HYDRAZINE DISPROPORTIONATION CATALYZED

BY Pincer RhoDium Complexes

By

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Alan S. Goldman

And approved by

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ABSTRACT OF THE THESIS

HYDRAZINE DISPROPORTIONATION CATALYZED

BY PINCER RHODIUM COMPLEXES

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JIA SONG

Thesis Director:

Alan S. Goldman

In order to achieve the process from nitrogen and hydrogen to ammonia under mild conditions thus save energy cost, possible intermediates have to be located and good catalysts need to be found. Hydrazine (N₂H₄) is believed to be one of the intermediates in this process.

This thesis aims to find a comparatively good catalyst towards hydrazine to establish a potential catalytic nitrogen fixation cycle.

At the very beginning of this project, a preliminary screening was done to locate a potentially good catalyst towards hydrazine. The pincer rhodium fragment gave promising result: disproportionation ratio products (N₂ and NH₃) were achieved in comparatively short time under room temperature.

A mechanism of this disproportionation reaction was then calculated. It contains of two pathways: hydrogenation and dehydrogenation. The calculated barriers show that
dehydrogenation should be slower than hydrogenation. Thus the supply of hydrogen to the hydrogenation pathway is constrained. Reactions under hydrogen atmosphere proved this result. And also, kinetic studies were done to partially prove the calculated mechanism.

When the reaction was carried out with pincer rhodium hydridochloride as the catalyst precursor, base (NaO\text{\text{-}Bu}) was needed to provide the 14 electron species to start the catalytic cycle. It was found that reactions under more base gave less ammonia with similar reaction rate. This means hydrogenation pathway was hindered under basic condition.

Then reactions with substituted hydrazines were done to stop the reaction at the diazene stage to prove the calculated dehydrogenation pathway. In these reactions, C-H activation and double N-H activation on the same nitrogen atom were observed.
Dedication

To my parents, Yongping and Zewen, my husband, Shengbo,

You support me with care and love everyday.
Acknowledgements

Firstly, I would like to thank my advisor Prof. Alan S. Goldman. He guided me throughout the challenging project. His enthusiasm in science and generosity as an advisor really inspired me in these three years.

I would also like to thank my committee member Prof. Karsten Krogh-Jespersen (along with Goldman group member Tian Zhou). They supported my project with calculated results.

I would like to thank my previous committee member Dr. Kai Hultszch. He gave me suggestions and advice on my project and led me to the deep scientific world as my first advisor during my rotation time.

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I would like to thank all Goldman group members. Especially to Tian Zhou. He provided all the computational results and discussed with me about the relations between the experimental parts and theoretical parts. I would like to thank Dr. Michael Haibach, Yang Gao and Michael Blessent for all the discussions we have had and advice you gave to me. Those really inspired me a lot.
Finally, I would like to thank my family and friends. My mom, Yongping, taught me to be strong. I cannot always be at her side during her hardest time, which is the most regretful thing in my life, but she supported my every decision and led me to face everything with super positive attitude. Although she’s not here any more, I'll live with her spirit forever, just like she’s here by my side. My dad, Zewen, the best husband and dad in this world, taught me highest level of love, gave me unconditional support and has been my closest friend. My husband, Shengbo Huang, held my hands, walked through my most difficult time together with me and tried his best to hang smile on my face. Thank you all for the true love you gave me. That is the motivation of my future.
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I. Introduction

Ammonia is very important in our everyday life. Fertilizers made from ammonia feed a great population’s sustaining. And ammonia is also the precursor to a wide range of nitrogenous compound. Natural plants can fix nitrogen to nitrogenous compound using their own nitrogenase, while main industrial way to fix nitrogen to produce ammonia is Habor-Bosch process. However, this is an energy-consuming process, accounting for 1%-2% of the world’s energy supply. The hush reaction condition of this process arises from the high first bond dissociation energy of dinitrogen. Acetylene is a similar compound to dinitrogen. Its first dissociation energy of the triple bond is 53 kcal/mol. However, this number is as high as 98 kcal/mol for dinitrogen. And also, dinitrogen has poor \( \sigma \)-donating and weak \( \pi \)-accepting as ligand. All these make the activation of dinitrogen the main problem of the fixing process. So better catalyst that can be used under milder conditions should be explored.

Nishibayashi’s group found that dinitrogen can be reduced to ammonia with the use of pincer molybdenum catalyst under room temperature, together with an electron source and a proton source, similar process to nature (Scheme 1). Bimetallic ruthenium pincer complex is also reported to try to mimic the natural progress.
Scheme 1 Dinitrogen Reduction by Nishibayashi’s Group

However, we want a process without the strong acid and reductant—a process similar to Habor-Bosch: start from only nitrogen and hydrogen, but with milder condition, end only to ammonia, thus to give it a promising future application in industrial production. This process is believed to go through two intermediate, diazene and hydrazine (Equation 1). Due to the fact mentioned before: the first bond dissociation of nitrogen triple bond is as high as 98kcal/mol, the first hydrogen addition step to make diazene will be highly endothermic and difficult. But the following steps are much more favorable. Thus made hydrazine a good start to study this process.

\[
\begin{align*}
N_2 + H_2 & \xrightarrow{H_2} N_2H_4 \xrightarrow{H_2} \quad \text{NH}_3
\end{align*}
\]

(1)

There are several previous examples shown the disproportionation reaction of hydrazine to give ammonia and dinitrogen with different kinds of catalyst. Nune’s group reported this reaction with the help of a high-oxidation state molybdenum complex \([\text{MoO}_2(\text{acac})_2]\) \((\text{acac}=\text{acetylacetonate})\)^3. 10 TON can be achieved and no hydrogen was observed. A mechanism cycle was proposed including the proton transfers between hydrazine and molybdenum center. A later example includes a NNN pincer iron catalyst reported by Ikariya’s group, where proton transfers happened between hydrazine and the
ligand backbone according to the proposed mechanism (Figure 1). Similar to the previous example, no hydrogen was formed during this process. The protons of hydrides produced in the dehydrogenation process were stored in the catalyst in both of these two cases.

**Figure 1** Structure of the Catalyst Used by Ikariya’s Group

The pincer-ligated iridium fragment \((\text{tBu}^4\text{PCP})\text{Ir}\) \((\text{PCP}=\kappa^3\cdot 3\cdot 2\cdot 6\cdot\text{bis}[\text{di-tert-butylphosphino}]\text{methyl}]\text{phenyl})\) can do C-H activation of a wide range of substrates based on the previous work of our group. These gave the basic foundation of trying these catalysts on N-H activation of hydrazine and the following steps.

Hartwig’s group reported the N-H activation of substituted hydrazines by using \((\text{tBu}^4\text{PCP})\text{Ir}\) complex in 2010. Several kinds of oxidative addition product was observed (Scheme 2). The reaction will not stop at here, it will continue via a second N-H activation on the same nitrogen atom to give an isodiazene complex or \(\alpha\)-methyl C-H activation and N-N bond cleavage to give isocyanide complex and ammonia (Scheme 3).
Scheme 2 Hydrido-iridium Hydrazido Complex Formation via N-H Bond Activation

Scheme 3 Double N-H Activation and α-methyl C-H Bond Activation

The feasibility of reductive elimination forming ammonia from the metal center of (tBu₄PCP)Ir catalyst was also reported by Hartwig’s group. (Scheme 4)

Scheme 4 Reductive Elimination from Iridium Center to Form Ammonia

Based on all the above result, hydrazine is a good start point to get into the process forming ammonia from nitrogen and hydrogen. Kathleen D. Field in our group found that (tBuPCP)Ir show dual reactivity towards hydrazine under different conditions (Scheme 5).

This thesis reports some catalysts that showed good activity towards hydrazine disproportionation. Experimental and computational studies are combined to give a raw
scheme of both the reduction route and oxidation route.

**Scheme 5** Dual Reactivity of (tBu₅PC)(PCP)Ir towards Hydrazine

II. Results and Discussion

2.1 Preliminary screening

As mentioned above, catalysts bearing a pincer-ligated backbone are a good starting point. However, other catalysts showed activity in different kinds of C-H activation and N-H activation are still worth trying. Table 1 listed the catalysts tried at the screening stage. The highly stable Cp*-Ir(III) complexes with N-heterocyclic carbene ligands (1 and 2) are known to activate C-H bond of a wide range of substrates and can be used in the deuteration of organic molecules.11,12 As for the catalytic activity towards hydrazine, although there seemed to be some reaction of 1, only 10% hydrazine were consumed in two days and products are not clear. Another Cp*-Ir(III) catalyst 3 was also tried, but no reaction showed in two days. So this kind of catalyst may not be a good category to give further study.

(PNP)Rh (PNP = (2-IP₆PC₆H₄)₂N) complex 4 are mostly studies in C-H and O-H oxidation.13
(iprXanPOP)RhH₂ cationic pincer complex 5 was reported to catalyze alkane dehydrogenation.¹⁴ (tBu₄PCP)Rh complexes (6, 7 and others not listed at here) have been studied widely by Milstein's group.¹⁵⁻¹⁸ Among these pincer rhodium catalyst (4, 5, 6, 7), Only 5 showed poor reactivity towards hydrazine. All other three showed good reactivity of hydrazine. They all consumed hydrazine 100% in two days and give ammonia (0.2ppm in ¹H NMR spectrum, Figure 2) as product. With the basis of the studies of (tBu₄PCP)Ir complexes in our group, (tBu₄PCP)Rh is a good start in this project.

Table 1 Preliminary Result of Catalysts in Catalytic Hydrazine Reactions

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Solvent</th>
<th>Additive</th>
<th>Temperature</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CD₂Cl₂</td>
<td>1 equiv. AgOTf</td>
<td>reflux</td>
<td>48h</td>
</tr>
<tr>
<td>2</td>
<td>CD₂Cl₂</td>
<td>N/A</td>
<td>reflux</td>
<td>48h</td>
</tr>
</tbody>
</table>

Figure 2 Ammonia formation in ¹H NMR spectrum
<table>
<thead>
<tr>
<th>Structure</th>
<th>CD$_2$Cl$_2$</th>
<th>Reaction Conditions</th>
<th>Percentage</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Structure 3" /></td>
<td>1 equiv. AgOTf</td>
<td>reflux</td>
<td>48h</td>
<td>NR</td>
</tr>
<tr>
<td><img src="image" alt="Structure 4" /></td>
<td>$p$-xylene-$d_{10}$</td>
<td>rt</td>
<td>98% hydrazine consumed, ammonia detected</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Structure 5" /></td>
<td>benzene-$d_6$</td>
<td>75 °C</td>
<td>5% hydrazine consumes, ammonia detected</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Structure 6" /></td>
<td>$p$-xylene-$d_{10}$</td>
<td>rt</td>
<td>98% hydrazine consumed, ammonia detected</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Structure 7" /></td>
<td>1 equiv. NaO'Bu</td>
<td>rt</td>
<td>98% hydrazine consumed, ammonia detected</td>
<td></td>
</tr>
</tbody>
</table>

All observations were got from NMR spectrum

2.2 Proposed Mechanism

A mechanism was proposed and the energies of the intermediates were calculated (Scheme 6, 7). This process was calculated to have two pathways: hydrogenation and dehydrogenation. Right cycle of Scheme 6 is dehydrogenation pathway. Starting from
(tBu4PCP)RhN2H4 (from substitution reaction of (tBu4PCP)RhN2), N-H activation first happens to give the oxidative addition product (tBu4PCP)Rh(H)(NHNH2). Then with β-H elimination, first molecule of dihydrogen was released. Then diazene N-H activation followed by another β-H elimination gives the second molecule of dihydrogen and give back the starting catalyst (tBu4PCP)RhN2. As for the hydrogenation pathway on the left side of Scheme 6, it also starts from the first N-H activation product (tBu4PCP)Rh(H)(NHNH2). With the next H-transfer, it will release the first molecule of ammonia. Then with the hydrogen produced in the dehydrogenation cycle coordinated to the rhodium center, two subsequent H-transfers give the second molecule of ammonia. One of the right cycle with two of the left cycle will give the disproportionation reaction of hydrazine (Equation 2).

**Scheme 6** Proposed Mechanism of Hydrazine Disproportionation Catalyzed by (tBu4PCP)RhN2

\[
3N_2H_4 \xrightarrow{\text{cat}} N_2 + 4NH_3 \quad (2)
\]

The energies of the proposed intermediates were also calculated (Scheme 7,8). Rate determine step of both the pathways are the steps after first N-H activation. For dehydrogention, it's β-H elimination (40 kcal/mol). And for hydrogenation, it's the
H-transfer from rhodium center to β-N (39.7 kcal). Although these numbers are too high for these reactions to happen under room temperature, which is the experimental results, however, at least it shows the barrier of dehydrogenation is higher than that of the hydrogenation. So we should expect a lower rate of dehydrogenation. But the dihydrogen produced in dehydrogenation is one of the substrate in hydrogenation pathway. Thus theoretically, even with a higher reaction rate, the limited of dihydrogen supply rate may constrain the hydrogenation pathway. Experimentally, no free dihydrogen was observed, this agrees with the calculated results.

With all the above theoretically and experimental results in hand, more research should be done to further test the proposed mechanism.

**Scheme 7** Calculated Energies of Dehydrogenation Pathway (kcal/mol)
Scheme 8 Calculated Energies of Hydrogenation Pathway (kcal/mol)

2.3 Reactions under Hydrogen Atmosphere

From the above results, hydrogenation pathway may be constrained by the limited supply of dihydrogen from dehydrogenation pathway. Experimental results are listed in Table 2. First is the normal catalytic reaction under argon atmosphere. 50% conversion was achieved in 4h and the reaction was complete in 29h. Yield of ammonia is 130mM, which means the reaction was a disproportionation reaction, as listed on the left below.

Then the following three reactions were carried out under 0.5 atm, 1 atm, 2 atm hydrogen atmospheres. Let’s first see the production of ammonia. Under 0.5 atm hydrogen, when 50% conversion was reached, ammonia concentration was 85mM, higher than that of reaction under argon atmosphere; and at 50h, when 90% of hydrazine was consumed, ammonia concentration is 140mM, already larger than the disproportionation 100% yield. Under 1 atm hydrogen atmosphere, when less than 50% hydrazine was consumed (10h), the concentration of ammonia product has already reached 90mM and in 50h, when 70mM
hydrazine was consumed, 135mM was produced—almost the hydrogenation only ratio.

Furthermore, for the reaction under 2 atm hydrogen atmosphere, the ratio between the amount of hydrazine consumed and the amount of ammonia produced is exactly 2—the hydrogenation reaction ratio. From all these results, we know under higher pressure of hydrogen atmosphere, more ammonia can be got. This means with enough hydrogen source, hydrogenation pathway now showed its full power to react much faster than the dehydrogenation pathway. This is the same result as the calculated barriers.

Another fact should be noticed from Table 2 is the slower rate under higher hydrogen atmosphere. And also, more (tBu₄PCP)RhH₂ complex was formed under higher hydrogen atmosphere reactions. Thus we know (tBu₄PCP)RhH₂ is not one of the intermediate in the mechanism cycle. Under higher atmosphere, the equilibrium between active (tBu₄PCP)Rh and (tBu₄PCP)RhH₂ slow down the whole reaction. Under 0.5 atm hydrogen atmosphere, starting (tBu₄PCP)RhH₂ amount was 50%, this means the reaction rate was slowed down by 50% and under 2 atm hydrogen atmosphere, almost 90% of the whole rhodium species were (tBu₄PCP)RhH₂, so the reaction rate is only 10% of what it should be. Under argon atmosphere, the only source of hydrogen was from dehydrogenation pathway. It was rapidly consumed by hydrogenation pathway, blocked the opportunity of form (tBu₄PCP)RhH₂. So formation of (tBu₄PCP)RhH₂ is the reason of the relative reaction rates in Table 2.
Table 2 Catalytic Reactions of Hydrazine under Hydrogen Atmosphere

\[
\begin{align*}
[\text{PCP}]\text{RhN}_2 + \text{N}_2\text{H}_4 & \xrightarrow{\text{gas, cat}} \text{p-xylene-}d_{10}, \text{rt} \\
10\text{mM} & \quad 100\text{mM} \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>Gas</th>
<th>Time</th>
<th>[N\textsubscript{2}H\textsubscript{4}]</th>
<th>[NH\textsubscript{3}]</th>
<th>Observed Intermediate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar, 1 atm</td>
<td>4h</td>
<td>50mM</td>
<td>67mM</td>
<td>2% 0% 51% 47%</td>
</tr>
<tr>
<td></td>
<td>29h</td>
<td>2mM</td>
<td>130mM</td>
<td>20% 0% 14% 66%</td>
</tr>
<tr>
<td>H\textsubscript{2}, 0.5 atm</td>
<td>7h</td>
<td>50mM</td>
<td>85mM</td>
<td>0% 48% 16% 25%</td>
</tr>
<tr>
<td></td>
<td>50h</td>
<td>10mM</td>
<td>140mM</td>
<td>60% 2% 5% 24%</td>
</tr>
<tr>
<td>H\textsubscript{2}, 1 atm</td>
<td>10h</td>
<td>55mM</td>
<td>90mM</td>
<td>0% 89% 0% 9%</td>
</tr>
<tr>
<td></td>
<td>50h</td>
<td>30mM</td>
<td>135mM</td>
<td>0% 80% 0% 19%</td>
</tr>
<tr>
<td>H\textsubscript{2}, 2 atm</td>
<td>23h</td>
<td>53mM</td>
<td>95mM</td>
<td>0% 91% 0% 7%</td>
</tr>
<tr>
<td></td>
<td>50h</td>
<td>42mM</td>
<td>110mM</td>
<td>0% 87% 0% 9%</td>
</tr>
</tbody>
</table>

All observations were got from NMR spectrum

2.4 Synthesis of Catalyst with Agostic C-H Bond

In section 2.2, it is proved that the barrier of hydrogenation is lower than that of dehydrogenation. If we want ammonia as the only main product, we should push hydrogen
into the reaction system. However, the formation of \((^{t\text{Bu}_4\text{PCP}})\text{RhH}_2\) under hydrogen atmosphere slow down the reaction. To solve this problem, catalyst should be modified to further lower the barrier of the hydrogenation pathway. Thus we can still rapidly get ammonia as the only main product, and at the same time, block the dehydrogenation pathway.

In 1998, Milstein's group found that an \(\eta^2\) C-H agostic bond can be formed by direct addition of proton acid (Scheme 9)\(^{17}\). If we apply the agostic \((^{t\text{Bu}_4\text{PC}(H)P})\text{Rh}\) core into the catalytic hydrazine reaction, DFT calculations show that (Scheme 10) the barrier of dehydrogenation will be raised from 40 kcal/mol (green numbers) to 43.2 kcal/mol (red numbers). And the barrier of hydrogenation will be greatly reduced: from 39.7 kcal/mol (green numbers) to 28.2 kcal/mol (red numbers). So this kind of agostic rhodium complex may realize the hypothesis mentioned above.

**Scheme 9** Reversible Agostic C-H Bond formation

![Scheme 9](image-url)
Scheme 10 Calculated Energies of Catalytic Hydrazine Reaction with Agostic (tBu4PC(H)P)Rh Catalyst

Then experiment trying to get agostic (tBu4PC(H)P)RhN2 was carried out (Scheme 11). Comparable to the reaction shown in Scheme 8, complex bearing an agostic bond was supposed to get (Figure 3). According to Milstein's result, the agostic C-H bond has a doublet peak at 4.13 ppm ($J_{RhH} = 18.1$Hz) in $^1$H NMR. However, such kind of peak was not observed in the product of the reaction in Scheme 8. $^{31}$P NMR spectrum showed full conversion of the starting (tBu4PC)RhN2 (81.27ppm, d, $J_{RhP}$=160.9Hz) to a new complex bearing a doublet peak at 77.01ppm ($J_{RhP}$=115.7Hz). $^1$H NMR of the product gave a new hydride peak at -28.03ppm (d, $J_{RhH}$= 50.4Hz).

Scheme 11 Addition of Acid into (tBu4PC)RhN2 Solution

Figure 3 Expected Product of the Reaction in Scheme 11
All of the above results implied that the expected product shown in Figure 3 has not been formed. Then what was the real product 6-1-a? \((\text{tBu}^4\text{PCP})\text{RhHCl} \) 7 has a doublet peak at -27.50 ppm with \(J_{\text{RhH}} = 50.8\text{Hz}\) in \(^1\text{H}\text{NMR}\). As for \(^{31}\text{P}\text{NMR}\), it has a doublet peak at 74.91 with \(J_{\text{RhP}} = 115.5\text{Hz}\). With both similar hydride shift and coupling constants, the result of the reaction in Scheme 11 may just be that the acid just substitute dinitrogen and coordinate to the rhodium center (Scheme 12). To further testify this hypothesis, reactions with other kinds of protic acids were carried out (Scheme 12). NMR data of the products were summarized in Table 3.

**Scheme 12** Reactions between \((\text{tBu}^4\text{PCP})\text{RhN}_2\) with Different Acid and Further with Hydrazine

![Diagram]
Table 3 NMR Data for Reactions in Scheme 12

<table>
<thead>
<tr>
<th></th>
<th>Hydride peak in $^1$H NMR (ppm)</th>
<th>Coupling $^3$P NMR (ppm)</th>
<th>Coupling</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-1-a</td>
<td>-28.03</td>
<td>d, $J_{RhH} = 50.4$ Hz</td>
<td>77.01</td>
</tr>
<tr>
<td>6-1-b</td>
<td>-17.15</td>
<td>m</td>
<td>75.50</td>
</tr>
<tr>
<td>6-2-a</td>
<td>-27.40</td>
<td>d, $J_{RhH} = 58.2$ Hz</td>
<td>76.05</td>
</tr>
<tr>
<td>6-2-b</td>
<td>-17.17</td>
<td>m</td>
<td>75.60</td>
</tr>
<tr>
<td>6-3-a</td>
<td>-23.85</td>
<td>d, $J_{RhH} = 42.0$ Hz</td>
<td>79.08</td>
</tr>
<tr>
<td>7</td>
<td>-27.50</td>
<td>d, $J_{RhH} = 50.8$ Hz</td>
<td>74.91</td>
</tr>
<tr>
<td>7-1</td>
<td>-17.22</td>
<td>m</td>
<td>76.16</td>
</tr>
</tbody>
</table>

Reactions of (tBu₄PCP)RhN₂ 6 with three different kind of protic acids (HOTf, HBF₄.OEt₂, TFA) together with (tBu₄PCP)RhHCl all gave a high-field doublet peak around -25ppm, oxidative addition of the acid. HBF₄.OEt₂ was tried to avoid the coordination of the anion part of the acid thus would probably gave the agostic product. However, the strong coordination ability of the ether still killed this proposal, gave an ionic rhodium complex 6-2-a. The five coordinated rhodium complexes 6-1-a, 6-3-a and 7 further react with hydrazine can gave the six coordinated 6-1-b, 6-3-b and 7-1. All hydride peaks moved towards low field.

In Milstein’s reaction, they use (tBu₄PCP)Rh(CO) as the substrate. This is an air-stable complex, more stable than others with a “non-CO” ligand. Similarly in (tBu₄PCP)Ir complexes,
based on our group's research, \((\text{tBu}_4\text{PCP})\text{Ir}(\text{CO})\) is regarded as the “end” of the this series. It's so stable that CO can hardly be replaced. So when \((\text{tBu}_4\text{PCP})\text{Rh}(\text{CO})\) reacted with HOTf, the strong coordination between CO and rhodium center prevent the substitution, then the proton can be added to the coordinated carbon. In other \((\text{tBu}_4\text{PCP})\text{Rh}\) complexes, the ligand can be easily substituted by the acid thus agostic complex cannot be obtained.

2.5 Base Effect

In the reactions starting from \((\text{tBu}_4\text{PCP})\text{RhHCl}\), base (NaO\text{tBu}) is needed to drag away HCl from rhodium center to give the catalytically active species. It was found that if more than 1 equiv. base was added to the reaction system, less ammonia product would form. (Scheme 13, second and third reactions) When 0.2 equiv. extra base was added to the reaction, a comparable could be got but with 5mM less ammonia yield. It also should be noticed that \((\text{tBu}_4\text{PCP})\text{RhH}_2\) was detected during the reaction process, which means there exist free dihydrogen that can not be consumed by hydrogenation pathway in a timely manner. To further illustrate this phenomenon, 0.6 equiv. base was added to the reaction with \((\text{tBu}_4\text{PCP})\text{RhN}_2\) as the starting catalyst (last reaction in Scheme 13). Also, reaction rate was not changed by the addition of extra base with the observation of the existence of \((\text{tBu}_4\text{PCP})\text{RhH}_2\) and even less ammonia yield as low as 50mM. Since ammonia is the product of hydrogenation pathway, these may imply that additional base will slow down the hydrogenation pathway to a number lower than the rate of dehydrogenation pathway. However, dehydrogenation pathway is not restrained by any substrate supply (compare
with hydrogenation) since hydrazine is the only substrate, it maintains the same rate which is faster than hydrogenation now and is still the rate-determine part. This can explain the decreasing yield of ammonia as well as the maintaining reaction rate with the addition of base.

**Scheme 13** Reactions with Extra Base Addition

\[
\text{[PCP]RhN}_2 + N_2H_4 \xrightarrow{\text{no base}} \text{Conv. (Hydrazine): 55\% in 3.5h} \\
10\text{mM} \quad 50\text{mM} \quad p\text{-xylene-}d_{10}, \text{ rt} \\
[NH_3]_{\text{final}} = 65\text{mM}
\]

\[
\text{[PCP]RhHCl + N}_2H_4 \xrightarrow{1 \text{ equiv. NaO}^\text{Bu}_\text{t}} \text{Conv. (Hydrazine): 55\% in 4h} \\
10\text{mM} \quad 50\text{mM} \quad p\text{-xylene-}d_{10}, \text{ rt} \\
[NH_3]_{\text{final}} = 65\text{mM}
\]

\[
\text{[PCP]RhHCl + N}_2H_4 \xrightarrow{1.2 \text{ equiv. NaO}^\text{Bu}_\text{t}} \text{Conv. (Hydrazine): 55\% in 4h} \\
10\text{mM} \quad 50\text{mM} \quad p\text{-xylene-}d_{10}, \text{ rt} \\
[NH_3]_{\text{final}} = 60\text{mM} \\
[\text{[PCP]RhH}_2 \text{ detected}]
\]

\[
\text{[PCP]RhN}_2 + N_2H_4 \xrightarrow{0.6 \text{ equiv. NaO}^\text{Bu}_\text{t}} \text{Conv. (Hydrazine): 55\% in 4h} \\
10\text{mM} \quad 50\text{mM} \quad p\text{-xylene-}d_{10}, \text{ rt} \\
[NH_3]_{\text{final}} = 50\text{mM} \\
[\text{[PCP]RhH}_2 \text{ detected}]
\]

With the proposed mechanism, how can base play such kind of role? From the hydride hydrazindo complex III, hydride transfer from rhodium center to terminal nitrogen is the next step of hydrogenation pathway to release the first molecule of ammonia. Base induced dehydrogenation of ruthenium hydrazine complex was reported before by McIntosh’s group.\(^{19}\) So with the existence of base, the hydride connected to rhodium center may be “stolen” by the base (Scheme 14), and then there will not be enough H to form
ammonia, thus lead to the prevention of hydrogenation pathway. On the other hand, even without that “central” hydride, diazene intermediate can still be formed without the formation of the first molecule of hydrogen in dehydrogenation pathway and continues to release nitrogen and hydrogen. This proposed mechanism can explain all the observations in base effect.

**Scheme 14** Proposed Mechanism for Base Effect

Then a series of reactions were carried out with different amount of base. Different from the results observed before. Higher reaction rate were observed with more base addition. Previously, 0.6 equiv is the highest extra amount of base used, this may lead to inconspicuous rate change. Besides the increasing reaction rate, the steady observed amount of (tBu₄PCP)RhH₂ and decreasing yield of ammonia should also be noticed. Based on
the proposed mechanism, more base will disfavor hydrogenation more to give less ammonia and more nitrogen and hydrogen thus more \((\text{tBu}^4\text{PCP})\text{RhH}_2\). Whereas, the latter inference opposites the experimental results. Even a little less \((\text{tBu}^4\text{PCP})\text{RhH}_2\) was observed under higher base concentration. It is possible that the extra base drag more than one hydride from the rhodium center. So most of the hydrogen atoms in hydrazine become HO-tBu. If this is true, the new peak of the HO-tBu in NMR spectrum would overlap with the peak of THF (initial hydrazine was 0.1M THF solution), thus made it impossible to prove this. Now, only lower yield of ammonia under higher base concentration can be confirmed.

The real mechanism of this base effect still needs further study, experimentally and theoretically.

**Table 4** Further Experimental Base Effect Study

<table>
<thead>
<tr>
<th>Base Amount</th>
<th>50% Conversion Time</th>
<th>98% Conversion Time</th>
<th>(\text{[NH]}_3) Yield</th>
<th>Observed Intermediates</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 equiv.</td>
<td>4 h</td>
<td>29 h</td>
<td>130 mM</td>
<td>20% 0%</td>
</tr>
<tr>
<td>1 equiv.</td>
<td>2 h</td>
<td>&lt;20 h</td>
<td>60 mM</td>
<td>30% 6%</td>
</tr>
<tr>
<td>2 equiv.</td>
<td>1 h</td>
<td>7 h</td>
<td>45 mM</td>
<td>50% 6%</td>
</tr>
<tr>
<td>4 equiv.</td>
<td>1 h</td>
<td>7 h</td>
<td>35 mM</td>
<td>40% 1%</td>
</tr>
<tr>
<td>8 equiv.</td>
<td>1 h</td>
<td>5 h</td>
<td>30 mM</td>
<td>48% 1%</td>
</tr>
</tbody>
</table>
2.6 Kinetic Study

The disproportionation reaction was studied using varying concentrations of \((tBu_4\text{PCP})\text{RhN}_2\) or hydrazine. Consumption of hydrazine and release of ammonia were monitored by \(^1\text{H}\) NMR. Every reaction were monitored all through the 0-100% conversion process, to best eliminate the effect of decreasing rate with increasing consumption of hydrazine and the error introduced by \(^1\text{H}\) NMR spectrum integration at early stage of the reaction because of small peaks of product, data at 30min were chosen as the kinetic results. These data were graphed ammonia release versus substrate concentration to get the order of each substrate. (Figure 4, Figure 5) It is clear from the graphs that this reaction is first order to catalyst \((tBu_4\text{PCP})\text{RhN}_2\) and zeroth order to hydrazine. As for computational results shown in Scheme 6,7,8, rate determine steps do not involve hydrazine, identified with experimental results.
**Figure 4** Ammonia Concentration at 30min in Disproportionation Reaction with Fixed Catalyst (tBu4PCP)RhN₂ Concentration at 10mM and Varied Hydrazine Concentration from 25mM to 150mM
**Figure 5** Ammonia Concentration at 30min in Disproportionation Reaction with Varied Catalyst (tBu₄PCP)RhN₂ Concentration from 5mM to 20mM and Fixed Hydrazine Concentration at 100mM

\[ \text{N}_2\text{H}_4 + \text{PtBu}_2\text{Rh}-\text{N}_2\text{PtBu}_2 \rightarrow \text{rt, p-xylene-d}_10, \text{30min} \]
2.7 Disproportionation of Substituted Hydrazines

Based on the mechanism proposed in Scheme 6, several kinds of substituted hydrazines can be used to let the reaction stop at certain stage (diazene).

2.7.1 Phenylhydrazine

If phenyl hydrazine are used to carry out the catalytic reaction shown in the above contents, according to the proposed mechanism, dehydrogenation pathway should give phenyl diazene and dihydrogen (Equation 3), then hydrogenation pathway can use this dihydrogen to produce aniline and ammonia (Equation 4).

\[
\begin{align*}
\text{PhNHNH}_2 & \rightarrow \text{PhN=NH} + \text{H}_2 \quad (3) \\
\text{PhNHNH}_2 + \text{H}_2 & \rightarrow \text{PhNH}_2 + \text{NH}_3 \quad (4)
\end{align*}
\]

Staring with 10mM of catalyst \((tBu_4\text{PCP})\text{RhN}_2\) and 100mM phenylhydrazine, after more than 2 days, all original phenyl hydrazine disappeared. Aniline was detected and concentration was determined to be 50mM compared with an authentic aniline sample. Ammonia was also detected with 50mM yield. No diazene product detected. But even if phenyldiazene existed, the aromatic hydrogen would probably overlapped with the solvent \(p\)-xylene. And same situation may be applied to the other hydrogen connected to nitrogen atom. Based on the existence and yield of ammonia, it's still safe to conclude that the proposed two pathways (Equation 3,4) happened and gave a total reaction as Equation 5.

\[
\begin{align*}
2\text{PhNHNH}_2 & \rightarrow 0.1 \text{ equiv. (}tBu_4\text{PCP})\text{RhN}_2 \rightarrow \text{2PhN=NH + PhNH}_2 + \text{NH}_3 \\
\text{100mM} & \rightarrow \text{PhN=NH + PhNH}_2 + \text{NH}_3 \quad (5)
\end{align*}
\]
2.7.2 1,1-Diphenylhydrazine

With proposed mechanism, dehydrogenation pathway cannot be applied to 1,1-diphenylhydrazine since there’s no hydrogen atom on one of the nitrogen, so β-H elimination is impossible to release free dihydrogen and give diazene product. However, the catalytic reaction with 1,1-diphenylhydrazine (same condition shown in Equation 5) still gave ammonia as product with 10mM yield after two days. $^{31}$P NMR spectrum monitoring the reaction showed fully conversion from starting ($^{tBu_4}$PCP)RhN$_2$ to a new complex 11 at δ 82.77 (d, $j_{RhP} = 177.0$ Hz). Production of ammonia implied there still exist dehydrogenation reaction. As shown in Scheme 3, Hartwig’s group found double N-H activation on same nitrogen atom can happen to 1,1-dimethylhydrazine with ($^{tBu_4}$PCP)Ir(H)(Ph) as catalyst to give isodiazene complex and release hydrogen. In the case shown here with ($^{tBu_4}$PCP)RhN$_2$, this is the possible way of dehydrogenation (Equation 6). With the hydrogen produced here, hydrogenation pathway can happen to give ammonia and diphenylamine as product (Equation 7).

$$\text{Ph}_2\text{NNH}_2 + (^{tBu_4}\text{PCP})\text{RhN}_2 \rightarrow (^{tBu_4}\text{PCP})\text{Rh} = \text{NNPh}_2 + \text{H}_2 \quad (6)$$

$$\text{Ph}_2\text{NNH}_2 + \text{H}_2 \rightarrow \text{NH}_3 + \text{HNPh}_2 \quad (7)$$

After forming the isodiazene complex, the catalyst will be “killed”. So this reaction is not a catalytic reaction anymore, but a stoichiometric one. Then the total reaction should be Equation 8. Since all species in $^{31}$P NMR spectrum was ($^{tBu_4}$PCP)Rh=NNPh$_2$ experimentally, the yield of this was 10mM. Concentration of HNPh$_2$ was confirmed by comparison with an
authentic sample and integration in $^1$H NMR spectrum. Ratios between these species agreed with proposed double N-H activation on same nitrogen. However, it took more than two days for this kind of double N-H activation to complete: much slower than the other way on different nitrogen atoms. So when original β-H is possible, that will be the dominant way for dehydrogenation.

$$\text{Ph}_2\text{NNH}_2 + (\text{tBu}_4\text{PCP})\text{RhN}_2 \rightarrow (\text{tBu}_4\text{PCP})\text{Rh=NNPh}_2 + \text{HNPh}_2 + \text{NH}_3$$

The isodiazene (or diazenido) complex is proposed to be a intermediate in nitrogenase function process.$^{20}$ The catalytic formation of ammonia from dinitrogen at mononuclear molybdenum center follows this pathway.$^{21,22}$

2.7.3 1,2-Diphenylhydrazine

To further confirm β-H elimination is the dominant pathway when it is possible, 1,2-diphenylhydrazine was then used to carry out the catalytic reaction. Based on the proposed mechanism, azobenzene and aniline should be the product of dehydrogenation and hydrogenation pathways respectively. Free hydrogen produced in dehydrogenation pathway should be consumed.

Experimentally, no aniline product was detected. Free dihydrogen (4.7 ppm broad peak in $^1$H NMR) was detected in this reaction, different from all previous reactions. Free dihydrogen means the occurrence of dehydrogenation pathway. There was fully conversion in $^{31}$P NMR from $(\text{tBu}_4\text{PCP})\text{RhN}_2$ to a new complex 12 at δ 80.72 (d, $J_{\text{RhP}}$ = 138.1 Hz)(Equation 9). This was proposed to be the complex formed between 14 electron rhodium pincer
backbone and the azobenzene product. It was confirmed by direct formation of this complex 12 from (tBu4PCP)RhN₂ and 6 equiv. azobenzene PhN=NPh (Equation 10). It showed a doublet of triplet hydride peak on ¹H NMR spectrum, integrated to one hydrogen atom (δ -14.98 (dt, J = 15.9, 12.7 Hz)).

\[
\begin{align*}
\text{(tBu4PCP)RhN}_2 + \text{PhN=NPh} & \rightarrow \text{12} + \text{H}_2 + \text{10mM} + \text{100mM} + \text{p-xylene-d}_{10}, \text{rt} + \text{9} \\
\text{(tBu4PCP)RhN}_2 + \text{PhN=NPh} & \rightarrow \text{12} + \text{10mM} + \text{60mM} + \text{p-xylene-d}_{10}, \text{rt} + \text{10}
\end{align*}
\]

Complex 12 showed a doublet of triplet hydride peak on ¹H NMR spectrum, integrated to one hydrogen atom (δ -14.98 (dt, J = 15.9, 12.7 Hz)). In Hartwig’s research, when PhMeNNH₂ is used as the substrate, isodiazene is first obtained product. Then C-H activation can happen on phenyl ring to form a five-member ring as the final product. Based on this, the structures of complex 12 was proposed as below in Figure 6. Different from Hartwig’s situation, C-H activation can either happen to the phenyl ring on α-N or the phenyl ring on β-N to give four member ring or five member ring rhodium complex respectively.

**Figure 6** Proposed Structures of Complex 12
III. Conclusion

Catalytic hydrazine disproportionation reactions using \((t\text{Bu}4\text{PCP})\text{Rh}\) complexes were studied and some intermediates were characterized by NMR spectrum. Both experimental and computational results showed there exist two pathways: dehydrogenation to give nitrogen, hydrogen and hydrogenation to give ammonia. Although hydrogenation has a lower barrier, its dependence on the supply of dihydrogen from dehydrogenation pathway when there’s no external source limits its rate. Kinetically, this reaction is first-order to the catalyst and zeroth-order to hydrazine, also agreed with computational result. Several substituted hydrazines were used to carry out the catalytic reaction to further confirm the proposed pathways. Appropriate ones can also give disproportionation products. For the ones bear no hydrogen on one of the nitrogen, a slower double N-H activation on the same nitrogen was observed.

IV. Experimental Methods

General Methods

Unless otherwise specified, all reactions were carried out under argon atmosphere using standard Schlenk techniques, in an argon atmosphere glovebox or in J. Young NMR tubes under argon atmosphere. C₆D₆, CD₂Cl₂ and \(p\)-xylene-\(d_{10}\) were stirred with activated aluminum for 48h, filtered then stored with molecular sieves. Hydrazine and ammonia were purchased from Sigma-Aldrich as solutions in THF, with 1M and 0.01M as concentrations respectively. All other substrates were degassed before bringing into glovebox. Complexes 1
to 7 were synthesized according to literature.\textsuperscript{11-18} NMR spectrums were obtained on 400 MHz and 500 MHz Varian instruments. The residue peak of the deuterated solvent was used as reference to $^1$H NMR spectrum. $^{31}$P NMR spectrum were referenced with P(Me)$_3$ in a capillary.

An internal capillary of ferrocene was used as standard to determine the concentration of ammonia during reaction process. This capillary was inserted into 10mM-200mM (every 10mM) ammonia solutions (0.5ml, same as reaction volume) in $p$-xylene-$d_{10}$ to get the precise ratios between ferrocene peak and ammonia peaks.

$(t$Bu$_4$PCP)RhNH$_3$, 8

It was already reported in 1983\textsuperscript{23} Can be obtained by pumping 1 atm hydrogen atmosphere into 10mM $(t$Bu$_4$PCP)RhN$_2$ solution (2.6mg in 0.5ml $p$-xylene-$d_{10}$). $^{31}$P NMR ($p$-xylene-$d_{10}$, 161.9MHz): $\delta$93.4 (d, $J_{RhP}$ = 154.2Hz) $^1$H NMR ($p$-xylene-$d_{10}$, 400MHz):

$\delta$-4.48 (d, $J_{RhH}$ = 17.2Hz).

$(t$Bu$_4$PCP)RhNH$_3$, 9

2.6mg of $(t$Bu$_4$PCP)RhN$_2$ (0.005mmol) was dissolved in $p$-xylene-$d_{10}$ to make a 0.45ml solution in J. Young NMR tube. 50\,$\mu$L 1M hydrazine solution in THF was then added. Full conversion showed to product at 0.5h under room temperature. $^{31}$P NMR ($p$-xylene-$d_{10}$, 161.9MHz): $\delta$75.3 (d, $J_{RhP}$ = 162.1Hz).

$(t$Bu$_4$PCP)RhNH$_3$, 10
2.6mg of \((\text{tBu}_4\text{PCP})\text{RhN}_2\) (0.005mmol) was dissolved in 0.4ml \(p\)-xylene-\(d_{10}\). 100\(\mu\)L of 0.5M ammonia solution in THF was then added. No obvious color change with the addition of ammonia solution. \(^{31}\text{P} \) NMR showed 80% conversion to the product. \(^{31}\text{P} \) NMR

\((p\text{-}xylene\text{-}d_{10}, 161.9\text{MHz})\): \(\delta 73.8 \) (d, \(J_{\text{RhP}} = 171.1\text{Hz}\)).

**Catalytic Disproportionation of Hydrazine**

Preliminary screening: 0.005mmol catalyst was dissolved in \(p\)-xylene-\(d_{10}\) to make a 0.48ml solution in J. Young NMR tube. 20\(\mu\)L 1M hydrazine solution in THF was then added. Other reactions without any extra additives: 0.005mmol catalyst (2.6mg for \((\text{tBu}_4\text{PCP})\text{RhN}_2\) and \((\text{tBu}_4\text{PCP})\text{RhH}_2\)) was dissolved in \(p\)-xylene-\(d_{10}\) to make a 0.45ml solution in J. Young NMR tube. 50\(\mu\)L 1M hydrazine solution in THF was then added. The solution changed color from light yellow to dark green immediately. The solution was left under room temperature and monitored by NMR spectroscopy at different time intervals. The solution gradually changed color from dark green light green in the reaction process. Ammonia yield was determined by getting the ratio peak area of ammonia produced to the peak area of the inserted ferrocene capillary standard. This ratio was then compared of the ratios of known ammonia solutions to the same capillary to determine

**Catalytic Disproportionation of Hydrazine under Hydrogen Atmosphere**

2.6mg of \((\text{tBu}_4\text{PCP})\text{RhN}_2\) (0.005mmol) was dissolved in \(p\)-xylene-\(d_{10}\) to make a 0.45ml solution in J. Young NMR tube. 50\(\mu\)L 1M hydrazine solution in THF was then added. This solution was immediately frozen by liquid nitrogen after taking out of glovebox. It was then
degassed and pumped in different pressure of hydrogen atmosphere respectively. To get the best interaction between liquid phase and gas phase, a rotary motor was used rotate the J. Young NMR tubes to mix these solutions. Monitoring method and ways to determine product yield are same as above.

**Attempt to Get Agostic C-H Bond**

Every acid (HOTf, TFA, HBF₄OEt₂) was made into a 0.5mM stock solution in p-xylene-d₁₀. 2.6mg of (tBu₄PCP)RhN₂ (0.005mmol) and 50µL acid stock solution was added to J-Young NMR tube. Then 0.45ml of p-xylene-d₁₀ was added to make a total 0.5ml solution. The solution was left under room temperature with the same method of monitoring and determining product yield as shown above.

**Catalytic Disproportionation of Hydrazine with Base**

NaO₄Bu was used as base at here. 9.6mg of NaO₄Bu was added to 1ml in p-xylene-d₁₀ to make a stock solution of base (0.5mM).

2.6mg of (tBu₄PCP)RhN₂ (0.005mmol) and corresponding base stock solution was added to J-Young NMR tube (1equiv. base is 50µL of the stock solution). Then p-xylene-d₁₀ was added to make a total 0.5ml solution. The solution was left under room temperature with the same method of monitoring and determining product yield as shown above.

**Kinetic Experiments**

Reaction conditions were same as the one stated in “catalytic disproportionation of
hydrazine”. Different amount of catalyst and hydrazine were used. All solutions were made finally into 0.5ml in \( p\text{-xylene-d}_{10} \). Monitoring and yield determination were still same as above.

**Reactions with Substituted Hydrazines**

Reaction conditions were same as the ones using simple hydrazine as substrate. 2.5mg \((^{t\text{Bu}4}\text{PCP})\text{RhN}_2\) and 0.05mmol of the corresponding substituted hydrazine were dissolved in 0.45ml \( p\text{-xylene-d}_{10} \) in J. Young NMR tubes. Reactions were left under room temperature and monitored by NMR spectroscopy. Products were confirmed by comparison of NMR spectrum of the reaction with the NMR spectrum of the authentic samples of proposed products. Products yields were determined peak area integration.

**Computational Methods**

All computational results were done by Tian Zhou. All calculations used DFT methodologies implemented in the Gaussian 09 program\(^{23}\). All the data presented in this thesis results from calculations that employed TPSS set of functionals\(^{24}\). Calculation results from these two functionals also support the mechanism we proposed in this work. For Rh, we applied the Hay-Wadt relativistic effective (small) core potential\(^{25}\) and the LANL2TZ basis set\(^{26}\) augmented by a diffuse d-type function (exponent=0.07645)\(^{27}\); all other atoms (P, N, C and H) were assigned 6-311G(d, p) basis set\(^{28}\).

All the geometrics and potential energies were calculated for all the stationary points along the reaction paths by standard optimization procedures. Normal mode analysis
was performed to further verify the nature of a particular stationary point (intermediate or transition state). The resulting set of vibrational frequencies was employed (without scaling) to determine zero-point energy corrections. Enthalpies (ΔH, ΔH°) and Gibbs’ free energies (ΔG, ΔG°; T = 298.15 K, P = 1 atm) were subsequently obtained from the potential energies (ΔE, ΔE°) using standard thermodynamic corrections. In order to enhance computational stability and accuracy in geometry optimization and normal mode calculations, we used increased atomic grid size setting (grid= ultrafine option).
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