Synthesis and Reactivity Study of Rhodium Porphyrin Amido Complexes

AU, Ching Chi

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Thesis/ Assessment Committee

Professor CHOW, Hak Fun (Chair)

Professor CHAN, Kin Shing (Thesis Supervisor)

Professor LEUNG, Ken Cham Fai (Committee member)

Professor LAM, Michael Hon Wah (External Examiner)
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Department of Chemistry

The Chinese University of Hong Kong
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<td>δ</td>
<td>chemical shift</td>
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<tr>
<td>Anal</td>
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<tr>
<td>Ar</td>
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</tr>
<tr>
<td>BDE</td>
<td>Bond dissociation energy</td>
</tr>
<tr>
<td>br</td>
<td>broad peak</td>
</tr>
<tr>
<td>Bn</td>
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<td>tol</td>
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<td>4-toluenesulfonyl</td>
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ABSTRACT

The rhodium porphyrin amido complex, Rh(ttp)NH\textsubscript{2}SO\textsubscript{2}Ph, was successfully synthesized from rhodium porphyrin chloride and benzenesulfonamide in the presence of base. Shorter reaction time and stronger base were found to be beneficial, with KOH found to give the highest rate and yield.

\[
\text{Rh(ttp)Cl} + \text{PhSO}_2\text{NH}_2 \xrightarrow{(3 \text{ equiv})} \text{C}_6\text{H}_6, \text{KOH (10 equiv)} \xrightarrow{\text{N}_2, 80 ^\circ\text{C}, 3.5 \text{ h}} \text{Rh(ttp)NH}\text{SO}_2\text{Ph} \xrightarrow{80 \%}
\]

Rh(ttp)NH\textsubscript{2}SO\textsubscript{2}Ph underwent various types of bond activation, 1) benzylic carbon-hydrogen bond activation (CHA) with toluene, 2) carbon-nitrogen bond activation (CNA) with tri-\textit{n}-butylamine as well as 3) carbon-carbon bond activation (CCA) of di-\textit{n}-butyl ether with high selectivity.

Rh(ttp)NH\textsubscript{2}SO\textsubscript{2}Ph was found to be thermally unstable upon heating to give [Rh(ttp)]\textsubscript{2} and PhSO\textsubscript{2}NH\textsubscript{2}. The mechanism of thermolysis was elucidated to go through homolytic cleavage. Through equilibrium studies, the Rh(ttp)-NH\textsubscript{2}SO\textsubscript{2}Ph bond strength was estimated to be 62 kcal mol\textsuperscript{-1}.

\[
2\text{Rh(ttp)NHSO}_2\text{Ph} \xrightarrow{\text{C}_6\text{D}_6, 60-110 ^\circ\text{C}, 11 \text{ d}} \xrightarrow{23\%} [\text{Rh(ttp)}]_2 + \text{PhSO}_2\text{NH}_2 \xrightarrow{28\%} 30\%
\]
摘要

在鹼性條件下，Rh(ttp)Cl 和苯磺酰胺可以成功地合成銠吖嗪醯胺絡合物
Rh(ttp)NH2SO2Ph。較短的時間或較強的鹼有助於提高反應速度和產率，氫氧化鉀
可以以最快的速度提供最高的產率。

Rh(ttp)NH2SO2Ph 可以以高選擇性活化各種類型的化學鍵，如 1) 可與甲苯進
行基碳氫鍵活化，2) 可與三正丁胺進行碳氮鍵活化，3) 還可與正丁醚進行碳
碳鍵活化。

研究發現 Rh(ttp)NH2SO2Ph 在加熱條件下不穩定，會產生 [Rh(ttp)]2 和
PhSO2NH2。機理研究顯示 Rh(ttp)NH2SO2Ph 的熱解是以均裂的方式進行。通過化
學平衡的研究，Rh(ttp)-NH2SO2Ph 的鍵強估計為 62 kcal mol⁻¹。
Chapter 1 Introduction

1.1 Importance of Transition Metal Amido Complexes

Transition metal amido complexes refer to compounds containing NH$_2^-$ ligands or its derivatives, such as NHMe$_2^-$, NMe$_2^-$ or N(SiMe$_3$)$_2^-$, attached to a transition metal. Figure 1.1 shows the general structural unit of transition metal amido complexes, with R and R' being the same or different and each is H, alkyl, alkenyl, alkynyl, aryl or M'R$_3$ (M' = Si, Ge or Sn). Late transition metal amido complexes, especially of the 4d- and 5d- series, are sparse.$^1$ Transition metal amido complexes are chemically interesting due to their important roles in carbon-nitrogen bond formation reactions and efficient catalysts in organic transformations.$^2,^3$

\[
\text{M} - \ddot{\text{N}} - \text{R} - \text{R'}
\]

Figure 1.1 Structural unit of metal amido complex

1.1.1 Transition Metal Amido Complexes as Catalysts

Transition metal amido complexes can act as catalysts for different chemical transformations. The amido ligand acts as an ancillary ligand in these systems. One of the examples is the chelation assisted Kumada coupling of Grignard reagents with aryl halides catalyzed by amido pincer complexes of nickel. Both aryl and alkyl Grignard reagents successfully couple with phenyl halides in the presence of a catalytic amount of [Ph-PNP]NiCl. ([Ph-PNP] = [N(o-C$_6$H$_4$PPh$_2$)$_2$]) (Scheme 1.1).$^4$
Scheme 1.1 Catalytic Kumada Coupling by [Ph-PNP]NiCl

Bifunctional iridium amido complex can also catalyze the enantioselective direct amination of α-cyanoacetates to provide the corresponding hydrazine adducts in high yields. (Scheme 1.2).^5

Scheme 1.2 Iridium amido complex catalyzed amination of α-cyanoacetates

1.1.2 Transition Metal Amido Complexes as Reaction Intermediates

Transition metal amido complexes are often found to be active intermediates in different carbon-heteroatom bond formations, such as carbon-nitrogen bond and carbon-flourine bond formations. This type of reaction is important since amines and their derivatives are often be used as dyes, surfactants and pharmaceutical agents.^6 Reported examples of C-N bond formation involving transition metal amido complexes include hydroamination of olefin^7 and arylamination.^8 In both processes, reductive elimination from the corresponding amido complex generates the desired
products.

Scheme 1.3 shows the proposed mechanism for hydroamination of olefins. An amido hydrido complex is first generated by the oxidative addition of amine N-H bond to the catalyst. Then, insertion of the coordinated olefin to this complex occurs, followed by product formation through C-H reductive elimination.²

Scheme 1.3 Proposed mechanism for hydroamination of olefins

The proposed mechanism of the coupling reaction between secondary amine and aryl bromide is shown in Scheme 1.4. In this reaction, reductive elimination of transition metal amido complex generated by the deprotonation of a coordinated amine gives the desired aryl amine.²⁶
1.2 Bonding Nature of Late Transition Metal Amido Complexes

Late transition metal-nitrogen bonded complexes are relatively difficult to synthesize compared with their early transition metal counterparts. This could be explained by their bonding nature. Three theories that could be used to explain their bonding nature are i) hard-soft acid-base theory, ii) \( \pi \)-conflict theory and iii) \( E-C \) approach.

Hard-soft acid-base (HSAB) theory suggests that the transition metal-heteroatom complexes should have weak bonds and are highly reactive due to the mismatch of hard ligand bases with soft metal centres. However, there are examples that contradict to the HSAB theory. For example, exchange reactions conducted by
Bergman et al. using complexes of type (PMe₃)₄Ru(H)X (X = H, OAr, NHAr, CH₂Ph) have shown that the relative order of bond strengths was Ru-H > Ru-OPh > Ru-NHPh > Ru-CH₂Ph.¹² This is inconsistent with the HSAB theory which predicts that the softer N-based ligand should form a stronger bond than the harder O-based ligand.¹³ This study indicates that HSAB theory is not comprehensive to describe the bonding of late transition metal amido complexes. Besides, this theory only deals with gas phase conditions,¹⁴ thus an alternative model is required to explain the trend.

1.2.1 Theory of π Conflict

A molecular orbital approach has been developed to explain the relatively high bond dissociation energy and high reactivity of metal-nitrogen bond.

The π-conflict theory suggests that the high reactivity of late transition metal (≥d⁶) amido complexes arises from the filled-filled π-interaction (Figure 1.2).³

![Figure 1.2 Filled-filled π-interaction between late transition metal and heteroatom](image)

Early transition metals usually have low d-electron counts and possess empty d-orbitals of correct symmetry. These conditions result in the formation of π-bonding
lowering both the energy of the complex and the reactivity of the heteroatom lone pair. On the other hand, in many late transition metals, the appropriate d-orbitals are filled. Therefore, both $\pi$ bonding and the $\pi^*$ antibonding molecular orbital are occupied, resulting in a repulsive four-electron destabilization which increases the ground state energy and makes the heteroatom lone pair more nucleophilic. The $\pi$-conflict model is similar to the filled-filled interactions which cause weakening of the N-N bond in hydrazines or the F-F bond in difluorine.

This model can also account for the thermodynamic trends in bonding. The stronger metal-oxygen bond than metal-nitrogen bond can be explained by the stronger $\pi$-donating ability of nitrogen-based ligands. With less donating oxide ligands, the extent of $\pi\pi$-$d\pi$ repulsion is reduced, thus the $\text{M-O}$ bond is thermodynamically more stable. Moreover, aryl substituents on the ligand are favoured over the alkyl ones because of the ability of an aryl ring to delocalize the lone pair electron and to lower the energy level of the high-lying heteroatom $\pi$-orbital. To conclude, the relative bond energy of $\text{M-X}$ moieties is in the following order: $\text{M-OAryl} > \text{M-OAlkyl} \approx \text{M-NH} \text{Aryl} > \text{M-NH} \text{Alkyl}$.

However, in the exchange reaction between $\text{Cp}^*\text{Ni(PEt}_3\text{)}\text{NHTol}$ and different anilido ligands reported by Bergman et al, there was little difference between the equilibrium constants for an aniline containing a para-dimethylamino group (a
resonance π-donor) and one with a meta-dimethylamino group (a weak π-donating ligand) (Scheme 1.5). This could not be explained by the π-conflict model which predicts that π-donating substituents would be much favoured. Therefore a better way to interpret relative M-N bond energies is needed.

\[
\text{Cp}^*\text{Ni(PEt}_3\text{)}\text{NH}_2 + \text{XC}_6\text{H}_4\text{NH}_2 \rightleftharpoons \frac{K_{eq}}{C_6\text{D}_6} \ \text{Cp}^*\text{Ni(PEt}_3\text{)}\text{NCH}_6\text{H}_4\text{X} + \text{TolNH}_2
\]

\[
X = \text{p-NMe}_2, K_{eq} = 0.2
\]

\[
X = \text{m-NMe}_2, K_{eq} = 1.1
\]

**Scheme 1.5** Equilibrium constants for amide/amine exchange

1.2.2 *E-C* Approach

According to the *E-C* theory, the bond enthalpy for a covalent bond can be separated into electrostatic and covalent components, \( E_AE_B \) and \( C_AC_B \), respectively. \( E_A \) and \( C_A \) represent the electrostatic and covalent bonding tendencies of the catimer (the positive end of the polar covalent bond), while \( E_B \) and \( C_B \) describe the electrostatic and covalent bonding tendencies of the animer (negative end of a polar covalent bond). Since \( E_AE_B \) and \( C_AC_B \) represent properties of the formed molecule, an additional term, \( T_AR_B \), is needed to describe homolytic bond energies, where \( T_A \) is the transference of the catimer and \( R_B \) is the receptance of the animer and their product describes the energy of shifting charge in neutral radicals to the polar bond in the molecule. The bond dissociation energy (BDE) can be described by equation 1.1.

\[
\text{BDE} = E_AE_B + C_AC_B + T_AR_B \quad (1.1)
\]
Due to the great difference in electronegativity between metal and the heteroatom, a M-X bond is highly polar in nature (Scheme 1.6). The greater the electronegativity difference, the larger the coulombic contribution (larger $E_A E_B$), resulting in a stronger, yet reactive M-X moiety.

\[ \begin{array}{c}
\text{M-X} \\
\leftrightarrow \\
\text{M} \quad \text{X}
\end{array} \]

**Scheme 1.6** Resonance structure of M-X bonds

Both the reactivity and the thermodynamic trends of late transition metal-heteroatom bonds could be explained by the $E-C$ theory. The nucleophilicity of M-X bond can be account by the significant negative charge localization on the electronegative heteroatom. The preference for oxide over amido ligands results from the higher polarity of the bond which stabilizes the complex. In addition, electron withdrawing groups on X, which favour negative charge on X and increase the bond polarity, would stabilize M-X complexes.

![Figure 1.3](image)

**Figure 1.3** Evolution of bonding theories for transition metal-nitrogen bond

### 1.3 Synthesis of Transition Metal Amido Complexes

A few methods exist for the synthesis of late transition metal amido complexes, including transmetallation with an alkali metal amide, deprotonation of coordinated
amines and hydride addition across an organic azide.

1.3.1 Transmetallation

The first method utilizes the transmetallation of a transition metal halide with alkali metal amide, MX (X = Cl, F and so on) (eq 1.2).

\[
L_nM-X + LiNRR' \rightarrow L_nM-NRR' + LiX \quad (1.2)
\]

In 1979, the first rhodium amido complex was prepared by transmetallation between a 16-electron rhodium chloride complex and a lithium amide. The use of the bulky \( \beta \)-elimination-stable amide \([N(SiMe_3)_2]^+\) led to the isolation of the 14-electron complex (eq 1.3).\(^{17}\)

\[
\text{RhCl(PPh}_3)_3 + \text{LiN(SiMe}_3)_2 \rightarrow \text{Rh(PPh}_3)_2[N(SiMe}_3)_2] + \text{LiCl + PPh}_3 \quad (1.3)
\]

When \((\text{dmpe})_2\text{RuHCl}\) (dmpe = 1,2-\( \text{bis(dimethylphosphino)ethane}\)) was treated with \(\text{NaNH}_2\), \((\text{dmpe})_2\text{RuH(NH}_2)\) was formed with 81% yield and it was the first characterized monomeric late transition metal parent amido complex (eq 1.4).\(^{18}\)

\[
\begin{array}{c}
\text{Me}_2\text{Cl} \\
\text{Me}_2\text{H} \\
\text{Me}_2
\end{array}
\text{P} \quad \text{P} \quad \text{P} \\
\text{P} \quad \text{P} \quad \text{P} \\
\text{Me}_2 \\
\text{Me}_2 \\
\text{Me}_2
\begin{array}{c}
\text{Me}_2 \\
\text{Me}_2 \\
\text{Me}_2
\end{array}
\text{Cl} \\
\text{H} \\
\text{NH}_2
\begin{array}{c}
\text{NaNNH}_2 \\
\text{NH}_3 (\ell) \rightarrow \text{THF} \\
\end{array}

\begin{array}{c}
\text{Me}_2\text{Cl} \\
\text{Me}_2\text{H} \\
\text{Me}_2
\end{array}
\text{P} \quad \text{P} \quad \text{P} \\
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\text{Me}_2 \\
\text{Me}_2
\begin{array}{c}
\text{Me}_2 \\
\text{Me}_2 \\
\text{Me}_2
\end{array}
\text{NH}_2 \text{Me}_2 \\
\text{Me}_2 \\
\text{Me}_2
\begin{array}{c}
\text{Me}_2 \\
\text{Me}_2 \\
\text{Me}_2
\end{array}
\text{81%}
\end{array}
\]

Transmetallation of nickel fluoride complex with lithium amide also gave nickel amido complex, the formation of stable and insoluble salt LiF provided the driving force for the reaction (Scheme 1.7).\(^{19}\)
1.3.2 Deprotonation of Coordinated Amine

The second approach makes use of the deprotonation of a coordinated amine to obtain late transition metal amido complexes; this process is driven by the enhanced acidity of the amino proton after coordination (eq 1.5).\textsuperscript{20}

\[
\text{L}_n\text{M}(\text{HNRR'})^+ + \text{B} \rightarrow \text{L}_n\text{M-NRR'} + \text{BH}^+ \quad (1.5)
\]

The successive deprotonation of the ethylenediamine $N$-hydrogen atom of [Rh(en)$_3$I$_3$] with KNH$_2$ in liquid ammonia gave a series of rhodium amides which were all very moisture sensitive (Scheme 1.8).\textsuperscript{21}

\[
[\text{Rh}(\text{en})_3]_3 \xrightarrow{\text{KNH}_2} \text{NH}_3 (\ell), -70 \, ^\circ\text{C} \rightarrow [\text{Rh}(\text{en})_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH})]_2
\]

\[
3 \text{KNH}_2 \xrightarrow{\text{NH}_3 (\ell), -33.5 \, ^\circ\text{C}} [\text{Rh}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH})_3]
\]

\[
2 \text{KNH}_2 \rightarrow [\text{Rh}(\text{en})(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH})_2]_2
\]

**Scheme 1.8** Formation of rhodium amido complexes by deprotonation of [Rh(en)$_3$I$_3$]

Ruthenium parent amido complexes can also be prepared by this method, however their solubility and sensitivity characteristics prohibited their isolation in a pure state (Scheme 1.9).\textsuperscript{22}
Scheme 1.9 Preparation of parent ruthenium amido complex by deprotonation of coordinated amine

1.3.3 Hydride Addition across Organic Azide

The third approach for the preparation of transition metal amido complexes involves hydride addition across an organic azide with the extrusion of dinitrogen (eq 1.6).

$$\text{L}_n\text{M-H} + \text{R}_n\text{N}_3 \rightarrow \text{L}_n\text{M-NRH} + \text{N}_2 \quad (1.6)$$

For examples, the reactions of p-tolylazide with (bipy)Ni(R)$_2$ (R=Me, Et, bipy = 2.2'-bipyridine) and nickelacylopentane complex (bipy)Ni(CH$_2$)$_4$ gave the corresponding nickel(II) amido complexes. In both reactions, dinitrogen gas was generated as a co-product (eqs 1.7 and 1.8).
1.4 Reactivity of Transition Metal Amido Complexes

1.4.1 β-Elimination

Since NR$_2^-$ is isoelectric with an alkyl CR$_3^-$, late transition metal amido complexes share similar decomposition pathway with their alkyl counterparts, for example, β-elimination (Scheme 1.10).$^{24}$

\[
\begin{align*}
\text{H} & \quad \text{C} \quad \text{X} \\
\text{L}_n\text{M} & \quad \text{L}_n\text{M} \\
\text{X} = & \text{CR}_2, \text{NR}
\end{align*}
\]

**Scheme 1.10** β-Elimination of metal amides and metal alkyls

β-Elimination of late transition metal amido complexes is important as it provides a way for the preparation of late transition metal hydride. Lithium dimethylamide, LiNMe$_2$, reacts with late transition metal chloride to give late transition metal amido complexes which rapidly undergo β-elimination to produce late transition metal hydride (Scheme 1.11).$^{25}$

\[
\begin{align*}
(P\text{Ph}_3)_3\text{RhCl} + \text{LiN(CH}_3)_2 & \rightarrow [(P\text{Ph}_3)_3\text{RhN(CH}_3)_2] \rightarrow (P\text{Ph}_3)_3\text{RhH} + \text{N}_2 \\
(P\text{Ph}_3)_4\text{RuCl}_2 + \text{LiN(CH}_3)_2 & \rightarrow [(P\text{Ph}_3)_4\text{Ru}[\text{N(CH}_3)_2]\text{Cl}] \rightarrow (P\text{Ph}_3)_3\text{RuHCl} + \text{N}_2
\end{align*}
\]

**Scheme 1.11** β-Elimination of transition metal amides to give transition metal hydride

The first example of direct observation of β-hydrogen elimination in a monomeric late transition metal amido complex was reported in 1996 by Hartwig et al. In the thermal reaction of iridium benzylanilide, the stable N-phenyltoluenimine together with iridium hydride was formed in high yield (eq 1.9).$^{26}$
Through β-elimination of transition metal amido complexes, a metal-coordinated imine complex can also be formed. Methylnickel amido complexes of type [Ni(Me)(ECHRR')(dippe)] (dippe = 1,2-bis(diisopropylphosphino)ethane, ECHR = pyrrolidino, dibenzylamido) are thermolabile and generate the corresponding Ni(0) η²-imine derivatives and methane (Scheme 1.12).²⁷

\[
\text{ECHRR'} = \text{NC}_4\text{H}_8, \text{N(CH}_2\text{Ph})_2
\]

**Scheme 1.12** β-Elimination of nickel(II) amido complex to give nickel-coordinated imine

### 1.4.2 Insertion

Late transition metal amido complexes are well-known to undergo insertion reactions with various electrophilic agents including carbon monoxide and carbon dioxide as well as organic compounds like olefins and isocyanates (eq 1.10 and Scheme 1.13).

\[
\text{L}_n\text{M-NRR} + Z \longrightarrow \text{L}_n\text{M-Z-NRR'} \quad (1.10)
\]

\[
Z = \text{CO}_2, \text{CO}, \text{SO}_2, S=\text{CNR}, \quad \text{CH}_2=\text{CO}, =\]
Scheme 1.13 Insertion reaction of transition metal amido complexes

The first example of CO insertion into late transition metal-nitrogen bonds was observed in 1985 by Brynda et al. Carbon monoxide was inserted into the Pt-N bond of (dppe)Pt(CH$_3$)[N(CH$_2$Ph)H] and (dppe)Pt(CH$_3$)(NMe$_2$) (dppe = 1,2-\textit{bis}(diphenylphosphino)ethane) to give (dppe)Pt(CH$_3$)[C(0)N(CH$_2$Ph)(H)] and (dppe)Pt(CH$_3$)[C(0)NMe$_2$], respectively in high yields (eq 1.11 and 1.12).$^{28}$

\[
\begin{align*}
\text{Ph$_2$P-Pt-NH} & \quad \text{CO (3 atm)} \quad \text{25 °C} \quad \text{Ph$_2$P-Pt-C-NH} \quad 80\% \\
\text{Ph$_2$P-Pt-NMe$_2$} & \quad \text{CO (3 atm)} \quad \text{25 °C} \quad \text{Ph$_2$P-Pt-C-NMe$_2$} \quad 76\%
\end{align*}
\]

Similar CO insertion into the Ru-N bond of Cp*Ru(dcpe)NH$_2$ (dcpe = 1,2-\textit{bis}(dicyclohexylphosphino)ethane) gave the foramide complex (eq 1.13).$^{22}$

\[
\begin{align*}
\text{H$_2$N-Ru-PCy$_2$} + \text{CO} \quad \text{THF} \quad \text{H$_2$N(O)-Ru-PCy$_2$} \\
\text{Cy$_2$P} & \quad \text{96%}
\end{align*}
\]
One of the early examples of insertion of heterocumulenes (CO₂, CS₂, RNCO) to late transition metal amido complexes is the insertion of electrophilic acrylonitrile into the Pt-N bond of hydrido amido complex trans-Pt(PEt₃)₂H(NHPh) to form trans-PtH[CH(CN)(CH₂NHPh)](PEt₃)₂, which reductively eliminates 3-anilinopropionate (Scheme 1.14).²⁹

Scheme 1.14 Olefin insertion of acrylonitrile into platinum amido complex

In 1991, Bergman and co-workers reported that Cp*IrPPh₃(NHR)H reacted with carbon disulfide to give Cp*IrPPh₃(SC(S)NHPh)(H) (eq 1.14).³⁰

Nickel(II) amido complex also reacts with carbon dioxide to give an addition product. Isocyanate and isothiocyanate also react with the amido complex to give the corresponding insertion products (Scheme 1.15).¹⁹
1.4.3 Reductive Elimination

Reductive elimination is commonly observed for transition metal amido complexes, this process is important for the formation of carbon-heteroatom bond.

In 1994, Boncella and co-workers discovered that monomeric PMe₃-ligated palladium amido complex containing an imido substituted aryl group gave diarylamine via reductive elimination (eq 1.15).[^31]

\[
\begin{align*}
\text{Ph-NHPh} & \xrightarrow{80 \, ^\circ \text{C}} \text{Ph-NHPh} + \text{Pd}^0 \quad (1.15)
\end{align*}
\]

In addition, Hartwig et al. reported that a palladium amido aryl complex underwent reductive elimination of arylamine in high yields (Scheme 1.16 and eq 1.16).[^32][^33]
Scheme 1.16 Reductive elimination of arylamine from palladium amido complexes

1.4.4 Bond Activation

Examples of bond activation by late transition metal amido complexes are limited. Bergman and co-workers reported that a ruthenium amido complex activated the carbon-hydrogen bond in phenylacetylene, 1,2-propadiene as well as cyclobutanone via elimination of ammonia in moderate to good yields (Scheme 1.17).34
1.5 Structural Features of Rhodium Porphyrin Complexes

Since my research work uses rhodium prophyrin complexes, its chemistry is briefly reviewed below.

Porphyrin ligand is heteroatom marcoycles consisting of four modified pyrrole subunits with methine linkages (=CH-). It is a tetradebate and dianionic ligand with an 18π-electron conjugated system. The highly conjugated system results in intense absorptions at the visible region which lead to its intense colour.\(^{35}\)
Electronic and steric properties of porphyrins can be modified at the meso (R) and β (X) positions. Table 1.1 lists some examples of porphyrins and their abbreviation.

**Table 1.1 Examples of Porphyrin and their Abbreviation**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Porphyrin</th>
<th>X</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂(oep)</td>
<td>Octaethylporphyrin</td>
<td>Ethyl</td>
<td>H</td>
</tr>
<tr>
<td>H₂(tmp)</td>
<td>Tetramesitylporphyrin</td>
<td>H</td>
<td>2,4,6-(CH₃)C₆H₂</td>
</tr>
<tr>
<td>H₂(tpp)</td>
<td>Tetraphenylporphyrin</td>
<td>H</td>
<td>C₆H₅</td>
</tr>
<tr>
<td>H₂(tpp)</td>
<td>Tetratolyporphyrin</td>
<td>H</td>
<td>4-CH₃C₆H₄</td>
</tr>
</tbody>
</table>

The four nitrogen atoms in the porphyrin ligand are planar, with diagonal radii to the centre of the macrocycle equal to 2.098 Å. This allows for the coordination of different metals. Metalloporphyrins can be formed by replacing two inner pyrrole protons by a metal ion (eq 1.18).

\[
M^{n+} + H₂(por) \xrightarrow{\text{metallation}} 2H^+ + [M(por)]^{(n-2)+} \xrightarrow{\text{demetallation}} (1.18)
\]

1.6 Examples of Metalloporphyrin Complexes Containing Nitrogen Ligands

Early examples of metalloporphyrins with nitrogen containing ligands were mainly metal nitrene complexes. The first nitrene complex of a metalloporphyrin was reported by Mansuy et al. in 1982. The complex was formed from the reaction of
Fe(tpp)Cl and 1-amino-2,2,6,6-tetramethylpiperidine by an O2-dependent oxidation (eq 1.19).  

\[
\text{Fe(tpp)Cl} + \text{H}_2\text{N-NH}_2 \xrightarrow{\Delta, \text{CH}_2\text{Cl}_2, 20^\circ \text{C}, 10 \text{ min}} \text{Fe} \quad \text{90%} 
\]

Iron porphyrin nitrene complexes had been proposed to be active intermediates of alkene aziridination by [(tosylimido)iodo]benzene, PhI=NTs (Scheme 1.18).  

\[
\text{Fe} = \text{Fe(tpp)} 
\]

**Scheme 1.18** Catalytic alkene aziridination by [(tosylimido)iodo]benzene using Fe(tpp)Cl

In the 1990s, various metalloporphyrin imido complexes have been reported, such as Ru\textsuperscript{VI}O(por)(N\textsuperscript{tBu}) (por = tpp, ttp)\textsuperscript{40} and Zr\textsuperscript{IV}(ttp)NAr\textsuperscript{Pr} (Ar\textsuperscript{Pr} = 2,6-diisopropylphenyl).\textsuperscript{41} It was discovered that the zirconium porphyrin imido complex reacted with isocyanate to give an \(\eta^2\)-ureato-N,O complex (eq 1.20).\textsuperscript{41}

\[
\text{Zr} + \text{tBuNCO} \xrightarrow{20-25^\circ \text{C}, 13 \text{ h \ toluene}} \text{Zr} \quad \text{32%} 
\]

\[
\text{Zr} = \text{Zr(tpp)} 
\]
Fewer examples of middle transition metalloporphyrin amido complexes were reported, for example Ru$^{IV}$(ttp)(NH-$p$-C$_6$H$_4$Cl)$_2$ and Os$^{IV}$(por)(NPh$_2$)(OH) (por $=$ tpp, ttp). However, examples of rhodium porphyrin amido complexes have not yet been reported.

### 1.7 Bond Activation by Rhodium Porphyrins

Bond activation by rhodium(II) and rhodium(III) porphyrins has been well studied. Examples of bond activation by rhodium(II) porphyrin include the carbon-hydrogen bond activation (CHA) of aldehyde, carbon-nitrogen bond activation (CNA) of isocyanides as well as methane activation (eq 1.21-1.23).

**CHA of aldehyde**

\[
[Rh(oep)]_2 + (CH_3)_2CHCHO \xrightarrow{23 \, ^\circ C} \frac{C_6D_5}{C_6D_5} \xrightarrow{23 \, ^\circ C} \text{Rh(oep)C(CH}_3\text{)_2CHO} + \text{Rh(oep)H} \quad (1.21)
\]

**CNA of isocyanides**

\[
[Rh(oep)]_2 + 2 \text{CNR} \xrightarrow{22 \, ^\circ C} \frac{C_6D_5}{C_6D_5} \xrightarrow{22 \, ^\circ C} \text{Rh(oep)R} + \text{Rh(oep)(CN)(RNC)} \quad (1.22)
\]

**methane activation**

\[
\text{Rh(tmp) + CH}_4 \xrightarrow{80 \, ^\circ C} \frac{C_6D_6}{C_6D_6} \xrightarrow{80 \, ^\circ C} \text{Rh(tmp)H} + \text{Rh(tmp)CH}_3 \quad (1.23)
\]

In addition, Chan’s group has discovered the carbon-carbon bond activation (CCA) of nitroxides, ketones, amides, esters and nitriles by Rh$^{II}$(tmp) (eq 1.24-1.28).
aliphatic CCA of nitrooxide

\[
\text{Rh(tmp) + } \begin{array}{c}
\text{R} \\
\text{N} \\
\text{O} \\
\text{R}
\end{array} \xrightarrow{70-110 \degree C, \text{benzene}} \text{Rh(tmp)R} \\
R = \text{Me, Et} >70\% 
\]

aliphatic CCA of ketone

\[
\text{Rh(tmp) + } \begin{array}{c}
\text{O}
\end{array} \xrightarrow{100 \degree C, 2 \text{ d}, \text{PPh}_3} \text{Rh(tmp)Me} \\
>70\% 
\]

aliphatic CCA of amide

\[
\text{Rh(tmp) + } \begin{array}{c}
\text{O}
\end{array} \xrightarrow{100 \degree C, 6 \text{ h}, \text{PPh}_3} \text{Rh(tmp)Me} \sim 40\% 
\]

aliphatic CCA of ester

\[
\text{Rh(tmp) + } \begin{array}{c}
\text{O}
\end{array} \xrightarrow{130 \degree C, 1 \text{ d}, \text{PPh}_3} \text{Rh(tmp)Me} \\
29\% 
\]

aliphatic CCA of nitrile

\[
\text{Rh(tmp) + } \begin{array}{c}
\text{Me}
\end{array} \xrightarrow{150 \degree C, 2 \text{ d}, \text{PPh}_3} \text{Rh(tmp)Me} \\
52\% 
\]

Recently, Chan's group has discovered the base-promoted benzylic carbon-hydrogen bond activation (BnCHA) of toluene\textsuperscript{47}, CHA of alkane\textsuperscript{48}, CCA of ethers\textsuperscript{49} as well as CHA of aldehydes\textsuperscript{50} by rhodium(III) porphyrins (eqs 1.29-1.32).
BnCHA of toluene
\[ \text{Rh(ttp)Cl} + \text{PhCH}_3 \xrightarrow{10 \text{ equiv of } \text{K}_2\text{CO}_3} \text{Rh(ttp)Bn} \xrightarrow{120 \, ^\circ \text{C}, 30 \text{ min}, \text{N}_2} \]
\[ 97\% \]  

CHA of alkane
\[ \text{Rh(ttp)Cl} + \text{PhCH}_3 \xrightarrow{10 \text{ equiv of } \text{K}_2\text{CO}_3} \text{Rh(ttp)} \xrightarrow{120 \, ^\circ \text{C}, 6 \text{ h}, \text{N}_2} \]
\[ 59\% \]  

CCA of ether
\[ \text{Rh(tmp)I} + \text{"Bu}_2\text{O} \xrightarrow{10 \text{ equiv of KOH}} \text{Rh(tmp)"Pr} \xrightarrow{100 \, ^\circ \text{C}, 1 \text{ d}, \text{N}_2} \]
\[ 86\% \]  

CHA of aldehyde
\[ \text{Rh(ttp)Me} + \text{PhCHO} \xrightarrow{200 \, ^\circ \text{C}, 0.5 \text{ h}} \text{Rh(ttp)C(O)Ph} + \text{Rh(ttp)Me} \]
\[ 82\% \]  

1.8 Objectives of the Work

In order to extend the scope of bond activation by rhodium(III) porphyrin complexes, my thesis focuses on the:


2. Examination of the reactivity and bond activation chemistry of rhodium porphyrin amido complex.
Chapter 2 Synthesis and Reactivity Studies of Rhodium Porphyrin Amido Complexes

2.1 Synthesis of Porphyrin and Rhodium Porphyrin Chloride

Tetratolyporphyrin (H_{ttp}) was prepared in 12% yield by the tetramerization of pyrrole and 4-methylbenzaldehyde in refluxing propionic acid (eq 2.1).\(^{51}\)

\[
\begin{align*}
4 \quad \text{pyrrole} &+ 4 \quad \text{4-methylbenzaldehyde} \quad \text{reflux, 30 min} \quad \to \quad \text{H}_{ttp} \\
\text{(2.1)} &+ 12\%
\end{align*}
\]

Rh(ttp)Cl was prepared in 68% yield by refluxing H_{ttp} with rhodium trichloride in benzonitrile for 3 hours (eq 2.2).\(^{52}\)

\[
\begin{align*}
\text{H}_{ttp} &+ \text{RhCl}_3 \cdot x\text{H}_2\text{O} \quad \text{reflux, 3 h} \quad \to \quad \text{Rh(ttp)Cl} \\
\text{(2.2)} &+ 268\%
\end{align*}
\]

2.2 Synthesis of Rhodium Porphyrin Amido Complexes from Rhodium Porphyrin Chloride

Rhodium porphyrin amido complexes were synthesized from Rh(ttp)Cl by i) transmetallation with lithium amides\(^{53}\) and ii) base-promoted ligand substitution.\(^{47-49}\) (Scheme 2.1)
Scheme 2.1 Synthetic methods for rhodium porphyrin amido complexes

2.2.1 By Transmetallation with Lithium Amide

Transmetallation of metal complexes with lithium amide has been used to prepare metal amido complexes.17-19 Therefore lithium benzenesulfonamidate, freshly prepared from PhSO₂NH₂ and "BuLi, was reacted with Rh(ttp)Cl to produce rhodium porphyrin amido complexes (eq 2.3).

\[
\text{PhSO}_2\text{NH}_2 + "\text{BuLi} \xrightarrow{\text{THF, -78 °C, 6 h}} \text{PhSO}_2\text{NH}^+\text{Li}^+ \xrightarrow{\text{r.t., 1d}} \text{Rh(ttp)NHSO}_2\text{Ph}}
\]

(2.3)

Table 2.1 Transmetallation of Rh(ttp)Cl with lithium salt of PhSO₂NH₂

<table>
<thead>
<tr>
<th>Entry</th>
<th>PhSO₂NH₂:&quot;BuLi:Rh(ttp)Cl</th>
<th>Yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.3 : 2.0 : 1.0</td>
<td>29</td>
</tr>
<tr>
<td>2</td>
<td>2.5 : 4.0 : 1.0</td>
<td>53</td>
</tr>
<tr>
<td>3</td>
<td>1.3 : 4.0 : 1.0</td>
<td>60</td>
</tr>
</tbody>
</table>

When the ratio of the lithium amide to Rh(ttp)Cl was 1.3:1, only 29% yield of Rh(ttp)NHSO₂Ph was isolated after 1 day (Table 2.1, entry 1). Doubling the ratio increased the yield of Rh(ttp)NHSO₂Ph to 53% (Table 2.1, entry 2). The enhanced yield is likely due to the increased amount of PhSO₂NHLi⁺ generated for more facile transmetallation. Increasing the amount of "BuLi also increased the yield of
Rh(ttp)NHSO$_2$Ph to 60% (Table 2.1, entries 1 and 3), again for more facile transmetallation.

The successful preparation of Rh(ttp)NHSO$_2$Ph by transmetallation, has led to the attempted preparation of other rhodium porphyrin amide by the reaction of Rh(ttp)Cl with various amide anions (eq 2.4).

\[
\text{HNRR'} + \text{LiNRR'} \rightarrow \text{product (2.4)}.
\]

| Table 2.2 Transmetallation of Rh(ttp)Cl with different lithium salt |
|---|---|---|---|---|
| Entry | Substrate | $pK_a$ in DMSO$^{54}$ | Time | Product | Yield/% |
| 1 | PhSO$_2$NH$_2$ | 16.1 | 1 d | Rh(ttp)NHSO$_2$Ph (3a) | 53 |
| 2 | PhNH$_2$ | 30.6 | 1 d | unknowns | --- |

Lithium phthalimide also reacted successfully with Rh(ttp)Cl to give the corresponding rhodium porphyrin amido complex, Rh(ttp)(C$_8$H$_4$NO$_2$) (3b) in 32% yield (Table 2.2, entry 1). However, the rate of reaction was much slower and the reaction completed only after 5 days. When more basic substrates, such as benzamide, 2-pyrrolidone and aniline, were used, no rhodium porphyrin amido complexes were
obtained (Table 2.2, entries 3-5). The unsuccessful isolation of the rhodium porphyrin amide is probably due to its instability under the reaction conditions (Section 2.2.2.1).

2.2.2 By Base-promoted Ligand Substitution Using Rh(ttp)Cl

A few disadvantages of transmetallation exist. Firstly, highly reactive "BuLi is needed. Secondly, the reaction takes a long time. Thirdly, it is a multi-step process. Lithium salt needs to be prepared separately before reacting with Rh(ttp)Cl.

Previously, Chan's group has reported the base-promoted bond activations of various hydrocarbons using Rh(ttp)Cl. For example, Rh(ttp)Cl reacts with toluene in the presence of K$_2$CO$_3$ to give Rh(ttp)Bn in high yield. To our delight, Rh(ttp)NH$_2$SO$_2$Ph was obtained in 56% yield when Rh(ttp)Cl was reacted with benzenesulfonamide in the presence of K$_2$CO$_3$ after 1 day at 120 °C (eq 2.5). Likely the fairly active nitrogen-hydrogen bond of benzenesulfonamide was deprotonated in situ to facilitate the ligand substitution.

$$\text{Rh(ttp)Cl} + \text{PhSO$_2$NH$_2$} \xrightarrow{\text{10 equiv}} \text{C$_6$D$_6$, K$_2$CO$_3$ (10 equiv)} \xrightarrow{\text{N$_2$, 120 °C, 1 d}} \text{Rh(ttp)NH$_2$SO$_2$Ph} \quad (2.5)$$

2.2.2.1 Optimization of Reaction Conditions

After the successful preparation of Rh(ttp)NH$_2$SO$_2$Ph from Rh(ttp)Cl and K$_2$CO$_3$, the reaction conditions were further optimized.
i) Effect of Reaction Time

The previously reported late transition metal amido complexes were not stable,\textsuperscript{22,25} therefore the reaction time was shortened to minimize decomposition of Rh(ttp)NHSO\textsubscript{2}Ph upon heating (eq 2.6).

\[
\text{Rh}(\text{ttp})\text{Cl} \ 2 + \text{PhSO}_2\text{NH}_2 \ (10 \text{ equiv}) \xrightarrow{\text{C}_6\text{H}_6, \text{K}_2\text{CO}_3 \ (10 \text{ equiv}) \ N_2, 120 \degree\text{C}, \text{time}} \text{Rh}(\text{ttp})\text{NHSO}_2\text{Ph} \ (3a)
\]

When the reaction time was shortened from 1 day to 2 hours, the yield of Rh(ttp)NHSO\textsubscript{2}Ph increased from 56\% to 75\%. This suggests that Rh(ttp)NHSO\textsubscript{2}Ph is not stable upon prolonged heating.

ii) Effect of Substrate Loading

Then, the effect of different substrate loading was investigated (eq 2.7). With 1 equivalent of PhSO\textsubscript{2}NH\textsubscript{2}, only 20\% of Rh(ttp)NHSO\textsubscript{2}Ph was produced after 2 hours (Table 2.3, entry 1). When the substrate loading was increased to 3 equivalents, the yield of Rh(ttp)NHSO\textsubscript{2}Ph increased to 70\% (Table 2.3, entry 2). When the substrate loading was further increased to 5 or 10 equivalents, the yield of Rh(ttp)NHSO\textsubscript{2}Ph leveled off in 78\% and 75\%, respectively (Table 2.3, entries 3 and 4). Therefore, 3 equivalents of PhSO\textsubscript{2}NH\textsubscript{2} were used in further preparation.
\[
\text{Rh(ttp)Cl} + \text{PhSO}_2\text{NH}_2 \rightarrow \text{Rh(ttp)NHSO}_2\text{Ph} \quad (2.7)
\]

### Table 2.3 Effect of substrate loading on the preparation of Rh(ttp)NHSO\(_2\)Ph

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate loading (equiv)</th>
<th>Yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>70</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>78</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>75</td>
</tr>
</tbody>
</table>

**iii) Effect of Temperature**

Next, the effect of temperature on the formation of Rh(ttp)NHSO\(_2\)Ph was investigated (eq 2.8). When the reaction temperature was lowered to 80 °C, Rh(ttp)NHSO\(_2\)Ph was obtained in 74% after 18 hours. Previously, it was shown that Rh(ttp)NHSO\(_2\)Ph decomposed upon prolong heating at 120 °C. As a result, despite the lower reaction rate, further reactions were carried out at 80 °C.

\[
\text{Rh(ttp)Cl} + \text{PhSO}_2\text{NH}_2 \rightarrow \text{Rh(ttp)NHSO}_2\text{Ph} \quad (2.8)
\]

**iv) Effect of Solvent**

It has been reported that late transition metal amido complexes were synthesized in polar solvents, such as THF, in high yield.\(^{17-19,21}\) Hence, effect of solvent polarity on the formation of Rh(ttp)NHSO\(_2\)Ph by ligand substitution was examined (eq 2.9).
Changing the solvent from benzene to the more polar THF (dielectric constant of benzene and THF are 2.27 and 7.52, respectively)\textsuperscript{55} was not beneficial to either the reaction rate or yield (eq 2.9). The reaction conducted in THF completed after 1 day to give Rh(ttp)NHSO\textsubscript{2}Ph in a similar yield of 72%.

\textit{v) Effect of Counter Anion}

When Rh(ttp)I with a more labile counterion was used instead of Rh(ttp)Cl, Rh(ttp)NHSO\textsubscript{2}Ph was formed in a lower yield of 63% after 18 hours. The use of more labile anion was not beneficial. Therefore, Rh(ttp)Cl was used for the preparation of Rh(ttp)NHSO\textsubscript{2}Ph.

\[
\begin{align*}
\text{Rh(ttp)Cl} & \quad + \quad \text{PhSO}_{2}\text{NH}_{2} \quad \xrightarrow{\text{solvent, K}_2\text{CO}_3 (10 \text{ equiv}), \text{N}_2, 80 \degree \text{C}, \text{time}} \quad \text{Rh(ttp)NHSO}_2\text{Ph} \\
\text{(2.9)} & \quad \text{(3 equiv)} & \quad \text{(3 equiv)} & \quad \text{(2.10)} \\
\text{solvent} = \text{C}_6\text{H}_6, \text{time} = 18 \text{ h, 74\%} & \quad = \text{THF, time} = 1 \text{ d, 72\%} \\
\end{align*}
\]

\textit{vi) Effect of Base}

Since the successful preparation of Rh(ttp)NHSO\textsubscript{2}Ph was carried out with 10 equivalents of K\textsubscript{2}CO\textsubscript{3}, the effect of different bases on the formation of Rh(ttp)NHSO\textsubscript{2}Ph was examined (eq 2.11).

\[
\begin{align*}
\text{Rh(ttp)X} & \quad + \quad \text{PhSO}_{2}\text{NH}_{2} \quad \xrightarrow{\text{C}_6\text{H}_6, \text{K}_2\text{CO}_3 (10 \text{ equiv}), \text{N}_2, 80 \degree \text{C}, 18 \text{ h}} \quad \text{Rh(ttp)NHSO}_2\text{Ph} \\
\text{X} = \text{Cl, 74\%} & \quad = \text{I, 63\%} \\
\text{3a} & \quad \text{(2.10)} \\
\end{align*}
\]
Table 2.4 Effect of base on the preparation of Rh(ttp)NHSO₂Ph

<table>
<thead>
<tr>
<th>Entry</th>
<th>Time</th>
<th>Base</th>
<th>Yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3 d</td>
<td>nil</td>
<td>33*</td>
</tr>
<tr>
<td>2</td>
<td>18 h</td>
<td>K₂CO₃</td>
<td>74</td>
</tr>
<tr>
<td>3</td>
<td>3.5 h</td>
<td>KOH</td>
<td>84</td>
</tr>
</tbody>
</table>

* recovery yield of Rh(ttp)Cl

In the absence of base, no Rh(ttp)NHSO₂Ph was obtained and 33% yield of Rh(ttp)Cl was recovered after 3 days (Table 2.4, entry 1). When a stronger base of KOH was used instead of K₂CO₃, both the rate and yield were enhanced. The reaction time was shortened from 18 to 3.5 hours and the yield of Rh(ttp)NHSO₂Ph increased from 74% to 84% (Table 2.4, entries 2 and 3). With a stronger base, the rate of deprotonation of benzenesulfonamide likely increases. As a result, the reaction is faster.

2.2.2.2 Substrate Scope

The optimized conditions for the preparation of Rh(ttp)NHSO₂Ph required 80 °C, 10 equivalents of KOH and 3 equivalents of PhSO₂NH₂ using benzene as the solvent.
Rh(ttp)Cl + substrate (3 equiv) → product (2.12)

**Table 2.6 Scope of preparation of rhodium porphyrin amido complexes**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>pKₐ in DMSO⁵⁴</th>
<th>BDE of N-H bond (kcal/mol)⁵⁶</th>
<th>Product</th>
<th>Yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PhNH₂</td>
<td>8.3ᵃ</td>
<td>89.1</td>
<td>Rh(ttp)-N</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>PhSO₂NH₂</td>
<td>16.1</td>
<td>105</td>
<td>Rh(ttp)NHSO₂Ph</td>
<td>84</td>
</tr>
<tr>
<td>3</td>
<td>PhNH₂</td>
<td>23.3</td>
<td>107</td>
<td>unknowns</td>
<td>---</td>
</tr>
<tr>
<td>4</td>
<td>PhNH₂</td>
<td>30.6</td>
<td>103.2</td>
<td>PhNH₂</td>
<td>15</td>
</tr>
</tbody>
</table>

ᵃ pKₐ in water was shown.

The substrate scope of the reaction was further investigated using the optimized reaction conditions (eq 2.12). Rh(ttp)Cl successfully reacted with phthalimide to give Rh(ttp)(C₈H₄N₉O₂) (3b) in 50% yield (Table 2.6, entry 1). For the less acidic benzamide, no corresponding rhodium amido complex was obtained (Table 2.6, entry 3). The least acidic aniline only yield the coordination product (PhNH₂)Rh(ttp)Cl (3c) in 15% yield (Table 2.6, entry 4).

The pKₐ values of the amides can be used to rationalize the reactivity pattern.
The pKa values of amide follow the order: phthalimide (8.3) < PhSO2NH2 (16.1) < benzamide (23.2) < aniline (30.6). Only the more acidic amides give the rhodium porphyrin amides. The deprotonation of N-H is important.

In addition, the difference in stability of rhodium porphyrin amide of phthalimide, benzenesulfonamide and benzamide can be explained by the $E$-$C$ approach. According to the $E$-$C$ theory, the more polar Rh-N bond is stronger and leads to a more stable complex. Thus the more polar Rh-N bond in Rh(ttp)NHSO2Ph accounts its higher stability than the rest.

2.3 X-ray Structure of Rh(ttp)NHSO2Ph

The structure of Rh(ttp)NHSO2Ph was elucidated by single-crystal X-ray diffraction studies and is shown in Figure 2.1 (30% thermal ellipsoids). Crystal of (H2O)Rh(ttp)NHSO2Ph was grown from toluene/hexane solution. Table 2.5 shows the selected bond lengths and bond angles of this complex.

The Rh-N(amide) bond length is 2.011Å which is comparable to the Os-NPh2 distance in Os(ttp)(NPh2)OH (1.944Å) and the Ru-NHAr distance in Ru(ttp)(NH-p-C6H4Cl)2 (1.956Å) reported by Che and co-workers. This suggests that the Rh-N bond in Rh(ttp)NHSO2Ph is single bond in nature. The rhodium centre is displaced from the mean porphyrin plane by 0.072Å. The dihedral angles between
toyl plane and the mean porphyrin plane are 79.1°, 74.0°, 83.6°, and 82.6°. The
dihedral angles between NC₄ pyrrole and the mean porphyrin plane are 5.0°, 3.9°, 3.8°
and 6.6°. The porphyrin structure is slightly distorted and adopts a ruffle form (Figure
2.2).

Figure 2.1 ORTEP presentation of molecular structure of (H₂O)Rh(ttp)NH₂SO₂Ph
(30% thermal ellipsoids)
**Figure 2.2a**

**Figure 2.2b**

**Figure 2.2** The conformations of porphyrins in (H₂O)Rh(ttp)NHSO₂Ph showing the displacement of the core atoms and of Rh from the 24-atom least squares plane of porphyrin core (in pm; negative values correspond to displacement towards the amido ligands). Absolute values of the angles between pyrrole rings and least-squares plane and angles between tolyl substituents and the least-squares plane are shown in bold.

<table>
<thead>
<tr>
<th>Table 2.5 Selected bond lengths and bond angles of (H₂O)Rh(ttp)NHSO₂Ph</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bond Lengths/ Å</strong></td>
</tr>
<tr>
<td>Rh(1)-N(1)</td>
</tr>
<tr>
<td>Rh(1)-N(3)</td>
</tr>
<tr>
<td>Rh(1)-N(5)</td>
</tr>
<tr>
<td><strong>Bond Angles/ deg</strong></td>
</tr>
<tr>
<td>N(5)-Rh(1)-N(1)</td>
</tr>
<tr>
<td>N(5)-Rh(1)-N(3)</td>
</tr>
<tr>
<td>S(1)-N(5)-Rh(1)</td>
</tr>
</tbody>
</table>
2.4 Bond Activation Chemistry of Rh(ttp)NH$_2$O$_2$Ph

With Rh(ttp)NH$_2$O$_2$Ph at hand, its bond activation chemistry with different organic substrates at both 60 °C and 120 °C were investigated (eq 2.13). At 60 °C, Rh(ttp)NH$_2$O$_2$Ph reacted with tri-$n$-butylamine to yield the carbon-nitrogen bond activation (CNA) product$^{57}$, Rh(ttp)$^{n}$Bu, in 13% yield after 3 days (Table 2.7, entry 1). Di-$n$-butyl ether also reacted to give the selective carbon-carbon bond activation (CCA)$^{49}$ to give Rh(ttp)$^{n}$Pr in 10% yield after 3 days (Table 2.7, entry 2). On the other hand, no reaction was observed for toluene$^{47}$ and hexane$^{48}$ with 70% and 71% of Rh(ttp)NH$_2$O$_2$Ph recovered after 3 days, respectively (Table 2.7, entries 3 and 4).

At a higher temperature of 120 °C, the CNA of tri-$n$-butylamine was also observed, both rate and yield were enhanced with 67% yield of Rh(ttp)$^{n}$Bu isolated after 4 hours (Table 2.7, entry 5). Di-$n$-butyl ether, however gave, according to the $^1$H NMR spectrum, the CCA product of Rh(ttp)$^{n}$Pr and the carbon-oxygen bond activated (COA) product of Rh(ttp)CO$^{n}$Pr in the ratio of 2:1, together with some unidentified rhodium porphyrin species with a total yield of 50% (Table 2.7, entry 6). Selective benzylic carbon-hydrogen bond activation (BnCHA) of toluene was also observed at 120 °C and 76% of Rh(ttp)Bn was produced after 2 hours (Table 2.7, entry 7). However, no bond activation was observed for $n$-hexane at 120 °C and 26% of Rh(ttp)NH$_2$O$_2$Ph was recovered after 1 day (Table 2.7, entry 8).
The above results show that Rh(ttp)NHSO₂Ph can undergo various types of bond activation to generate Rh(ttp)R in moderate yields.

\[ \text{Rh(ttp)NHSO₂Ph} + \text{substrate} \xrightarrow{\text{temp, time}} \text{product} \]  

Table 2.7 Bond activation by Rh(ttp)NHSO₂Ph

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Temp/°C</th>
<th>Time</th>
<th>Type of activation</th>
<th>Product</th>
<th>Yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>&quot;Bu₂N</td>
<td>60</td>
<td>3 d</td>
<td>CNA</td>
<td>Rh(ttp)&quot;Bu (4a)</td>
<td>13</td>
</tr>
<tr>
<td>2</td>
<td>&quot;Bu₂O</td>
<td>60</td>
<td>3 d</td>
<td>CCA</td>
<td>Rh(ttp)&quot;Pr (4b)</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>PhCH₃</td>
<td>60</td>
<td>3 d</td>
<td>---</td>
<td>---</td>
<td>70⁷⁺</td>
</tr>
<tr>
<td>4</td>
<td>n-hexane</td>
<td>60</td>
<td>3 d</td>
<td>---</td>
<td>---</td>
<td>71⁷⁺</td>
</tr>
<tr>
<td>5</td>
<td>&quot;Bu₂N</td>
<td>120</td>
<td>4 h</td>
<td>CNA</td>
<td>Rh(ttp)&quot;Bu (4a)</td>
<td>67</td>
</tr>
<tr>
<td>6</td>
<td>&quot;Bu₂O</td>
<td>120</td>
<td>3 h</td>
<td>CCA, COA</td>
<td>Rh(ttp)&quot;Pr (4b), Rh(ttp)CO&quot;Pr (4c)</td>
<td>50⁰⁺</td>
</tr>
<tr>
<td>7</td>
<td>PhCH₃</td>
<td>120</td>
<td>2 h</td>
<td>BnCHA</td>
<td>Rh(ttp)Bn (4d)</td>
<td>76</td>
</tr>
<tr>
<td>8</td>
<td>n-hexane</td>
<td>120</td>
<td>1 d</td>
<td>---</td>
<td>---</td>
<td>26⁷⁺</td>
</tr>
</tbody>
</table>

⁷⁺ recovery yield of Rh(ttp)NHSO₂Ph
⁰⁺ total yield of 4b, 4c and unidentified rhodium porphyrin species

2.5 Conclusion

Rh(ttp)NHSO₂Ph and Rh(ttp)(C₈H₆NO₂) were synthesized successfully from (i) the transmetallation of Rh(ttp)Cl with the lithium benzenesulfonamidate and lithium phthalimide, and (ii) the reaction of benzenesulfonamide and phthalimide with Rh(ttp)Cl in the presence of KOH.
Rh(ttp)NHSO₂Ph activated the carbon-nitrogen bond of tri-\textit{n}-butylamine and carbon(\(\alpha\))-carbon(\(\beta\)) bond of di-\textit{n}-butyl ether at 60 °C. The carbon-nitrogen bond activation of tri-\textit{n}-butylamine, carbon-carbon bond activation and carbon-oxygen bond cleavage of di-\textit{n}-butyl ether as well as selective benzylic carbon-hydrogen bond activation of toluene by Rh(ttp)NHSO₂Ph were observed at 120 °C.
Chapter 3 Reactivity Studies of Rh(ttp)NHSO₂Ph

3.1 Thermal Reaction of Rh(ttp)NHSO₂Ph in Benzene-⁺₆

Chapter 1 already introduces that metal-nitrogen bonded complexes share similar bonding features with metal-oxygen bonded complexes. Recently, Chan’s group has discovered that the reductive dimerization of Rh(ttp)OH generates [Rh(ttp)]₂ together with H₂O₂ in benzene solvent at 120 °C (eq 3.1).⁵⁸ Therefore, the thermal reaction of Rh(ttp)NHSO₂Ph in benzene-⁺₆ was investigated to probe the expected reductive dimerization.

\[
\text{Rh(ttp)Cl} + \text{KOH} \xrightarrow{(10 \text{ equiv}) \text{C₆D₆}} \text{Rh(ttp)OH} \xrightarrow{120 \text{ °C, } 0.5 \text{ h}} \text{"Rh(ttp)OH"} \xrightarrow{} [\text{Rh(ttp)}]₂ + \text{H₂O₂} \quad (3.1)
\]

The thermal stability of Rh(ttp)NHSO₂Ph in benzene-⁺₆ in a sealed NMR tube was monitored periodically by ¹H NMR spectroscopy (eq 3.2). Figure 3.1 and Table 3.1 show the results.

\[
2\text{Rh(ttp)NHSO₂Ph} \xrightarrow{\text{time, temp C₆D₆}} [\text{Rh(ttp)}]₂ + \text{PhSO₂NH₂} \quad (3.2)
\]

![Figure 3.1 Time profile of the thermal reaction of Rh(ttp)NHSO₂Ph in benzene-⁺₆](image-url)

Figure 3.1 Time profile of the thermal reaction of Rh(ttp)NHSO₂Ph in benzene-⁺₆
Table 3.1 Thermal reaction of Rh(ttp)NHSO₂Ph in benzene-
de

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temp/ °C</th>
<th>Time</th>
<th>Yield/%</th>
<th>Total Rh yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>[Rh]NHSO₂Ph&lt;sub&gt;a&lt;/sub&gt;</td>
<td>[Rh]&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>1</td>
<td>60</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>2 d</td>
<td>84</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>80</td>
<td>0</td>
<td>84</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>1 d</td>
<td>60</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>110</td>
<td>0</td>
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<td>9</td>
</tr>
<tr>
<td>6</td>
<td>6 d</td>
<td>43</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>25</td>
<td>22</td>
<td>10</td>
<td>25</td>
</tr>
<tr>
<td>8</td>
<td>8 d</td>
<td>23</td>
<td>28</td>
<td>19</td>
</tr>
</tbody>
</table>

<sup>a</sup> [Rh] = Rh(ttp)

<sup>b</sup> Rhodium porphyrin complexes

Reductive dimerization of Rh(ttp)NHSO₂Ph was also observed but the rate of generation of [Rh(ttp)]₂ was slower than that of Rh(ttp)OH. At 60 °C, Rh(ttp)NHSO₂Ph was mostly stable, with about 84% yield of Rh(ttp)NHSO₂Ph remained and only 3% of [Rh(ttp)]₂ generated after 2 days (Table 3.1, entry 2). At 80 °C, [Rh(ttp)]₂ formed in 9% yield and 60% yield of Rh(ttp)NHSO₂Ph still remained after 1 day (Table 3.1, entry 4). When the temperature was further increased to 110 °C, 16% yield of PhSO₂NH₂ and 9% yield of [Rh(ttp)]₂ formed after 1 day. In addition, the Rh(ttp)NHSO₂Ph left further decreased to 43% (Table 3.1, entry 6). After heating at 110 °C for 8 days, the yield of [Rh(ttp)]₂ and PhSO₂NH₂ increased to 28% and 30%,
respectively. Furthermore, 23% yield of Rh(ttp)NHSO₂Ph was recovered (Table 3.1, entry 8). To summarize, Rh(ttp)NHSO₂Ph is thermally unstable above 60 °C producing [Rh(ttp)]₂ and PhSO₂NH₂, though in poor yields, but with high total rhodium porphyrin yields.

3.2 Mechanistic Studies of the Conversion from Rh(ttp)NHSO₂Ph to [Rh(ttp)]₂

In the reductive dimerization of Rh(ttp)OH, H₂O₂ was formed. However, in the reductive dimerization of Rh(ttp)NHSO₂Ph, only PhSO₂NH₂ was observed. The formation of PhSO₂NH₂, instead of the expected (PhSO₂NH)₂, was puzzling. Further mechanistic studies were thus carried out to gain a better understanding of the reaction.

Scheme 3.1 shows three possible mechanisms for the generation of [Rh(ttp)]₂ and PhSO₂NH₂ from Rh(ttp)NHSO₂Ph: (A) hydrolysis of Rh(ttp)NHSO₂Ph, (B) Rh-N bond homolysis - (PhSO₂NH)₂ hydrolysis and (C) Rh-N bond homolysis - (PhSO₂NH)₂ nitrogen-hydrogen bond activation. These proposed mechanisms will be explained one by one.
Mechanism A (Hydrolysis of Rh(ttp)NHSO$_2$Ph):

\[
\text{Rh(ttp)NAr + H}_2\text{O} \rightarrow \text{Rh(ttp)OH + ArNH}_2 \\
\text{Ar} = \text{PhSO}_2
\]

\[
2\text{Rh(ttp)OH} \rightarrow [\text{Rh(ttp)}]_2 + \text{H}_2\text{O}_2
\]

Mechanism B (Rh-N Bond Homolysis - (PhSO$_2$NH)$_2$ Hydrolysis):

\[
\text{Rh(ttp)NAr} \rightarrow \text{Rh(ttp)$^\cdot$ + ArNH}$^\cdot$ \\
\text{Ar} = \text{PhSO}_2
\]

\[
2\text{Rh(ttp)$^\cdot$} \rightarrow [\text{Rh(ttp)}]_2
\]

\[
(\text{ArNH})_2 + \text{H}_2\text{O} \rightarrow \text{ArNH}_2 + \text{ArNHOH}
\]

Mechanism C (Rh-N Bond Homolysis - (PhSO$_2$NH)$_2$ Nitrogen-Hydrogen Bond Activation):

\[
\text{Rh(ttp)NAr} \rightarrow (i) \rightarrow [\text{Rh(ttp)}]_2 + (\text{ArNH})_2 \\
\text{Ar} = \text{PhSO}_2
\]

\[
[i] \text{nitrogen-nitrogen bond activation} \rightarrow 2 \text{Rh(ttp)NAr}
\]

\[
[iii] \text{nitrogen-hydrogen bond activation} \rightarrow \begin{align*}
\text{Rh(ttp)NAr} & \rightarrow (\text{tp})\text{Rh}_\text{Ar}^\cdot \begin{array}{c}
\text{n} \\
\text{n}
\end{array} + \text{Rh(ttp)H} \\
\text{Ar}^\cdot \begin{array}{c}
\text{H}
\end{array}
\end{align*}
\]

Scheme 3.1 Proposed mechanisms for the thermolysis of Rh(ttp)NHSO$_2$Ph

3.2.1 Mechanism A (Hydrolysis of Rh(ttp)NHSO$_2$Ph)

\[
\text{Rh(ttp)NAr + H}_2\text{O} \xrightarrow{\text{hydrolysis}} \text{Rh(ttp)OH + ArNH}_2 \\
\text{Ar} = \text{PhSO}_2
\]

\[
2\text{Rh(ttp)OH} \xrightarrow{\text{dimerization}} [\text{Rh(ttp)}]_2 + \text{H}_2\text{O}_2
\]

Scheme 3.2 Hydrolysis of Rh(ttp)NHSO$_2$Ph

Transition metal amido complexes are known to undergo ligand exchange reactions with various oxide ligands forming the corresponding transition metal-oxygen bonded complexes.$^{230}$ Thus, we proposed that Rh(ttp)NHSO$_2$Ph
initially undergoes ligand substitution with water to give Rh(ttp)OH and PhSO₂NH₂.

Then, Rh(ttp)OH further converts to [Rh(ttp)]₂ upon heating (Scheme 3.2). Water therefore should enhance the reaction rate. Hence, the rate-enhancement by added water was tested (eq 3.3, Figure 3.2, Table 3.2).

\[
2\text{Rh(ttp)NHSO}_2\text{Ph} + 2\text{H}_2\text{O} \xrightarrow{\text{C}_6\text{D}_6, \text{temp} \text{sealed tube}} \text{[Rh(ttp)]}_2 + 2\text{PhSO}_2\text{NH}_2 + \text{H}_2\text{O}_2 \quad (3.3)
\]

**Figure 3.2** Time profile of thermal reaction of Rh(ttp)NHSO₂Ph in C₆D₆ with the addition of 100 equivalents of H₂O

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temp/ Time</th>
<th>Yield/ %</th>
<th>Total Rh yield/ %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>o°C</td>
<td>[Rh]NHSO₂Ph</td>
<td>[Rh]₂</td>
</tr>
<tr>
<td>1</td>
<td>80</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>1d</td>
<td>65</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>65</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>110</td>
<td>1d</td>
<td>40</td>
</tr>
<tr>
<td>5</td>
<td>2d</td>
<td>37</td>
<td>13</td>
</tr>
</tbody>
</table>

\[a \text{[Rh]} = \text{Rh(ttp)}\]

\[b \text{Rhodium porphyrin complexes}\]
After the addition of 100 equivalents of H₂O, at 80 °C, 35% of Rh(ttp)NHSO₂Ph was consumed after 1 day to give only 5% yield of [Rh(ttp)]₂ (Table 3.2, entry 2). Both the reaction rate and product yield were similar to that without water (Table 3.1, entries 3 and 4). At 110 °C, the reaction rate and product yield were higher but were still similar to that without water (Table 3.2, entries 3 and 4). These results show that the addition of water has no significant effect on both the rate and the yield of the reaction. Hence, the proposed mechanism A is ruled out.

### 3.2.2 Mechanism B (Rh-N bond Homolysis - (PhSO₂NH)₂ Hydrolysis)

$$\text{Rh(ttp)NHar} \xrightarrow{\text{homolysis}} \text{Rh(ttp).} + \text{ArNH.}$$

$$2\text{Rh(ttp).} \xrightarrow{\text{dimerization}} [\text{Rh(ttp)}]_2$$

$$\text{(ArNH)₂} + \text{H₂O} \rightarrow \text{ArNH₂} + \text{ArNHOH}$$

**Scheme 3.3** Homolysis of Rh-N bond followed by hydrolysis of (PhSO₂NH)₂

Analogous to the reductive dimerization of Rh(ttp)OH, homolysis of rhodium-nitrogen bond accounts for the generation of [Rh(ttp)]₂ and (PhSO₂NH)₂ (Scheme 3.3). Subsequently, (PhSO₂NH)₂ is hydrolyzed to give PhSO₂NH₂.

With the addition of 100 equivalents of water, TsNHNHTs reacted at 120 °C in 1 day to give TsNH₂ in 20% yield and with 63% yield of TsNHNHTs remained unreacted (eq 3.4). The result apparently supports the proposal. However, even in the presence of huge excess of water and higher temperature, only 20% of TsNH₂ was generated and TsNHNHTs still did not completely reacted. The rate of hydrolysis was
therefore much slower than the thermolysis of Rh(ttp)NSO₂Ph. Furthermore, the slow rate of (PhSO₂NH)₂ hydrolysis should have allowed its detection. However, it was not detected. Therefore, the proposed mechanism B is ruled out.

\[
\text{TsNHNHTs} + \text{H}_2\text{O} \xrightarrow{\text{C}_6\text{D}_6, 120 \degree \text{C}, 1 \text{ d}} \frac{63\%}{\text{(100 equiv)}} \xrightarrow{20\%} \text{TsNH}_2 \quad (3.4)
\]

3.2.3 Mechanism C (Rh-N Bond Homolysis - (PhSO₂NH)₂ Nitrogen-Hydrogen Bond Activation)

We proposed that [Rh(ttp)]₂ is generated from the homolysis of Rh-N bond of [Rh(ttp)NHAr] slow → [Rh(ttp)]₂ + (ArNH)₂

\[
[\text{Rh(ttp)}]_2 \xrightarrow{\text{(i) homolysis slow}} [\text{Rh(ttp)}]_2 + (\text{ArNH})_2
\]

\[
[\text{Rh(ttp)}]_2 + (\text{ArNH})_2 \xrightarrow{\text{(ii) } \text{NNA, major}} 2\text{Rh(ttp)NHAr}
\]

\[
[\text{Rh(ttp)}]_2 + (\text{ArNH})_2 \xrightarrow{\text{(iii) } \text{NNA, minor}} (\text{ttp})\text{RhArN} + \text{Rh(ttp)H}
\]

\[
(\text{ttp})\text{RhArN} \xrightarrow{\text{(v) } \text{NNA}} \text{Rh(ttp)NAr} + \text{ArNH}
\]

\[
\text{ArNH} \xrightarrow{\text{(vi) } \text{HAT}} \text{ArNH} + \text{Rh(ttp)}
\]

\[
\text{ArNH} \xrightarrow{\text{(vii) } \text{HAT}} \text{Rh(ttp)NAr} + \text{ArNH}_2
\]

\[
\text{Rh(ttp)NAr} \xrightarrow{\text{(viii) } \text{decompose}} \text{Rh(ttp)NAr} + \text{ArNH}_2
\]

Scheme 3.4 Rh-N bond Homolysis - (PhSO₂NH)₂ nitrogen-hydrogen bond activation
Rh(ttp)NHSO₂Ph and PhSO₂NH₂ is formed from the nitrogen-hydrogen bond activation product of (PhSO₂NH)₂ with [Rh(ttp)]₂ (Scheme 3.4).

i) NNA of (PhSO₂NH)₂

To verify step iii of the proposed mechanism, first the reaction between [Rh(ttp)]₂ and the sulfonyl hydrazine (TsNHNHTs) was investigated (eq 3.5, Figure 3.3, Table 3.3).

\[
[\text{Rh(ttp)}]_2 + \text{TsNHNHTs} \xrightarrow{\text{CsD₅, r.t.}} 2[\text{Rh(ttp)NHTs}] \quad (3.5)
\]

Figure 3.3 Time profile of the reaction between [Rh(ttp)]₂ and TsNHNHTs at room temperature
Table 3.3 Reaction between [Rh(ttp)]$_2$ and TsHNHTs at room temperature

<table>
<thead>
<tr>
<th>Entry</th>
<th>Time</th>
<th>[Rh]$_2$%</th>
<th>TsHNHTs</th>
<th>[Rh]NHTs%</th>
<th>Total Rh yield/%</th>
<th>Total N yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>100</td>
<td>100</td>
<td>0</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>1 h</td>
<td>94</td>
<td>99</td>
<td>7</td>
<td>101</td>
<td>106</td>
</tr>
<tr>
<td>3</td>
<td>1 d</td>
<td>80</td>
<td>87</td>
<td>21</td>
<td>101</td>
<td>107</td>
</tr>
<tr>
<td>4</td>
<td>2 d</td>
<td>62</td>
<td>77</td>
<td>34</td>
<td>96</td>
<td>115</td>
</tr>
<tr>
<td>5</td>
<td>5 d</td>
<td>42</td>
<td>46</td>
<td>61</td>
<td>103</td>
<td>106</td>
</tr>
<tr>
<td>6</td>
<td>6 d</td>
<td>31</td>
<td>38</td>
<td>69</td>
<td>100</td>
<td>117</td>
</tr>
<tr>
<td>7</td>
<td>9 d</td>
<td>32</td>
<td>42</td>
<td>67</td>
<td>99</td>
<td>109</td>
</tr>
</tbody>
</table>

$^a$ [Rh] = Rh(ttp)

TsHNHTs, which is structurally similar to (PhSO$_2$NH)$_2$, was synthesized and was reacted with [Rh(ttp)]$_2$. The reaction proceeded even at room temperature and Rh(ttp)NHTs was formed in 69% yield after 6 days with [Rh(ttp)]$_2$ remained in 31% (Table 3.3, entry 6). Likely, the reaction has reached an equilibrium.

There are two possible mechanisms for the reaction to occur. First, [Rh(ttp)]$_2$ dissociate into Rh(ttp) monomer and attack the N-N bond in a linear transition state to form 2 Rh-N bond (Scheme 3.5, mechanism C-ii-1)$^{59}$ However, the presence of bulky −SO$_2$Ph group on the nitrogen atom should disfavour the Rh(ttp)$^\cdot$ attack on the nitrogen atom. The sterically difficult termolecular transition state is also entropically demanding. This pathway is less probable. Second, a radical chain mechanism can operate. [Rh(ttp)]$_2$ first dissociates into Rh(ttp)$^\cdot$$^{60}$ to initiate the chain reaction. Chain
propagation continues. Rh(ttp)• then reacts with the N-N bond in the sulfonyl hydrazine to form Rh(ttp)NHTs and TsNH• which further reacts with [Rh(ttp)]2 to give Rh(ttp)NHTs and Rh(ttp)•. Lastly, Rh(ttp)• either combine with another Rh(ttp)• or TsNH• to form [Rh(ttp)]2 or Rh(ttp)NHTs, respectively (Scheme 3.5, mechanism C-ii-2).61

The fast rate of the reaction between [Rh(ttp)]2 and TsNHNHTs shows that once (PhSO2NH)2 is formed, it would react with [Rh(ttp)]2.

**Mechanism C-ii-1**

\[
[Rh(ttp)]_2 \rightleftharpoons 2Rh(ttp)•
\]

\[2Rh(ttp)^\cdot + (ArNH)_{2} \xrightarrow{\text{high temp}} \text{Ar} = \text{PhSO}_2 \]

**Mechanism C-ii-2**

**Initiation**

\[ [Rh(ttp)]_2 \rightleftharpoons 2Rh(ttp)^\cdot \]

**Propagation**

\[ Rh(ttp)^\cdot \rightarrow Rh(ttp)(ArNH \cdot) \rightarrow Rh(ttp)NHAr + ArNH^\cdot \]

\[ Ar = \text{PhSO}_2, \text{Ts} \]

**Termination**

\[ ArNH^\cdot \rightarrow Rh(ttp)^\cdot \rightarrow Rh(ttp)NHAr \]

\[ Rh(ttp)^\cdot \rightarrow [Rh(ttp)]_2 \]

**Scheme 3.5** Possible mechanism of reaction between [Rh(ttp)]2 and (ArNH)2
ii) NHA of (PhSO₂NH)₂

\[
[\text{Rh(ttp)}]_2 + (\text{ArNH})_2 \xrightarrow{\text{high temp}} [\text{Rh(ttp)}]_2 + \text{NHA (PhSO₂NH)}
\]

**Scheme 3.6 Non-selective bond cleavage of hydrazine at high temperature**

The thermolysis of Rh(ttp)NHSO₂Ph can give [Rh(ttp)]₂ and (PhSO₂NH)₂. The absence of (PhSO₂NH)₂ must be caused by a new reaction. We thus proposed that at elevated temperature, both N-N and N-H cleavages of the hydrazine by [Rh(ttp)]₂ occur (Scheme 3.6). The less bulky N-H bond is cleaved despite its higher bond dissociation energy (BDE of N-H bond and N-N bond in hydrazines are about 80 and 60 kcal mol⁻¹, respectively (Figure 3.4)). A four-centred transition state is probably involved during the reaction based on the reported four-centred transition state mechanism of the reaction of Rh(tmp) with CH₄ (Scheme 3.7).

\[
[\text{Rh(ttp)}]_2 + (\text{ArNH})_2 \xrightarrow{\text{high temp}} \begin{array}{c}
\text{Ar}^- \text{N}^+ \text{H} \\
(ttp)\text{Rh} \cdots \text{N}^+ \text{H}^+ \text{Rh(ttp)}
\end{array} + \text{N-N} + \text{Rh(ttp)H}
\]

**Scheme 3.7 NHA of (PhSO₂NH)₂ at high temperature**

![Figure 3.4 BDE of N-N and N-H bond in hydrazine](image)

* hydrazinophenyl sulfone was used as the reference
* tetramethyldydrazone was used as the reference
iii) N-N cleavage of the NHA product of the hydrazine

Since the NHA product contains a Rh-N bond and a relatively weak N-N bond, it is likely to be thermally unstable. N-N bond cleavage of Rh(ttp)(NArNHAr) can occur to give Rh(ttp)NAr• and ArNH• (Ar = PhSO2) (Scheme 3.8).\(^6^2\)

\[
\text{Scheme 3.8 N-N cleavage of NHA product at high temperature}
\]

iv) Formation of PhSO\textsubscript{2}NH\textsubscript{2}

ArNH\textsubscript{2} probably forms from the reaction between ArNH• and Rh(ttp)H or Rh(ttp)NHar (Ar = PhSO2). Exothermic hydrogen atom abstraction from Rh(ttp)H by ArNH• likely occurs and generates ArNH\textsubscript{2} and Rh(ttp)• (Scheme 3.9, pathway i).\(^6^3\)

The process is thermodynamically favoured since the stronger PhSO\textsubscript{2}NH-H bond (105 kcal mol\(^{-1}\))\(^5^6\) is formed while the weaker (ttp)Rh-H bond (60 kcal mol\(^{-1}\))\(^6^4\) is cleaved.

\[
\text{Scheme 3.9 Formation of PhSO}_{2}\text{NH}_{2} \text{from PhSO}_{2}\text{NH}^{•}
\]

Alternatively, hydrogen atom abstraction can occur at the N-H hydrogen of Rh(ttp)NHar to form ArNH\textsubscript{2} and Rh(ttp)NAr• (Scheme 3.9, pathway ii).\(^6^5\) Hydrogen
atom transfer (HAT) occurs at the N-H hydrogen instead of the aromatic C-H hydrogen due to the lower bond dissociation energy of N-H bond (Figure 3.5). From pathways i and ii in Scheme 3.9, pathway i is more favoured since Rh(ttp)H is more accessible and the hydrogen atom on Rh(ttp)NHSO₂Ph is sterically hindered. The other nitrogen-centred radical formed probably decomposes under the reaction conditions.

![Figure 3.5 BDE of N-H bond and aromatic C-H bond in PhSO₂NH₂](image)

**Figure 3.5** BDE of N-H bond and aromatic C-H bond in PhSO₂NH₂

**v) Incomplete Consumption of Rh(ttp)NHSO₂Ph**

From Table 3.1 and Figure 3.1, Rh(ttp)NHSO₂Ph was not completely consumed in its thermolysis and 23% yield of Rh(ttp)NHSO₂Ph remained after heating at 110 °C for 8 days (Table 3.1, entry 8). We reason that PhSO₂NH₂ once formed in the thermolysis further reacts with rhodium porphyrin complexes, i) Rh(ttp)H or ii) [Rh(ttp)]₂ as both species have been reported to be the intermediate in various types of bond activation.⁵⁰,⁵⁷,⁶⁶

However, PhSO₂NH₂ did not react with Rh(ttp)H even at 120 °C and Rh(ttp)H was recovered quantitatively (eq 3.6). Thus, regeneration of Rh(ttp)NHSO₂Ph from Rh(ttp)H and PhSO₂NH₂ is not possible.
Then, the reaction between [Rh(ttp)]_2 and PhSO_2NH_2 was carried out. The two species reacted instantaneously at room temperature to give Rh(ttp)NHSO_2Ph and Rh(ttp)H. After 5 days, 60% yield of Rh(ttp)NHSO_2Ph and 5% yield of Rh(ttp)H were generated. In addition, 32% yield of [Rh(ttp)]_2 and 51% yield of PhSO_2NH_2 was remained (eq 3.7).

\[
[Rh(ttp)]_2 + PhSO_2NH_2 \xrightarrow{C_6D_6, r.t., 5 \text{ d}} Rh(ttp)NHSO_2Ph + Rh(ttp)H \quad (3.7)
\]

The fast rate and high yield of the reaction show that once these two species are formed, they react to regenerate Rh(ttp)NHSO_2Ph and leads to its incomplete consumption.\(^{59}\) Rh(ttp)H generated in the process probably reacts with the nitrogen-centred radical, PhSO_2NH^•, generated from the NHA product of (PhSO_2NH)_2.

Therefore, the above lines of evidence support that mechanism C is operating.

### 3.3 Implication of Proposed Mechanism C on Synthesis of Rh(ttp)NHSO_2Ph

#### 3.3.1 Estimation of Rhodium-Nitrogen Bond Dissociation Energy

The incomplete reaction of [Rh(ttp)]_2 with PhSO_2NH_2 gave Rh(ttp)NHSO_2Ph after 5 days (eq 3.7) suggested that an equilibrium has been reached. To test this proposed equilibrium, both the forward and backward reaction were studied at room
Forward Reaction. [Rh(ttp)]_2 reacted with PhSO_2NH_2 to give Rh(ttp)NHSO_2Ph and Rh(ttp)H at room temperature (eq 3.8, Figure 3.6, Table 3.4). Rh(ttp)NHSO_2Ph was formed instantaneously in 17% yield (Table 3.4, entry 1). After 2 days, 45% yield of [Rh(ttp)]_2 was observed in the system and 56% yield of Rh(ttp)NHSO_2Ph was generated (Table 3.4, entry 3). The reaction was incomplete even after 5 days. At this point, 32% of [Rh(ttp)]_2 and 51% of PhSO_2NH_2 were yielded. Rh(ttp)NHSO_2Ph and Rh(ttp)H were obtained in 60% and 5% yield, respectively (Table 3.4, entry 4).

\[
[Rh(ttp)]_2 + PhSO_2NH_2 \xrightarrow{[R = D_8, r.t.] suggest} Rh(ttp)NHSO_2Ph + Rh(ttp)H \] (3.8)

Figure 3.6 Time profile of the reaction between [Rh(ttp)]_2 and PhSO_2NH_2 at room temperature.
Table 3.4 Reaction between [Rh(ttp)]₂ and PhSO₂NH₂ at room temperature

<table>
<thead>
<tr>
<th>Entry</th>
<th>Time/h</th>
<th>[Rh]₂&lt;sup&gt;a&lt;/sup&gt;</th>
<th>PhSO₂NH₂</th>
<th>[Rh]NHSO₂Ph&lt;sup&gt;a&lt;/sup&gt;</th>
<th>[Rh]H&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Yield/%</th>
<th>Total Rh yield/%</th>
<th>Total N yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>82</td>
<td>100</td>
<td>18</td>
<td>0</td>
<td>100</td>
<td>118</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>54</td>
<td>64</td>
<td>44</td>
<td>0</td>
<td>98</td>
<td>108</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>48</td>
<td>45</td>
<td>56</td>
<td>56</td>
<td>0</td>
<td>101</td>
<td>112</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>120</td>
<td>32</td>
<td>51</td>
<td>60</td>
<td>5</td>
<td>97</td>
<td>111</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>144</td>
<td>30</td>
<td>55</td>
<td>60</td>
<td>12</td>
<td>102</td>
<td>115</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> [Rh] = Rh(ttp)

Backward reaction. To our delight, when Rh(ttp)NHSO₂Ph was reacted with Rh(ttp)H, [Rh(ttp)]₂ and PhSO₂NH₂ were formed (eq 3.9, Figure 3.7, Table 3.5). After 2 hours, 16% yield of Rh(ttp)H and 40% yield of Rh(ttp)NHSO₂Ph remained and 34% yield of [Rh(ttp)]₂ and 25% yield of PhSO₂NH₂ were obtained (Table 3.5, entry 2). At longer reaction time, the four species had reached a constant ratio (Table 3.5, entries 3 and 4).
Rh(ttp)H + Rh(ttp)NHSO₂Ph → \[\text{r.t., time} \quad C₆D₆ \quad [\text{Rh(ttp)}]₂ + \text{PhSO₂NH₂} \] (3.9)

**Figure 3.7** Time profile of reaction between Rh(ttp)H and Rh(ttp)NHSO₂Ph at room temperature

**Table 3.5 Reaction between Rh(ttp)H and Rh(ttp)NHSO₂Ph at room temperature**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Time/h</th>
<th>[Rh]H</th>
<th>[Rh]NHSO₂Ph</th>
<th>[Rh]₂</th>
<th>PhSO₂NH₂</th>
<th>Total Rh</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>35</td>
<td>53</td>
<td>12</td>
<td>23</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>16</td>
<td>40</td>
<td>34</td>
<td>29</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>48</td>
<td>16</td>
<td>45</td>
<td>30</td>
<td>25</td>
<td>91</td>
</tr>
<tr>
<td>4</td>
<td>72</td>
<td>24</td>
<td>49</td>
<td>27</td>
<td>30</td>
<td>100</td>
</tr>
</tbody>
</table>

*a [Rh] = Rh(ttp)*

Furthermore, the same ratio was obtained from both the forward and backward reactions. It was concluded that \([\text{Rh(ttp)}]₂\) and PhSO₂NH₂ established an equilibrium with Rh(ttp)NHSO₂Ph and Rh(ttp)H.

It should be noted that a board signal instead of a sharp doublet was observed for Rh(ttp)-H (Figure 3.8). The observed broad Rh(ttp)-H signal is in line with a fast
exchange in the equilibrium.\textsuperscript{5,67}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.8.png}
\caption{Selected region of the $^1$H NMR spectra of the reaction between Rh(ttp)NHSO\textsubscript{2}Ph and Rh(ttp)H}
\end{figure}

Once the equilibrium has been confirmed, the bond dissociation energy of the rhodium-nitrogen bond in Rh(ttp)NHSO\textsubscript{2}Ph can be estimated. The equilibrium constant of the backward reaction was calculated to be 0.344 based on the yields of Rh(ttp)H, Rh(ttp)NHSO\textsubscript{2}Ph, [Rh(ttp)]\textsubscript{2} and PhSO\textsubscript{2}NH\textsubscript{2} at the equilibrium (Table 3.5, entry 4).
Rh(ttp)H + Rh(ttp)NHSO2Ph $\xrightleftharpoons^{\text{rt}}_{C_6D_6}^{}$ [Rh(ttp)]$_2$ + PhSO$_2$NH$_2$

| Yield (Rh) at equilibrium | 24% | 49% | 27% | 30% |

\[
K = \frac{[[\text{Rh(ttp)}]_2][\text{PhSO}_2\text{NH}_2]}{[\text{Rh(ttp)NHSO}_2\text{Ph}][\text{Rh(ttp)H}]} = \frac{(27/2)(30)}{(49)(24)} = 0.344
\]

With the equilibrium constant in hand, the enthalpy change ($\Delta H$) of the reaction was estimated by eqs 3.10 and 3.11$^{57}$

\[
\Delta G = -RT \ln K \quad (3.10)
\]

\[
\Delta G = \Delta H - T\Delta S \quad (3.11)
\]

\[\therefore \Delta S \sim 0\]

\[\therefore \Delta G \sim \Delta H\]

In addition, BDE of (ttp)Rh-H bond, (ttp)Rh-Rh(ttp) bond as well as the PhSO$_2$NH-H bond were reported to be 60, 16 and 105 kcal mol$^{-1}$,$^{56,64}$ respectively. Since the entropy change of the reaction ($\Delta S$) was close to 0, BDE of (ttp)Rh-NHSO$_2$Ph bond was calculated to be 62 kcal mol$^{-1}$. The BDE of (ttp)Rh-NHSO$_2$Ph bond is the same as that of [(H$_2$O)Rh(tspp)-OH]$^{4-}$.$^{64}$

By $\Delta G = -RT \ln K$

\[
= -1.9859 \times 10^{-3} \text{ kcal mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} \times \ln 0.344
\]

\[
= 0.631 \text{ kcal mol}^{-1}
\]

By $\Delta G \sim \Delta H$
\[ \Delta H = 0.631 \text{ kcal mol}^{-1} \]

and

\[ \Delta H = \text{BDE of (Rh-H)} + \text{BDE of (Rh-N)} - \text{BDE of (Rh-Rh)} - \text{BDE of (N-H)} \]

\[ 0.631 = 60 + \text{BDE of (Rh-N)} - 16 - 105 \]

\[ \therefore \text{BDE of (Rh-N)} = 62 \text{ kcal mol}^{-1} \]

3.3.2 Effect of Excess PhSO₂NH₂ in the Synthesis of Rh(ttp)NHSO₂Ph

The discovery of the equilibrium has a bearing on the synthesis of Rh(ttp)NHSO₂Ph. In Section 2.2.2.1, it was shown that when Rh(ttp)Cl reacted with 1 equivalent of PhSO₂NH₂, the yield of Rh(ttp)NHSO₂Ph was only 20%. However, when the loading of PhSO₂NH₂ was increased to 3 equivalents, the yield of Rh(ttp)NHSO₂Ph increased to 70% (eq 3.12). This can be reasoned that once [Rh(ttp)]₂ is formed from Rh(ttp)NHSO₂Ph upon heating, in the presence of excess PhSO₂NH₂, [Rh(ttp)]₂ reacts with PhSO₂NH₂ to form Rh(ttp)NHSO₂Ph. The increase in the yield of Rh(ttp)NHSO₂Ph therefore results.

\[
\begin{align*}
\text{Rh(ttp)Cl} + 2 \text{PhSO₂NH₂} & \xrightarrow{\text{C₆H₆, K₂CO₃ (10 equiv)}} \text{N₂, 120 °C, 2 h}} \text{Rh(ttp)NHSO₂Ph} (3.12) \\
\text{substrate loading} & = 1 \text{ equiv, 20%} \\
& = 3 \text{ equiv, 70%}
\end{align*}
\]

3.4 Conclusion

The mechanism of the thermal reactions of Rh(ttp)NHSO₂Ph were elucidated. It
was proposed that upon heating, homolysis of the Rh-N bond of Rh(ttp)NHSO₂Ph occurs to give [Rh(ttp)]₂ and (PhSO₂NH)₂ followed by NNA and NHA of (PhSO₂NH)₂. The observed organic co-product, PhSO₂NH₂, is generated from PhSO₂NH• through hydrogen atom abstraction. The incomplete reaction can be explained by the fact that [Rh(ttp)]₂ and PhSO₂NH₂ formed would react and regenerate Rh(ttp)NHSO₂Ph.

The bond dissociation energy of Rh-N bond in Rh(ttp)NHSO₂Ph was estimated to be 62 kcal mol⁻¹ which is the same as that of [Rh(tspp)OH(H₂O)]⁴⁺.
Chapter 4 Experimental Section

4.1 General Procedures

All materials were purchased from commercial suppliers and used without further purification unless otherwise specified. Rhodium trichloride (RhCl₃·xH₂O) was obtained from Johnson Matthey. Benzonitrile was distilled from P₂O₅ under N₂. n-Hexane for chromatography was distilled from calcium hydride. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl under N₂. Benzene was distilled from sodium under N₂. Di-n-butyl ether was purified by sodium in vacuum. All reactions were conducted under N₂ and shielded from light with aluminum foil wrapping. Thin-layer chromatography was performed on percoated silica gel 60 F₂₅₄ plates. Column chromatography was performed on silica gel (70-230 and 230-400 mesh).

4.2 Experimental Instrumentation

¹H NMR spectra were recorded on either a Bruker DPX-300 (300 MHz) or Bruker AV 400 (400 MHz) spectrometer. Chemical shifts were referenced with the residual solvent protons in CDCl₃ (δ 7.26 ppm) or C₆D₆ (δ 7.15 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in scale downfield from TMS (δ 0.00 ppm). ¹³C NMR spectra were recorded on Bruker AV
400 (100 MHz) spectrometer. Chemical shifts were referenced to the solvent peak of CDCl₃ (δ 77.0 ppm). Coupling constants (J) were reported in Hertz (Hz).

High resolution mass spectra (HRMS) were performed on a ThermoFinnigan MAT 95 XL mass spectrometer in fast atom bombardment (FAB) mode using 3-nitrobenzyl alcohol (NBA) matrix.

4.3 Synthesis of Starting Material

**Preparation of Tetratolyporphyrin, H₂ttp (1)**

Pyrrole (24 mL, 346 mmol) and 4-methylbenzaldehyde (35 mL, 297 mmol) were added to refluxing propionic acid (1.25 L). The mixture was refluxed for 30 minutes and then cooled to room temperature. The purple solid was collected after crystallization from methanol and further dried by vacuum at 70 °C for 2 hours. H₂ttp 1 obtained was purple solid (6.03 g, 8.99 mmol, 12%). Rf = 0.87 (CH₂Cl₂). ¹H NMR (CDCl₃, 300 MHz) δ -2.78 (s, 2 H), 2.70 (s, 12 H), 7.55 (d, 8H, J= 7.8 Hz), 8.09 (d, 8 H, J= 7.8 H), 8.85 (s, 8 H).

**Preparation of 5,10,15,20-Tetratolyporphyrinorhodium(III) Chloride, [Rh(ttp)Cl] (2)**

RhCl₃.xH₂O (233.9 mg, 0.89 mmol) was added to the solution of H₂ttp 1 (365.4 mg, 0.54 mmol) in benzonitrile (30 mL). The mixture was refluxed for 4 hours. After the removal of solvent under vacuum at elevated temperature, the resulting red residue
was purified by column chromatography using silica gel (70-230 mesh) eluting with CH₂Cl₂. A major red band was collected. A red solid (299.0 mg, 0.37 mmol, 68%) was collected after recrystallization from CH₂Cl₂/MeOH and further dried under vacuum at 70 °C for 2 hours. Rf = 0.31 (CH₂Cl₂). ¹H NMR (CDCl₃, 300 MHz) δ 2.71 (s, 12 H), 7.59 (d, 8 H, J = 8.1 Hz), 8.08 (d, 4 H, J = 7.2 Hz), 8.14 (d, 4 H, J = 6.9 Hz), 8.94 (s, 8 H).

Preparation of 5,10,15,20-Tetratolyporphyrinorhodium(III) Iodide, (Rh(ttp)I)₆⁷

A red suspension of Rh(ttp)Cl₂ (79 mg, 0.098 mmol in EtOH (30 mL) and a solution of NaBH₄ (7.46 mg, 0.196 mmol) in aqueous NaOH (0.1 M, 2 mL) were purged with N₂ for 15 minutes separately. The solution of NaBH₄ was added slowly to the suspension of Rh(ttp)Cl₂ via a cannula. The reaction was heated at 60 °C for 1 hour and the colour changed to deep brown. The solution was then cooled down to 0 °C and degassed 0.1 M HCl (40 mL) was added via a cannula. Once the reaction mixture became orange, excess I₂ (210 mg, 0.827 mmol) was added and reaction mixture turned dark brown immediately and stirred for further 5 minutes. Solvent was then removed by rotary evaporation. The residue was then purified by chromatography on silica gel using a solvent mixture of hexane: CH₂Cl₂ = 5:3. The slow moving orange band was collected and the solvent was evaporated off to give purple solids of Rh(ttp)I (68.5 mg, 0.076 mmol, 82%). The product was further purified from
recrystallization from CH₂Cl₂/methanol. Rᵣ = 0.35 (CH₂Cl₂). ¹H NMR(300 MHz, CDCl₃) δ 2.70 (s, 12H), 7.53 (d, 4 H, J = 6.9 Hz), 7.55 (d, 4 H, J = 7.2 Hz), 8.05 (d, 4 H, J = 7.8 Hz), 8.10 (d, 4 H, J = 7.8 Hz), 8.89 (s, 8 H).

Preparation of 5, 10, 15, 20-Tetratolyloporphyrinatorhodium(III) Hydride, [Rh(ttp)H] (8).⁵³,⁶⁸b,⁶⁹

A red suspension of Rh(ttp)Cl₂ (100 mg, 0.11 mmol) in EtOH (50 mL) and a solution of NaBH₄ (17 mg, 0.45 mmol) in aqueous NaOH (0.1 M, 2 mL) were purged with N₂ for 15 minutes separately. The solution of NaBH₄ was added slowly to the suspension of Rh(ttp)Cl₂ via a cannula. The mixture was heated at 60 °C for 1 hour and the colour changed to deep brown. The solution was then cooled down to 0 °C and degassed 0.1 M HCl (40 mL) was added via a cannula. A brick red suspension was formed. After stirred at room temperature for another 15 minutes under N₂, the brick red precipitate was collected after filtration and washing with water (2 x 10 mL) under N₂. The brick red residues of Rh(ttp)H 8 (80 mg, 0.10 mmol, 92 %) were obtained after vacuum dried. ¹H NMR (C₆D₆, 300 MHz) δ -40.12 (d, 1 H, J₉⁻H = 43.5 Hz), 2.42 (s, 12 H), 7.16 (d, 4 H, J = 8.2 Hz), 7.35 (d, 4 H, J = 8.2 Hz), 7.95 (d, 4 H, J = 8.1 Hz), 8.22 (d, 4 H, J = 8.1 Hz), 9.03 (s, 8 H).

Preparation of Rh₂(ttp)₂ (5)⁵³,⁶⁹

Rh(ttp)H 8 (10.0 mg, 0.013 mmol) was dissolved in degassed benzene (4.0 mL). The
reaction mixture was then degassed by three freeze-pump-thaw method and refilled with N₂. The solution was irradiated under a 400 W Hg-lamp at 6-11 °C until all the starting material was consumed to give [Rh(tp)]₂ in quantitative yield.

**Preparation of N,N'-ditosylhydrazine, [TsNHNHTs]⁷⁰**

*p*-Toluenesulfonyl hydrazide (2.33 g, 12.5 mmol) and *p*-toluenesulfonyl chloride (3.6g, 18.8 mmol) were added to CH₂Cl₂. The reaction mixture was stirred at room temperature while pyridine (1.5 mL, 18.8 mmol) was added dropwise over 1 minute. During the addition, the reaction mixture became homogenous and turned yellow. White precipitate was observed and the reaction mixture was stirred for 1.5 hours. Diethyl ether (50 mL) and H₂O (25 mL) were added and stirred at 0 °C for 15 minutes. The white solid which precipitate were collected by suction filtration and washed with diethyl ether. The solid thus obtained was dissolved in boiling methanol. After cooling to the room temperature, half of the solvent was removed by rotary evaporation and cooled to 0 °C. The precipitate was collected using suction filtration and washed with cold methanol and diethyl ether. *N,N'*-ditosylhydrazine⁷⁰ (2.8 g, 8.2 mmol, 66%) was collected. ³¹H NMR (C₆D₆, 400 MHz) δ 1.77 (s, 3 H), 5.38 (s, 1 H), 6.52 (d, 2 H, J = 8.4 Hz), 7.53 (d, 2 H, J = 8 Hz).
4.4 Synthesis of Various Rhodium Porphyrin Amido Complexes

Transmetallation between Rh(ttp)Cl and Lithium Benzenesulfonamidate

(1) Ratio of PhSO₂NH₂: "BuLi: Rh(ttp)Cl = 1.3:2.0:1.0

n-Butyllithium (10 μL of 2.5 M n-hexane solution) was added to a solution of benzenesulfonamide (2.6 mg, 0.016 mmol) in THF (2 mL) under N₂ and stirred for 6 hours at -78 °C. Rh(ttp)Cl 2 (10.1 mg, 0.012 mmol) was added to this mixture. The mixture was then stirred at room temperature for 1 day. The solvent was then removed under vacuum and the red crude mixture was purified by silica gel column (230-400 mesh) chromatography eluting with a solvent mixture of hexane: EtOAc (1:1). A red product Rh(ttp)NHSO₂Ph 3a (3.3 mg, 0.003 mmol, 29%), with Rf = 0.76 (hexane/EtOAc = 1:1) was collected. ¹H NMR (CD₂Cl₂, 400 MHz) δ -6.56 (s, 1 H), 2.43 (s, 12 H), 5.15 (d, 2 H, J = 6.8 Hz), 6.37 (t, 2 H, J = 7.6 Hz), 6.6 (t, 1 H, J = 7.2 Hz), 7.31 (d, 8 H, J = 7.6 Hz), 8.05 (d, 4 H, J = 7.2 Hz), 8.11 (d, 4 H, J = 7.2 Hz), 9.05 (s, 8 H). ¹³C NMR (CDCl₃, 100 MHz) δ 21.5, 121.1, 123.2, 126.7, 127.1, 127.4, 128.6, 131.9, 133.8, 134.5, 137.0, 142.7; HRMS (FABMS): calcd for (C₅₄H₄₂N₅S₂O₂Rh)⁺ m/z 927.2109, found m/z 927.2093.

(2) Ratio of PhSO₂NH₂: "BuLi: Rh(ttp)Cl = 2.5:4.0:1.0

n-Butyllithium (20 μL of 2.5 M n-hexane solution) was added to a solution of benzenesulfonamide (4.9 mg, 0.031 mmol) in THF (2 mL) under N₂ and stirred for 6 hours at -78 °C. Rh(ttp)Cl 2 (10.1 mg, 0.012 mmol) was added to this mixture. The
mixture was then stirred at room temperature for 1 day. The solvent was then removed under vacuum and the red crude mixture was purified by silica gel column (230-400 mesh) chromatography eluting with a solvent mixture of hexane: EtOAc (1:1). A red product Rh(ttp)NH\textsubscript{2}SO\textsubscript{2}Ph \textit{3a} (6.1 mg, 0.007 mmol, 53 %), with \( R_f = 0.76 \) (hexane/EtOAc = 1:1) was collected.

(3) Ratio of PhSO\textsubscript{2}NH\textsubscript{2}: 'BuLi: Rh(ttp)Cl = 1.3:4.0:1.0

\( \text{n-Butyllithium (20 } \mu\text{L of 2.5 M } n\text{-hexane solution) was added to a solution of benzenesulfonamide (2.6 mg, 0.016 mmol) in THF (2 mL) under N}_2 \text{ and stirred for 6 hours at } -78 \degree \text{C. Rh(ttp)Cl } 2 \text{ (10.1 mg, 0.012 mmol) was added to this mixture. The mixture was then stirred at room temperature for 1 day. The solvent was then removed under vacuum and the red crude mixture was purified by silica gel column (230-400 mesh) chromatography eluting with a solvent mixture of hexane: EtOAc (1:1). A red product Rh(ttp)NH\textsubscript{2}SO\textsubscript{2}Ph } \textit{3a} \text{ (7.0 mg, 0.008 mmol, 60 %), with } R_f = 0.76 \text{ (hexane/EtOAc = 1:1) was collected.} \\

\textbf{Transmetallation between Rh(ttp)Cl and Lithium Phthalimide}

\( \text{n-Butyllithium (20 } \mu\text{L of 2.5 M } n\text{-hexane solution) was added to a solution of phthalimide (4.7 mg, 0.032 mmol) in THF (2 mL) under N}_2 \text{ and stirred for 6 hours at } -78 \degree \text{C. Rh(ttp)Cl } 2 \text{ (10.3 mg, 0.013 mmol) was added to this mixture. The mixture was then stirred at room temperature for 5 days. The solvent was then removed under vacuum and the red crude mixture was purified by silica gel column (230-400 mesh)
chromatography eluting with CH$_2$Cl$_2$ followed by a solvent mixture of CH$_2$Cl$_2$: EtOAc (9:1). Rh(ttp)(C$_8$H$_4$NO$_2$)$_3$b (3.7 mg, 0.004 mmol, 32%), with $R_f$ = 0.9 (EtOAc / CH$_2$Cl$_2$ = 1:9) was collected. $^1$H NMR (CD$_2$D$_6$, 400 MHz) $\delta$ 2.38 (s, 12 H), 5.85 (dd, 2 H, $J$ = 2.8, 5.6 Hz), 5.92 (dd, 2 H, $J$ = 3, 5.4 Hz), 7.22 (d, 4 H, $J$ = 5.2 Hz), 7.31 (d, 4 H, $J$ = 7.2 Hz), 8.18 (d, 4 H, $J$ = 6.4 Hz), 8.26 (d, 4 H, $J$ = 6.8 Hz), 9.16 (s, 8 H).

HRMS (FABMS): calcd for (C$_{56}$H$_{40}$N$_5$Rh$_2$O$_2$)$^+$ m/z 917.2232, found m/z 917.2216.

The complex is not stable upon recrystallization from CH$_2$Cl$_2$/hexane and $^{13}$C NMR was not preformed.

**Transmetallation between Rh(ttp)Cl and Lithium Benzamidate**

$n$-Butyllithium (20 $\mu$L of 2.5 M $n$-hexane solution) was added to a solution of benzamide (3.8 mg, 0.032 mmol) in THF (2 mL) under $N_2$ and stirred for 6 hours at -78 °C. Rh(ttp)Cl 2 (10.2 mg, 0.013 mmol) was added to this mixture. The mixture was then stirred at room temperature for 2 days. The solvent was then removed under vacuum and the red crude mixture was analyzed by $^1$H NMR and unknowns were obtained.

**Transmetallation between Rh(ttp)Cl and Lithium Salt of 2-Pyrrolidone**

$n$-Butyllithium (20 $\mu$L of 2.5 M $n$-hexane solution) was added to a solution of 2-pyrrolidone (3 $\mu$L, 0.036 mmol) in THF (2 mL) under $N_2$ and stirred for 6 hours at -78 °C. Rh(ttp)Cl 2 (11.5mg, 0.014 mmol) was added to this mixture. The mixture
was then stirred at room temperature for 2 days. The solvent was then removed under vacuum and the red crude mixture was analyzed by $^1$H NMR and unknowns were obtained.

**Transmetallation between Rh(ttp)Cl and Lithium Salt of Aniline**

$n$-Butyllithium (20 µL of 2.5 M $n$-hexane solution) was added to a solution of aniline (3 µL, 0.034 mmol) in THF (2 mL) under N$_2$ and stirred for 6 hours at -78 °C. Rh(ttp)Cl$_2$ (10.9 mg, 0.014 mmol) was added to this mixture. The mixture was then stirred at room temperature for 1 day. The solvent was then removed under vacuum and the red crude mixture was analyzed by $^1$H NMR and unknowns were obtained.

**Reactions between Rh(ttp)Cl and Benzenesulfonamide at Different Reaction Time**

(1) **Reaction for 1 day**

Rh(ttp)Cl$_2$ (10.1 mg, 0.013 mmol), K$_2$CO$_3$ (17.3 mg, 0.13 mmol) and benzenesulfonamide (19.8 mg, 0.13 mmol) were added to benzene (1.5 mL) and the mixture was degassed for three freeze-thaw-pump cycles and filled with N$_2$. The mixture was then heated at 120 °C for 1 day. The solvent was then removed under vacuum and the red crude mixture was purified by silica gel column (230-400 mesh) chromatography eluting with a solvent mixture of hexane: EtOAc (1:1). A red product
(Rh(ttp)NHSO$_2$Ph 3a (6.5 mg, 0.007 mmol, 56%), with $R_f = 0.76$ (hexane/ EtOAc = 1:1) was collected.

(2) Reaction for 2 hours

Rh(ttp)Cl 2 (10.1 mg, 0.013 mmol), K$_2$CO$_3$ (17.3 mg, 0.13 mmol) and benzenesulfonamide (19.8 mg, 0.13 mmol) were added to benzene (1.5 mL) and the mixture was degassed for three freeze-thaw-pump cycles and filled with N$_2$. The mixture was then heated at 120 °C for 2 hours. The solvent was then removed under vacuum and the red crude mixture was purified by silica gel column (230-400 mesh) chromatography eluting with a solvent mixture of hexane: EtOAc (1:1). A red product Rh(ttp)NHSO$_2$Ph 3a (8.7 mg, 0.009 mmol, 75%), with $R_f = 0.76$ (hexane/ EtOAc = 1:1) was collected.

Reactions between Rh(ttp)Cl and Benzenesulfonamide with Different Substrate Loadings

(1) Addition of 1 equivalent of benzenesulfonamide

Rh(ttp)Cl 2 (10.6 mg, 0.013 mmol), K$_2$CO$_3$ (18.1 mg, 0.13 mmol) and benzenesulfonamide (2.1 mg, 0.013 mmol) were added to benzene (1.5 mL) and the mixture was degassed for three freeze-thaw-pump cycles and filled with N$_2$. The mixture was then heated at 120 °C for 2 hours. The solvent was then removed under vacuum and the red crude mixture was purified by silica gel column (230-400 mesh)
chromatography eluting with a solvent mixture of hexane: EtOAc (1:1). A red product Rh(ttp)NH$_2$SO$_2$Ph 3a (2.4 mg, 0.003 mmol, 20%), with $R_f = 0.76$ (hexane/ EtOAc = 1:1) was collected.

(2) Addition of 3 equivalents of benzenesulfonamide

Rh(ttp)Cl 2 (10.1 mg, 0.013 mmol), K$_2$CO$_3$ (17.3 mg, 0.13 mmol) and benzenesulfonamide (5.9 mg, 0.04 mmol) were added to benzene (1.5 mL) and the mixture was degassed for three freeze-thaw-pump cycles and filled with N$_2$. The mixture was then heated at 120 °C for 2 hours. The solvent was then removed under vacuum and the red crude mixture was purified by silica gel column (230-400 mesh) chromatography eluting with a solvent mixture of hexane: EtOAc (1:1). A red product Rh(ttp)NH$_2$SO$_2$Ph 3a (8.1 mg, 0.009 mmol, 70%), with $R_f = 0.76$ (hexane/ EtOAc = 1:1) was collected.

(3) Addition of 5 equivalents of benzenesulfonamide

Rh(ttp)Cl 2 (10.1 mg, 0.013 mmol), K$_2$CO$_3$ (17.3 mg, 0.13 mmol) and benzenesulfonamide (9.8 mg, 0.06 mmol) were added to benzene (1.5 mL) and the mixture was degassed for three freeze-thaw-pump cycles and filled with N$_2$. The mixture was then heated at 120 °C for 2 hours. The solvent was then removed under vacuum and the red crude mixture was purified by silica gel column (230-400 mesh) chromatography eluting with a solvent mixture of hexane: EtOAc (1:1). A red product
Rh(ttp)NHSO₂Ph 3a (9.0 mg, 0.001 mmol, 78%), with R_f = 0.76 (hexane/ EtOAc = 1:1) was collected.

(4) Addition of 10 equivalents of benzenesulfonamide

As mentioned in 4.4.2.1 (2).

Reactions between Rh(ttp)Cl and Benzenesulfonamide at Different Temperatures

(1) Reaction at 120 °C

As mentioned in 4.4.2.2 (2).

(2) Reaction at 80 °C

Rh(ttp)Cl 2 (10.1 mg, 0.013 mmol), K₂CO₃ (17.3 mg, 0.13 mmol) and benzenesulfonamide (5.9 mg, 0.04 mmol) were added to benzene (1.5 mL) and the mixture was degassed for three freeze-thaw-pump cycles and filled with N₂. The mixture was then heated at 80 °C for 18 hours. The solvent was then removed under vacuum and the red crude mixture was purified by silica gel column (230-400 mesh) chromatography eluting with a solvent mixture of hexane: EtOAc (1:1). A red product Rh(ttp)NHSO₂Ph 3a (8.6 mg, 0.009 mmol, 74%), with R_f = 0.76 (hexane/ EtOAc = 1:1) was collected.
Reactions between Rh(ttp)Cl and Benzenesulfonamide in Different Solvents

(1) Reaction in benzene

As mentioned in 4.4.2.3 (2).

(2) Reaction in THF

Rh(ttp)Cl 2 (10.1 mg, 0.013 mmol), K₂CO₃ (17.3 mg, 0.13 mmol) and benzenesulfonamide (5.9 mg, 0.04 mmol) were added to THF (1.5 mL) and the mixture was degassed for three freeze-thaw-pump cycles and filled with N₂. The mixture was then heated at 80°C for 1 day. The solvent was then removed under vacuum and the red crude mixture was purified by silica gel column (230-400 mesh) chromatography eluting with a solvent mixture of hexane:EtOAc (1:1). A red product Rh(ttp)NH₂SO₂Ph 3a (8.4 mg, 0.009 mmol, 72%), with Rᵣ = 0.76 (hexane/ EtOAc = 1:1) was collected.

Reactions between Different Rh(ttp)X and Benzenesulfonamide

(1) Reaction using Rh(ttp)Cl

As mentioned in 4.4.2.3 (2).

(2) Reaction using Rh(ttp)I

Rh(ttp)I (10.5 mg, 0.012 mmol), K₂CO₃ (16.1 mg, 0.12 mmol) and benzenesulfonamide (5.5 mg, 0.035 mmol) were added to benzene (1.5 mL) and the mixture was degassed for three freeze-thaw-pump cycles and filled with N₂. The
mixture was then heated at 80 °C for 18 hours. The solvent was then removed under vacuum and the red crude mixture was purified by silica gel column (230-400 mesh) chromatography eluting with a solvent mixture of hexane: EtOAc (1:1). A red product Rh(ttp)NHSO₂Ph 3a (6.8 mg, 0.007 mmol, 63%), with Rf = 0.76 (hexane/ EtOAc = 1:1) was collected.

Reactions between Rh(ttp)Cl and Benzenesulfonamide with Different Base

(1) Without base added

Rh(ttp)Cl₂ (11.5 mg, 0.014 mmol) and benzenesulfonamide (6.7 mg, 0.043 mmol) were added to benzene (1.5 mL) and the mixture was degassed for three freeze-thaw-pump cycles and filled with N₂. The mixture was then heated at 80 °C for 3 days. The solvent was then removed under vacuum and the red crude mixture was purified by silica gel column (70-230 mesh) chromatography eluting with dichloromethane. Rh(ttp)Cl₂ (3.8 mg, 0.005 mmol, 33%) was collected.

(2) Addition of 10 equivalents of K₂CO₃

As mentioned in 4.4.2.3 (2).

(3) Addition of 10 equivalents of KOH

Rh(ttp)Cl₂ (10.7 mg, 0.013 mmol), KOH (7.0 mg, 0.13 mmol) and benzenesulfonamide (6.2 mg, 0.040 mmol) were added to benzene (1.5 mL) and the mixture was degassed for three freeze-thaw-pump cycles and filled with N₂. The
mixture was then heated at 80 °C for 3.5 hours. The solvent was then removed under vacuum and the red crude mixture was purified by silica gel column chromatography eluting with a solvent mixture of hexane: EtOAc (1:1). A red product Rh(ttp)NH$_2$SO$_2$Ph 3a (10.3 mg, 0.011 mmol, 84%), with $R_f$ = 0.76 (hexane/ EtOAc = 1:1) was collected.

**Substrate Scope of Base-promoted Ligand Substitution**

**(1) Reaction between Rh(ttp)Cl and phthalimide**

Rh(ttp)Cl 2 (10.4 mg, 0.013 mmol), KOH (7.2 mg, 0.13 mmol) and phthalimide (5.7 mg, 0.039 mmol) were added to benzene (1.5 mL) and the mixture was degassed for three freeze-thaw-pump cycles and filled with N$_2$. The mixture was then heated at 80 °C for 3.5 hours. The solvent was then removed under vacuum and the red crude mixture was purified by silica gel column chromatography (230-400 mesh) eluting with CH$_2$Cl$_2$ followed by a solvent mixture of CH$_2$Cl$_2$: EtOAc (9:1). Rh(ttp)(C$_8$H$_4$N$_2$O$_2$) 3b (5.9 mg, 0.006 mmol, 50%) was collected.

**(2) Reaction between Rh(ttp)Cl and benzenesulfonamide**

As mentioned in 4.4.2.6 (3).

**(3) Reaction between Rh(ttp)Cl and benzamide**

Rh(ttp)Cl 2 (10.5 mg, 0.013 mmol), KOH (7.3 mg, 0.13 mmol) and benzamide (4.7 mg, 0.039 mmol) were added to benzene (1.5 mL) and the mixture was degassed
for three freeze-thaw-pump cycles and filled with N\textsubscript{2}. The mixture was then heated at 80 °C for 3.5 hours. The solvent was then removed under vacuum and the red crude mixture was analyzed by \textsuperscript{1}H NMR and unknowns were obtained.

(4) Reaction between Rh(ttp)Cl and aniline

Rh(ttp)Cl \textsubscript{2} (10.8 mg, 0.013 mmol), KOH (7.5 mg, 0.13 mmol) and aniline (4 µL, 0.13 mmol) were added to benzene (1.5 mL) and the mixture was degassed for three freeze-thaw-pump cycles and filled with N\textsubscript{2}. The mixture was then heated at 80 °C for 3.5 hours. The solvent was then removed under vacuum and the red crude mixture was purified by silica gel column chromatography (230-400 mesh) eluting with CH\textsubscript{2}Cl\textsubscript{2} followed by a solvent mixture of hexane: EtOAc (2:1). A red product (PhNH\textsubscript{2})Rh(ttp)Cl \textsubscript{3c} (0.2 mg, 0.002 mmol, 15%), with R\textsubscript{f} = 0.8 (hexane/ EtOAc = 2:1) was collected. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz) \textsuperscript{\delta} -3.68 (s, 2 H), 2.3 (d, 2 H, J = 7.8 Hz), 2.71 (s, 12 H), 5.94 (t, 2 H, J = 7.8 Hz), 6.47 (t, 1 H, J = 7.5 Hz), 7.55 (d, 8 H, J = 7.8 Hz), 7.98 (d, 4 H, J = 7.8 Hz), 8.17 (d, 4 H, J = 7.4 Hz) , 8.84 (s, 8 H). HRMS (FABMS): calcd for (C\textsubscript{54}H\textsubscript{43}N\textsubscript{5}RhCl-Cl\textsuperscript{+}) \textsuperscript{m/z} 864.2568, found m/z 864.2532
4.5 Bond Activation Chemistry of Rh(ttp)NHSO₂Ph

Reactions at 60 °C

(1) Reaction between Rh(ttp)NHSO₂Ph and tri-n-butylamine

Rh(ttp)NHSO₂Ph 3a (10.5 mg, 0.011 mmol) and tri-n-butylamine (1.5 mL) were degassed for three freeze-thaw-pump cycles and filled with N₂. The mixture was then heated at 60 °C for 3 days. The solvent was then removed under vacuum and the red crude mixture was purified by silica gel column chromatography (70-230 mesh) eluting with a solvent mixture of hexane: CH₂Cl₂ (1:1). A red product Rh(ttp)"Bu⁷⁷ 4a (1.2 mg, 0.001 mmol, 13%), with Rₚ = 0.72 (hexane/ CH₂Cl₂ = 1:1) was collected. ¹H NMR (CDCl₃, 300 MHz) δ -4.95 (dt, 2 H, \( J_{\text{Rh-H}} = 3.0 \) Hz, \( J = 8.1 \) Hz), -4.50 (qu, 2 H, \( J = 7.9 \) Hz), -1.57 (sext, 2 H, \( J = 7.4 \) Hz), -0.83 (t, 3 H, \( J = 7.2 \) Hz), 2.70 (s, 12 H), 7.53 (t, 8 H, \( J = 6 \) Hz), 7.99 (dd, 4 H, \( J = 2.1 \) Hz, \( J = 7.8 \) Hz), 8.08 (dd, 4 H, \( J = 2.1 \) Hz, \( J = 7.8 \) Hz), 8.71 (s, 8 H).

(2) Reaction between Rh(ttp)NHSO₂Ph and di-n-butyl ether

Rh(ttp)NHSO₂Ph 3a (10.7 mg, 0.012 mmol) and di-n-butyl ether (1.5 mL) were degassed for three freeze-thaw-pump cycles and filled with N₂. The mixture was then heated at 60 °C for 3 days. The solvent was then removed under vacuum and the red crude mixture was purified by silica gel column chromatography (70-230 mesh) eluting with a solvent mixture of hexane: CH₂Cl₂ (1:1). A red product Rh(ttp)"Pr⁷¹ 4b...
(0.9 mg, 0.001 mmol, 64%), with $R_f = 0.72$ (hexane/CH$_2$Cl$_2$ = 1:1) was collected. $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ -4.98 (dt, 2 H, $^2J_{Rh-H} = 3.3$ Hz, $J = 8.3$ Hz), -4.46 (sext, 2 H, $J = 8.7$ Hz), -1.75 (t, 3 H, $J = 7.2$ Hz), 2.69 (s, 12 H), 7.53 (t, 8 H, $J = 5.7$ Hz), 8.00 (dd, 4 H, $J = 2.1$ Hz, 7.7 Hz), 8.07 (dd, 4 H, $J = 2.1$ Hz, 8.0 Hz), 8.71 (s, 8 H).

(3) Reaction between Rh(ttp)NHSO$_2$Ph and toluene

Rh(ttp)NHSO$_2$Ph 3a (10.7 mg, 0.012 mmol) and toluene (1.5 mL) were degassed for three freeze-thaw-pump cycles and filled with N$_2$. The mixture was then heated at 60°C for 3 days. The solvent was then removed under vacuum and the red crude mixture was purified by silica gel column chromatography (230-400 mesh) eluting with a solvent mixture of hexane: EtOAc (1:1). Rh(ttp)NHSO$_2$Ph 3a (7.5 mg, 0.008 mmol, 70%) was collected.

(4) Reaction between Rh(ttp)NHSO$_2$Ph and $n$-hexane

Rh(ttp)NHSO$_2$Ph 3a (10.9 mg, 0.012 mmol) and $n$-hexane (1.5 mL) were degassed for three freeze-thaw-pump cycles and filled with N$_2$. The mixture was then heated at 60°C for 3 days. The solvent was then removed under vacuum and the red crude mixture was purified by silica gel column chromatography (230-400 mesh) eluting with a solvent mixture of hexane: EtOAc (1:1). Rh(ttp)NHSO$_2$Ph 3a (7.7 mg, 0.008 mmol, 71%) was collected.
Reactions at 120 °C

(1) Reaction between Rh(ttp)NHSO₂Ph and tri-\textit{n}-butylamine

Rh(ttp)NHSO₂Ph 3a (10.3 mg, 0.011 mmol) and tri-\textit{n}-butylamine (1.5 mL) were degassed for three freeze-thaw-pump cycles and filled with N₂. The mixture was then heated at 120 °C for 4 hours. The solvent was then removed under vacuum and the red crude mixture was purified by silica gel column chromatography (70-230 mesh) eluting with a solvent mixture of hexane: CH₂Cl₂ (1:1). A red product Rh(ttp)"Bu 4a (6.2 mg, 0.007 mmol, 67%), with Rᵢ = 0.72 (hexane/ CH₂Cl₂ = 1:1) was collected.

(2) Reaction between Rh(ttp)NHSO₂Ph and di-\textit{n}-butyl ether

Rh(ttp)NHSO₂Ph 3a (10.8 mg, 0.012 mmol) and di-\textit{n}-butyl ether (1.5 mL) were degassed for three freeze-thaw-pump cycles and filled with N₂. The mixture was then heated at 120 °C for 3 hours. The solvent was then removed under vacuum and the red crude mixture was purified by silica gel column chromatography (70-230 mesh) eluting with a solvent mixture of hexane: CH₂Cl₂ (1:1). A mixture of product containing Rh(ttp)CO"Pr 4c, Rh(ttp)"Pr 71 4b and unknowns (5.4 mg, 50%) was obtained. Rh(ttp)CO"Pr 4c. \(^1\text{H}\) NMR (CDCl₃, 300 MHz) \(\delta\) -3.10 (t, 2 H, \(J = 6.9\) Hz), -1.30 (sext, 2 H, \(J = 7.0\) Hz), -1.16 (t, 3 H, \(J = 7.1\) Hz), 2.70 (s, 12 H), 7.54 (d, 8 H, \(J = 8.1\) Hz), 8.03 (dd, 4 H, \(J = 2.0\) Hz, 7.5 Hz), 8.08 (dd, 4 H, \(J = 2.0\) Hz, 7.5 Hz), 8.79 (s, 8 H). \(^{13}\text{C}\) NMR (CDCl₃, 100 MHz) \(\delta\) 11.3, 16.3, 24.5, 45.6, 122.6, 127.4, 131.5,
133.7, 134.1, 137.2, 143.1, 202.6 (d, $J = 29$ Hz). HRMS (FABMS): calcd for $(C_{52}H_{43}N_{4}RhO)^{+}$ m/z 843.2565, found m/z 843.2544.

(3) Reaction between Rh(ttp)NHSO$_2$Ph and toluene

Rh(ttp)NHSO$_2$Ph 3a (10.7 mg, 0.012 mmol) and toluene (1.5 mL) were degassed for three freeze-thaw-pump cycles and filled with N$_2$. The mixture was then heated at 120 °C for 2 hours. The solvent was then removed under vacuum and the red crude mixture was purified by silica gel column chromatography (230-400 mesh) eluting with a solvent mixture of hexane: CH$_2$Cl$_2$ (1:1). A red product Rh(ttp)Bn 4d (7.6 mg, 0.009 mmol, 76%), with $R_f = 0.55$ (hexane/ CH$_2$Cl$_2$ = 1:1) was collected. $^1$H NMR (CDCl$_3$, 300 MHz) δ -3.79 (d, 2 H, $J = 3.6$ Hz), 2.70 (s, 12 H), 2.95 (d, 2 H, $J = 7.2$ Hz), 5.87 (t, 2 H, $J = 7.5$ Hz), 6.40 (t, 1 H, $J = 6.9$ Hz), 7.54 (t, 8 H, $J = 5.7$ Hz), 8.00 (dd, 4 H, $J = 2.1$, 7.1 Hz), 8.06 (dd, 4 H, $J = 2.1$, 7.1 Hz), 8.67 (s, 8 H).

(4) Reaction between Rh(ttp)NHSO$_2$Ph and $n$-hexane

Rh(ttp)NHSO$_2$Ph 3a (10.7 mg, 0.012 mmol) and $n$-hexane (1.5 mL) were degassed for three freeze-thaw-pump cycles and filled with N$_2$. The mixture was then heated at 120°C for 1 day. The solvent was then removed under vacuum and the red crude mixture was purified by silica gel column chromatography (230-400 mesh) eluting with a solvent mixture of hexane: EtOAc (1:1). Rh(ttp)NHSO$_2$Ph 3a (2.8 mg, 0.003 mmol, 26 %) was collected.
4.6 Mechanistic Investigation

(1) Thermolysis of Rh(ttp)NH\textsubscript{2}OPh in Benzene-\textit{d}\textsubscript{6}

Rh(ttp)NH\textsubscript{2}OPh \textit{3a} (1.5 mg, 0.002 mmol) was added into benzene-\textit{d}\textsubscript{6} (500 \mu\text{L}) in an NMR tube under N\textsubscript{2}. The red solution was degassed for three freeze-thaw-pump cycles and the NMR tube was flame-sealed under vacuum. The reaction mixture was heated at 60 °C for 2 day, then at 80 °C for 1 day, finally at 110 °C for 8 days. The reaction mixture was monitored with \textsuperscript{1}H NMR spectroscopy with NMR yields measured using the residual benzene signal as the internal standard.

(2) Thermolysis of Rh(ttp)NH\textsubscript{2}OPh in Benzene-\textit{d}\textsubscript{6} in the Presence of 100 Equivalents of H\textsubscript{2}O

Rh(ttp)NH\textsubscript{2}OPh \textit{3a} (1.4 mg, 0.002 mmol) and water (3 \mu\text{L}, 0.167 mmol) were added into benzene-\textit{d}\textsubscript{6} (500 \mu\text{L}) in an NMR tube under N\textsubscript{2}. The red solution was degassed for three freeze-thaw-pump cycles and the NMR tube was flame-sealed under vacuum. The reaction mixture was heated at 80 °C for 1 day and then at 110 °C for 2 days. The reaction mixture was monitored with \textsuperscript{1}H NMR spectroscopy with NMR yields measured using the residual benzene signal as the internal standard.

(3) Thermolysis of TsNH\textsubscript{2}HTs in Benzene-\textit{d}\textsubscript{6} in the presence of 100 equiv of H\textsubscript{2}O

TsNH\textsubscript{2}HTs (0.7 mg, 0.002 mmol) and H\textsubscript{2}O (3 \mu\text{L}, 0.167 mmol) were added into benzene-\textit{d}\textsubscript{6} (500 \mu\text{L}) in an NMR tube under N\textsubscript{2}. The colourless solution was degassed
for three freeze-thaw-pump cycles and the NMR tube was flame-sealed under vacuum.

The reaction mixture was heated at 120 °C for 1 day. The reaction mixture was monitored with $^1$H NMR spectroscopy with NMR yields measured using the residual benzene signal as the internal standard.

(4) Reaction between [Rh(ttp)]$_2$ and TsNHNHTs

TsNHNHTs (0.5 mg, 0.002 mmol) was added into benzene-$d_6$ (500 µL) solution of [Rh(ttp)]$_2$ 5 (0.002 mmol) in an NMR tube under N$_2$. The red solution was degassed for three freeze-thaw-pump cycles and the NMR tube was flame-sealed under vacuum. The reaction mixture was stored at room temperature for 6 days and was monitored with $^1$H NMR spectroscopy with NMR yields measured using the residual benzene signal as the internal standard. Rh(ttp)NHTs. $^1$H NMR (CDC$_3$, 400 MHz) δ 2.73 (s, 12 H), 3.65 (d, 2 H, $J = 7.9$ Hz), 6.11 (d, 2 H, $J = 7.5$ Hz), 7.58 (dd, 8 H, $J = 7.8$ Hz, 13.4 Hz), 8.07 (dd, 8 H, $J = 7.7$ Hz, 12 Hz), 8.84 (s, 8 H). The proton signal for the N-H hydrogen were not located. $^{13}$C NMR (CDCl$_3$, 100 MHz) 21.5, 22.04, 122.4, 123.8, 126.9, 127.9, 128.0, 128.6, 132.3, 134.1, 134.6, 137.9, 139.4, 142.7; HRMS (FABMS): calcd for (C$_{55}$H$_{44}$N$_5$S$_2$Rh)$^+$ m/z 941.2265, found m/z 941.2305.

(5) Reactions of Rh(ttp)H and PhSO$_2$NH$_2$ in Benzene-$d_6$

PhSO$_2$NH$_2$ (0.3 mg, 0.002 mmol) was added into benzene-$d_6$ (500 µL) solution of Rh(ttp)H 8 (0.002 mmol) in an NMR tube under N$_2$. The red solution was degassed
for three freeze-thaw-pump cycles and the NMR tube was flame-sealed under vacuum.

The reaction mixture was heated at 120 °C for 2 days and was monitored with $^1$H NMR spectroscopy with NMR yields measured using the residual benzene signal as the internal standard.

(6) Reaction between [Rh(ttp)]$_2$ and PhSO$_2$NH$_2$

PhSO$_2$NH$_2$ (0.3 mg, 0.002 mmol) was added into benzene-$d_6$ (500 µL) solution of [Rh(ttp)]$_2$ 5 (0.002 mmol) in an NMR tube under N$_2$. The red solution was degassed for three freeze-thaw-pump cycles and the NMR tube was flame-sealed under vacuum. The reaction mixture was stored at room temperature for 6 days and was monitored with $^1$H NMR spectroscopy with NMR yields measured using the residual benzene signal as the internal standard.

(7) Reactions of Rh(ttp)H and Rh(ttp)NH$_2$SO$_2$Ph in Benzene-$d_6$

Rh(ttp)NH$_2$SO$_2$Ph 3a (1.5 mg, 0.002 mmol) was added into benzene-$d_6$ (500 µL) solution of Rh(ttp)H 8 (0.001 mmol) in an NMR tube under N$_2$. The red solution was degassed for three freeze-thaw-pump cycles and the NMR tube was flame-sealed under vacuum. The reaction mixture was stored at room temperature for 3 days and was monitored with $^1$H NMR spectroscopy with NMR yields measured using the residual benzene signal as the internal standard.
References:


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


(54) (a) Lyman, W. J.; Reehl, W. F.; Rosenblatt, D. H. Handbook of Chemical Property Estimation Methods: Environmental Behavior of Organic Compounds;


(58) Choi, K. S. Unpublished result, 2009


Appendix I

X-ray Data of (H$_2$O)Rh(ttp)NHSO$_2$Ph

Figure 1 ORTEP presentation of molecular structure of (H$_2$O)Rh(ttp)NHSO$_2$Ph (30% thermal ellipsoids)

Figure 2

- The conformations of porphyrins in (H$_2$O)Rh(ttp)NHSO$_2$Ph showing the displacement of the core atoms and of Rh from the 24-atom least squares plane of porphyrin core (in pm; negative values correspond to displacement towards the amido ligands). Absolute values of the angles between pyrrole rings and least-squares plane and angles between tolyl substituents and the least-squares plane are shown in bold.
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## Appendix II

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