydrogenation to olefin→metathesis→ hydrogenation)

$$n\text{-}C_6H_{14} \xrightarrow[\substack{\text{Mo cat (0.22 mol\%)} \\ 125\ ^\circ\text{C, 1 d}}]{\text{Ir cat (0.14 mol\%)}} \text{linear } C_2 \text{ to } C_{15}$$

135 TON
w.r.t. Ir

Ir cat = (structure: $O-P(^tBu)_2$ ... $Ir-(C_2H_4)$ ... $O-P(^tBu)_2$)

Mo cat = (structure: ^iPr ... ^iPr, N, $Ph(H_3C)_2CHC=Mo\cdots OC(CF_3)_2(CH_3)$, $OC(CF_3)_2(CH_3)$)

Radius 2006[79]

$$Ni(Me_2Im)_3 + \text{(biphenylene)} \xrightarrow[\text{r.t., overnight}]{\text{toluene}} \text{(product)}$$

$(Me_2Im)\ Ni\ (ImMe_2)$
84%

Radius 2006[79]

$$\text{(biphenylene)} + \text{(PhC≡CPh)} \xrightarrow[\text{toluene, 80 }^\circ\text{C, overnight}]{Ni_2(^iPr_2Im)_4(COD)\ (1\ mol\%)} \text{(product)}$$

Ph Ph

1 equiv

91%

	Shi 2006[80]
	$$\text{(cyclopropylidene-Me-Ph)} + TsNH_2 \xrightarrow[\text{toluene, 85 }^\circ\text{C, 12 h}]{\substack{Au(PPh_3)Cl\ (5\ mol\%) \\ AgOTf\ (5\ mol\%)}} \text{(product)}$$

Me, Ph, N, Ts

1 equiv

68%

Eisch 2007[81]

$$Zr(OEt)_2(Bu)_2 + Ph_2CH\text{-}CHPh_2 \xrightarrow[\text{THF, 25 }^\circ\text{C, 3 d}]{\substack{75\ W\ \text{bulb (> 300 nm)} \\ Fe(acac)_3\ (1\ mol\%)}} Zr(OEt)_2(CHPh_2)_2$$

2 equiv

quantitative

	Shi 2009[82]

Shi 2009[82]

$$\text{(vinylcyclopropane-Ph)} + PhI(OAc)_2 \xrightarrow[\text{CH}_3\text{CN, 60 }^\circ\text{C, 10 h}]{\substack{Pd(OAc)_2\ (10\ mol\%) \\ Bu_4NI\ (1\ equiv)}} \text{(product)}$$

Ph ... OAc ... OAc

3 equiv

76%

Esteruelas, López, Mascareñas 2010[83]

$$[Tp\ Os(O)(O)(P^iPr_3)]^+ BF_4^- + \text{(vinylidenecyclopropane-Ph)} \xrightarrow[\text{r.t., 30 min}]{C_6H_5F} [Tp\ Os=C=C(H)Ph(P^iPr_3)]^+ BF_4^-$$

1.4 equiv

quantitative

Parkin 2010[84]

$$\text{(Me}_3\text{P)}_x\text{W(H)(CH}_2)\text{(PMe}_3)_x + \text{(quinoxaline)} \xrightarrow[\text{90 }^\circ\text{C, 18 h}]{C_6D_6} \text{(product 15\%)} + \text{(product 24\%)}$$

1 equiv

15%

24%

	Marek 2010[85] **Marek 2010[86]**
Chan 2010[87] 	
Chaplin 2010[88] 	
	Matsuda 2011[89]

	Shi 2011[90]
Chan 2012[91] 	**Chan 2012**[91]
	Tilley, Bergman 2013[92]
Hou 2014[93] 	

1.5 Water as Transfer Hydrogenating Agent

Water protonates carbanions readily due to its lower pKa value than most carbanions of hydrocarbon (Table 1.5).[94] This is why anhydrous solvents are used for Grignard type reactions. However, water seldom served as a hydrogen atom donor because of the strong O-H bond (Table 1.5).[95] Therefore, catalytic hydrogenation of C-C σ-bond using H_2O is a challenging research (eq 1.27).

Table 1.5 pKa and X-H BDE Values of H_2O and Selected Hydrocarbons.

Substrate	pKa (in H_2O)	X-H BDE / kcalmol^{-1}
HO-H	15.7	118.8
H_3C-H	48	105.0
Bn-H	41	89.7
Ph_3C-H	31.5	81
$PhC\equiv C$-H	23	133

$$\text{R}-\text{R'} + \text{H}_2\text{O} \xrightarrow{\text{catalyst}} \text{R}-\text{H} + \text{R'}-\text{H} + 1/2\text{O}_2 \qquad (1.27)$$
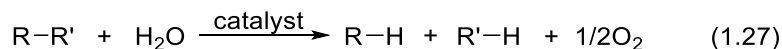
H_2 gas is a commonly employed hydrogenating agent nowadays because of its atom economical nature and much cheaper than most organic H atom donors like silane. However, H_2 exhibits poor solubility in most organic solvents under ambient conditions and low energy density. The storage and transfer via gas cylinder is inconvenient as well. In contrast, H_2O does not have the drawbacks mentioned above.

There are only three reported systems for the stoichiometric hydrogenation of carbon center using water via radical mechanism: (1) titanium/H_2O system; (2) cobalt/H_2O system; and (3) borane/H_2O system.

1.5.1 Titanium/H_2O System

Barrero and Oltra probably observed the first H atom transfer from H_2O to carbon skeleton mediated by titanium complex in 2002. During their investigations on the Cp_2TiCl mediated transannular cyclization of epoxygermacrolide in the presence of H_2O, the unexpected reduction product was obtained in high yield (eq 1.28).[96a] Labeling experiment using D_2O confirmed water as the hydrogen source. Later, the Cp_2TiCl/H_2O system has been utilized to reduce epoxides[96b] and ketones[96c] into alcohols (eqs 1.29 and 1.30).

(1.28)

epoxygermacrolide

Cp$_2$TiCl (3.3 equiv)
H$_2$O (28 equiv)
THF, 30 min

71%

Cp$_2$TiCl (2.2 equiv)
H$_2$O (40 equiv)
THF, r.t., 6 h

(1.29)

60 - 85%

Cp$_2$TiCl (3 equiv)
H$_2$O (100 equiv)
25 °C, 60 h

(1.30)

94%
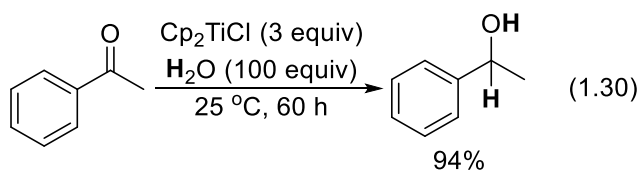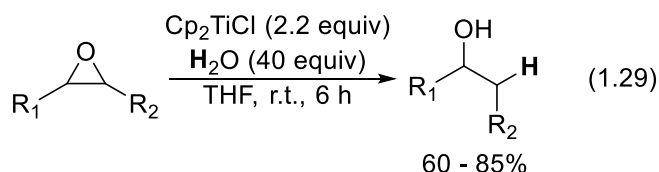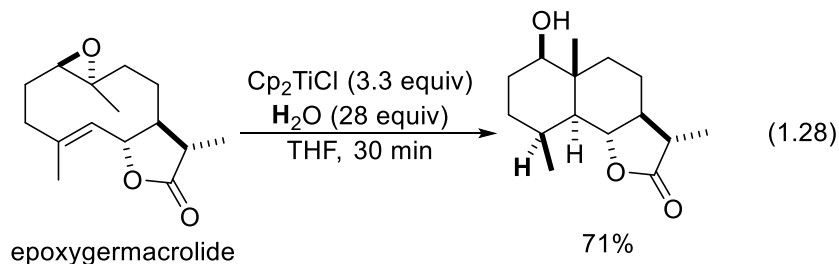
The authors suggested that coordination of H$_2$O to Cp$_2$TiCl to form Cp$_2$Ti(OH$_2$)Cl[96b,d] or Cp$_2$Ti(OH$_2$)$_2$[96c] intermediates as the active hydrogen atom donor (Scheme 1.6). The coordination of H$_2$O to the titanium metal center weakens the O-H bond. Computational analysis shows that the reaction energy of eq 1.31 is endothermic by 49.4 kcal/mol, which is about 70 kcal/mol lesser than the BDE of O-H bond in water.[96d] Replacing the water with more acidic phenol resulted in very low yield of reduction product, suggesting that protonation of carbon center is unlikely.

Cp$_2$Ti^{III}(OH$_2$)Cl
-Cp$_2$Ti^{IV}(OH)Cl

hydrolysis
work up
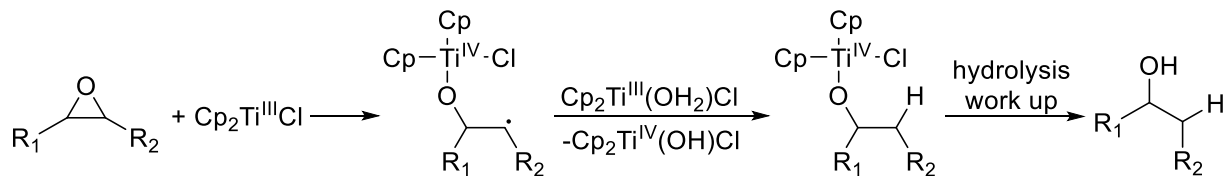
Scheme 1.6 Proposed Mechanism for the Epoxide Reduction

ΔH = 49.4 kcal/mol

+ "H·"   (1.31)

28
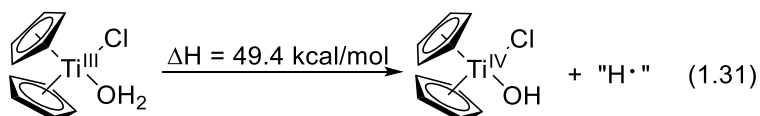
1.5.2 Cobalt/H$_2$O System

Selective reduction of α,β-unsaturated aldehydes and ketones to the corresponding saturated carbonyl compounds by Co$_2$(CO)$_8$/H$_2$O system has been reported (eq 1.32).[97] In situ formation of CoH(CO)$_4$ was proposed to reduce the C=C double bond. Since the author did not discuss how CoH(CO)$_4$ was formed from Co$_2$(CO)$_8$, these two mechanistic possibilities may be operating based on known cobalt chemistry: (1) oxidative addition of H$_2$O with Co$_2$(CO)$_8$ (eq 1.33);[98] and (2) disproportionation of Co$_2$(CO)$_8$ to form Co(CO)$_4^-$ followed by protonation with H$_2$O (Scheme 1.7).[99]

$$Co_2(CO)_8 + H_2O \rightleftharpoons CoH(CO)_4 + Co(OH)(CO)_4 \qquad (1.33)$$

$$3/2 Co_2(CO)_8 \longrightarrow 2 Co(CO)_4^- + Co^{2+} + 4CO$$

$$Co(CO)_4^- + H_2O \longrightarrow CoH(CO)_4 + OH^-$$
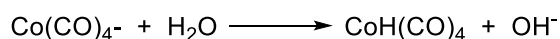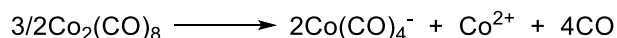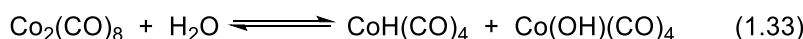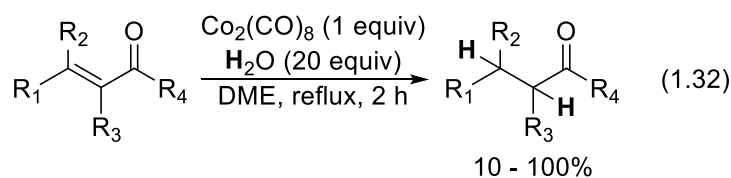
Scheme 1.7 Proposed CoH(CO)$_4$ Formation from Disproportionation Channel.

1.5.3 Borane/H$_2$O System

Hydrogenation of O-alkyl thiocarbonate ester to give alkane has been reported using BMe$_3$/H$_2$O combination (eq 1.34 and scheme 1.5).[100] The role of BMe$_3$ is similar to Cp$_2$TiCl mentioned previously. Computational analysis suggested that coordination of H$_2$O to BMe$_3$ to form H$_2$O-BMe$_3$ intermediate weakened the O-H bond by 30 kcal/mol.

BMe$_3$ (2.5-4 equiv)

H$_2$O (5 equiv)

benzene, air, r.t., 1 h

R−H + (1.34)

MeS SMe

42 - 99%

initiation

BMe$_3$ + O$_2$ ⟶ Me·

propagation

Me·

MeS SMe

R·

Me$_2$B-OH + R-H   Me$_3$B-OH$_2$
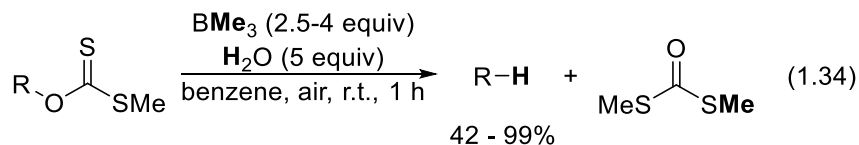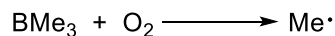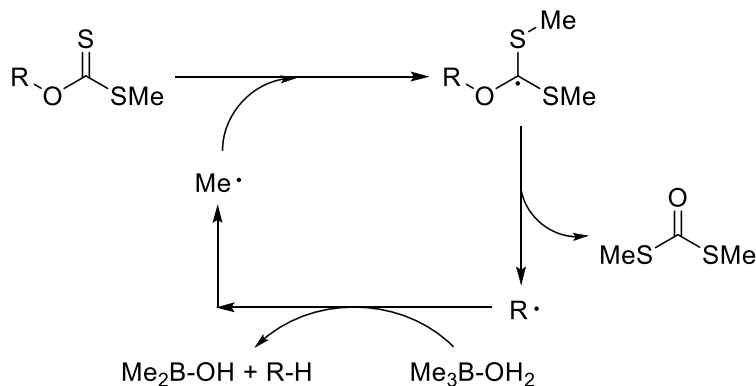
Scheme 1.7 Proposed Mechanism for Xanthate Reduction.

1.6 Porphyrins and Group 9 Metalloporphyrins

1.6.1 Porphyrin Ligands

Porphyrins are planar heterocyclic macrocycles with four pyrrole subunits interconnected by at their α carbons by methane bridges (Figure 1.1). They contain 22 π electrons with 18 of them in delocalization to contribute the aromaticity.[101] Various *meso-* and *β*-substituted porphyrins can be prepared easily by condensation.[102] Substituting four aryl groups at *meso-*positions gives tetraarylporphyrins which generally show better solubility in organic solvents. The first synthesis of porphyrin was reported by Rothemund in 1935.[103]

Porphyrins commonly act as macrocyclic dianionic tetradentate ligands upon deprotonation of the two pyrrolic protons. The diagonal radii of the central cavity is 2.098 Å,

which allow the coordination of various metal of suitable sizes.[104] Metalloporphyrin is formed when metal is coordinated.

meso

β

α

N HN

2.098 Å

C_t

NH N
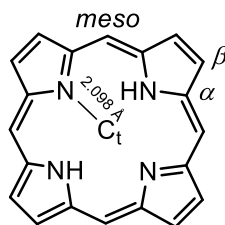
Figure 1.1 Structure of Porphyrin

1.6.2 Metalloporphyrins

Naturally occurring metalloporphyrins are the most common and best known metal complexes in nature. The universal coordination ability of porphyrin and the conformational flexibility allow diverse biological functions.[105] Hemoglobins (heme b) function as oxygen carrier by reversible oxygen binding (Figure 1.2a).[106] Coenzymes B_{12} work as rearrangement catalyst due to its weak Co-C bond (Figure 1.2b).[107] Chlorophylls are green pigments that harvest light and transform light energy into chemical energy (Figure 1.2c).[108]

Synthetic metalloporphyrins can be made by replacing the pyrrole protons with metal ions (eq 1.35).[109]

heme b

coenzymes B$_{12}$
R = 5'-deoxyadenosyl, Me, OH, CN

chlorophyll a; R = Me
chlorophyll b; R = CHO
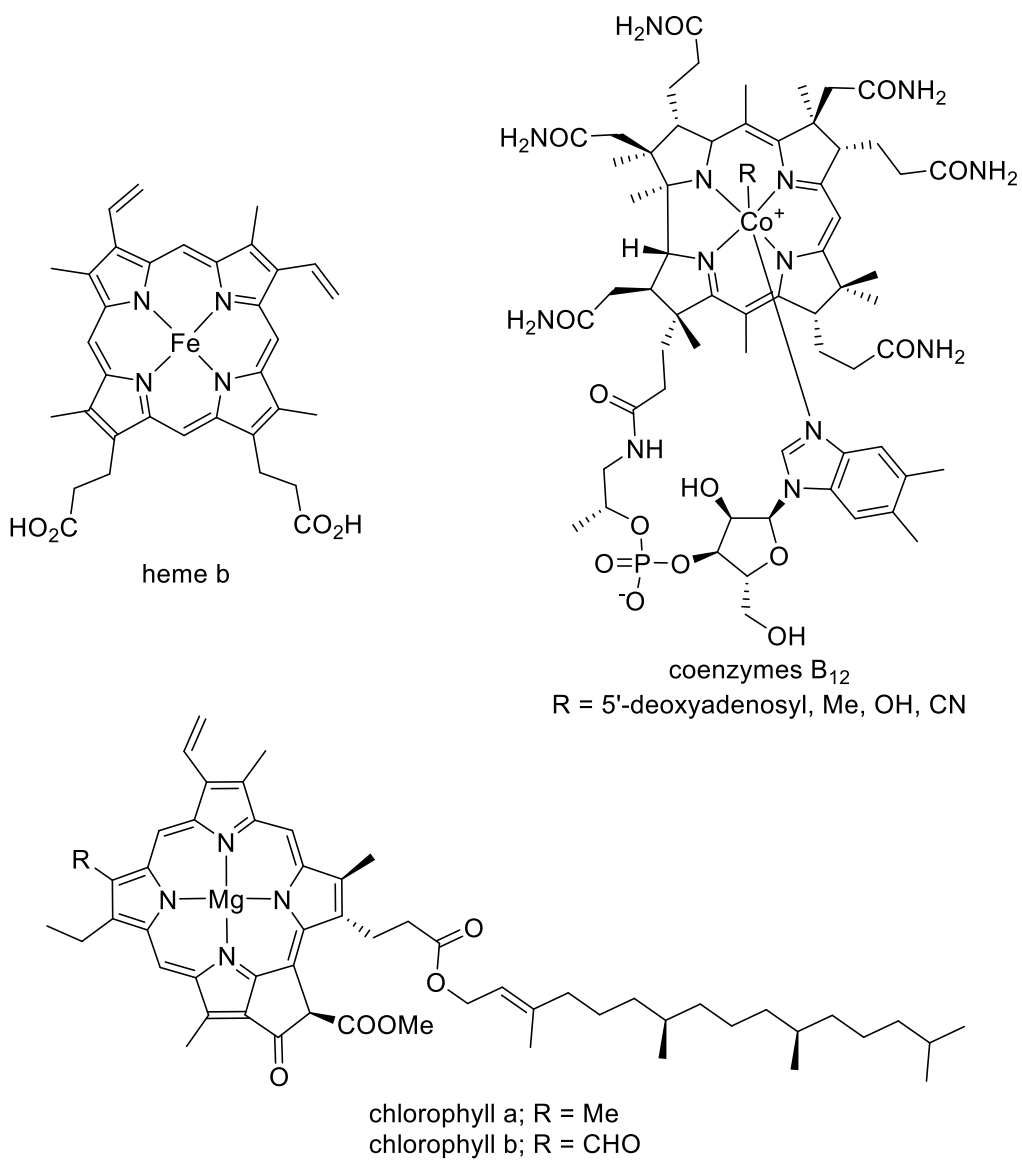
Figure 1.2(a) Structure of Heme b; (b) Structure of Coenzymes B$_{12}$; (c) Structure of Chlorophylls.

$$M^{n+} + \text{porphyrin} \underset{\text{demetalation}}{\overset{\text{metalation}}{\rightleftharpoons}} \text{metalloporphyrin} + 2H^+ \quad (1.35)$$
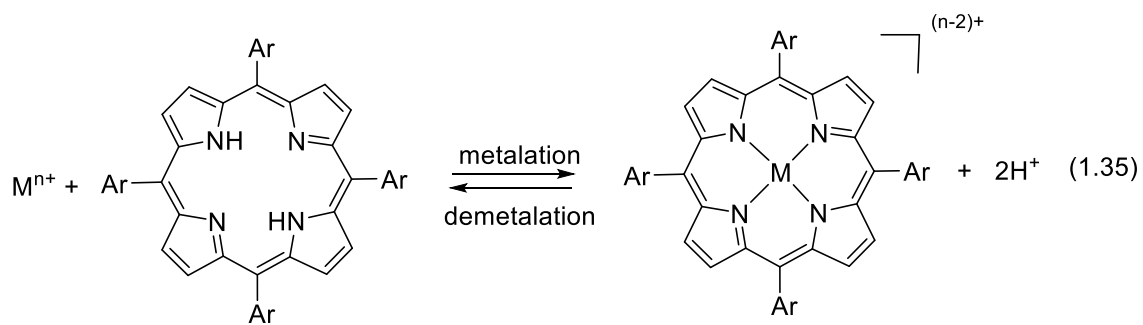
Porphyrin ligands are selective towards coordination of metal ions with ionic radii ranging from 60 to 70 pm. Therefore, 1st row transition metal ions usually fit into the central cavity to form in-plane square planar complexes.[110] However, 2nd and 3rd row transition metal ions with larger ionic radii form complexes with slightly out-of-plane structures (Figure 1.3 and Table 1.6).
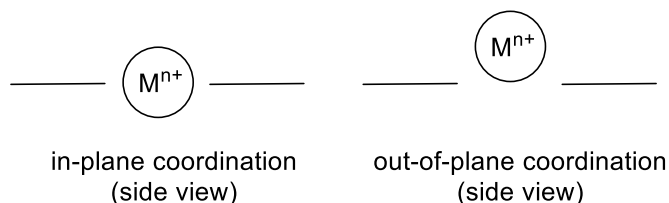
Figure 1.3 In-plane and out-of-plane coordination of metal ions with porphyrins

Table 1.6 Suitability of Various Transition Metal Ions with Porphyrin Coordination[110]

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)

1.6.3 Chemistry of Group 9 Metalloporphyrins

Air stable cobalt, rhodium and iridium porphyrin complexes can be easily prepared by refluxing the porphyrin with corresponding metal salts (eqs 1.36 to 1.38). The common oxidation states of group 9 metalloporphyrins are +1 (d^8), +2 (d^7) and +3 (d^6).[110a] M^I(por), M^{II}(por) and M^{III}(por) (M = Co, Rh or Ir) behave like nucleophile, radical and electrophile, respectively, as

reflected from their energy level diagrams (Figure 1.4). The reactivities of rhodium and iridium porphyrin complexes, especially $M^{II}(por)$ chemistry, will be discussed in details.

$$H_2(ttp) \ + \ Co(OAc)_2 \ \xrightarrow[\text{reflux}]{\text{DMF}} \ Co^{II}(ttp) \qquad\qquad (1.36)$$

$$H_2(ttp) \ + \ RhCl_3 \cdot xH_2O \ \xrightarrow[\text{reflux}]{\text{PhCN}} \ Rh^{III}(ttp)Cl \qquad\qquad (1.37)$$

$$H_2(ttp) \ + \ [Ir(COD)Cl]_2 \ \xrightarrow[\text{reflux}]{\textit{p}\text{-xylene}} \ Ir^{III}(ttp)(CO)Cl \qquad (1.38)$$
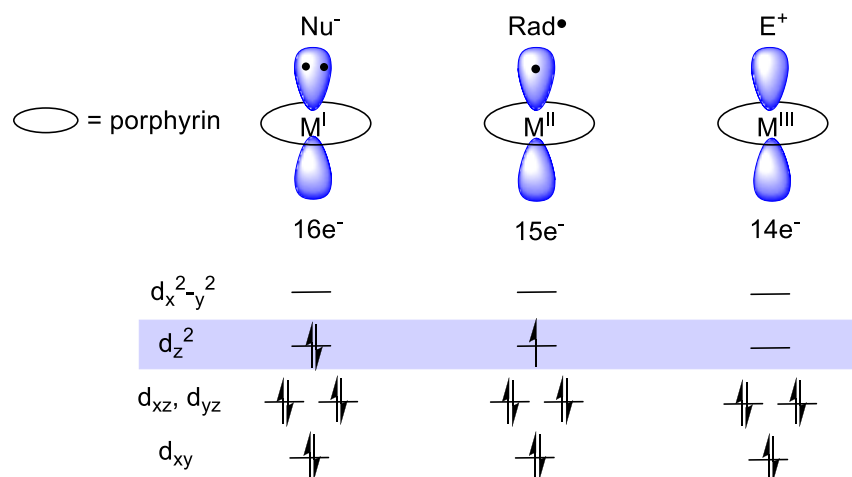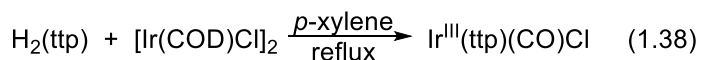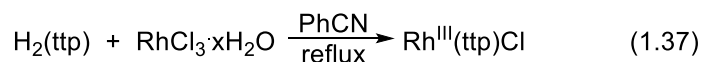
Figure 1.4 Energy Level Diagrams for Square Planar Group 9 Metalloporphyrins

1.6.3.1 $M^I(por)$ Chemistry

Both anionic $Rh^I(por)^-$ and $Ir^I(por)^-$ contains a pair of electron in the dz^2 orbital. Hence, they react like nucleophile. Examples of $M^I(por)^-$ nucleophilic attack to alkyl halides (eq 1.39),[111] lactones (eq 1.40),[112] methanol (eq 1.41)[113] and electron poor olefins (eq 1.42)[111a,b] have been reported. Interestingly, Ogoshi demonstrated the nucleophilic substitution of non-polar C-C bond with $Rh^I(oep)^-$ (eqs 1.43 and 1.44).[40,44]

C-I Bond Cleavage

$$M^I(por)^- \ + \ Me\text{-}I \ \longrightarrow \ M^{III}(por)Me \qquad (1.39)$$

$$Co(oep)^-, \text{ r.t., 10 min} \qquad 65\%$$
$$Rh(oep)^-, \text{ r.t., 10 min} \qquad 46\%$$
$$Ir(ttp)^-, \text{ 70 }^oC, \text{ 2 h} \qquad 88\%$$

C-O Bond Cleavage

$$Rh^I(oep)^- \ + \ \underset{O}{\overset{O}{\Box}} \ \xrightarrow[\text{r.t., 30 min}]{EtOH} \ Rh^{III}(oep)\diagdown\diagup\diagdown^{O}_{OH} \qquad (1.40)$$
$$72\%$$

$$Ir^I(ttp)^- \ + \ MeOH \ \xrightarrow[\text{1 d}]{200\ ^oC} \ Ir^{III}(ttp)Me \qquad (1.41)$$
$$87\%$$
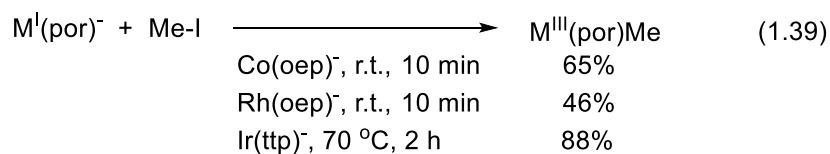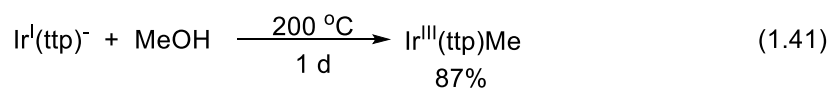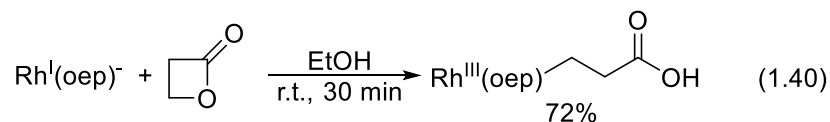
Nucleophilic Addition[73a-b]

$$M^I(oep)^- \ + \ \diagup\!\!\diagdown_{CN} \ \xrightarrow{EtOH, \text{ r.t.}} \ M^{III}(oep)\diagdown\diagup\diagdown_{CN} \qquad (1.42)$$

$$M = Co, \text{ 15 min} \qquad 44\%$$
$$= Rh, \text{ 3 h} \qquad 58\%$$

C-C Bond Cleavage

$$Rh(oep)^{\ominus} \ + \ \text{[quadricyclane]} \ \xrightarrow[\text{50 }^oC, \text{ 10 h}]{EtOH} \ \text{[norbornene-Rh(oep)]} \qquad (1.43)$$
$$23\%$$

$$Rh(oep)^- \ + \ \text{[bicyclopropyl]} \ \xrightarrow[\text{50 }^oC, \text{ 27 h}]{EtOH} \ \text{[Rh(oep)]} \qquad (1.44)$$
$$24\%$$
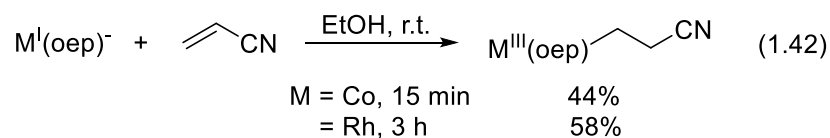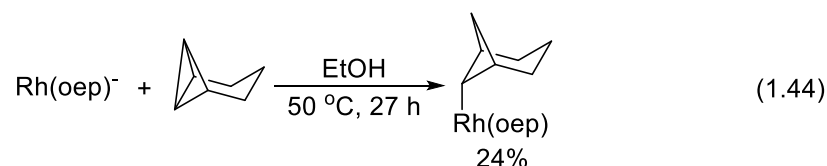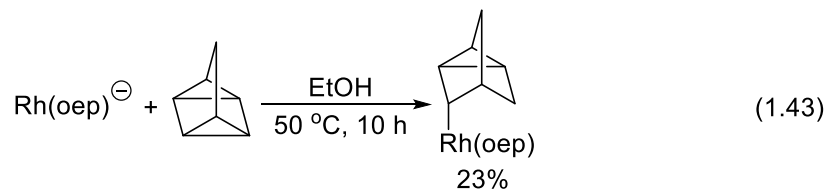
1.6.3.2 $M^{II}(por)$ Chemistry

Monomeric $M^{II}(por)$ has singly occupied dz^2 orbital. It is a metal-centered radical and often called metalloradical. Sterically non-bulky $Rh^{II}(por)$ and $Ir^{II}(por)$ dimerize to give M-M bonded $Rh^{II}_2(por)_2$ and $Ir^{II}_2(por)_2$ dimers, respectively.[114] Sterically bulky $Rh^{II}(tmp)$ and $Ir^{II}(TTiPP)$ remain as monomer.[114] Due to the weak and short Co-Co bond and inter-porphyrin π-π repulsion,[115a] $Co^{II}(por)$ does not form dimer (Table 1.7).

Table 1.7. Formation of M^{II}(por) Dimer.

3.2Å

M = Rh, Ir
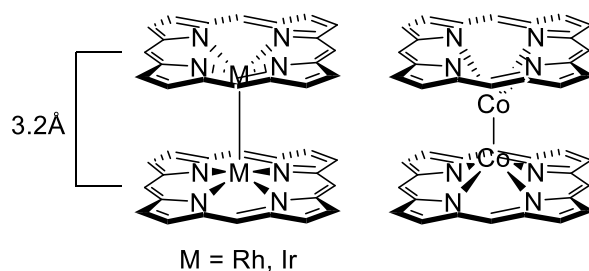
M	Covalent Radii[115b] / Å	Theoretical M-M Bond Length in M^{II}_2(por)$_2$ / Å
Co	1.26	2.52
Rh	1.42	2.84
Ir	1.41	2.82

Due to the weak Rh-Rh and Ir-Ir bonds in M^{II}_2(por)$_2$ dimer, they equilibrate to give back monomeric M^{II}(por) when subjected to heating (Table 1.8 and eq 1.45).

Table 1.8. Equilibrium between M^{II}_2(por)$_2$ and M^{II}(por).[114,116]

$$M^{II}_2(por)_2 \xrightleftharpoons{K} 2M^{II}(por) \qquad (1.45)$$
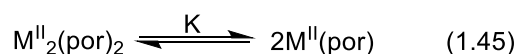
M^{II}_2(por)$_2$	BDE / kcal mol^{-1}	Estimated K	
		25 ºC	200 ºC
Rh^{II}_2(oep)$_2$	16.5	5.3×10^{-6}	0.16
Rh^{II}_2(txp)$_2$	12	0.011	19
Ir^{II}_2(oep)$_2$	24	1.7×10^{-11}	5.5×10^{-5}
Ir^{II}_2(txp)$_2$	20	1.4×10^{-8}	3.8×10^{-3}

The reactivity of Rh^{II}(por) has been extensively investigated. Various chemical transformations involving Rh^{II}(por) are summarized in eqs 1.46-1.59, including H-H activation (eq 1.46),[117] C-H activation (eqs 1.47 and 1.48),[118] C-N activation (eq 1.49),[119] C-Si activation (eq 1.50),[120] C-X activation (X = Br, I) (eqs 1.51 and 1.52),[121] CO reduction and coupling (eqs 1.53-1.55),[122] oxidative addition with H_2O_2 (eq 1.56),[123] alkene insertion (eq 1.57),[121a,124] reaction with diazo compounds (eq 1.58)[125] and ligand induced disproportionation (eq 1.59).[126]

H-H Bond Cleavage

$$2Rh^{II}(tmp) + H_2 \xrightleftharpoons[\substack{C_6H_6 \\ 400\text{ -}600\text{ Torr}}]{\substack{23\ ^oC \\ k = 1.6\ M^{-2}\ s^{-1}}} 2Rh^{III}(tmp)H \qquad (1.46)$$

C-H Bond Cleavage

$$2Rh^{II}(tmp) + CH_4 \xrightleftharpoons[C_6H_6]{\substack{80\ ^oC,\ K = 7300 \\ k = 0.83\ M^{-2}\ s^{-1}}} Rh^{III}(tmp)Me + Rh^{III}(tmp)H \qquad (1.47)$$

$$2Rh^{II}(tmp) + PhCH_3 \xrightleftharpoons[C_6H_6]{\substack{80\ ^oC \\ k = 6.12 \times 10^{-2}\ M^{-2}\ s^{-1}}} Rh^{III}(tmp)CH_2Ph + Rh^{III}(tmp)H \qquad (1.48)$$

C-N Bond Cleavage

$$Rh^{II}_2(oep)_2 + 2CNCH_3 \xrightleftharpoons{C_6D_6,\ 22\ ^oC,\ 1\ h} Rh^{III}(oep)CH_3 + Rh^{III}(oep)(CN)(CNCH_3) \qquad (1.49)$$

C-Si Bond Cleavage

$$2Rh^{II}(tmp) + Me_3SiCN + py \xrightarrow[N_2,\ 1\ h]{C_6H_6,\ 110\ ^oC} \underset{88\%}{Rh^{III}(oep)SiMe_3} + \underset{81\%}{(py)Rh^{III}(oep)CN} \qquad (1.50)$$

C-X Bond Cleavage (X = Br, I)

$$Rh^{II}_2(oep)_2 + BnBr \xrightarrow[instant]{C_6H_6,\ r.t.} \underset{50\%}{Rh^{III}(oep)Bn} + \underset{50\%}{Rh^{III}(oep)Br} \qquad (1.51)$$

$$Rh^{II}_2(ttp)_2 + PhX \xrightarrow[120\ ^oC,\ 5\ min]{C_6D_6} Rh^{III}(ttp)Ph + Rh^{III}(ttp)X \qquad (1.52)$$

$$X = Br \qquad\qquad 37\% \qquad 34\%$$
$$= I \qquad\qquad 30\% \qquad 30\%$$

CO Activation

$$Rh^{II}_2(oep)_2 + 2CO + H_2 \xrightleftharpoons{C_6D_6,\ 25\ ^oC} 2Rh(oep)CHO \qquad (1.53)$$

$$Rh^{II}_2(oep)_2 + 3CO + H_2O \xrightleftharpoons{C_6D_6,\ 25\ ^oC} 2Rh(oep)CHO + CO_2 \qquad (1.54)$$

Reductive Coupling of CO
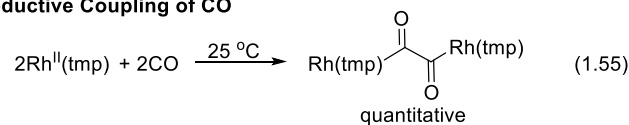
$$2Rh^{II}(tmp) + 2CO \xrightarrow{25\ ^oC} \underset{quantitative}{Rh(tmp)\overset{O}{\underset{O}{C-C}}Rh(tmp)} \qquad (1.55)$$

O-O Bond Cleavage

$$Rh^{II}_2(ttp)_2 + H_2O_2 \xrightarrow[C_6D_6]{r.t.,\ 1\ h} \underset{55\%}{2Rh^{III}(ttp)OH} \qquad (1.56)$$

Alkene Insertion

$$Rh^{II}_2(oep)_2 + {\underset{X = Ph,\ CO_2H,\ CO_2Me,\ CO_2Et}{\diagup\!\!\!=\!\!X}} \xrightleftharpoons[C_6D_6]{r.t.} Rh^{III}(oep)\diagdown\!\!\!\diagup\!\!\!\underset{Rh^{III}(oep)}{\overset{X}{\diagup}} \qquad (1.57)$$

Reaction with diazo compounds

$$Rh^{II}(tmp) + RCHN_2 \xrightarrow[r.t.,\ 30\ min]{C_6H_6} Rh(tmp)CH_2R + N_2 \qquad (1.58)$$

$$R = CO_2Et\ 75\%,\ SiMe_3\ 70\%$$

Disproportionation

$$Rh^{II}_2(oep)_2 + 2py \xrightleftharpoons{25\ ^oC,\ K = 129} Rh^{III}(oep)(py)_2{}^+ + Rh^I(oep)^- \qquad (1.59)$$
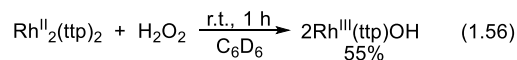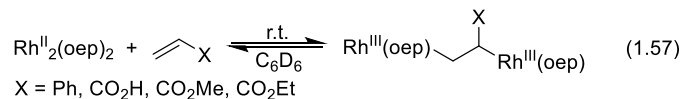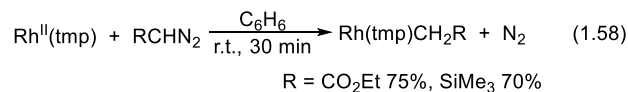
Ir^{II}(por) shares similar reactivities with Rh^{II}(por), but the scopes are limited to H-H bond (eq 1.60),[127] C-H bonds (eqs 1.61 and 1.62),[127] aryl C-X bonds (X = Cl, Br and I) bonds (eq 1.63),[128] alkene (eq 1.64)[114] and CO (eqs 1.65 and 1.66).[114] The temperature dependent spin density equilibrium between Ir metal center and porphyrin π orbital renders difficulties for detailed mechanistic studies.[129]

H-H Bond Cleavage

$$Ir^{II}_2(oep)_2 \ + \ H_2 \ \xrightarrow[200 \ Torr]{C_6D_6, \ 25 \ ^oC} \ 2Ir^{III}(oep)H \qquad (1.60)$$

C-H Bond Cleavage

$$Ir^{II}_2(oep)_2 \ + \ PhCH_3 \ \xrightarrow{120 \ ^oC} \ Ir^{III}(oep)CH_2Ph \ + \ Ir^{III}(oep)H \qquad (1.61)$$

$$Ir^{II}_2(oep)_2 \ + \ CH_3CHO \ \xrightarrow{C_6D_6, \ 25 \ ^oC} \ Ir^{III}(oep)CH_2CHO \ + \ Ir^{III}(oep)H \qquad (1.62)$$

C-Br Bond Cleavage

$$Ir^{II}_2(ttp)_2 \ + \ PhX \ \xrightarrow{C_6D_6} \ Ir^{III}(ttp)Ph \ + \ Ir^{III}(ttp)X \qquad (1.63)$$
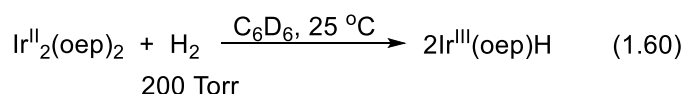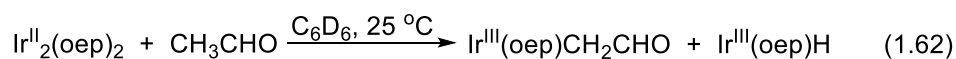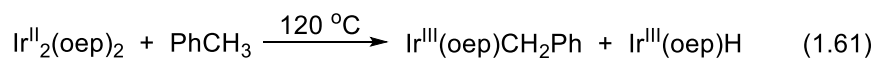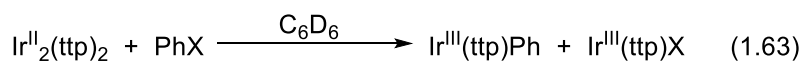
X = Cl	200 ^oC, 5 h	57%	4%
= Br	200 ^oC, 2 min	34%	32%
= I	200 ^oC, 1 min	37%	36%

Alkene Insertion

$$Ir^{II}_2(oep)_2 \ + \ {=\!=} \ \underset{1 \ atm}{\overset{C_6D_6, \ 25 \ ^oC}{\rightleftharpoons}} \ Ir^{III}(oep)CH_2CH_2Ir^{III}(oep) \qquad (1.64)$$

Reaction with CO

$$Ir^{II}_2(oep)_2 \ + \ 2CO \ \underset{1 \ atm}{\overset{C_6D_6}{\rightleftharpoons}} \ (CO)[(oep)Ir^{II}\text{-}Ir^{II}(oep)](CO) \qquad (1.65)$$

$$Ir^{II}(TTiPP) \ + \ nCO \ \overset{C_6D_6}{\rightleftharpoons} \ (TTiPP)^{\bullet-} Ir^{III}(CO)n \qquad (1.66)$$

1 atm
n = 1 or 2
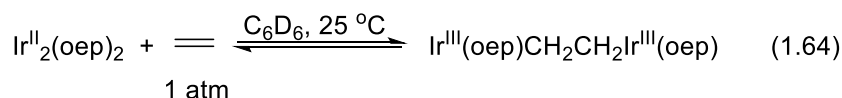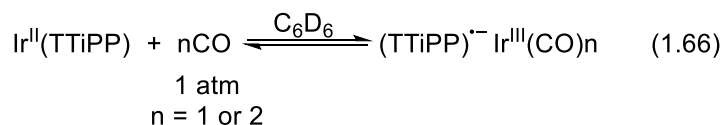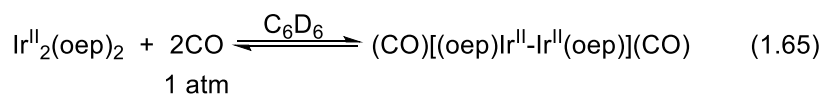
For CCA chemistry, $Rh^{II}(tmp)$ is known to activate aliphatic C-C bonds in functionalized substrates such as TEMPO and its derivatives (eq 1.67),[130] nitriles (eq 1.68),[131] non-enolizable ketones (eq 1.69),[132] esters and amides (eqs 1.70-1.72).[133] A homolytic radical substitution mechanism (S_H2) was proposed (Scheme 1.8). The fate of organic co-product was not observed in most cases.
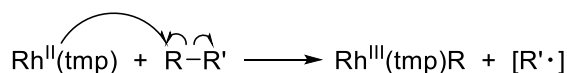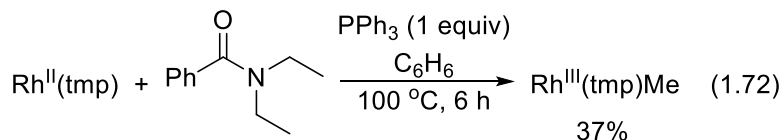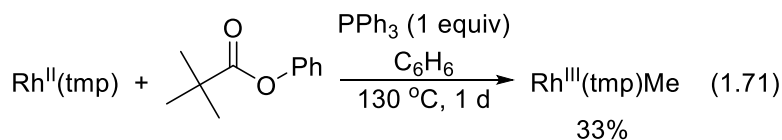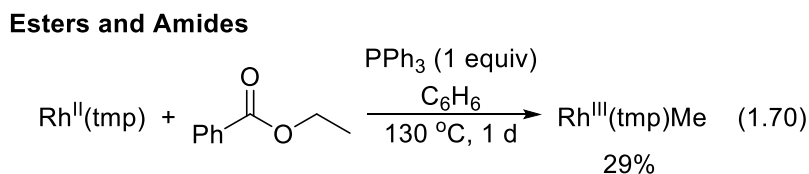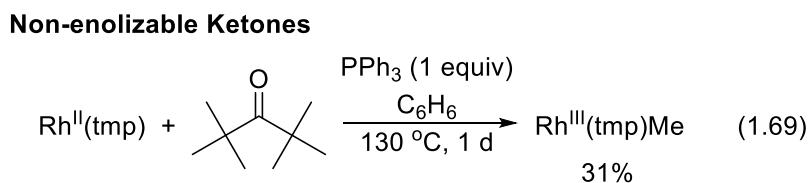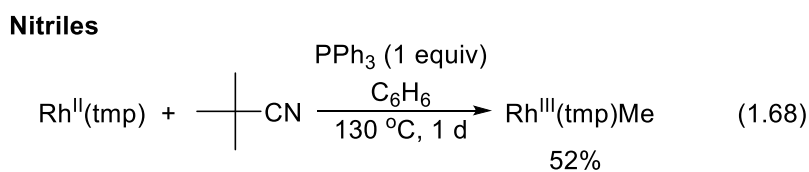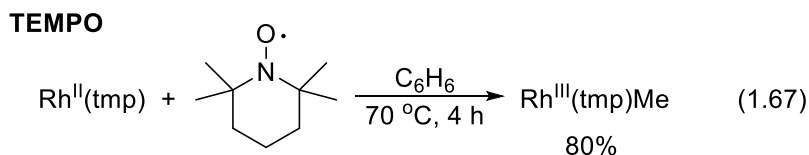
Scheme 1.8 Homolytic Radical Substitution (S_H2) of C-C bond by $Rh^{II}(tmp)$.

In 2010, the Chan group reported the aliphatic CCA in cyclooctane with $Rh^{II}_2(ttp)_2/Rh^{III}(ttp)H$ system (eq 1.73).[134] $Rh^{II}_2(ttp)_2$, employed at lower concentration, cleaves the C-C bond efficiently at 120 °C via radical attack to first generate $Rh^{III}(ttp)(CH_2)_7CH_2$• radical, followed by H atom transfer from $Rh^{III}(ttp)H$ to yield $Rh^{III}(ttp)(n\text{-octyl})$ in 73% yield (Scheme 1.9).

$$Rh^{III}(ttp)H \ + \ Rh^{II}_2(ttp)_2 \ + \ \bigcirc \quad \xrightarrow[\text{15 h, N}_2]{\text{120 }^o\text{C}} \quad Rh^{III}(ttp)(c\text{-octyl}) \qquad (1.73)$$

$$10 \quad : \quad 1 \qquad\qquad\qquad\qquad\qquad 73\%$$

$$\bigcirc \xrightarrow{Rh^{II}(ttp)} Rh^{III}(ttp)(CH_2)_7CH_2\bullet \xrightarrow[-Rh^{II}(ttp)]{H\text{-}Rh^{III}(ttp)} Rh^{III}(ttp)(CH_2)_7CH_3$$
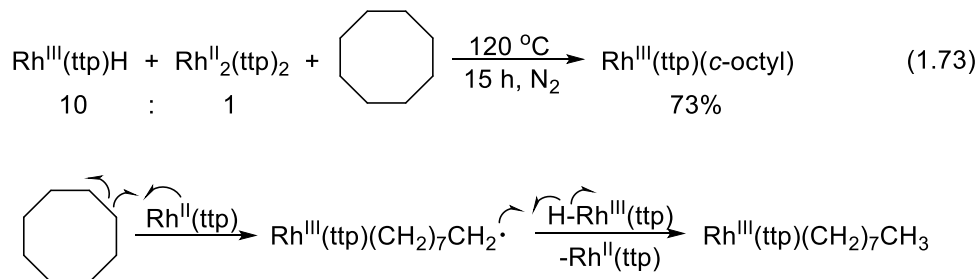
Scheme 1.9 $Rh^{II}(ttp)$ Catalyzed CCA of Cyclooctane with $Rh^{III}(ttp)H$.

Until now, the aliphatic CCA chemistry by $Ir^{II}(por)$ is still unknown.

1.6.3.3 $M^{III}(por)$ Chemistry

Most $M^{III}(por)$ are air stable such as $M^{III}(por)(halide)$ and $M^{III}(por)(alkyl)$, which makes them common starting materials to generate reactive metalloporphyrin species like $M^{II}(por)$ and $M^{III}(por)OH$ for bond activation studies. Rhodium porphyrin examples are outlined, including thermal decomposition (eq 1.74),[135] oxidation (eq 1.75),[135] photolysis (eq 1.76),[104b] intermolecular reductive elimination (eq 1.77),[136] alkyl 1,2-rearrangement (eq 1.78),[137] C-H bond activation (eqs 1.79-1.82)[138] and C-C bond activation (eq 1.83).[139]

Thermal decomposition

$$2Rh^{III}(oep)CH_2CH(Ph)CH_3 \; \underset{\text{r.t., 30d}}{\rightleftharpoons} \; Rh^{II}_2(oep)_2 \; + \; 2PhC(CH_3)=CH_2 \; + \; H_2 \quad (1.74)$$
$$40\%$$

Oxidation

$$Rh^{III}(oep)CH_2Ph \; \xrightarrow[\text{130 }^o\text{C, 20 h}]{\text{air (200 torr)}} \; PhCHO \quad (1.75)$$
$$40\%$$

Photolysis

$$Rh^{III}(tmp)Me \; \xrightarrow[\text{r.t., 6 h}]{h\nu,\ C_6H_6} \; Rh^{II}(tmp) \quad (1.76)$$

Intermolecular reductive elimination

$$Rh^{III}(oep)CH_2OH \; + \; Rh^{III}(oep)H \; \xrightarrow{\text{80 }^o\text{C, 8 h}} \; Rh^{II}_2(oep)_2 \; + \; CH_3OH \quad (1.77)$$
$$\text{quantitative} \quad \text{quantitative}$$

Alkyl 1,2-rearrangement

$$Rh^{III}(bocp)CH_2CH_2Ph \; \underset{\text{80 }^o\text{C, 10 h}}{\overset{C_6D_6}{\rightleftharpoons}} \; Rh(bocp)CH(CH_3)Ph \quad (1.78)$$
$$87\%$$

C-H Bond Cleavage

$$Rh^{III}(ttp)Cl \; + \; PhCHO \; \xrightarrow[\text{1 d}]{\text{200 }^o\text{C}} \; Rh^{III}(ttp)\overset{\displaystyle O}{\underset{}{C}}Ph \quad (1.79)$$
$$79\%$$

$$Rh^{III}(ttp)Cl \; + \; PhCH_3 \; \xrightarrow[\text{120 }^o\text{C, 30 min}]{K_2CO_3 \text{ (10 equiv)}} \; Rh^{III}(ttp)CH_2Ph \quad (1.80)$$
$$97\%$$

$$Rh^{III}(ttp)Me \; + \; PhCH_3 \; \xrightarrow[\text{150 }^o\text{C, 4 d}]{} \; Rh^{III}(ttp)CH_2Ph \quad (1.81)$$
$$97\%$$

$$Rh^{III}(ttp)Cl \; + \; PhCN \; \xrightarrow[\text{3 d}]{\text{reflux}} \; Rh^{III}(ttp)\!-\!\!\bigcirc\!\!-CN \quad (1.82)$$
$$28\%$$

C-C Bond Cleavage

$$Rh^{III}(tmp)X \; + \; (PrCH_2)_2O \; \xrightarrow[\text{80 }^o\text{C, 1 d, N}_2]{KOH \text{ (10 equiv)}} \; Rh^{III}(tmp)^nPr \quad (1.83)$$
$$X = I$$
$$= Cl$$
$$53\%$$
$$23\%$$

1.6.4 Equilibrium Between M^I(por), M^{II}(por) and M^{III}(por)

Wayland has established the equilibria of water soluble Rh(I), Rh(II) and Rh(III) porphyrins in aqueous medium quantitatively (Scheme 1.10).[140] The distribution of these rhodium porphyrins depends on the pH of the medium. In analogy, the respective major species in organic solvent, for example benzene, will be Rh^I(por)$^-$, Rh^{II}(por), Rh^{III}(por)H and Rh^{III}(por)OH (Scheme 1.11).
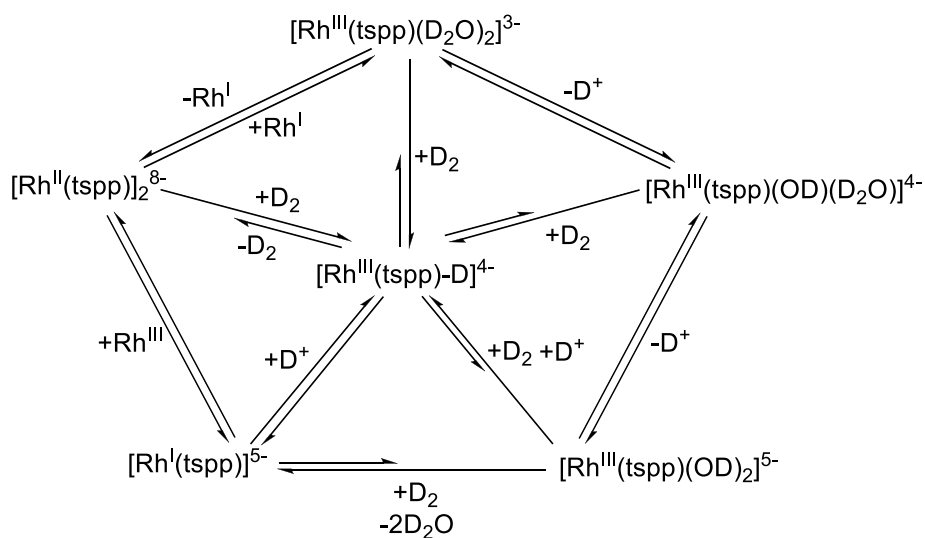
Scheme 1.10 Equilibrium of Rhodium Porphyrins in Water.
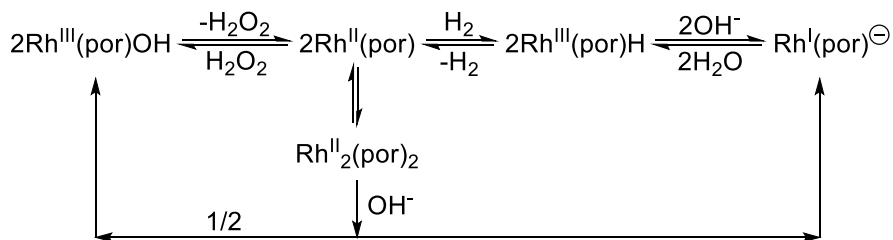
Scheme 1.11 Equilibrium of Rhodium Porphyrins in Organic Solvent.

1.7 Scope of Thesis

This thesis focuses on the catalytic carbon-carbon σ-bond hydrogenation of [2.2]paracyclophane (PCP) using water by group 9 metalloporphyrins. The thesis is outlined in the following sections:

(i) mechanistic investigations on the stoichiometric and catalytic CCA of PCP with rhodium porphyrins;

(ii) discovery on the reaction rate and yield enhancement with iridium porphyrins;

(iii) preliminary results on catalytic hydrogenation of PCP with economical cobalt porphyrins.

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Chapter 2   Catalytic Carbon-Carbon Bond Hydrogenation of [2.2]Paracyclophane

with Water by Rhodium Porphyrin Complexes

2.1 Introduction

Catalytic carbon-carbon σ-bond hydrogenation using water involves two fundamental steps: (1) carbon-carbon bond activation (CCA) and (2) hydrogenation using water (Scheme 2.1).

$$R-R' + M \xrightarrow{\text{CCA}} \begin{array}{c} R-M-R' \\ \\ M-R \\ + \\ M-R' \end{array} \xrightarrow[\text{hydrogenation}]{H_2O} R-H + R'-H + M + 1/2O_2$$
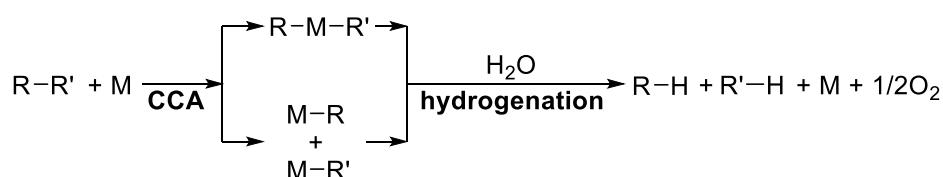
Scheme 2.1 Catalytic Carbon-Carbon σ-Bond Hydrogenation using Water

The Chan group has reported the stoichiometric intermolecular aliphatic CCA in TEMPO and derivatives,[1] nitriles,[2] non-enolizable ketones,[3] ester[4] and amides[4] by monomeric $Rh^{II}(tmp)$ metalloradical. $Rh^{II}(tmp)$ undergoes homolytic substitution (S_H2) at the carbon center which leads to carbon-carbon bond cleavage and rhodium-carbon bond formation (eq 2.1).

$$Rh^{II}(tmp) + R-R' \xrightarrow[\text{temp, time}]{\substack{\text{additives} \\ \text{solvent}}} Rh^{III}(tmp)R + "R'\cdot" \qquad (2.1)$$

$$R = Me, Et, {}^nPr, Bn, (CH_2)_3Ph$$
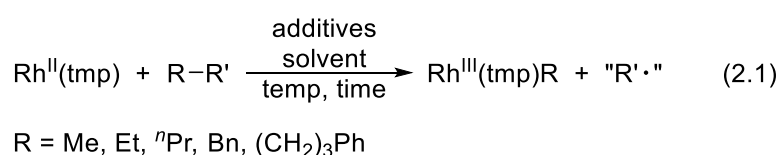
The Chan group also discovered the $Rh^{II}(ttp)$ catalyzed 1,2-insertion of $Rh^{III}(ttp)H$ into the carbon-carbon bond of cyclooctane (eq 2.2 and Scheme 2.2).[5] This ascertained the potency of rhodium(II) porphyrins for CCA of hydrocarbon substrates.

$$\text{Rh}^{III}(\text{ttp})\text{H} + \text{Rh}^{II}_2(\text{ttp})_2 + \bigcirc \xrightarrow[\text{15 h, N}_2]{120\ ^\circ\text{C}} \text{Rh}^{III}(\text{ttp})(c\text{-octyl}) \qquad (2.2)$$

10 : 1   73%

$$\bigcirc \xrightarrow{\text{Rh}^{II}(\text{ttp})} \text{Rh}^{III}(\text{ttp})(\text{CH}_2)_7\text{CH}_2\cdot \xrightarrow[-\text{Rh}^{II}(\text{ttp})]{\text{H-Rh}^{III}(\text{ttp})} \text{Rh}^{III}(\text{ttp})(\text{CH}_2)_7\text{CH}_3$$
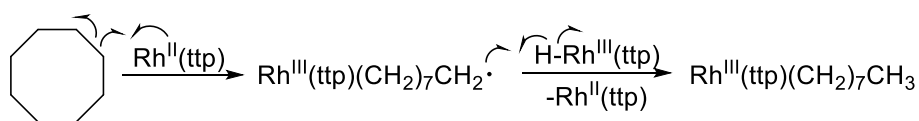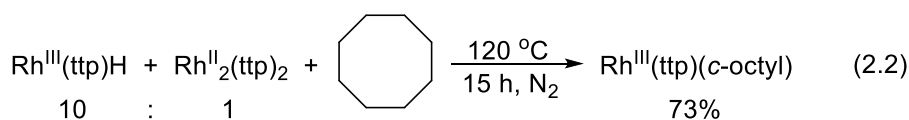
Scheme 2.2 CCA of Cyclooctane by Rh^{II}(ttp) Catalyzed 1,2-Insertion of Rh^{III}(ttp)H.

Rhodium(III) porphyrin alkyls undergo hydrolysis at elevated temperature. This allows the hydrogenation of alkyl fragment using H$_2$O. Rh^{III}(ttp)Me, Rh^{III}(ttp)CH$_2$COPh and Rh^{III}(ttp)CH$_2$CH$_2$COPh have been shown to undergo hydrolysis in C$_6$D$_6$ at 200 $^\circ$C to produce CH$_4$, PhCOMe and PhCOEt, respectively (eqs 2.3-2.5).[6] At the same time, Rh$^{II}_2$(ttp)$_2$ is generated and capable for CCA.

$$\text{Rh}^{III}(\text{ttp})\text{Me} + \text{H}_2\text{O} \xrightarrow[\text{C}_6\text{D}_6,\ 30\ \text{min}]{200\ ^\circ\text{C}} \text{Rh}^{III}(\text{ttp})\text{H} + \text{Rh}^{II}_2(\text{ttp})_2 + \text{CH}_4 \quad (2.3)$$

60%   100 equiv   trace   34%   11%
recovery

$$\text{Rh}^{III}(\text{ttp})\underset{}{\overset{\text{O}}{\diagup\diagdown}}\text{Ph} + \text{H}_2\text{O} \xrightarrow[\text{C}_6\text{D}_6,\ 5\ \text{min}]{200\ ^\circ\text{C}} \text{Rh}^{III}(\text{ttp})\text{H} + \text{Rh}^{II}_2(\text{ttp})_2 + \underset{}{\overset{\text{O}}{\diagup\diagdown}}\text{Ph} \quad (2.4)$$

42%   100 equiv   42%   13%   57%
recovery

$$\text{Rh}^{III}(\text{ttp})\underset{}{\overset{\text{O}}{\diagdown\diagup\diagdown}}\text{Ph} + \text{H}_2\text{O} \xrightarrow[\text{C}_6\text{D}_6,\ 5\ \text{min}]{200\ ^\circ\text{C}} \text{Rh}^{III}(\text{ttp})\text{H} + \text{Rh}^{II}_2(\text{ttp})_2 + \underset{}{\overset{\text{O}}{\diagdown\diagup\diagdown}}\text{Ph} \quad (2.5)$$

71%   100 equiv   9%   18%   29%
recovery
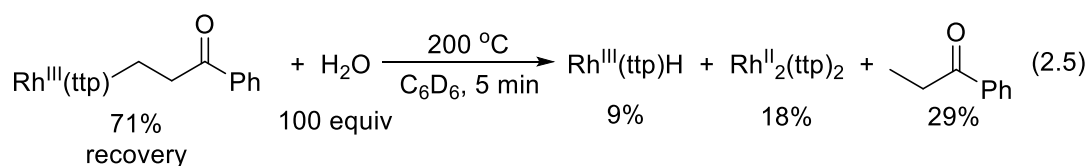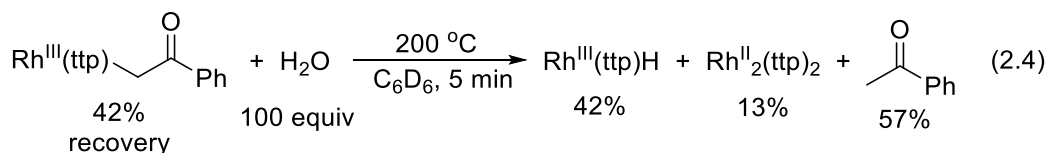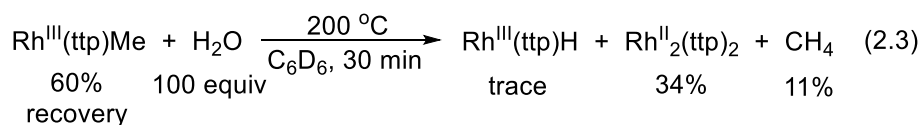
Therefore, by combining the reactivity of Rh^{II}(por) towards CCA and hydrolysis of Rh^{III}(por)R, catalytic carbon-carbon σ-bond hydrogenation using H$_2$O by rhodium porphyrins is achievable.

2.2 Objectives of the Work

We aim to achieve catalytic carbon-carbon σ-bond hydrogenation of hydrocarbons using H_2O by rhodium porphyrins.

2.3 Preparation of Starting Materials

2.3.1 Synthesis of Porphyrins

Various *meso*-aryl substituted free base porphyrins $H_2(tpp)$, $H_2(ttp)$, $H_2(tap)$ and $H_2(t_{p\text{-}CF_3}pp)$ were prepared by the condensation of corresponding aldehydes and pyrrole in refluxing propionic acid for 30 min in 18%, 20%, 20% and 17% yields, respectively, according to the literature procedures (eq 2.6).[7]

$$\text{(2.6)}$$

R = H, $H_2(tpp)$ **1a**, 18%
= Me, $H_2(ttp)$ **1b**, 20%
= OMe, $H_2(tap)$ **1c**, 20%
= CF_3, $H_2(t_{p\text{-}CF_3}pp)$ **1d**, 17%
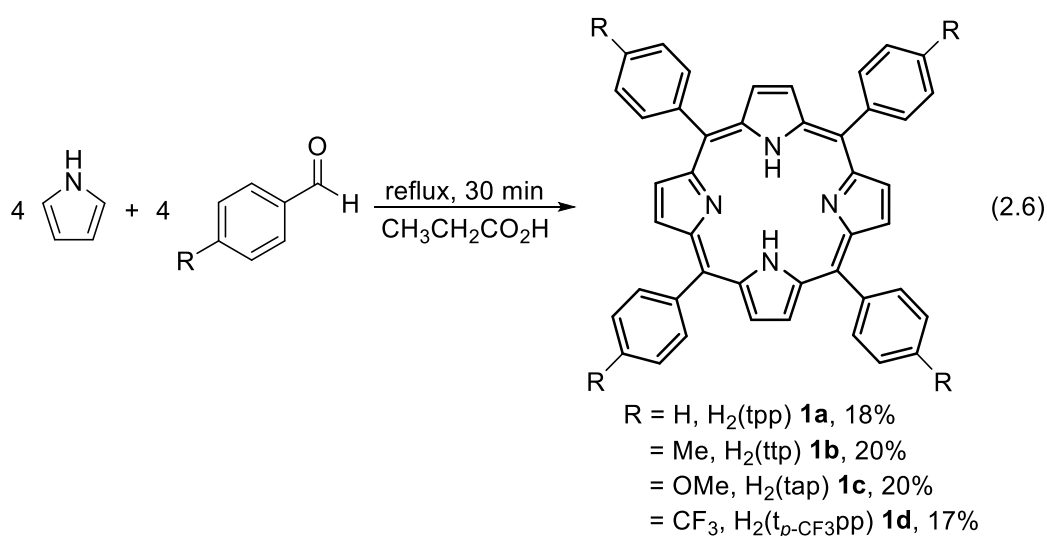
$H_2(tmp)$ **1e** was prepared in 32% yield from mesitaldehyde and pyrrole according to literature procedures (eq 2.7).[8]

$$\text{(2.7)}$$

1. $BF_3 \cdot Et_2O$, CHCl3, N_2, 25 °C, 1 h
2. DDQ, reflux, 1 h

$H_2(tmp)$ **1e**, 32%
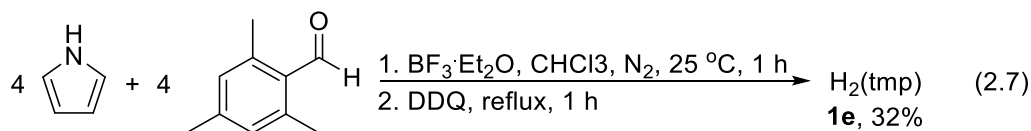
The electron deficient porphyrin $H_2(ocp)$ was prepared in three steps from $H_2(tpp)$ (Scheme 2.3).[9,10]

$$H_2(tpp) \xrightarrow[\text{DMF, reflux, 2 h}]{\text{Ni(OAc)}_2 \text{ (4 equiv)}} \underset{87\%}{\text{Ni(tpp)}} \xrightarrow[\substack{\text{1,2-dichlorobenzene} \\ \text{reflux, 3 h}}]{\text{NCS (12 equiv)}} \underset{75\%}{\text{Ni(ocp)}} \xrightarrow[\substack{\text{CHCl}_3 \\ \text{r.t., 15 min}}]{\text{conc. H}_2\text{SO}_4} \underset{60\%}{H_2(ocp)}$$
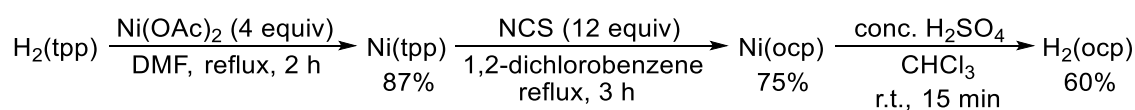
Scheme 2.3 Preparation of $H_2(ocp)$ from $H_2(tpp)$

2.3.2 Synthesis of Metalloporphyrins

2.3.2.1 Synthesis of Rhodium(III) Porphyrin Halides

$Rh^{III}(ttp)Cl$, $Rh^{III}(tap)Cl$, $Rh^{III}(t_{p\text{-CF3}}pp)Cl$, $Rh^{III}(ocp)Cl$ and $Rh^{III}(tmp)Cl$ were synthesized by refluxing the corresponding free base porphyrin with $Rh^{III}Cl \cdot xH_2O$ in PhCN in 72%, 77%, 70%, 62% and 75% yields, respectively, according to literature procedures (eq 2.8).[11]

$$H_2(por) + Rh^{III}Cl_3 \cdot xH_2O \xrightarrow[\text{PhCN}]{\text{reflux, 3-4 h}} Rh^{III}(por)Cl \qquad (2.8)$$

$$\begin{aligned} &\text{por = ttp } \mathbf{1a}, 72\% \\ &\quad = \text{tap } \mathbf{1b}, 77\% \\ &\quad = t_{p\text{-CF3}}\text{pp } \mathbf{1c}, 70\% \\ &\quad = \text{ocp } \mathbf{1d}, 62\% \\ &\quad = \text{tmp } \mathbf{1e}, 75\% \end{aligned}$$
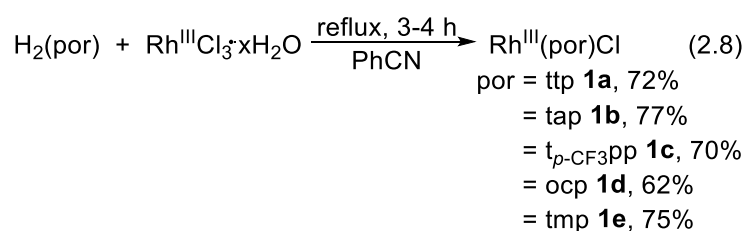
$Rh^{III}(ttp)I$[12] was prepared from modified procedures by reacting $Rh^{III}(ttp)Cl$ with KI in C_6H_6 at 120 °C in 96% yield (eq 2.9).

$$Rh^{III}(ttp)Cl + \underset{\substack{20 \\ \text{equiv}}}{KI} \xrightarrow[\text{120 °C, 1 d}]{C_6H_6} \underset{96\%}{Rh^{III}(ttp)I} \qquad (2.9)$$
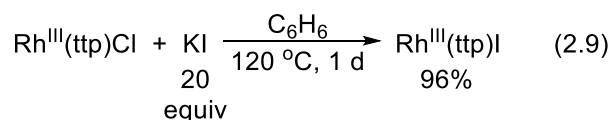
2.3.2.2 Synthesis of Rhodium(III) Porphyrin Alkyls

$Rh^{III}(ttp)Me$, $Rh^{III}(tap)Me$, $Rh^{III}(t_{p-CF3}pp)Me$, $Rh^{III}(ocp)Me$, $Rh^{III}(tmp)Me$ and $Rh^{III}(ttp)^iPr$ were synthesized by reductive alkylation of the corresponding $Rh^{III}(por)Cl$ with alkyl iodide in 90%, 90%, 88%, 85%, 89% and 80% yields, respectively (eqs 2.10 and 2.11).[13]

$$Rh^{III}(por)Cl \xrightarrow[\text{2. MeI, 5 min, 0 }^{\circ}\text{C}]{\substack{\text{1. NaBH}_4/\text{NaOH(aq)} \\ \text{EtOH, 50 }^{\circ}\text{C, 1 h}}} Rh^{III}(por)Me \qquad (2.10)$$

$$\begin{aligned} por &= ttp \ \mathbf{2a}, 90\% \\ &= tap \ \mathbf{2b}, 90\% \\ &= t_{p-CF3}pp \ \mathbf{2c}, 88\% \\ &= ocp \ \mathbf{2d}, 85\% \\ &= tmp \ \mathbf{2e}, 89\% \end{aligned}$$

$$Rh^{III}(ttp)Cl \xrightarrow[\text{2. }^i\text{PrI, 5 min, 0 }^{\circ}\text{C}]{\substack{\text{1. NaBH}_4/\text{NaOH(aq)} \\ \text{EtOH, 50 }^{\circ}\text{C, 1 h}}} Rh^{III}(ttp)^iPr \qquad (2.11)$$
$$\mathbf{2f}, 80\%$$
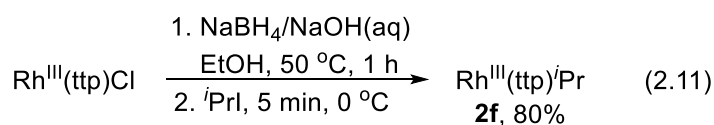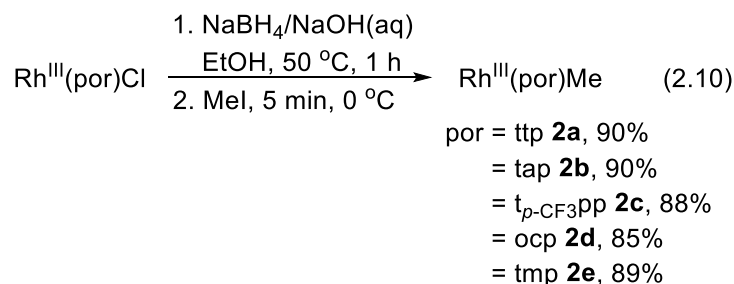
$Rh^{III}(ttp)Bn$ was prepared by the base promoted BnCHA of toluene with $Rh^{III}(ttp)Cl$ (eq 2.12).[14]

$$Rh^{III}(ttp)Cl + toluene \xrightarrow[\text{120 }^{\circ}\text{C, N}_2\text{, 1 h}]{\text{K}_2\text{CO}_3 \text{ (10 equiv)}} Rh^{III}(ttp)Bn \qquad (2.12)$$
$$\mathbf{2g}, 89\%$$
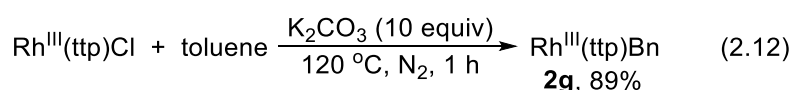
2.3.2.3 Synthesis of $Rh^{II}(tmp)$

$Rh^{II}(tmp)$ was prepared by the photolysis of $Rh^{III}(tmp)Me$ at 6-10 °C in C_6H_6 (eq 2.14).[15]

$$Rh^{III}(tmp)Me \xrightarrow[\text{6-10 }^{\circ}\text{C, 6 h}]{h\nu, \text{C}_6\text{H}_6, \text{N}_2} Rh^{III}(tmp) \qquad (2.14)$$
$$\mathbf{4a}, 80\%$$
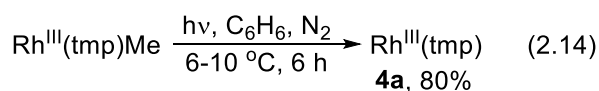
2.4 Optimization of Catalytic PCP Hydrogenation with H_2O

2.4.1 Initial Screenings

Initially, PCP with KOH (1 equiv) and H_2O (100 equiv) heated at 200 °C in the presence of 10 mol% Rh^{III}(ttp)I in C_6D_6 for 25 h yielded 83% of 4,4'-dimethylbibenzyl **5** (Table 2.1, eq 2.15, entry 1). The saturated [NaOH] in toluene at 25 °C has been reported to be ~9 mM.[16] It is assumed that KOH has the same solubility in C_6D_6 at 25 °C. Therefore, KOH was completely dissolved in the catalysis to give [KOH] = 9.6 mM. In addition, the saturated [H_2O] in C_6H_6 at 200 °C has been reported to be ~2 M. It is assumed that H_2O/C_6D_6 system would behave similarly.[17] Therefore, H_2O was completely dissolved in the catalysis to give [H_2O] = 0.96 M. Hence, the reaction mixture was homogeneous at 200 °C.

Table 2.1 Catalytic PCP Hydrogenation using H_2O.
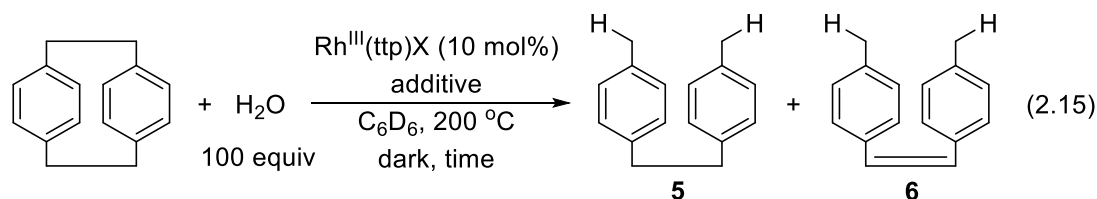
entry	X	additive	time	yield / %				
				PCP recovery	**5**	**6**	X-H[a]	Rh^{III}(ttp)H[a]
1	I	KOH (1 equiv)	25 h	0	83	12	--	29
2[b]	I	KOH (1 equiv)	5 d	9	52	4	--	0
3	Me	--	54 h	0	78	9	79	55
4	^{i}Pr	--	50 h	0	68	10	20[c]	41
5	none	none	4.5 d	100	0	0	--	--

[a] w.r.t. Rh^{III}(ttp)X
[b] carried out under room light, see experimental for details
[c] propene was formed in 18% yield

In the presence of room light, the catalysis was greatly retarded (Table 2.1, eq 2.15, entry 2). The rhodium porphyrin complexes might be photochemically decomposed at elevated temperature as formation of dark purple precipitate was observed. The catalytic hydrogenation proceeded smoothly under neutral conditions using Rh^{III}(ttp)Me pre-catalyst to produce **5** in 78% yield after 54 h (Table 2.1, eq 2.15, entry 3). Rh^{III}(ttp)^{i}Pr was a good pre-

catalyst and **5** was formed in 68% yield after 50 h (Table 2.1, eq 2.15, entry 4). Control experiment showed that PCP was stable at 200 °C in the presence of H_2O up to 4.5 d with quantitative recovery (Table 2.1, eq 2.15, entry 5).

All pre-catalysts produced small amounts of 4,4'-dimethylstilbene **6** (Table 2.1, eq 2.15, entries 1-4). The stoichiometric dehydrogenation of bibenzyl to trans-stilbene promoted by rhodium porphyrin complex has been studied by the Chan group (eq 2.16).[18] Hence, two possible pathways can lead to product **6**: (1) dehydrogenation of PCP to [2.2]paracyclophane-1-ene followed by CCA and hydrogenation; or (2) direct dehydrogenation of **5** to **6**. The former pathway is less likely because dehydrogenation of PCP to give more strained [2.2]paracyclophane-1-ene is energetically uphill by 4.6 kcal/mol based on their corresponding strain energies.[19]

$$Rh^{III}(ttp)Cl \ + \ \underset{10 \ equiv}{\text{(Ph-CH}_2\text{-CH}_2\text{-Ph)}} \ \xrightarrow[\text{C}_6\text{D}_6, \ 120 \ °\text{C}, \ 7 \ \text{d}]{\text{KOH (10 equiv)}} \ Rh^{I}(ttp)^{\ominus} \ + \ \underset{74\% \ \text{w.r.t.} \ Rh^{III}(ttp)Cl}{\text{(Ph-CH=CH-Ph)}} \qquad (2.16)$$

$$72\%$$
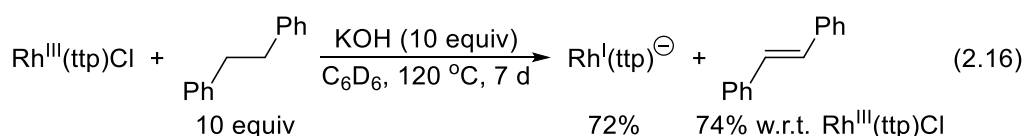
We reasoned that the CCA of PCP is associated with the $Rh^{II}(ttp)$ metalloradical attack at the benzylic C-C bond. Indeed, $Rh^{III}(ttp)I$, $Rh^{III}(ttp)Me$ and $Rh^{III}(ttp)^iPr$ are readily available precursors of $Rh^{II}_2(ttp)_2$, via a common intermediate $Rh^{III}(ttp)OH$. $Rh^{III}(ttp)I$ undergoes fast ligand substitution with KOH to give $Rh^{III}(ttp)OH$, followed by thermal rapid reduction to give $Rh^{II}_2(ttp)_2$ (Scheme 2.4, and further explained in details in mechanistic discussion part below).[20] Similarly, hydrolysis of $Rh^{III}(ttp)Me$ and $Rh^{III}(ttp)^iPr$ first generate $Rh^{III}(ttp)OH$ and then converted to $Rh^{II}_2(ttp)_2$ under neutral conditions (Scheme 2.4).[6] The detection of CH_4 and propane further supports the hydrolysis step.

$$Rh^{III}(ttp)I + KOH \longrightarrow Rh^{III}(ttp)OH + KI \qquad (i)$$

$$Rh^{III}(ttp)R + H_2O \longrightarrow Rh^{III}(ttp)OH + RH \qquad (ii)$$

$$2Rh^{III}(ttp)OH \longrightarrow Rh^{II}_2(ttp)_2 + H_2O_2 \qquad (iii)$$

$$(R = Me, {}^iPr)$$
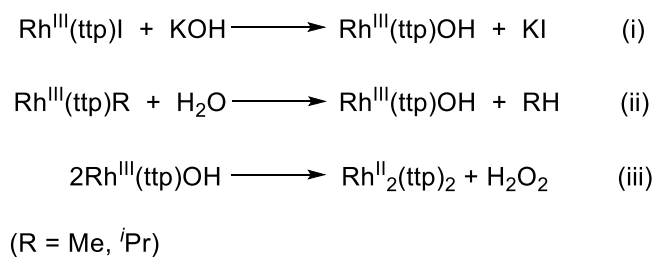
Scheme 2.4 Conversion of Pre-Catalysts to $Rh^{II}_2(ttp)_2$.

In addition, the propene co-formation from $Rh^{III}(ttp)^iPr$ pre-catalyst suggests a parallel β-H elimination process to first give $Rh^{III}(ttp)H$ intermediate.[21] $Rh^{III}(ttp)H$ then undergoes bi-molecular thermal dehydrogenation to give $Rh^{II}_2(ttp)_2$ and H_2 (Scheme 2.5).[22]

$$2Rh^{III}(ttp)H \longrightarrow Rh^{II}_2(ttp)_2 + H_2 \qquad (ii)$$
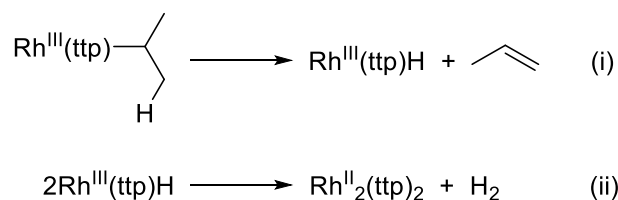
Scheme 2.5 Alternative Conversion Pathway from $Rh^{III}(ttp)^iPr$ to $Rh^{II}_2(ttp)_2$.

2.4.2 Porphyrin Ligand Electronic Effects

The electronic effects of the porphyrin ligand on catalytic PCP hydrogenation were then examined with both electron rich and poor $Rh^{III}(por)Me$ (Table 2.2, eq 2.16). The rate of PCP consumption increased with electron deficiency of the porphyrin, e.g. t4-CF3pp > ttp > tap (Table 2.2, eq 2.17, entries 1-3). CCA of PCP would be more favorable with electron rich rhodium porphyrin since the oxidation of Rh^{II} to Rh^{III} in the CCA step is better stabilized. Electron rich ligand usually gives complex with stronger Rh-C bond than electron poor one.[23] The reverse reactivity trend observed probably reflects that CCA of PCP is not the rate determining step in the catalysis.

Table 2.2 Catalytic PCP Hydrogenation by Various $Rh^{III}(por)Me$.

$$+ Rh^{III}(por)H + CH_4 \quad (2.17)$$
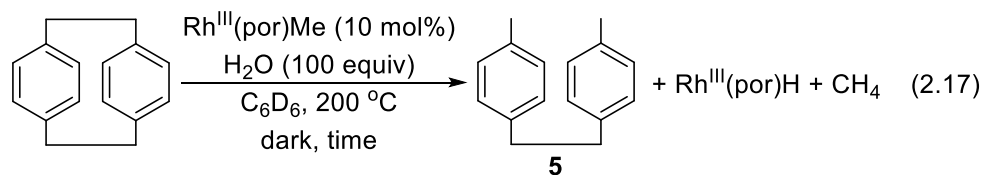
entry	por	time / h	yield / %			
			5	**6**	$Rh^{III}(por)H^a$	$CH_4{}^a$
1	tap	84	62	7	30	33
2	ttp	54	78	9	55	79
3[b]	t4-CF3pp	40	59	14	4	13
4	ocp	4 d	54	15	not observed	58
5[c]	tmp	7 d	39	14	$Rh^{III}(tmp)D$, 16	--

^{a} w.r.t. $Rh^{III}(por)Me$

^{b} $Rh^{III}(t4\text{-}CF3pp)H$ was observed after 24 h

^{c} D_2O was used

Alternatively, the formation of electron richer $Rh^{II}_2(por)_2$ for CCA is slower. In the base-promoted reduction of $Rh^{III}(por)I$ to $Rh^{II}_2(por)_2$ via $Rh^{III}(por)OH$ intermediate, the reaction with $Rh^{III}(tap)I$ is about 4 times slower than $Rh^{III}(ttp)I$.[20] Since hydrolysis of $Rh^{III}(por)Me$ is proposed to go through $Rh^{III}(por)OH$ intermediate, which is reduced to $Rh^{II}_2(por)_2$ and favored by electron poor porphyrin ligand. However, the half-life of $Rh^{III}(ttp)OH$ reduction to $Rh^{II}_2(ttp)_2$ is estimated to be 15 min at 120 °C (assume 4 half-lives for complete reaction).[20] This suggests a short half-life of about 4 s at 200 °C. Despite the carry over effect in the catalysis, the rate of conversion of $Rh^{III}(por)Me$ pre-catalyst to $Rh^{II}_2(por)_2$ is unlikely to affect the catalysis time in hour scale.

The hydrogenation catalyzed by very electron deficient $Rh^{III}(ocp)Me$ required 4 d to give 54% yield of **5** (Table 2.2, eq 2.16, entry 4). The saddle-shaped ocp ligand may induce steric hindrance on CCA and slowed down the catalysis.[24] Similarly, the sterically bulky $Rh^{III}(tmp)Me$ catalyzed the PCP hydrogenation very slowly to give only 39% yield of **5** after 7 d (Table 2.2, eq 2.16, entry 5). After the completion of catalytic PCP hydrogenation, $Rh^{III}(por)H$ was the organometallic end product obtained in low to moderate yields.

2.4.3 Additive Effects

In order to promote the hydrolysis by enhancing the mixing of H_2O in non-polar benzene solvent, various polar additives were introduced to the catalytic system. ^{t}BuOH, BnEt$_3$NCl and PPh$_4$Br at various loadings did not give significant improvements (Table 2.3, eq 2.17). Extensive decomposition of phase transfer catalyst PPh$_4$Br to PPh$_3$ and O=PPh$_3$ was observed (Table 2.3, eq 2.18, entry 6). PPh$_4$Br was hydrolyzed to first give O=PPh$_3$, followed by reduction to produce PPh$_3$ (Scheme 2.6).[25] Higher additive loadings were not examined because rhodium porphyrins are known to cleave the C-N bond in amine[26] or reacts with alcohol.[3b,27]

Table 2.3 Polar Additive Effects on Catalytic PCP Hydrogenation.
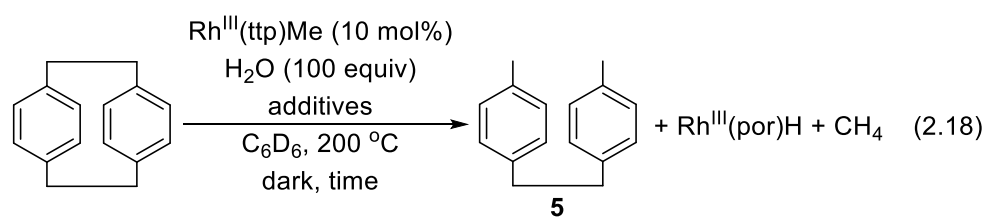
| entry | additives | equiv | time / h | yield / % | |
				5	Rh^{III}(por)H[a]
1	--	--	54	78	55
2	^{t}BuOH	2	54	68	0
3	^{t}BuOH	10	47	74	0
4	BnEt$_3$NCl	0.1	50	56	9
5	BnEt$_3$NCl	1	41	75	0
6[b]	PPh$_4$Br	0.1	61	70	9

[a] w.r.t. Rh^{III}(ttp)Me
[b] 73% PPh$_3$ and 21% O=PPh$_3$ were formed w.r.t. PPh$_4$Br

$$Ph_4P^+ \ + \ OH^- \ \rightleftharpoons \ Ph_4POH$$

$$Ph_4POH \ + \ OH^- \ \rightleftharpoons \ Ph_4PO^- \ + \ H_2O$$

$$Ph_4PO^- \ \longrightarrow \ Ph_3P=O \ + \ Ph^-$$

$$Ph^- \ + \ H_2O \ \longrightarrow \ PhH \ + \ OH^-$$
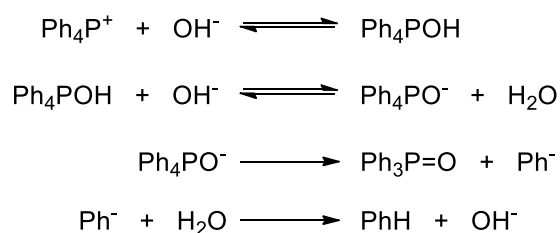
Scheme 2.6 Hydrolysis of PPh$_4^+$ to O=PPh$_3$.

2.5 Mechanistic Investigations

2.5.1 Deuterium Labeling Experiments

To test whether water was the hydrogen source to enrich PCP to give **5**, a series of deuterium labeling experiments using D_2O were performed. Under the standard catalytic PCP hydrogenation conditions with H_2O replaced with D_2O, PCP was converted to deuterium-enriched **5**-*d* in 64% yield (eq 2.18).[28] ^{1}H NMR analysis of the isolated **5**-*d* gave proton integration ratio with aromatic : internal benzylic : terminal benzylic = 8.00 : 2.12 : 3.3, assuming no aromatic H/D exchange (Figure 2.1). Hence, the terminal benzylic positions are ((6 - 3.31) / 6) x 100% = 45% deuterated, while the internal benzylic positions are ((4 - 2.12) / 4) x 100% = 47% deuterated. Attempted detection of 4-d_1,4'-d_1-dimethylbibenzyl upon its initial formation by ^{1}H NMR spectroscopy was unsuccessful because the benzylic ^{1}H signal of PCP (δ = 2.81 ppm) partially overlapped with the internal benzylic ^{1}H signal of deuterated **5** (δ = 2.79 ppm), giving non-conclusive ^{1}H integration. Nevertheless, no deuterated PCP was observed during the catalysis.

$$\text{Rh}^{III}\text{(ttp)Me (10 mol\%)}$$
$$D_2O \text{ (100 equiv)}$$
$$C_6D_6, 200\ ^oC$$
$$\text{dark, 3 d}$$

(2.19)

5-*d*
64%
mixture of isotopomers
terminal benzylic D% = 45%
internal benzylic D% = 47%
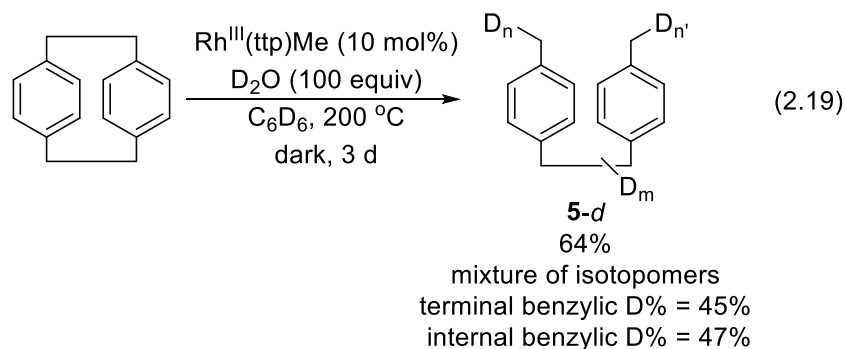
Since H/D exchange at the internal benzylic positions was observed, we independently examined the H/D exchange activity of **5** under identical conditions (eq 2.19). The isolated **5**-*d'* was analyzed by ^{1}H NMR spectroscopy to give proton integration ratio with aromatic : internal benzylic : terminal benzylic = 8.00 : 1.15 : 5.51 (Figure 2.1). Hence, the terminal benzylic positions are ((6 - 5.51) / 6) x 100% = 8% deuterated, while the internal

benzylic positions are ((4 - 1.15) / 4) x 100% = 71% deuterated. This suggested that the post-exchange activity at the terminal benzylic positions was minor within the catalysis time scale. The more extensive internal benzylic H/D exchange was due to the more rapid benzylic CHA with ethylbenzene than toluene, governed by the weaker C-H bond.[29] These observations, in addition to the control experiment in Table 2.1, eq 2.21, further support that water is the hydrogen source.
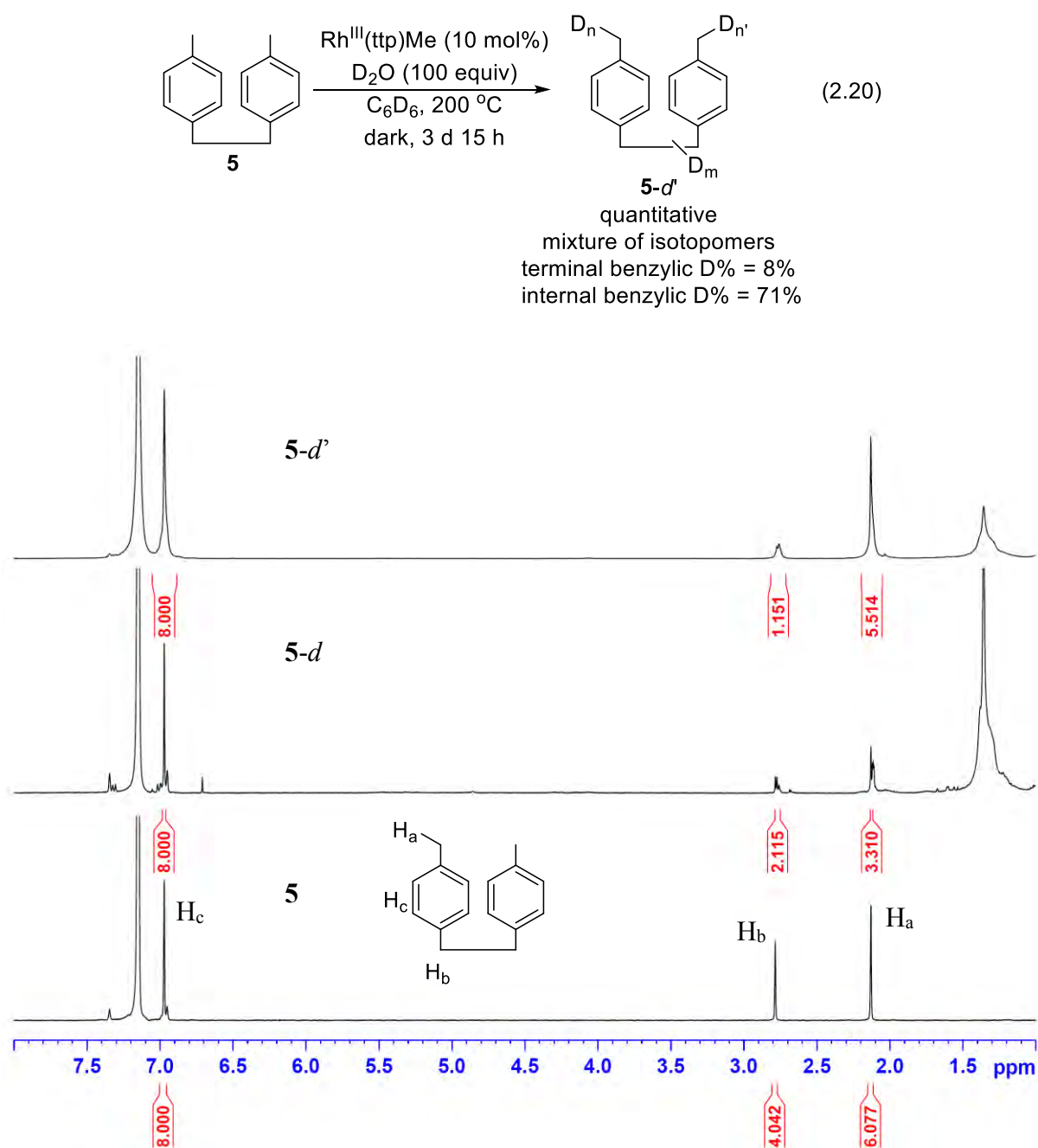
Figure 2.1 ^{1}H NMR Spectra of Product **5**, **5-**d and **5-**d'.

2.5.2 CCA via CHA Intermediate

As Milstein and Jones have shown CHA is a prior step to the CCA in α,α'-diphosphino-m-xylenes[30] and biphenylene,[31] respectively, we investigated whether benzylic CHA would also take place for the CCA of PCP. The stoichiometric reaction of $Rh^{III}(ttp)Cl$ with PCP (10 equiv) in the presence of KOH (10 equiv) and D_2O (1000 equiv) was closely monitored by ^1H NMR spectroscopy (Table 2.4, eq 2.20, Figure 1). After 12 d of heating at 60 ^oC and then at 120 ^oC, PCP remained unreacted and undeuterated. At the same time, $Rh^{III}(ttp)Cl$ was completely consumed to give $Rh^{II}_2(ttp)_2$ in 71% yield. The poor mass balance for rhodium porphyrin complexes, especially at 60 ^oC, was due to the poor solubility of $Rh^{II}_2(ttp)_2$. No benzylic CHA of PCP with $Rh^{II}_2(ttp)_2$ to give $Rh^{III}(ttp)(cyclophanyl)$ was observed.[14,29,32b] The rigid structure of PCP may induces steric repulsion between the benzene rings and $Rh^{II}(ttp)$, such that the four-centered transition state for benzylic CHA is not accessible (Scheme 2.7).[32] Upon further heating at 130 ^oC for 1 d the reaction mixture yielded 6% of di-rhodium benzyl intermediate **7**. Therefore, CCA of PCP occurred directly without any observable CHA process.

Table 2.4 Reaction Time Profile of Rh^{III}(ttp)Cl with PCP under Basic Conditions.
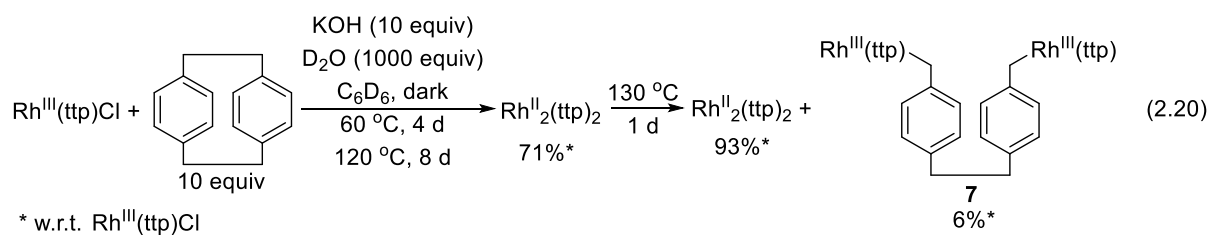
entry	temp / °C	time / h	yield / %				
			Rh^{III}(ttp)Cl	Rh$^{II}_2$(ttp)$_2$	Rh^{III}(ttp)H	7	Total [Rh]
1	r.t.	0	100	0	0	0	100
2	60	1	35	8	2	0	45
3	60	18	0	22	14	0	36
4	60	72	0	24	4	0	28
5	60	96	0	30	4	0	34
6	120	104	0	53	7	0	60
7	120	120	0	60	9	0	69
8	120	144	0	55	9	0	64
9	120	216	0	56	5	0	61
10	120	288	0	71	7	0	78
11	130	312	0	93	0	6	99
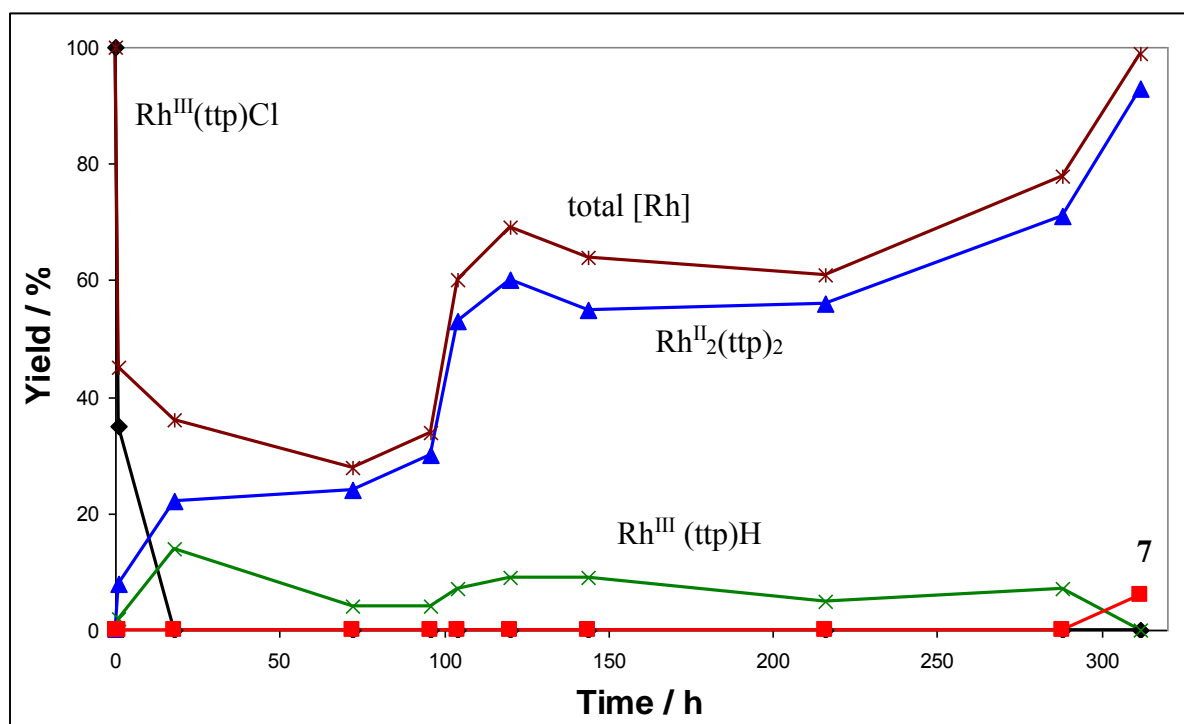
Figure 2.1 Reaction Time Profile of Reaction of Rh^{III}(ttp)Cl with [2.2]Paracyclophane in the presence of KOH and D$_2$O
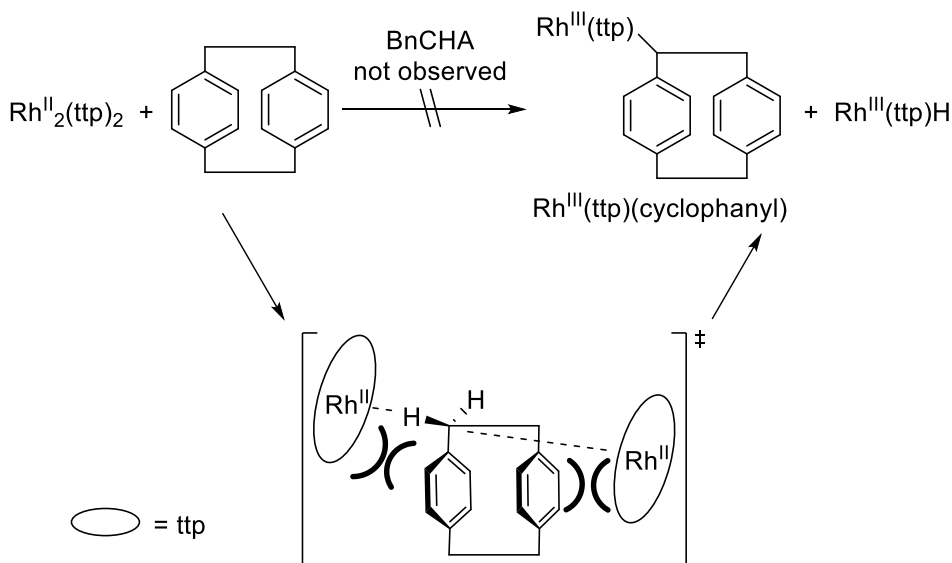
Scheme 2.7 Absence of BnCHA of PCP with $Rh^{II}_2(ttp)_2$.

2.5.3 ^{1}H NMR Kinetics of Stoichiometric CCA

In order to gain a deeper understanding on the CCA step of PCP with rhodium(II) porphyrins, the reaction kinetics of stoichiometric CCA of PCP with monomeric $Rh^{II}(tmp)$ were monitored by ^{1}H NMR spectroscopy. $Rh^{II}(tmp)$, pioneered by Wayland et al, is an ideal candidate since it exists as a persistent metalloradical.[33] $Rh^{II}(tmp)$ reacted smoothly with PCP at 150 °C in C_6D_6 for 23 h to yield 85% of di-rhodium benzyl CCA product **8** without any intermediates observed, establishing the high yielding stoichiometric reaction (eq 2.21).

$$(2.21)$$
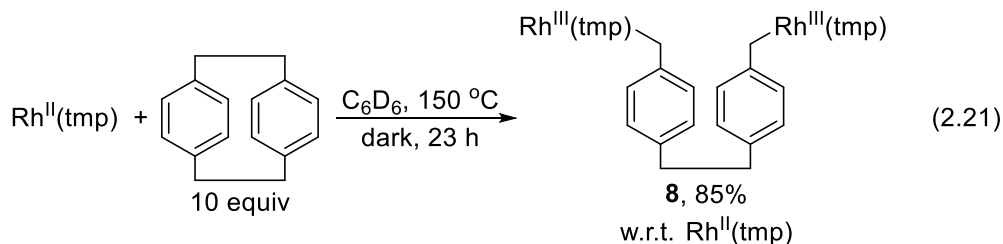
Attempt to search for any pre-coordination between PCP and $Rh^{II}(tmp)$ by ^{1}H NMR spectroscopy was not fruitful. No change in chemical shift was observed both for $Rh^{II}(tmp)$ ($\delta = 18.38$ ppm for pyrrole proton) and PCP ($\delta = 6.33$ ppm for aromatic proton and $\delta = 2.81$

ppm for benzylic proton). The kinetic runs were then conducted with $[Rh^{II}(tmp)] = 0.24\text{-}0.48$ mM, $[PCP] = 4.8\text{-}14.4$ mM in at least 10 fold excess and temperature of 140-170 $^{\circ}$C till the disappearance of $Rh^{II}(tmp)$ for at least 4 half-lives.

2.5.3.1 Determination of Reaction Orders

The rate equation can be expressed as eq 2.22. Since PCP was employed in excess, eq 2.22 is simplified to eq 2.23 where $k_{obs} = k[PCP]^n$.

$$\text{rate} = k[Rh^{II}(tmp)]^m[PCP]^n \quad (2.22)$$

$$= k_{obs}[Rh^{II}(tmp)]^m \quad (2.23)$$

First, the value of m was evaluated with typical conditions $[Rh^{II}(tmp)] = 0.24\text{-}0.48$ mM and $[PCP] = 9.6$ mM at 150 $^{\circ}$C. The disappearance of $Rh^{II}(tmp)$ fitted best with pseudo second order kinetics (Figure 2.2 and Appendix II for other plots). The kinetic order of $Rh^{II}(tmp)$ was measured to be two and hence m = 2. The corresponding derivation of the second order integrated rate equation is as follow:

$$\text{rate} = -d[Rh^{II}]/dt = k_{obs}[Rh^{II}]^2$$

$$-d[Rh^{II}]/[Rh^{II}]^2 = k_{obs}dt$$

Integrate both sides of the equation from time = 0 to time = t.

$$1/[Rh^{II}]_t - 1/[Rh^{II}]_0 = k_{obs}t$$

$$1/[Rh^{II}]_t = 1/[Rh^{II}]_0 + k_{obs}t$$

Where $1/[Rh^{II}]_t$ and t are the y-axis and x-axis, respectively.
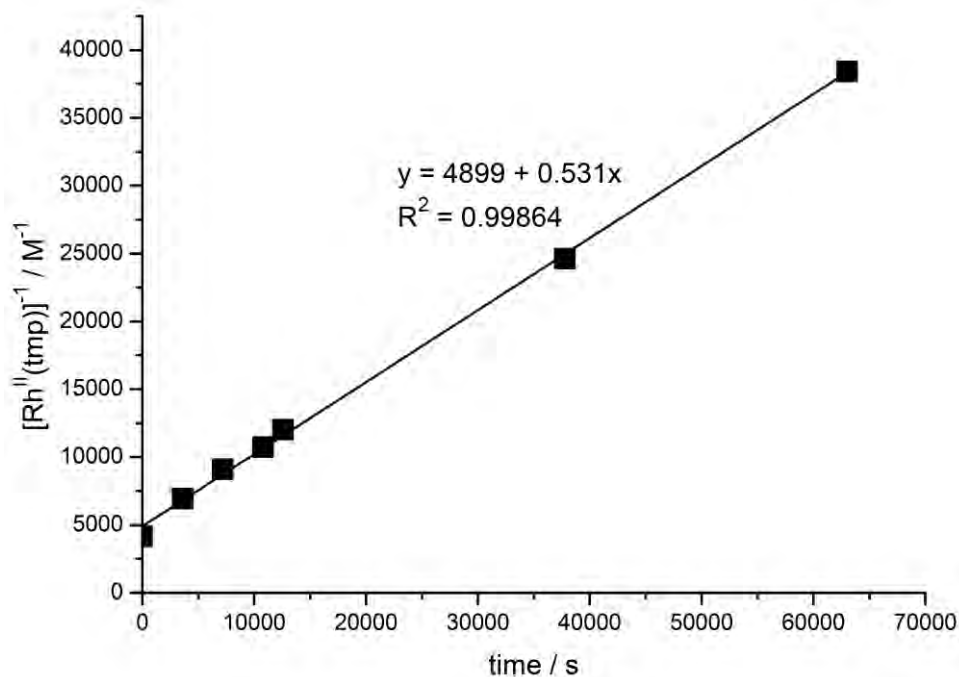
Figure 2.2 A Typical Pseudo 2nd Order Kinetic Plot with $[Rh^{II}(tmp)] = 0.24$ mM and $[PCP] = 9.6$ mM at 150 °C.

The value of n was then evaluated with typical conditions $[Rh^{II}(tmp)] = 0.24$ mM and $[PCP] = 4.8\text{-}14.4$ mM at 150 °C. The results also fitted best with pseudo second order kinetic plot (Appendix II). The rate of disappearance of $Rh^{II}(tmp)$ increases linearly with increasing $[PCP]$ from 4.8 mM to 14.4 mM, giving a pseudo first order kinetic plot (Figure 2.3). The kinetic order of PCP was measured to be one and hence n = 1.
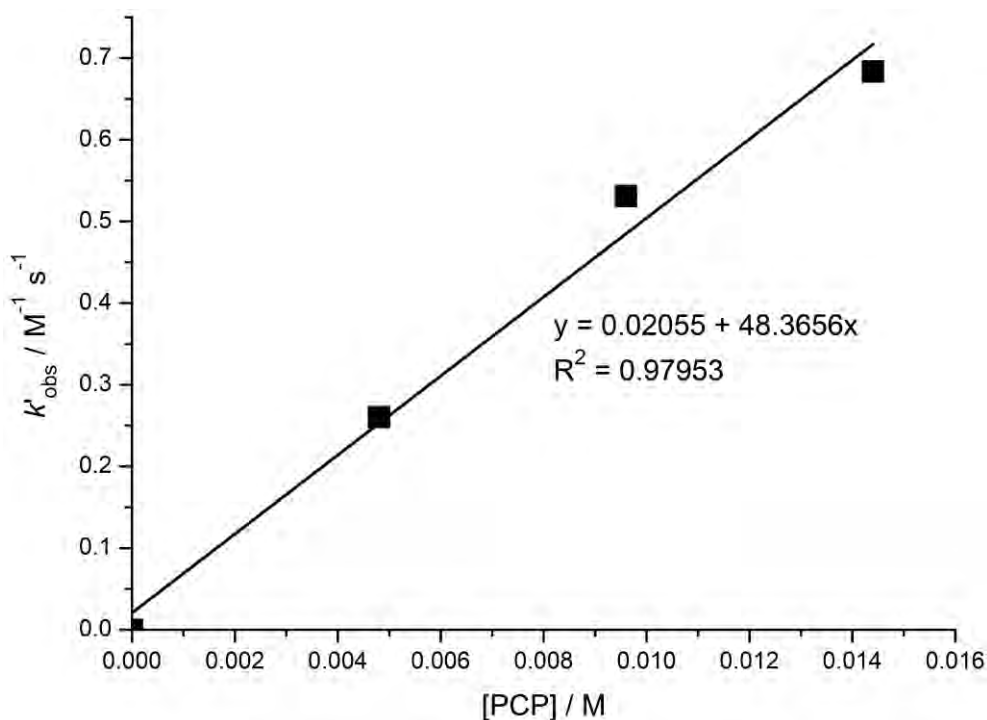
Figure 2.3 Plot of k_{obs} against [PCP] with [Rh^{II}(tmp)] = 0.24 mM and [PCP] = 4.8-14.4 mM.

Table 2.5 summarizes the k_{obs} measured at various conditions. The kinetic orders of Rh^{II}(tmp) and PCP were fitted to be two and one, respectively. The rate equation can be expressed as rate = k[Rh^{II}(tmp)]^2[PCP].

Table 2.5 k_{obs} Measured at Various Conditions.

entry	[Rh^{II}(tmp)] / mM	[PCP] / mM	k_{obs} / M^{-1} s^{-1}
1	0.24	9.6	0.53±0.01
2	0.24	9.6	0.56±0.03
3	0.48	9.6	0.55±0.03
4	0.24	4.8	0.26±0.02
5	0.24	14.4	0.68±0.04

2.5.3.2 Activation Parameters

The rates were measured at typical conditions [Rh^{II}(tmp)] = 0.24 mM and [PCP] = 9.6 mM at 140 °C to 170 °C. Table 2.6 summarized the temperature dependent rate constants (Appendix II for kinetic plots). These data were used to evaluate the activation parameters.

Table 2.6 k_{obs} Measured at Various Conditions.

entry	[Rh^{II}(tmp)] / mM	[PCP] / mM	T / °C	k_{obs} / M^{-1} s^{-1}	k / M^{-2} s^{-1}
1	0.24	9.6	140	0.152±0.007	15.8
2	0.24	9.6	150	0.53±0.01	55.3
3	0.48	9.6	160	2.0±0.2	205
4	0.24	4.8	170	3.1±0.3	319

where $k = k_{obs}/[PCP]$

The Eyring equation describes the relationships between the temperature dependent rate constants and activation parameters (eq 2.24).[34]

$$\ln(k/T) = -\Delta H^{\ddagger}/(RT) + \ln(\kappa/h) + \Delta S^{\ddagger}/R \quad (2.24)$$

(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 $\ln(\kappa/h) + \Delta S^{\ddagger}/R$ (Table 2.7 and Figure 2.4).

Table 2.7 $\ln(k_{obs}/T)$ at Various $1/T$.

entry	T / °C	$1/T$ / K^{-1}	k / M^{-2} s^{-1}	$\ln(k/T)$
1	140	0.00242	15.8	-3.262
2	150	0.00236	55.3	-2.036
3	160	0.00231	205	-0.746
4	170	0.00226	319	-0.328
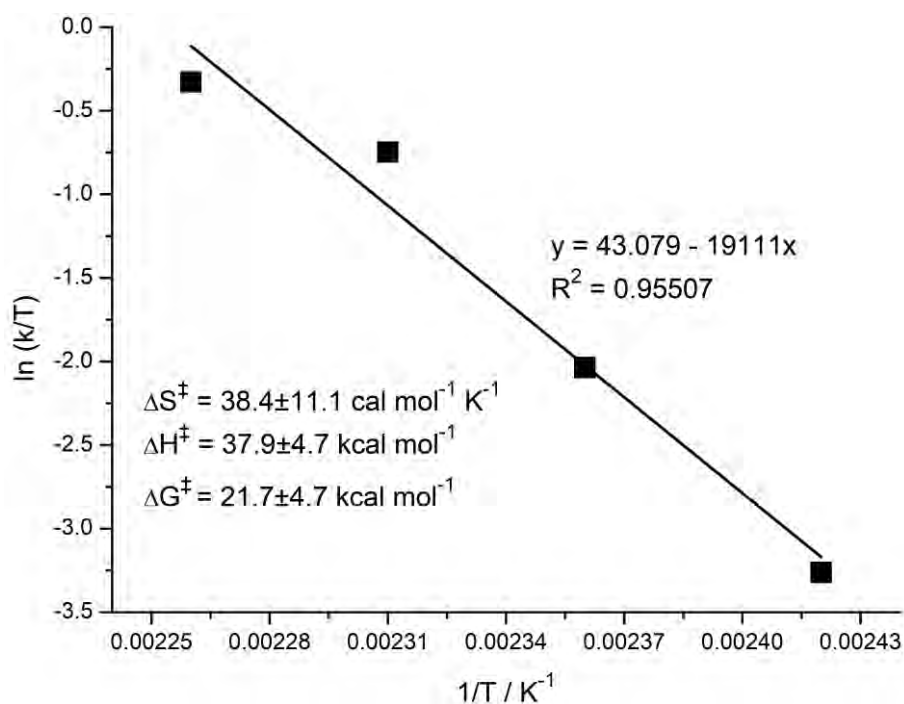
Figure 2.4 Eyring Plot of the CCA of PCP with $Rh^{II}(tmp)$ at 140 $^\circ$C to 170 $^\circ$C.

Since	y-intercept	=	$\ln(\kappa/h) + \Delta S^{\ddagger}/R$
	43.079	=	$\ln(1.3807 \times 10^{-23}/6.6261 \times 10^{-34}) + \Delta S^{\ddagger}/1.9859$
	$\Delta S^{\ddagger}$	=	38.4$\pm$11.1 cal mol^{-1} K^{-1}
And	slope	=	$\Delta H^{\ddagger}/R$
	-19111	=	$\Delta H^{\ddagger}/1.9859$
	$\Delta H^{\ddagger}$	=	37.9$\pm$4.7 kcal mol^{-1}
Then	$\Delta G^{\ddagger}$	=	$\Delta H^{\ddagger}\text{-}T\Delta S^{\ddagger}$
	$\Delta G^{\ddagger}$	=	21.7$\pm$4.7 kcal mol^{-1} (150 $^\circ$C)

Roth has reported the computed activation parameters of PCP thermolysis at 188 $^\circ$C (eq 2.25).[35] These values were compared with the current experimental results in Table 2.8. The activation enthalpies were very similar, agreeing the cleavage of benzylic C-C bond. The activation entropy $\Delta S^{\ddagger}$ of 38.4$\pm$11.1 cal mol^{-1} K^{-1} is much greater than the computed value of

2.7±1.1 cal mol^{-1} K^{-1}.[35] This positive value suggests a dissociative nature of the transition state, however, does not simply resembles a simple thermal PCP ring-opening situation.

(eq 2.25)

$\Delta H^{\ddagger} = 37.7 \pm 0.5$ kcal mol^{-1}

$\Delta S^{\ddagger} = 2.7 \pm 1.1$ cal mol^{-1} K^{-1}

$\Delta G^{\ddagger} = 36.5 \pm 0.5$ kcal mol^{-1}

188 $^{\circ}$C
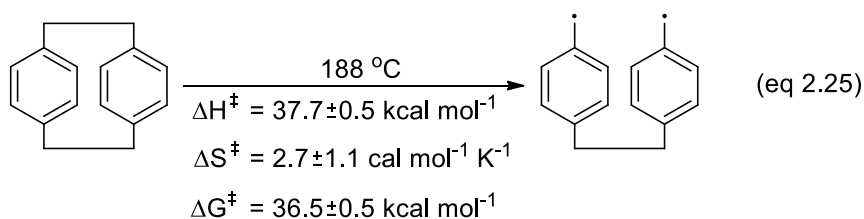
Table 2.8 Comparison of Activation Parameters

	reaction 2.21 (this work)	reaction 2.25
$\Delta H^{\ddagger}$ / kcal mol^{-1}	37.9±4.7	37.7±0.5
$\Delta S^{\ddagger}$ / cal mol^{-1} K^{-1}	38.4±11.1	2.7±1.1
$\Delta G^{\ddagger}$ / kcal mol^{-1}	21.7±4.7 (150 $^{\circ}$C)	36.5±0.5 (188 $^{\circ}$C)

2.5.4 Mechanistic Implications

2.5.4.1 Rh^{II}(tmp) as a Trap

Rh^{II}(tmp) can be a reagent for CCA or a radical trap. If it is a trap, the kinetic scheme would follows the one illustrated in Scheme 2.8, such that the consumption of PCP, i.e. the reaction rate, is independent of [Rh^{II}(tmp)]. The current experimental results show that the reaction rates are [Rh^{II}(tmp)] dependent. Saturation kinetics is unable to determine since data points are limited at this moment.
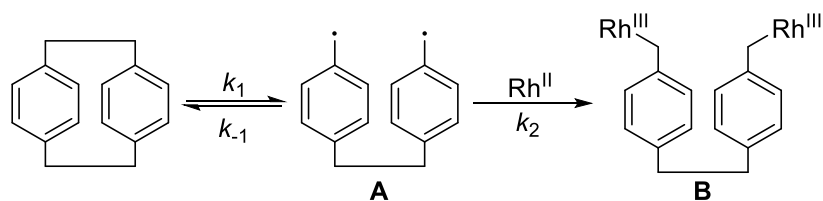
with steady state approximation on diradical intermedate **A**

$$d[\mathbf{A}]/dt = k_1[\text{PCP}] - k_{-1}[\mathbf{A}] - k_2[\text{Rh}^{II}]^2[\mathbf{A}] = 0$$

$$[\mathbf{A}] = k_1[\text{PCP}]/(k_{-1} + k_2[\text{Rh}^{II}]^2)$$

$$-d[\text{PCP}]/dt = d[\mathbf{B}]/dt = k_2[\text{Rh}^{II}]^2[\mathbf{A}]$$

$$= k_1 k_2[\text{Rh}^{II}]^2[\text{PCP}]/(k_{-1} + k_2[\text{Rh}^{II}]^2)$$

case 1: $k_2[\text{Rh}^{II}]^2 \gg k_{-1}$, i.e. Rh^{II} is a fast trap

then $-d[\text{PCP}]/dt = k_1[\text{PCP}]$

case 2: $k_2[\text{Rh}^{II}]^2 \ll k_{-1}$, i.e. Rh^{II} is a slow trap

then $-d[\text{PCP}]/dt = (k_1 k_2/k_{-1})[\text{Rh}^{II}]^2[\text{PCP}]$

case 3: $k_2[\text{Rh}^{II}]^2 \sim k_{-1}$

then $-d[\text{PCP}]/dt = k_1 k_2[\text{Rh}^{II}]^2[\text{PCP}]/(2k_2[\text{Rh}^{II}]^2)$

$$= (k_1/2)[\text{PCP}]$$

Scheme 2.8 Kinetic Scheme of Trapping by Rh^{II}.

The kinetics of PCP thermolysis in the presence of NO or O_2 as radical trap have been investigated by Roth (Table 2.8, eqs. 2.25 and 2.26).[35] The trapping rate constants are in the range of 10^{-6} to 10^{-3} s^{-1} with saturation rate constants at about 10^{-3} s^{-1}. In contrast, the rate constants of CCA of PCP with $\text{Rh}^{II}(\text{tmp})$ are in the range of 10 to 10^2 M^{-2} s^{-1}, which is greater than the saturation rate constants by at least four orders of magnitude. The superior performance of $\text{Rh}^{II}(\text{tmp})$ suggests that it is unlikely a radical trap.

Table 2.8 Trapping Rate Constants of PCP with NO and O$_2$.
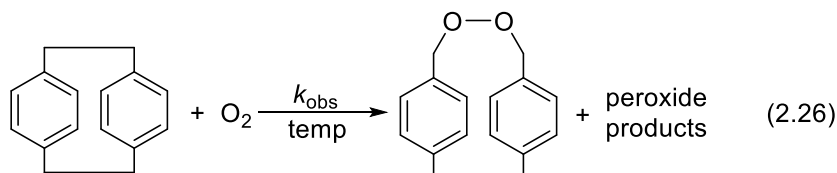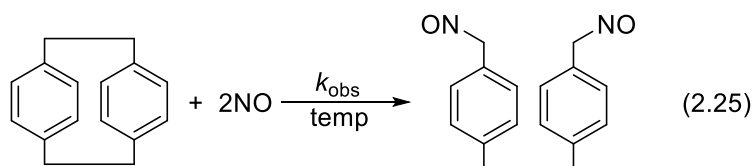
$$rate = k_{obs}[PCP]$$

entry	trap (pressure)	temperature range / °C	k_{obs} range / s^{-1}
1	NO (51.5 to 448.31 mbar)	168.90 to 208.40	5.43×10^{-6} to 2.34×10^{-3}
2	O$_2$ (300.5 to 931.1 mbar)	178.90 to 218.29	2.16×10^{-5} to 5.57×10^{-4}

2.5.4.2 PCP Homolysis Rate at 200 °C

Even though Rh^{II}(tmp) is not a trap, the benzylic C-C bond of PCP may undergo homolysis with sufficient rate upon heating when the bond is weak. In the presence of H atom donor, e.g. Rh^{III}(por)H, the bis-benzylic radical intermediate **A** will be trapped to yield the hydrogenation product **5** (eq 2.27).
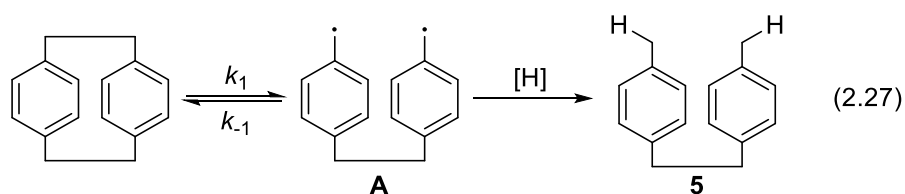
The benzylic C-C BDE of PCP is estimated to be 26.8 kcal mol^{-1} based on the method employed by Jones, which the C-C BDE of biphenylene was estimated (Scheme 2.7).[36]

$\Delta H_{rxn} = BDE(C\text{-}C)$

$\Delta H_f^o = 36.9 \text{ kcal mol}^{-1[37]}$ $\Delta H_f^o{}_1$

ΔH_{rxn2}

$\Delta H_f^o = -10.1 \text{ kcal mol}^{-1[38]}$ $\Delta H_f^o{}_1$ $+ \ 2H\cdot$

$\Delta H_f^o = 52.1 \text{ kcal mol}^{-1[36]}$

$\Delta H_{rxn2} = 2BDE(p\text{-xylene BnC-H})^{[39]} = 2(89) = 178 \text{ kcal mol}^{-1}$

$178 = \Delta H_f^o{}_1 + 2\Delta H_f^o(H\cdot) - \Delta H_f^o(4,4'\text{-dimethylbibenzyl})$

$178 = \Delta H_f^o{}_1 + 2(52.1) - (-10.1)$

$\Delta H_f^o{}_1 = 178 - 104.2 - 10.1 = 63.7 \text{ kcal mol}^{-1}$

$BDE(C\text{-}C) = \Delta H_f^o{}_1 - \Delta H_f^o(PCP)$

$= 63.7 - 36.9 = 26.8 \text{ kcal mol}^{-1}$
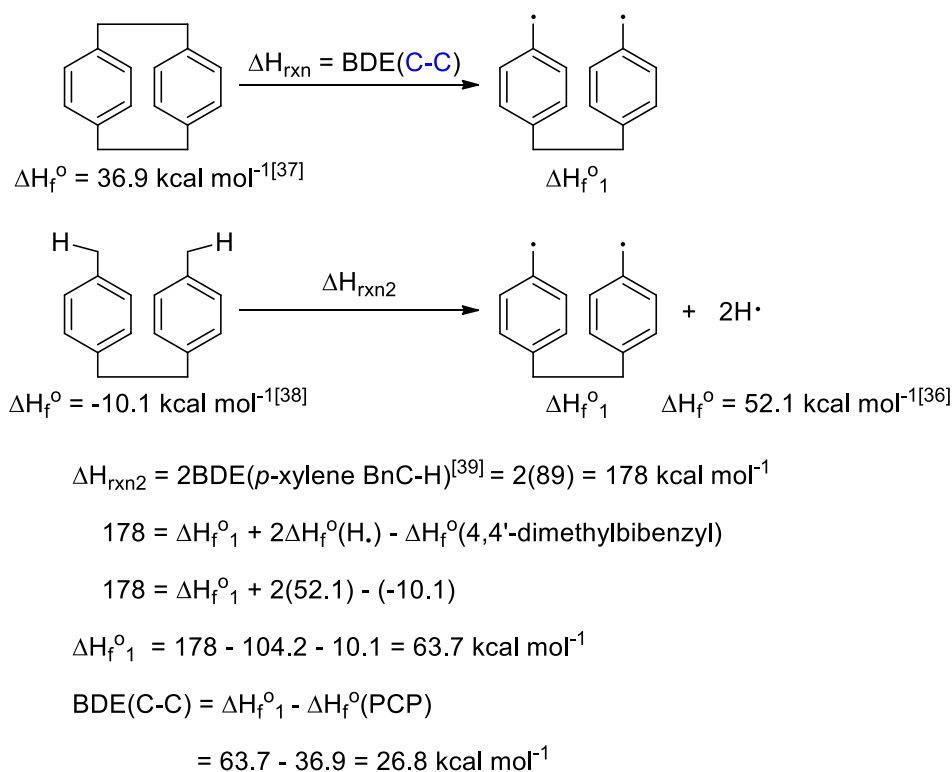
Scheme 2.7 Estimation of Benzylic C-C BDE of PCP.

Assume the $\Delta G^{\ddagger}$ of homolysis in eq 2.27 equals the benzylic C-C BDE of PCP, i.e. 26.8 kcal mol^{-1}, it yields $k_1 = 4.1$ s^{-1} at 200 °C calculated from the eq 2.28. This is equivalent to a fast half-life of 0.17 s. In other words, the reaction in eq 2.27 can reach completion in about 1 s in the presence of sufficient H atom donor as trap.

$$\ln k = \ln(k_B T/h) - (\Delta G^{\ddagger}/RT) \qquad (2.28)$$

(k_B is the Boltzman constant, h is the Plank constant, R is the ideal gas constant)

The present experimental results on catalytic PCP hydrogenation contradict with this fast homolysis rate. This probably implies (1) the intramolecular radical recombination of **A** is very fast such that trapping is impossible; or (2) H atom donor is very limited in the reaction and most **A** is converted back to PCP.

2.5.4.3 Possible CCA Transition State

The second order dependence of $Rh^{II}(tmp)$ and first order dependence of PCP suggest a termolecular CCA process which have been proposed by Wayland for the $Rh^{II}(tmp)$ bi-metalloradical CHA process (Scheme 2.8).[32] The simultaneous breaking of one bond and formation of two bonds provide a synergistic effect to lower down the activation barrier. However, with the best understanding at this stage, we are unclear about the dissociative nature of the transition state based on the positive $\Delta S^{\ddagger}$.

$$2Rh^{II}(tmp) + CH_4 \longrightarrow \left[\begin{array}{c} H \\ | \\ (tmp)Rh\text{-}\text{-}\text{-}C\text{-}\text{-}\text{-}H\text{-}\text{-}\text{-}Rh(tmp) \\ \diagup \quad \diagdown \\ H \quad H \end{array} \right]^{\ddagger} \longrightarrow Rh^{III}(tmp)H + Rh^{III}(tmp)CH_3$$
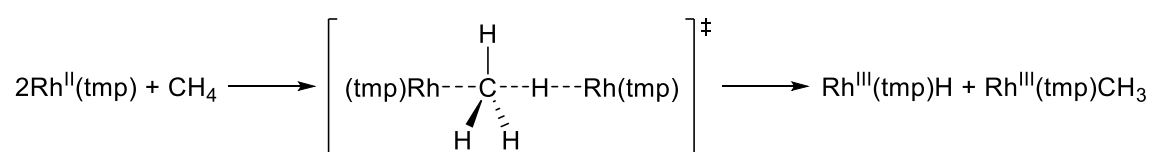
Scheme 2.8 Termolecular Reaction in CHA of CH_4 with $Rh^{II}(tmp)$.

2.5.4.4 Computational Study

To better understand the interaction between $Rh^{II}(tmp)$ and PCP in the CCA process, transition state geometry analysis by Spartan '10 software at PM3 level has been performed, as limited by our theoretical capability. The *meso*-aryl groups omitted rhodium porphyrins were used to shorten the calculation steps without over simplify the system. The transition state geometry was optimized under the following two constrains: (1) the Rh_1-C_1 and Rh_2-C_2 distance does not exceed 3.100 Å, which is about 1.5 times of the Rh-C(benzylic) bond length in $Rh^{III}(ttp)Bn(p\text{-}^tBu)$ (2.085 Å) and $Rh^{III}(ttp)Bn(p\text{-}F)$ (2.064 Å);[40] (2) the C_1-C_2 distance does not exceed 2.350 Å, which is 1.5 times of a intact benzylic C-C bond length in PCP.

From the optimized transition state geometry shown in Figure 2.5, the C_1-C_2 bond is lengthened from 1.556 Å (C_3-C_4) to 1.793 Å. Rh_1 interacts with C_1 at an angle of 33° to the C_1-C_2 bond and a distance of 2.349 Å away. Rh_2 interacts with C_2 at an angle of 49° to the C_1-C_2 bond and a distance of 2.239 Å away. Distortion of rhodium porphyrin from planarity

is observed, probably due to steric congestion. A zig-zag Rh-C-C-Rh interaction is observed (Figure 2.6).

key data:	
C_1-C_2	1.793 Å
C_3-C_4	1.556 Å
Rh_1-C_1	2.349 Å
Rh_2-C_2	2.239 Å
α	33º
β	49º
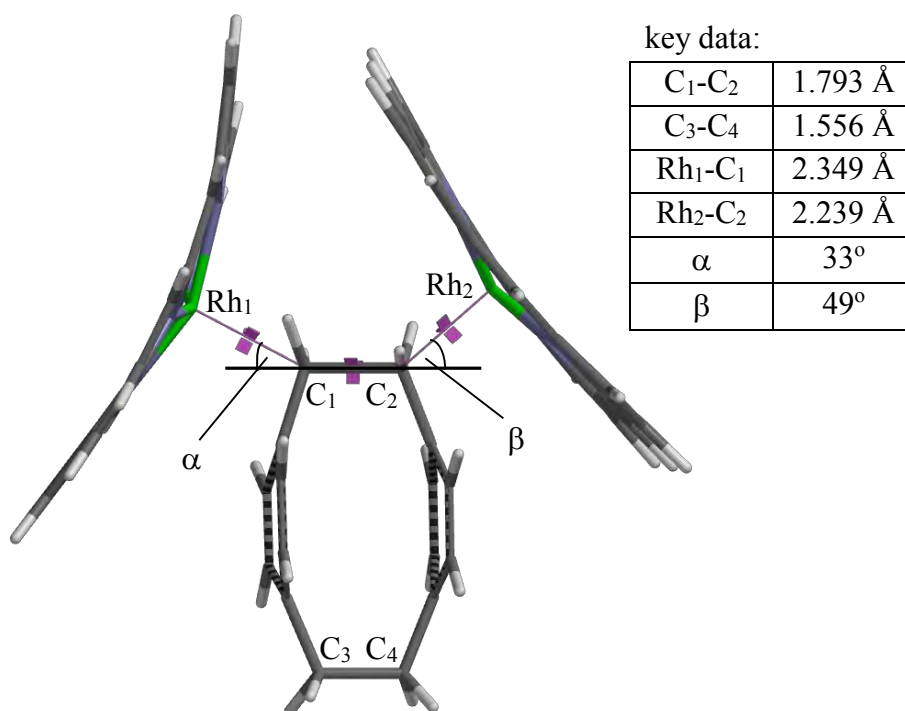
Figure 2.5 Computed Transition State Geometry of CCA of PCP with Rh(por) (side view).
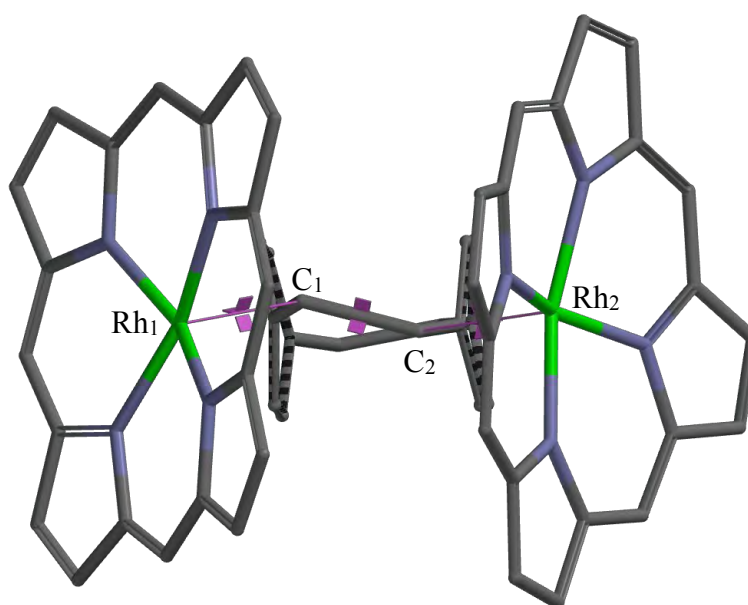
Figure 2.6 Computed Transition State Geometry of CCA of PCP with Rh(por) (top view, hydrogen omitted for clarity).

2.5.5 Hydrolysis of $Rh^{III}(ttp)R$

To further confirm that hydrolysis of $Rh^{III}(ttp)R$ indeed releases alkane from the rhodium porphyrin, $Rh^{III}(ttp)R$ (R = Me, Bn and ^{i}Pr) was subjected to hydrolysis study. The 1° alkyls $Rh^{III}(ttp)Me$ and $Rh^{III}(ttp)Bn$ were hydrolyzed to give good yields of CH_4 and toluene, respectively (Table 2.9, eq 2.29, entries 1 and 2). The hydrolysis of $Rh^{III}(ttp)Bn$ serves as a mimic of the hydrolysis of CCA product di-rhodium benzyl **7** to give 4,4'-dimethylbibenzyl **5**. The 2° alkyl $Rh^{III}(ttp)^i$Pr underwent competitive hydrolysis and β-H elimination to give a mixture of propane and propene (Table 2.9, eq 2.29, entry 3).

Table 2.9 Hydrolysis of $Rh^{III}(ttp)R$.

$$Rh^{III}(ttp)R \; + \; H_2O \; \xrightarrow[\substack{1000 \\ equiv}]{\substack{C_6D_6 \\ 200\ ^oC,\ dark \\ time}} \; Rh^{III}(ttp)H \; + \; Rh^{II}{}_2(ttp)_2 \; + \; \substack{Rh\ porphyrin \\ unknowns} \; + \; RH \qquad (2.29)$$
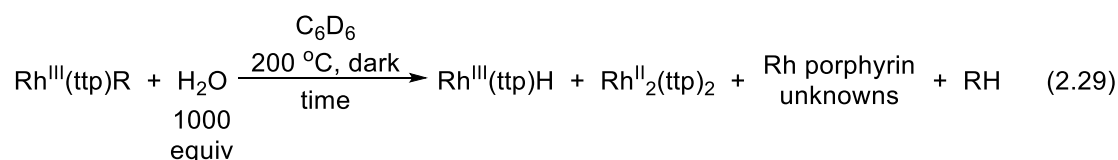
entry	R	time	yield / %					
			$Rh^{III}(ttp)R$	$Rh^{III}(ttp)H$	$Rh^{II}{}_2(ttp)_2$	Rh porphyrin unknowns	Total [Rh]	RH
1[a]	Me	1 d	13	6	11	20	50	87
2	Bn	3.5 d	2	15	0	41	58	66
3	^{i}Pr	50 h	2	36	2	20	60	45[b]

[a] conducted at 150 ^{o}C, Fung, H. S. *Unpublished Results*, CUHK, 2011
[b] 35% yield of propene was formed

During the hydrolysis of $Rh^{III}(ttp)^i$Pr, rapid alkyl 1,2-rearrangement of $Rh^{III}(ttp)^i$Pr was observed and attained equilibrium after 1 h to give a mixture of $Rh^{III}(ttp)^i$Pr, $Rh^{III}(ttp)^n$Pr and $Rh^{III}(ttp)H$ in 13%, 23% and 58% yields, respectively, together with 47% yield of propene (eq 2.30).[21] The secondary : primary ratio of 0.57 agrees with the previous reported ratio of 0.70 measured at 120 ^{o}C.[21b] $Rh^{III}(ttp)H$ is the dominant product since elimination is favored by high temperature.

$$\text{Rh}^{III}(\text{ttp})^i\text{Pr} + \text{H}_2\text{O} \xrightarrow[\substack{1\text{ h}}]{\substack{\text{C}_6\text{D}_6 \\ 200\ ^\circ\text{C, dark}}} \text{Rh}^{III}(\text{ttp})^n\text{Pr} + \text{Rh}^{III}(\text{ttp})\text{H} + \text{Rh}^{II}_2(\text{ttp})_2 + \text{\Large \diagup\!\!\diagdown} \qquad (2.30)$$

| 13% | 1000 | | 23% | 58% | 2% | 47% |
| recovery | equiv | | | | | |
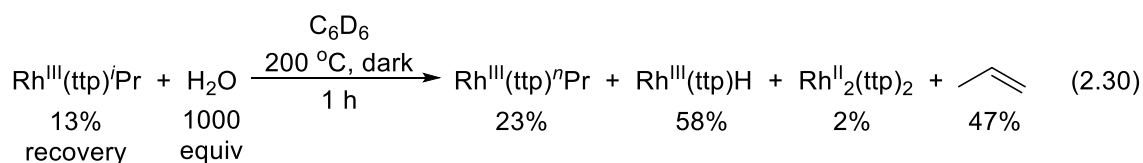
2.6 Proposed Mechanism

Based on the previous studies and current findings, Scheme 2.9 illustrates the proposed catalytic cycle for the catalytic PCP hydrogenation using H_2O.
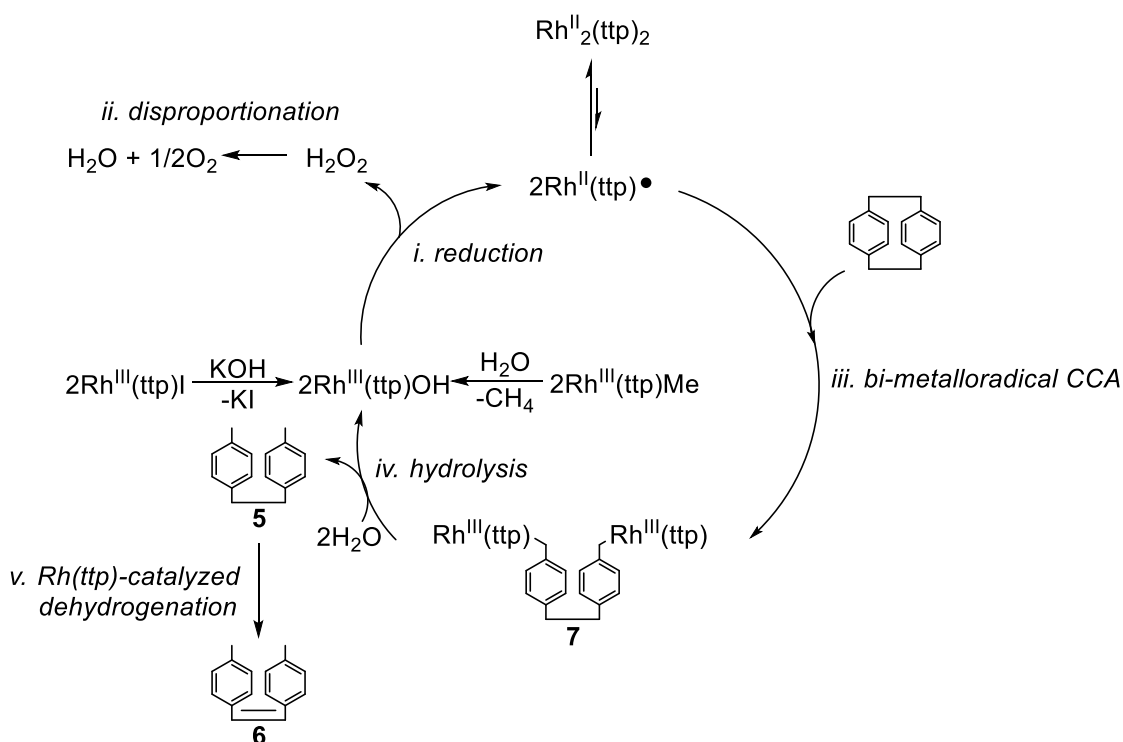
Scheme 2.9 Proposed Catalytic Cycle for the Catalytic Hydrogenation of PCP using H_2O.

$Rh^{III}(ttp)I$ pre-catalyst undergoes rapid ligand substitution with KOH to first give $Rh^{III}(ttp)OH$.[20] The hydroxide then donates one electron to the ligated Rh^{III} metal center and reduces it to Rh^{II}, with itself oxidized to hydroxyl radical (step i).[41] Electron poor porphyrin ligand may further favor this reduction process to Rh(II). Hydroxyl radicals combine to form H_2O_2. In the presence of OH^-, I^- or transition metals, they catalyze the disproportionation of

H_2O_2 to H_2O and O_2 (step ii).[42] Previous study by Chan group shows that $Rh^{III}(ttp)I$ reacted

with 10 equiv of KOH at 80 °C in C_6D_6 for 1.5 h to yield 72% of $Rh^{II}_2(ttp)_2$ (eq 2.31).[20]

Alternatively, $Rh^{III}(ttp)Me$ pre-catalyst is hydrolyzed by H_2O to give CH_4 and $Rh^{III}(ttp)OH$,

which is converted to $Rh^{II}_2(ttp)_2$ accordingly.[6]

$$2Rh^{III}(ttp)I \ + \ 2KOH \ \xrightarrow[\substack{80\ °C,\ 1.5\ h}]{C_6D_6} \ Rh^{II}_2(ttp)_2 \ + \ "2KI" \ + \ "H_2O_2" \quad (2.31)$$

$$\text{10 equiv} \qquad\qquad\qquad\qquad\qquad 72\%$$
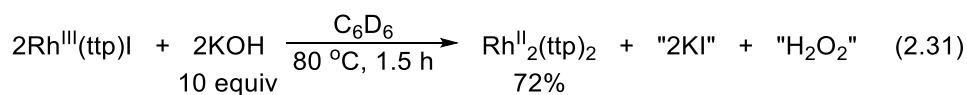
Under thermal conditions, $Rh^{II}_2(ttp)_2$ dissociates to form $Rh^{II}(ttp)$ with equilibrium

constant estimated to be 19 at 200 °C (eq 2.32 and Scheme 2.10).[43] $Rh^{II}(ttp)$ cleaves the

benzylic carbon-carbon bond of PCP, in a termolecular manner similar to $Rh^{II}(tmp)$, to yield

the di-rhodium benzyl **7** (step iii).

$$Rh^{II}_2(ttp)_2 \ \underset{}{\overset{\substack{200\ °C \\ K = 19}}{\rightleftharpoons}} \ 2Rh^{II}(ttp) \quad (2.32)$$
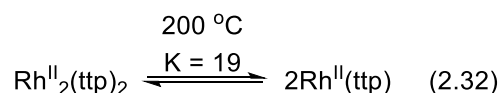
$\Delta G = \Delta H - T\Delta S$

$\Delta H = \text{Rh-Rh BDE in } Rh^{II}_2(txp)_2 = 12 \text{ kcal mol}^{-1}$

$\text{assume } S = S(H_2) = 31.2 \text{ cal mol}^{-1}\text{ K}^{-1}$

$\Delta G = 12 - (473)(0.0312) = -2.8 \text{ kcal mol}^{-1}$

$\Delta G = -RT\ln K$

$-2.8 = -(1.9872 \times 10^{-3})(473)\ln K$

$K = 19$

Scheme 2.10 Equilibrium Estimation for $Rh^{II}_2(ttp)_2$.

Subsequently, hydrolysis of **7** produces the hydrogenation product 4,4'-

dimethylbibenzyl **5** and regenerates $Rh^{III}(ttp)OH$ to complete the catalytic cycle (step iv),

which is supported by the hydrolysis of $Rh^{III}(ttp)Bn$ to give toluene. Rhodium porphyrin

catalyzes dehydrogenation of **5** occurs to give **6** (step v).

2.7 Conclusions

We have discovered the rhodium porphyrin catalyzed carbon-carbon σ-bond hydrogenation of PCP using H_2O as the convenient hydrogen source. This demonstrates that H_2O is a transfer hydrogenating agent. Kinetic studies suggest a $Rh^{II}(tmp)$ bi-metalloradical CCA process. Hydrogenation via hydrolysis of rhodium porphyrin alkyls is a general process to produce hydrocarbons.

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Experimental Section

General Procedures

Unless otherwise specified, all reagents were purchased from commercial suppliers and directly used without further purification. [2.2]paracyclophane was further tested by melting point (m.p. = 288.6-289.4 °C, lit. = 285-287.2 °C).[1] Hexane for chromatography was distilled from anhydrous $CaCl_2$. Benzene-d_6 was distilled from sodium under N_2, degassed with three freeze-pump-thaw cycles and stored in a Teflon screw head stoppered flask. Benzonitrile was distilled from anhydrous P_2O_5. Thin layer chromatography was performed on pre-coated silica gel 60 F_{254} plates. Silica gel (Merck, 70-230 mesh) was used for column chromatography under air.

Melting points were recorded on an MPA100 Automated Melting Point System. ^{1}H NMR spectra were recorded on a Bruker AV-400 MHz at 400 MHz. Chemical shifts were referenced internally to the residual solvent proton resonance in C_6D_6 (δ = 7.15 ppm), $CDCl_3$ (δ = 7.26 ppm) or with tetramethylsilane (δ = 0.00 ppm) as the internal standard. Chemical shifts (δ) are reported in parts per million (ppm). Coupling constants (J) are reported in hertz (Hz). High resolution mass spectra (HRMS) were recorded on a Thermofinnigan MAT 95 XL mass spectrometer. Fast atom bombardment was performed with 3-nitrobenzyl alcohol (NBA) as the matrix.

All reactions in 0.5 mL benzene-d_6 were carried out in a flame-sealed NMR tube in vacuum with the reaction mixture degassed with three freeze(77 K)-pump(0.005 mmHg)-thaw cycles, then heated in oven in dark and wrapped with aluminum foil to protect from exposure to room light before ^{1}H NMR measurements. The NMR yields were with benzene residue as the internal standard. Aqueous stock solution of KOH was prepared separately, transferred to the reaction vessel and dried under vacuum at r.t. to obtain anhydrous starting materials. Benzene stock solutions of Rh^{III}(ttp)X (X = Cl, I, Me, Bn and ^{i}Pr) were prepared

separately, transferred to the reaction vessel and dried under vacuum at r.t. to obtain anhydrous starting materials. Benzene-d_6 stock solution of [2.2]paracyclophane was prepared separately and transferred to the reaction vessel.

All free base porphyrins,[2] $Rh^{III}(ttp)X$ (X = Cl, I, Me, Bn, ^iPr),[3,4] $Rh^{III}(tap)X$ (X = Cl and Me),[4] $Rh^{III}(t_{4\text{-}CF3}pp)X$ (X = Cl and Me),[4] $Rh^{III}(tmp)X$ (X = Cl and Me),[3,5] $Rh^{II}(tmp)$[5] were prepared according to the literature procedures.

$Rh^{III}(ttp)^iPr$ has been reported earlier but spectroscopic characterization was not provided.[6] Its ^1H and $^{13}C\{^1H\}$ NMR spectra are now attached.

^1H NMR (C_6D_6, 400 MHz) δ -4.00 (d, $^3J_{H\text{-}H}$ = 6.2 Hz, 6 H, H_a), -3.89 (br, 1 H, H_b), 2.41 (s, 12 H, H_c), 7.27 (d, $^3J_{H\text{-}H}$ = 7.6 Hz, 4 H, H_d), 7.34 (d, $^3J_{H\text{-}H}$ = 7.5 Hz, 4 H, H_d'), 8.07 (d, $^3J_{H\text{-}H}$ = 7.5 Hz, 4 H, H_e), 8.19 (d, $^3J_{H\text{-}H}$ = 7.5 Hz, 4 H, H_e'), 8.97 (s, 8 H, H_f). $^{13}C\{^1H\}$ NMR (CDCl$_3$, 175 MHz) δ 21.7, 22.6, 27.7 (d, $^1J_{Rh\text{-}C}$ = 27.5 Hz), 122.8, 127.4, 127.5, 131.5, 133.7, 134.2, 137.2, 139.5, 143.4.
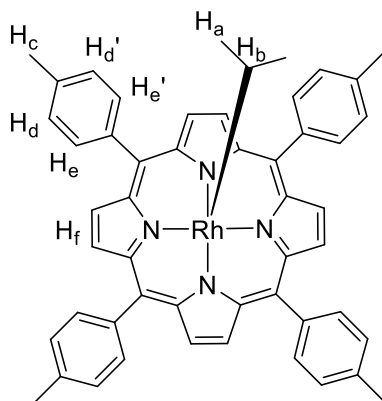
Experimental Procedures

Catalytic PCP Hydrogenation with H_2O Catalyzed by 10 mol% of $Rh^{III}(ttp)X$.

With $Rh^{III}(ttp)I$ and KOH (1 equiv). $Rh^{III}(ttp)I$ (0.43 mg, 0.00048 mmol), KOH (0.27 mg, 0.0048 mmol) and H_2O (8.6 μL, 0.48 mmol) were added into benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) in a NMR tube. The orange mixture was

degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 $^\circ$C in the dark for 25 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. 4,4'-dimethylbibenzyl **5** was isolated by column chromatography on silica gel eluting with hexane. R_f = 0.31 (hexane). m.p. = 81.8-83.1 $^\circ$C, lit. = 81-82 $^\circ$C.[7] ^{1}H NMR (CDCl$_3$, 400 MHz) δ 2.32 (s, 6 H, H$_a$), 2.86 (s, 4 H, H$_b$), 7.09 (s, 8 H, H$_c$).
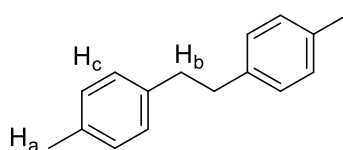
With Rh^{III}(ttp)I, KOH (1 equiv) and Under Light. Rh^{III}(ttp)I (0.43 mg, 0.00048 mmol), KOH (0.27 mg, 0.0048 mmol) and H$_2$O (8.6 μL, 0.48 mmol) were added into benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) in a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated in an oil bath at 200 $^\circ$C under the light conditions (Philips Master TL5 HE 21W/835, 21 W, approx. 1 m above) for 5 d. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. 1 was formed in 52% yield and 9% of [2.2]paracyclophane was remained. Therefore light did not catalyze the hydrogenation of PCP.

With Rh^{III}(ttp)Me. Rh^{III}(ttp)Me (0.38 mg, 0.00048 mmol) and H$_2$O (8.6 μL, 0.48 mmol) were added into benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) in a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 $^\circ$C in the dark for 54 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

With Rh^{III}(ttp)^{i}Pr. Rh^{III}(ttp)^{i}Pr (0.39 mg, 0.00048 mmol) and H$_2$O (8.6 μL, 0.48 mmol) were added into benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) in a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 °C in the dark for 50 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

Without Rh^{III}(ttp)X. H$_2$O (8.6 μL, 0.48 mmol) was added into benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) in a NMR tube. The colorless mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 °C in the dark for 4.5 d. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. [2.2]Paracyclophane remained quantitative.

Porphyrin Ligand Electronic Effects.

With Rh^{III}(tap)Me. Rh^{III}(tap)Me (0.41 mg, 0.00048 mmol) and H$_2$O (8.6 μL, 0.48 mmol) were added into benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) in a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 °C in the dark for 84 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

With Rh^{III}(t$_{4-CF3}$pp)Me. Rh^{III}(t$_{4-CF3}$pp)Me (0.48 mg, 0.00048 mmol) and H$_2$O (8.6 μL, 0.48 mmol) were added into benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) in a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 °C in the dark

for 40 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

With Rh[III](ocp)Me. Rh[III](ocp)Me (0.49 mg, 0.00048 mmol) and H_2O (8.6 μL, 0.48 mmol) were added into benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) in a NMR tube. The red mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 ºC in the dark for 4 d. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

With Rh[III](tmp)Me. Rh[III](tmp)Me (0.43 mg, 0.00048 mmol) and D_2O (8.7 μL, 0.48 mmol) were added into benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) in a NMR tube. The red mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 ºC in the dark for 7 d. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

Additive Effects.

With 'BuOH (2 equiv). Rh[III](ttp)Me (0.38 mg, 0.00048 mmol), 'BuOH (0.9 μL, 0.0096 mmol) and H_2O (8.6 μL, 0.48 mmol) were added into benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) in a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 ºC in the dark for 54 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

With 'BuOH (10 equiv). Rh[III](ttp)Me (0.38 mg, 0.00048 mmol), 'BuOH (4.6 μL, 0.048 mmol) and H_2O (8.6 μL, 0.48 mmol) were added into benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) in a NMR tube. The orange mixture was

degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 °C in the dark for 47 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

With BnEt$_3$NCl (0.1 equiv). Rh^{III}(ttp)Me (0.38 mg, 0.00048 mmol), BnEt$_3$NCl (0.11 mg, 0.00048 mmol) and H$_2$O (8.6 μL, 0.48 mmol) were added into benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) in a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 °C in the dark for 50 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

With BnEt$_3$NCl (1 equiv). Rh^{III}(ttp)Me (0.38 mg, 0.00048 mmol), BnEt$_3$NCl (1.1 mg, 0.0048 mmol) and H$_2$O (8.6 μL, 0.48 mmol) were added into benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) in a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 °C in the dark for 41 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

With PPh$_4$Br (0.1 equiv). Rh^{III}(ttp)Me (0.38 mg, 0.00048 mmol), PPh$_4$Br (0.2 mg, 0.00048 mmol) and H$_2$O (8.6 μL, 0.48 mmol) were added into benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) in a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 °C in the dark for 61 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

Deuterium Labeling Experiments.

Catalytic Deuteration of [2.2]Paracyclophane with Rh^{III}(ttp)Me. Rh^{III}(ttp)Me (0.38 mg, 0.00048 mmol) and D$_2$O (8.7 μL, 0.48 mmol) were added into benzene-d_6 stock solution (500

μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) in a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 ℃ in the dark for 3 d. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. **5-*d*** was isolated by column chromatography on silica gel eluting with hexane. ^{1}H NMR (C$_6$D$_6$, 400 MHz) δ 2.11-2.13 (m), 2.76-2.79 (m), 6.97 (s, 8 H).

Benzylic H/D Exchange of 4,4'-Dimethylbibenzyl 5. Rh^{III}(ttp)Me (0.38 mg, 0.00048 mmol) and D$_2$O (8.7 μL, 0.48 mmol) were added into benzene-*d$_6$* stock solution (500 μL) of 4,4'-dimethylbibenzyl (1.0 mg, 0.0048 mmol) in a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 ℃ in the dark for 3 d 15 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. **5-*d'*** was isolated by column chromatography on silica gel eluting with hexane. ^{1}H NMR (C$_6$D$_6$, 400 MHz) δ 2.13 (s), 2.76-2.77 (m), 6.97 (s, 8 H).

Reaction of Rh^{III}(ttp)Cl with [2.2]Paracyclophane at Lower Temperature. Rh^{III}(ttp)Cl (0.39 mg, 0.00048 mmol), KOH (0.27 mg, 0.0048 mmol) and D$_2$O (8.7 μL, 0.48 mmol) were added into benzene-*d$_6$* stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) in a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated in the dark at 60 ℃ for 4 d, 120 ℃ for 8 d and 130 ℃ for 1 d. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

Independent Synthesis of Di-rhodium Benzyl 7. Rh^{III}(ttp)I (0.43 mg, 0.00048 mmol) and KOH (0.27 mg, 0.0048 mmol) were added into benzene-*d$_6$* stock solution (500 μL) of
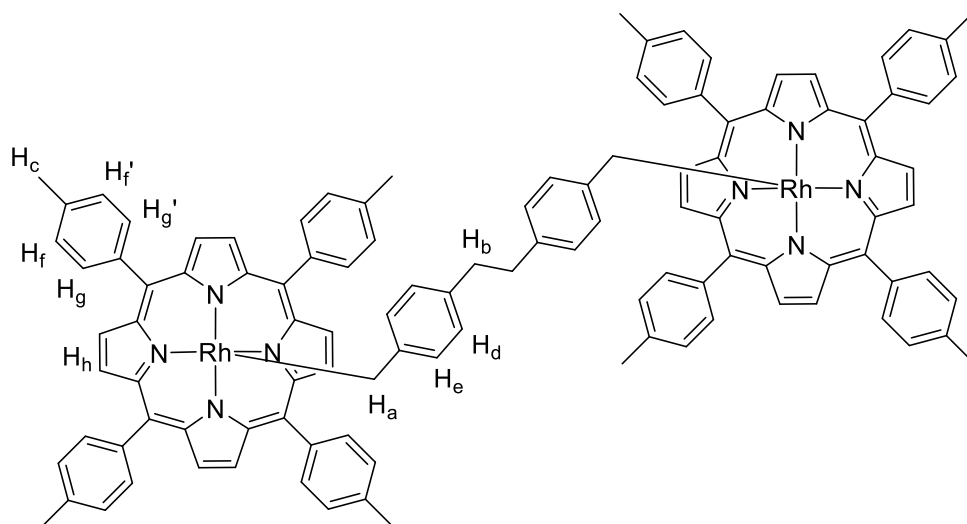
[2.2]paracyclophane (1.0 mg, 0.0048 mmol) in a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 150 °C in the dark for 15 h to give 82% yield of **7**. Attempted isolation of **7** by column chromatography led to decomposition to intractable products. ^{1}H NMR (C_6D_6, 400 MHz) δ -3.42 (d, $^2J_{Rh-H}$ = 3.3 Hz, 4 H, H_a), 1.96 (s, 4 H, H_b), 2.42 (s, 24 H, H_c), 3.16 (d, $^3J_{H-H}$ = 7.7 Hz, 4 H, H_d), 5.61 (d, $^3J_{H-H}$ = 8.0 Hz, 4 H, H_e), 7.31 (d, $^3J_{H-H}$ = 7.8 Hz, 8 H, H_f), 7.35 (d, $^3J_{H-H}$ = 6.8 Hz, 8 H, H_f'), 8.04 (d, $^3J_{H-H}$ = 7.6 Hz, 8 H, H_g), 8.21 (d, $^3J_{H-H}$ = 7.4 Hz, 8 H, H_g'), 8.93 (s, 16H, H_h). HRMS calcd. for $(C_{112}H_{88}N_8Rh_2)^+$: m/z 1751.5269. Found: m/z 1751.5269.

Reaction of Rh^{II}(tmp) with [2.2]Paracyclophane. Rh^{II}(tmp) (0.42 mg, 0.00048 mmol) was added into benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) in a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 150 °C in the dark for 23 h to give **8** in 85% yield. ^{1}H NMR (C_6D_6, 400 MHz) δ -3.20 (d, $^2J_{Rh-H}$ = 2.8 Hz, 4 H, H_a), 1.62 (s, 4 H, H_b), 1.89 (s, 24 H, H_c), 1.97 (s, 24 H, H_c'), 2.43 (s, 24 H, H_d), 3.50 (d, $^3J_{H-H}$ = 7.4 Hz, 4

H, H$_e$), 5.38 (d, $^3J_{H-H}$ = 8.0 Hz, 4 H, H$_f$), 7.12 (*meso*-aryl *meta* protons overlapped with solvent residual C$_6$H$_6$, H$_g$), 8.66 (s, 16H, H$_h$).

General Procedures for Kinetic Experiments.

Rh^{II}(tmp) was added into benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane in a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at designated temperature in the dark. The reaction was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. The collected kinetic data were analyzed and plotted into graphs using OriginPro 7.5 software.

Hydrolysis of Rh^{III}(ttp)R.

Rh^{III}(ttp)Bn. Rh^{III}(ttp)Bn (0.41 mg, 0.00048 mmol) and H$_2$O (8.6 μL, 0.48 mmol) were added into benzene-d_6 (500 μL) in a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 °C in the dark for 3.5 d. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

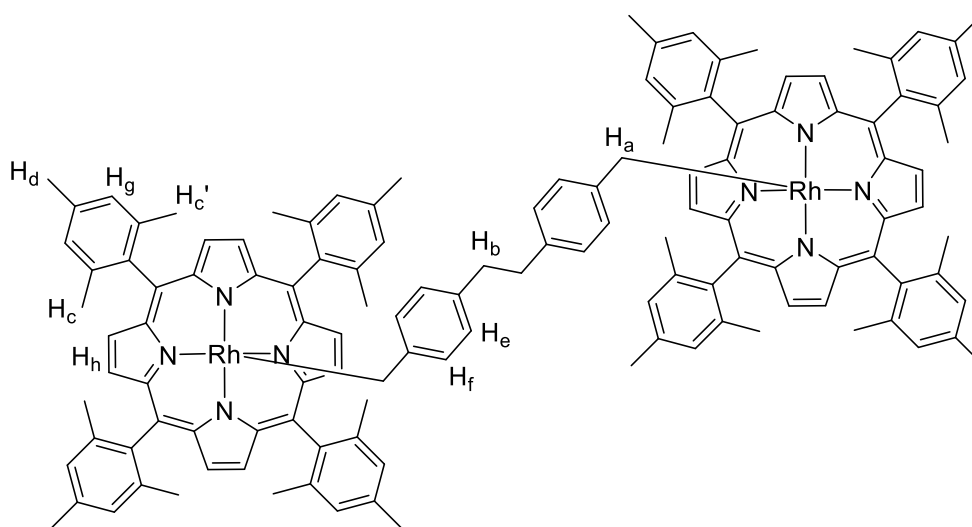**Rh^{III}(ttp)^{i}Pr.** Rh^{III}(ttp)^{i}Pr (0.39 mg, 0.00048 mmol) and H$_2$O (8.6 µL, 0.48 mmol) were added into benzene-d_6 (500 µL) in a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 °C in the dark for 50 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken.

Appendix I   List of Spectra

Rh^{III}(ttp)^{*i*}Pr (¹H)

Rh^{III}(ttp)^{*i*}Pr (¹³C{¹H})
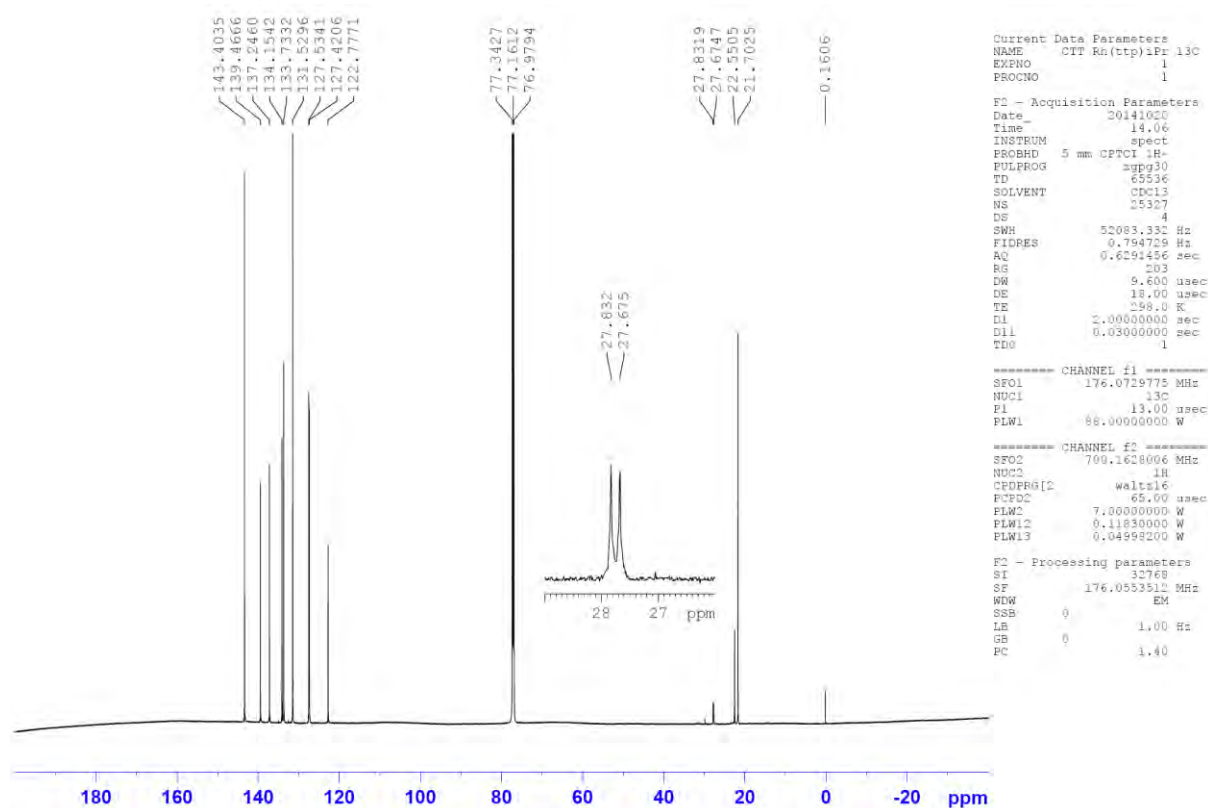
4,4'-Dimethylbibenzyl 5 (^{1}H)
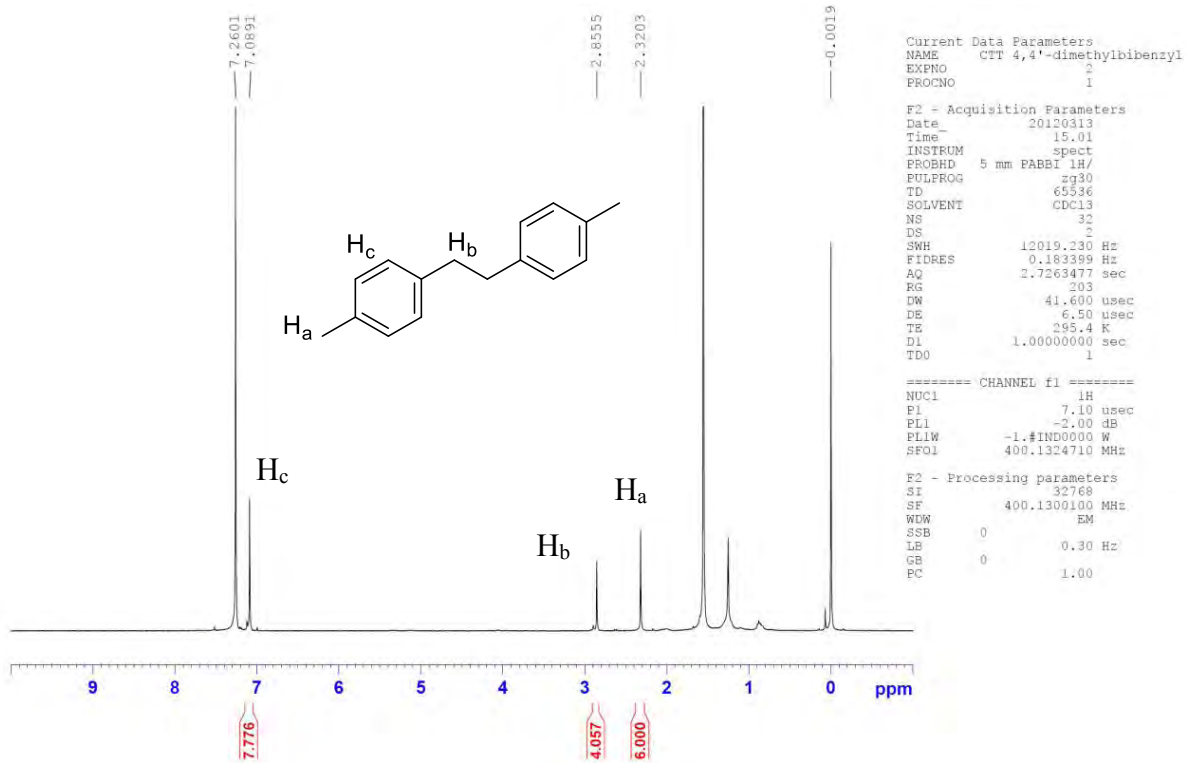
5-*d* (^{1}H)
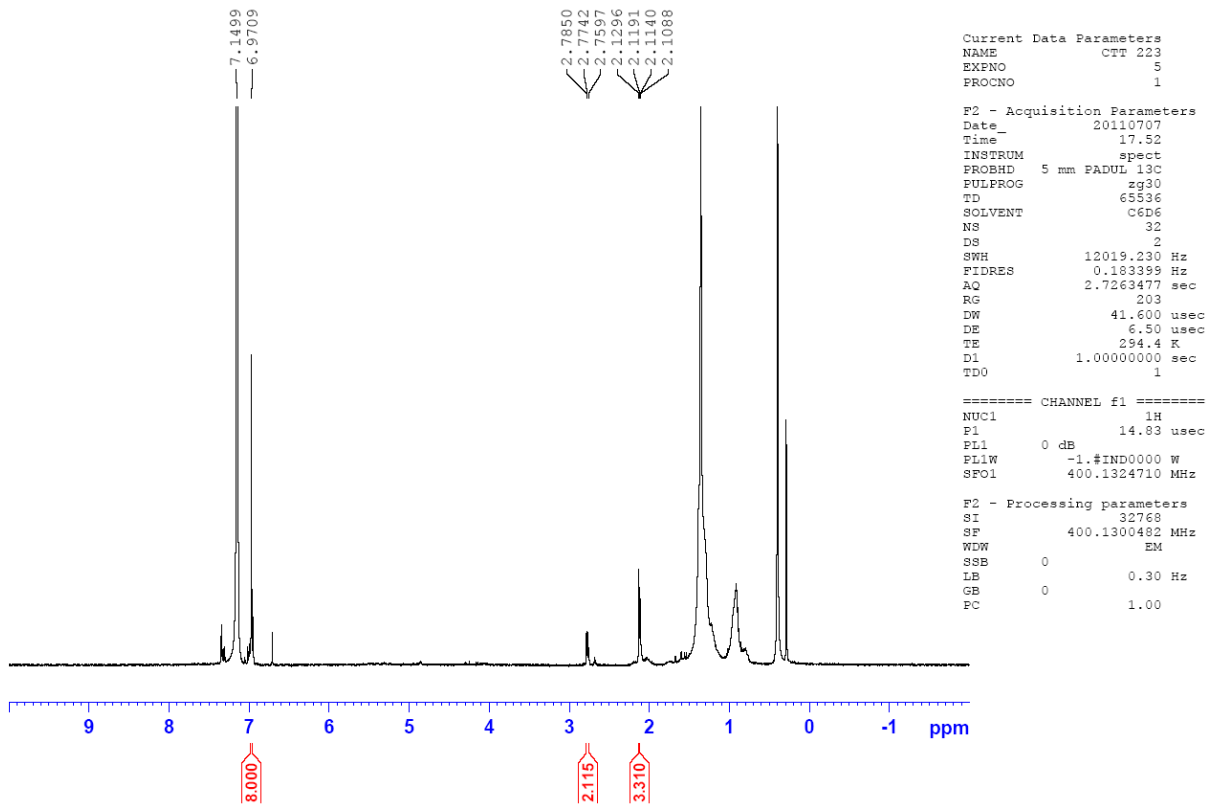
5-*d'* (^{1}H)
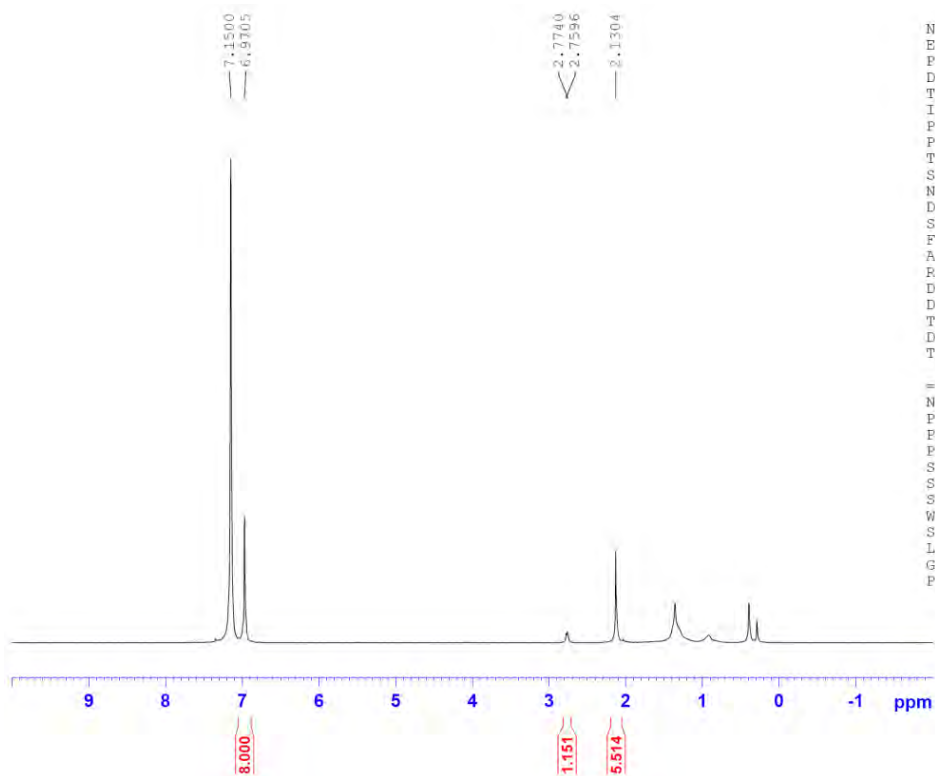
NAME   CTT 265
EXPNO   10
PROCNO   1
Date_   20120116
Time   12.52
INSTRUM   spect
PROBHD   5 mm PABBI 1H/
PULPROG   zg30
TD   65536
SOLVENT   C6D6
NS   32
DS   2
SWH   12019.230 Hz
FIDRES   0.183399 Hz
AQ   2.7263477 sec
RG   203
DW   41.600 usec
DE   6.50 usec
TE   295.5 K
D1   1.00000000 sec
TD0   1

======== CHANNEL f1 ========
NUC1   1H
P1   7.10 usec
PL1   -2.00 dB
PL1W   13.17734718 W
SFO1   400.1324710 MHz
SI   32768
SF   400.1300480 MHz
WDW   EM
SSB   0
LB   0.30 Hz
GB   0
PC   1.00

Di-rhodium benzyl 7 (^{1}H)
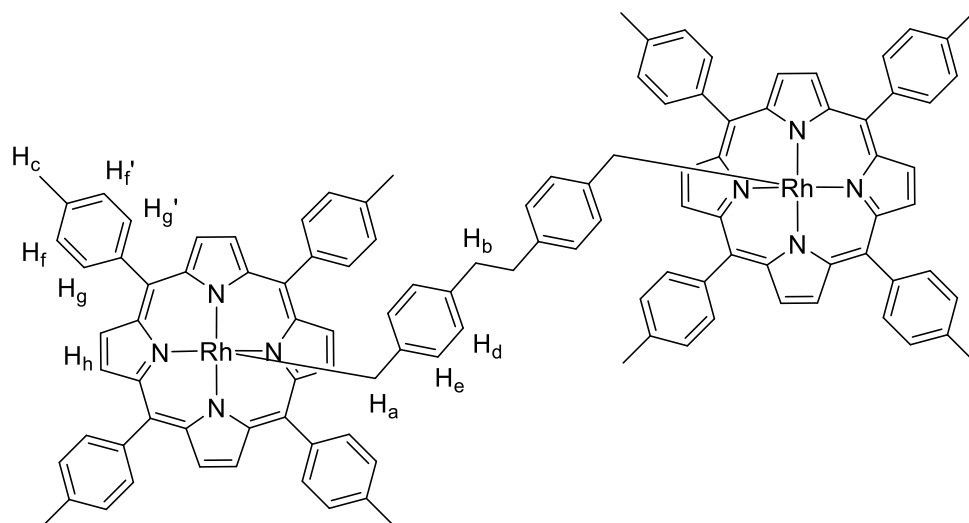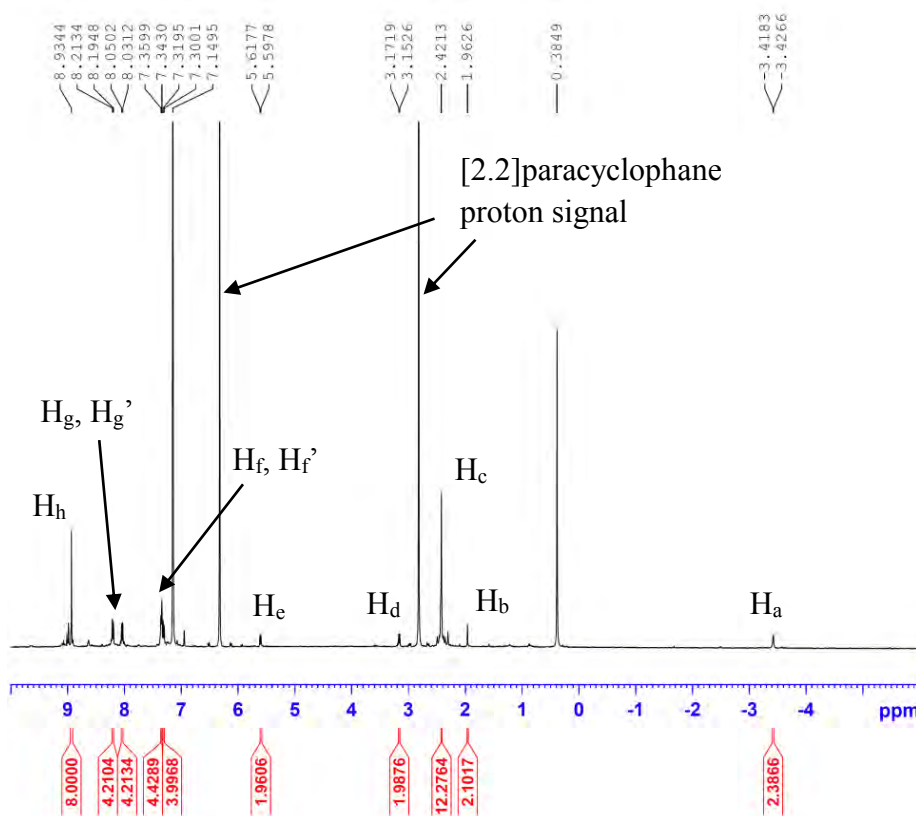
Di-rhodium benzyl 8 (^{1}H)
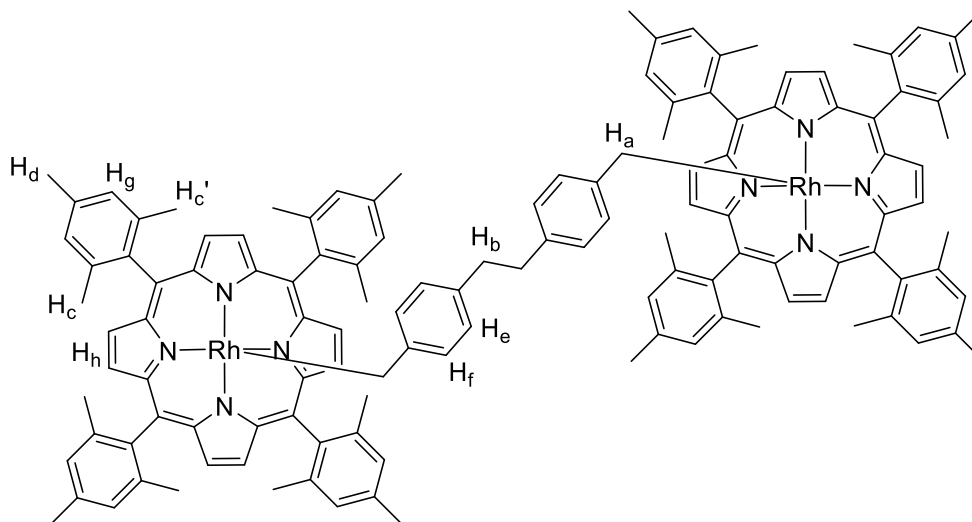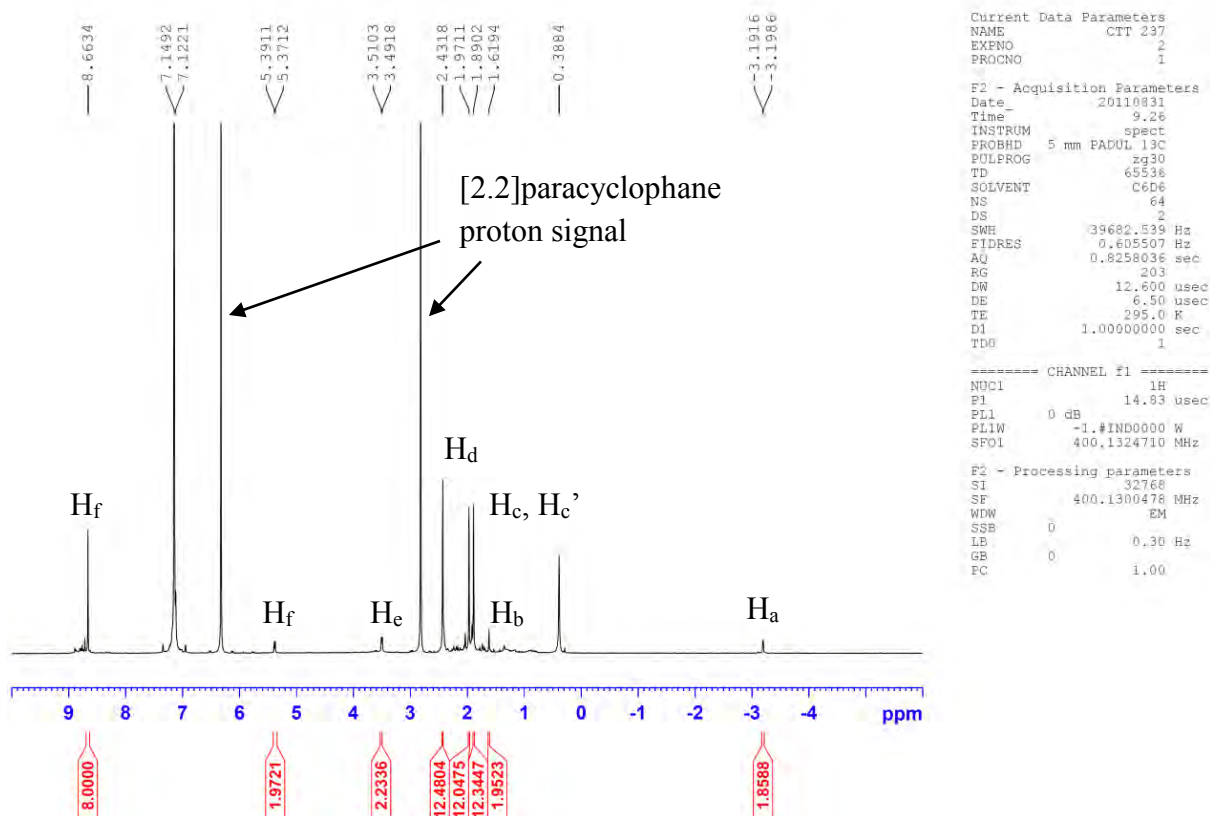
HRMS Spectra

Di-rhodium benzyl 7 (FAB)
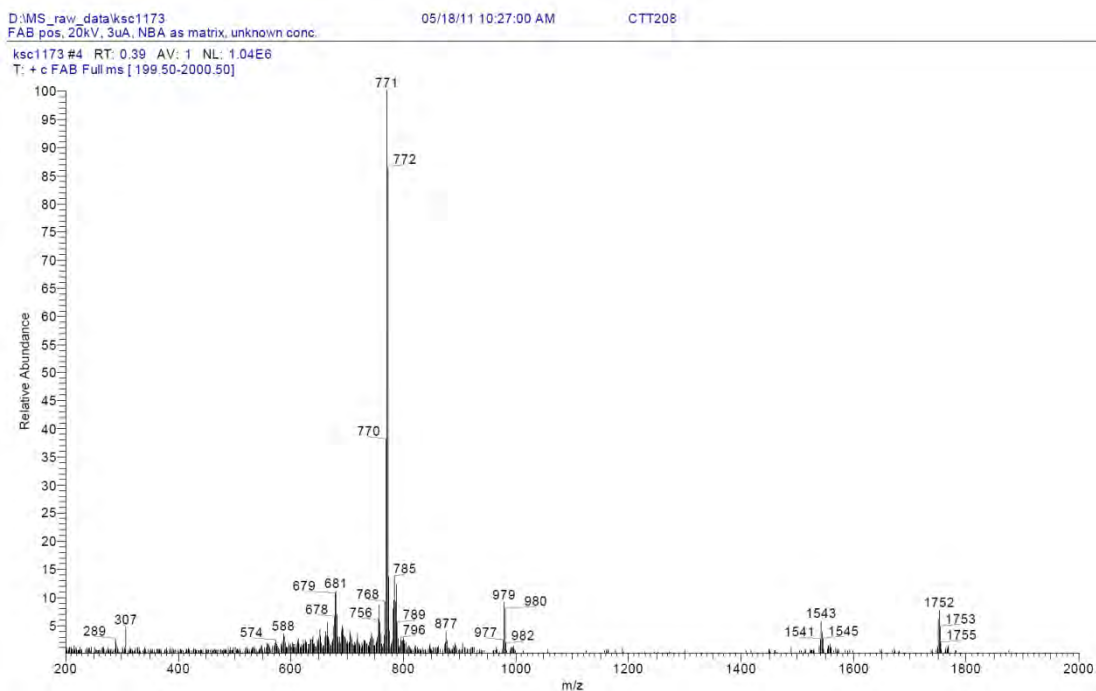
Accurate Mass Measurement
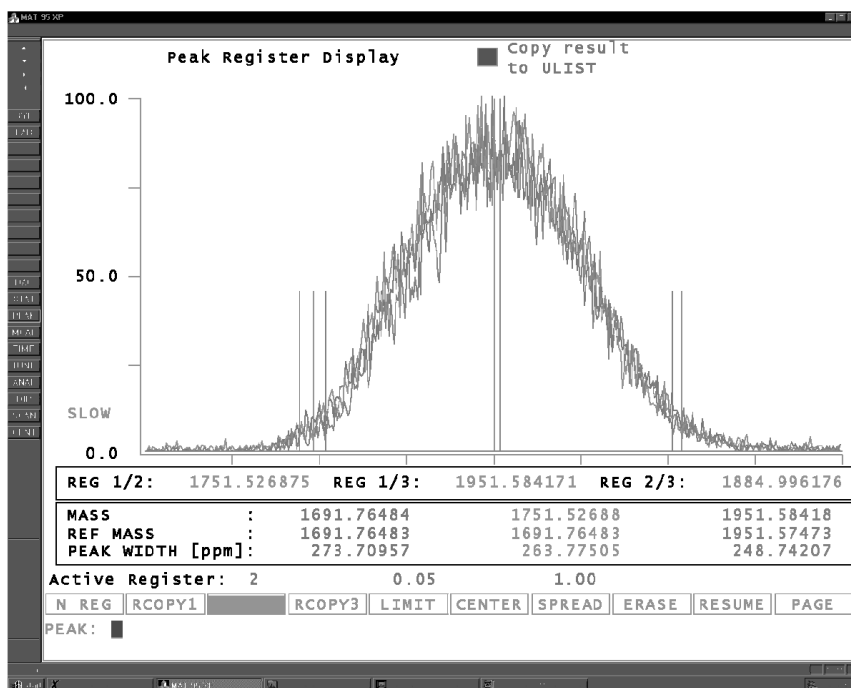
Molecular formula
$C_{112}H_{88}N_8Rh_2$
$[M]^+$ (theoretical)
= 1751.5269

Appendix II ¹H NMR Kinetic Data

[PCP] = 9.6 mM, 150 ºC					
[Rh^{II}(tmp)] = 0.24 mM				**[Rh^{II}(tmp)] = 0.48 mM**	
Trial 1			Trial 2		
time / s	[Rh^{II}(tmp)] / mM	time / s	[Rh^{II}(tmp)] / mM	time / s	[Rh^{II}(tmp)] / mM
0	0.240	0	0.240	0	0.480
3600	0.144	3600	0.147	1800	0.377
7200	0.110	10800	0.104	12600	0.134
10800	0.093	18000	0.063	23400	0.112
12600	0.083	27900	0.053	28800	0.094
37800	0.041	36000	0.042	32400	0.075
63000	0.026			39600	0.064

[Rh^{II}(tmp)] = 0.24 mM, 150 ºC			
[PCP] = 4.8 mM		**[PCP] = 14.4 mM**	
time / s	[Rh^{II}(tmp)] / mM	time / s	[Rh^{II}(tmp)] / mM
0	0.240	0	0.240
1800	0.174	1800	0.156
3600	0.168	3600	0.139
7200	0.140	7200	0.096
11700	0.109	11700	0.085
18900	0.103	18900	0.052
33300	0.079	33300	0.037
52000	0.053		

[Rh^{II}(tmp)] = 0.24 mM, [PCP] = 9.6 mM					
140 ºC		160 ºC		170 ºC	
time / s	[Rh^{II}(tmp)] / mM	time / s	[Rh^{II}(tmp)] / mM	time / s	[Rh^{II}(tmp)] / mM
0	0.240	0	0.240	0	0.240
18000	0.158	3600	0.081	3600	0.080
28200	0.119	5400	0.062	5400	0.053
46800	0.092	6300	0.058	6300	0.047
52000	0.083	8100	0.056	8100	0.034
		9900	0.042		
		10800	0.037		

Pseudo 2nd Order Kinetic Plot with [Rh^{II}(tmp)] = 0.24 mM and [PCP] = 9.6 mM at 150 ^{o}C.

Pseudo 2nd Order Kinetic Plot with [Rh^{II}(tmp)] = 0.24 mM and [PCP] = 9.6 mM at 150 ^{o}C.

Pseudo 2nd Order Kinetic Plot with [Rh^{II}(tmp)] = 0.48 mM and [PCP] = 9.6 mM at 150 ^{o}C.

Pseudo 2nd Order Kinetic Plot with [Rh^{II}(tmp)] = 0.24 mM and [PCP] = 4.8 mM at 150 ^{o}C.
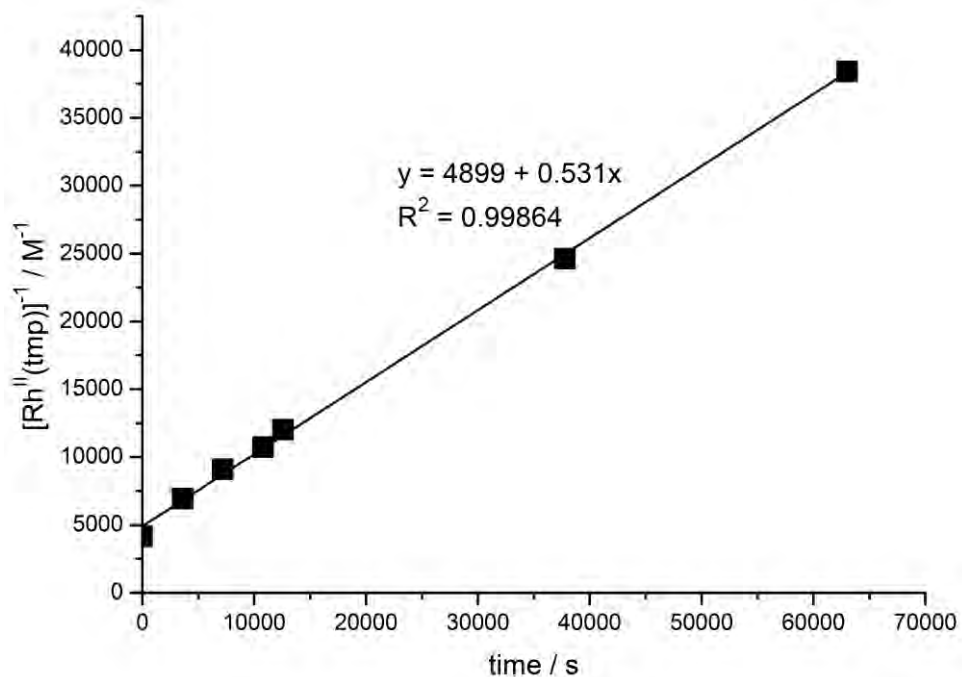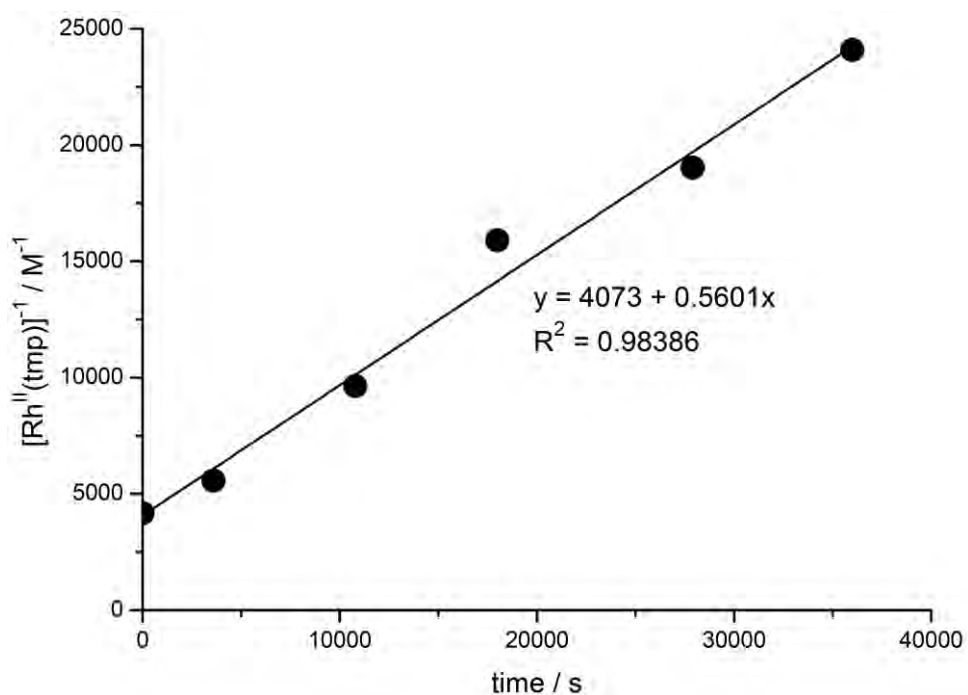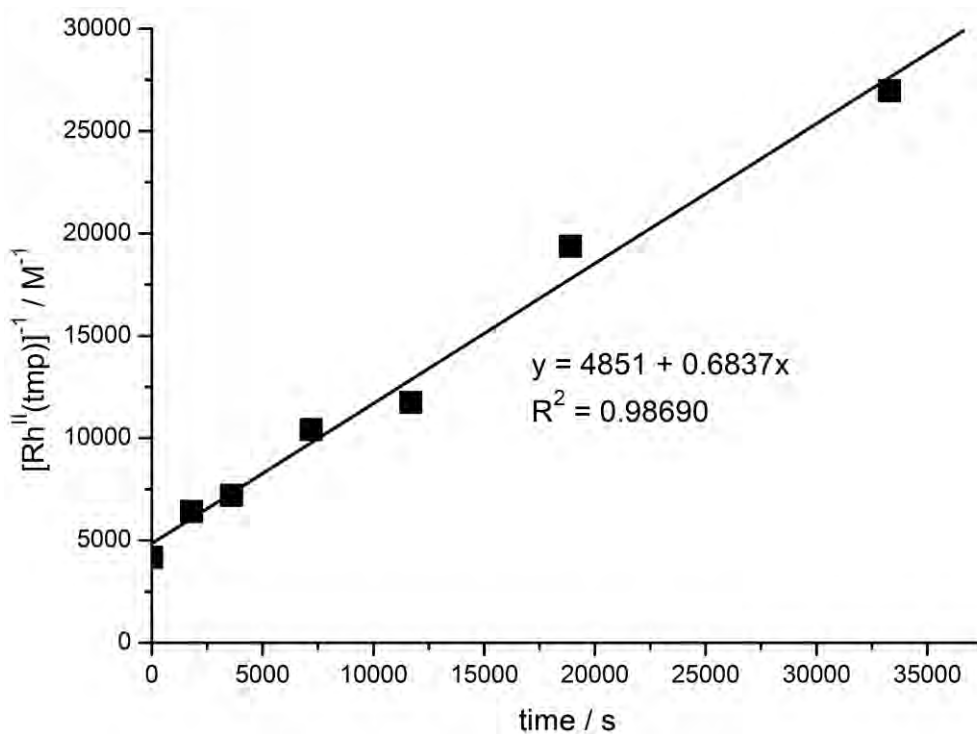
Pseudo 2nd Order Kinetic Plot with [Rh^{II}(tmp)] = 0.24 mM and [PCP] = 14.4 mM at 150 °C.
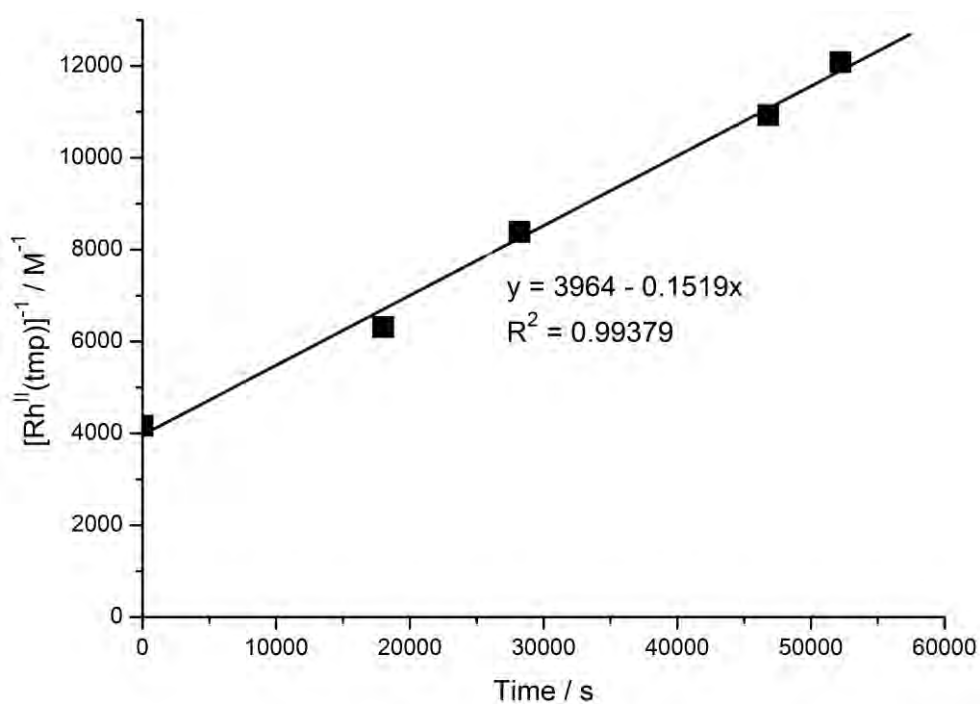
Pseudo 2nd Order Kinetic Plot with [Rh^{II}(tmp)] = 0.24 mM and [PCP] = 9.6 mM at 140 °C.
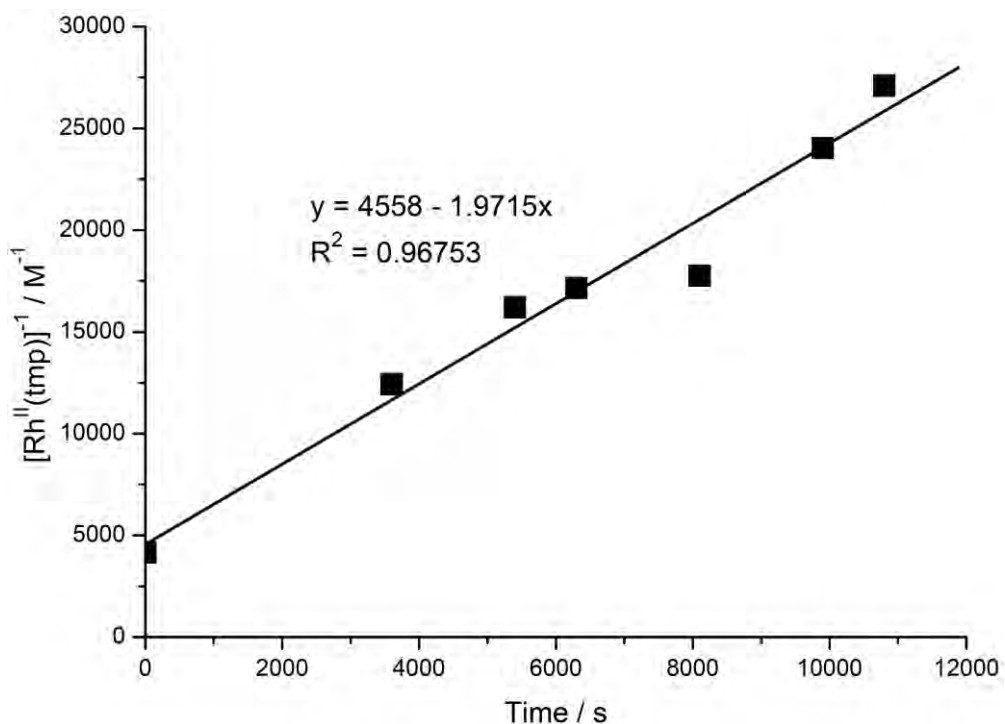
Pseudo 2nd Order Kinetic Plot with [Rh^{II}(tmp)] = 0.24 mM and [PCP] = 9.6 mM at 160 °C.
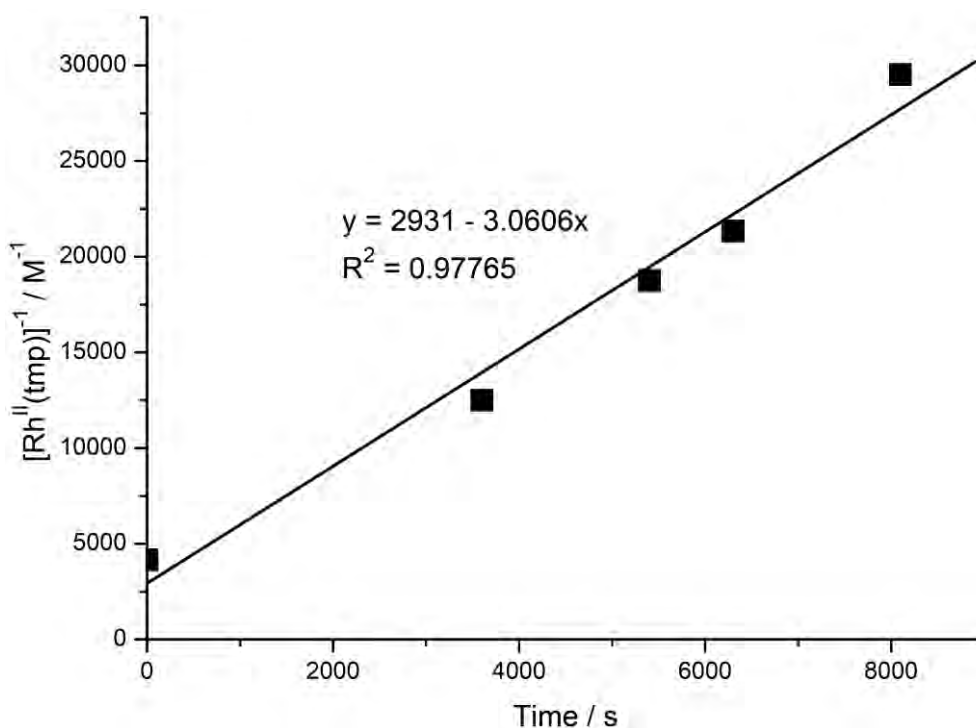
Pseudo 2nd Order Kinetic Plot with [Rh^{II}(tmp)] = 0.24 mM and [PCP] = 9.6 mM at 170 °C.

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Chapter 3   Catalytic Carbon-Carbon Bond Hydrogenation of [2.2]Paracyclophane with Water by Iridium Porphyrin Complexes

3.1 Introduction

Chapter 2 describes the rhodium porphyrin catalyzed hydrogenation of PCP using water. The CCA of PCP with rhodium(II) porphyrin metalloradical is proposed with the cleavage of benzylic C-C bond of PCP and the formation of two Rh-C bonds (Scheme 3.1). Since the reaction enthalpy is solely governed by the BDE of M-C bond being formed, the CCA step can be made more exothermic by forming a M-C bond that is stronger than Rh-C bond.
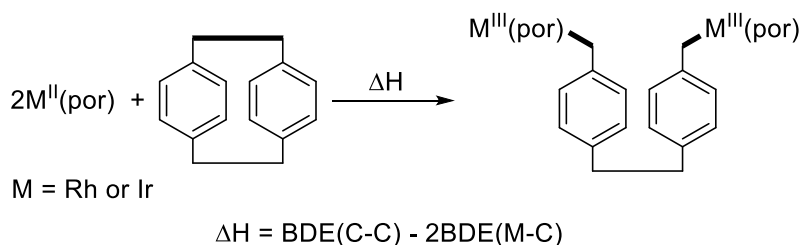
Scheme 3.1 CCA of PCP with M^{II}(por).

Table 3.1 lists the M-CH$_3$ BDEs for group 9 metalloporphyrin complexes as examples. The strengths of the M-CH$_3$ bonds follow the trend: Ir > Rh >> Co. Hence, the CCA of PCP with iridium(II) porphyrin should be thermodynamically more favorable. Without the resting state or rate determining step well defined at this stage, we hope that better efficiency for the catalytic hydrogenation of PCP with H$_2$O can be achieved using iridium porphyrin catalyst. The iridium porphyrin catalyzed hydrogenation protocol is thus examined.

Table 3.1 M-CH$_3$ BDE in M^{III}(por)-CH$_3$ Complexes.

M	M^{III}(por)-CH$_3$ BDE / kcal mol^{-1}
Co	18.7[1]
Rh	56.9[2]
Ir	62[3]

3.2 Objectives of the Work

We aim to develop a more facile iridium porphyrin catalyzed C-C σ-bond hydrogenation protocol using H_2O.

3.3 Preparation of Starting Materials

3.3.1 Synthesis of Metalloporphyrins

3.3.1.1 Synthesis of Iridium(III) Porphyrin Halides

Ir^{III}(ttp)(CO)Cl, the starting material for other iridium porphyrin complexes, can be prepared from H_2(ttp) using $[Ir^I$(cod)Cl$]_2$ complex as the iridium source. $[Ir^I$(cod)Cl$]_2$ was first prepared by refluxing $Ir^{III}Cl_3 \cdot xH_2O$ with 1,5-cyclooctadiene in $EtOH/H_2O$ mixed solvent for 2 d in 64% yield according to the literature method (eq 3.1).[4] Ir^{III}(ttp)(CO)Cl was then prepared by refluxing H_2(ttp) with $[Ir^I$(cod)Cl$]_2$ in p-xylene for 4 d in 63% yield (eq 3.2).[5]

$$Ir^{III}Cl_3 \cdot xH_2O \ + \ cod \ \xrightarrow[\text{reflux, 2 d, } N_2]{\text{EtOH/}H_2O} \ [Ir^I(cod)Cl]_2 \qquad (3.1)$$
$$64\%$$

$$2H_2(ttp) \ + \ [Ir^I(cod)Cl]_2 \ \xrightarrow[\text{reflux, 4 d}]{p\text{-xylene}} \ 2Ir^{III}(ttp)(CO)Cl \qquad (3.2)$$
$$63\%$$
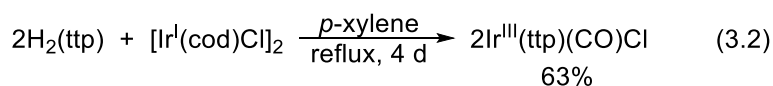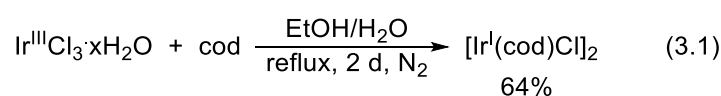
3.3.1.2 Synthesis of Iridium(III) Porphyrin Alkyls

Ir^{III}(ttp)Me and Ir^{III}(ttp)^{i}Pr, were synthesized by reductive alkylation of Ir^{III}(ttp)(CO)Cl with alkyl iodide in 52% and 65% yields, respectively (eq 3.3).[5b,6] Ir^{III}(ttp)Bn was prepared by base-promoted benzylic CHA of toluene with Ir^{III}(ttp)(CO)Cl (eq 3.4).[7]

$$Ir^{III}(ttp)(CO)Cl \ \xrightarrow[\text{2. RI, 70 °C, } N_2, \text{ 2 h}]{\substack{\text{1. NaBH}_4/\text{NaOH(aq)} \\ \text{THF, 70 °C, } N_2 \text{ 2 h}}} \ Ir^{III}(ttp)R \qquad (3.3)$$
$$R = Me \ \mathbf{2a}, \ 52\%$$
$$= \ ^iPr \ \mathbf{2b}, \ 65\%$$

$$Ir^{III}(ttp)(CO)Cl \ + \ PhCH_3 \ \xrightarrow[\text{150 °C, } N_2, \text{ 3 d}]{K_2CO_3 \text{ (10 equiv)}} \ Ir^{III}(ttp)Bn \qquad (3.4)$$
$$\mathbf{2c}, \ 65\%$$
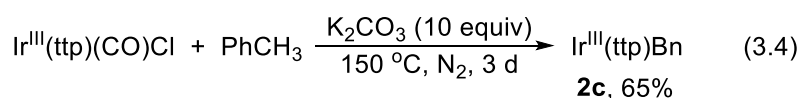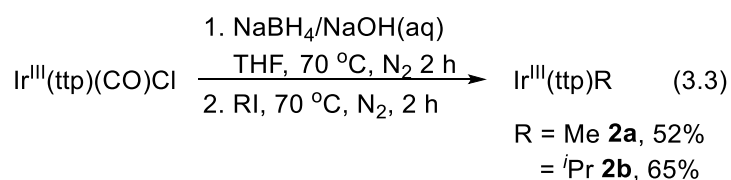
3.3.1.3 Synthesis of $Ir^{III}(ttp)H$ and $Ir^{II}_2(ttp)_2$

$Ir^{III}(ttp)H$ was prepared by the reductive protonation of $Ir^{III}(ttp)(CO)Cl$ (eq 3.5).[5a,7] $Ir^{II}_2(ttp)_2$ was then prepared by reacting $Ir^{III}(ttp)H$ with TEMPO followed by removal of TEMPO-H (eq 3.6).[7,8]

$$Ir^{III}(ttp)(CO)Cl \xrightarrow[\text{2. HCl (aq), 0-5 }^{o}\text{C, N}_2\text{, 5 min}]{\substack{\text{1. NaBH}_4\text{/NaOH(aq)} \\ \text{THF, 70 }^{o}\text{C, N}_2\text{, 2 h}}} Ir^{III}(ttp)H \qquad (3.5)$$
$$\mathbf{3}, 90\%$$

$$Ir^{III}(ttp)H \xrightarrow[\text{C}_6\text{H}_6\text{, r.t., N}_2\text{, 1 min}]{\text{TEMPO (1.1 equiv)}} Ir^{II}_2(ttp)_2 \qquad (3.6)$$
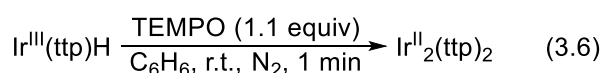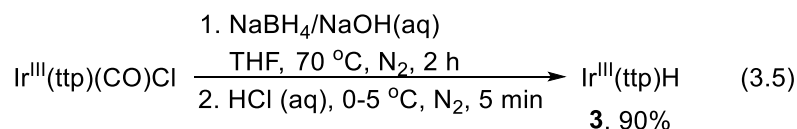
3.4 Optimization of Catalytic PCP Hydrogenation with H_2O

3.4.1 With $Ir^{III}(ttp)R$ Pre-catalysts

Based on the successful catalytic hydrogenation of PCP with H_2O using $Rh^{III}(ttp)Me$ pre-catalyst, we first examined the reaction with $Ir^{III}(ttp)R$ pre-catalysts (R = Me, Bn and ^{i}Pr). To our delight, PCP was catalytically hydrogenated to give **5** in over 90% yields. (Table 3.2, eq 3.8, entries 1-3). The dehydrogenation product of **5**, 4,4'-dimethylstilbene, was not observed. This accounts for the neat and high yielding conversion from PCP to **5**.

$Ir^{III}(ttp)SiEt_3$ was a poor pre-catalyst (Table 3.2, eq 3.8, entry 4). It underwent very slow hydrolysis with 81% recovery yield after 48 h. In constrast, hydrolysis of $Rh^{III}(ttp)SiEt_3$ occurred readily at 150 ^{o}C in C_6D_6 to give $Rh^{III}(ttp)H$ and organic co-product $HOSiEt_3$ (eq 3.9).[9] H_2O undergoes S_N2 at the Si center of $Rh^{III}(ttp)SiEt_3$ and $Rh^{I}(ttp)^-$ is the leaving group (pK_a of $Rh^{III}(ttp)H \approx 11$).[10] However, $Ir^{I}(ttp)^-$ is a poorer leaving group because $Ir^{III}(ttp)H$ is less acidic.[11] Hence, $Ir^{III}(ttp)SiEt_3$ is less reactive towards hydrolysis.

$$Rh^{III}(ttp)SiEt_3 + H_2O \xrightarrow[\text{150 }^{o}\text{C, 2 d}]{\text{C}_6\text{D}_6} Rh^{III}(ttp)H + HOSiEt_3 \qquad (3.9)$$
$$\text{1000 equiv} \qquad\qquad\qquad 99\% \qquad\quad 94\%$$
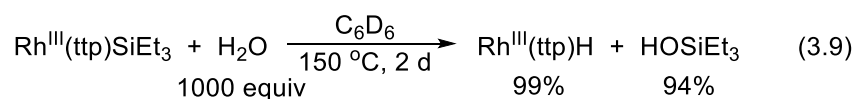
Table 3.2 Catalytic Hydrogenation of PCP using H_2O.

$$\text{(3.8)}$$
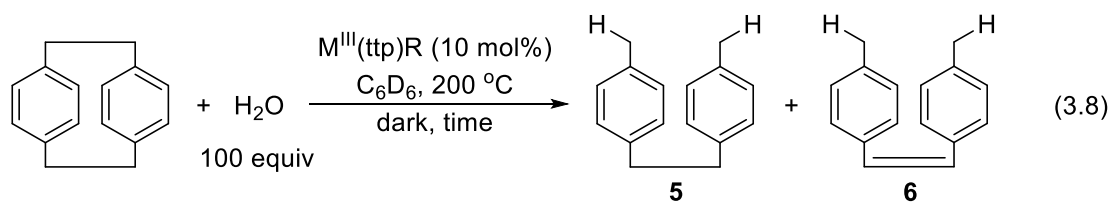
entry	M	R	time / h	yield / %			
				PCP recovery	5	6	R-H[a]
1	Ir	Me	53	0	94	0	0
2	Ir	Bn	48	0	95	0	42
3	Ir	^{i}Pr	41	0	98	0	24[b]
4[c]	Ir	SiEt$_3$	48	70	10	0	0[d]
5	Ir	H	35	0	96	0	0
6	Rh	Me	54	0	78	9	79
7	Rh	^{i}Pr	50	0	68	10	20[e]

[a] w.r.t. M^{III}(ttp)R
[b] 29% propene
[c] 81% recovery of Ir^{III}(ttp)SiEt$_3$
[d] HOSiEt$_3$ was not observed
[e] 18% propene

The use of Ir^{III}(ttp)H pre-catalyst resulted in the shortest reaction time (Table 3.2, eq 3.8, entry 5), suggesting a facile conversion of Ir^{III}(ttp)H to Ir^{II}_2(ttp)$_2$ for CCA. Previous investigations showed that Ir^{II}_2(ttp)$_2$ was formed from the thermal dehydrogenation of Ir^{III}(ttp)H (eq 3.10).[7]

$$2Ir^{III}(ttp)H \xrightarrow[\text{150 °C, 1.5 h}]{C_6D_6} Ir^{II}_2(ttp)_2 + \text{"}H_2\text{"} \quad \text{(3.10)}$$
$$74\%$$
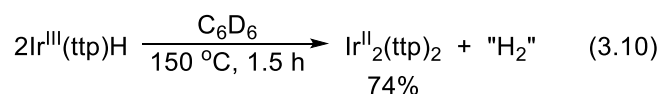
The catalytic efficiency using Ir^{III}(ttp)R pre-catalysts (R = Me, Bn and ^{i}Pr) followed the order: Ir^{III}(ttp)^{i}Pr > Ir^{III}(ttp)Bn > Ir^{III}(ttp)Me. The improved catalytic efficiency from Ir^{III}(ttp)Me to Ir^{III}(ttp)^{i}Pr was unique since similar improvement was not observed for Rh^{III}(ttp)Me and Rh^{III}(ttp)^{i}Pr (Table 3.2, eq 3.8, entries 6 and 7).

3.4.2 $Ir^{III}(ttp)^iPr$ Pre-Catalyst Loading

With $Ir^{III}(ttp)^iPr$ as the best and convenient pre-catalyst chosen, we then examined the catalytic hydrogenation of PCP at various $Ir^{III}(ttp)^iPr$ loadings. The reaction was very slow with 2.5 mol% of $Ir^{III}(ttp)^iPr$ and did not reach completion after 3 d (Table 3.3, eq 3.11, entry 1). Increasing the loading to 5, 10 and 20 mol% gave almost quantitative conversion of PCP to **5** with shortened reaction time, respectively (Table 3.3, eq 3.11, entries 2-4).

Table 3.3 Catalytic PCP Hydrogenation at Various $Ir^{III}(ttp)^iPr$ Loadings.
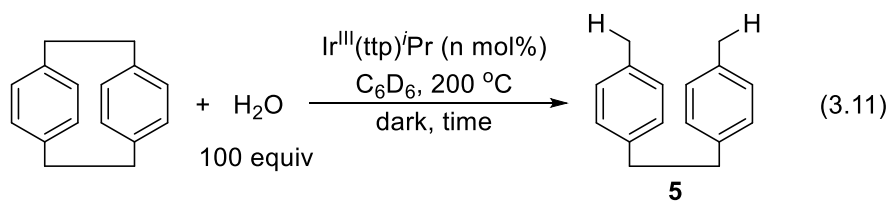
| entry | $Ir^{III}(ttp)^iPr$ / mol% | time / h | yield / % | | TOF / h^{-1} |
			PCP recovery	**5**	
1	2.5	76	10	74	0.39
2	5	58	0	97	0.33
3	10	41	0	98	0.24
4	20	33	0	95	0.14

Interestingly, the catalytic efficiency in terms of turnover frequency (TOF) decreased with increasing $Ir^{III}(ttp)^iPr$ loadings in a slightly concave manner (Figure 3.1). This probably implies that there were non-productive resting states in the catalysis and became dominant at high concentration of iridium porphyrin complexes.
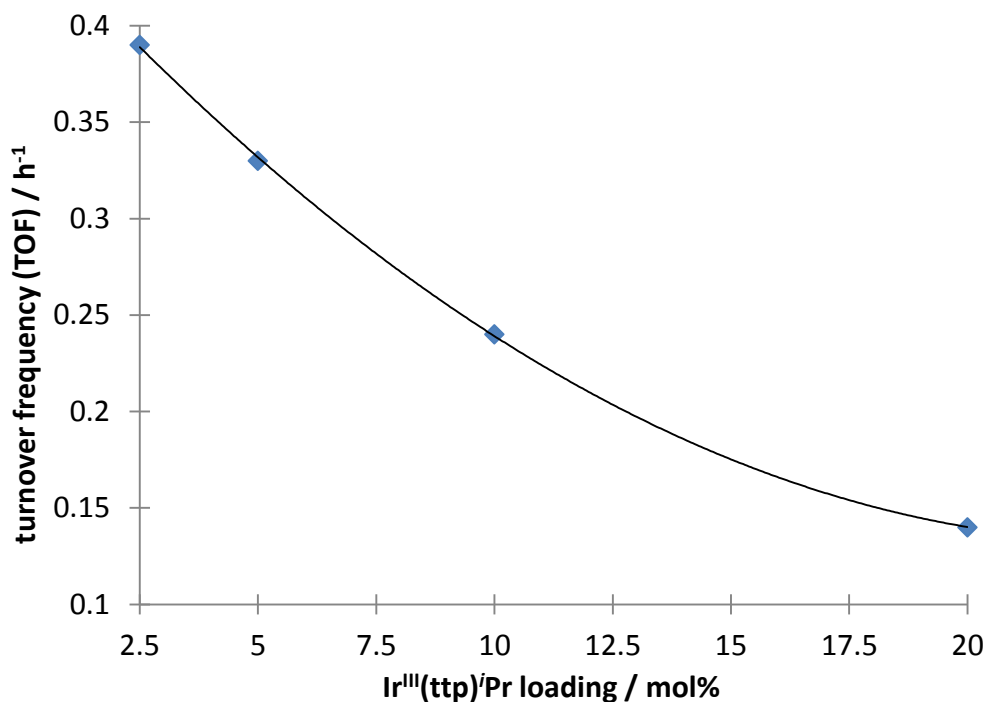
Figure 3.1 Plot of Turnover Frequency Against $Ir^{III}(ttp)^iPr$ Loadings.

3.4.3 Water loading Effects

Since H_2O is proposed to be the hydrogenating agent, its loadings were examined. Without any H_2O added, the catalytic hydrogenation of PCP still proceeded to afford **5** in 97% yield after 55 h (Table 3.4, eq. 3.12, entry 1). The C_6D_6 solvent was found to contain ~3 equiv of residual H_2O, it was already excess to PCP. Adding 2.3 equiv of H_2O to the catalytic system yielded 98% of **5** in 59 h (Table 3.3, eq 3.12, entry 2). Since it was difficult to maintain an absolute anhydrous reaction conditions even from using Na metal purified C_6D_6, it was unable to examine whether the hydrogenation would be stopped or not without any H_2O.

Table 3.4 Water Loading Effects.
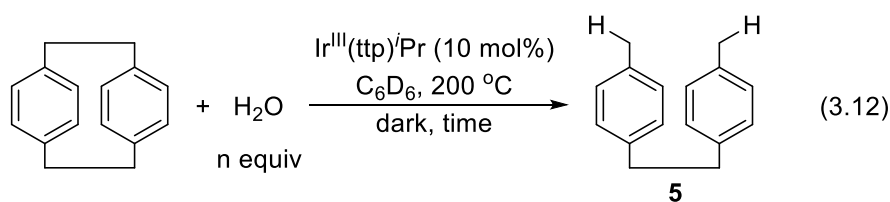
entry	H_2O loading[a] / equiv	time / h	yield **5** / %
1	$0^{[b]}$	55	97
2	$2.3^{[b]}$	59	98
3	100	41	98

[a] refer to external H_2O added
[b] ~3 equiv of solvent residual H_2O estimated from ^1H NMR

Comparing entries 1 and 3 in Table 3.4, it was surprising that the H_2O loading affected minimally on the reaction rate. The $[H_2O]$ in C_6D_6 at 200 °C reached ~1 M when 100 equiv of H_2O was added, which was 33 times higher than without H_2O added.[12] Hence, direct uncatalyzed hydrogenation using H_2O is unlikely. An alternative hydrogen source may be generated in situ and derived from H_2O.

Wayland has estimated that the oxidative addition of D_2O with water soluble rhodium porphyrin $[(TMPS)Rh^{II}(D_2O)]^{8-}$ to form $[(TMPS)Rh^{III}D(D_2O)]^{8-}$ and $[(TMPS)Rh^{III}OD(D_2O)]^{8-}$ was exergonic by -2.4 kcal/mol at 25 °C (Scheme 3.2).[13] Analogous oxidative addition with $[(TMPS)Ir^{II}(D_2O)]^{8-}$ has been suggested to be more exergonic due to the stronger (TMPS)Ir-D bond than (TMPS)Rh-D bond by 4-6 kcal/mol, and (TMPS)Ir-OD bond than (TMPS)Rh-OD bond by 7-9 kcal/mol (Scheme 3.3).[14]
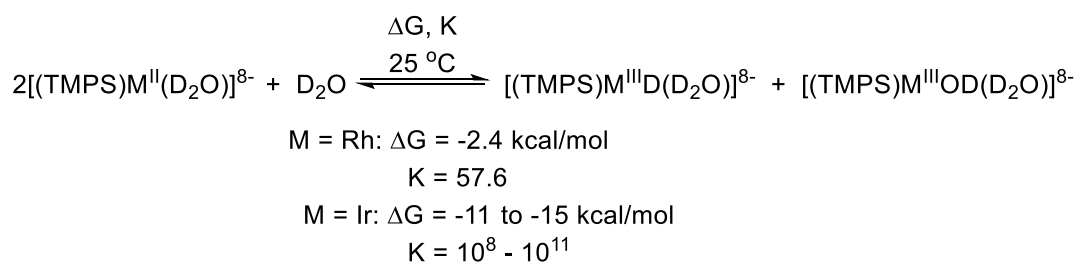
Scheme 3.2 Oxidative Addition of H_2O with Rhodium and Iridium Porphyrin Complexes.

Similarly, $Ir^{II}(ttp)$ may react with H_2O to give $Ir^{III}(ttp)H$ and $Ir^{III}(ttp)OH$. $Ir^{III}(ttp)H$ is a better hydrogen atom donor than H_2O because of the much weaker Ir-H bond (70 kcal/mol)[3] than the HO-H bond (118.8 kcal/mol).[15]

3.4.4 Additive Effects

Despite insignificant effects were observed for adding polar additives in the rhodium catalyzed system, we examined two more active benzene/water emulsifying agents in the iridium catalyzed protocol. Dioctyl sodium sulfosuccinate (DSS) and benzyldimethylhexadecylammonium chloride (BDHA) help to solubilize H_2O in non-polar organic solvents by forming reverse micelles.[15] However, no significant enhancement on reaction rate was observed with added DSS and BDHA (Table 3.5, eq 3.13, entries 2-3). The reverse micelles might not survive at 200 °C and hence addition of DSS and BDHA showed no effects. Alternatively, H_2O was already sufficiently soluble in C_6D_6 at 200 °C.

Table 3.5 Polar Additive Effects on Catalytic PCP Hydrogenation.
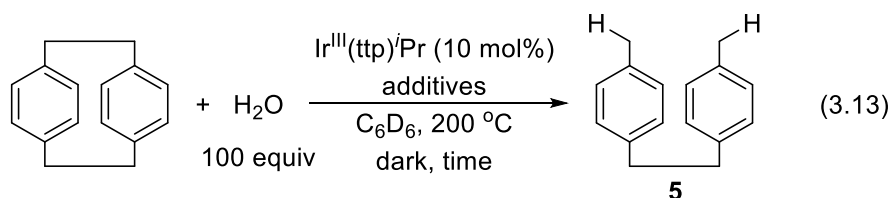
entry	additives	mol%	time / h	yield / %	
				PCP recovery	5
1	--	--	41	0	98
2	DSS[a]	2.3	45	0	97
3	BDHA[b]	13	41	0	86
4	DMF-d_7 solvent	--	53	51	30

[a] DSS = Dioctyl sodium sulfosuccinate
[b] BDHA = benzyldimethylhexadecylammonium chloride

Changing the solvent from C_6D_6 to DMF-d_7 was attempted to provide a homogeneous reaction conditions. However, the catalytic hydrogenation was greatly retarded and the reaction was stopped after 53 h (Table 3.5, eq 3.13, entry 4). $Ir^{III}(ttp)H$ and $(L)Ir^{III}(ttp)H$,

where L might be DMF-d_7, CO or $(CD_3)_2ND$, were found to be the major resting species. The three characteristic Ir-H ^{1}H signals observed at δ = -32.2, -37.2 and -41.6 ppm supported the coordination of ligands (Figure 3.2). At this stage it was unable to differentiate which ligands were coordinated due to their dueterated nature or lack of ^{1}H NMR signals.
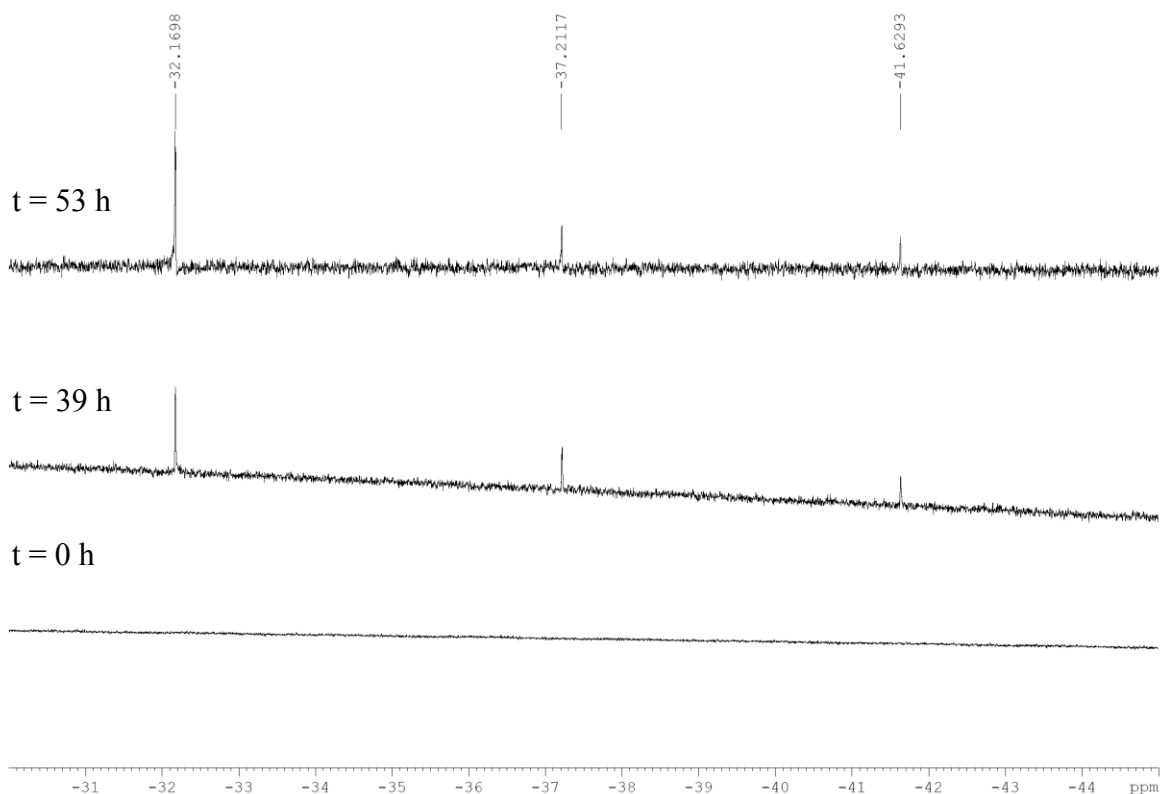
Figure 3.2 Expanded ^{1}H NMR Spectra Showing Upfield Ir-H Signals in DMF-d_7.

3.5 Mechanistic Investigations

3.5.1 Deuterium Labeling Experiments

To verify whether water also acted as the hydrogen source in the iridium catalyzed hydrogenation of PCP, D_2O was employed and the deuterium content of the resultant product was analyzed. Under the standard conditions for catalytic hydrogenation of PCP using D_2O, a high yielding conversion from PCP was obtained to yield 97% of deuterium enriched **5-*d*** (eq 3.14).[24] No deuterated PCP was observed during the catalysis.
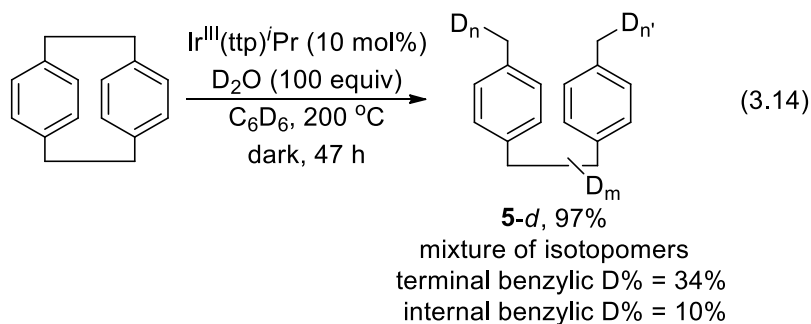
$$\text{Ir}^{III}\text{(ttp)}^{i}\text{Pr (10 mol\%)}$$
$$\text{D}_2\text{O (100 equiv)}$$
$$\overrightarrow{\text{C}_6\text{D}_6,\ 200\ ^\text{o}\text{C}}$$
$$\text{dark, 47 h}$$

(3.14)

5-*d*, 97%
mixture of isotopomers
terminal benzylic D% = 34%
internal benzylic D% = 10%

^{1}H NMR analysis of the isolated **5**-*d* gave proton integration ratio with aromatic : internal benzylic : terminal benzylic = 8.00 : 3.60 : 3.95. Hence, the terminal benzylic positions were ((6-3.95)/6)x100% = 34% deuterated. This suggested that there were in average two deuterium atoms incorporated at the terminal benzylic positions. The internal benzylic positions were ((4-3.60)/4)x100% = 10% deuterated.

The degree of internal benzylic H/D exchange was minor when comparing with the rhodium catalyzed H/D exchange. The reduced metalloradical character of iridium(II) porphyrin may lead to less extensive benzylic C-H activation. Indeed, the K_2CO_3-promoted benzylic C-H activation of toluene in solvent free conditions required higher temperature (200 $^\text{o}$C vs 120 $^\text{o}$C) and base loading (20 equiv vs 10 equiv) for iridium than rhodium porphyrin complexes.[7,16]

To further verify this hypothesis, we then examined the H/D exchange activity of **5** under identical conditions (eq 3.15). ^{1}H NMR analysis of the isolated **5'**-*d* gave proton integration ratio with aromatic : internal benzylic : terminal benzylic = 8.00 : 2.87 : 6.04. Hence, the terminal benzylic positions were ((6-6.04)/6)x100% ≈ 0% deuterated, while the internal benzylic positions were ((4-2.87)/4)x100% = 28% deuterated. The absence of terminal benzylic H/D exchange strongly supported that the deuterium incorporation via post-exchange of **5**-*d* in reaction 3.14 is unlikely. Hence, water was the hydrogenating agent.

Ir^{III}(ttp)^{i}Pr (10 mol%)
D$_2$O (100 equiv)
C$_6$D$_6$, 200 °C
dark, 48 h

(3.15)

1

5'-d, 99%
mixture of isotopomers
terminal benzylic D% = ~0%
internal benzylic D% = 28%
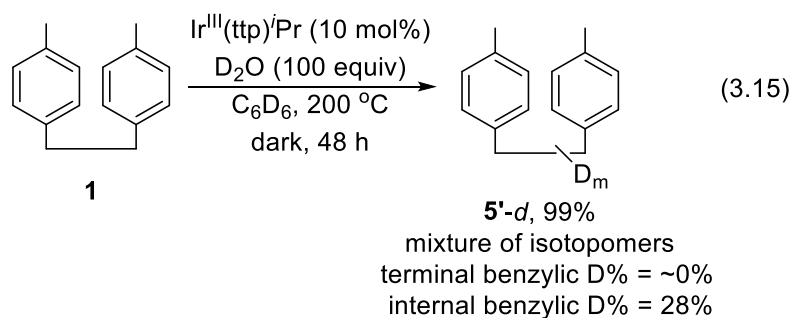
3.5.2 CCA via CHA Intermediate

It has been demonstrated that PCP was inert towards benzylic CHA with rhodium porphyrin complexes. To examine whether this is general to iridium porphyrin complexes, we attempted to observe any benzylic C-H activation intermediates Ir^{III}(ttp)(cyclophanyl) or catalyzed H/D exchanged product deuterated PCP using analogous strategy. Ir^{III}(ttp)(CO)Cl, a convenient precursor of Ir$^{II}_2$(ttp)$_2$ upon reaction with base, was allowed to react with PCP (10 equiv) in the presence of KOH (10 equiv) and D$_2$O (1000 equiv) in C$_6$D$_6$ with gradual heating from 60 °C to 150 °C (Table 3.6, eq 3.16). The reaction progress was closely monitored by ^{1}H NMR spectroscopy. After 9 d of heating from 60 °C to 120 °C, Ir^{III}(ttp)(CO)Cl was completely consumed to give 93% yield of Ir^{III}(ttp)D, without any Ir^{III}(ttp)(cyclophanyl) formed. PCP remained unreacted and undeuterated. Upon further heating at 130 °C for 1 d the reaction mixture produced two CCA products di-Ir **7** and mono-Ir **8** in 5% total yield, with 88% recovery of Ir^{III}(ttp)D. Finally, **7** and **8** were formed in 19% and 23% yields, with 52% recovery of Ir^{III}(ttp)D. Therefore, CCA of PCP occurred directly without prior benzylic CHA process. The rigid structure of PCP discussed in Chapter 2 should be the conclusive reason for the absence of benzylic CHA of PCP.

Table 3.6 Reaction Time Profile of $Ir^{III}(ttp)(CO)Cl$ with PCP under Basic Conditions.

(3.16)
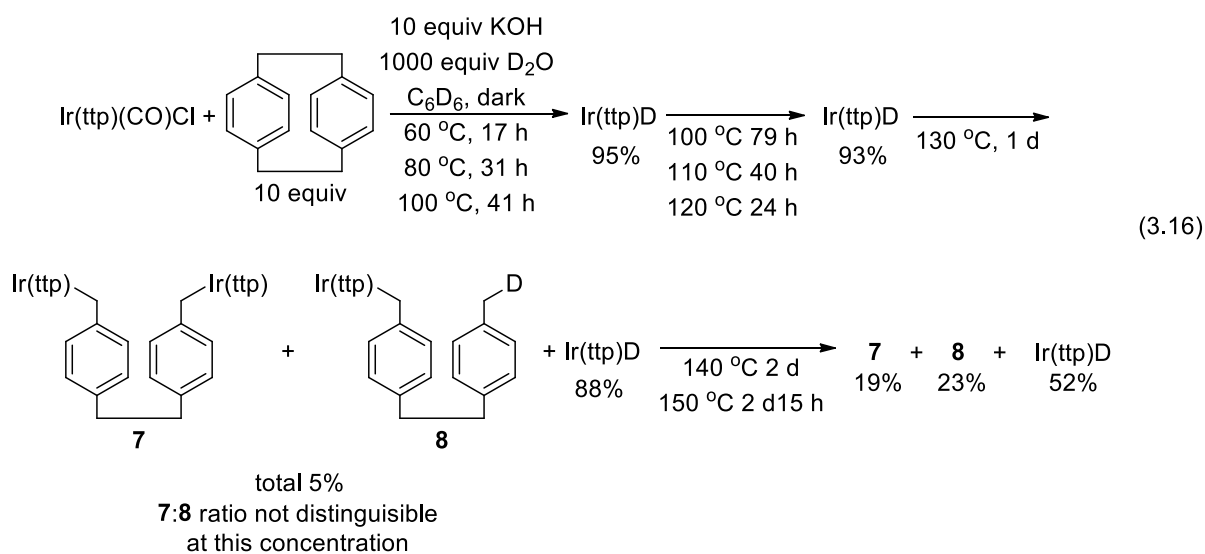
Time / h	Temp / °C	Yield / %				
		$Ir^{III}(ttp)(CO)Cl$	$Ir^{III}(ttp)D$	**7**	**8**	total [Ir]
0	--	100	0	0	0	100
1.5	60	91	7	0	0	98
17	80	66	29	0	0	95
21	80	52	37	0	0	89
24	80	43	50	0	0	93
40	80	33	54	0	0	87
48	100	27	63	0	0	90
64	100	14	80	0	0	94
88	100	0	95	0	0	95
167	110	0	93	0	0	93
191	110	0	83	0	0	83
207	120	0	95	0	0	95
215	120	0	89	0	0	89
231	130	0	94	0	0	94
238	130	0	93	0	0	93
255	140	0	88	5% in total		93
263	140	0	90	3% in total		93
279	140	0	83	6% in total		89
294	140	0	88	8% in total		96
303	150	0	87	9% in total		96
318	150	0	76	7	11	94
342	150	0	62	14	20	96
366	150	0	52	19	23	94

3.5.3 Hydrolysis of $Ir^{III}(ttp)R$

After figuring out the hydrogenating agent, we examined the reasons behind the pre-catalyst effect on shortening the catalysis time. Based on the proposed catalytic cycle for rhodium catalyzed hydrogenation of PCP, we suggested that the iridium catalyzed protocol operated similarly and the hydrolysis of $Ir^{III}(ttp)R$ pre-catalyst to $Ir^{II}(ttp)$ for CCA (the induction period) was the only factor that differentiated the catalysis time. Therefore we investigated the hydrolysis of $Ir^{III}(ttp)R$ (R = Me, Bn and ^{i}Pr).[17]

Table 3.7. Hydrolysis of $Ir^{III}(ttp)R$

$$Ir^{III}(ttp)R \ + \ H_2O \ \xrightarrow[\text{dark, time}]{C_6D_6, \ 200 \ ^oC} \ Ir^{III}(ttp)H \ + \ R\text{-H} \quad (3.17)$$
$$\text{1000 equiv}$$
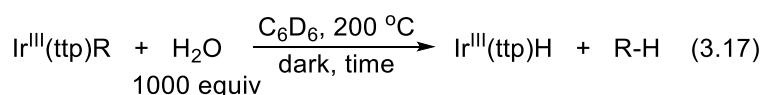
entry	R	time / h	yield / %		
			$Ir^{III}(ttp)R$ recovery	$Ir^{III}(ttp)H$	R-H
1	Me	75	81	8	0[a]
2	Bn	43	3	56	72
3	^{i}Pr	44	0	76	26[b]

[a] the $[CH_4]$ in C_6D_6 might be too low to be observed
[b] 68% yield of propene was formed

Unexpectedly, $Ir^{III}(ttp)Me$ was quite stable towards hydrolysis (Table 3.7, eq 3.17, entry 1). 81% of $Ir^{III}(ttp)Me$ was recovered after 75 h of heating at 200 ^oC with 8% yield of $Ir^{III}(ttp)H$. The organic co-product CH_4 was not observed. It might be formed in little amount due to the partial hydrolysis of $Ir^{III}(ttp)Me$. Hence CH_4 was too diluted in C_6D_6 to be detected by ^1H NMR spectroscopy.

$Ir^{III}(ttp)Bn$ and $Ir^{III}(ttp)^{i}Pr$ were hydrolyzed in similar reaction time of 44 h to give 56% and 76% yields of $Ir^{III}(ttp)H$, respectively (Table 3.7, eq 3.17, entries 2 and 3). Toluene was formed exclusively in 72% yield in the hydrolysis of $Ir^{III}(ttp)Bn$. $Ir^{III}(ttp)^{i}Pr$ underwent competitive hydrolysis and β-H elimination to give the organic co-products propane and

propene in 26% and 68% yields, respectively. The propane : propene ratio of about 1 : 2.5 reflected that β-H elimination is a more facile process (Scheme 3.3).

$$Ir^{III}(ttp)^iPr + H_2O \xrightarrow{\text{hydrolysis}} Ir^{III}(ttp)OH + \text{/\\}$$

$$Ir^{III}(ttp)^iPr \xrightarrow{\beta\text{-H elimination}} Ir^{III}(ttp)H + \text{/\\}$$
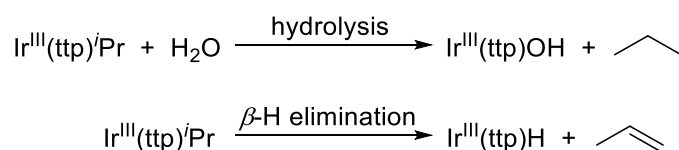
Scheme 3.3 Competitive Hydrolysis and β-H Elimination of $Ir^{III}(ttp)^iPr$.

The generally slow hydrolysis of $Ir^{III}(ttp)R$ were unable to account for the fast turnovers in catalytic hydrogenation of PCP. The hydrolytic stable $Ir^{III}(ttp)Me$ requires amendments in the initial mechanistic assumption. The parallel decomposition of $Ir^{III}(ttp)^iPr$ was mechanistic interesting. Therefore, we pursued further investigations on $Ir^{III}(ttp)Me$ and $Ir^{III}(ttp)^iPr$.

3.5.3.1 Investigation with $Ir^{III}(ttp)CD_3$

To investigate how $Ir^{III}(ttp)Me$ pre-catalyst was consumed in the catalytic hydrogenation of PCP, we traced the fate of deuterium by reacting $Ir^{III}(ttp)CD_3$ with PCP in C_6D_6. $Ir^{III}(ttp)CD_3$ reacted with PCP at 200 ${}^oC$ for 11 h to yield the CCA products di-Ir **7** and mono-Ir **8** in 27% total yields w.r.t. $Ir^{III}(ttp)CD_3$, with 17% recovery of $Ir^{III}(ttp)CD_3$ (eq 3.18). PCP was catalytically converted to 48% of **5''**-*d*, with 47% recovery of PCP. The solvent residual H_2O was in excess to PCP and therefore catalytic conversion was occurred.
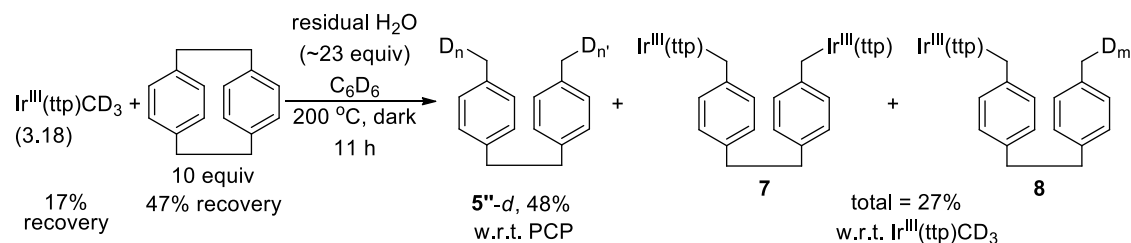
The ^{2}H NMR spectrum of this reaction mixture at t = 11 h showed characteristic resonances at δ = -5.95 ppm and 2.02 ppm, which were assigned as Ir^{III}(ttp)-CD$_3$ and terminal benzylic D of **5''**-*d*, respectively (Figure 3.3). A ^{2}H signal at δ = 1.28 ppm was also observed, which its identity was unclear. Based on its chemical shift, it might be dueterated alkane. At this stage, it could be concluded that the D atoms in Ir^{III}(ttp)CD$_3$ were transferred to the terminal benzylic positions of **5''**-*d*.
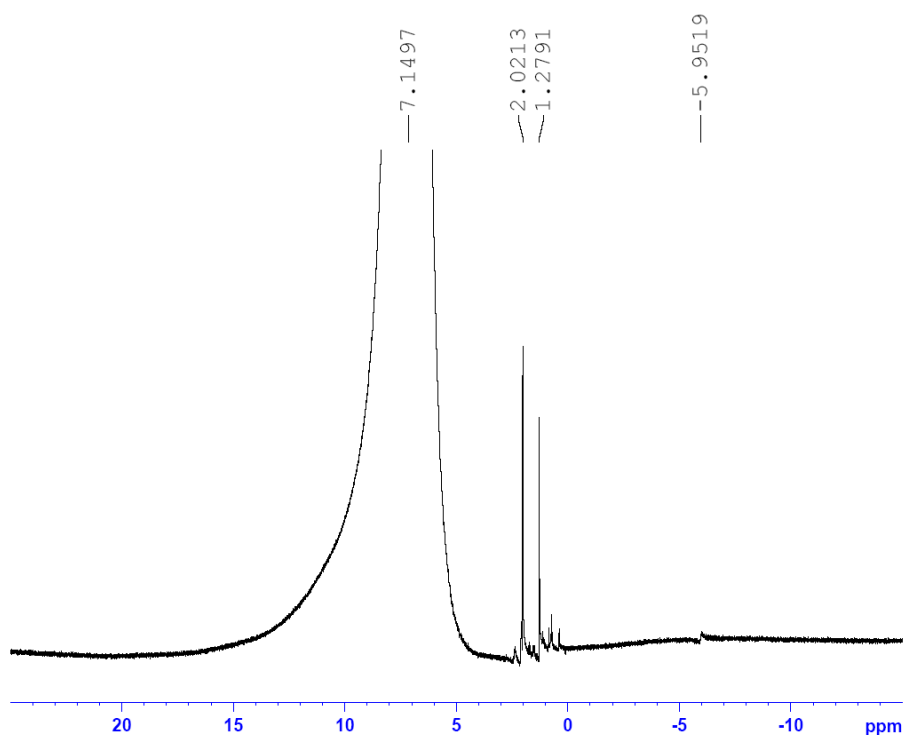
Figure 3.3 ^{2}H NMR Spectrum of Reaction 3.18 at t = 11h.

To account for this observation, a possible reaction mechanism was proposed in Scheme 3.4. Initially, trace amount of Ir^{II}(ttp), formed from the slow hydrolysis of Ir^{III}(ttp)CD$_3$, undergoes homolytic radical substitution at the benzylic carbon of PCP to give the iridium benzylic radical intermediate **A** (step i), analogous to the Rh^{II}(ttp)-catalyzed ring-opening of *c*-octane with Rh^{III}(ttp)H.[18] It then abstracts a deuterium atom from the abundant Ir^{III}(ttp)CD$_3$ to give mono-Ir **8**-*d*$_1$ and Ir^{III}(ttp)CD$_2$ carbon-centered radical, which was estimated to be 16.6 kcal/mol uphill (step ii).[19] Two Ir^{III}(ttp)CD$_2$ carbon-centered radicals

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combine to form $Ir^{III}(ttp)CD_2CD_2(ttp)Ir^{III}$ (step iii). It might be formed in very little amount such that the characteristic very up-field $Ir-CD_2CD_2-Ir$ signal at around -10 ppm was not observed in the ^2H NMR spectrum.[21] Hydrolysis of $Ir^{III}(ttp)CD_2CD_2(ttp)Ir^{III}$ yields partial deuterated ethane which accounted for the ^2H NMR signal observed at $\delta = 1.28$ ppm (step iv).
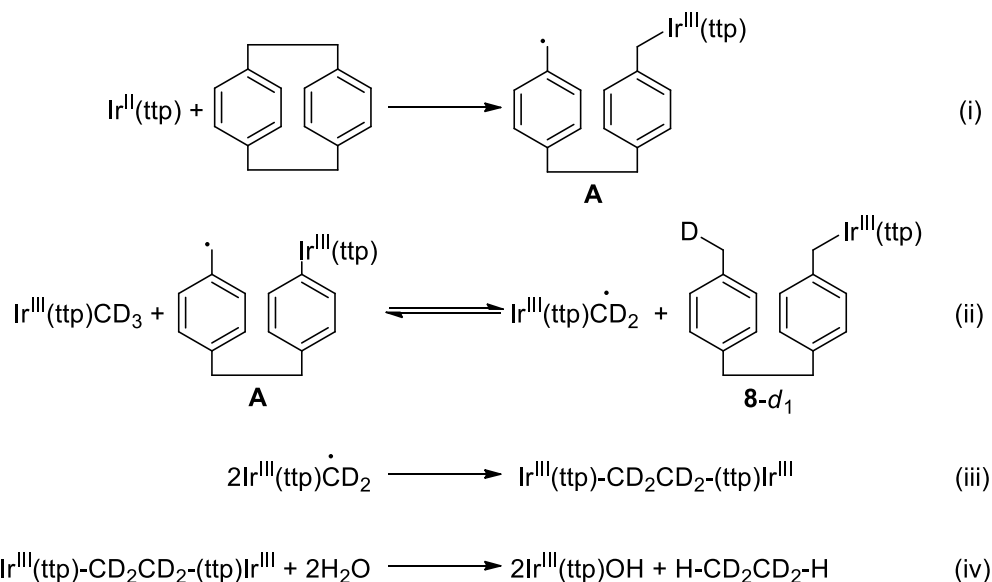
Scheme 3.4 Proposed Mechanism for the Reaction between $Ir^{III}(ttp)CD_3$ and PCP.

3.5.3.2 Investigation with $Ir^{III}(ttp)^iPr$

$Ir^{III}(ttp)^iPr$ underwent parallel hydrolysis and β-H elimination in its hydrolysis study and in catalytic hydrogenation of PCP both supported by the formation of propane and propene. To investigate whether these parallel processes aided $Ir^{III}(ttp)^iPr$ as the most active pre-catalyst, the initial stage of the catalytic hydrogenation of PCP was closely monitored by ^1H NMR spectroscopy. In order to slow down any fast transformations or to observe unstable intermediates, the reaction was carried out at 170 °C instead of 200 °C.

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Table 3.8 Initial Stage of Catalytic Hydrogenation of PCP using $Ir^{III}(ttp)^iPr$ at 170 °C
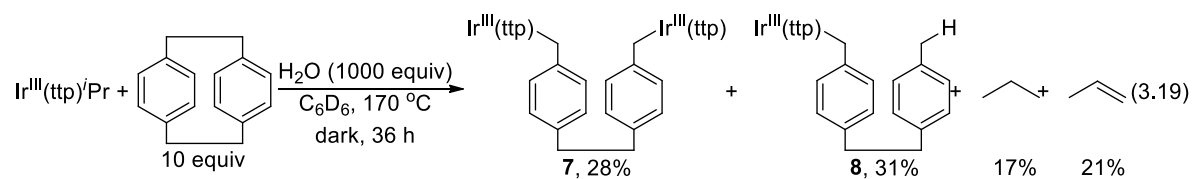
*all yields w.r.t. $Ir^{III}(ttp)^iPr$

Time / h	Yield / %						
	$Ir^{III}(ttp)^iPr$	**7**	**8**	total Ir complexes	propane	propene	total gases
0	100	0	0	100	0	0	0
3	85	10	0	95	0	6	6
6	61	16	8	85	5	10	15
8	46	19	10	75	7	12	19
10.5	39	24	14	77	8	16	24
14	30	32	25	87	15	18	33
18	14	29	25	68	20	23	43
21	7	30	32	69	15	24	39
36	0	28	31	59	17	21	38
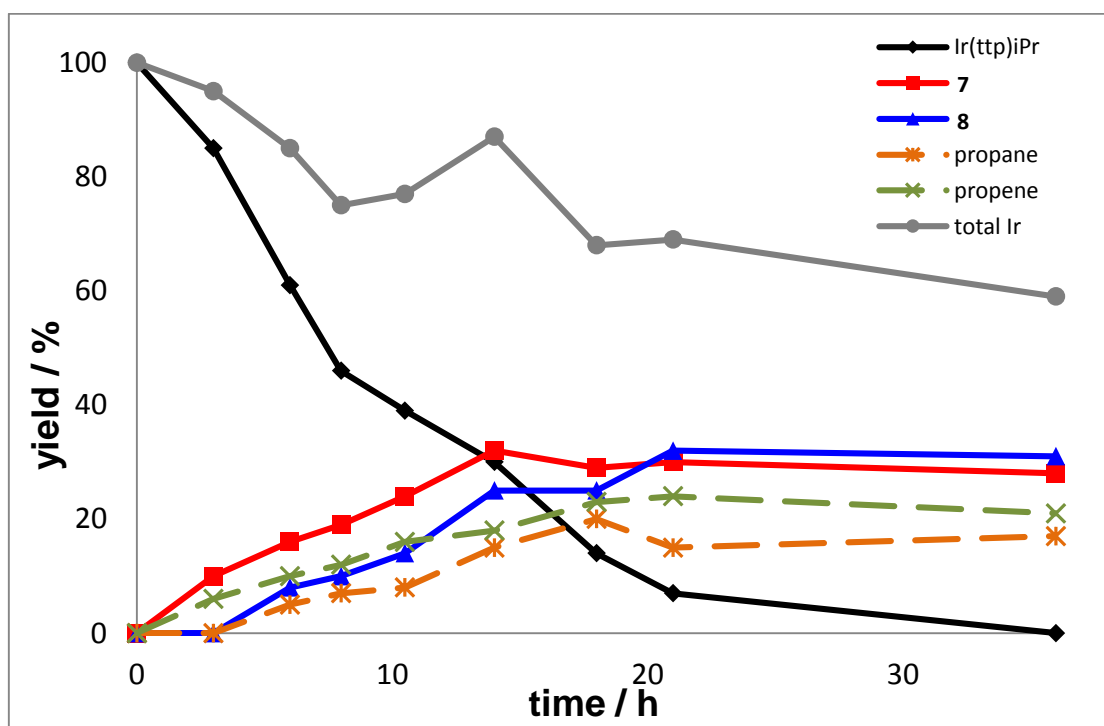
Figure 3.3 Reaction Profile of Reaction 3.19.

Initially, 15% of $Ir^{III}(ttp)^iPr$ was consumed to produce 10% of CCA product di-Ir **7** and 6% of propene after 3 h (Table 3.8, eq 3.19, Figure 3.3). $Ir^{III}(ttp)^iPr$ first reacted via β-H elimination to give propene (Scheme 3.5, step i).[21] $Ir^{III}(ttp)H$ underwent facile dehydrogenation to give $Ir^{II}_2(ttp)_2$ rapidly (step ii).[7] $Ir^{II}_2(ttp)_2$ then dissociated to give $Ir^{II}(ttp)$ for CCA to give **7** (steps iii and iv).

$$Ir^{III}(ttp)^iPr \longrightarrow Ir^{III}(ttp)H + \text{propene} \qquad (i)$$

$$2Ir^{III}(ttp)H \longrightarrow Ir^{II}_2(ttp)_2 \qquad (ii)$$

$$Ir^{II}_2(ttp)_2 \rightleftharpoons 2Ir^{II}(ttp) \qquad (iii)$$

$$2Ir^{II}(ttp) + \text{[PCP]} \longrightarrow \mathbf{7} \qquad (iv)$$
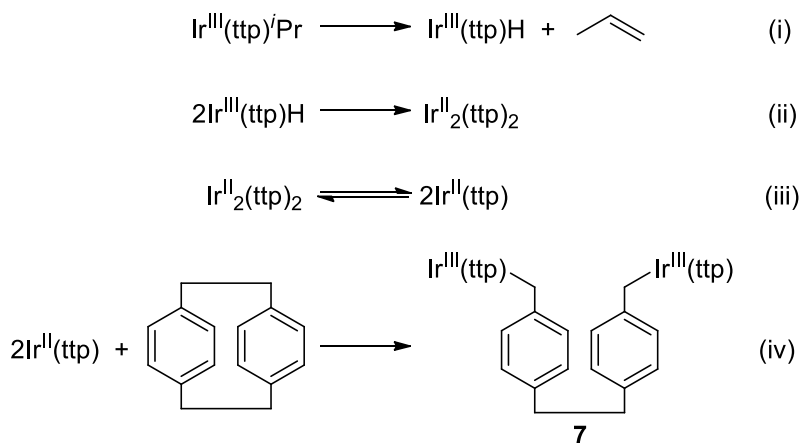
Scheme 3.5 Initial Reaction Pathway of $Ir^{III}(ttp)^iPr$ via β-H Elimination.

Further heating to 6 h produced both CCA products di-Ir **7** and mono-Ir **8** in 16% and 8% yields, respectively. Hydrolysis of $Ir^{III}(ttp)^iPr$ was now observed to yield 5% of propane and $Ir^{III}(ttp)OH$, which was quickly reduced to $Ir^{II}_2(ttp)_2$.[23] $Ir^{II}_2(ttp)_2$ reacted rapidly with PCP to yield **7** (Scheme 3.5, steps iii and iv, and see eq 3.20). After 36 h, $Ir^{III}(ttp)^iPr$ was completely consumed to yield 28% of **7**, 31% of **8**, 17% of propane and 21 % of propene. No benzylic C-H activation of PCP was observed to form any $Ir^{III}(ttp)(cyclophanyl)$ intermediates.[7]

Hence, β-H elimination of $Ir^{III}(ttp)^iPr$ followed by thermal dehydrogenation was a faster pathway than hydrolysis to provide $Ir^{II}_2(ttp)_2$ for CCA. Alternatively, $Ir^{III}(ttp)H$ reacted with PCP directly to afford the CCA product mono-Ir **8**. $Ir^{III}(ttp)H$ and $Ir^{II}_2(ttp)_2$ were the possible intermediates for the CCA of PCP. Their stoichiometric reactions with PCP were then examined independently.

3.5.4 Reaction of $Ir^{II}_2(ttp)_2$ with PCP

At 150 °C, $Ir^{II}_2(ttp)_2$ was completely reacted with PCP to give 55% yield of CCA product di-Ir **7** after 28 h (eq 3.20). Under thermal conditions, $Ir^{II}_2(ttp)_2$ equilibrates with $Ir^{II}(ttp)$ due to the weak Ir-Ir bond.[24] The Ir-Ir BDE in $Ir^{II}_2(ttp)_2$ was estimated 20 kcal/mol using the sterically similar $Ir^{II}_2(txp)_2$ as reference.[3] The equilibrium constant for $Ir^{II}_2(ttp)_2$ dissociation at 150 °C was evaluated to be 3.1 x 10^{-4} (Scheme 3.6). This closely resembled the bi-metalloradical CCA of PCP with $Rh^{II}(tmp)$.

$$Ir^{II}_2(ttp)_2 + \underset{\text{5 equiv}}{\boxed{\text{PCP}}} \xrightarrow[\text{150 °C, 28 h}]{\text{C}_6\text{D}_6, \text{dark}} \quad \underset{\textbf{7}, 55\%}{\boxed{\text{di-Ir product}}} \qquad (3.20)$$

$$Ir^{II}_2(ttp)_2 \underset{K = 3.1\times10^{-4}}{\overset{150\ ^{\circ}\text{C}}{\rightleftharpoons}} 2Ir^{II}(ttp)$$
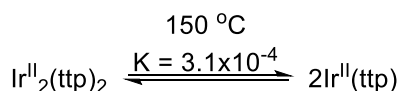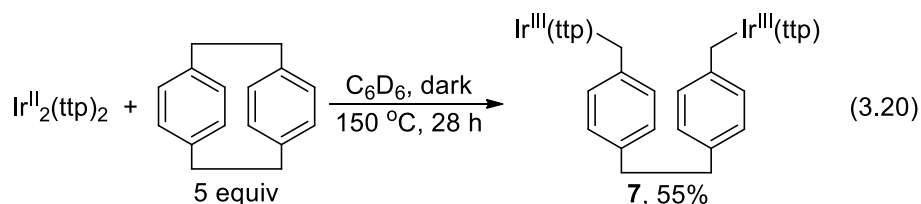
$\Delta G = \Delta H - T\Delta S$

$\Delta H = $ Ir-Ir BDE in $Ir^{II}_2(txp)_2 = 20$ kcal mol^{-1}

assume $S = $ entropy of $H_2 = 31.2$ cal mol^{-1} K^{-1} [25]

$\Delta G = 20 - (423)(0.0312) = 6.8$ kcal mol^{-1}

$\Delta G = -RTlnK$

$6.8 = -(1.9872\times10^{-3})(423)lnK$

$K = 3.1\times10^{-4}$

Scheme 3.6 Equilibrium Estimation for the $Ir^{II}_2(ttp)_2$ Dissociation.

3.5.5 Reaction of $Ir^{III}(ttp)H$ with PCP

$Ir^{III}(ttp)H$ reacted with PCP at 150 °C in 35 h to give di-Ir **7** and mono-Ir **8** in 12% and 21% yields, respectively, with 37% recovery yield of $Ir^{III}(ttp)H$ (Table 3.9, eq 3.21 and Figure 3.4). Interestingly, the mono-Ir **8** was the major CCA product throughout the first 35 h

of the reaction. Then, di-Ir **7** took the lead as the major product upon further heating from 35

h to 69 h, yielding 50% of **7** and 33% of **8** as the minor product, with complete consumption

of $Ir^{III}(ttp)H$.

Table 3.9 Reaction of $Ir^{III}(ttp)H$ with PCP at 150 ºC.

$$\text{(3.21)}$$
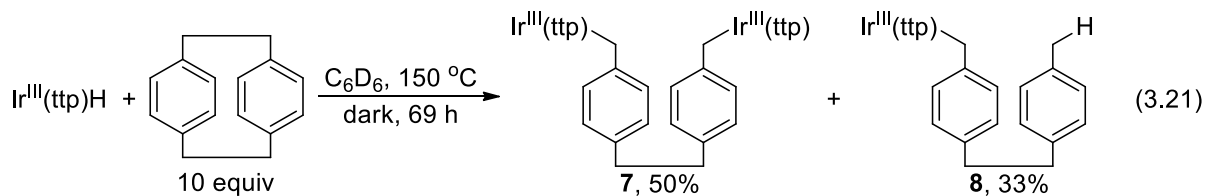
Time / h	Yield / %			
	$Ir^{III}(ttp)H$	**7**	**8**	total Ir complexes
0	100	0	0	100
2	100	0	0	100
5.5	92	3	7	102
9.5	80	4	9	93
28.5	53	11	19	83
35	37	12	21	70
52	22	29	24	75
69	0	50	33	83
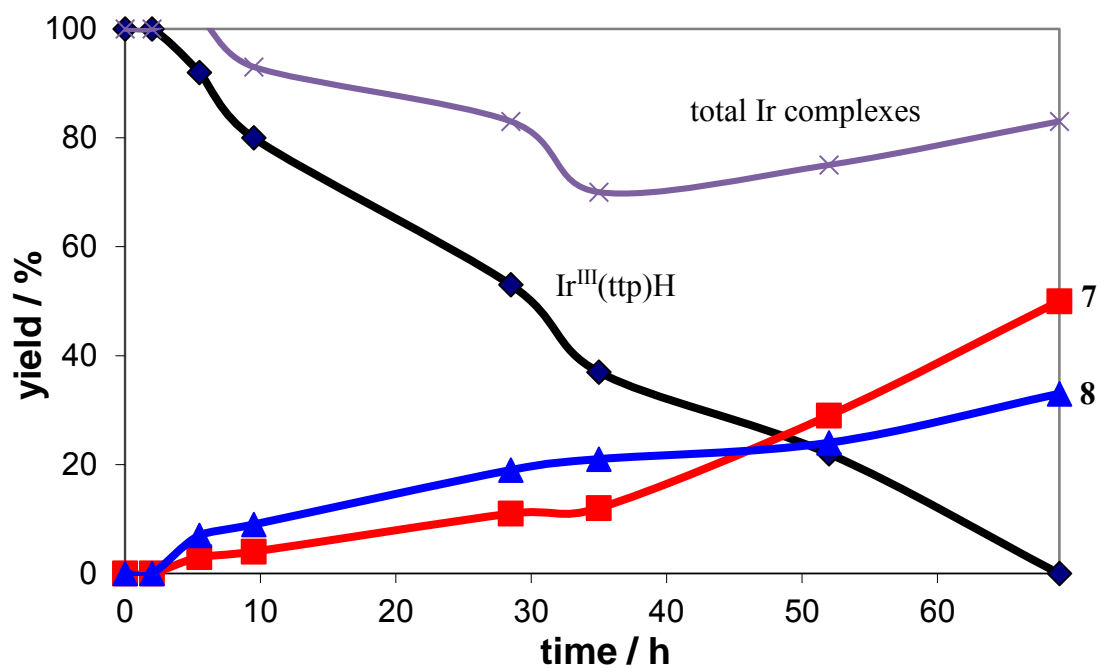
Figure 3.4 Reaction Profile of Reaction 3.21.

The formation of di-Ir **7** can be well accounted by the in situ formation of $Ir^{II}(ttp)$ from $Ir^{III}(ttp)H$ followed by CCA with PCP as discussed previously. However, the preferential formation of mono-Ir **8** at the initial stage of reaction contradicted with the bi-metalloradical CCA proposal. Since the hydrolysis of $Ir^{III}(ttp)Bn$, as a simplified structural model of **7**, was slow at 200 °C, the hydrolysis of **7** by the solvent residual water at 150 °C was unlikely a source of **8**. We suspected that the abundant $Ir^{III}(ttp)H$ present in the reaction mixture has promoted two reaction channels to form **8** in a much faster manner. The two pathways are: (1) $Ir^{II}(ttp)$-catalyzed 1,2-addition of $Ir^{III}(ttp)H$ across the benzylic C-C bond of PCP to form **8**, bypassing the formation of **7** (Scheme 3.7)[18] and (2) bi-molecular reductive elimination from $Ir^{III}(ttp)H$ and **7** to give **8** and $Ir^{II}_2(ttp)_2$ (eq 3.22).[26] These two possibilities were then investigated.
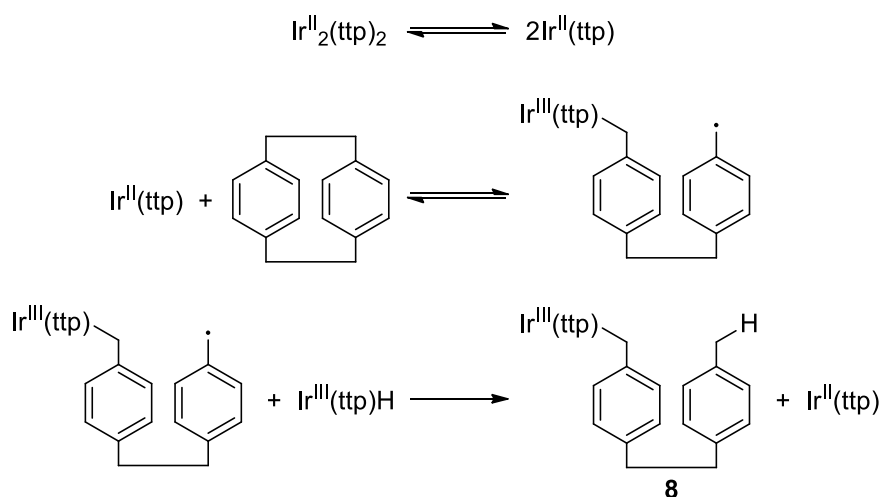
Scheme 3.7 $Ir^{II}(ttp)$-Catalyzed 1,2-Addition of $Ir^{III}(ttp)H$.
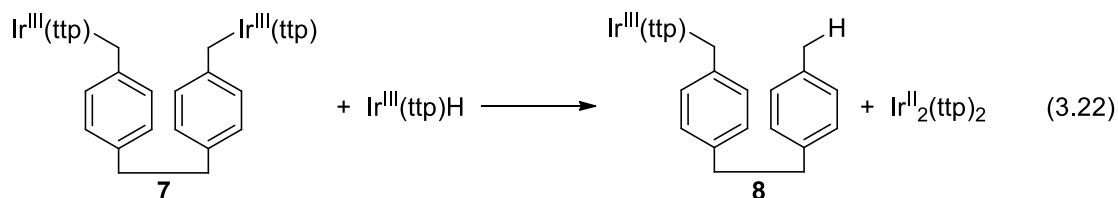
3.5.5.1 Ir^{II}(ttp)-Catalyzed 1,2-Addition of Ir^{III}(ttp)H

With catalytic amount of Ir^{II}_2(ttp)$_2$ (3 mol%), Ir^{III}(ttp)H reacted with PCP at 150 °C in C_6D_6 to yield 49% of **7** and 39% of **8** in 75 h (Table 3.10, eq 3.23, Figure 3.5). The reaction profile was very similar to reaction 3.21 without Ir^{II}_2(ttp)$_2$ added. The mono-Ir **8** was the major CCA product at initial and then shifted to di-Ir **7** as the major product. In addition, the rate of formation of **8** was not enhanced in the presence of Ir^{II}_2(ttp)$_2$ (Figure 3.6). Therefore, the Ir^{II}(ttp)-catalyzed 1,2-addition of Ir^{III}(ttp)H pathway does not operate at 150 °C. Kinetically, the much lower equilibrium concentration of Ir^{II}(ttp) than that of Rh^{II}(ttp) at same temperature should be a key reason.

Table 3.10. Reaction Ir^{III}(ttp)H with PCP with 3 mol% of Ir^{II}_2(ttp)$_2$ at 150 °C.
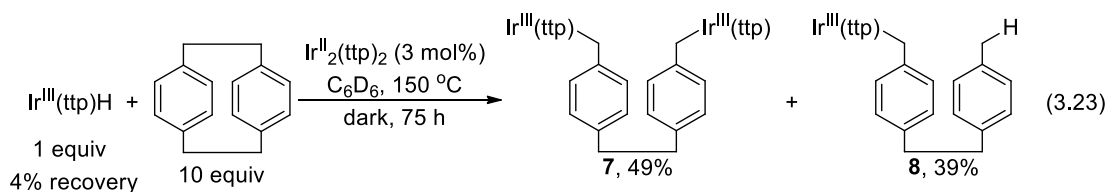
Time / h	Yield / %			
	Ir^{III}(ttp)H	**6**	**7**	total Ir complexes
0	100	0	0	100
6	95	1	3	99
12	87	3	9	99
27	67	11	15	93
36	53	17	21	91
51	30	36	32	98
75	4	49	39	92
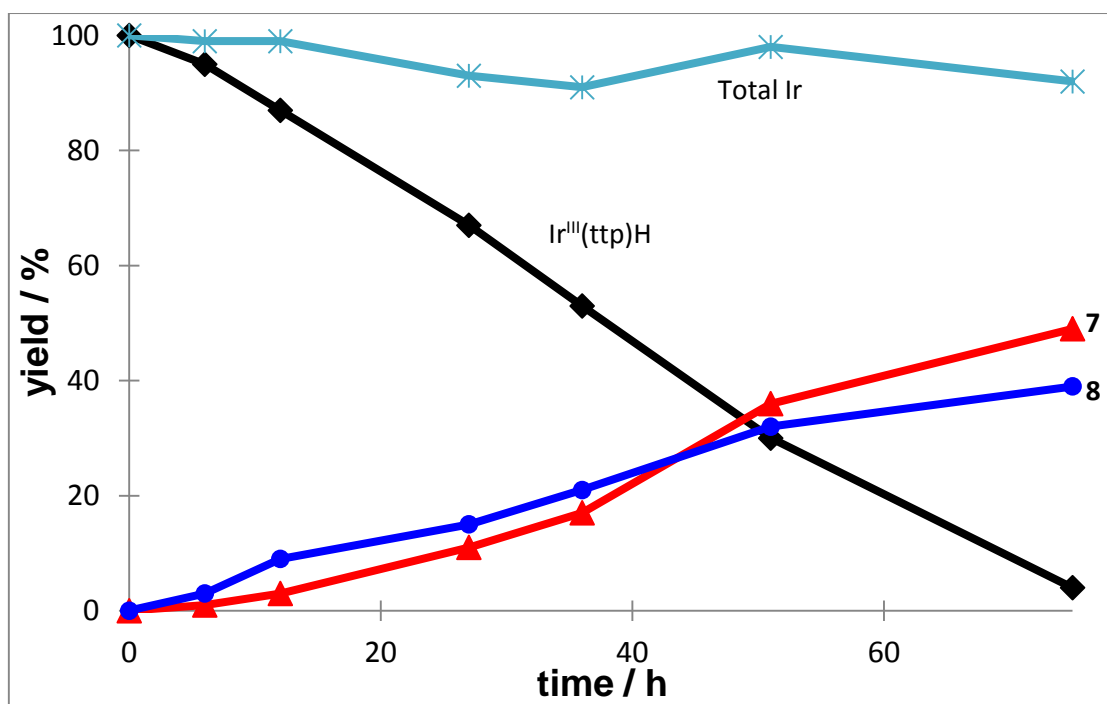
Figure 3.5 Reaction Time Profile of Reaction 3.23.
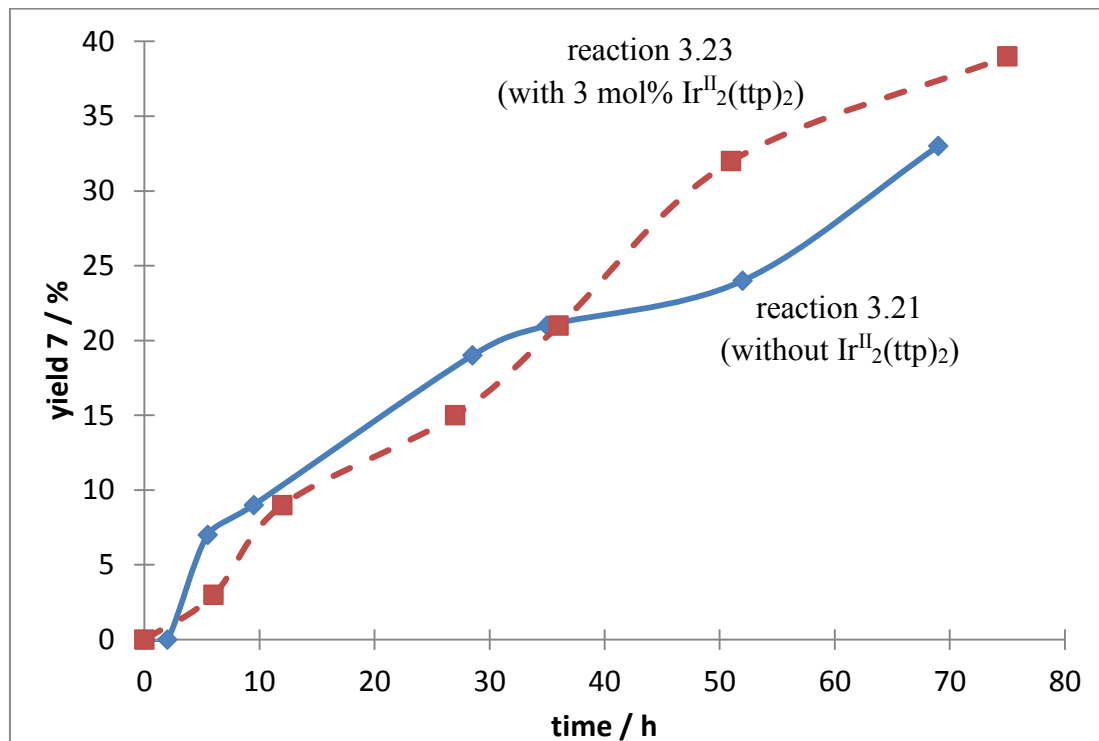
Figure 3.6 Comparison of the Formation of Mono-Ir **8** from Reactions 3.21 and 3.23.

To better understand why the Ir^{II}(ttp)-catalyzed 1,2-addition of Ir^{III}(ttp)H pathway was

not operating, the reaction thermodynamics of this pathway and bi-metalloradical CCA with

rhodium and iridium scenarios were estimated (Scheme 3.8).

In the M^{II}(ttp)-catalyzed 1,2-addition of M^{III}(ttp)H pathway, the breaking of stronger

Ir-H bond is 10 kcal/mol uphill than the breaking of Rh-H bond.[27] This energetically uphill

demand cannot be compensated by forming the Ir-C bond since it is only 5.1 kcal/mol

stronger than the Rh-C bond.[28] On the contrary, the bi-metalloradical activation of PCP with

Ir^{II}_2(ttp)$_2$ is more favored than with Rh^{II}_2(ttp)$_2$. Although the breaking of stronger Ir-Ir bond is

8 kcal/mol uphill than the breaking of Rh-Rh bond, it can be compensated by forming of two

Ir-C bonds which is 10.2 kcal/mol downhill than forming two Rh-C bonds.

M^{II}(ttp)-catalyzed 1,2-addition of M^{III}(ttp)H

BDE (kcal/mol)

M = Rh	60	26.8	37.1	89.7
M = Ir	70	26.8	42.2	89.7
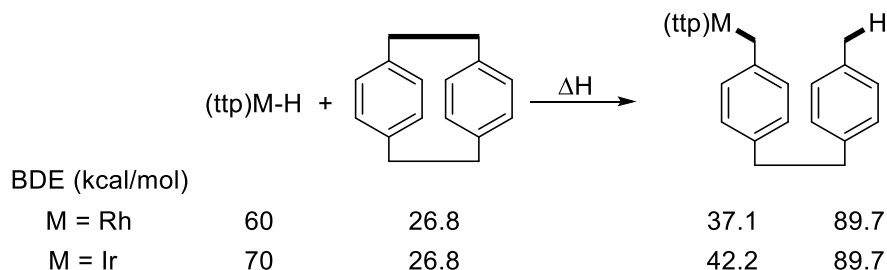
For Rh: ΔH = 60 + 26.8 – 37.1 – 89.7 = -40.0 kcal/mol
For Ir: ΔH = 70 + 26.8 – 42.2 – 89.7 = -35.1 kcal/mol
Ir is **less favorable** than Rh in this process by 4.9 kcal/mol.

CCA with M^{II}_2(ttp)$_2$

BDE (kcal/mol)

M = Rh	12	26.8	37.1 x 2
M = Ir	20	26.8	42.2 x 2
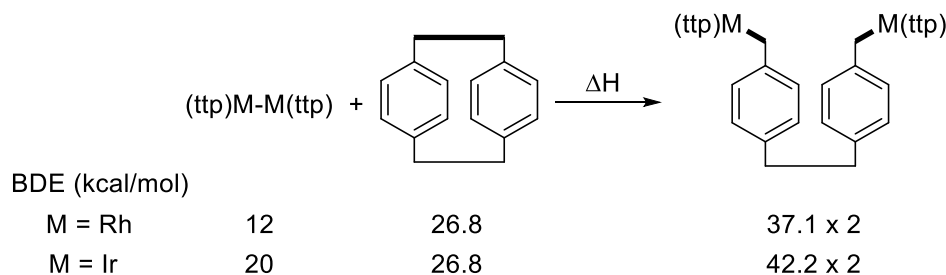
For Rh: ΔH = 12 + 26.8 – (37.1 x 2) = -35.4 kcal/mol
For Ir: ΔH = 20 + 26.8 – (42.2 x 2) = -37.6 kcal/mol
Ir is **more favorable** than Rh in this process by 2.2 kcal/mol.

Scheme 3.8 Thermodynamic Comparison on Two CCA Pathways.

3.5.5.2 Bi-molecular Reductive Elimination with $Ir^{III}(ttp)H$

Wayland has reported various examples of intermolecular reductive elimination from $Rh^{III}(por)H$ and $Rh^{III}(por)R$ to give $Rh^{II}(por)$ and alkanes,[29] alkylaromatics[26] and MeOH.[30] The bi-molecular reductive elimination from $Rh^{III}(oep)H$ and $Rh^{III}(oep)(CH(Ph)CH_2CH_3)$ at 100 °C in C_6D_6 gave *n*-propylbenzene (eq 3.24).[26] Similarly, quantitative bi-molecular reductive elimination of MeOH from $Rh^{III}(oep)CH_2OH$ and $Rh^{III}(oep)H$ has been reported (eq 3.25).[30]

$$Rh^{III}(oep)H + Rh^{III}(oep)(CH(Ph)CH_2CH_3) \xrightarrow[100 \text{ °C}]{C_6D_6} Rh^{II}_2(oep)_2 + PhCH_2CH_2CH_3 \quad (3.24)$$

$$Rh^{III}(oep)H + Rh^{III}(oep)CH_2OH \xrightarrow[\text{quantitative}]{\substack{C_6D_6 \\ 80 \text{ °C, 8 h}}} Rh^{II}_2(oep)_2 + CH_3OH \quad (3.25)$$
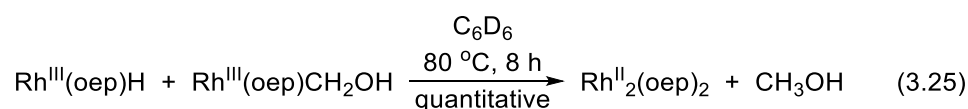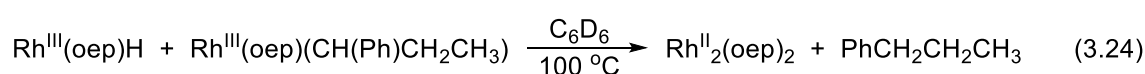
In the reversible C-H bond activation of CH_4 with $Rh^{II}(tmp)$ to give $Rh^{III}(tmp)CH_3$ and $Rh^{III}(tmp)H$, the bi-molecular reductive elimination of CH_4 proceeded favorably at elevated temperatures (Table 3.11, eq 3.26).[29]

Table 3.11 Reversible C-H Activation of CH_4 with $Rh^{II}(tmp)$.

$$2Rh^{II}(tmp) + CH_4 \underset{C_6D_6, \text{ temp}}{\overset{K}{\rightleftharpoons}} Rh^{III}(tmp)H + Rh^{III}(tmp)CH_3 \quad (3.26)$$
$$\text{1 atm}$$
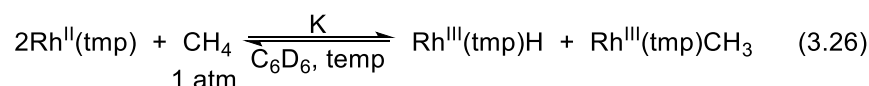
entry	Temp / °C	K
1	80	7300±700
2	100	3300±400
3	120	1100±200

We propose that this kind of bi-molecular reductive elimination is general to iridium porphyrin system. If the formation of R-H from $Ir^{III}(ttp)H$ and $Ir^{III}(ttp)R$ (Scheme 3.9, pathway i) is faster than the hydrolysis of $Ir^{III}(ttp)R$ (Scheme 3.9, pathway ii), this will provide an additional and faster pathway for C-H bond formation.

Faster
(i) bi-molecular reductive elimination
$Ir^{III}(ttp)H$
$-Ir^{II}_2(ttp)_2$

$Ir^{III}(ttp)R \longrightarrow$ | | $\longrightarrow$ R-H

(ii) hydrolysis
H_2O
$-Ir^{III}(ttp)OH$
Slower
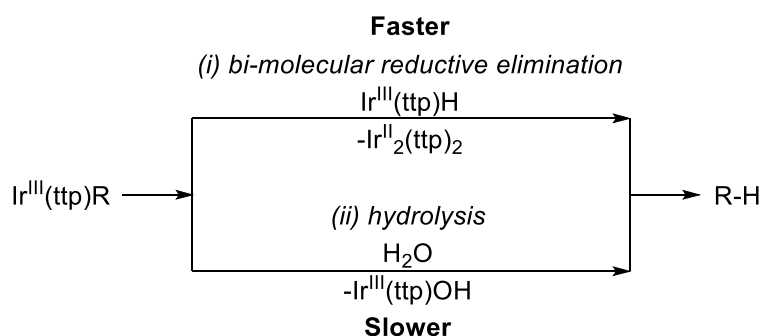
Scheme 3.9 Parallel Pathway for the Formation of R-H.

To our delight, $Ir^{III}(ttp)H$ reacted with $Ir^{III}(ttp)Bn$ at 200 °C to give 78% yield of toluene in 43 h (Table 3.12, eq 3.27, Figures 3.7). The initial rates of $Ir^{III}(ttp)Bn$ consumption and toluene formation were both 3 times faster than that of $Ir^{III}(ttp)Bn$ hydrolysis, estimated from the initial 3 h of the two reactions (Figures 3.8 and 3.9), supporting the promoting effect of $Ir^{III}(ttp)H$ towards faster hydrogenation.

Table 3.12 Reaction Time Profile of Bi-molecular Reductive Elimination between $Ir^{III}(ttp)Bn$ and $Ir^{III}(ttp)H$

$$Ir^{III}(ttp)Bn \ + \ Ir^{III}(ttp)H \xrightarrow[43 \text{ h}]{\substack{C_6D_6 \\ 200 \ ^oC}} BnH \ + \ \substack{\text{Ir porphyrin} \\ \text{unknowns}} \quad (3.27)$$
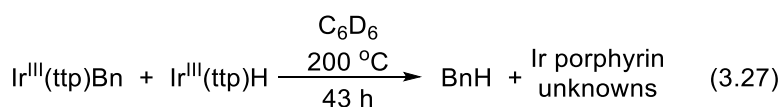
Time / h	Yield / %			
	$Ir^{III}(ttp)Bn^a$	$Ir^{III}(ttp)H^b$	BnH^a	Ir por unknowns^c
0	100	100	0	0
1	74	117	25	11
2	64	95	32	10
6	53	116	48	17
21	27	117	66	22
28	19	120	73	26
43	11	107	78	30

[a] w.r.t. $Ir^{III}(ttp)Bn$
[b] w.r.t. $Ir^{III}(ttp)H$
[c] w.r.t. total [Ir] at initial
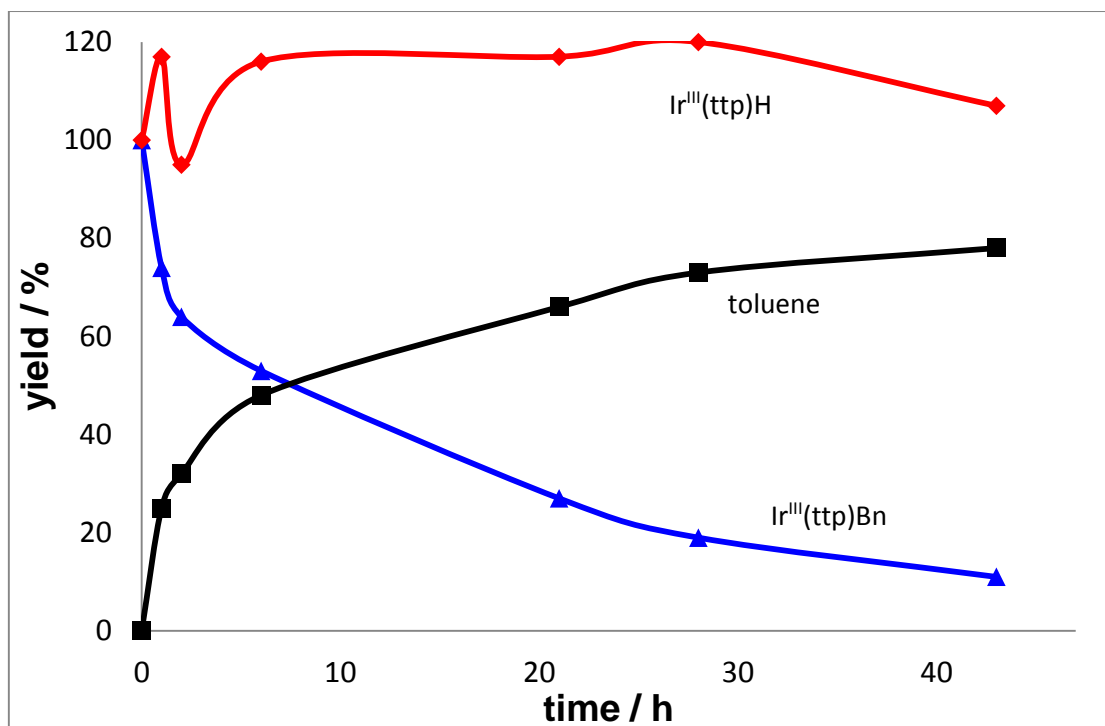
Figure 3.7 Reaction Time Profile of Reaction 3.27.
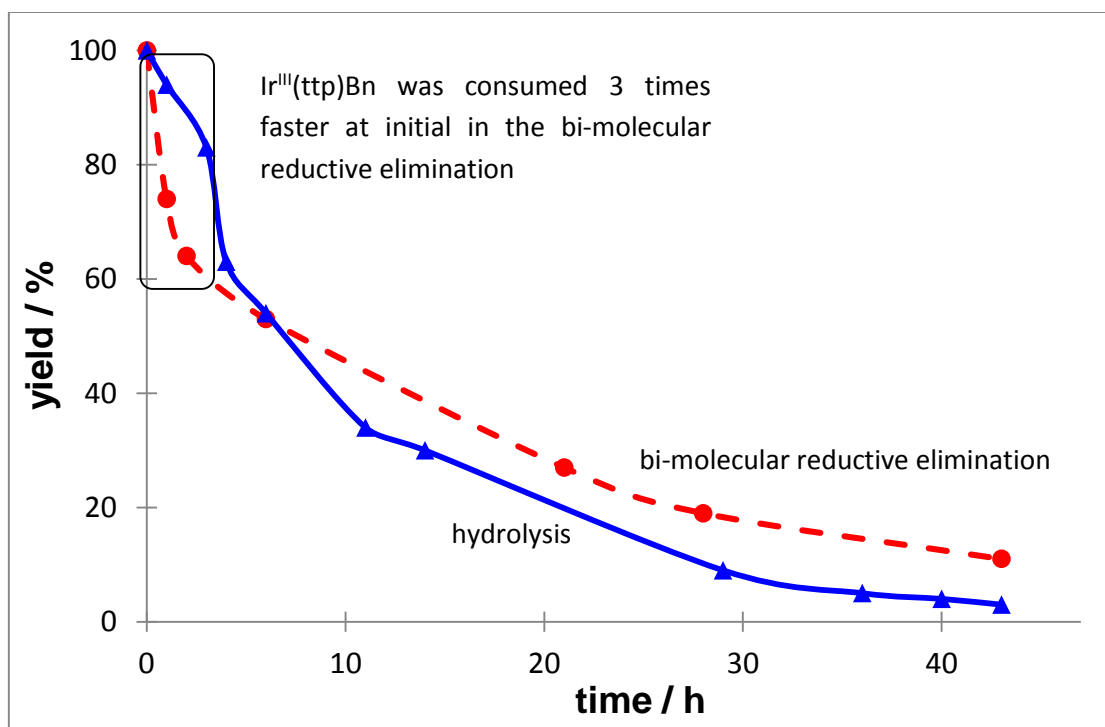
Figure 3.8 Comparison on Ir^{III}(ttp)Bn Consumption between Bi-molecular Reductive Elimination and Hydrolysis.
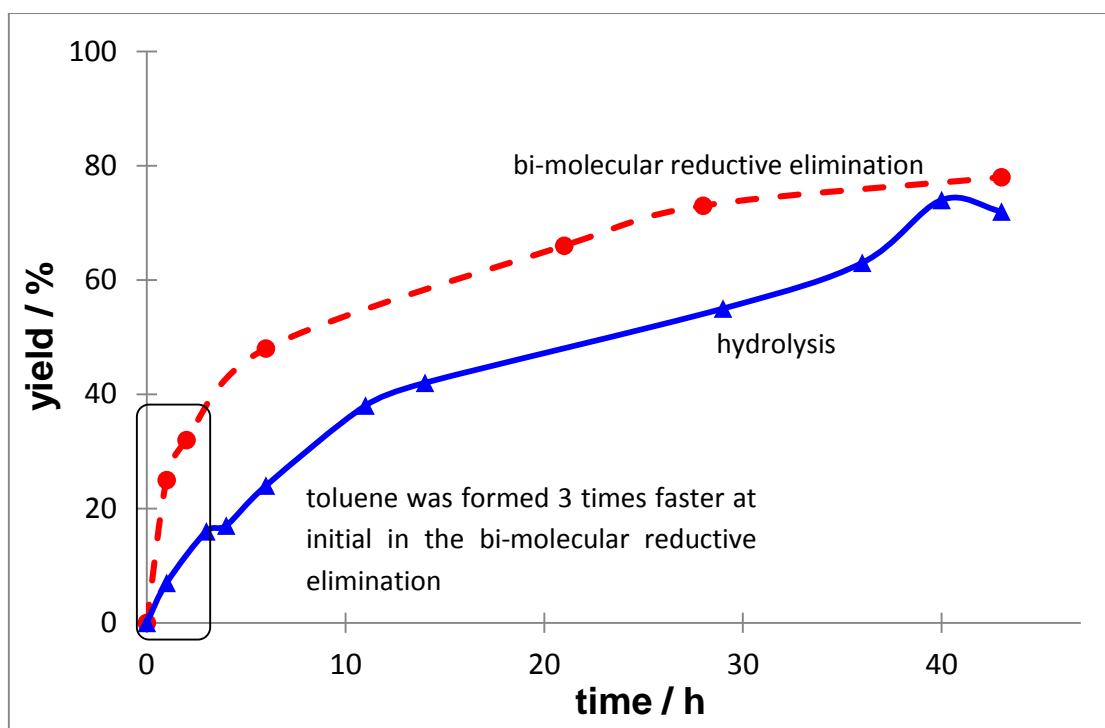
Figure 3.9 Comparison on Toluene Formation between Bi-molecular reductive elimination and Hydrolysis.

Therefore, in the reaction of $Ir^{III}(ttp)H$ with PCP (Table 3.9, eq 3.21, Figure 3.4), the intermolecular elimination of mono-Ir **8** from $Ir^{III}(ttp)H$ and di-Ir **7** occurred rapidly right after **7** was formed provided that the $[Ir^{III}(ttp)H]$ was still high at the initial stage of reaction (eq 3.28). In analogy, $Ir^{III}(ttp)H$ can react with **8** to yield the hydrogenation product **5** (eq 3.29). These two sequential reaction pathways can operate in the catalytic hydrogenation of PCP to achieve a faster hydrogenation process, bypassing the slower hydrolysis.
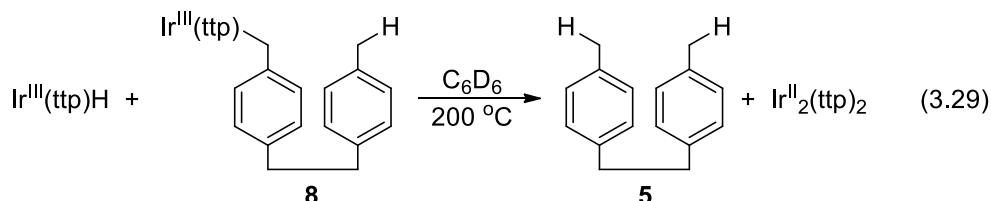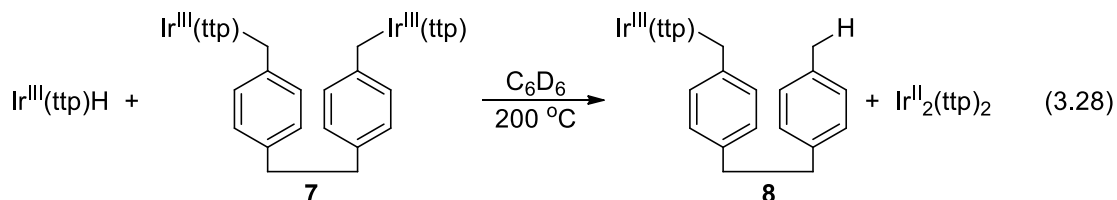
3.5.6 Reaction of $Ir^{II}_2(ttp)_2$ with H_2O

A continuous generation of $Ir^{III}(ttp)H$ in the catalytic hydrogenation of PCP is essential to sustain the fast intermolecular elimination reaction. β-H elimination of $Ir^{III}(ttp)^iPr$ pre-catalyst only provides $Ir^{III}(ttp)H$ at the beginning of the catalysis. Oxidative addition of H_2O with group 9 metalloradical is another channel. The reaction of $Co^{II}(CN)_5^{3-}$ with H_2O to give $Co^{III}(CN)_5H^{3-}$ and $Co^{III}(CN)_5OH^{3-}$ occurs readily at 25 ^oC in aqueous medium (eq 3.30).[31]

$$2Co^{II}(CN)_5^{3-} + H_2O \xrightarrow[25\ ^oC]{\overset{k = 1.0\times10^{-3}\ M^{-1}\ s^{-1}}{\Delta G^{\ddagger} = 9.84\ kcal\ mol^{-1}}} Co^{III}(CN)_5H^{3-} + Co^{III}(CN)_5OH^{3-} \qquad (3.30)$$
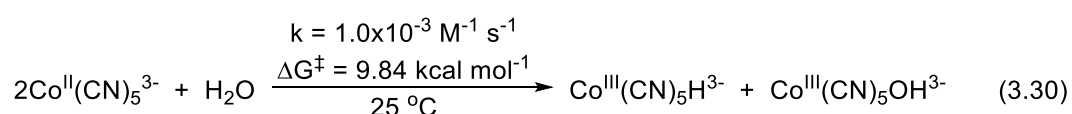
Wayland has reported the thermodynamic favorable oxidative addition of D_2O with water soluble rhodium porphyrin $[(TMPS)Rh^{II}(D_2O)]^{-8}$ (eq 3.31).[13] The analogous reaction with $[(TMPS)Ir^{II}(D_2O)]^{-8}$ has been suggested to be more exergonic by -11 to -15 kcal/mol due to the stronger Ir-D and Ir-OD bonds than the corresponding Rh-D and Rh-OD bonds.[32]

$$2[(TMPS)Rh^{II}(D_2O)]^{-8} + D_2O \xrightleftharpoons[\ \ ]{\overset{\Delta G = -2.4\ kcal/mol}{K(25\ ^oC) = 57.6}} [(TMPS)Rh^{III}D(D_2O)]^{-8} + [(TMPS)Rh^{III}D(D_2O)]^{-8} \qquad (3.31)$$
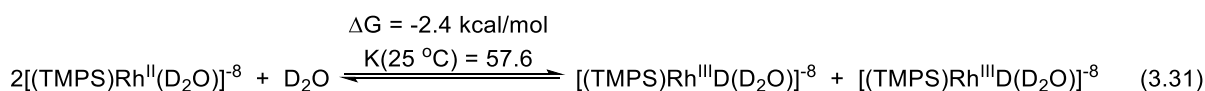
Similarly, the lipophilic $Ir^{II}(ttp)$ may undergo oxidative addition with H_2O to generate $Ir^{III}(ttp)H$ and $Ir^{III}(ttp)OH$. The $Ir^{III}(ttp)OH$ once formed, quickly reverts back to $Ir^{II}_2(ttp)_2$ with elimination of H_2O_2.[22] Indeed, $Ir^{II}_2(ttp)_2$ reacted readily with excess H_2O in C_6D_6 at 27 ^oC to 50 ^oC to give 55% yield of $Ir^{III}(ttp)H$, with 8% recovery of $Ir^{II}_2(ttp)_2$ after 110 h (Table 3.13, eq 3.32, Figure 3.10). Prolonged heating at 50 ^oC gave no further conversions. The saturated $[H_2O]$ in C_6D_6 at 27 ^oC and 50 ^oC were estimated to be 35 mM and 78 mM, respectively.[11] Deep brown precipitates were formed gradually during the reaction and led to

the decreased total yield. The H_2O_2 formed, if not decomposed quickly to less oxidizing O_2 and H_2O, probably induced the oxidative decomposition of iridium porphyrin complexes.

Table 3.13 Reaction of $Ir^{II}_2(ttp)_2$ with H_2O.

$$Ir^{II}_2(ttp)_2 \ + \ H_2O \ \xrightarrow[\text{dark, temp, time}]{C_6D_6} \ Ir^{III}(ttp)H \quad (3.32)$$
$$3200 \text{ equiv}$$
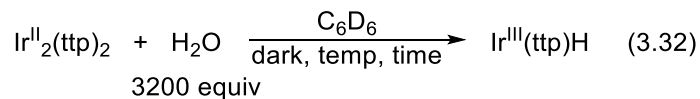
Time / h	Temp / °C	Yield / %		
		$Ir^{II}_2(ttp)_2$	$Ir^{III}(ttp)H$	total Ir complexes
0	27	100	0	100
1.5	27	82	0	82
16.5	27	60	6	66
24	27	60	10	70
41	27	43	10	53
44	50	34	16	50
48	50	29	21	50
63	50	22	35	57
91	50	10	44	54
110	50	8	55	63
134	50	7	60	67
209	50	8	58	66
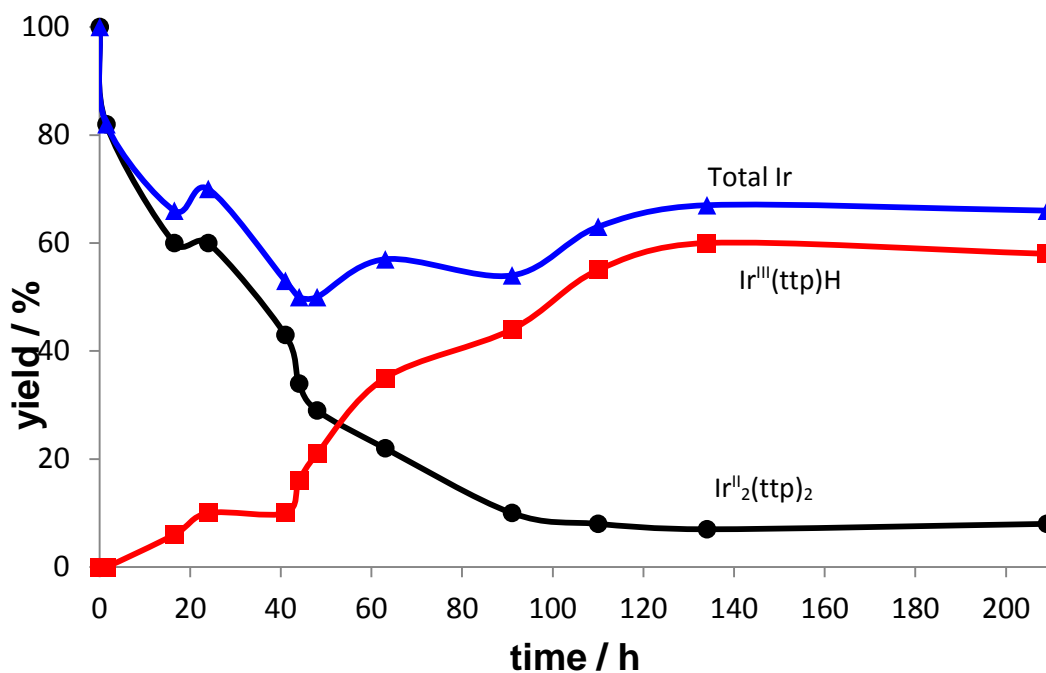
Figure 3.10 Reaction Time Profile of Reaction of $Ir^{II}_2(ttp)_2$ with H_2O.

(H$_2$O)Ir^{III}(ttp)-O-Ir^{III}(ttp)(H$_2$O), the condensation product of Ir^{III}(ttp)OH, was not observed based on reported characteristic pyrrole ^{1}H signal at δ = 8.36 ppm in C$_6$D$_6$ (Figure 3.11).[22] Rapid hydrolysis of (H$_2$O)Ir^{III}(ttp)-O-Ir^{III}(ttp)(H$_2$O) to give back Ir^{III}(ttp)OH and then Ir$^{II}_2$(ttp)$_2$ at 27 °C or 50 °C was unlikely, since it was prepared in good yields by heating Ir^{III}(ttp)CH$_2$CH$_2$OH at 120 °C in C$_6$D$_6$ for 23 d (eq 3.33). In addition, stability test showed that the μ-oxo complex decomposed very slowly to Ir^{III}(ttp)H at 200 °C under basic conditions (eq 3.34). This suggested that (H$_2$O)Ir^{III}(ttp)-O-Ir^{III}(ttp)(H$_2$O) should be reasonably stable to be observed at 27 °C or 50 °C, if it had been present.
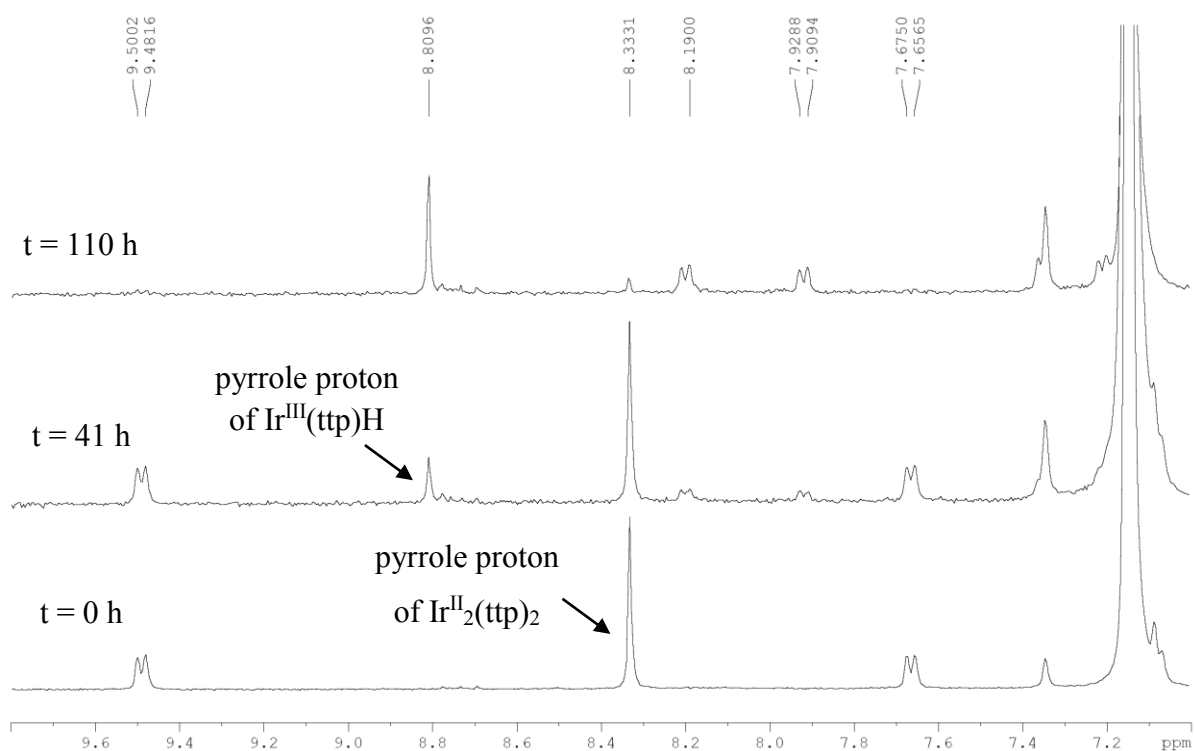
Figure 3.11 Expanded ^{1}H NMR Spectra at Selected Time Intervals from Reaction 3.32.

$$\text{Ir}^{III}\text{(ttp)CH}_2\text{CH}_2\text{OH} \xrightarrow[\text{120 °C, 23 d}]{\text{C}_6\text{D}_6} \text{(H}_2\text{O)Ir}^{III}\text{(ttp)-O-Ir}^{III}\text{(ttp)(H}_2\text{O)} \quad (3.33)$$
$$72\%$$

$$\text{(H}_2\text{O)Ir}^{III}\text{(ttp)-O-Ir}^{III}\text{(ttp)(H}_2\text{O)} \xrightarrow[\text{C}_6\text{D}_6,\ 200\ °\text{C, 10 d}]{\text{KOH (20 equiv)}} \text{Ir}^{III}\text{(ttp)H} \quad (3.34)$$
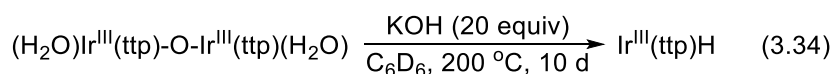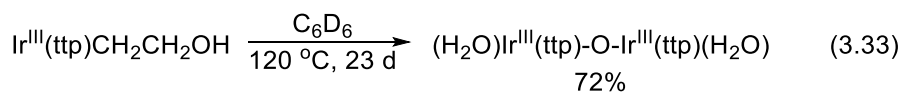
3.6 Proposed Mechanism

Based on the previous understandings of rhodium porphyrin catalyzed hydrogenation of PCP and current findings on the reactivity of iridium porphyrin complexes, Scheme 3.10 illustrates the proposed mechanism for the iridium catalyzed hydrogenation of PCP with H_2O. Using $Ir^{III}(ttp)^iPr$ pre-catalyst as example, the proposed mechanism contains three major steps: (1) pre-catalyst activation; (2) C-C bond activation and (3) hydrogenation.

1. pre-catalyst activation

$2Ir^{III}\text{-}^iPr$ $Ir^{III}\text{-}^iPr$

1a. hydrolysis (slow) $2H_2O$ | -2 ⌢ $-$ ⌿   *1b. β-H elimination (fast)*

$2Ir^{III}\text{-OH}$

$-H_2O_2$

$Ir^{II}_2 \rightleftharpoons 2Ir^{II} \underset{-"H_2"}{\overset{H_2O \;\; -Ir^{III}\text{-OH}}{\rightleftharpoons}} Ir^{III}\text{-H}$

2. C-C bond activation

2. CCA with Ir^{II} metalloradical

3. hydrogenation

3a. bi-molecular reductive elimination (fast)

Ir^{III} Ir^{III} Ir^{III}

7 $\xrightarrow[-Ir^{II}_2]{Ir^{III}\text{-H}}$ **8** $\xrightarrow[-Ir^{II}_2]{Ir^{III}\text{-H}}$ **5**

3b. hydrolysis (slow) $\xrightarrow[-Ir^{III}\text{-OH}]{H_2O}$ $\xrightarrow[-Ir^{III}\text{-OH}]{H_2O}$

$Ir = Ir(ttp)$
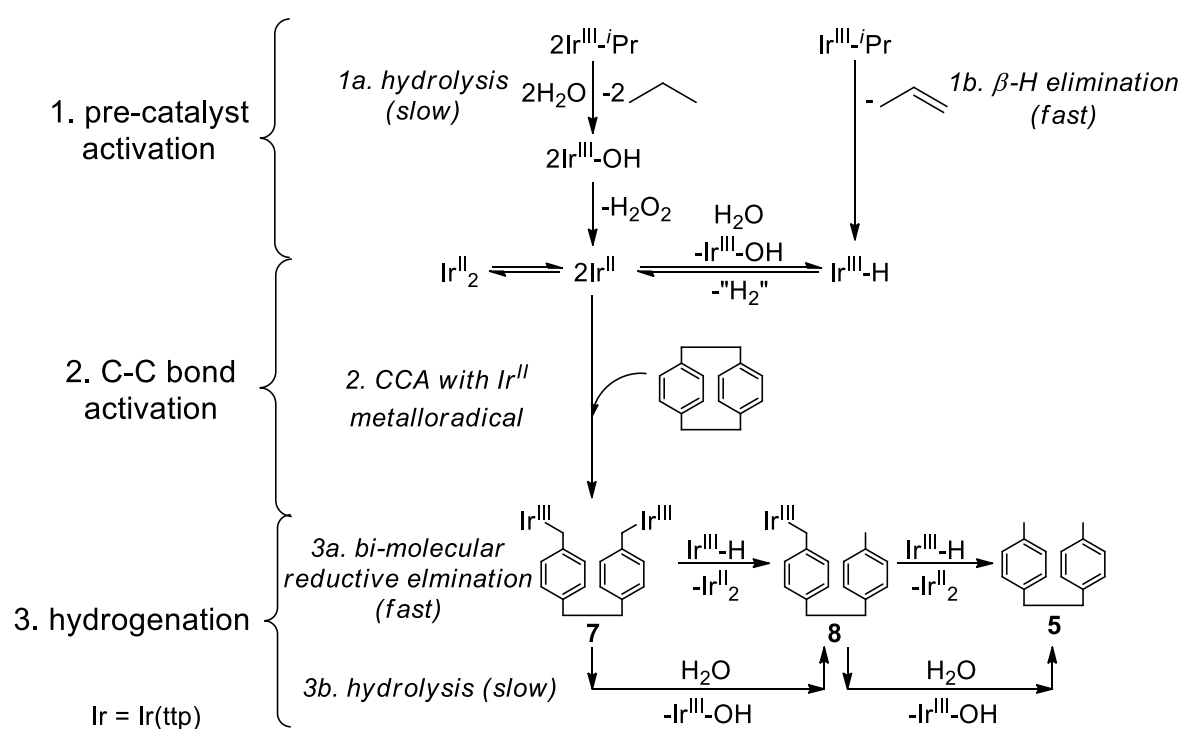
Scheme 3.10 Proposed Mechanism for the Iridium Catalyzed Hydrogenation of PCP with H_2O.

(1) Pre-catalyst activation: $Ir^{III}(ttp)^iPr$ undergoes slow hydrolysis to generate $Ir^{III}(ttp)OH$ and propane (step 1a). In aprotic solvent, the hydroxide ligand in $Ir^{III}(ttp)OH$ acts as an efficient single electron reductant to reduce the Ir(III) metal center to Ir(II), forming $Ir^{II}(ttp)$ and H_2O_2 as co-product. The oxidation potentials of OH⁻ in MeCH and H_2O have been reported to be +0.68 V and +1.65V, respectively (vs SCE).[33] Therefore OH⁻ is more reducing in non-polar C_6D_6 due to the even poorer solvation. The 1st reduction potential of

Ir^{III}(tpp)(CO)Cl in PhCN has been reported to be -1.15 V (vs SCE).[34] This yields the reaction potential of (-1.15) + (+0.68) = -0.47 V (vs SCE) in aprotic solvent (eq 3.35). It is equivalent to ΔG = 10.8 kcal/mol using ΔG = nFE^o relationships (n = 1 and F = 23.0 kcal/mol) and has equilibrium constant K = 1.0 x 10^{-5} at 200 ^{o}C.

$$E^o = -0.47 \text{ V}$$
$$\Delta G = 10.8 \text{ kcal/mol}$$
$$Ir(III) + OH^- \xrightarrow{\ K = 1.0 \times 10^{-5} \ (200\ ^oC)\ } Ir(II) + OH^\cdot \quad (3.35)$$
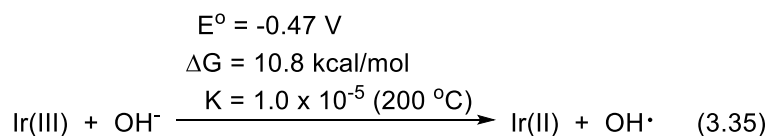
Concurrently, fast β-H elimination of Ir^{III}(ttp)^{i}Pr occurs to give Ir^{III}(ttp)H and propene (step 1b). Ir^{II}(ttp) and Ir^{III}(ttp)H can be interconverted via oxidative addition with H$_2$O or dehydrogenation, respectively.

(2) C-C bond activation: Ir$^{II}_2$(ttp)$_2$ dissociates to give Ir^{II}(ttp) upon heating. The equilibrium constant at 200 ^{o}C is estimated to be 3.8 x 10^{-3} (Scheme 3.11). Ir^{II}(ttp) then cleaves the benzylic carbon-carbon bond of PCP to yield the CCA product **7**.
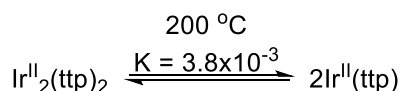
$$200\ ^oC$$
$$Ir^{II}_2(ttp)_2 \xrightleftharpoons{\ K = 3.8 \times 10^{-3}\ } 2Ir^{II}(ttp)$$

ΔG = ΔH - TΔS

ΔH = Ir-Ir BDE in Ir$^{II}_2$(txp)$_2$ = 20 kcal mol^{-1}

assume S = entropy of H$_2$ = 31.2 cal mol^{-1} K^{-1} [25]

ΔG = 20 - (473)(0.0312) = 5.2 kcal mol^{-1}

ΔG = -RTlnK

5.2 = -(1.9872x10^{-3})(473)lnK

K = 3.8x10^{-3}

Scheme 3.11 Equilibrium Constant Estimation for Ir$^{II}_2$(ttp)$_2$ Dissociation.

(3) Hydrogenation: With continuous production of Ir^{III}(ttp)H via the oxidative addition of H$_2$O with Ir^{II}(ttp), the CCA products **7** and **8** undergo fast bi-molecular reductive

elimination with $Ir^{III}(ttp)H$ to yield **5** as the final hydrogenation product (step 3a). The slow hydrolysis of **7** and **8** acts as the minor hydrogenation process.

3.7 Conclusions

We have discovered the fast and high yielding catalytic hydrogenation of PCP with H_2O by iridium porphyrin complexes. $Ir^{II}_2(ttp)_2$ undergoes oxidative addition with H_2O readily to produce $Ir^{III}(ttp)H$ for bi-molecular reductive elimination of alkyl-H with $Ir^{III}(ttp)(alkyl)$, which can furnish concurrent hydrogenation much faster than hydrolysis. This provides a new insight towards designing new catalytic hydrogenation using H_2O with iridium porphyrin system by enhancing the rate of in situ formation of $Ir^{III}(ttp)H$.

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Experimental Section

General Procedures

Unless otherwise specified, all reagents were purchased from commercial suppliers and directly used without further purification. The purity of [2.2]paracyclophane was further tested by melting point (m.p. = 288.6-289.4 $^{\circ}$C, lit. = 285-287.2 $^{\circ}$C).[1] Hexane for chromatography was distilled from anhydrous $CaCl_2$. Benzene-d_6 was distilled from sodium under vacuum, degassed with three freeze-pump-thaw cycles and stored in a Teflon screw head stoppered flask under N_2. Thin layer chromatography was performed on pre-coated silica gel 60 F_{254} plates. Silica gel (Merck, 70-230 mesh) was used for column chromatography under air.

Melting points were recorded on an MPA100 Automated Melting Point System. ^{1}H NMR spectra were recorded on a Bruker AV-400 MHz at 400 MHz. Chemical shifts were referenced internally to the residual solvent proton resonance in C_6D_6 (δ = 7.15 ppm), $CDCl_3$ (δ = 7.26 ppm) or with tetramethylsilane (δ = 0.00 ppm) as the internal standard. Chemical shifts (δ) are reported in parts per million (ppm). Coupling constants (J) are reported in hertz (Hz). High resolution mass spectra (HRMS) were recorded on a Thermofinnigan MAT 95 XL mass spectrometer. Fast atom bombardment was performed with 3-nitrobenzyl alcohol (NBA) as the matrix.

All reactions in 0.5 mL benzene-d_6 were carried out in a flame-sealed NMR tube in vacuum with the reaction mixture degassed with three freeze(77 K)-pump(0.005 mmHg)-thaw(r.t.) cycles, then heated in oven in dark and wrapped with aluminum foil to protect from exposure to room light before ^{1}H NMR measurements. The NMR yields were with benzene residue as the internal standard. Aqueous stock solution of KOH was prepared separately, transferred to the reaction vessel and dried under vacuum at r.t. to obtain anhydrous starting materials. Benzene stock solutions of Ir(ttp)X (X = Me, Bn, ^{i}Pr, H and Ir(ttp)) were prepared separately, transferred to the reaction vessel and dried under vacuum at r.t. to obtain

anhydrous starting materials. Benzene-d_6 stock solution of [2.2]paracyclophane was prepared separately, degassed and stored under N_2 before transferred to the reaction vessel.

[Ir(cod)Cl]$_2$,[2] Ir^{III}(ttp)(CO)Cl,[3] Ir^{III}(ttp)Me,[3b,4] Ir^{III}(ttp)Bn,[5] Ir^{III}(ttp)H[3a,5] and Ir$^{II}_2$(ttp)$_2$[5,6] were prepared according to the literature procedures. Ir^{III}(ttp)SiEt$_3$ and Ir^{III}(ttp)CD$_3$ were borrowed from group members.

Experimental Procedures

Preparation of Ir^{III}(ttp)^{i}Pr. The reductive alkylation of Ir^{III}(ttp)(CO)Cl is described as a typical example for the preparation of Ir^{III}(ttp)-alkyl complexes, adapting the literature procedure.[3b,4] A suspension of Ir^{III}(ttp)(CO)Cl (20 mg, 0.022 mmol) in 2 mL THF in a Teflon screw head stoppered tube and a solution of NaBH$_4$ (8.2 mg, 0.22 mmol) in aqueous NaOH (1 M, 1 mL) in a Schlenk tube were purged with N_2 for 15 min separately. The NaBH$_4$ solution was added slowly to the suspension of Ir^{III}(ttp)(CO)Cl via a cannula. The mixture was heated at 70 °C under N_2 for 2 h to give a brown suspension. The reaction was then cooled to r.t. and 2-iodopropane (4.4 μL, 0.044 mmol) was added under N_2. The reaction mixture was further heated at 70 °C for 2 h to give a reddish brown suspension. It was worked up by extraction with CH$_2$Cl$_2$/H$_2$O. The organic layer was rotary evaporated. The crude solid was purified by column chromatography on silica gel eluting with CH$_2$Cl$_2$/hexane = 1:1. The major red fraction was collected and dried to give reddish purple solid Ir^{III}(ttp)^{i}Pr (13 mg, 0.014 mmol, 65%). R_f = 0.84 (CH$_2$Cl$_2$/hexane = 1:1). ^{1}H NMR (CDCl$_3$, 400 MHz) δ -5.09 (septet, $^3J_{H-H}$ = 6.6 Hz, 1 H), -4.45 (d, $^3J_{H-H}$ = 6.6 Hz, 6 H), 2.68 (s, 12 H), 7.51 (two d overlapped, 8 H), 7.98 (d, $^3J_{H-H}$ = 7.4 Hz, 4 H), 8.03 (d, $^3J_{H-H}$ = 7.4 Hz, 4 H), 8.49 (s, 8 H). ^{1}H NMR (C$_6$D$_6$, 400 MHz) δ -4.74 (h, $^3J_{H-H}$ = 6.6 Hz, 1 H), -4.06 (d, $^3J_{H-H}$ = 6.6 Hz, 6 H), 2.40 (s, 12 H), 7.24 (d, $^3J_{H-H}$ = 7.8 Hz, 4 H), 7.35 (d, $^3J_{H-H}$ = 6.1 Hz, 4 H), 8.03 (dd, $^4J_{H-H}$ = 1.5, $^3J_{H-H}$ = 7.6 Hz, 4 H), 8.18 (dd, $^4J_{H-H}$ = 1.5, $^3J_{H-H}$ = 7.6 Hz, 4 H), 8.75 (s, 8 H). ^{13}C NMR (CDCl$_3$,

100 MHz) δ -3.0, 21.6, 21.7, 124.8, 127.6, 127.7, 131.5, 133.6, 134.0, 137.3, 138.9, 143.7. HRMS calcd. for $(C_{51}H_{43}N_4Ir)^+$: m/z 904.3115. Found: m/z 904.3119.

Catalytic Hydrogenation of [2.2]Paracyclophane with Water by Ir^{III}(ttp)R Pre-Catalyst.

With Ir^{III}(ttp)Me. Ir^{III}(ttp)Me (0.42 mg, 0.00048 mmol), H_2O (8.6 μL, 0.48 mmol) and benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) were added successively to a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 °C in the dark for 53 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. 4,4'-Dimethylbibenzyl **5** was formed in 94% yield.

With Ir^{III}(ttp)Bn. Ir^{III}(ttp)Bn (0.46 mg, 0.00048 mmol), H_2O (8.6 μL, 0.48 mmol) and benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) were added successively to a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 °C in the dark for 48 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. 4,4'-Dimethylbibenzyl **5** was formed in 95% yield.

With Ir^{III}(ttp)^{i}Pr. Ir^{III}(ttp)^{i}Pr (0.43 mg, 0.00048 mmol), H_2O (8.6 μL, 0.48 mmol) and benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) were added successively to a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 °C in the dark for 41 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. 4,4'-Dimethylbibenzyl **5** was formed in 98% yield.

With Ir^{III}(ttp)SiEt$_3$. Ir^{III}(ttp)SiEt$_3$ (0.47 mg, 0.00048 mmol), H_2O (8.6 μL, 0.48 mmol) and benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) were added successively to a NMR tube. The orange mixture was degassed for three freeze-pump-

thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 ℃ in the dark for 48 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. 4,4'-Dimethylbibenzyl **5** was formed in 10% yield. PCP was recovered in 70% yield.

With Ir^{III}(ttp)H. Ir^{III}(ttp)H (0.41 mg, 0.00048 mmol), H_2O (8.6 μL, 0.48 mmol) and benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) were added successively to a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 ℃ in the dark for 35 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. 4,4'-Dimethylbibenzyl **5** was formed in 96% yield.

Ir^{III}(ttp)^{i}Pr Pre-Catalyst Loading.

With 2.5 mol%. Ir^{III}(ttp)^{i}Pr (0.11 mg, 0.00012 mmol) and H_2O (8.6 μL, 0.48 mmol) and benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) were added successively to a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 ℃ in the dark for 76 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. 4,4'-Dimethylbibenzyl **5** was formed in 74% yield. PCP was recovered in 10% yield.

With 5 mol%. Ir^{III}(ttp)^{i}Pr (0.22 mg, 0.00024 mmol) and H_2O (8.6 μL, 0.48 mmol) and benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) were added successively to a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 ℃ in the dark for 58 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. 4,4'-Dimethylbibenzyl **5** was formed in 97% yield.

With 20 mol%. $Ir^{III}(ttp)^iPr$ (0.86 mg, 0.00096 mmol) and H_2O (8.6 μL, 0.48 mmol) and benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) were added successively to a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 ºC in the dark for 33 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. 4,4'-Dimethylbibenzyl **5** was formed in 95% yield.

Water loading Effects.

Without H$_2$O added. $Ir^{III}(ttp)^iPr$ (0.43 mg, 0.00048 mmol) and benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) were added successively to a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. ^{1}H NMR analysis at t = 0 showed that the reaction mixture already contained ~3 equiv of H_2O. It was heated at 200 ºC in the dark for 55 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. 4,4'-Dimethylbibenzyl **5** was formed in 97% yield.

With 2.3 equiv of H$_2$O added. $Ir^{III}(ttp)^iPr$ (0.43 mg, 0.00048 mmol), H_2O (0.2 μL, 0.011 mmol) and benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) were added successively to a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 ºC in the dark for 59 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. 4,4'-Dimethylbibenzyl **5** was formed in 98% yield.

Additive Effects.

With DSS added. $Ir^{III}(ttp)^iPr$ (0.43 mg, 0.00048 mmol), H_2O (0.2 μL, 0.011 mmol), DSS (0.049 mg, 0.11 μmol) and benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0

mg, 0.0048 mmol) were added successively to a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 °C in the dark for 45 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. 4,4'-Dimethylbibenzyl **5** was formed in 97% yield.

With BDHA added. Ir^{III}(ttp)^{i}Pr (0.43 mg, 0.00048 mmol), H_2O (0.2 μL, 0.011 mmol), BDHA (0.25 mg, 0.11 μmol) and benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.62 μmol) were added successively to a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 °C in the dark for 41 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. 4,4'-Dimethylbibenzyl **5** was formed in 86% yield.

With DMF-d_7 solvent. Ir^{III}(ttp)^{i}Pr (0.43 mg, 0.00048 mmol), H_2O (0.2 μL, 0.011 mmol) and DMF-d_7 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) were added successively to a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 °C in the dark for 53 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. 4,4'-Dimethylbibenzyl **5** was formed in 30% yield. PCP was recovered in 51% yield.

Deuterium Labeling Experiments.

Catalytic Deuteration of [2.2]Paracyclophane with Ir^{III}(ttp)^{i}Pr. Ir^{III}(ttp) ^{i}Pr (0.43 mg, 0.00048 mmol), D_2O (8.7 μL, 0.48 mmol) and benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) were added successively to a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was

flame-sealed under vacuum. It was heated at 200 °C in the dark for 47 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. **5**-*d* was formed in 97% yield. Upon breaking the sealed NMR tube, **5**-*d* was isolated by column chromatography on silica gel eluting with hexane. ^{1}H NMR (C$_6$D$_6$, 400 MHz) δ 2.13 (s), 2.78 (s), 6.97 (s, 8 H). The internal benzylic D% = (1-3.596/4) x 100% = 10%. The terminal benzylic D% = (1-3.949/6) x 100% = 34%.

Benzylic H/D Exchange of 4,4'-Dimethylbibenzyl 5. Ir^{III}(ttp) ^{i}Pr (0.43 mg, 0.00048 mmol), D$_2$O (8.7 μL, 0.48 mmol) and benzene-*d$_6$* stock solution (500 μL) of 4,4'-dimethylbibenzyl (1.0 mg, 0.0048 mmol) were added successively to a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 °C in the dark for 48 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. **5'**-*d* was formed in 99% yield. Upon breaking the sealed NMR tube, **5'**-*d* was isolated by column chromatography on silica gel eluting with hexane. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 2.32 (s, 6 H), 2.83-2.86 (m), 7.09 (s, 8 H). The internal benzylic D% = (1-2.869/4) x 100% = 28%. The terminal benzylic D% = (1-6.039/6) x 100% ≈ 0%.

Reaction of Ir^{III}(ttp)(CO)Cl with [2.2]Paracyclophane. Ir^{III}(ttp)(CO)Cl (0.44 mg, 0.00048 mmol), KOH (0.27 mg, 0.0048 mmol), D$_2$O (8.7 μL, 0.48 mmol) and benzene-*d$_6$* stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) were added to a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated in the dark from 60 °C to 150 °C. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. Neither Ir^{III}(ttp)(cyclophanyl) intermediates nor deuterated PCP were observed. After heating at 130 °C for 1 d, CCA of PCP was occurred.

Hydrolysis of Ir^{III}(ttp)R.

Hydrolysis of Ir^{III}(ttp)Me. Ir^{III}(ttp)Me (0.42 mg, 0.00048 mmol) and H$_2$O (8.6 μL, 0.48 mmol) were added to a NMR tube, followed by addition of 500 μL benzene-d_6. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 °C in the dark for 75 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. Ir^{III}(ttp)H was formed in 8 % yield. Ir^{III}(ttp)CH$_3$ was recovered in 81% yield.

Hydrolysis of Ir^{III}(ttp)Bn. Ir^{III}(ttp)Bn (0.46 mg, 0.00048 mmol) and H$_2$O (8.6 μL, 0.48 mmol) were added to a NMR tube, followed by addition of 500 μL benzene-d_6. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 °C in the dark for 43 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. Ir^{III}(ttp)H and toluene were formed in 56% and 72% yields, respectively. Ir^{III}(ttp)Bn was recovered in 3 % yield.

Hydrolysis of Ir^{III}(ttp)^{i}Pr. Ir^{III}(ttp)^{i}Pr (0.43 mg, 0.00048 mmol) and H$_2$O (8.6 μL, 0.48 mmol) were added to a NMR tube, followed by addition of 500 μL benzene-d_6. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 °C in the dark for 44 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. Ir^{III}(ttp)H, propane and propene were formed in 76%, 26% and 68% yields, respectively.


Reaction of Ir^{III}(ttp)CD$_3$ with PCP. Ir^{III}(ttp)CD$_3$ (0.42 mg, 0.00048 mmol) and benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) were added successively to a NMR tube. The orange mixture was degassed for three freeze-pump-thaw

cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 °C in the dark for 11 h. It was monitored with ^{1}H and ^{2}H NMR spectroscopy at particular time intervals.

Initial Stage of Catalysis using Ir^{III}(ttp)^{i}Pr at 170 °C. Ir^{III}(ttp)^{i}Pr (0.43 mg, 0.00048 mmol), H_2O (8.6 μL, 0.48 mmol) and benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) were added successively to a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 170 °C in the dark for 36 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. Di-Ir **7**, mono-Ir **8**, propane and propene were formed in 28%, 31%, 17% and 21% yields, respectively.

Reaction of Ir^{II}$_2$(ttp)$_2$ with [2.2]Paracyclophane. Ir^{II}$_2$(ttp)$_2$ (0.83 mg, 0.00048 mmol) and benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (0.5 mg, 0.0024 mmol) were added to a NMR tube under N$_2$. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated from 30 °C to 150 °C in the dark. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. The CCA product di-Ir **7** was formed in 55% yield.

Reaction of Ir^{III}(ttp)H with [2.2]Paracyclophane. Ir^{III}(ttp)H (0.41 mg, 0.00048 mmol) and benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) were added to a NMR tube under N$_2$. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 150 °C in the dark for 69 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. The CCA products di-Ir **7** and mono-Ir **8** were formed in 50% and 33% yields, respectively.

In a separate experiment with identical conditions except that 1.4 mg Ir^{III}(ttp)H was used, **7** and **8** were isolated by dropper-scale column chromatography on silica gel eluting with DCM/hexane = 1:1 for characterizations.
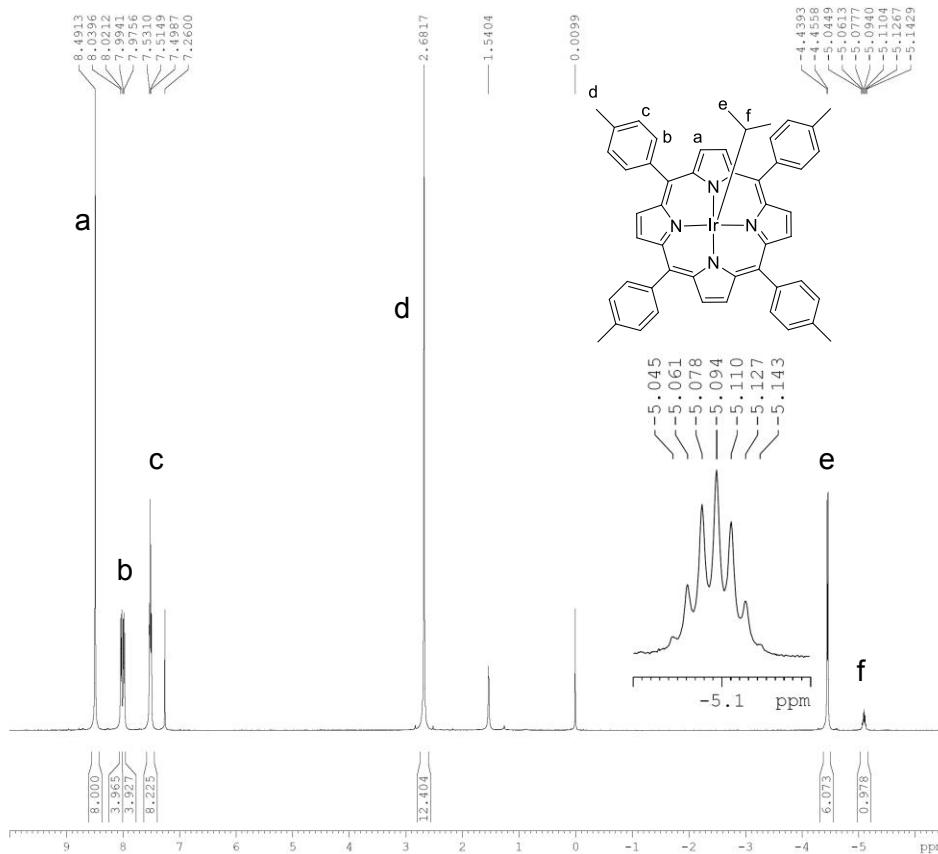
Compound **7**: R_f = 0.71 (CH_2Cl_2/hexane = 1:1). ^1H NMR (C_6D_6, 400 MHz) δ -3.67 (s, 4 H, H_a), 2.03 (s, 4 H, H_b), 2.42 (s, 24 H, H_c), 3.39 (d, $^3J_{H-H}$ = 9.6 Hz, 4 H, H_d), 5.69 (d, $^3J_{H-H}$ = 8.7 Hz, 4 H, H_e), 7.30 (d, $^3J_{H-H}$ = 7.6 Hz, 8 H, H_f), 7.36 (peak overlapped with residual solvent, $H_{f'}$), 8.01 (d, $^3J_{H-H}$ = 7.6 Hz, 8 H, H_g), 8.20 (d, $^3J_{H-H}$ = 8.2 Hz, 8 H, $H_{g'}$), 8.73 (s, 16H, H_h). Attempted $^{13}C\{^1H\}$ NMR measurement for overnight at r.t. resulted in complete decomposition of **7** and no characteristic porphyrin signals could be recorded. The ^1H NMR spectrum of **7** is closely similar to the rhodium analogue reported. HRMS calcd. for ($C_{112}H_{88}N_8Ir_2$+H)$^+$: m/z 1931.6484. Found: m/z 1931.6483.
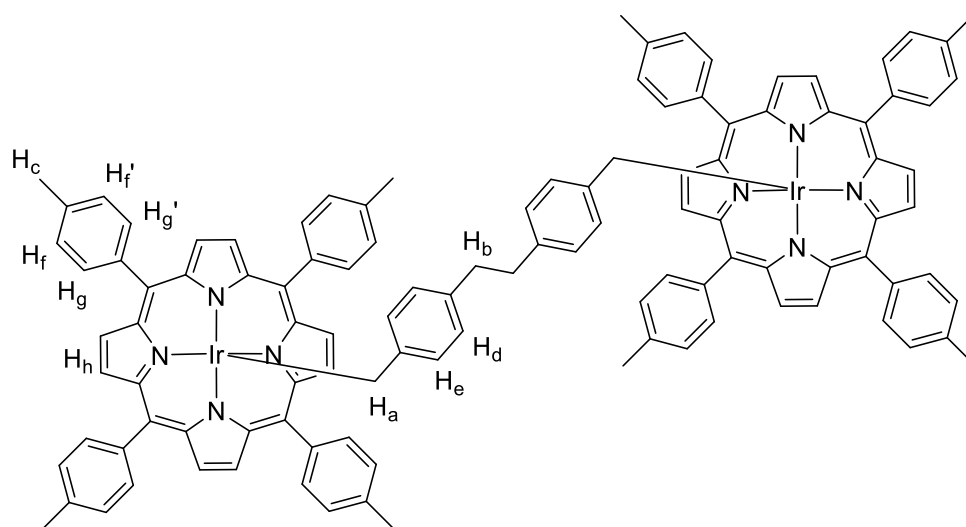
Compound **8**: R_f = 0.80 (CH_2Cl_2/hexane = 1:1). ^1H NMR (C_6D_6, 400 MHz) δ -3.64 (s, 2 H, H_a), 2.10 (s, 3 H, H_b), 2.29 (t, $^3J_{H-H}$ = 8.2 Hz, 2 H, H_c), 2.43 (s, 12 H, H_d), 2.54 (t, $^3J_{H-H}$ = 8.4 Hz, 2 H, H_e), 3.45 (d, $^3J_{H-H}$ = 8.0 Hz, 2 H, H_f), 5.83 (d, $^3J_{H-H}$ = 7.8 Hz, 2 H, H_g), 6.85 (d, $^3J_{H-H}$ = 8.2, 2 H, H_h), 6.92 (d, $^3J_{H-H}$ = 8.0 Hz, 2 H, H_i), 8.07 (d, $^3J_{H-H}$ = 7.8 Hz, 4 H, H_j), 8.20 (d, $^3J_{H-H}$ = 7.7 Hz, 4 H, $H_{j'}$), 8.74 (s, 8H, H_k). There were 8 *meso*-aryl protons masked by the

residual solvent. HRMS calcd. for $(C_{64}H_{53}N_4Ir+H)^+$: m/z 1071.3978. Found: m/z 1071.3990.

Standing of this C_6D_6 solution for overnight at r.t. resulted in complete decomposition of **8**.
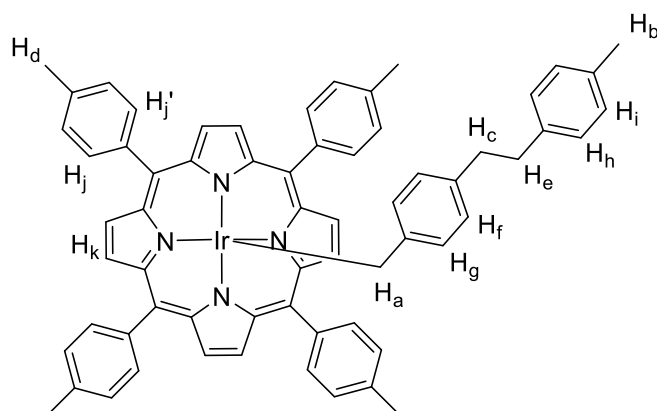
The mini-scale experiment and the close R_f values of **7**, **8** and PCP rendered difficulties in product purifications. Attempted column chromatography still retained some minor impurities and solvent peaks in their ^{1}H NMR spectra.

Reaction of Ir^{III}(ttp)H with [2.2]Paracyclophane with 3 mol% Ir$^{II}_2$(ttp)$_2$. Ir^{III}(ttp)H (0.41 mg, 0.00048 mmol), Ir$^{II}_2$(ttp)$_2$ (0.02 mg, 1.4x10^{-5} mmol) and benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) were added to a NMR tube under N$_2$. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 150 °C in the dark for 98 h. The CCA products di-Ir **7** and mono-Ir **8** were formed in 49% and 39% yields, respectively. Ir^{III}(ttp)H was recovered in 4% yield.

Bi-molecular Reductive Elimination from Ir^{III}(ttp)H and Ir^{III}(ttp)Bn. Ir^{III}(ttp)Bn (0.46 mg, 0.00048 mmol) and Ir^{III}(ttp)H (0.41 mg, 0.00048 mmol) were added to a NMR tube, followed by addition of 500 μL benzene-d_6 under N$_2$. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was

heated at 200 °C in the dark for 43 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. Toluene was formed in 78% yield.

Reaction of Ir$^{II}_2$(ttp)$_2$ with H$_2$O. Ir$^{II}_2$(ttp)$_2$ (0.26 mg, 0.00015 mmol) and H$_2$O (8.6 μL, 0.48 mmol) were added to a NMR tube, followed by addition of 500 μL benzene-d_6 under N$_2$. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated in the dark from 27 °C to 50 °C for 209 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals and the NMR yields were taken. Ir^{III}(ttp)H was formed in 58% yield. Ir$^{II}_2$(ttp)$_2$ was recovered in 8% yield.

Appendix I   List of Spectra

Ir^{III}(ttp)^{i}Pr (CDCl$_3$, 400 MHz)

Ir^{III}(ttp)^{i}Pr (C$_6$D$_6$, 400 MHz)

Ir^III(ttp)^*i*Pr ($^{13}C\{^1H\}$, CDCl$_3$, 100 MHz)

5-*d* (C$_6$D$_6$, 400 MHz)

terminal benzylic D% = 34%
internal benzylic D% = 10%

5-*d'* (CDCl₃, 400 MHz)

terminal benzylic D% = 0%
internal benzylic D% = 28%

Di-Ir 7 (C$_6$D$_6$, 400 MHz)

Mono-Ir 8 (C$_6$D$_6$, 400 MHz)

HRMS Spectra

Ir^{III}(ttp)^{i}Pr (FAB)

D:\MS_raw_data\ksc1304   03/03/14 04:41:21 PM   CTT452
fab pos, 20kV, 4uA, NBA as matrix, unknown conc.

ksc1304 #5   RT: 0.42   AV: 1   NL: 2.57E5
T: + c FAB Full ms [199.50-1500.50]
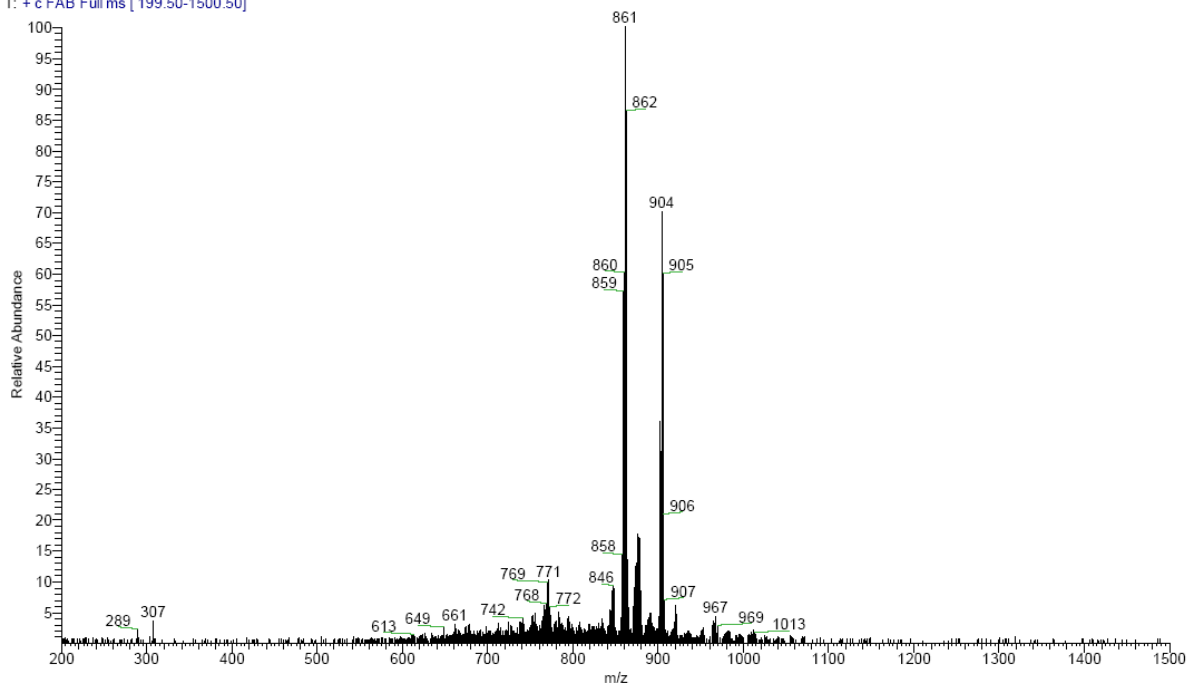
Accurate Mass Measurement
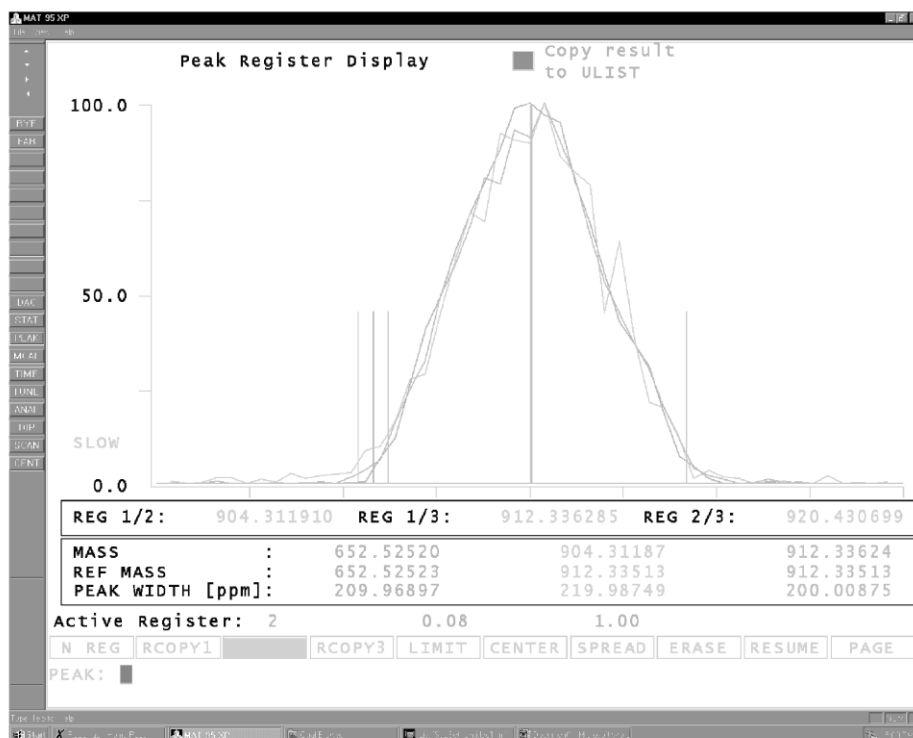
Molecular formula
C$_{51}$H$_{43}$N$_4$Ir
[M]$^+$ (theoretical)
= 904.3115

Di-Ir 7 (FAB)

D:\MS_raw_data\ksc1295_131211170025   12/11/13 05:00:25 PM   CTT442 f2
fab pos, 20kV, 4uA, NBA as matrix, unknown conc.

ksc1295_131211170025 #2-38 RT: 0.16-2.87 AV: 37 SM: 5G NL: 1.45E5
T: + p FAB Full ms [199.50-2400.50]
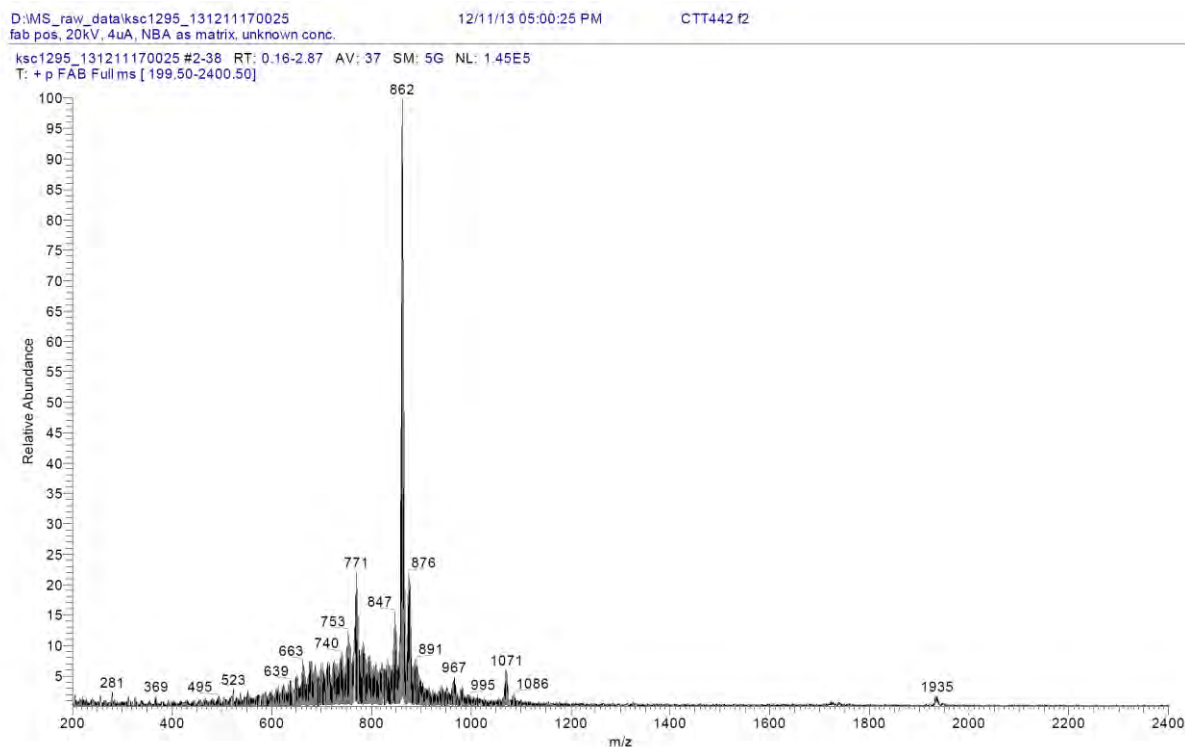
Accurate Mass Measurement
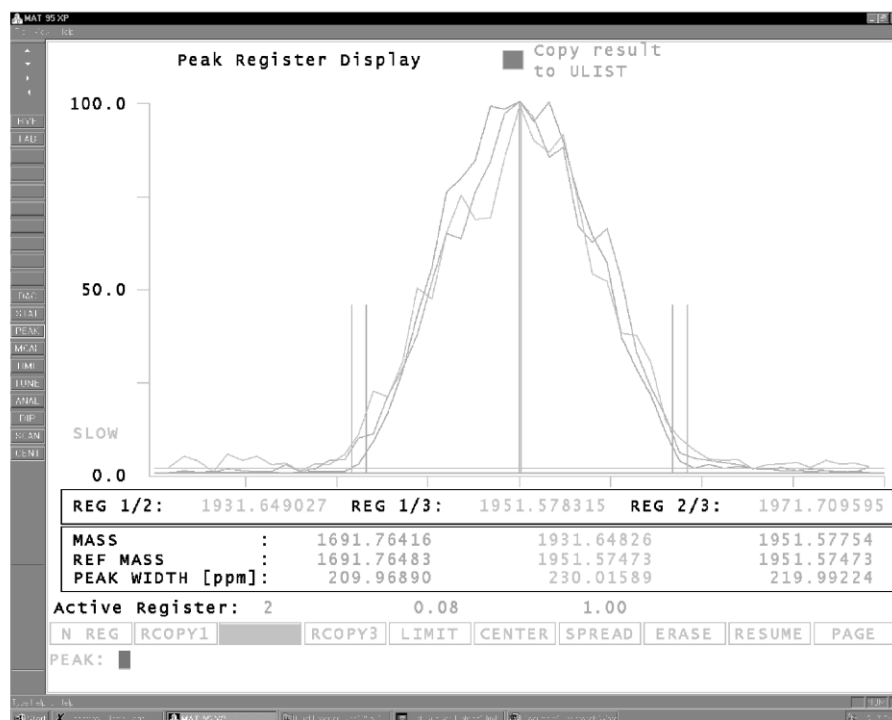
Molecular formula
$C_{112}H_{88}N_8Ir_2$
$[M+H]^+$ (theoretical)
= 1931.6484

Mono-Ir 8 (FAB)

D:\MS_raw_data\ksc1294_131211132850   12/11/13 01:28:50 PM   CTT442 f1
fab pos, 20kV, 4uA, NBA as matrix, unknown conc.
ksc1294_131211132850 #1 RT: 0.12 AV: 1 NL: 4.15E5
T: + c FAB Full ms [199.50-1600.50]
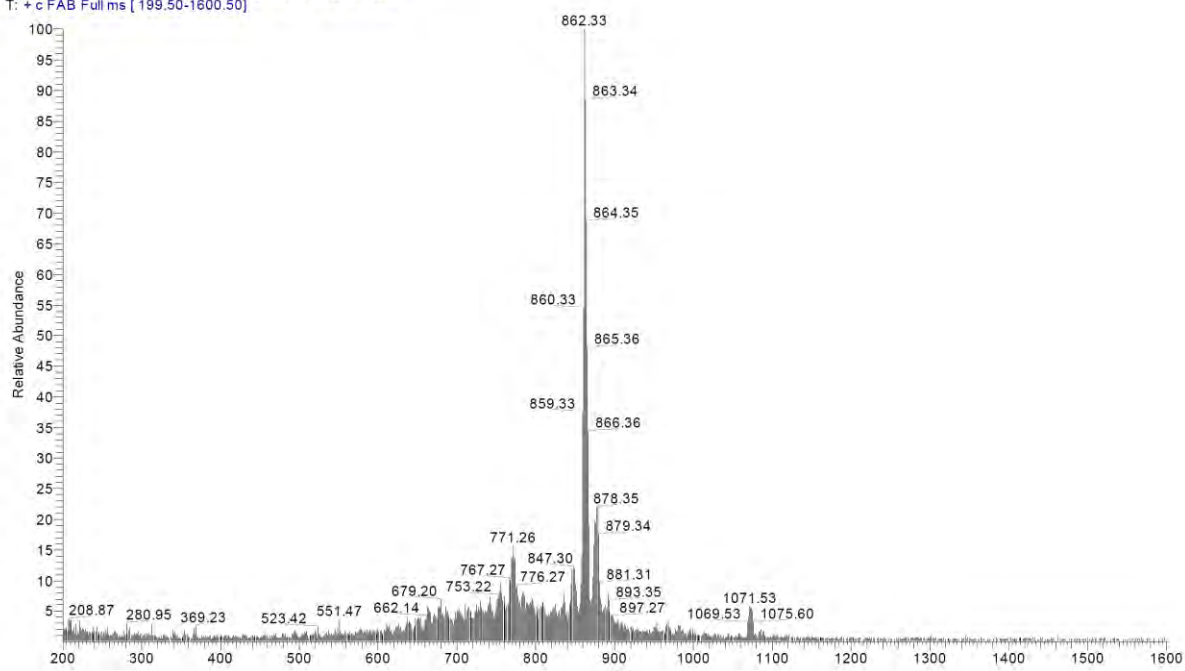
Accurate Mass Measurement
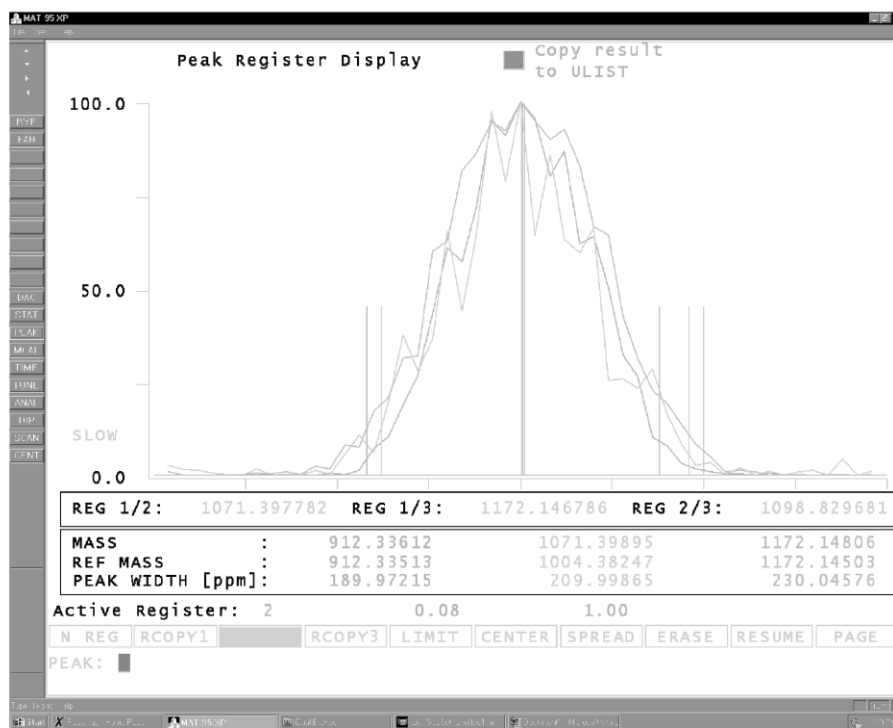
Molecular formula
$C_{64}H_{53}N_4Ir$
$[M+H]^+$ (theoretical)
= 1071.3978

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2. Van der Ent, A.; Onderdelinden, A. L. *Inorg. Synth.* **1973**, *14*, 92-95.

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

5. Cheung, C. W.; Chan, K. S. *Organometallics* **2008**, *27*, 3043-3055.

6. Chan, K. S.; Leung, Y.-B. *Inorg. Chem.* **1994**, *33*, 3187.

Chapter 4   Catalytic Carbon-Carbon Bond Hydrogenation of [2.2]Paracyclophane with Water by Cobalt Porphyrin Complexes

4.1 Introduction

In the rhodium and iridium porphyrin catalyzed hydrogenation of PCP with water, activation of $M^{III}(ttp)R$ pre-catalyst to $M^{II}(ttp)$ for CCA is a prerequisite reaction step. In addition, $M^{II}(ttp)$ is in equilibrium with its dimer $M^{II}_2(ttp)_2$. The use of $M^{III}(ttp)R$ pre-catalyst is beneficial from easy reaction setup, it suffers the drawback of lengthened reaction time. Direct utilization of rhodium(II) or iridium(II) metalloporphyrin radicals as catalyst requires multistep preparation and extra manipulation precautions due to their air-sensitiveness.

Cobalt(II) porphyrin complexes are attractive alternative choices of catalyst. They can be readily accessed by the simple metallation of free base porphyrins. They are air stable and allow easy reaction setup. Previously, the Chan group has successfully utilized the metalloradical character of cobalt(II) porphyrin complexes for stoichiometric and catalytic transformation of aryl C-X bond (X = I and Br).[1] In addition, the economic competitiveness of cobalt compared with rhodium and iridium is of more practical use. In this chapter, the examination of cobalt(II) porphyrin catalyzed hydrogenation of PCP with H_2O is reported.

4.2 Objectives of the Work

We aim to develop a cheap and user-friendly cobalt porphyrin catalyzed C-C σ-bond hydrogenation protocol using H_2O.

4.3 Preparation of Cobalt(II) Porphyrins

$Co^{II}(ttp)$, $Co^{II}(tap)$, $Co^{II}(t_{3,4,5\text{-OMe}}pp)$ and $Co^{II}(t_{4\text{-CF}3}pp)$ were prepared in 92%, 94%, 89% and 90% yields, respectively, by refluxing $Co^{II}(OAc)_2 \cdot 4H_2O$ with the corresponding free base prophyrins in DMF according to the literature method (eq 4.1).[2]

$$H_2(por) + Co^{II}(OAc)_2 \cdot 4H_2O \xrightarrow[\text{DMF}]{\text{reflux, 3-5 h}} Co^{II}(por) \qquad (4.1)$$

$$por = ttp \ \mathbf{1a}, 92\%$$
$$= tap \ \mathbf{1b}, 94\%$$
$$= t_{3,4,5\text{-OMe}}pp \ \mathbf{1c}, 89\%$$
$$= t_{4\text{-CF3}}pp \ \mathbf{1d}, 90\%$$
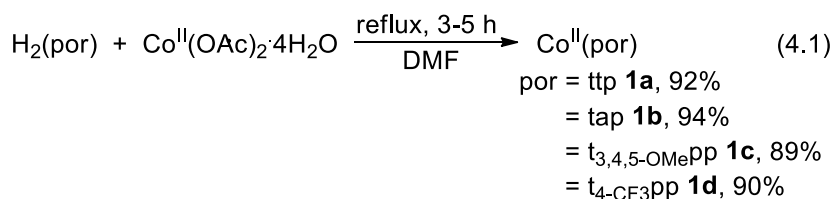
4.4 Discovery of Selective Hydrogenation of PCP in DMF Solvent

Initially, we suspected that $Co^{II}(ttp)$ would be less reactive than $Rh^{II}(ttp)$ and $Ir^{II}(ttp)$ in the CCA of PCP due to the formation of much weaker Co-C bond than Rh-C and Ir-C bonds.[3] Hence, a high loading of $Co^{II}(ttp)$, e.g. 50 mol%, was employed to investigate the catalytic hydrogenation of PCP with H_2O. The first attempt yielded only trace amount of the hydrogenation product **2**, together with a mixture of at least three organic unknowns **a**, **b** and **c** (Table 4.1, eq 4.2, entry 1). Preliminary information from their ^1H NMR spectra suggested that **a** and **b** were PCP ring-opening products due to the downfield shifted aromatic signals (Figure 4.1).[4] The organic unknowns **a** and **b** were unlikely the dimer or trimer of **2** based on their ^1H NMR spectra (see experimental). $Co^{II}(ttp)$ was successfully recovered in 80% yield, supporting its true catalyst nature.

Table 4.1 Catalytic Hydrogenation of PCP with H_2O.
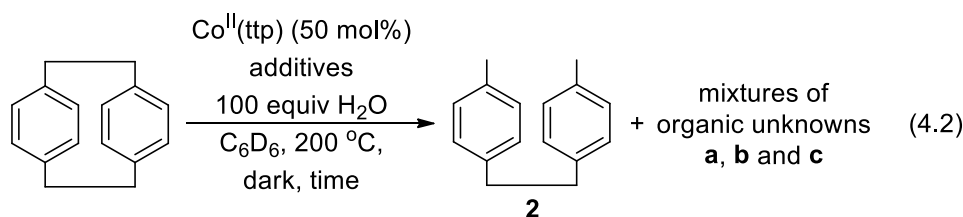
entry	additives	Time / h	Total Organics / %	$Co^{II}(ttp)$ recovery / %	Remarks
1	--	20	45	80	only trace amount of **2**
2	5 mol% PPh$_3$	16	57	95	
3	2 equiv KOH	38	66	85	
4	DMF-d_7 solvent	41	14	0	**2** was formed selectively with trace unknown **b**
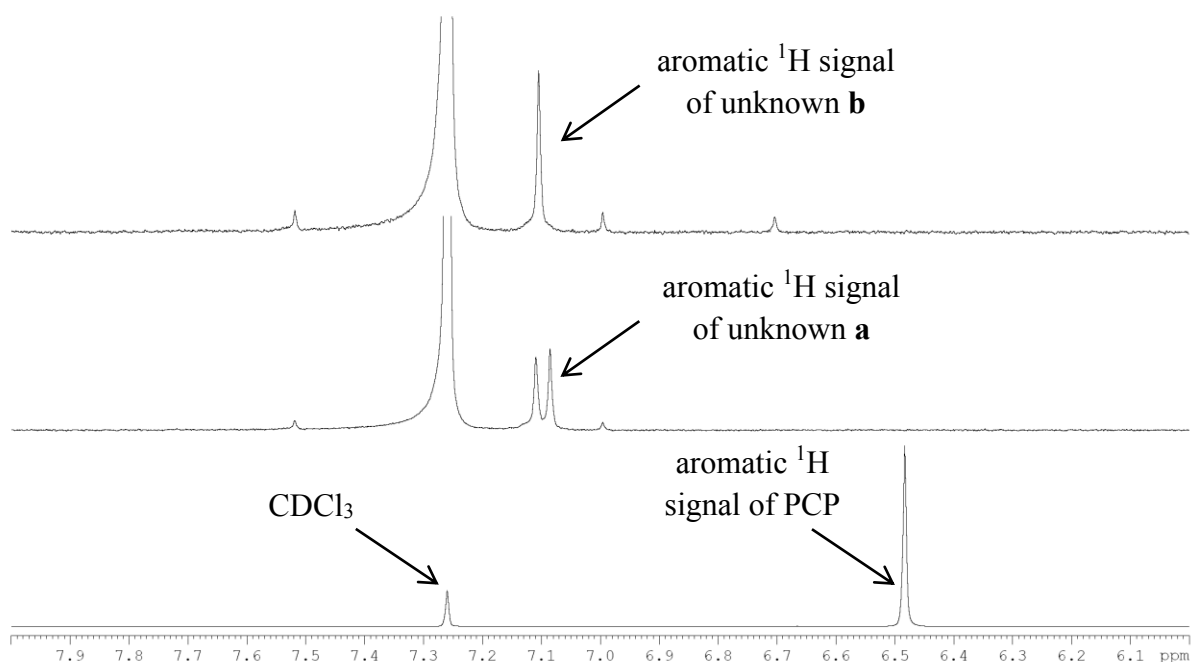
Figure 4.1 Expanded ^{1}H NMR Spectra of PCP, unknown **a** and **b** in CDCl$_3$.

Addition of PPh$_3$ to generate the more electron rich (PPh$_3$)Co^{II}(ttp) in situ was attempted.[5] The coordination of PPh$_3$ also helps stabilize the Co(III) state after the CCA step. However, the same mixture of organic products was still obtained with the addition of 5 mol% of PPh$_3$ (Table 4.1, entry 2, eq 4.2). Owing to the high reaction temperature at 200 °C and low loading of PPh$_3$, the concentration of (PPh$_3$)Co^{II}(ttp) was reasoned to be low in the reaction mixture.[6]

We reasoned that the organic products **a**, **b** and **c** were originated from the homolysis of Co-C bond in the CCA intermediates (Scheme 4.1). The Co-C bond is very weak with BDE reported as 23.8 kcal/mol in (PPh$_3$)Co^{III}(oep)-Bn.[7] Kinetic measurements by Halpern revealed fast homolysis rate constant $k_{obs} = 5.2 \times 10^4$ s^{-1} at 70.4 °C (eq 4.3).
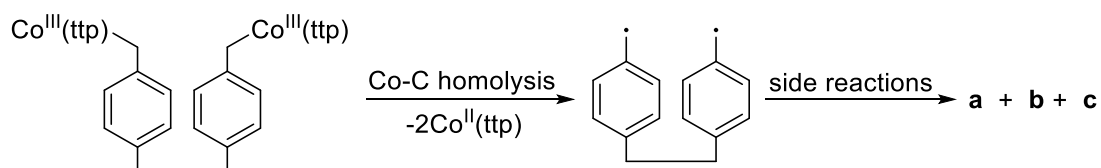
Scheme 4.1 Decomposition of CCA Intermediates.

$$(PPh_3)Co^{III}(oep)\text{-}CH_2Ph \xrightarrow[\text{toluene, 70.4 °C}]{k_{obs} = 5.2 \times 10^4 \text{ s}^{-1}} (PPh_3)Co^{II}(oep) + Ph\overset{\bullet}{C}H_2 \quad (4.3)$$
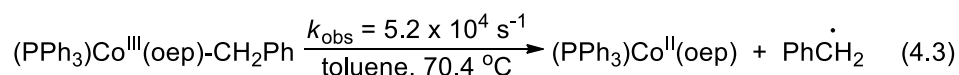
Thus, 2 equiv of KOH was added to promote the hydrolysis. However, the hydrogenation product **2** was not formed selectively with added KOH (Table 4.1, eq 4.2, entry 3). Moreover, the reaction time became longer. The addition of KOH might have promoted the ligand induced disproportionation of $Co^{II}(ttp)$ to give $Co^{I}(ttp)^-$ and $Co^{III}(ttp)OH$ (eq 4.4). This significantly reduced the concentration of $Co^{II}(ttp)$ for CCA of PCP. Analogous disproportionation of macrocyclic cobalt(II) tetra(neopentoxy)phthalocyanine, $Co^{II}(Pc)$, in the presence of OH^- to give 1:1 mixture of $[Co^{III}(Pc)(OH)_2]^-$ and $Co^{I}(Pc)^-$ has been reported (eq 4.5).[8]

$$2Co^{II}(ttp) + OH^- \longrightarrow Co^{III}(ttp)OH + Co^{I}(ttp)^- \quad (4.4)$$

$$2Co^{II}(Pc) + 2OH^- \xrightarrow[\text{instant}]{C_6H_4Cl_2, N_2} [Co^{III}(Pc)(OH)_2]^- + Co^{I}(Pc)^- \quad (4.5)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad 1 \quad : \quad 1$$

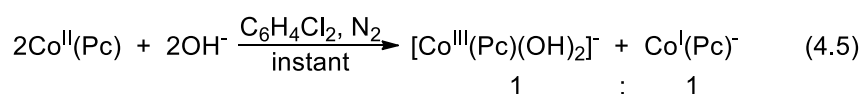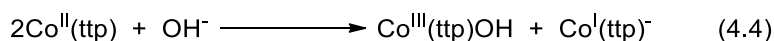Finally, we employed DMF-d_7 polar solvent to facilitate the hydrolysis. To our delight, PCP was catalytically hydrogenated to yield **2** selectively in 14% yield (Table 4.1, eq 4.2, entry 4). $Co^{II}(ttp)$ could not be recovered after the catalysis. Although the reaction yield was low, it led to a correct direction to further optimize the cobalt(II) porphyrin catalyzed hydrogenation of PCP with H_2O. In order to minimize the cost of DMF-d_7 for further investigations, DMF was employed as the solvent and the reactions were monitored by TLC analysis.

4.5 Optimization of Catalytic Hydrogenation of PCP with H$_2$O

4.5.1 Porphyrin Ligand Electronic Effects

We then examined the porphyrin ligand electronic effects. $Co^{II}(ttp)$ and more electron rich $Co^{II}(tap)$ catalysts performed similarly to give 29% and 28% yields of **2** selectively in 32

h (Table 4.2, eq 4.6, entries 1 and 2). $Co^{II}(t_{4\text{-}CF3}pp)$ dissolved poorly in DMF at r.t. and resulted

in a longer reaction time (Table 4.2, eq 4.6, entry 3). Hence, no significant porphyrin electronic

effects were observed and $Co^{II}(ttp)$ was the most cost-effective catalyst.

Table 4.2 Porphyrin Ligand Electronic Effects.
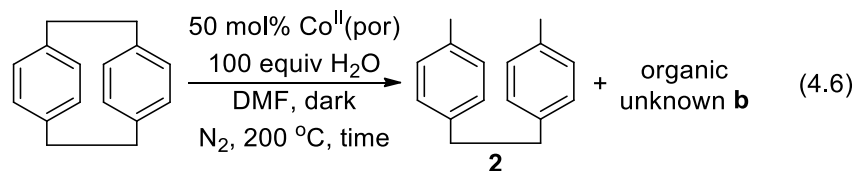
| entry | por | Time / h | GC yield / % | | | | $Co^{II}(por)$ recovery / % |
			2	unknown b^a	PCP recovery	total	
1	ttp	32	29	2	1	32	0
2	tap	32	28	2	< 1	30	0
3	$t_{4\text{-}CF3}pp$	48	35	1	0	36	0

^{a} estimated from the ^1H NMR of crude reaction mixture

4.5.2 Solvent Effects

In view of the importance of DMF for achieving selective catalytic hydrogenation of

PCP with H_2O, we investigated the potential of using other polar solvents, e.g. CH_3CN and *N*-

methyl-2-pyrrolidone (NMP), to see whether the polar solvent effect was general. Due to the

poor solubility of $Co^{II}(ttp)$ in CH_3CN and NMP at r.t., $Co^{II}(t_{3,4,5\text{-}OMe}pp)$ and $Co^{II}(tap)$ were

utilized in CH_3CN and NMP solvents, respectively, to ensure complete solubility with the

assumption of insignificant porphyrin ligand electronic effects based on previous results.[9]

The catalytic hydrogenation of PCP carried out in CH_3CN and NMP yielded only less

than 10% of **2**, even though the corresponding $Co^{II}(por)$ catalysts could be recovered (Table

4.3, entries 2 and 3, eq 4.7). The dielectric constants of DMF, CH_3CN and NMP are 38.3, 36.6

and 32.6, respectively, suggesting that they are similarly polar.[10] Hence, the role of DMF was

likely unique.

Table 4.3 Solvent Effects.

$$\text{50 mol\% Co}^{II}\text{(por)}, \text{100 equiv H}_2\text{O}, \text{solvent, dark, N}_2, 200\ ^\circ\text{C, time} \qquad (4.7)$$
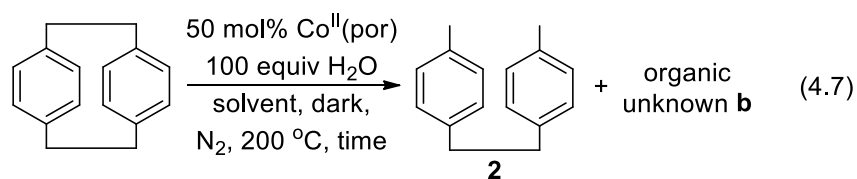
entry	por	solvent	Time / h	GC yield / %				Co^{II}(por) recovery / %
				2	unknown **b**[a]	PCP recovery	total	
1	ttp	DMF	32	29	2	1	32	0
2	t$_{3,4,5\text{-OMe}}$pp	CH$_3$CN	60	trace	5	34	39	71
3	tap	NMP	48	7	0	1	8	91

[a] estimated from the ^{1}H NMR of crude reaction mixture

4.5.3 Catalyst Loading Effects

The Co^{II}(ttp) catalyst loading effects were then examined. In general, the yields of hydrogenation product **2** increased with decreasing Co^{II}(ttp) loadings with the compromise of longer reaction times (Table 4.4, eq 4.8). At 10 mol% of Co^{II}(ttp) loading, a good mass balance of the reactants and products was observed (Table 4.4, eq 4.8, entry 1). On the contrary, employing 2 equiv of Co^{II}(ttp) led to almost complete decomposition of the organic compounds (Table 4.4, eq 4.8, entry 6). In addition, 41% total yield of Co^{II}(ttp) and suspected (DMF)Co^{II}(ttp) were recovered (Figure 4.2). Hence, the decomposition of Co^{II}(ttp) catalyst and the organic compounds was very likely in a stoichiometric relationships. The reactions carried out in air resulted in slightly lower yield of **2** (Table 4.4, entries 2 vs 3, eq 4.8).

Table 4.4 Co^{II}(ttp) Catalyst Loading Effects.

$$\text{(4.8)}$$
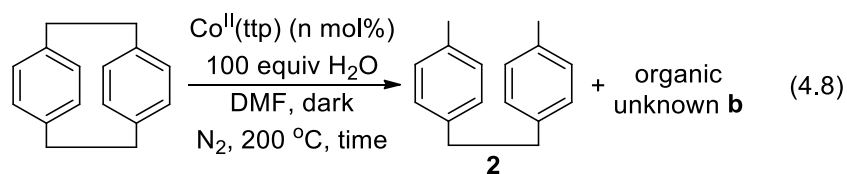
entry	Co^{II}(ttp) mol%	time	GC yield / %				Co^{II}(ttp) recovery / %
			2	unknown **b**[a]	PCP recovery	total	
1	10	4 d	38	0	34	72	0
2	20	3 d	44	1	5	50	0
3[b]	20	2 d	31	1	2	34	0
4	50	32 h	29	2	1	32	0
5	100	19 h	13	1	< 1	14	0
6	200	19 h	3	N/A[c]	1	4	41[d]

[a] estimated from the ^{1}H NMR of crude reaction mixture

[b] in air

[c] unable to determine because of messy crude ^{1}H NMR spectrum

[d] total yield of Co^{II}(ttp) and suspected (DMF)Co^{II}(ttp)
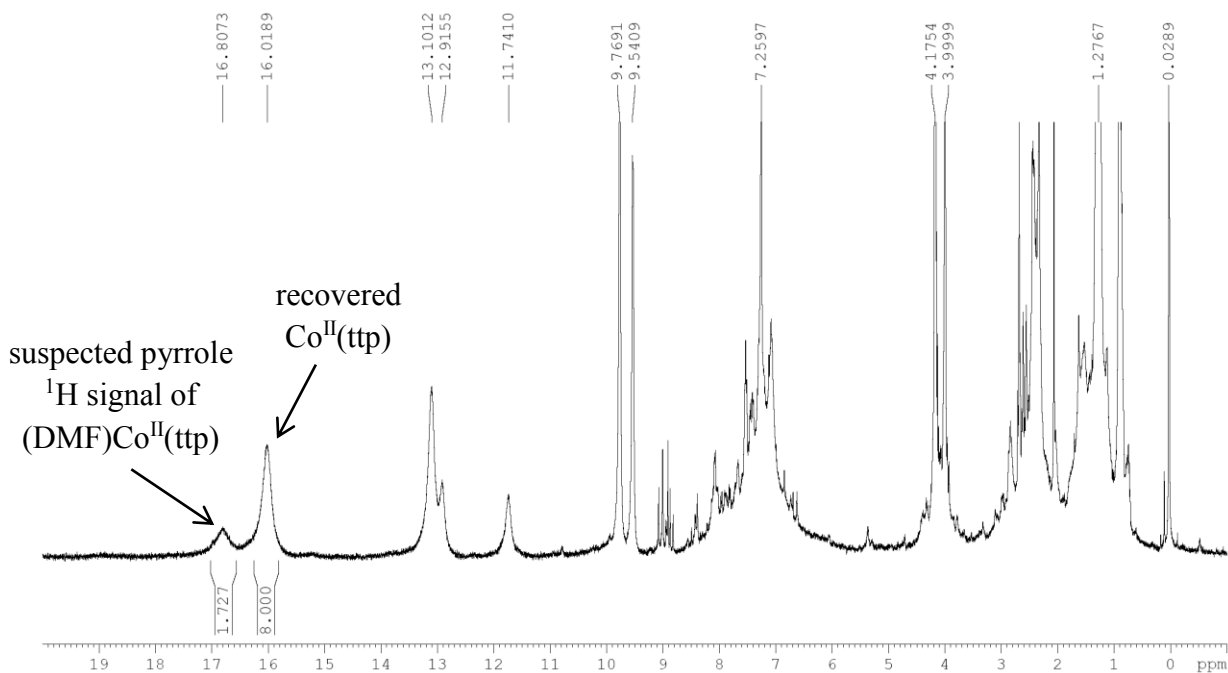

Figure 4.2 Suspected (DMF)Co^{II}(ttp) with Pyrrole ^{1}H Signal at δ = 16.81 ppm in CDCl$_3$.

4.5.4 Temperature Effects

In order to minimize the excessive decompositions, the catalysis carried out at milder reaction temperatures was attempted. In addition, the loading of Co^{II}(ttp) catalyst was reduced to 20 mol%. At 150 °C, only trace amount of **2** was yielded with PCP recovered in 50% yield (Table 4.5, eq 4.9, entry 1). Moreover, an unknown Co^{III}(ttp)R or (DMF)Co^{III}(ttp)R were observed from the ^{1}H NMR spectrum of crude reaction mixture with characteristic pyrrole ^{1}H signal at δ = 9.11 ppm and upfield ^{1}H signals at δ = -2.43, -3.84 and -6.79 ppm (Figure 4.3). It decomposed to intractable unknowns after purification by column chromatography in dark.

Catalytic hydrogenation of PCP carried out at 170 °C and 180 °C was very slow and yielded only 10% and 33% of **2**, respectively (Table 4.5, eq 4.9, entries 2 and 3). Therefore, milder reaction temperature was insufficient for the catalytic hydrogenation of PCP to occur.

Table 4.5 Temperature Effects.
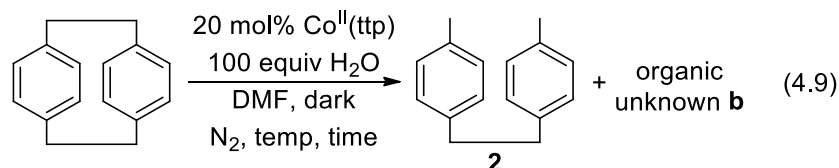
| entry | temp / °C | time / d | GC yield / % | | | | Co^{II}(ttp) recovery / % |
			2	unknown **b**[a]	PCP recovery	total	
1	150	2	trace	0	50	50	93[b]
2	170	4	10	trace	24	34	0
3	180	5	33	1	6	40	0
4	200	3	44	1	5	50	0

[a] estimated from the ^{1}H NMR of crude reaction mixture
[b] together with decomposed unknowns
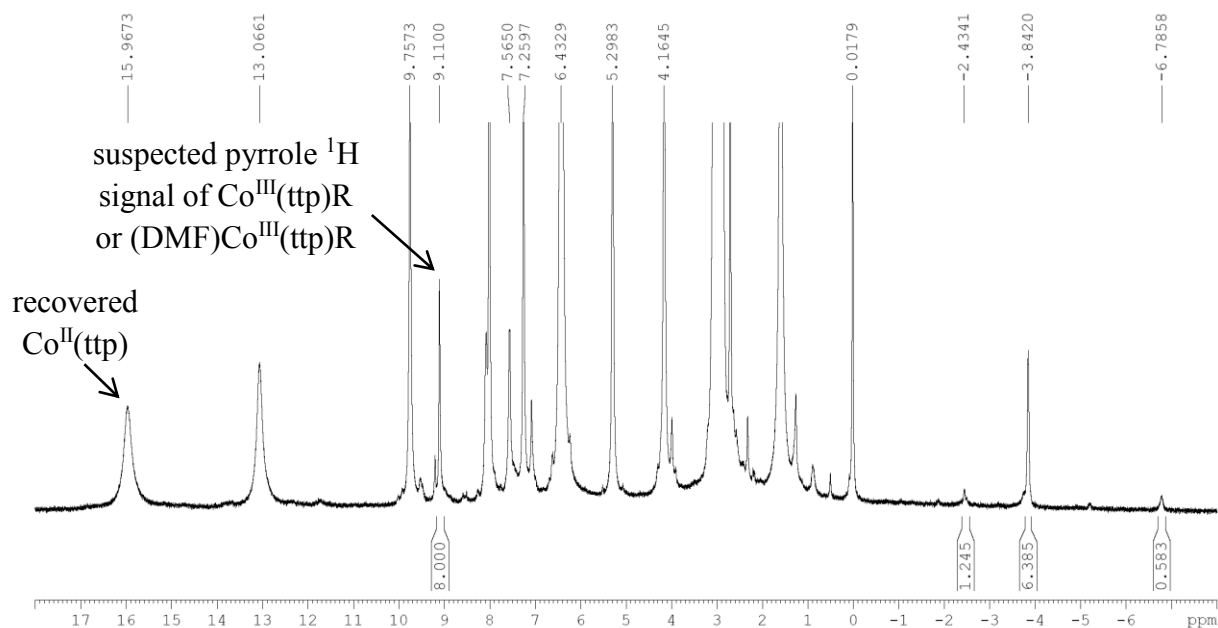
Figure 4.3 Suspected Co^{III}(ttp)R or (DMF)Co^{III}(ttp)R Formation.

4.5.5 Improved Catalytic Hydrogenation of PCP at Higher Temperatures

From the results obtained in previous sections, two critical parameters were essential to the cobalt(II) porphyrin catalyzed hydrogenation of PCP: (1) low Co^{II}(ttp) catalyst loading to achieve good mass balance; and (2) high temperature to give enough driving force. Therefore, we attempted to further increase the reaction temperature and to reduce the loading of Co^{II}(por) catalyst to 10 mol% to avoid any accelerated decomposition at the same time.

To our delight, PCP was successfully hydrogenated at 220 ºC and 240 ºC to yield 86% and 97% of **2** in 20 h, respectively (Table 4.6, eq. 4.10, entries 2 and 3). A longer reaction time at 240 ºC led to decreased yield of **2** by about 10% (Table 4.6, eq 4.10, entry 4), suggesting that the decomposition of the organic compounds at high temperature. Re-examining the porphyrin ligand electronic effects revealed that both electron rich Co^{II}(tap) and electron poor Co^{II}(t$_{4-CF3}$pp) were poorer catalysts than Co^{II}(ttp) (Table 4.6, entries 5 and 6, eq 4.10).

Table 4.6 Improved Catalytic Hydrogenation of PCP at Higher Temperatures.

$$(4.10)$$
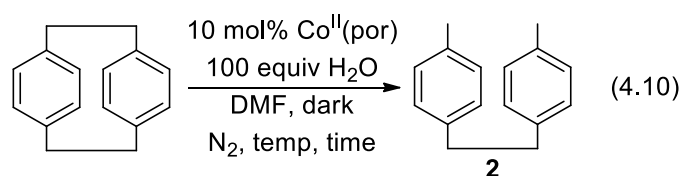
entry	por	temp / °C	time / h	GC yield / %			Co^{II}(por) recovery / %
				2	PCP recovery	total	
1	ttp	200	72	44	5	50	0
2	ttp	220	20	86	3	89	0
3	ttp	240	20	97	1	98	0
4	ttp	240	48	84	0	84	0
5	tap	240	20	83	< 1	83	0
6	t_{4-CF3}pp	240	20	72	0	72	0

Control experiment at 240 °C showed that PCP was decomposed extensively and yielded 10% of the hydrogenation product **2** (eq 4.11). Homolysis of the weak benzylic carbon-carbon bond of PCP probably took place at 240 °C to form the bi-radical intermediate (Scheme 4.2). It then abstract hydrogen atoms, likely from the aldehydic hydrogen of DMF to form **2**. This process is thermodynamically favorable because the BDE of aldehydic C-H bond in DMF is 81.7 kcal/mol, while that of benzylic C-H bond in toluene is 89.7 kcal/mol. The fate of amino acyl radical is unclear. Fast decarbonylation of this radical is a possible decomposition pathway.[11]

$$(4.11)$$
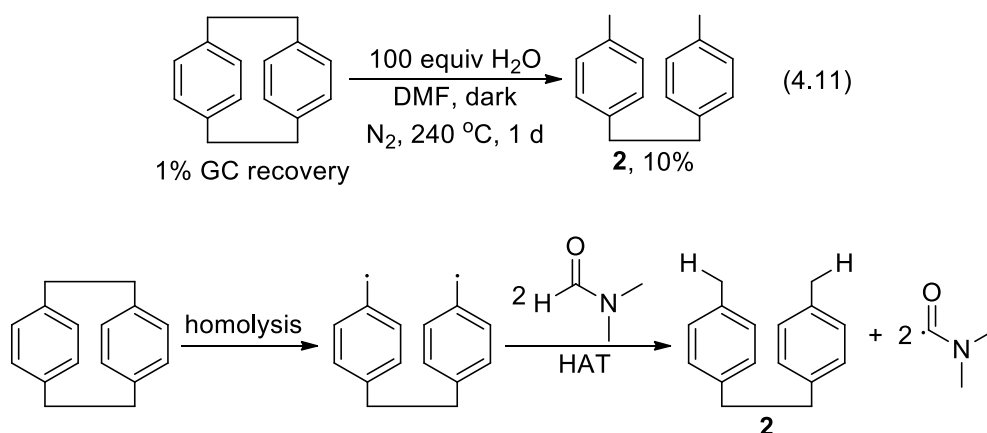
Scheme 4.2 Proposed Decomposition of PCP to **2** in DMF.

Fortunately, PCP was stable when heated with H_2O in DMF at 220 °C for 1 d (eq 4.12).

Formation of the hydrogenation product **2** was not observed.

$$\text{98\% isolated recovery} \xrightarrow[\substack{\text{DMF, dark} \\ N_2,\ 220\ ^{\circ}C,\ 1\ d}]{100\ \text{equiv}\ H_2O} \text{2 not observed} \qquad (4.12)$$
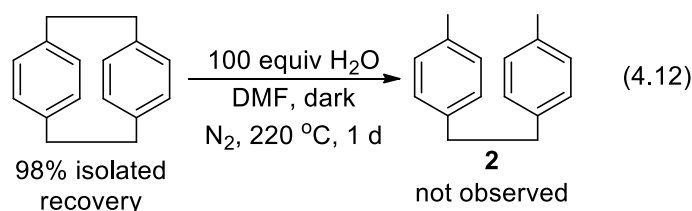
4.6 Mechanistic Investigations

4.6.1 Pre-coordination of DMF to Co^{II}(ttp)

The binding constant of DMF to cobalt(II) protoporphyrin IX dimethyl ester (CoP) at 23 °C in toluene has been reported to be 15.1 M^{-1} (eq 4.13).[12]

$$K = 15.1\ M^{-1}$$
$$\Delta H = -7.9\ \text{kcal mol}^{-1}$$
$$\Delta S = -21\ \text{cal mol}^{-1}\ K^{-1}$$

$$Co^{II}P\ +\ DMF\ \underset{\text{toluene, 23 }^{\circ}C}{\xrightleftharpoons{\hspace{2cm}}}\ (DMF)Co^{II}P \qquad (4.13)$$
$$5\ \mu M \quad 200\ \text{equiv}$$
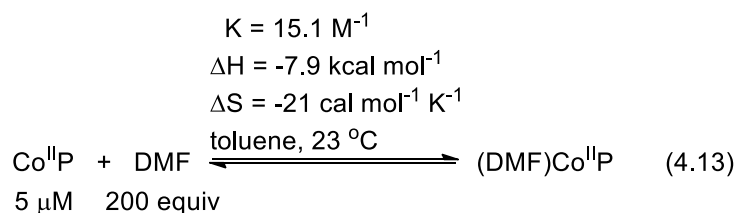
The corresponding binding free energy at 220 °C is estimated to be 2.5 kcal/mol and a weak binding constant of 0.082 M^{-1}. Assume the affinity of DMF towards Co^{II}P is similar to Co^{II}(ttp), the relative ratio of Co^{II}(ttp) and (DMF)Co^{II}(ttp) at 220 °C is only 1:1 for 10 mol% loading of Co^{II}(ttp) even though DMF is employed as the solvent. Therefore, both Co^{II}(ttp) and (DMF)Co^{II}(ttp) are likely the active catalysts in the hydrogenation of PCP.

4.6.2 Stability Test of Co^{II}(ttp) with H_2O in DMF

In view of the excessive Co^{II}(ttp) decomposition observed in most reactions examined, independent experiments were performed to investigate the stability of Co^{II}(ttp) with H_2O in DMF at elevated temperature. Co^{II}(ttp) was decomposed completely into brownish black

unknown solids at 200 °C in 2 d, regardless of N$_2$ or air atmosphere (Table 4.7, eq 4.14). The

unknowns did not give characterizable signals in ^{1}H NMR analysis. Alternatively, the unknown

products obtained from N$_2$ conditions were dissolved in CH$_2$Cl$_2$ for UV-Vis spectroscopic

analysis. The Soret band at 409 nm was almost disappeared, supporting the decomposition of

Co^{II}(ttp) (Figure 4.4). A new absorption peak at 509 nm was observed. However these data

were insufficient to suggest structural assignment for the unknowns.

Table 4.7 Stability Test of Co^{II}(ttp) with H$_2$O in DMF.

$$Co^{II}(ttp) \xrightarrow[\text{dark, 2 d}]{\substack{\text{500 equiv H}_2\text{O} \\ \text{DMF, 200 °C}}} \text{unknowns} \qquad (4.14)$$
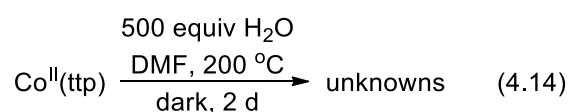
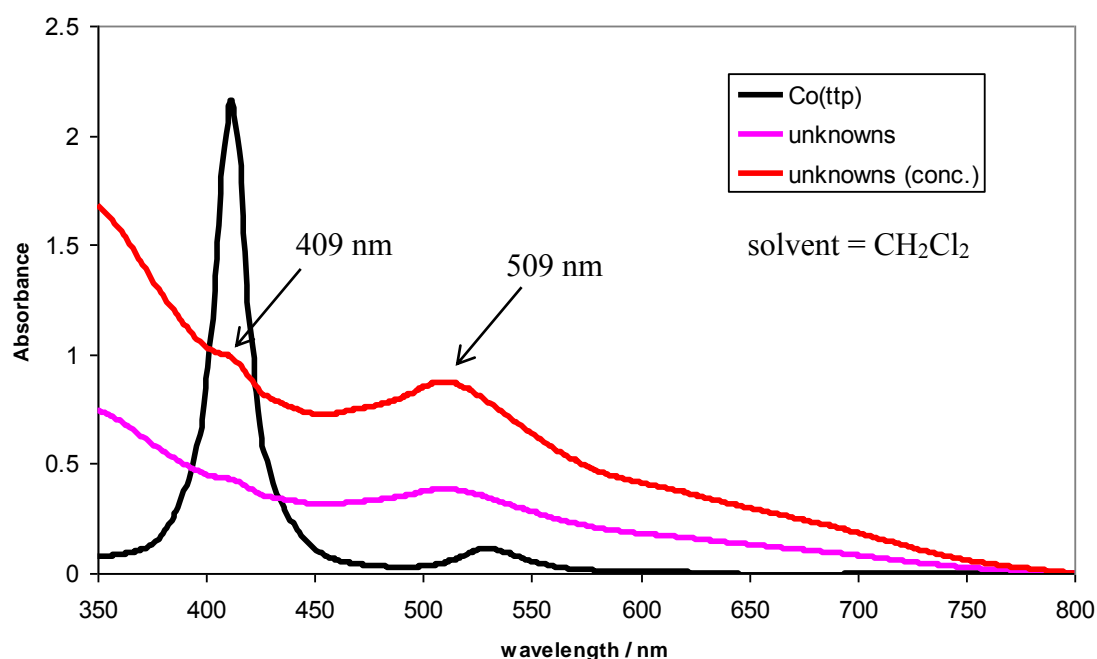| entry	conditions	Co(ttp) recovery / %
1	Air	0
2	N$_2$	0

Figure 4.4 Comparison of UV-Vis Spectra of Co^{II}(ttp) and Unknowns.

The oxidative addition of H$_2$O with Co^{II}(ttp) to give Co^{III}(ttp)H and Co^{III}(ttp)OH in

polar DMF may proceed much faster than in non-polar benzene. Coordination of DMF can

stabilize the high valent Co(III) state. The oxidative addition of H$_2$O with Co^{II}(CN)$_5$$^{3-}$ occurs

readily at 25 °C in aqueous medium.[13] Dehydrogenation of $Co^{III}(ttp)H$ produces H_2 and regenerates $Co^{II}(ttp)$.[14] $Co^{III}(ttp)OH$ is quickly reduced by the OH^- ligand to gives back $Co^{II}(ttp)$ and produce H_2O_2, which subsequently oxidizes $Co^{II}(ttp)$. The oxidation of other cobalt(II) tetradentate-N_4 macrocycle by H_2O_2 has been suggested to occur by the $OH\cdot$ attack at the imine nitrogen.[15]

4.7 Proposed Mechanism

At this stage we lacked in-depth investigations on the cobalt(II) porphyrin catalyzed hydrogenation of PCP with H_2O. Based on the previous understanding on the rhodium and iridium porphyrin catalyzed protocols, a preliminary catalytic cycle is proposed for the cobalt system (Scheme 4.3). $Co^{II}(ttp)$ first undergoes CCA with PCP to give the di-Co intermediate **3**, though not observed (step i). In polar DMF solvent, hydrolysis of **3** takes place readily to yield **2** and $Co^{III}(ttp)OH$ (step ii). $Co^{III}(ttp)OH$ is rapidly reduced to regenerate $Co^{II}(ttp)$ and give H_2O_2. At the same time, $Co^{II}(ttp)$ reacts quickly with H_2O to produce $Co^{III}(ttp)OH$ and $Co^{III}(ttp)H$, facilitated by the DMF solvent (step iv). Dehydrogenation of $Co^{III}(ttp)H$ affords $Co^{II}(ttp)$ and H_2. Finally, rapid production of H_2O_2 induces the decomposition of $Co^{II}(ttp)$.
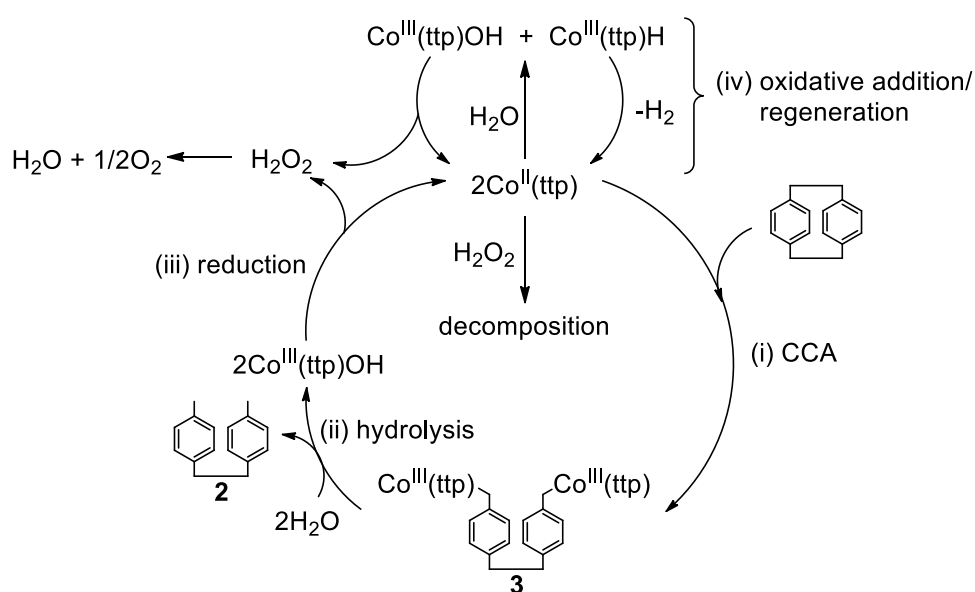
Scheme 4.3 Proposed Catalytic Cycle.

4.8 Co^{II}(ttp) Catalyzed Carbon-Carbon Bond Hydration in DMSO

As an extended study from the solvent effects, attempted catalytic hydrogenation of PCP in DMSO solvent gave unexpected results. When PCP was heated with 20 mol% of Co^{II}(ttp) and 100 equiv of H_2O at 200 °C in DMSO, **2** was formed in only 3% yield (eq 4.15). In addition, an oxygen incorporated product **4** was formed in 16% yield. ^1H NMR analysis of the isolated product suggested an aldehyde functionality. Further experiments are needed to investigate whether H_2O or DMSO act as the oxygen source and Co^{III}(ttp)OH is involved to cleave the benzylic carbon-carbon bond of PCP.
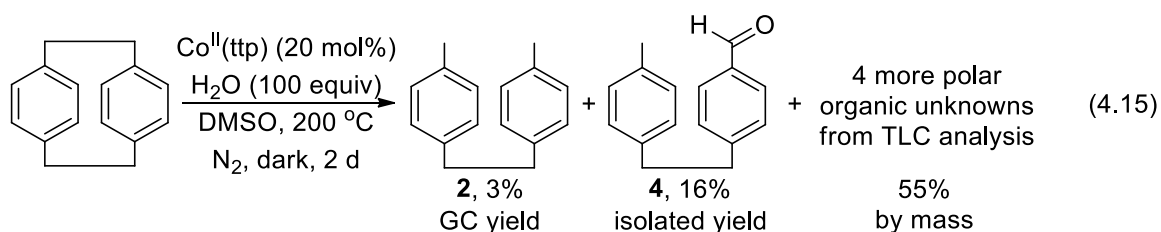
Control experiment was carried out to investigate whether the benzylic C-H bond of **2** could be oxidized in the reaction conditions. Conversion of **2** to **4** was not observed with 88% recovery yield of **2** (eq 4.16).
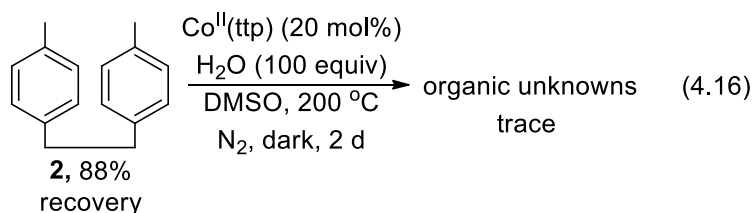
4.9 Conclusions

The economical Co^{II}(ttp) catalyst shows its promising ability in the catalytic hydrogenation of PCP. Deuterium labeling experiments using D_2O are needed to examine whether H_2O is acting as the hydrogen source. In addition, carbon-carbon σ-bond oxidation of hydrocarbon with H_2O is possible using PCP as the substrate.

References

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3. Please refer to Chapter 3, section 3.1 for details.

4. The aromatic signal of PCP is more upfield than simple aromatics because of more alkene character due to its bent structure.

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13. This has been discussed in details in Chapter 3, section 3.5.6. For reference, see: Sokol, C. S.; Brubaker, Jr. C. H. *J. Inorg. Nucl. Chem.* **1968**, *30*, 3267-3271.

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Experimental Section

General Procedures

Unless otherwise specified, all reagents were purchased from commercial suppliers and directly used without further purification. Hexane for chromatography was distilled from anhydrous $CaCl_2$. Benzene-d_6 was distilled from sodium under vacuum, degassed with three freeze-pump-thaw cycles and stored in a Teflon screw head stoppered flask under N_2. Thin layer chromatography was performed on pre-coated silica gel 60 F_{254} plates. Silica gel (Merck, 70-230 mesh) was used for column chromatography under air or N_2.

Melting points were recorded on an MPA100 Automated Melting Point System. ^{1}H NMR spectra were recorded on a Bruker AV-400 MHz at 400 MHz. Chemical shifts were referenced internally to the residual solvent proton resonance in C_6D_6 (δ = 7.15 ppm), CDCl$_3$ (δ = 7.26 ppm) or with tetramethylsilane (δ = 0.00 ppm) as the internal standard. Chemical shifts (δ) are reported in parts per million (ppm). Coupling constants (J) are reported in hertz (Hz).

All reactions in 0.5 mL benzene-d_6 or 0.5 mL DMF-d_7 were carried out in a flame-sealed NMR tube in vacuum with the reaction mixture degassed with three freeze(77 K)-pump(0.005 mmHg)-thaw(r.t.) cycles, then heated in oven in dark and wrapped with aluminum foil to protect from exposure to room light before ^{1}H NMR measurements. The NMR yields were with benzene residue as the internal standard. GC yields were taken using naphthalene as internal standard. Aqueous stock solution of KOH was prepared separately, transferred to the reaction vessel and dried under vacuum at r.t. to obtain anhydrous starting materials. Benzene-d_6 and DMF-d_7 stock solutions of [2.2]paracyclophane were prepared separately, degassed and stored under N_2 before transferred to the reaction vessel. All the Co^{II}(por) complexes were prepared according to the literature procedures.[1]

Experimental Procedures

Discovery of Selective Hydrogenation of PCP in DMF Solvent

In C$_6$D$_6$ without additives. Co^{II}(ttp) (1.7 mg, 0.0024 mmol), H$_2$O (8.6 μL, 0.48 mmol) and benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) were added successively to a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 °C in the dark for 20 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals. The organic products were isolated by column chromatography eluting with hexane to remove Co^{II}(ttp). Total yield was taken by mass balance. Product **2**, unknowns **a**, **b** and **c** were re-purified from TLC plate eluting with hexane for 4 times.

Product **2**: ^{1}H NMR (CDCl$_3$, 400 MHz) δ 2.32 (s, 6 H, H$_a$), 2.86 (s, 4 H, H$_b$), 7.09 (s, 8 H, H$_c$).
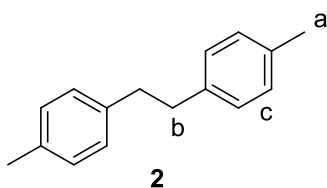
Unknown **a**: ^{1}H NMR (CDCl$_3$, 400 MHz) δ 2.32 (s, 3 H), 2.86 (s, 4 H), 3.96 (s, 2 H), 7.10 (d, J = 9.6 Hz, 8 H). The integration of proton numbers may reflect the empirical ratio only.

Unknown **b**: ^{1}H NMR (CDCl$_3$, 400 MHz) δ 2.86 (s, 8 H), 3.96 (s, 8 H), 6.70 (s, 1 H), 7.10 (s, 16 H). The integration of proton numbers may reflect the empirical ratio only.

Unknown **c**: ^{1}H NMR (C$_6$D$_6$, 400 MHz) δ 2.77 (s, 6 H), 2.79 (s, 7 H), 3.77 (s, 3 H), 4.25 (s, 1 H), 6.98 (s, 16 H). The integration of proton numbers may reflect the empirical ratio only.

In C$_6$D$_6$ with 5 mol% PPh$_3$. Co^{II}(ttp) (1.7 mg, 0.0024 mmol), PPh$_3$ (0.06 mg, 0.24 μmol), H$_2$O (8.6 μL, 0.48 mmol) and benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) were added successively to a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 °C in the dark for 16 h. It was monitored with ^{1}H NMR spectroscopy at particular

time intervals. The organic products were isolated by column chromatography eluting with hexane to remove Co^{II}(ttp). Total yield was taken by mass balance.

In C_6D_6 with 2 equiv of KOH. Co^{II}(ttp) (1.7 mg, 0.0024 mmol), KOH (0.54 mg, 0.0096 mmol), H_2O (8.6 μL, 0.48 mmol) and benzene-d_6 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) were added successively to a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 °C in the dark for 38 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals. The organic products were isolated by column chromatography eluting with hexane to remove Co^{II}(ttp). Total yield was taken by mass balance.

In DMF-d_7. Co^{II}(ttp) (1.7 mg, 0.0024 mmol), H_2O (8.6 μL, 0.48 mmol) and DMF-d_7 stock solution (500 μL) of [2.2]paracyclophane (1.0 mg, 0.0048 mmol) were added successively to a NMR tube. The orange mixture was degassed for three freeze-pump-thaw cycles and the NMR tube was flame-sealed under vacuum. It was heated at 200 °C in the dark for 41 h. It was monitored with ^{1}H NMR spectroscopy at particular time intervals. The organic products were isolated by column chromatography eluting with hexane. Total yield was taken by mass balance.

Porphyrin Ligand Electronic Effects

With Co^{II}(ttp) Catalyst. Co^{II}(ttp) (7.0 mg, 0.0096 mmol), H_2O (34 μL, 1.9 mmol) and [2.2]paracyclophane (4.0 mg, 0.019 mmol) were dissolved in 2 mL DMF in a rotaflo tube. The orange mixture was degassed for three freeze-pump-thaw cycles and flushed with N_2. The tube was heated at 200 °C in the dark for 32 h. After complete consumption of PCP from TLC analysis, the reaction was extracted with CH_2Cl_2 and H_2O to remove DMF. The organic layer was collected and rotary evaporated. The crude mixture was purified by column chromatography eluting with hexane to afford the organic products. GC yields were taken.

With Co^{II}(tap) Catalyst. Co^{II}(ttp) (7.7 mg, 0.0096 mmol), H$_2$O (34 μL, 1.9 mmol) and [2.2]paracyclophane (4.0 mg, 0.019 mmol) were dissolved in 2 mL DMF in a rotaflo tube. The orange mixture was degassed for three freeze-pump-thaw cycles and flushed with N$_2$. The tube was heated at 200 ^{o}C in the dark for 32 h. After complete consumption of PCP from TLC analysis, the reaction was extracted with CH$_2$Cl$_2$ and H$_2$O to remove DMF. The organic layer was collected and rotary evaporated. The crude mixture was purified by column chromatography eluting with hexane to afford the organic products. GC yields were taken.

With Co^{II}(t$_{4-CF3}$pp) Catalyst. Co^{II}(t$_{4-CF3}$pp) (9.1 mg, 0.0096 mmol), H$_2$O (34 μL, 1.9 mmol) and [2.2]paracyclophane (4.0 mg, 0.019 mmol) were dissolved in 2 mL DMF in a rotaflo tube. The orange mixture was degassed for three freeze-pump-thaw cycles and flushed with N$_2$. The tube was heated at 200 ^{o}C in the dark for 32 h. After complete consumption of PCP from TLC analysis, the reaction was extracted with CH$_2$Cl$_2$ and H$_2$O to remove DMF. The organic layer was collected and rotary evaporated. The crude mixture was purified by column chromatography eluting with hexane to afford the organic products. GC yields were taken.

Solvent Effects.

With CH$_3$CN solvent. Co^{II}(t$_{3,4,5-OMe}$pp) (9.9 mg, 0.0096 mmol), H$_2$O (34 μL, 1.9 mmol) and [2.2]paracyclophane (4.0 mg, 0.019 mmol) were dissolved in 2 mL CH$_3$CN in a rotaflo tube. The orange mixture was degassed for three freeze-pump-thaw cycles and flushed with N$_2$. The tube was heated at 200 ^{o}C in the dark for 60 h. The reaction was then extracted with CH$_2$Cl$_2$ and H$_2$O to remove DMF. The organic layer was collected and rotary evaporated. The crude mixture was purified by column chromatography eluting with hexane to afford the organic products. GC yields were taken. Co^{II}(t$_{3,4,5-OMe}$pp) was recovered by eluting with CH$_2$Cl$_2$ (7.0 mg, 71%).

With NMP solvent. Co^{II}(tap) (7.7 mg, 0.0096 mmol), H_2O (34 μL, 1.9 mmol) and [2.2]paracyclophane (4.0 mg, 0.019 mmol) were dissolved in 2 mL NMP in a rotaflo tube. The orange mixture was degassed for three freeze-pump-thaw cycles and flushed with N_2. The tube was heated at 200 °C in the dark for 60 h. After complete consumption of PCP from TLC analysis, the reaction was extracted with CH_2Cl_2 and H_2O to remove DMF. The organic layer was collected and rotary evaporated. The crude mixture was purified by column chromatography eluting with hexane to afford the organic products. GC yields were taken. Co^{II}(tap) was recovered by eluting with CH_2Cl_2 (7.0 mg, 91%).

Co^{II}(ttp) Catalyst Loading Effects.

With 10 mol% Co^{II}(ttp). Co^{II}(ttp) (1.4 mg, 0.0019 mmol), H_2O (34 μL, 1.9 mmol) and [2.2]paracyclophane (4.0 mg, 0.019 mmol) were dissolved in 2 mL DMF in a rotaflo tube. The orange mixture was degassed for three freeze-pump-thaw cycles and flushed with N_2. The tube was heated at 200 °C in the dark for 4 d. The reaction was then extracted with CH_2Cl_2 and H_2O to remove DMF. The organic layer was collected and rotary evaporated. The crude mixture was purified by column chromatography eluting with hexane to afford the organic products. GC yields were taken.

With 20 mol% Co^{II}(ttp). Co^{II}(ttp) (2.8 mg, 0.0038 mmol), H_2O (34 μL, 1.9 mmol) and [2.2]paracyclophane (4.0 mg, 0.019 mmol) were dissolved in 2 mL DMF in a rotaflo tube. The orange mixture was degassed for three freeze-pump-thaw cycles and flushed with N_2. The tube was heated at 200 °C in the dark for 3 d. After complete consumption of PCP from TLC analysis, the reaction was extracted with CH_2Cl_2 and H_2O to remove DMF. The organic layer was collected and rotary evaporated. The crude mixture was purified by column chromatography eluting with hexane to afford the organic products. GC yields were taken.

With 20 mol% Co^{II}(ttp) in air. Co^{II}(ttp) (2.8 mg, 0.0038 mmol), H$_2$O (34 μL, 1.9 mmol) and [2.2]paracyclophane (4.0 mg, 0.019 mmol) were dissolved in 2 mL DMF in a rotaflo tube. The tube was heated at 200 °C in the dark for 2 d. After complete consumption of PCP from TLC analysis, the reaction was extracted with CH$_2$Cl$_2$ and H$_2$O to remove DMF. The organic layer was collected and rotary evaporated. The crude mixture was purified by column chromatography eluting with hexane to afford the organic products. GC yields were taken.

With 100 mol% Co^{II}(ttp). Co^{II}(ttp) (14.0 mg, 0.019 mmol), H$_2$O (34 μL, 1.9 mmol) and [2.2]paracyclophane (4.0 mg, 0.019 mmol) were dissolved in 2 mL DMF in a rotaflo tube. The orange mixture was degassed for three freeze-pump-thaw cycles and flushed with N$_2$. The tube was heated at 200 °C in the dark for 19 h. After complete consumption of PCP from TLC analysis, the reaction was extracted with CH$_2$Cl$_2$ and H$_2$O to remove DMF. The organic layer was collected and rotary evaporated. The crude mixture was purified by column chromatography eluting with hexane to afford the organic products. GC yields were taken.

With 200 mol% Co^{II}(ttp). Co^{II}(ttp) (28.0 mg, 0.038 mmol), H$_2$O (34 μL, 1.9 mmol) and [2.2]paracyclophane (4.0 mg, 0.019 mmol) were dissolved in 2 mL DMF in a rotaflo tube. The orange mixture was degassed for three freeze-pump-thaw cycles and flushed with N$_2$. The tube was heated at 200 °C in the dark for 19 h. After complete consumption of PCP from TLC analysis, the reaction was extracted with CH$_2$Cl$_2$ and H$_2$O to remove DMF. The organic layer was collected and rotary evaporated. The crude mixture was purified by column chromatography eluting with hexane to afford the organic products. GC yields were taken. Cobalt(II) porphyrin complexes were recovered by eluting with CH$_2$Cl$_2$ (11.5 mg, 41%).

Temperature Efefcts.

At 150 °C. Co^{II}(ttp) (2.8 mg, 0.0038 mmol), H$_2$O (34 μL, 1.9 mmol) and [2.2]paracyclophane (4.0 mg, 0.019 mmol) were dissolved in 2 mL DMF in a rotaflo tube. The orange mixture was

degassed for three freeze-pump-thaw cycles and flushed with N_2. The tube was heated at 150 ^{o}C in the dark for 2 d. The reaction was then extracted with CH_2Cl_2 and H_2O to remove DMF. The organic layer was collected and rotary evaporated. The crude mixture was purified by column chromatography eluting with hexane to afford the organic products. GC yields were taken. Cobalt porphyrin complexes were recovered by eluting with CH_2Cl_2 (2.6 mg, 93%).

At 170 ^{o}C. Co^{II}(ttp) (2.8 mg, 0.0038 mmol), H_2O (34 μL, 1.9 mmol) and [2.2]paracyclophane (4.0 mg, 0.019 mmol) were dissolved in 2 mL DMF in a rotaflo tube. The orange mixture was degassed for three freeze-pump-thaw cycles and flushed with N_2. The tube was heated at 170 ^{o}C in the dark for 4 d. The reaction was then extracted with CH_2Cl_2 and H_2O to remove DMF. The organic layer was collected and rotary evaporated. The crude mixture was purified by column chromatography eluting with hexane to afford the organic products. GC yields were taken.

At 180 ^{o}C. Co^{II}(ttp) (2.8 mg, 0.0038 mmol), H_2O (34 μL, 1.9 mmol) and [2.2]paracyclophane (4.0 mg, 0.019 mmol) were dissolved in 2 mL DMF in a rotaflo tube. The orange mixture was degassed for three freeze-pump-thaw cycles and flushed with N_2. The tube was heated at 180 ^{o}C in the dark for 5 d. After complete consumption of PCP from TLC analysis, the reaction was extracted with CH_2Cl_2 and H_2O to remove DMF. The organic layer was collected and rotary evaporated. The crude mixture was purified by column chromatography eluting with hexane to afford the organic products. GC yields were taken.

Improved Catalytic Hydrogenation of PCP at Higher Temperatures

At 220 ^{o}C. Co^{II}(ttp) (1.4 mg, 0.0019 mmol), H_2O (34 μL, 1.9 mmol) and [2.2]paracyclophane (4.0 mg, 0.019 mmol) were dissolved in 2 mL DMF in a rotaflo tube. The orange mixture was degassed for three freeze-pump-thaw cycles and flushed with N_2. The tube was heated at 220

ºC in the dark for 20 h. After complete consumption of PCP from TLC analysis, the reaction was extracted with CH_2Cl_2 and H_2O to remove DMF. The organic layer was collected and rotary evaporated. The crude mixture was purified by column chromatography eluting with hexane to afford the organic products. GC yields were taken.

At 240 ºC for 20 h. Co^{II}(ttp) (1.4 mg, 0.0019 mmol), H_2O (34 μL, 1.9 mmol) and [2.2]paracyclophane (4.0 mg, 0.019 mmol) were dissolved in 2 mL DMF in a rotaflo tube. The orange mixture was degassed for three freeze-pump-thaw cycles and flushed with N_2. The tube was heated at 240 ºC in the dark for 20 h. After complete consumption of PCP from TLC analysis, the reaction was extracted with CH_2Cl_2 and H_2O to remove DMF. The organic layer was collected and rotary evaporated. The crude mixture was purified by column chromatography eluting with hexane to afford the organic products. GC yields were taken.

At 240 ºC for 48 h. Co^{II}(ttp) (1.4 mg, 0.0019 mmol), H_2O (34 μL, 1.9 mmol) and [2.2]paracyclophane (4.0 mg, 0.019 mmol) were dissolved in 2 mL DMF in a rotaflo tube. The orange mixture was degassed for three freeze-pump-thaw cycles and flushed with N_2. The tube was heated at 240 ºC in the dark for 48 h. After complete consumption of PCP from TLC analysis, the reaction was extracted with CH_2Cl_2 and H_2O to remove DMF. The organic layer was collected and rotary evaporated. The crude mixture was purified by column chromatography eluting with hexane to afford the organic products. GC yields were taken.

At Co^{II}(tap). Co^{II}(tap) (1.5 mg, 0.0019 mmol), H_2O (34 μL, 1.9 mmol) and [2.2]paracyclophane (4.0 mg, 0.019 mmol) were dissolved in 2 mL DMF in a rotaflo tube. The orange mixture was degassed for three freeze-pump-thaw cycles and flushed with N_2. The tube was heated at 240 ºC in the dark for 20 h. After complete consumption of PCP from TLC analysis, the reaction was extracted with CH_2Cl_2 and H_2O to remove DMF. The organic layer was collected and rotary evaporated. The crude mixture was purified by column chromatography eluting with hexane to afford the organic products. GC yields were taken.

At Co^{II}(t$_{4\text{-CF3}}$pp). Co^{II}(t$_{4\text{-CF3}}$pp) (1.8 mg, 0.0019 mmol), H$_2$O (34 μL, 1.9 mmol) and [2.2]paracyclophane (4.0 mg, 0.019 mmol) were dissolved in 2 mL DMF in a rotaflo tube. The orange mixture was degassed for three freeze-pump-thaw cycles and flushed with N$_2$. The tube was heated at 240 °C in the dark for 20 h. After complete consumption of PCP from TLC analysis, the reaction was extracted with CH$_2$Cl$_2$ and H$_2$O to remove DMF. The organic layer was collected and rotary evaporated. The crude mixture was purified by column chromatography eluting with hexane to afford the organic products. GC yields were taken.

Control Experiment at 240 °C. H$_2$O (34 μL, 1.9 mmol) and [2.2]paracyclophane (4.0 mg, 0.019 mmol) were dissolved in 2 mL DMF in a rotaflo tube. The colorless solution was degassed for three freeze-pump-thaw cycles and flushed with N$_2$. The tube was heated at 240 °C in the dark for 1 d. After complete consumption of PCP from TLC analysis, the reaction was extracted with CH$_2$Cl$_2$ and H$_2$O to remove DMF. The organic layer was collected and rotary evaporated. The crude mixture was purified by column chromatography eluting with hexane to afford the organic products. GC yields were taken.

Control Experiment at 220 °C. H$_2$O (34 μL, 1.9 mmol) and [2.2]paracyclophane (4.0 mg, 0.019 mmol) were dissolved in 2 mL DMF in a rotaflo tube. The colorless solution was degassed for three freeze-pump-thaw cycles and flushed with N$_2$. The tube was heated at 220 °C in the dark for 1 d. The reaction was then extracted with CH$_2$Cl$_2$ and H$_2$O to remove DMF. The organic layer was collected and rotary evaporated. The crude mixture was purified by column chromatography eluting with hexane to recover the PCP (3.9 mg, 98%).

Stability Test of Co^{II}(ttp).

Under air. Co^{II}(tp) (2.8 mg, 0.0019 mmol) and H$_2$O (34 μL, 1.9 mmol) were dissolved in 2 mL DMF in a rotaflo tube. The tube was heated at 200 °C in the dark for 2 d. After complete

consumption of Co^{II}(ttp) from TLC analysis, the reaction was extracted with CH_2Cl_2 and H_2O to remove DMF. The organic layer was collected and rotary evaporated to afford crude solids.

Under N$_2$. Co^{II}(tp) (2.8 mg, 0.0019 mmol) and H_2O (34 μL, 1.9 mmol) were dissolved in 2 mL DMF in a rotaflo tube. The orange mixture was degassed for three freeze-pump-thaw cycles and flushed with N_2. The tube was heated at 200 °C in the dark for 2 d. After complete consumption of Co^{II}(ttp) from TLC analysis, the reaction was extracted with CH_2Cl_2 and H_2O to remove DMF. The organic layer was collected and rotary evaporated to afford crude solids. The solids were dissolved in CH_2Cl_2 for UV-Vis spectroscopic analysis.

Catalytic Hydration of PCP in DMSO. Co^{II}(ttp) (2.8 mg, 0.0038 mmol), H_2O (34 μL, 1.9 mmol) and [2.2]paracyclophane (4.0 mg, 0.019 mmol) were dissolved in 2 mL DMSO in a rotaflo tube. The orange mixture was degassed for three freeze-pump-thaw cycles and flushed with N_2. The tube was heated at 200 °C in the dark for 2 d. After complete consumption of PCP from TLC analysis, the reaction was extracted with ethyl acetate and H_2O to remove DMSO. The organic layer was collected and rotary evaporated. **2** was first purified by column chromatography eluting with hexane, then **4** was obtained by eluting with hexane/CH_2Cl_2 = 2:1, finally the unknowns were collected by eluting with CH_2Cl_2. GC yield was taken for **2**. Isolated yields were taken for **4** (0.7 mg, 16%) and the organic unknowns (2.2 mg, 55%).

Control Experiment of 2. Co^{II}(ttp) (2.8 mg, 0.0038 mmol), H_2O (34 μL, 1.9 mmol) and 4,4'-dimethylbibenzyl **2** (4.0 mg, 0.019 mmol) were dissolved in 2 mL DMSO in a rotaflo tube. The orange mixture was degassed for three freeze-pump-thaw cycles and flushed with N_2. The tube was heated at 200 °C in the dark for 2 d. The reaction was then extracted with ethyl acetate and H_2O to remove DMSO. The organic layer was collected and rotary evaporated. The crude mixture was purified by column chromatography eluting with hexane to afford the organic products. GC yields were taken.

Appendix I   List of Spectra

2 (CDCl₃, 400 MHz)

unknown **a** (CDCl₃, 400 MHz)

unknown **b** (CDCl₃, 400 MHz)

unknown **c** (C₆D₆, 400 MHz)

4 (CDCl₃, 400 MHz)

GCMS Spectra of 4

The peak at m/z = 224 agrees with the molecular mass of **4**

Sample Information

Analyzed by	: Admin
Analyzed	: 1/14/2013 9:20:53 AM
Sample Type	: Unknown
Level #	: 1
Sample Name	: CTT 363 f2
Sample ID	:
IS Amount	: [1]=1
Sample Amount	: 1
Dilution Factor	: 1
Vial #	: 1
Injection Volume	: 1.00
Data File	: C:\GCMSsolution\Data\Project1\CTT 363 f2.qgd
Org Data File	: C:\GCMSsolution\Data\Project1\CTT 363 f2.qgd
Method File	: C:\GCMSsolution\Data\Project1\TTT5.qgm
Org Method File	: C:\GCMSsolution\Data\Project1\TTT5.qgm
Report File	:
Tuning File	: C:\GCMSsolution\System\Tune1\12012013(filament 2).qgt
Modified by	: Admin
Modified	: 1/14/2013 9:31:53 AM

Chromatogram CTT 363 f2 C:\GCMSsolution\Data\Project1\CTT 363 f2.qgd

References

1. Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2445-2448.

Chapter 5   Analysis on the Carbon-Carbon Bond Activation with Group 9 Metalloporphyrins

5.1 Introduction

There are two reported CCA of unfunctionalized hydrocarbons with detailed experimental investigations: (1) Rh^{II}(ttp)-catalyzed 1,2-addition of Rh^{III}(ttp)H with c-octane[1] and (2) Rh^{II}(tmp) bi-metalloradical CCA of PCP.[2] This chapter will discuss these two modes of CCA in a more general approach based on the reaction thermodynamics and kinetics. Secondly, the bi-molecular reductive elimination between M^{III}(ttp)H and M^{III}(ttp)R to generate R-H and M^{II}_2(ttp)$_2$ will also be discussed as an alternative hydrogenation process. Finally, the reduction potentials of M^{III}(por)L complexes (M = Co, Rh and Ir) will be compared in relation to CCA.

5.2 Thermodynamics

5.2.1 Equilibrium Concentration of M^{II}(ttp) Metalloradical

Sterically non-bulky rhodium(II) and iridium(II) porphyrin radicals, e.g. Rh^{II}(ttp) and Ir^{II}(ttp), are in thermal equilibrium with its dimer in solutions.[3] The degree of dimer dissociation to give the monomer increases with temperatures. Due to the much stronger (ttp)Ir-Ir(ttp) bond (20 kcal/mol) than the (ttp)Rh-Rh(ttp) bond (12 kcal/mol),[4] Rh^{II}_2(ttp)$_2$ dissociates to give high concentration of Rh^{II}(ttp) than the iridium analogue under the same temperature. Table 5.1 tabulates the selected ΔG, K, [M^{II}(ttp)] at equilibrium and [Rh^{II}(ttp)]/[Ir^{II}(ttp)] ratio at equilibrium using 1 M Rh^{II}_2(ttp)$_2$ and Ir^{II}_2(ttp)$_2$ at initial as the examples from 0 ^{o}C to 200 ^{o}C.

Table 5.1 Selected Equilibria of $M^{II}_2(ttp)_2$ and $M^{II}(ttp)$ from 0 °C to 200 °C (M = Rh and Ir).

$$M^{II}_2(ttp)_2 \underset{}{\overset{K}{\rightleftharpoons}} 2M^{II}(ttp)$$

initial:　　1 M　　　　　0 M
eqm:　(1 - x) M　　　　2x M

$$\begin{cases} \Delta G = \Delta H - T\Delta S \\ \Delta G = -RT\ln K \end{cases}$$

where ΔH = M-M BDE
$S = S$ of H_2 = 31.2 cal mol^{-1} K^{-1} [5]
$R = 1.9872 \times 10^{-3}$ kcal mol^{-1} K^{-1}
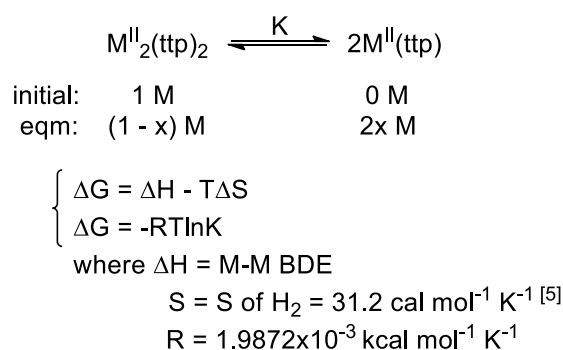
| T / °C	M = Rh			M = Ir			Rh^{II}/Ir^{II} ratio
	ΔG / kcal mol^{-1}	K	2x / M	ΔG / kcal mol^{-1}	K	2x / M	
0	3.5	0.0016	0.04	11.5	6.4×10^{-10}	2.5×10^{-5}	1577
20	2.9	0.0074	0.08	10.9	8.0×10^{-9}	8.9×10^{-5}	942
25	2.7	0.0104	0.10	10.7	1.4×10^{-8}	1.2×10^{-4}	836
40	2.2	0.0275	0.16	10.2	7.1×10^{-8}	2.7×10^{-4}	596
60	1.6	0.0877	0.28	9.6	4.9×10^{-7}	7.0×10^{-4}	392
80	1.0	0.2451	0.44	9.0	2.7×10^{-6}	1.7×10^{-3}	265
100	0.4	0.6133	0.64	8.4	1.3×10^{-5}	3.5×10^{-3}	182
120	-0.3	1.3979	0.88	7.7	5.0×10^{-5}	7.0×10^{-3}	125
140	-0.9	2.9419	1.13	7.1	1.7×10^{-4}	0.013	87
160	-1.5	5.7801	1.36	6.5	5.3×10^{-4}	0.023	59
180	-2.1	10.6988	1.55	5.9	0.0015	0.038	41
200	-2.8	18.7987	1.69	5.2	0.0038	0.061	28

5.2.2 Reaction Free Energy Estimations

The thermodynamic feasibilities of bi-metalloradical CCA with $Co^{II}(ttp)$, $Rh^{II}_2(ttp)_2$ and $Ir^{II}_2(ttp)_2$ at 150 °C are estimated from the bond energy approach. In order to achieve a complete reaction, it is assumed that the reaction equilibrium constant must be greater than 100. This corresponds to a reaction free energy lower than -4 kcal/mol at 150 °C. Scheme 5.1 illustrates the estimation method. Similarly, scheme 5.2 illustrates the estimation for the $M^{II}(ttp)$-catalyzed 1,2-addition of $M^{III}(ttp)H$.
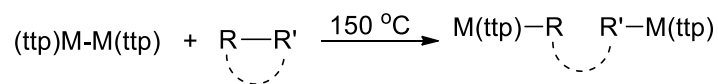
(ttp)M-M(ttp) + R—R' $\xrightarrow{150\ ^oC}$ M(ttp)—R   R'—M(ttp)

at 150 °C, for a complete reaction with K > 100, then ΔG < -4 kcal/mol

for non-ring substrate, ΔS ~ 0

  ΔH = (M-M) + (C-C) - 2(M-C)

  ΔG = ΔH - TΔS

  -4 > (M-M) + (C-C) - 2(M-C)

2(M-C) > (M-M) + (C-C) + 4

for ring substrate with ring opening, TΔS ~ -13 kcal/mol

  ΔG = ΔH - TΔS

  -4 > (M-M) + (C-C) - 2(M-C) + 13

2(M-C) > (M-M) + (C-C) + 17

* there is no (M-M) term for Co(ttp)

Scheme 5.1 Thermodynamic Estimation for the Bi-metalloradical CCA.
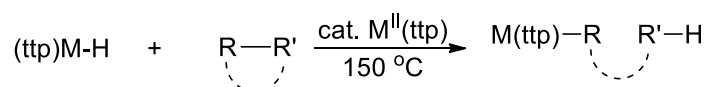
(ttp)M-H   +   R—R' $\xrightarrow[150\ ^oC]{\text{cat. } M^{II}(ttp)}$ M(ttp)—R   R'—H

at 150 °C, for a complete reaction with K > 100, then ΔG < -4 kcal/mol

for non-ring substrate, ΔS ~ 0

  ΔH = (M-H) + (C-C) - (M-C) - (C-H)

  ΔG = ΔH - TΔS

  -4 > (M-H) + (C-C) - (M-C) - (C-H)

(M-C) + (C-H) > (M-H) + (C-C) + 4

for ring substrate with ring opening, TΔS ~ -13 kcal/mol

  ΔG = ΔH - TΔS

  -4 > (M-H) + (C-C) - (M-C) - (C-H) + 13

(M-C) + (C-H) > (M-H) + (C-C) + 17

Scheme 5.2 Thermodynamic Estimation for the M^{II}(ttp)-Catalyzed 1,2-Addition of M^{III}(ttp)H.

Substituting the bond energies of M-M and M-H bonds in $M^{II}_2(ttp)_2$ and $M^{III}(ttp)$-H, respectively, listed in Table 5.2 into Scheme 5.1 and Scheme 5.2, the minimum free energies estimated for the corresponding CCA reaction to occur are summarized in Table 5.3.

Table 5.2 Summary of the M-M and M-H Bond Energies.

M(ttp)-X	Bond Energy (kcal/mol)	
	X = M(ttp)	X = H
Co(ttp)-X	N/A	52
Rh(ttp)-X	12	60
Ir(ttp)-X	20	70

Table 5.3 Estimations of the Energetic Requirement for the Two Types of CCA.

Substrate	Free Energy Estimation / kcal mol^{-1}					
	$M^{II}(ttp)$ bi-metalloraidcal CCA 2(M-C) > (C-C)			$M^{II}(ttp)$-catalyzed 1,2-addition of $M^{III}(ttp)H$ (M-C) + (C-H) > (C-C)		
	Co	Rh	Ir	Co	Rh	Ir
R—R' (ring)	17	29	37	69	77	87
R—R'	4	16	24	56	64	74

Comparing rhodium and iridium in the bi-metalloradical CCA, despite the apparently thermodynamic more demanding for $Ir^{II}_2(ttp)_2$, the Ir-C bond formed is stronger than the Rh-C bond formed by about 5 kcal/mol.[4b] It sums up to 10 kcal/mol for two Ir-C bonds formation. It is well enough to compensate for the breaking of Ir-Ir bond which is 8 kcal/mol stronger than the Rh-Rh bond. Therefore, the bi-metalloradical CCA with $Ir^{II}_2(ttp)_2$ is thermodynamically more favorable than with $Rh^{II}_2(ttp)_2$.

$Co^{II}(ttp)$ is considered a special case because it exists as a monomer without the need to break the M-M bond. Therefore, it only requires the two M-C bonds formed in total to be 4 kcal/mol stronger than the C-C bond being broken in order for the non-ring opening CCA to occur.

In the $M^{II}(ttp)$-catalyzed 1,2-addition of $M^{III}(ttp)H$, the estimated trend in energetic requirements increases with the M-H bond energy in $M^{III}(ttp)$-H.
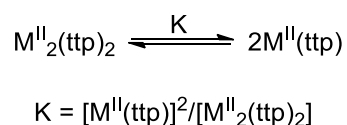
5.3 Kinetics

The proposed rate laws of $M^{II}(por)$ bi-metalloradical CCA and $M^{II}(por)$-catalyzed 1,2-addition of $M^{III}(por)H$ with a hydrocarbon substrate in a general case are expressed in eqs 5.1 and 5.2, respectively.[2] Although the rate law for the latter reaction has not yet been measured experimentally for both Rh and Ir, we assumed that it follows a radical chain type reaction (for which $M^{II}_2(por)_2$ dimer exist) and 1st order in both $[M^{II}(por)]$ and $[M^{III}(por)H]$.[6]

$$\text{rate} = k[M^{II}(por)]^2[\text{substrate}] \quad (5.1)$$

$$\text{rate} = k[M^{II}(por)][M^{III}(por)H][\text{substrate}] \quad (5.2)$$

The two equations above is general to $M^{II}(por)$ that only exists as monomer, e.g. $Rh^{II}(tmp)$. For $M^{II}_2(por)_2$ which is in equilibrium with $M^{II}(por)$, e.g. $Rh^{II}_2(ttp)_2$, Scheme 5.3 applies. Therefore, the corresponding rate laws for $M^{II}_2(ttp)_2$ now become eqs 5.3 and 5.4.

$$M^{II}_2(ttp)_2 \ \underset{}{\overset{K}{\rightleftharpoons}} \ 2M^{II}(ttp)$$

$$K = [M^{II}(ttp)]^2/[M^{II}_2(ttp)_2]$$

Scheme 5.3 Equilibrium of $M^{II}_2(ttp)_2$ and $M^{II}(ttp)$.

$$\text{rate} = K^{1/2}k[M^{II}_2(ttp)_2]^{1/2}[\text{substrate}] \quad (5.3)$$
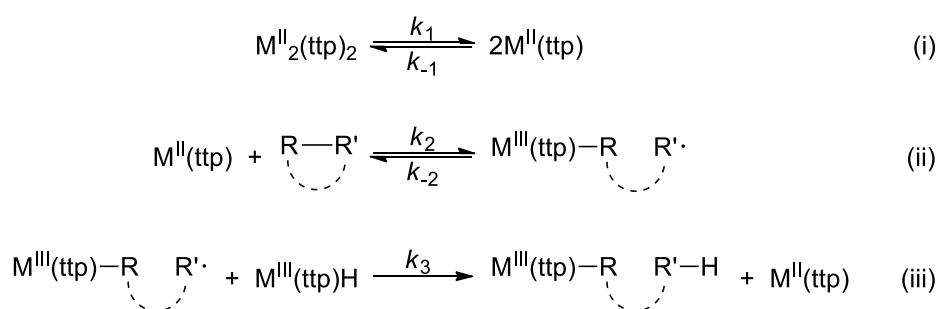
$$\text{rate} = K^{1/2}k[M^{II}_2(por)_2]^{1/2}[M^{III}(por)H][\text{substrate}] \quad (5.4)$$

Apart from the 1st order dependence on the substrate, the rate of bi-metalloradical CCA is 2nd order dependent on $M^{II}(ttp)$, which requires high temperatures to facilitate the $M^{II}_2(ttp)_2$ dimer dissociation. Although rate enhancement effect is significant with increased $[M^{II}(ttp)]$,
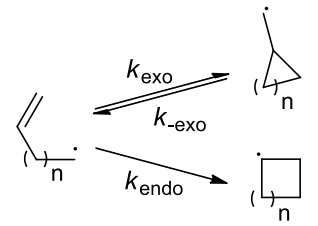
it also promotes the bi-metalloradical CHA at the same time.[7] In other words, the bi-metalloraidcal CCA is more practical for CHA inactive substrates, for example [2.2]paracyclophane.

Such drawback is minimized in the M^{II}-catalyzed 1,2-addition of $M^{III}(ttp)H$ since it is 1st order dependent on $M^{II}(ttp)$. Alternatively, the reaction rate can be increased by employing a higher $[M^{III}(ttp)H]$. This combination allows milder reaction temperatures and probably lower operating $[M^{II}(ttp)]$. The extensive thermal dehydrogenation of $M^{III}(ttp)H$ and bi-molecular CHA can be avoided.

Unlike the $M^{II}(ttp)$ bi-metalloradical CCA, the $M^{II}(ttp)$-catalyzed 1,2-addition of $M^{III}(ttp)H$ is essentially a three-step reaction (Scheme 5.4).[1] $M^{II}_2(ttp)_2$ first dissociates to give $M^{II}(ttp)$ (step i). After the initial CCA with $M^{II}(ttp)$ to generate a $M^{III}(ttp)$-alkyl radical, it must possess sufficient life time to undergo the subsequent H atom abstraction from $M^{III}(ttp)H$ to furnish the reaction (step iii), otherwise it cyclizes back to regenerate the reactants (step ii). Since the values for k_2, k_{-2} and k_3 are not reported, the rate constants of olefin-radical cyclization and H atom abstraction from common H atom sources are compared for reference (Tables 5.4 and 5.5).

$$M^{II}_2(ttp)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2M^{II}(ttp) \qquad \text{(i)}$$

$$M^{II}(ttp) + R\!-\!R' \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} M^{III}(ttp)\!-\!R \quad R'\!\cdot \qquad \text{(ii)}$$

$$M^{III}(ttp)\!-\!R \quad R'\!\cdot + M^{III}(ttp)H \xrightarrow{k_3} M^{III}(ttp)\!-\!R \quad R'\!-\!H + M^{II}(ttp) \qquad \text{(iii)}$$

Scheme 5.4 Stepwise $M^{II}(ttp)$-Catalyzed 1,2-Addition of $M^{III}(ttp)H$.

Table 5.4 Rate Constants of *exo* and *endo* Cyclization of Olefin Alkyl Radicals at 25 °C.[8]

| $\overset{//}{\underset{n}{\diagdown}}\cdot$	k_{exo} / s^{-1}	k_{-exo} / s^{-1}	k_{endo} / s^{-1}
n = 1	1.8 x 10^4	2.0 x 10^8	not observed
n = 2	1.0	4.7 x 10^3	not observed
n = 3	2.3 x 10^5	--	4.1 x 10^3
n = 4	5.2 x 10^3	--	8.3 x 10^2
n = 5	<70	--	1.2 x 10^5

Table 5.5 Rate Constants of H Atom Abstraction of 1°, 2°, 3° Alkyl and Benzylic Radicals at 25-30 °C.[8]

H Atom Source	X-H BDE[8] / kcal mol^{-1}	k / M^{-1} s^{-1}			
		RCH$_2\cdot$	R$_2$CH$\cdot$	R$_3$C$\cdot$	PhCH$_2\cdot$
PhS-H	83.5	9.2 x 10^7	1.1 x 10^8	1.5 x 10^8	3.0 x 10^5
Et$_3$Si-H	94.6	7.0 x 10^3	N/A	3.0 x 10^3	N/A
Cy$_2$P-H	86.2	1.0 x 10^6	N/A	2.5 x 10^3	2.5 x 10^3
n-Bu$_3$Ge-H	~86	1.0 x 10^5	N/A	N/A	N/A
n-Bu$_3$Sn-H	78.0	2.7 x 10^6	1.5 x 10^6	1.7 x 10^6	3.6 x 10^4
1,4-cyclohexadiene	74.3	4.8 x 10^5	N/A	9.4 x 10^3	1.0 x 10^2

The rate constants of intramolecular cyclization are in the range of 10^3 to 10^5 s^{-1} (Table 5.4). The bi-molecular rate constants of H atom abstraction from non C-H sources are in the range of 10^3 to 10^8 M^{-1} s^{-1} (Table 5.5). Abstraction of H atom from donor with weaker X-H bond tends to be faster. Rh^{III}(ttp)H and Ir^{III}(ttp)H with M-H BDE to be 60 kcal/mol and 70 kcal/mol, respectively, serve as the much better H atom donors. Therefore, the latter process can compete with the cyclization in the presence of sufficient H atom donor.

The benzylic radical undergoes slower H atom abstraction than the 1°, 2° and 3° alkyl radicals by 2 to 3 orders of magnitude, probably due to the formation of weaker benzylic C-H bond (89.7 kcal/mol) than a typical alkyl C-H bond (~100 kcal/mol).[9] Therefore in the CCA of

PCP, even though M^{II}(ttp) cleaves the benzylic C-C bond of PCP bi-molecularly to form the M^{III}(ttp)-terminal benzylic radical intermediates **A**, it may re-cyclize much faster than abstracting a H atom from M^{III}(ttp)H, e.g. k_{-1}[**A**] $\gg$ k_2[**A**][M^{III}(ttp)H] (Scheme 5.5). CCA of PCP via M^{II}(ttp)-catalyzed 1,2-addition of M^{III}(ttp)H will not be observed. In contrast, the CCA of *c*-octane proceeds smoothly via the Rh^{II}(ttp)-catalyzed 1,2-addition of Rh^{III}(ttp)H pathway as it involves the H atom abstraction by 1° alkyl radical intermediate.
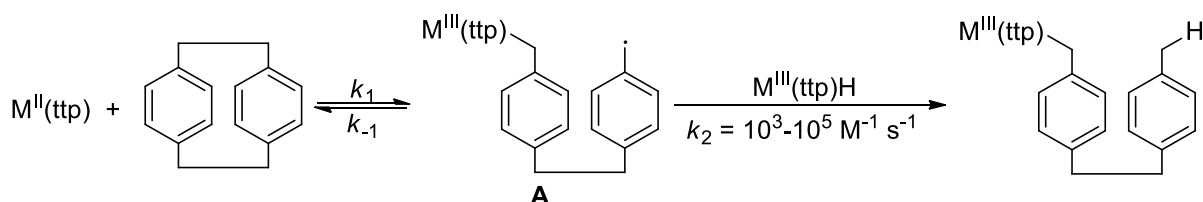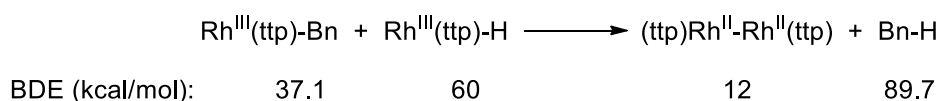

Scheme 5.5 Absence of M^{II}(ttp)-Catalyzed 1,2-Addition of M^{III}(ttp)H for PCP.

5.4 Bi-molecular Reductive Elimination with M^{III}(ttp)H

In Chapter 3, the reductive elimination of toluene and Ir^{II}_2(ttp)$_2$ from Ir^{III}(ttp)Bn and Ir^{III}(ttp)H is discussed. Here, the reaction thermodynamics will be analyzed as well as for the analogous reaction with rhodium porphyrin complexes.

Using the BDE values of Rh^{III}(ttp)-Bn (37.1 kcal/mol),[10] Rh^{III}(ttp)-H (60 kcal/mol),[4a] (ttp)Rh^{II}-Rh^{II}(ttp) (12 kcal/mol)[4a] and Bn-H (89.7 kcal/mol),[9] this yields the free energy of -4.6 kcal/mol for the reaction with rhodium porphyrin complexes (Scheme 5.6). The corresponding reaction free energy for iridium porphyrin complexes is estimated to be 2.5 kcal/mol, which is endergonic.

$$Rh^{III}(ttp)\text{-}Bn \ + \ Rh^{III}(ttp)\text{-}H \ \longrightarrow \ (ttp)Rh^{II}\text{-}Rh^{II}(ttp) \ + \ Bn\text{-}H$$

BDE (kcal/mol):   37.1   60   12   89.7

Assume $T\Delta S \sim 0$
then $\Delta G = \Delta H$
$= 37.1 + 60 - 12 - 89.7$
$= -4.6$ kcal/mol

$$Ir^{III}(ttp)\text{-}Bn \ + \ Ir^{III}(ttp)\text{-}H \ \longrightarrow \ (ttp)Ir^{II}\text{-}Ir^{II}(ttp) \ + \ Bn\text{-}H$$

BDE (kcal/mol):   42.2   70   20   89.7
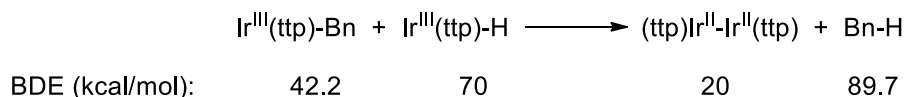
Assume $T\Delta S \sim 0$
then $\Delta G = \Delta H$
$= 42.2 + 70 - 20 - 89.7$
$= 2.5$ kcal/mol

Scheme 5.6 Thermodynamic Estimations for the Bi-molecular Reductive Eliminations.

This surprising results suggest that the bi-molecular reductive elimination of toluene and $Rh^{II}_2(ttp)_2$ from $Rh^{III}(ttp)Bn$ and $Rh^{III}(ttp)H$ may occur more readily than the iridium system studied. In the rhodium porphyrin catalytic hydrogenation of PCP with H_2O, the di-Rh and mono-Rh CCA intermediates may react with $Rh^{III}(ttp)H$ as an alternative hydrogenation pathway, in analogous to the iridium porphyrin system discussed in Chapter 3.

5.5 Redox Potentials of Group 9 Metalloporphyrins

The reduction potentials of group 9 metal(III) porphyrin complexes provide another useful insight on their reactivities in the CCA reactions. For example, the bi-metalloradical CCA of PCP with $Rh^{II}(tmp)$ accompanies the metal center oxidation from Rh(II) to Rh(III). This process would be more favorable with a more negative Rh(III)/Rh(II) reduction potential, suggesting a more stable Rh(III) state. Table 5.6 lists the reduction potentials of $M^{III}(tpp)L$ and $M^{III}(oep)L$ (M = Co, Rh and Ir) as the references.

Table 5.6 Comparison on the Reduction Potentials of $M^{III}(por)L$.

$$M^{III}(tpp)L + e^- \xrightarrow{E^o} M^{II}(tpp) + L^-$$
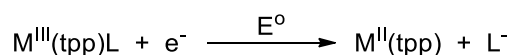
M	por	L	solvent	temp / °C	E° vs SCE / V
Co		Cl	CH_2Cl_2	N/A	-0.055[11]
Rh	tpp	Cl	THF	23	-1.01[12]
Ir		(CO)Cl	THF	22	-1.17[13]
Co		Br	CH_2Cl_2:MeOH (4:1)	N/A	-1.05[14]
Rh	oep	Cl	THF	23	-1.30[12]
Ir		(CO)Cl	THF	22	-1.49[13]

The tendency for the reduction of $M^{III}(por)L$ to $M^{II}(por)$ follows a general trend for both tpp and oep ligands: Co > Rh > Ir. As the electron richness increases down the group, the high valent M(III) oxidation state can be better stabilized. The reducing property is further enhanced with more electron rich oep ligand. This facilitates the oxidation of $M^{II}(por)$.

From the above table, it suggested that iridium(II) porphyrins are the most reducing. In other words, CCA using iridium(II) porphyrins will be thermodynamically more favorable than rhodium(II) and cobalt(II) porphyrins. This agrees with the energetic estimation discussed in section 5.2.2 for bi-metalloradical CCA process. In addition, electron rich porphyrin ligand increases the LUMO energy and the metalloradical character of $Ir^{II}(por)$

The reduction potentials of Co(III)/Co(II) reported varies greatly in the literatures, from +0.01 V to -1.05 V. Alternative report suggests that the reduction of $Co^{III}(tpp)R$ (R = Me, Et and CH_2Cl) occurs at the porphyrin ligand instead of the Co(III) center to form porphyrin π radical anion only at potentials from -1.37 V to -1.42 V (vs SCE) in THF or CH_2Cl_2.[15] These examples showed that cobalt porphyrins exhibit distinct reactivity depending on the reaction conditions. In contrast, the 1st oxidation potentials of $Co^{II}(tpp)$ from two separate reports are similar, e.g. +0.58 V and +0.52V (vs SCE), giving metal center oxidized $[Co^{III}(ttp)]^+$ complex.[16,17]

5.6 Conclusions

The M^{II}(por) bi-metalloradical CCA and M^{II}(por)-catalyzed 1,2-addition of M^{III}(por)H were analyzed from the thermodynamic and kinetic points of view. The M^{II}(por) bi-metalloradical CCA is ideal for CHA inactive hydrocarbon substrate. This process is thermodynamically more favorable with Ir^{II}$_2$(ttp)$_2$, in agreement with the estimation using the 1st reduction potentials of M^{III}(por)L. Alternatively, the M^{II}(por)-catalyzed 1,2-addition of M^{III}(por)H pathway avoids the bi-metalloradical CHA process by kinetic control. The bi-molecular reductive elimination with M^{III}(ttp)H as an alternative hydrogenation process is thermodynamically more favorable for rhodium porphyrin complexes.

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