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Functionalization of Dinitrogen Using a Historically Significant Ru Complex: A New Life for an Old Complex

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Dedicated to Prof. Ashoka G. Samuelson on the occasion of his 55th birthday

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DFT calculations reveal that molecular dinitrogen in the first reported dinitrogen complex, a historically significant complex $[Ru(NH_3)_5N_2]^{2+}$, can be functionalized to hydrazine and ammonia using suitable electron and proton sources in water. Thermodynamic barriers have been calculated for every electron transfer and protonation reaction in the Chatt and Schrock catalytic cycle. Although we adopt the Chatt and Schrock catalytic cycle for the functionalization of dinitrogen in $[Ru(NH_3)_5N_2]^{2+}$, we propose that reduction is the first step contrary to that previously reported. Different electron and proton sources have been probed, however, a copper and lutidinium combination shows a lower thermodynamic barrier than other combinations that are considered here. The thermodynamic barriers calculated also revealed that hydrazine formation is more favorable than ammonia formation.

Introduction

A low-temperature catalytic conversion of dinitrogen to ammonia has long been a challenge of fundamental importance.[1–4] In this regard, synthesis and reactivity studies of dinitrogen complexes have become more important.[5] Until Allen and Senoff synthesized the first water soluble dinitrogen complex, $[Ru(NH_3)_5N_2]^{2+}$ (**1**), in 1965, dinitrogen was believed to be an inert molecule.[6] In 1968 Taube et al. reported a dinuclear Ru^{II}-dinitrogen complex in which dinitrogen bridges two Ru^{II} centers in a head-on fashion.[7] Allen and Senoff treated their complex with $NaBH_4$ to produce ammonia in water.[8] However, later independent isotope substitution studies revealed that ammonia was formed from a hydrazine impurity and therefore concluded that the dinitrogen in **1** is not reactive.[9] A large number of dinitrogen complexes have been reported in the literature after the isolation of **1**; however, only few of these have been shown to generate ammonia and are not broadly applicable.[1,10–13] Chatt et al. have reported the synthesis and reactivity of Mo/W dinitrogen complexes which are known to generate ammonia but not catalytically.[14] More recently, Schrock et al. have reported a breakthrough catalyst (a triamidoamine-Mo^{III} complex) which produces ammonia catalytically in the presence of lutidinium and $CrCp_2^*$ in pentane, however, only six turnovers were achieved, which leaves room for further development.[15] In the Chatt and Schrock catalytic cycle the first step is believed to be a protonation on the N_β of the dinitrogen molecule.[14,15d,16–17]

$[Ru(NH_3)_5N_2]^{2+}$ (**1**) is considered to be an inert complex towards the functionalization of dinitrogen.[18] Nevertheless no considerable efforts have been taken, experimentally or computationally, to understand its inertness. Herein, we report the calculated energies for the functionalization of the Allen and Senoff complex. We also suggest a slightly different sequence of the addition of electrons and protons to the Chatt and Schrock catalytic cycle for the functionalization of dinitrogen in **1**.

Results and Discussion

Geometry optimization and frequency calculations for the model systems (**1**–**2**, **A**–**B**) have been carried out at DFT level using LANL2DZ and 6-31G* basis sets. The selected bond lengths, angles and energies have been tabulated (Table S1–S2, see the Supporting Information). Firstly, we compared the electronic structure of the Allen and Senoff complex with the reactive Schrock (**A**) and Chatt (**B**) model complexes and found that N_β of the dinitrogen molecule in the Chatt and Schrock model complexes carry negative charges (–0.04 and –0.02, respectively) and that of the Allen and Senoff complex carries a positive charge (0.16) (Table 1). For this reason, proton attack on N_β of the dinitrogen molecule in the Chatt and Schrock complexes is feasible but not in the Allen and Senoff complex. MO calculations show that the HOMO in both the Chatt and

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Schrock model complexes is located on the dinitrogen unit and thus proton attack is feasible, whereas in the Allen and Senoff complex the HOMO is located on the central metal ion and thus proton attack is unfeasible on the dinitrogen unit (Figure 1). This conclusion is based on the electronic structure requirements for the proton attack on dinitrogen suggested by Morokuma et al[19] and is further supported by the standard free energy Δ*G*° calculation for the first protonation of **1** with various proton sources $LutH^+$ (Lut = 2,6-dimethylpyridine), H_3O^+ (when acid is mixed with water), and H_2O in water, which was found to be more endergonic in nature (69.12, 35.39, and 130.23 kcal/mol, respectively). Therefore, protonation cannot be the first step in the sequence of protonation and reduction steps as proposed in the Chatt and Schrock catalytic cycle.[14,15d,16–17] Now, we consider the reduction of **1** to $[Ru(NH_3)_5N_2]^+$ (**2**) and compare the electronic structures with those of the Chatt and Schrock model complexes. The natural population analysis (NPA) charge calculation reveals that the N_β of the dinitrogen unit in **2** carries a negative charge (–0.14), and there is a feasible situation for a proton attack on N_β (Table 1). The dinitrogen unit in the reduced species is bent and shows somewhat hydrazinic character (Table S2). The MO calculation shows that the HOMO of **2** is located on the dinitrogen molecule as seen in the Chatt and Schrock model complexes (Figure 1) and therefore **2** can react with a proton. The Δ*G*° of the protonation in water medium with $LutH^+$, H_3O^+, and H_2O is calculated to be 5.35, –28.38, and –27.42 kcal/mol, respectively. Therefore, **2** can be protonated or functionalized by the aforementioned proton sources.

Table 1. NPA charges of the model complexes.

Systems	M	N_α	N_β
$[Ru(NH_3)_5(N_2)]^{2+}$ (**1**)	0.56	–0.07	0.16
$[Mo(HN_3N)(N_2)]$ (**A**)	1.09	–0.13	–0.02
$[Mo(N_2)_2(dpe)_2]$ (**B**)	–1.10	–0.02	–0.04
$[Ru(NH_3)_5(N_2)]^+$ (**2**)	0.46	–0.21	–0.14

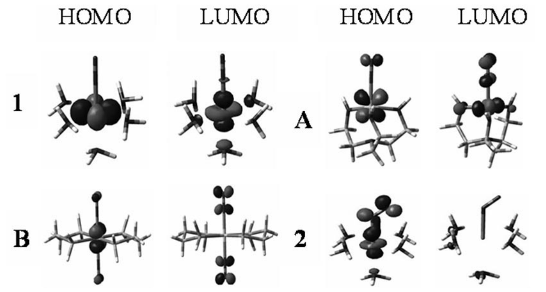

Figure 1. FMO of $[Ru(NH_3)_5N_2]^{2+}$ (**1**), $[Mo(N_2)(HN_3N)]$ (**A**), $[Mo(PH_2\text{-}(CH_2)_2\text{-}PH_2)]$ (**B**), and $[Ru(NH_3)_5N_2]^+$ (**2**).

We have probed several reducing agents (which are generally used for the dinitrogen reduction) to convert **1** to **2** including $NaBH_4$ which was used by Allen et al. and Chatt et al.[9] When the reductant is copper the Δ*G*° of the reduction reaction is slightly endergonic in nature (1.43 kcal/mol, Figure 3); for Mg (Figure S1–S3) and Cp^*_2Cr (Figure S4–S6) the reduction is found to be slightly more exergonic (–12.97 kcal/mol) and endergonic (20.53 kcal/mol) in nature, respectively. Reduction by $NaBH_4$ is found to be far more endergonic (62.21 kcal/mol). The Δ*G*° calculation shows that the reduction of **1** to **2** is thermodynamically feasible with Mg and Cu, possible with Cp^*_2Cr, and unfeasible with $NaBH_4$. The high thermodynamic barriers calculated for the reduction by $NaBH_4$ are in good agreement with experimental observations.[9]

From these results it is clear that reduction is thermodynamically more feasible than protonation of **1** and that the reduced complex, **2**, can be protonated. Based on these results we propose reduction to be first step in the catalytic cycle (Figure 2) (which is contrary to that proposed for the Chatt and Schrock catalytic cycle) and construct a different thermodynamic energy profile for all transformations with combinations of different electron and proton sources (Figures 3, 4 and Figures S1–S8 in the Supporting Information) similar to that reported for the Chatt and Schrock catalytic cycle.[16]

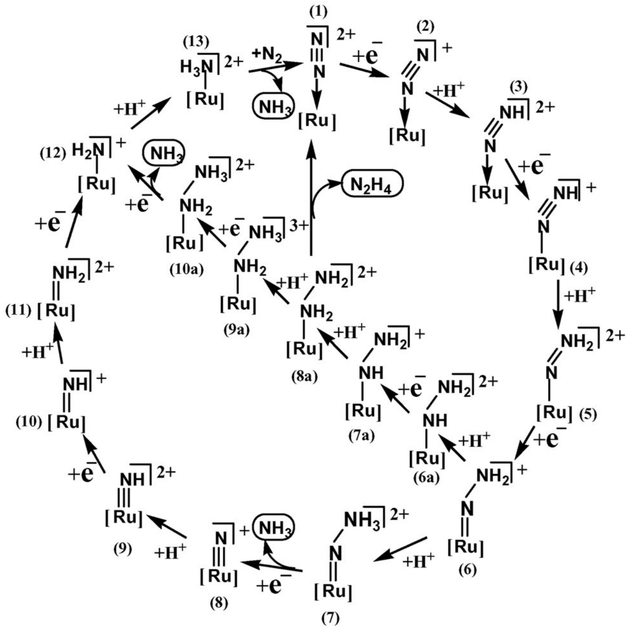

Figure 2. Proposed mechanism for the functionalization of N_2 in $[Ru(NH_3)_5N_2]^{2+}$ (**1**).

Combination of Cu with $LutH^+$ shows feasible thermodynamic barriers to produce two equivalents of ammonia and hydrazine from **1** (Figures 3 and 2).[20] Complex **1** is susceptible to reduction (1.43 kcal/mol) to yield **2**. Protonation of complex **2** is slightly endergonic (3.92 kcal/mol) in nature. Reduction of $[Ru(NH_3)_5(NNH)]^{2+}$ (**3**) is highly exergonic in nature (–29.77 kcal/mol). Protonation of $[Ru(NH_3)_5(NNH)]^+$ (**4**, 15.06 kcal/mol) and reduction of $[Ru(NH_3)_5(NNH_2)]^{2+}$ (**5**, 7.37 kcal/mol) are endergonic in nature. Protonation of $[Ru(NH_3)_5(NNH_2)]^+$(**6**) to yield $[Ru(NH_3)_5(NNH_3)]^{2+}$ (**7**) is about thermoneutral (–0.22 kcal/mol). Reduction of **7** and elimination of ammonia (N–N cleavage) is exergonic in nature (–11.87 kcal/mol) which is a similar

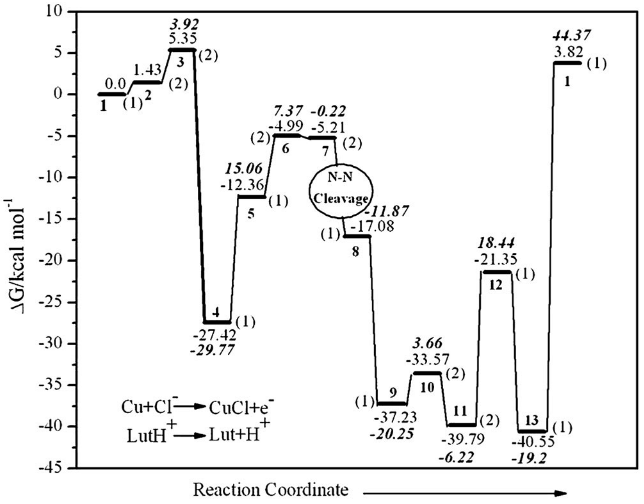

Figure 3. Calculated thermodynamic energy profile for the formation of ammonia from $[Ru(NH_3)_5N_2]^{2+}$ (**1**). Relative activation energy Δ*G* (plain), energy difference Δ*G* (italic), complex numbers (bold), and spin state (in brackets).

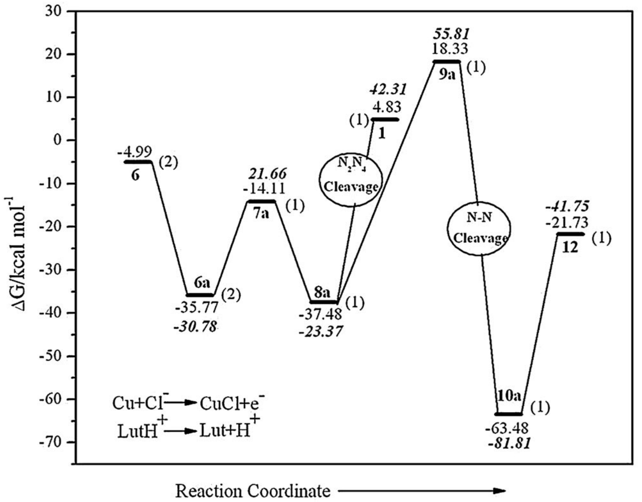

Figure 4. Calculated thermodynamic energy profile for the formation of hydrazine from $[Ru(NH_3)_5NNH_2]^+$ (**6**). Relative activation energy Δ*G* (plain), energy difference Δ*G* (italic), complex numbers (bold), and spin state (in brackets).

situation to that calculated for the Schrock system.[16] Protonation of $[Ru(NH_3)_5N]^+$ (**8**) to yield $[Ru(NH_3)_5NH]^{2+}$ (**9**) is more exergonic in nature (–20.25 kcal/mol). Reduction of **9** to produce $[Ru(NH_3)_5NH]^+$ (**10**) is slightly endergonic (3.66 kcal/mol). Complex **10** is susceptible to further protonation to yield $[Ru(NH_3)_5NH_2]^{2+}$, (**11**, –6.22 kcal/mol). Reduction of **11** to yield $[Ru(NH_3)_5NH_2]^+$ (**12**) is endergonic (18.44 kcal/mol). Further protonation of **12** to yield $[Ru(NH_3)_5NH_3]^{2+}$ (**13**) is exergonic (–19.2 kcal/mol). In **13**, replacement of ammonia by dinitrogen to yield **1** is more endergonic. The calculated endergonic steps (**1**–**3**, **4**–**6**, and **11**–**12** in Figure 3) are within the permissible range of thermodynamically feasible reactions.[16,17] The calculated thermodynamic barriers revealed that there is a possibility of functionalizing the dinitrogen in **1**, which has been considered as an inert complex for the last 45 years.

We have also examined other reaction pathways. Formation of hydrazine from **6** by the addition of a proton to the N_α of the dinitrogen unit (complexes **6**–**8a** in Figure 2) is found to be more exergonic (–30.78 kcal/mol, Figure 4) than the proton attack on N_β (–0.22 kcal/mol, Figure 3). Further reduction (**6a**–**7a**) and protonation (**7a**–**8a**) steps are endergonic (21.66 kcal/mol) and exergonic (–23.37 kcal/mol) in nature, respectively (Figure 4). Therefore, formation of the hydrazine complex $[Ru(NH_3)_5NH_2NH_2]^{2+}$ (**8a**) from **1** is also feasible. The replacement of hydrazine in **8a** by dinitrogen to form **1** is highly endergonic (42.31 kcal/mol in Figure 4), therefore, hydrazine replacement is not feasible. Another possibility is the protonation of N_β in **8a** to form $[Ru(NH_3)_5NH_2NH_3]^{3+}$ (**9a**) (Figure 2) which has a high thermodynamic barrier (55.81 kcal/mol in Figure 4) and is, therefore, unfeasible.

Conclusions

In summary, DFT calculations have revealed that the positive charge on N_β of the bound dinitrogen unit and the unsuitable location of the HOMO in the Allen and Senoff complex make this system unlikely to undergo protanation. However, this complex can be functionalized in water using copper and $LutH^+$ (Figure 2). Other reagents (Cp^*_2Cr and Mg with H_3O^+, $LutH^+$, and H_2O in water medium) may only yield complex **5**. Hydrazine formation is thermodynamically more feasible than ammonia formation when copper and $LutH^+$ are used. The next goal is to find a way to replace the hydrazine and ammonia by dinitrogen from complexes **8a** and **13** in order to make this process catalytic.

Experimental Section

G1–**13**, **6a**–**10a**, Cp^*_2Cr, $Cp^*_2Cr^+$, Cu, Cl, CuCl, Mg, $MgCl_2$, Lut, $LutH^+$, H_2O, H_3O^+, OH^-, N_2, NH_3, and H_2NNH_2 have been fully optimized using the B3LYP[21] functional. All metal atoms (Ru, Cr, Cu, Mg) were described using the LANL2DZ basis set,[22] and all nonmetal atoms were described using the 6-31G* basis set.[23] Vibrational frequency calculations were performed on these optimized structures to confirm minimum energy geometries by observing all positive frequencies and obtain the corresponding entropy and zero point energy correction. A solvent correction (for water) was performed using the polarized continuum model.[24] NPA was performed using the same level of theory.[25] All computational procedures were used as they are implemented in the Gaussian 03 package.[26] Contour plots of the molecular orbitals of the complexes were generated using Gaussview 3.0.

Supporting Information (see also the footnote on the first page of this article): Relevant geometry parameters, energy profiles, cartesian coordinates.

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