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Design and reactivity of pentapyridyl metal complexes for ammonia oxidation

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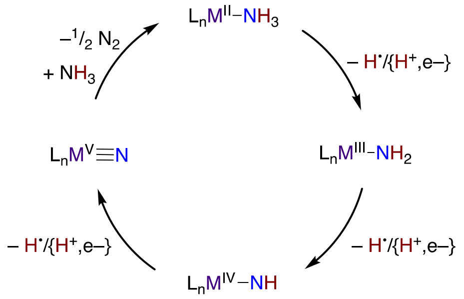
Oxidation of NH_3 to N_2 by pentapyridyl metal complexes via hydrogen atom abstraction was investigated computationally. Quantum chemical analysis reveals insights on orbital symmetry requirements for efficient NH_3 oxidation. The most promising complex, $[(PY5)Mo(NH_3)]^{2+}$, was studied experimentally. It shows conversion of NH_3 to N_2 upon treatment with 2,4,6-tri-tert-butylphenoxyl radical.



Scheme 1 - Ammonia oxidation by removal of three H atoms, or three protons and electrons, and formation of an N≡N bond.

Storing energy in chemical bonds is becoming increasingly important[1, 2] because of the expanded availability of intermittent sustainable energy sources, such as wind and solar. Storing protons and electrons in nitrogen-based fuel provides a readily transportable and carbon-free energy vector.[3] Ammonia is particularly appealing because of its transportability and high energy density. Catalysts for oxidation of NH_3 can release H_2[4] and N_2; the H_2 can be used in a fuel cell. Direct ammonia fuel cells are also known and give electricity upon electrochemical oxidation of NH_3.[5] Heterogeneous catalysts for oxidation of NH_3 are known[6, 7], but little is known of molecular catalysts for this reaction.[8]

For NH_3 oxidation, breaking the N-H bonds of an NH_3 ligand can be achieved by removal of protons and electrons in an electrochemical reaction (potentially involving proton-coupled electron transfer, PCET) or through a hydrogen atom transfer (HAT). In the simplest mechanism, shown in Scheme 1, three H atoms can be removed forming a metal nitrido complex. Homocoupling of the resulting nitridos would form an N–N bond. In principle this coupling can involve any combination of the M-(NH_x) species, yielding a variety of possible M-H_xN-NH_y-M adducts. HAT reactions can be accomplished using a chemical mediator, such as an organic radical. Metal complexes that can complete portions of this cycle are known. Chirik and co-workers reported a Mo terpyridine pincer complex that coordinatively weakens the ammonia N-H bonds, liberating H_2,[9] and complexes that interconvert between aryl amido (NR_2) and imido (NR) ligands via PCET.[10] Prior work showed that three hydrogen atoms of $[CpMo(NH_3)(CO)(P^{Ph}{}_2N^{tBu}{}_2)]^+$ can be abstracted using the organic radical 2,4,6-tri-*tert*-butylphenoxyl (ArO•). The intermediate molybdenum nitrido $[CpMo(≡N)(P^{Ph}{}_2N^{tBu}{}_2)]^+$ underwent N–C coupling with ArO• to form an arylimido complex.[11] Several Mn,[12-14] Ru,[15, 16] and Ir complexes are known to react by N–N coupling.[17, 18] Polypyridyl complexes of Ru and Os have been studied in detail by Meyer and co-workers in the electrochemical oxidation of NH_3.[16, 19-22] Recently, Smith, Hamann and co-workers reported a Ru polypyridyl electrocatalyst for oxidation of NH_3 that produces ~2.5 equivalents of N_2.[8] Fe and Mo-based polypyridyl catalysts for water oxidation have also been reported.[23, 24] These examples demonstrate that polypyridyl ligands are attractive for probing the chemistry of ammonia oxidation because of their ability to bind to many metals,[23, 25-27] as well as modularity that allows for tuning of the electronic structure.[28]

Quantum chemical methods can be efficiently employed to evaluate complexes as candidates for catalytic ammonia oxidation. We report here a detailed computational analysis based on density functional theory of the free energy landscape

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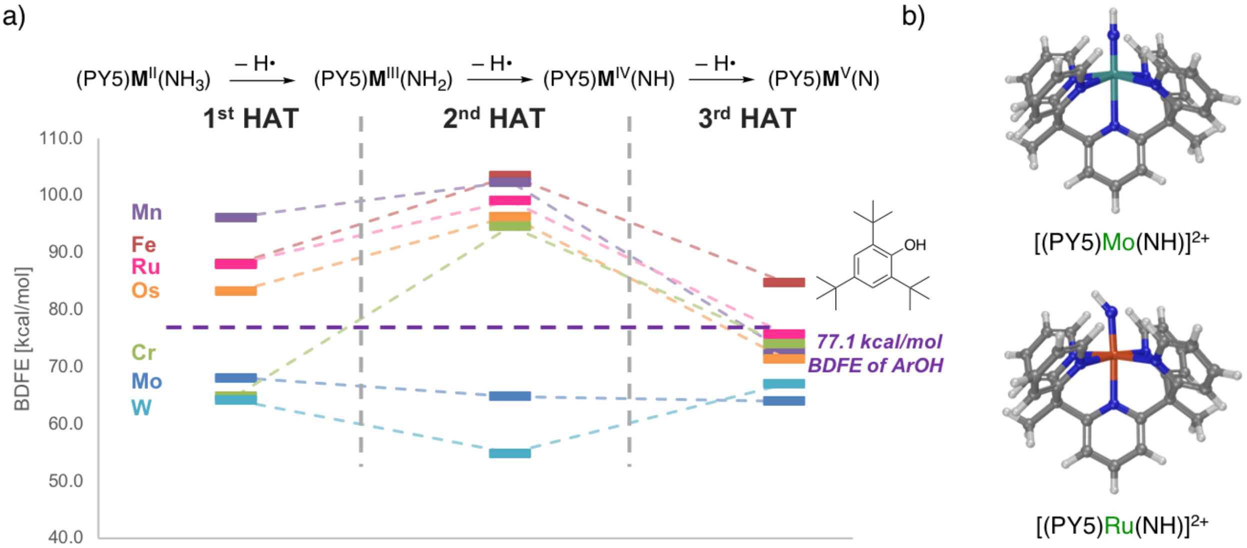

Figure 1 - a. Bond dissociation free energies of three H atom removals. Most metals have a higher second BDFE than first. Mo and W are exceptions to this. b. The geometries of (PY5)Mo and (PY5)Ru imidos are compared showing a linear imido and a bent imido geometry, respectively.

of NH_3 oxidation by pentapyridyl metal complexes (PY5)M for group VI, VII, and VIII metals. Specifically, we focus on $[(PY5)M(NH_3)]^{2+}$ in reactions with ArO• proceeding by HAT. Our investigation began with the calculation of the three N-H homolytic bond dissociation free energies (BDFEs) of metal-bound NH_3 in acetonitrile. We then studied the coupling of M-NH_x dehydrogenation intermediates with subsequent release of N_2 and regeneration of the ammonia-bound (PY5)M complex. The most promising candidate, $[(PY5)Mo(NH_3)]^{2+}$, was prepared *in situ* and its reactivity towards ArO• was investigated. Preliminary data suggest that NH_3 is indeed oxidized under these conditions to yield N_2.

Our calculations indicate that NH_3 displaces the bound acetonitrile ligand of $[(PY5)M(NCMe)]^{2+}$ with an exchange reaction free energy (equation 1) ranging from -8.0 kcal/mol (M = Mo) to -5.0 kcal/mol (M = Fe, Ru).

$$[(PY5)M\text{-}NCCH_3]^{2+} + NH_3 \rightleftharpoons [(PY5)M\text{-}NH_3]^{2+} + NCCH_3 \quad (1)$$

BDFEs were calculated from the free energies $\Delta G(NH_x)$ of the HAT reactions (equation 2) using the experimental BDFE for the ArO-H bond, $BDFE^{(exp)}(OH)$ = 77.1 kcal/mol in acetonitrile[29], as the reference value (equation 3).

$$(PY5)M(NH_x) + {}^tBu_3ArO\bullet \rightarrow (PY5)M(NH_{x-1}) + {}^tBu_3ArOH,$$
$$\Delta G^0(NH_x),\ x = 3, 2, 1 \quad (2)$$

$$BDFE(NH_x) = \Delta G(NH_x) - BDFE^{(exp)}(OH) \quad (3)$$

The computed values are shown graphically in Figure 1a and are listed in Table S1. Two patterns emerge from these data. Most of the metals analyzed (Mn, Fe, Os, Cr) show that the second BDFE is larger than the first, indicating that the imido complex (M=NH) is more difficult to form than the amido complex (M-NH_2). These metals also have a third N-H BDFE that is lower than the second. Remarkably, Mo and W stand out from this trend by displaying nearly flat BDFE profiles and relatively lower values, suggesting that they are good candidates for NH_3 oxidation by HAT. Indeed, it is desirable to have no variation in the BDFE's, with same organic mediator being used for optimum thermodynamic efficiency of all three HAT steps.

The difficulty in forming the imido intermediates for the majority of the metal complexes examined here can be interpreted in terms of simple orbital considerations. In the $[(PY5)M^{IV}(NH)]^{2+}$ complexes, the M-N-H can either be in a collinear or bent geometry. A linear imido yields a complex with C_{4v} symmetry, whereby the degeneracy of the metal *d* orbitals is affected by overlap with the *p* orbitals of the ligand.[30] Illustrative molecular orbital diagrams can be found in Figures S1 and S2 of the ESI. The group VI (Mo, W) imido complexes have a d^2 electronic configuration and can fill the C_{4v} symmetry orbital ladder such that a M≡NH triple bond is formed. For the group VIII metal (Fe, Ru, Os) complexes, $[(PY5)M^{IV}(NH)]^{2+}$, the d^4 electron configuration in a C_{4v} symmetry arrangement forces two electrons in degenerate π^* orbitals, which will result in a high-energy complex. This unfavourable situation for the VIII metal complexes is avoided by the lower symmetry of the bent geometry, which localizes electrons on the metal and the imido nitrogen atom and leads to the formation of a M=NH double bond. A similar electronic structure is anticipated for the d^3 Mn imido complex. An imido species with a M≡NH triple bond is expected to be more stable than that with a M=NH double bond. These considerations explain why the d^2 Mo and W imido complexes are more stable than the d^3 and d^4 complexes. Representative structures of the Ru and Mo complexes can be seen in Figure 1b, with characteristic M-N-H angles of 141.7° and 180.0°, respectively. Analysis within the Natural Bond Orbital (NBO) framework[31] confirms this picture. The exception to this trend is Cr, which also shows a higher second BDFE and bent imido despite its d^2 electronic structure.

In principle, N-N bond formation can involve any combination of the $M(NH_x)^{2+}$ species or reaction of NH_3 with an $M(NH_x)^{2+}$ species. We explored these reactions computationally and found that the coupling is energetically reasonable only for the nitrido intermediate. Therefore, we focus here only on the nitrido/nitrido coupling reaction. A detailed discussion of the other possibilities is reported in the ESI.

In acetonitrile solvent, formation of the N_2–bridged, bimetallic complex (Scheme S2) is favourable for Mo by 6.1 kcal/mol, despite the +2 charge of both metal complexes. In the less polar solvent fluorobenzene, N-N coupling is unfavourable by 16.2 kcal/mol. The reactivity of $[(PY5)Mo{\equiv}N]^{2+}$ seems to be at odds with its strong Mo≡N π bonds. For instance, it has been shown by Cummins and co-workers that the formation of strong $Mo^{VI}{\equiv}N$ bonds[32] drives the cleavage of the N≡N bond of N_2[33] by the tripodal complex $Mo^{III}[N(^tBu)Ar']_3$ (Ar' = 3,5-$Me_2C_6H_3$).[33] However, exceptions have also been documented in the literature.[11]

The overall energetics for the N–N coupling, followed by elimination of N_2 and regeneration of the ammonia-bound starting material (equation 4) is favourable for all metals, as reported in Table S3.

$$2\,[(PY5)M{\equiv}N]^{2+} + 2\,NH_3 \rightarrow 2\,[(PY5)M\text{-}NH_3]^{2+} + N_2 \quad (4)$$

As anticipated, later metals like Fe and Ru show highly exoergic coupling steps (ΔG^o = –194.4 and –167.4 kcal/mol, respectively).

To assess the underlying mechanism of N-N coupling for this class of complexes, the electronic structure of $[(PY5)M{\equiv}N]^{2+}$ molecules was analysed within the NBO framework. As the two nitrido complexes couple, the M≡N π bonds must be broken as the new N–N bond forms. Depending on the nature of the nitrido intermediate, this reaction can occur either by radical coupling[11] or by nucleophilic attack.[34, 35] Radical coupling is expected for an intermediate with an unpaired electron localized on the nitrido ligand. Homocoupling through nucleophilic attack requires ambiphilic nitrido intermediates, whereby the lone pair of an approaching nitrido (the nucleophile) is donated to the π* orbital of another nitrido (the electrophile). An ambiphilic nitrido results when the metal *d* orbitals are lower in energy than the ligand *p* orbitals, which yields π* orbitals that are more localized on the nitrido.[30, 36] The more ligand-centred the π* orbital, the more electrophilic the nitrido ligand.

The metal centre of most of the metal nitrido species can be formally assigned a V oxidation state. The Cr, W, and Mo complexes have no radical population on the nitrido ligand, in agreement with their formal assignment as $M^V{\equiv}N$. The Mn complex is a closed-shell singlet, which can be formally seen as $M^V{\equiv}N$. In contrast, the NBO bonding analysis indicates that the Ru and Os intermediates can be better described as $M^{IV}{=}N\bullet$ nitridyl radicals. The electronic structure of the Fe intermediate is unique, wherein the NBO analysis implies the formation of an unusual Fe^{III}-N: diradical. A nucleophilic attack mechanism is possible for metals with formal M^{IV} or M^V oxidation states. A radical mechanism is also possible for the $M^{IV}{=}N\bullet$ species, but is unlikely for the formal $M^V{\equiv}N$ species due to the lack of unpaired electrons on the N atom. To gauge the importance of nucleophilic attack, the nitrido electrophilicity was investigated by calculating the fraction of the π* orbital on the nitrido (or nitridyl) for the group VI-VIII metal complexes. This quantity was then compared to the change in the electronic energy in solution, ΔE_{el}, of equation 5.

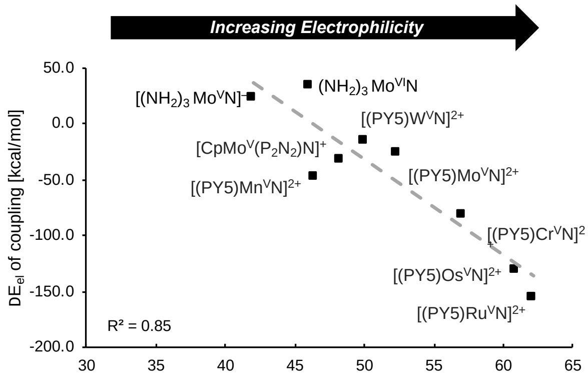

Figure 2 – Correlation between the change in electronic energy in acetonitrile for the coupling reaction and the amount of π* fraction of the nitrido/nitridyl ligand.

$$2\,[(PY5)M{\equiv}N]^{2+} \rightarrow [(PY5)M\text{-}N\text{-}N\text{-}M(PY5)]^{4+} \quad (5)$$

In addition to the series $[(PY5)M^V{\equiv}N]^{2+}$ series of complexes discussed so far, we extended the analysis to $(NH_2)_3Mo^{VI}{\equiv}N$, a truncated analogue of Cummins' complex that has been used in calculations[37], as well as the hypothetical $[(NH_2)_3Mo^VN]^-$ complex, in order to examine the effect of both ligand and oxidation state. We have also included the $[CpMo({\equiv}N)(P^{Ph}{}_2N^{tBu}{}_2)]^+$ complex previously studied in our group.[11] As can be seen from the data reported in Figure 2, there is a good correlation (R^2 = 0.85) between the amount of π* on the nitrido (nitridyl) and ΔE_{el} despite the range of complexes being examined. This analysis indicates that the more electrophilic the nitridos are, the more favourable N-N coupling (and N_2 evolution, Figure S4) is. This result can be attributed to the increased propensity for the electrophilic nitrido to accept another nitrido's lone pair, which will then go into the spatially and energetically accessible π* orbital, initiating the collapse of the π bonding structure and eventual N_2 evolution. Illustrative schematic molecular orbital diagrams are reported in the ESI. The Fe complex represents a clear exception to the general trend discussed above (see Table S5), whereby a radical coupling mechanism is the only possibility.

Based on the computational results discussed above, $[(PY5)Mo(NH_3)]^{2+}$ was selected for experimental studies on NH_3 oxidation because of its low BDFEs and ability to form an N-N bond. Treatment of $[(PY5)Mo(OTf)](OTf)$[24] with $^{15}NH_3$ in acetonitrile solvent led to the formation of $[(PY5)Mo(^{15}NH_3)](OTf)_2$ (Figure S5). This complex was treated with 22 equiv of ArO• and monitored by ^1H and $^{15}N\{^1H\}$ NMR spectroscopy (Figures S5-S8). $[(PY5)Mo(^{15}NH_3)]^{2+}$ was observed to react quickly with ArO•, as evidenced by the appearance of resonances for ArOH in the ^1H NMR spectrum. A $^{15}N\{^1H\}$ NMR spectrum displayed a resonance at -71.0 ppm that is characteristic of $^{15}N_2$. No $^{15}N_2$ was observed in a control reaction with ArO• and $^{15}NH_3$ but no $[(PY5)Mo(^{15}NH_3)]^{2+}$. To quantify the amount of $^{15}N_2$ formed, the headspace was sampled and analysed by GC (Figures S12-S17). Each reaction was run in parallel with a control reaction that did not contain $[(PY5)Mo(^{15}NH_3)]^{2+}$ to correct for background N_2 generation or contamination. In this manner, the reaction of $[(PY5)Mo(^{15}NH_3)]^{2+}$ with 22 equiv of ArO• was determined to yield 0.2(1) equiv of $^{15}N_2$ per Mo (Table S6), which is less than the 0.5 equiv of N_2 expected for the stoichiometric reaction.

A possible cause for the yield of $^{15}N_2$ is that the ArO• may be participating in undesired side reactions. Treatment of $[(PY5)Mo(OTf)]^+$ with ArO• led to the formation of a new unidentified species (Figure S9), possibly resulting from binding of ArO• to Mo. Further, no $^{15}N_2$ was detected by $^{15}N\{^1H\}$ NMR spectroscopy when ArO• was added to $[(PY5)Mo(OTf)]^+$ before addition of $^{15}NH_3$. Based on this experimental evidence, calculations of the free energy for ArO• binding were performed. Exchange of NH_3 for ArO• in (PY5)Mo was calculated to be favourable by 12.1 kcal/mol, which accounts for the dependence on order of addition of reagents, as well as the low overall turnover. Turnover could be hindered by reactivity with ArO• after N_2 production or by ArO• displacing bound NH_3.

In conclusion, we reported a systematic computational study of NH_3 oxidation by pentapyridyl group VI , VII, and VIII metals via HAT reactions mediated by the 2,4,6-tri-*tert*-butylphenoxyl radical. We found that changes in molecular orbital symmetry regulate the thermodynamics of H atom abstraction from the metal-bound ammonia and the propensity of the resulting nitrido intermediate to homocouple with the consequent release of N_2. Preliminary reactivity studies on the most promising complex, $[(PY5)Mo(^{15}NH_3)]^{2+}$, verify production of N_2.

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Conflicts of interest

There are no conflicts to declare.

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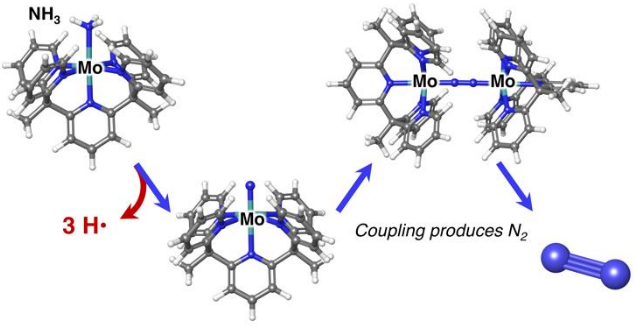
TOC Diagram



Computational and experimental work shows that Mo pentapyridal complexes can oxidize ammonia in the presence of a chemical mediator and evolve N_2.