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Communication

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Diversion of Catalytic C-N Bond Formation to Catalytic Oxidation of NH_3 Through Modification of the Hydrogen Atom Abstractor

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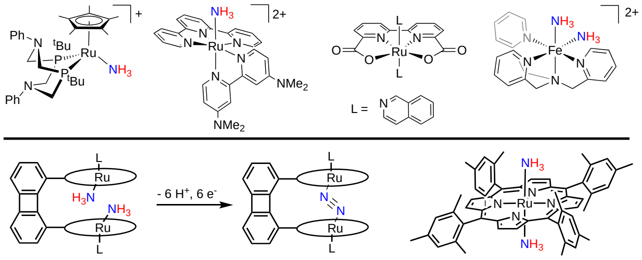
Supporting Information Placeholder

ABSTRACT: We report that (TMP)Ru(NH_3)$_2$ (TMP = tetramesitylporphryin) is a molecular catalyst for oxidation of ammonia to dinitrogen. An aryloxy radical, tri-*tert*-butylphenoxyl (**ArO•**), abstracts H atoms from a bound ammonia ligand of (TMP)Ru(NH_3)$_2$, leading to the discovery of a new catalytic C-N coupling to the para position of **ArO•**, forming 4-amino-2,4,6-tri-*tert*-butylcyclohexa-2,5-dien-1-one. Modification of the aryloxy radical to contain a trityl group at the para position, 2,6-di-*tert*-butyl-4-tritylphenoxyl radical, prevents C-N coupling and diverts the reaction to catalytic oxidation of NH_3 to give N_2. We achieve 125(±5) turnovers at 22 °C for oxidation of NH_3, the highest reported to date for a molecular catalyst.

Carbon-free fuels are attractive to meet worldwide demands for sustainable energy.[1] Ammonia is produced on a huge scale by the Haber-Bosch process;[2] it has a high energy density, and is readily transported as a liquid using a well-established infrastructure.[3] Direct ammonia fuel cells, where electricity is generated through oxidation of ammonia to N_2, offers appealing attributes compared to carbon-based fuels.[4-7] Ammonia has also been used as an H_2 storage medium.[8-11] However, the study of molecular ammonia oxidation catalysts has lagged behind studies of its microscopic reverse, nitrogen reduction.

The first N-H bond dissociation free energy (BDFE) of ammonia is 99.4 kcal/mol,[12] but the energy is decreased by coordination to a metal. Several approaches in transition metal systems have overcome the high bond strength to cleave N-H bonds, including N-H oxidative addition,[13] metal-ligand cooperativity,[14-15] 1,2 addition across a metal-metal bond,[16] and H atom abstraction.[17-20] Formation of an N-N bond is a requisite step in oxidation of NH_3 to N_2, so understanding the factors that control that reaction are crucial in the design of metal catalysts for oxidation of NH_3.[21-26] To the best of our knowledge, only four molecular systems have been reported to catalytically oxidize NH_3 to N_2 (Figure 1, top);[27-30] all have turnovers less than 20.



stoichiometric oxidation of NH_3
Collman *et al.*

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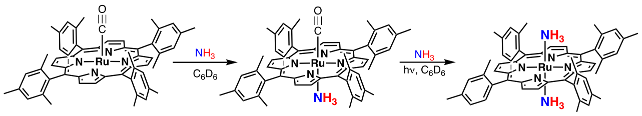
Figure 1: Stoichiometric and catalytic ammonia oxidation by molecular catalysts.

Molecular mediators to abstract or donate H atoms have been increasingly beneficial in the catalytic reduction of O_2,[31-32] using a variety of mediators that span a range of bond strengths.[12] We have recently shown that tri-*tert*-butylphenoxyl (**ArO•**)[12, 33] accomplishes H atom abstraction (HAA) from ammonia ligands: triple HAA from Mn diphosphine complexes resulting in cyclophosphazeniums,[34] triple HAA from a Mo(NH_3) complex, generating a metal imido formed by C-N coupling,[35] sub-stoichiometric ammonia oxidation from a Mo polypyridyl complex,[36] and ammonia oxidation catalyzed by a Cp*Ru complex.[27]

Collman and co-workers reported elegant studies on stoichiometric ammonia oxidation to dinitrogen (Figure 1), using cofacial diruthenium porphryins.[37-38] Starting from a [Ru(NH_3)]$_2$ complex, bridging hydrazine, diazene, and dinitrogen complexes were synthesized through double oxidation and deprotonation reactions. Inspired by their results, we investigated the reactivity of a Ru complex with a more readily accessible ligand.[39]

Treatment of (TMP)Ru(CO) (TMP = tetramesitylporphryin) with NH_3 (1 atm) results in formation of (TMP)Ru(CO)(NH_3). Photolysis of a solution of (TMP)Ru(CO)(NH_3) with excess NH_3 leads to (TMP)Ru(NH_3)$_2$ in 96% yield (Scheme 1). The ^1H NMR spectrum of (TMP)Ru(NH_3)$_2$ exhibits an upfield shifted ammonia resonance at -6.88 ppm due to porphyrin ring currents.[40] Single crystals of (TMP)Ru(NH_3)$_2$ were grown from slow evaporation of a concentrated THF solution, and the structure was determined by X-ray diffraction (Figure 2).



Scheme 1. Synthesis of (TMP)Ru(NH_3)$_2$

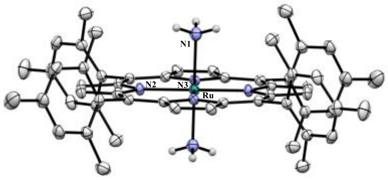
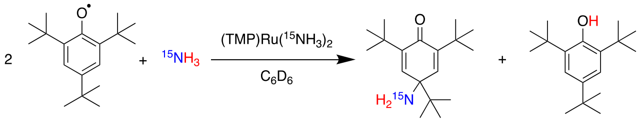


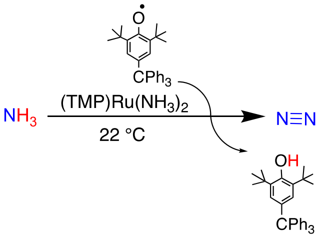
Figure 2: 50% thermal ellipsoid drawing of (TMP)Ru(NH_3)$_2$. Solvent and H atoms, except N-H bonds, are not shown. Bond distances (Å): Ru-N1: 2.108(3), Ru-N2: 2.037(2), and Ru-N3: 2.031(2).

No reaction was observed when (TMP)Ru(CO)(NH_3) was treated with **ArO•** and excess ammonia. In contrast, in the presence of NH_3 and **ArO•** at room temperature, (TMP)Ru(NH_3)$_2$ quenched the blue color of **ArO•**. ^{1}H NMR spectroscopic analysis showed formation of **ArOH** and 4-amino-2,4,6-tri-*tert*-butylcyclohexa-2,5-dien-1-one (**RNH₂**) that results from C-N bond formation with NH_3[41-42] (Scheme 2). Small amounts (<4%) of isobutylene are also observed by ^{1}H NMR spectroscopy; it was previously reported from decomposition of **ArO•**.[43] The catalytic reaction was optimized with as low as 0.05 mole % loading of Ru, resulting in 610±20 turnovers **RNH₂**, which can be isolated as a white solid (65% yield). Control reactions with **ArO•** and $^{15}NH_3$ in C_6D_6 (no Ru) show no coupling product or $^{15}N_2$ as measured by ^{15}N NMR spectroscopy.



Scheme 2. C-N coupling catalyzed by (TMP)Ru(NH_3)$_2$.

RNH₂ is proposed to result from C-N coupling between the para position of the aryl radical and a Ru-NH_x (x = 0, 1, 2) species that has significant radical character on the nitrogen atom.[44] Mayer and co-workers noted that the predominant resonance structure of **ArO•** has significant radical character on the para carbon.[33] Similar C-N coupling was observed in a CpMo system, where H atom abstractions from an ammonia ligand led to the formation of a Mo-NH_x (x = 0, 1, 2) species that couples with the aryloxy radical.[35] Oxidation at the 2- or 4- positions has been observed,[45-46] and coupling between anilido radicals and **ArO•** resulting in C-N bond formation at the para position has also been reported.[43] Attempts to use TEMPO or ABNO,[47] which form weaker O-H bonds,[12] did not lead to product formation in our system.



Scheme 3. Oxidation of ammonia to N_2 catalyzed by (TMP)Ru(NH_3)$_2$.

Recognizing the possibility of thwarting the C-N coupling by increasing the steric bulk at the para position of **ArO•**, we prepared an aryloxy radical with a trityl substituent in the para position, the previously reported 2,6-di-*tert*-butyl-4-tritylphenoxyl radical (**Ph₃C-ArO•**) (Figure 3).[48] **Ph₃C-ArO•** was isolated as dark green crystals; it shows good stability over months when stored as a solid at -35ºC.[49]

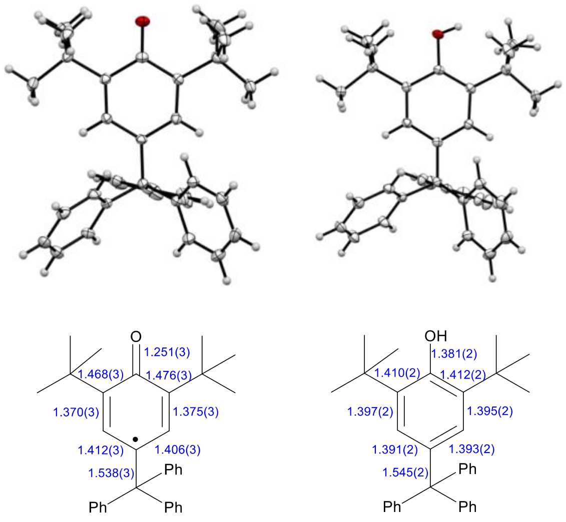


Figure 3. Structural drawings (50% thermal ellipsoids) of **Ph₃C-ArO•** (top left) and **Ph₃C-ArOH** (top right). Solvent of crystallization is not shown. Bond distance (Å) comparisons (bottom) are consistent with a radical centered on the para carbon: a dienone-like structure.[33]

When (TMP)Ru(NH_3)$_2$ was treated with **Ph₃C-ArO•** and excess $^{15}NH_3$, the intense green color of the radical dissipated over the course of a day. A ^{15}N NMR spectrum in C_6D_6 revealed a sharp singlet at -71.7 ppm (vs. $CH_3{}^{15}NO_2$ = 0 ppm), consistent with the formation of free $^{15}N_2$ (Scheme 3). The ^{1}H NMR spectrum showed conversion of **Ph₃C-ArO•** to **Ph₃C-ArOH.** Importantly, no C-N coupling product is observed, although, minor amounts of isobutylene are again observed. In a control experiment, we observed no resonance for $^{15}N_2$ after treating **Ph₃C-ArO•** with $^{15}NH_3$ in C_6D_6 for one month at 22 °C, as judged by an overnight ^{15}N NMR spectrum.

Catalytic turnover was determined by quantifying the liberated N_2 gas in the headspace by GC (Figure S19, SI).[27,36] Treatment of a 1.0 mM solution of (TMP)Ru(NH_3)$_2$ with **Ph₃C-ArO•** (450 equiv.), then saturated with NH_3, produces ~3.3 × 10^{-5} moles of N_2, giving 40(±0.5) turnovers of N_2 over the course of one day. Decreasing the catalyst concentrations to 0.5 mM or 0.25 mM gives increased turnovers, reaching 125(±5) per Ru (Table S1, SI). Recharging a spent 0.5 mM reaction with 540 more equivalents of **Ph_3C-ArO•** and NH_3 produces ~20 more turnovers of N_2, showing that the ruthenium porphyrin catalyst is still active. The current system is limited by the amount and stability of **Ph_3C-ArO•** in solution, as **Ph_3C-ArO•** has a half-life of ~ 1 day in C_6D_6, as shown by UV-Vis spectroscopy. Analysis of the reaction solution by ^1H NMR spectroscopy after catalysis shows only two main organic products: **Ph_3C-ArOH** (~90%) and isobutylene (~2%) (Table S2, SI).

We propose that the dramatically divergent catalysis mediated by **Ph_3C-ArO•** relative to **ArO•** is caused by steric differences. While the mesityl groups on the porphyrin ring were initially chosen to prevent dimerization, the added steric bulk appears to have a cooperative effect with **Ph_3C-ArO•** to prevent C-N coupling. From the crystal structure of (TMP)Ru$(NH_3)_2$, the porphyrin pocket, from ortho-methyl to ortho-methyl, is approximately ~8.5 Å across and ~3.5 Å deep. Comparing the crystal structures of **ArO•** and **Ph_3C-ArO•** lends insight. The height (oriented as in Figure 3) of **ArO•** is ~7.4 Å. Replacement of the *tert*-butyl by a trityl group increases the length to ~9.1 Å and the depth from ~4.1 to ~8.4 Å in **Ph_3C-ArO•**, making it too big to easily fit in the porphyrin pocket (see Figure S22, SI, for additional explanation and drawings). We suggest that this increase in size impedes the relative rate of C-N coupling compared to that of N_2 formation, such that oxidation to give N_2 predominates.

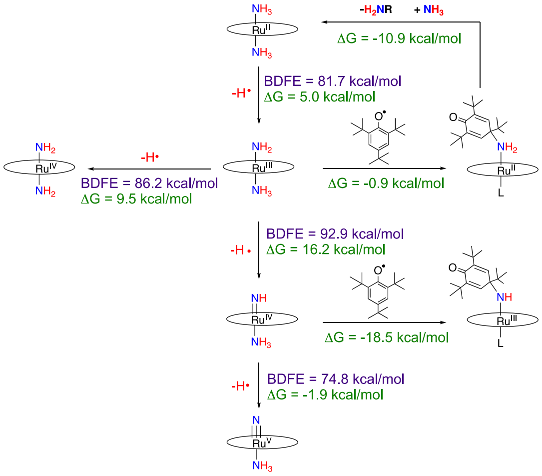


Figure 4. Computed free energies in benzene solvent.

DFT calculations provide further understanding of the observed reactivity (Figure 4). The first two N-H BDFEs were computed to be 81.7 and 92.9 kcal/mol, which are thermodynamically uphill by 5.0 and 16.2 kcal/mol, respectively, for hydrogen atom abstraction by **ArO•** (ArO-H BDFE = 77 kcal/mol).[12] The third BDFE is lower (74.8 kcal/mol). While the second BDFE is uphill, previous studies have also found this trend; when coupled to a more favorable step (C-N, N-N coupling or CO loss), thermodynamically unfavorable HAAs can occur.[34-35]

Computations show that C-N coupling is favorable from both the amido and imido complexes, by 0.9 and 18.5 kcal/mol (Fig. 4). These favorable steps appear to drive the reaction, leading to formation of **RNH_2**. Release of the **RNH_2** product and binding a fresh ammonia molecule is exergonic by 10.9 kcal/mol. While C-N coupling is more favorable from a Ru^{IV}=NH intermediate, generation of this species necessitates a second, more uphill HAA. Additionally, in order for product formation to occur *via* Ru^{IV}=NH, an additional H atom would have to be donated (not shown in Figure 4) from either previously formed **ArOH**, or possibly another $Ru(NH)_x$ (x = 2 or 3) species. Therefore, we favor the simplest and lowest energy route for C-N bond formation: C-N coupling from Ru^{III}-NH_2.

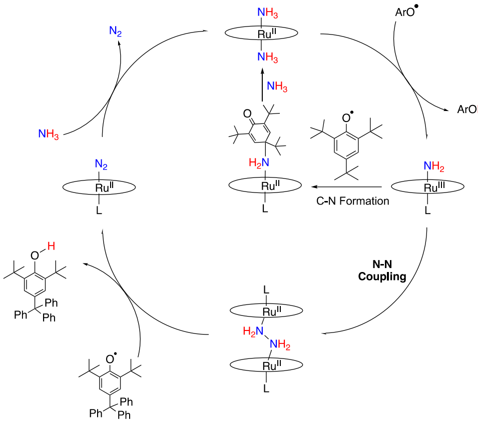


Figure 5. Possible mechanism for ammonia oxidation catalyzed by (TMP)Ru$(NH_3)_2$. L = NH_3 or vacant site.

Two types of mechanisms have been invoked for N-N bond formation in ammonia oxidation by molecular complexes: bimetallic N-N coupling, or nucleophilic attack of ammonia on an electrophilic $M(NH)_x$ (x = 0, 1, or 2) intermediate.[21-24, 27-30, 50-54] Multiple mechanistic possibilities should be considered, since bimetallic N-N coupling could occur at any of the possible intermediates: amide, imide, or nitride ligand on the metal. Using cofacial Ru porphyrins, Collman and co-workers reported stoichiometric N-N coupling through a cofacial $[Ru^{III}(NH_2)]_2$ intermediate.[37-38] Their proposal, in conjunction with our observed C-N coupling from a $Ru^{III}(NH_2)$ intermediate, leads us to favor N-N bond formation by a bimetallic coupling route of two Ru amides, forming a bridging hydrazine ligand (Figure 5). We are not aware, however, of additional precedents for coupling of two metal amides. Subsequent HAAs could then proceed from the bridged, bimetallic complex, akin to that proposed by Collman, or dissociation of a Ru center could lead to a terminal Ru hydrazine species.

HAA from both possible hydrazine intermediates should be facile compared to their NH_3 analogues. HAAs from the terminal hydrazine species would access higher oxidation states of Ru, which are well-documented for ruthenium porphryins bearing nitrogen-based axial ligands.[40, 55-58]

In conclusion, we report a new catalyst, (TMP)Ru(NH_3)$_2$, that catalyzes the oxidation of NH_3 to N_2 under mild conditions using **Ph_3C-ArO•**. The scalability (>10 g) and ease of preparation of **Ph_3C-ArO•** make it an attractive alternative to **ArO•**. This catalytic system achieves 125(±5) turnovers for oxidation of NH_3, a significant improvement compared to previously reported molecular catalysts. Ongoing work is focusing on investigating the mechanism of N-N coupling, translating this system to work with earth-abundant metals, and converting this system to work under mediated electrocatalytic conditions wherein the phenoxyl radical can be regenerated.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website. Experimental procedures, spectral data, computational procedures, molecular coordinates, X-ray procedures (pdf).

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Notes

The authors declare no competing financial interest.

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Artwork for Table of Contents: