REGULAR ARTICLE

Possibility of reducing the coordinated dinitrogen into ammonia and hydrazine using [Ru-L] (L = triamidoamine) and FLP-H₂: A DFT study

THAYALARAJ CHRISTOPHER JEYAKUMAR[✉], SAMBATH BASKARAN and CHINNAPPAN SIVASANKAR*

Catalysis and Energy Laboratory, Department of Chemistry, Pondicherry University, Kalapet, Puducherry 605 014, India

E-mail: chemistchris24@gmail.com; siva.che@pondiuni.edu.in; baskarsambath@gmail.com

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Abstract. DFT studies have been executed on a hypothetical Ru-triamidoamine complex to understand the possibility of synthesizing ammonia and hydrazine from the dinitrogen at normal temperature and pressure in heptane. In this present study, we utilized the H₂ in the form of FLP-H₂ complex and reacted with Ru-triamidoamine complex. We have added three H⁺ and H[−] parts of FLP-H₂ to the Ru complex in a stepwise manner as an alternate way to yield NH₃/N₂H₄. The catalytic cycle for the formation of NH₃ and N₂H₄ were found to be energetically feasible. We have also observed some thermodynamically feasible six coordinate [M]-H intermediates.

Keywords. Nitrogen fixation; reaction mechanism; homogeneous catalysis; density functional calculations; ammonia; FLP (frustrated Lewis pair).

1. Introduction

Generation of ammonia from N₂ and H₂ at low temperature and 1 atm pressure is still a great challenge for inorganic chemists.^{1–13} However, Haber-Bosch process generates more than 100 million tons of ammonia yearly for several applications, and this procedure involves experimental conditions such as high temperature and high pressure.^{14–16} Nevertheless, nitrogenase enzyme converts atmospheric dinitrogen into ammonia at ambient reaction conditions.^{17–23}

Reaction of H₂ with different dinitrogen complexes under different experimental conditions can be seen in Scheme 1, which clearly discriminates the present work. Hidai and co-workers reported that the Chatt complex (cis-[W(N₂)₂(PMe₂Ph)₄]) could be reacted with trans-[RuCl(η²-H₂)(dppp)₂](X = PF₆, BF₄, OTf, BPh₄) to generate ammonia and tungsten species under normal experimental conditions. They achieved only 8–55% of the ammonia with respect to the tungsten complex. In

this reaction, they had used only H⁺ from H₂, as well as this reaction is not catalytic.²⁴ Fryzuk *et al.*, reported a room temperature reaction of [[P₂N₂][Zr]₂(μ-η²-N₂)] (P₂N₂ = PhP(CH₂SiMe₂NSiMe₂CH₂)₂PPh) with dihydrogen to form [[P₂N₂][Zr]₂(2-N₂H)(H)] under longer reaction time.²⁵ Although there is no ammonia production in this report, the reaction is an important one owing to the formation of a new N-H bond by the direct addition of H₂. Chirik *et al.*, reported a direct reaction of [[η⁵-C₅Me₄H]₂Zr]₂(μ₂, η², η²-N₂)] with dihydrogen to produce ammonia (yield 10–15% with respect to the concentration of dinitrogen complex) at 85 °C.²⁶ Holland *et al.*, reported the reaction of (NACNAC)FeCl₂ (NACNAC = MeC[C(Me)N(2,6-Me₂C₆H₃)]₂) with N₂ in the presence of potassium as a reducing agent to yield corresponding nitride complex *via* direct N–N bond cleavage. More interestingly, this nitride complex produced ammonia (42 ± 2%) in the presence of acid. Although ammonia production was not catalytic, this reaction has become more relevant to understand the Haber–Bosch process in which Mittasch catalyzed

*For correspondence

Scheme 1. Dinitrogen complexes reaction with direct H_2 and FLP- H_2 .

produced ammonia from N_2 and H_2 in the presence of suitable electronic and structural promoters.²⁷

Schrock *et al.*,^{28–37} and Nishibayashi *et al.*,^{38–40} have generated ammonia catalytically (Schrock = 8 equiv. of ammonia, Nishibayashi = 23 equiv. of ammonia) using Mo complexes under normal experimental conditions by the addition of proton and electron sources as similar to nitrogenase enzymatic process.

Leitner *et al.*, predicted computationally the synthesis of ammonia using dihydrogen and dinitrogen in the presence of $[\text{M}(\text{H})_2(\text{H}_2)(\text{PXP})]$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$; $\text{X} = \text{N}, \text{O}, \text{S}$). In their proposed catalytic cycle, large thermodynamic barriers were observed for most of the fundamental steps except for the Ru-POP complex.⁴¹ Leitner *et al.*, theoretically attempted to use H_2 directly to reduce the coordinated N_2 using Schrock type model complexes and found more barriers for their approach.⁴² Later, Hölscher and Leitner reported some reactions similar to our previous report using $[\text{Ru}(\text{PNP})(\text{CO})_2(\text{N}_2)]^{2+}$ ($\text{PNP} = 2,6\text{-bis}(\text{di-tert-butylphosphanylmethyl})\text{pyridine}$) complex with tert-butylphosphane (PtBu_3) and H_2 .⁴³

A large number of computationally predicted reports are available for the reduction of dinitrogen using $[\text{N}_2\text{-Mo}\{(\text{N}(\text{HIPT})\text{CH}_2\text{CH}_2)_3\text{N}\}]$ ($\text{HIPT} = \text{hexaisopropylterphenyl-triamidoamine}$) complex.^{44–52} However, the efficiency of $[\text{N}_2\text{-Mo}\{(\text{N}(\text{HIPT})\text{CH}_2\text{CH}_2)_3\text{N}\}]$ catalyst gets lowered during the direct addition of dihydrogen owing to the tendency to bind competitively with metal center by eliminating N_2 .⁵³ In this regard, our group has recently investigated the methodology to utilize $[\text{AH}]^+[\text{BH}]^-$ (FLP- H_2) ($\text{A} = [\text{Lut}]$, $[\text{iPr}_2\text{NH}]$, $[\text{TMPh}]$ $\text{B} = [\text{B}(\text{C}_6\text{F}_5)_3]$, which can be generated from H_2) along with $[\text{N}_2\text{-M}\{(\text{NHCH}_2\text{CH}_2)_3\text{N}\}]$ ($\text{M} = \text{Mo}$ and W) to produce ammonia under mild reaction conditions. And also, we applied our methodology

Table 1. Structural parameters and vibrational frequencies of complexes **1–11**, **4a–7a** and **TS-I–III**, **Ia**, **IIa**.

Systems		Bond lengths (Å)			Bond angle (°)	Vibrational frequency (cm^{-1})		
		Ru- N_α	$\text{N}_\alpha\text{-N}_\beta$	Ru-H		$\text{N}_\alpha\text{-N}_\beta$	Ru- N_α	Ru-H
[Ru]	(1)	—	—	—	—	—	—	—
[Ru]- N_2	(2)	1.971	1.120	—	179	2288	406	—
[Ru]- NNH^+	(3)	2.019	1.189	—	144	1858	392	—
H-[Ru]- NNH	(4)	1.917	1.206	1.654	147	1751	447	1846
H-[Ru]- NNH	(TS-I)	1.974	1.244	1.876	106	1566	476	−1312
[Ru]- NNH_2	(5)	1.959	1.350	—	117	1182	552	—
[Ru]- NNH_3^+	(6)	1.957	1.496	—	109	737	555	−1000
H-[Ru]-N	(7)	1.641	—	1.635	—	—	1068	1924
H-[Ru]-N	(TS-II)	1.693	—	1.761	—	—	953	—
[Ru]-NH	(8)	1.937	—	—	—	—	572	—
[Ru]- NH_2^+	(9)	1.973	—	—	—	—	579	—
H-[Ru]- NH_2	(10)	1.920	—	1.641	—	—	635	1849
H-[Ru]- NH_2	(TS-III)	2.209	—	1.608	—	—	476	−479
[Ru]- NH_3	(11)	2.192	—	—	—	—	403	—
H-[Ru]- NNH	(TS-Ia)	1.975	1.247	1.789	136	1553	515	−1113
[Ru]- NHNH	(4a)	1.987	1.265	—	132	1530	544	—
[Ru]- NHNH_2^+	(5a)	2.075	1.349	—	124	1293	442	—
H-[Ru]- NHNH_2	(6a)	2.003	1.378	1.651	123	1188	484	1834
H-[Ru]- NHNH_2	(TS-IIa)	2.239	1.415	1.614	121	1129	253	−597
[Ru]- NH_2NH_2	(7a)	2.156	1.480	—	113	943	234	—

for Chatt-type complexes for the formation of ammonia and hydrazine.^{54–57} Recently, our group achieved experimentally a new N–H bond formation from coordinated N_2 in $trans$ -[W(dppe)₂(N₂)₂] by using FLP-H₂.⁵⁸ In continuation of our earlier work, herein we report a hypothetical Ru-triamidoamine [N₂-Ru-{(NHCH₂CH₂)₃N}] complex for the synthesis of ammonia and hydrazine using FLP-H₂ adduct.

2. Computational details

The model systems of **1–11**, **4a–7a**, transition state structures (**TS-I**, **TS-II**, **TS-III**, **TS-Ia** and **TS-IIa**), [Lut] (Lut = 2,6 dimethyl pyridine), [LutH]⁺, [*i*Pr₂NH], [*i*Pr₂NH₂]⁺, [TMP] (2,6-tetramethyl pyridine), [TMPH]⁺, [B(C₆F₅)₃], [HB(C₆F₅)₃][−], N₂, NH₃, N₂H₄ and H₂ have been fully optimized using the B3LYP functional.^{59–61} The metal center Ru was described using the LANL2DZ basis set,^{62–65} non-metal centers were described using the 6-31G* basis set.^{66–69} As earlier studies revealed, the combination of B3LYP with LANL2DZ and 6-31G* basis set can be used to describe transition metals and nonmetal centers respectively.⁷⁰ Frequency calculations were performed on the optimized geometries of all the model systems to confirm that the optimized geometries were energetically global minima (without imaginary frequency except for the transition state structures (TS)) and the zero point energy (ZPE) and thermal correction. All the transition state structures were confirmed by frequency calculations, which showed one imaginary frequency for each of them (Table 1). Further, IRC calculation was performed on all the TS to confirm the correct TS. A solvent correction (for heptane) was performed using the polarized continuum model (PCM).^{71–73} We have calculated the thermodynamic and kinetic barriers and presented in this work in terms of ΔG. All these computations were carried out using the Gaussian-03 program package.⁷⁴

3. Results and Discussion

In the present investigation, we used a hypothetical Ru-N₂ complex stabilized by triamidoamine ligand (Figure 1) to understand the feasibility of producing ammonia by computational methods. DFT calculations have been carried out for the Ru complexes **1–11**, **4a–7a** and related transition state structures. Selected structural parameters of all the optimized geometries are given in Table 1. Total energies of all the optimized structures are given in Table S1 (in Supporting Information) and the reaction sequence for the formation of ammonia can be seen in the Figure 2. The formation of [LutH]⁺ [(C₆F₅)₃BH][−] can be achieved by reacting B(C₆F₅)₃ with Lut (Lut = 2,6-Me₂C₅H₃N) in the presence of H₂ at normal pressure and room temperature.⁵⁹ The [LutH]⁺ and [(C₆F₅)₃BH][−] of FLP-H₂

Figure 1. Optimized geometry of the complex ([Ru]-N₂)(2).

Figure 2. Catalytic cycle for the formation of ammonia from dinitrogen.

Scheme 2. Proposed catalytic cycle for the functionalization of N₂ using H₂.

can donate protons and hydrides respectively to the [N₂-Ru-{(NHCH₂CH₂)₃N}] in order to produce ammonia/hydrazine (Scheme 2).

Figure 3. The energy profile for the reduction of N_2 to NH_3 in Ru-triamidoamine $[(N_3N)Ru]$ system using FLP- H_2 in heptane.

Figure 4. The free energy profile for the reduction of N_2 to NH_3 in the Ru-triamidoamine $[(N_3N)Ru]$ system. (Proton partner $iPr_2NH_2^+$ and solvent, Heptane).

Figure 5. The free energy profile for the reduction of N_2 to NH_3 in the Ru-triamidoamine $[(N_3N)Ru]$ system. (Proton partner TMPH and solvent, Heptane).

Figure 6. Catalytic cycle for the formation of hydrazine from dinitrogen.

3.1 Formation of dinitrogen complex $[Ru]-N_2$ (2)

Reaction of complex 1 $\{[Ru] = (Ru - N_3N)\}$ with dinitrogen to yield complex 2 $([Ru]-N_2)$ was calculated to be exergonic ($-3.81 \text{ kcal mol}^{-1}$), which indicates that the complex 2 $([Ru]-N_2)$ is thermally stable towards the

loss of N_2 . The atomic partial charge on β -nitrogen atom of $([Ru]-N_2)2$ was calculated and found to be negative ($Ru = -0.635$) indicating that it can be protonated if the reaction is charge controlled.

3.2 Ammonia synthesis from the reaction between complex 2 ($[Ru]-N_2$) and $FLP-H_2$

The catalytic cycle and the corresponding energy profile for the formation of ammonia from complex 2 and $FLP-H_2$ can be seen in the Figures 2 and 3.

The addition of $[LutH]^+$ to the complex 2 ($[Ru]-N_2$) to yield complex 3 ($[Ru]-NNH^+$) is slightly endergonic ($16.34 \text{ kcal mol}^{-1}$) in nature as similar to the earlier report by Tuzek *et al.*,⁴⁴ and this can be assigned to the reasonable degree of activation of N_2 . Hydride addition to the 3 ($[Ru]-NNH^+$) by $[(C_6F_5)_3BH]^-$ to yield six coordinate ruthenium hydride complex 4 ($[H-[Ru]-NNH]$) was calculated to be endergonic ($6.19 \text{ kcal mol}^{-1}$) in which a new $[Ru]-H$ bond is formed. The migration of a proton from the metal center to the β -N atom *via* reductive elimination to yield **TS-I** is found to be endergonic ($19.69 \text{ kcal mol}^{-1}$) and indicates that the reductive elimination of hydride may also be possible in this reaction. The complete transfer of proton from **TS-I** to β -N to yield **5** ($[Ru]-NNH_2$) was calculated to be

Figure 7. The energy profile for the reduction of N_2 to N_2H_4 in the Ru-triamidoamine $[(N_3N)Ru]$ system using FLP- H_2 in heptane.

highly exergonic in nature ($-35.46 \text{ kcal mol}^{-1}$). Further addition of $[LutH]^+$ to **5** ($[Ru]-NNH_2$) to yield **6** ($[Ru]-NNH_3^+$) was found to be endergonic ($1.21 \text{ kcal mol}^{-1}$) in nature. Subsequently, addition of $[(C_6F_5)_3BH]^-$ to **6** ($[Ru]-NNH_3^+$) to yield one equivalent of ammonia and hexa-coordinate ruthenium-hydride complex **7** ($[H-[Ru]-N]$) was calculated to be exergonic in nature ($25.01 \text{ kcal mol}^{-1}$).

Migration of coordinated hydride in **7** ($[H-[Ru]-N]$) to the nitride *via* **TS-II**, was calculated to be endergonic in nature ($9.18 \text{ kcal mol}^{-1}$). Formation of **8** ($[Ru]-NH$) from **TS-II** was calculated to be exergonic ($-39.62 \text{ kcal mol}^{-1}$) due to the formation of a new N-H bond. Further addition of $[LutH]^+$ to **8** ($[Ru]-NH$) to produce **9** ($[Ru]-NH_2^+$) was calculated to be highly exergonic in nature ($-42.56 \text{ kcal mol}^{-1}$). Further addition of $[(C_6F_5)_3BH]^-$ to **9** ($[Ru]-NH_2^+$) to yield Ru-hydride complex **10** ($[H-[Ru]-NH_2]$) was calculated to be endergonic in nature ($14.77 \text{ kcal mol}^{-1}$). The formation of **TS-III** from **10** ($[H-[Ru]-NH_2]$) was found to be endergonic by $7.79 \text{ kcal mol}^{-1}$ and the formation of **11** ($[Ru]-NH_3$) from **TS-III** was calculated to be highly exergonic in nature ($-39.37 \text{ kcal mol}^{-1}$). Finally, the elimination of second equivalent of ammonia from **11** ($[Ru]-NH_3$) is endergonic by $5.85 \text{ kcal mol}^{-1}$. From the above mentioned energy barriers, it can be concluded

that the formation of **TS-I** has relatively higher barrier when compared to **TS-II** and **TS-III** in the catalytic cycle (Figure 2) for the ammonia formation, and the **TS-I** can be the rate determining step (RDS) in this process. The above computed thermodynamic barriers (ΔG) reveal that there is a possibility to generate ammonia from complex **2** ($[Ru]-N_2$) using FLP- H_2 .

We have also studied the ammonia formation using different FLP- H_2 with the changes in the proton partner of $[iPr_2NH_2]^+$ and $[TMPh]^+$ instead of $[LutH]^+$ with $[(C_6F_5)_3BH]^-$ as the same hydride partner. We have observed energy barriers which are very similar to the $[LutH]^+ [(C_6F_5)_3BH]^-$ and the corresponding energy profiles we have plotted in the Figures 4 and 5.

3.3 Why H_2 gas is not used directly for the N_2 reduction?

It is worthwhile to mention here that in this methodology we avoided the direct contact of H_2 with Ru complex in order to overcome the problem of competition in binding of N_2 and H_2 with complex **1**. Binding of N_2 and H_2 with $[Ru]$ is thermodynamically feasible (Eqs. 1 and 2). However, the H_2 binding with the $[Ru]$ can be avoided using FLP- H_2 as we described in Scheme 2. Also we have analyzed the binding of H^- with **1** and **2**, and found to

Figure 8. The free energy profile for the reduction of N_2 to N_2H_4 in the Ru-triamidoamine $[(N_3N)Ru]$ system. (Proton partner $iPr_2NH_2^+$ and solvent Heptane).

be highly endergonic in nature therefore thermodynamically not feasible.

3.4 Hydrazine synthesis from the reaction of $[Ru]-N_2$ (2) with FLP- H_2

We also have studied the viability of formation of hydrazine as described in Figure 6. Up to the formation of **4** has been discussed in section 3.1. The formation of **TS-Ia** from **4** ($[H-[Ru]-NNH]$) for the proton migration from the metal center to the α -N (reductive elimination) is endergonic by $19.36 \text{ kcal mol}^{-1}$. The formation of **4a** ($[Ru]-NHNH$) from **TS-Ia** was calculated to be exergonic by $38.51 \text{ kcal mol}^{-1}$, therefore, complex **4a** can be accessed at low temperature.

Protonation of β -N in **4a** ($[Ru]-NHNH$) by the addition of $[LutH]^+$ to yield **5a** ($[Ru]-NHNH_2^+$) was found to be exergonic by $30.84 \text{ kcal mol}^{-1}$. Addition of $[(C_6F_5)_3BH]^-$ to **5a** ($[Ru]-NHNH_2^+$) to generate hydride coordinated **6a** ($[H-[Ru]-NHNH_2]$) was found to be endergonic by $17.67 \text{ kcal mol}^{-1}$. The formation of **TS-IIa** from **6a** ($[H-[Ru]-NHNH_2]$) via the migration of proton from Ru center (reductive elimination) to the α -N is endergonic by $9.96 \text{ kcal mol}^{-1}$. The complete hydrogen transfer from **TS-IIa** to form hydrazine bound Ru complex **7a** ($[Ru]-NH_2NH_2$) was calculated to be exergonic by $34.91 \text{ kcal mol}^{-1}$. Finally, the elimination of hydrazine from **7a** ($[Ru]-NH_2NH_2$) to regenerate **1** ($[Ru]$) was calculated to be endergonic by $5.81 \text{ kcal mol}^{-1}$. The calculated thermodynamic barriers reveal that hydrazine can also be prepared from **1** using $[(C_6F_5)_3BH]^-$ and $[LutH]^+$ (FLP- H_2).

We have also examined other alternate FLP- H_2 and found similar thermodynamic barriers (Figures 8 and 9) and therefore one can use these reagents also.

4. Conclusions

We have computationally examined the reduction of N_2 to NH_3 and N_2H_4 by H_2 using FLP. Calculated free energies (Figures 3–5 and 7–9) reveal that the formation

Figure 9. The free energy profile for the reduction of N_2 to N_2H_4 in the Ru-triamidoamine $[(N_3N)Ru]$ system. (Proton partner TMPH and solvent, Heptane).

of all the intermediates and transition states proposed in the catalytic cycles (Figures 2 and 6) are thermodynamically feasible. The calculated free energies also further reveal that the formation of NH_3 is more viable than the formation of N_2H_4 . Formation of six-coordinate $[Ru]-H$ intermediates have also been predicted in the reaction sequence. Since our methodology provides a way to handle the H_2 even in the presence of competitively binding other molecules, one can make use of FLP- H_2 for not only functionalization of coordinated dinitrogen but also for other reactions where similar competition occurs. The possibility of utilizing FLP- H_2 along with other suitable catalysts for fixing N_2 to NH_3 is under investigation in our laboratory.

Supplementary Information (SI)

Tables representing energies of optimized structures and their Cartesian coordinates are presented in the Supplementary Information, which is available at www.ias.ac.in/chemsci.

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