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Catalytic Nitrogen-to-Ammonia Conversion by Osmium and Ruthenium Complexes

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Abstract

Despite the critical role ruthenium and osmium complexes have played in the development of transition metal dinitrogen chemistry, they have not been previously shown to mediate catalytic N_2 -to- NH_3 conversion (N_2RR), nor have $\text{M}-\text{N}_x\text{H}_y$ complexes been derived from protonation of $\text{M}-\text{N}_2$ precursors ($\text{M} = \text{Ru}, \text{Os}$). To help delineate key factors for N_2RR catalysis, we report on isostructural tris(phosphino)silyl Ru and Os complexes that mediate catalytic N_2RR , and compare their activities with an isostructural iron complex. The Os system is most active, and is demonstrated to liberate more than 120 equiv NH_3 per Os center in a single batch experiment using Cp^*_2Co and $[\text{H}_2\text{NPh}_2][\text{OTf}]$ as the reductant and acid source. Isostructural Ru and Fe complexes generate very little NH_3 under the same conditions. Protonation of an anionic $\text{Os}-\text{N}_2^-$ state affords a structurally characterized $\text{Os}=\text{NNH}_2^+$ hydrazido species that itself mediates NH_3 generation, suggesting it is a plausible intermediate of the catalysis. Os-hydride species are characterized that form during catalysis as inactive species.

Synthetic Mo and Fe model systems have been identified as catalysts for N_2 -to- NH_3 conversion (N_2RR).^{1,2} The development of these catalytic systems has in part been motivated by the role(s) these metals may play in biological nitrogen fixation, and the desire to test various mechanistic hypotheses using well-defined inorganic model complexes.³ In contrast, synthetic models based on metals other than Fe or Mo that display efficacy for catalytic N_2RR are to date limited to two cobalt systems, both of which use a combination of strong acid and reductant in the form of $[\text{H}(\text{OEt}_2)_2][\text{BAr}^{\text{F}}_4]$ (HBAr^{F}_4 , BAr^{F}_4 = tetrakis (3,5-bis(trifluoromethyl)phenyl)borate) and KC_8 .⁴

The heavier group VIII elements Ru and Os have played a significant role in the history and development of ammonia synthesis and $\text{M}-\text{N}_2$ model chemistry. For example, a very active heterogeneous Ru catalyst is used in the industrial Kellogg Advanced Ammonia Process (KAAP),⁵ and the first metal-dinitrogen complex to be discovered featured ruthenium $((\text{NH}_3)_5\text{Ru}-\text{N}_2^{2+})$.⁶ Noteworthy achievements in Ru and Os model chemistry have included

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Synthetic and spectroscopic details:

Crystallographic information:

(1) the demonstration of terminal nitride ($M=N^{[2/3+]}$) coupling to form (iso- lable or transient) N_2 -bridged bimetallics of the type $L_nM-N_2-ML_n^{[4/5/6+]}$ ($M = Ru$ or Os);^{7,8} (2) photochemically induced homo- lytic N_2 cleavage to generate terminal $Os\equiv N$ products;⁹ (3) selective protonation and hydrogenation of terminal osmium nitrides to generate NH_3 ;¹⁰ and (4) step-wise NH_3 oxidation to N_2 via diimide ($HN=NH$) and hydrazine (N_2H_4) intermediates at cofacial Ru porphyrins.¹¹

Despite these advances, there remain no examples of synthetic Ru or Os complexes that demonstrate step-wise protonation of $M-N_2$ to generate $M-N_xH_y$ species, nor complexes featuring these metals that catalyze N_2RR .¹² Germane to our present interest, the identification and study of a homologous, isostructural series of complexes (Fe , Ru , Os) will help to better delineate some of the key factors for N_2RR catalyst design.

A limitation with respect to achieving N_2RR catalysis by either Ru or Os is that low-valent redox states ($< 2+$) can be difficult to access for these metals.¹³ In systems where such states may be accessed, it is common for the electron(s) to be ligand rather than metal-localized; this is especially true of d^7 systems.¹⁴ For $M-N_2$ species, this should in turn lead to a less activated, and thereby less readily functionalized, N_2 ligand. One notable exception in this context are the $[M]-N_2^{[0/1-]}$ redox pairs ($M = Ru$, Os ; Figure 1) previously reported by our group, where utilization of a rigid, chelating tris(phosphine)silyl ligand permits access to low-valent MI and M^0 terminal dinitrogen compounds.^{14a} These species exhibit $\nu(NN)$ stretching frequencies suggestive of highly activated, terminally bonded N_2 ligands. To our knowledge, $K(THF)_2^+[Os]-N_2^-$ (abbreviated hereafter as $[Os]-N_2^-$) exhibits the lowest $\nu(NN)$ stretching frequency (1931 cm^{-1}) known for a terminal N_2 adduct of Ru or Os (Figure 1).^{14a}

Herein, we establish that both $[Ru]-N_2^-$ and $[Os]-N_2^-$ mediate catalytic N_2RR . $[Os]-N_2^-$ is a particularly competent catalyst in the presence of Cp^*_2Co and mild acids. Moreover, the N_2 ligand of $[Os]-N_2^-$ can be protonated to afford a structurally characterized $[Os]=NNH_2^+$ hydrazido complex, a likely intermediate by analogy to related $[Fe]=NNH_2^+$ species that have been implicated as intermediates of N_2RR by our lab.¹⁵ Catalytically inactive Os -hydride species are characterized that appear to form as thermodynamic sinks of the spent catalyst system.

The N_2RR performance of $[Ru]-N_2^-$ and $[Os]-N_2^-$ was initially canvassed under conditions similar to those first studied in the context of N_2RR by related iron systems (46 equiv $HBAr^F_4$, 50 equiv KC_8 , 1 atm N_2 , Et_2O , $-78\text{ }^\circ\text{C}$).^{2a-d} $[Os]-N_2^-$ affords 1.6 ± 0.3 equiv of NH_3 (Table 1, entry 1) under these conditions, exceeding that observed for $[Na(12\text{-crown-}4)_2][P_3^{Si}Fe-N_2]$ ($[Fe]-N_2^-$; entry 2). $[Ru]-N_2^-$ performs better under these conditions (entry 3), affording 4.3 ± 0.3 equiv of NH_3 (28% selectivity for NH_3 based on H^+), confirming that N_2RR catalysis with Ru is viable. Related tripodal, tetra(phosphine) Ru^0-N_2 complexes have not yet shown selective reactivity at the coordinated N_2 ligand; the weak acids canvassed (e.g., 2,6-lutidinim tetrafluoroborate) tend to react at the metal center to yield oxidized $[Ru^{II}(N_2)(H)]^+$ products, whereas stronger acids (e.g., HCl , $HOTf$) have been shown to protonate at the phosphine ligand.¹⁶

With these results in hand, we next canvassed milder reagents.^{2f,17} These reactions highlight the far superior N₂RR activity of [Os]-N₂⁻ by comparison to either [Ru]-N₂⁻ or [Fe]-N₂⁻. Thus, treatment of a suspension of [Os]-N₂⁻ in Et₂O at -78 °C with 46 equiv of [H₂NPh₂][OTf] and 50 equiv of Cp*₂Co results in the generation of 7.1 ± 0.6 equiv of NH₃ per Os (Table 1, entry 6; 46% based on acid). An identical catalytic run performed under an ¹⁴N₂ atmosphere using [H₂¹⁵NPh₂][OTf] yields only [¹⁴NH₄][Cl], confirming that the NH₃ formed is derived from the N₂ atmosphere. Attempts to use either[(η⁶-C₆H₆)Os(Cl)(μ-Cl)]₂ or [Os]-Cl as the (pre)catalyst generates only < 0.1 and 2.5 equiv of NH₃, respectively, underscoring a privileged role for [Os]-N₂⁻ as the catalyst. For comparison, [Fe]-N₂⁻, whose [Fe]-N₂^[0/1-] redox couple (-2.2 V vs Fc/Fc⁺) is shifted ~220 mV cathodically from that of Cp*₂Co/Cp*₂Co⁺,¹⁸ generates only stoichiometric quantities of NH₃ under analogous conditions (entry 4); likewise [Ru]-N₂⁻ (E = - 2.14 V vs Fc/Fc⁺, Figure 1)^{14a} shows very poor N₂RR performance (0.8 ± 0.5 equiv of NH₃; entry 5).

Os-catalyzed N₂RR was found to proceed in the presence of correspondingly weaker and stronger anilinium acids with unperturbed yields for NH₃ production. For example, replacing [H₂NPh₂][OTf] with either [H₃NPh][OTf] or [H₃N-2,5-Cl₂C₆H₃][OTf] affords 7.9 equiv of NH₃ per Os, respectively (Table 1, entries 11 and 12). [*N*-Me-H₂NPh][OTf] gives a slightly diminished yield (6.3 ± 0.5 equiv of NH₃ per Os; entry 13). These observations contrast the behavior of P₃^BFe-N₂⁻, where the selectivity for N₂RR (vs HER) is substantially diminished when using [H₃NPh][OTf] compared to [H₂NPh₂][OTf].^{2f}

Attempts to replace Cp*₂Co with weaker metallocene reductants, such as cobaltocene (Cp₂Co) or decamethylchromocene (Cp*₂Cr), did not yield any detectable NH₃. Similarly, the Et₂O soluble acids [H₂NPh₂][BAR^F₄] and [H₃NPh][BAR^F₄] furnished much lower yields of NH₃ relative to their triflate counterparts (Table 1, entries 14 and 15), presumably due to increasing the background HER and possibly promoting catalyst deactivation (*vide infra*). Ether-miscible HOTf displays similar behavior (entry 16).

To explore the effect of increasing the acid/reductant loading with [Os]-N₂⁻, we tested 150 equiv of [H₂NPh₂][OTf] and 180 equiv of Cp*₂Co and detected 18 ± 1 equiv of NH₃ per Os (Table 1, entry 7), only a modestly diminished yield (35% based on H⁺) relative to the lower loading. Increasing the substrate loading leads to further increases in the total yield of NH₃, again with rather little impact on overall efficiency for NH₃ with respect to acid (Table 1, entries 8 and 9). Re-loading an 800 equiv acid run after stirring for 3 hours at -78 °C (1600 equiv total) affords a total of 122 equiv of NH₃, suggesting a substantial amount of active catalyst is still present at the end of the first run.

In a single run at the highest loading tested, 1500 equiv of [H₂NPh₂][OTf] and 1800 equiv of Cp*₂Co, a yield of 120 ± 11 equiv of NH₃ per Os (24 ± 2% for NH₃; entry 10) is observed. This total turnover number exceeds that of previously reported Fe catalysts, regardless of protocol,¹⁹ and also exceeds TON data for most Mo catalysts.¹ Noteworthy exceptions concern recent Mo catalysts supported by pincer-phosphine ligands, which have been shown to be both very active and selective for NH₃ generation under certain conditions.^{1d,f}

For a direct single-run comparison under the present conditions, we tested the best known Fe catalyst, $[\text{Na}(12\text{-crown-}4)_2][\text{P}_3^{\text{B}}\text{Fe-N}_2]$,^{2d,f} at 1500 equiv of $[\text{H}_2\text{NPh}_2][\text{OTf}]$ and 1800 equiv of Cp^*_2Co ; only 22 ± 5 equiv of NH_3 is produced (average of two runs). This $\text{P}_3^{\text{B}}\text{Fe-N}_2^-$ catalyst performs more efficiently than $[\text{Os}]\text{-N}_2^-$ at lower substrate loading, however.^{2f} The single-run TON value for $[\text{Os}]\text{-N}_2^-$ is hence noteworthy, despite its modest selectivity for NH_3 relative to H_2 overall.

With respect to formation of inactive osmium hydrides, we comment for comparison that $[\text{Fe}]\text{-N}_2^-$ reacts with stoichiometric acid (e.g., HBAr^{F}_4) to liberate 0.5 equiv of H_2 and its one-electron oxidized derivative, $[\text{Fe}]\text{-N}_2$, presumably via a diazenido intermediate, $[\text{Fe}]\text{-N=NH}$, that releases H_2 bimolecularly;²⁰ none of the thermally stable, and catalytically inactive, hydride product, $[\text{Fe}](\text{N}_2)(\text{H})$,²¹ is observed. By contrast, exposing $[\text{Os}]\text{-N}_2^-$ to stoichiometric HBAr^{F}_4 in THF-*d*₈ solution at -78°C affords a mixture of the hydride products $[\text{Os}](\text{N}_2)(\text{H})$ (major) and $[\text{Os}]\text{H}_3$ (minor), as determined by variable temperature NMR spectroscopy (Scheme 1).²² On warming, $[\text{Os}]\text{-N}_2$ is also observed as a byproduct.

$[\text{Os}]\text{H}_3$ can be synthesized independently by reacting $[\text{Os}]\text{-Cl}$ with LiEt_3BH , or by exposing either $[\text{Os}](\text{N}_2)(\text{H})$ or $[\text{Os}]\text{-N}_2$ to an atmosphere of H_2 (Scheme 1). Subjecting $[\text{Os}](\text{N}_2)(\text{H})$ or $[\text{Os}]\text{H}_3$ to 46 equiv of acid (HBAr^{F}_4 or $[\text{H}_2\text{NPh}_2][\text{OTf}]$) and 50 equiv of reductant (KC_8 or Cp^*_2Co ; 1 atm N_2 , Et_2O , -78°C) does not furnish any detectable NH_3 . Examination of the Os speciation after treatment of $[\text{Os}]\text{-N}_2^-$ with 10 equiv of acid and 12 equiv of reductant reveals $[\text{Os}](\text{N}_2)(\text{H})$ ($\text{HBAr}^{\text{F}}_4/\text{KC}_8$: 32%; $[\text{H}_2\text{NPh}_2][\text{OTf}]/\text{Cp}^*_2\text{Co}$: 0%) and $[\text{Os}]\text{H}_3$ ($\text{HBAr}^{\text{F}}_4/\text{KC}_8$: 48%; $[\text{H}_2\text{NPh}_2][\text{OTf}]/\text{Cp}^*_2\text{Co}$: 62%) as the only observable products by NMR and IR spectroscopies, providing strong evidence that these inactive Os-hydride species form during catalytic reactions. For the $\text{P}_3^{\text{B}}\text{Fe-N}_2^-$ catalyst system using $[\text{H}_2\text{NPh}_2][\text{OTf}]/\text{Cp}^*_2\text{Co}$, off-path hydrides are not observed;^{2f} they are observed, however, when using $\text{HBAr}^{\text{F}}_4/\text{KC}_8$.^{2d}

We hypothesized that access to zero-valent $[\text{Os}]\text{-N}_2^-$ is critical for productive N_2 functionalization, presumably proceeding via an initial $[\text{Os}]\text{-N=NH}$ intermediate formed via the first protonation step. The $[\text{Os}]\text{-N}_2^{[0/1]}$ redox couple is -1.94 V (vs Fc/Fc^+ , Figure 1),^{14a} suggesting that Cp^*_2Co should be a sufficiently strong reductant to (re)generate the $[\text{Os}]\text{-N}_2^-$ state during catalysis. By analogy, access to anionic $\text{P}_3^{\text{E}}\text{Fe-N}_2^-$ ($\text{E} = \text{B}, \text{C}, \text{Si}$) states has been shown to be chemically and electrochemically correlated with N_2RR catalysis.^{2d,f} Invoking $[\text{Os}]\text{-N}_2^-$ as “on-path” for catalysis helps rationalize the poor N_2^- to- NH_3 conversion exhibited by the osmium catalyst when Cp^*_2Co is replaced by either Cp_2Co ($E = -1.33$ vs Fc/Fc^+ , THF) or Cp^*_2Cr ($E = -1.55$ vs Fc/Fc^+ , THF); these reagents are not sufficiently reducing to regenerate $[\text{Os}]\text{-N}_2^-$.

To gauge whether Cp^*_2Co can competently reduce $[\text{Os}]\text{-N}_2$ to generate $[\text{Os}]\text{-N}_2^-$, a green Et_2O solution of $[\text{Os}]\text{-N}_2$ was treated with 5 equiv of Cp^*_2Co at room temperature. Surprisingly, analysis of the reaction mixture by ^{31}P NMR and IR spectroscopies, monitoring over several hours with vigorous stirring, shows none of the expected $[\text{Os}]\text{-N}_2^-$ species.

An analogous experiment, performed in THF-rfs and monitored by ^1H and d_8 NMR spectroscopies at room temperature, shows only unreacted $[\text{Os}]\text{-N}_2$ and Cp^*Co . However, upon cooling this mixture to -78°C , resonances consistent with the formation of $[\text{Os}]\text{-N}_2^-$ appear.²³ Accordingly, a color change from green-brown to red is observed within seconds, indicating a temperature-dependent redox process. This is conveniently monitored as a function of temperature by optical spectroscopy; a gradual decrease in the absorption bands at $\lambda = 670\text{ nm}$ and $\lambda = 1000\text{ nm}$ corresponding to $[\text{Os}]\text{-N}_2$ is observed, with a simultaneous increase in a feature attributable to $[\text{Os}]\text{-N}_2^-$ near $\lambda = 550\text{ nm}$ (Figure 2, left). This reaction mixture can be warmed and re-cooled multiple times, confirming a temperature-dependent redox equilibrium.

We conclude that, at the catalytically relevant temperature of -78°C , Cp^*Co is sufficiently capable of reducing $[\text{Os}]\text{-N}_2$ to $[\text{Os}]\text{-N}_2^-$. The VT optical data suggest that an observable population of $[\text{Os}]\text{-N}_2^-$ can be generated at temperatures as high as -40°C . Accordingly, a catalytic run carried-out at -40°C (46 equiv $[\text{H}_2\text{NPh}_2][\text{OTf}]$ and 50 equiv Cp^*Co) produces 6.2 equiv NH_3 .²⁴ By contrast, it appears that neither $[\text{Ru}]\text{-N}_2^-$ nor $[\text{Fe}]\text{-N}_2^-$ can be competently generated using Cp^*Co , helping explain their comparatively poor performance.

Having established the viability of an initial ET step to generate $[\text{Os}]\text{-N}_2^-$, we next probed its reactivity with protons. Tripodal tris(phosphine) hydrazido $\text{P}_3^{\text{E}}\text{Fe}=\text{NNH}_2^+$ complexes have been spectroscopically ($\text{E} = \text{B}$)^{15a} and structurally characterized ($\text{E} = \text{Si}$),^{15b} generated via double protonation of $\text{P}_3^{\text{E}}\text{Fe-N}_2^-$ at low temperature. Similarly, reaction of $[\text{Os}]\text{-N}_2^-$ with 3 equiv of HOTf in thawing 2-MeTHF (-135°C) produces an orange mixture, from which pale orange $\{[\text{Os}]=\text{NNH}_2\} \{\text{OTf}\}$ can be isolated upon precipitation (Scheme 1). Spectroscopic features of this diamagnetic hydrazido complex include a broad $\nu(\text{NH})$ stretch centered at 3232 cm^{-1} and a diagnostic ^1H NMR resonance (THF- d_8) at $\delta = 10.0\text{ ppm}$. For comparison, the related resonance for $\{[\text{Fe}]=\text{NNH}_2\} \{\text{OTf}\}$ is at 9.5 ppm .^{15b}

X-ray diffraction analysis of $\{[\text{Os}]=\text{NNH}_2\} \{\text{OTf}\}$ locates two protons bound to the sp^2 -hybridized β N-atom (N_2) with H-bonding to the triflate anion (Figure 2, right). The Os-N-NH_2 unit is linear ($\angle(\text{Os-N}_1\text{-N}_2) = 176^\circ$), the $\text{N}_1\text{-N}_2$ distance is $1.271(5)\text{ \AA}$, and the Os-N_1 distance is short ($1.815(3)\text{ \AA}$), in accord with a hydrazido(2-) featuring substantial Os-N multiple bond character. The Os-N and N-N distances in $[\text{Os}]=\text{NNH}_2^+$ are within the range observed for previous structurally characterized linear and bent hydrazido(2-) complexes of osmium,²⁵ prepared by trapping Os^{IV} -imido intermediates²⁶ or by the reaction between Os-nitride complexes with secondary amines.²⁷ A related osmium-imide complex prepared by our lab, $[\text{Os}]=\text{N-Ar}$ ($\text{Ar} = p\text{-trifluoro-methylphenyl}$),^{14a} displays remarkably similar structural parameters to $[\text{Os}]=\text{NNH}_2^+$, including comparable Os-N bond lengths, Os-P bond lengths, and degrees of pyramidalization at the Si and Os atoms (see Table S1). $[\text{Os}]=\text{NNH}_2^+$ represents the first instance of an Os-N_2 species to be converted to a protonated $\text{Os-N}_x\text{H}_y$ product.

To assess the possible intermediacy of $[\text{Os}]=\text{NNH}_2^+$ in the Os-mediated N_2RR catalysis described herein, $[\text{Os}]=\text{NNH}_2^+$ was treated with 46 equiv of $[\text{H}_2\text{NPh}_2][\text{OTf}]$ and 50 equiv of Cp^*Co at low temperature, generating greater-than-stoichiometric quantities of NH_3 (ca.

2.6 equiv; no hydrazine detected). $[\text{Os}]=\text{NNH}_2^+$ and its one-electron reduced state, $[\text{Os}]=\text{NNH}_2$, should be active toward bimolecular proton-coupled-electron-transfer (PCET) steps to generate inactive hydrides (or competing H_2) owing to very weak N-H bonds.^{2f,15c,20} Such reactivity likely explains the poor catalytic performance of isolated $[\text{Os}]=\text{NNH}_2^+$; catalysis is likely to be more efficient when such hydrazido species are formed in lower concentration in situ during catalysis. Combined with the observation that Cp^*_2Co can reduce $[\text{Os}]-\text{N}_2$ to $[\text{Os}]-\text{N}_2^-$ at low temperature, and that $[\text{Os}]-\text{N}_2^-$ can be protonated to yield $[\text{Os}]=\text{NNH}_2^+$, the observation that $[\text{Os}]=\text{NNH}_2^+$ can facilitate NH_3 formation lends support to an ET-PT N_2RR pathway that proceeds, initially at least, via a distal pathway.

To conclude, we have shown for the first time that both Ru and Os coordination complexes can serve as catalysts for N_2RR in the presence of reductant and acid sources under ambient pressure at low temperature. The tris(phosphine)silyl Os system is most active, displaying high turnover at high loadings of Cp^*_2Co and $[\text{H}_2\text{NPh}_2][\text{OTf}]$. Access to zero-valent $[\text{Os}]-\text{N}_2^-$ appears to be critical for N_2 functionalization, and a bona fide $[\text{Os}]=\text{NNH}_2^+$ hydrazido complex can be generated via protonation of $[\text{Os}]-\text{N}_2^-$ and is shown to facilitate NH_3 generation; $[\text{Os}]=\text{NNH}_2^+$ is hence a plausible intermediate. Os-hydrides, including $[\text{Os}](\text{N}_2)(\text{H})$ and $[\text{Os}]\text{H}_3$, form during the catalysis as catalytically inactive states. That a tris(phosphine)silyl ligand proves so effective for osmium-mediated N_2RR catalysis, but is largely ineffective for the isostructural $[\text{Fe}]-\text{N}_2^-$ and $[\text{Ru}]-\text{N}_2^-$ systems using Cp^*_2Co and $[\text{H}_2\text{NPh}_2][\text{OTf}]$, underscores the value in comparatively exploring highly related systems for N_2RR . In this case, the key $[\text{Os}]-\text{N}_2^{[0/1-]}$ redox couple is accessible with Cp^*_2Co , but only at low temperature, whereas a stronger reductant is needed to drive the $[\text{Fe}]-\text{N}_2^{[0/1-]}$ and $[\text{Ru}]-\text{N}_2^{[0/1-]}$ reductions. While other factors are most certainly at play, access to $\text{M}-\text{N}_2^-$ states is emerging as a common theme for N_2RR catalysis by group VIII metals.

Supplementary Material

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22. [Ru](N₂)(H) and [Ru]H₃ form as catalytically inactive species in the corresponding Ru-system. See SI for details.
23. Analogous experiments produce none of either [Ru]-N₂⁻ or [Fe]-N₂⁻, as probed by ¹H and ³¹P NMR spectroscopies.

24. The generation of $[\text{Os}]\text{-N}_2^-$ during catalysis does not preclude the possibility of productive PCET pathways.^{2f}
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Figure 1.
Ruthenium and osmium N_2RR catalysts studied herein and some relevant physical data (from references 14a and 18).

Figure 2.

Left: UV-visible absorbance spectra for the reaction of $[\text{Os}]\text{-N}_2$ (1.2 mM) and 5 equiv of Cp^*_2Co (6.0 mM) in THF at the listed temperature. Arrows represent the direction of change when the temperature is lowered. Right: XRD structure of $\{[\text{Os}]=\text{NNH}_2\} \{\text{OTf}\}$ with thermal ellipsoids set at 50% probability. Hydrogen atoms (except for N-H's) are omitted for clarity.

Scheme 1.

Synthesis of Os-hydride and Os-hydrazido(2-) Complexes

Table 1.

N₂-to-NH₃ Conversion Mediated by [M]-N₂[−] Complexes^a

	catalyst	acid (equiv)	reductant (equiv)	NH ₃ /M (equiv)	Yield NH ₃ /H ⁺ (%)
1	[Os]-N ₂ [−]	46 ^c	50 ^d	1.6 ± 0.3	10 ± 2
2 ^b	[Fe]-N ₂ [−]	46 ^c	50 ^d	0.8 ± 0.5	4.7 ± 2.9
3	[Ru]-N ₂ [−]	46 ^c	50 ^d	4.3 ± 0.3	28 ± 2
4	[Fe]-N ₂ [−]	46 ^e	50 ^f	1.4 ± 0.3	9.3 ± 1.8
5	[Ru]-N ₂ [−]	46 ^e	50 ^f	0.8 ± 0.5	4.9 ± 3.5
6	[Os]-N ₂ [−]	46 ^e	50 ^f	7.1 ± 0.6	46 ± 4
7	[Os]-N ₂ [−]	150 ^e	180 ^f	18 ± 1	35 ± 1
8	[Os]-N ₂ [−]	500 ^e	600 ^f	50 ± 3	30 ± 2
9	[Os]-N ₂ [−]	800 ^e	960 ^f	86 ± 5	32 ± 2
10	[Os]-N ₂ [−]	1500 ^e	1800 ^f	120 ± 11	24 ± 2
11	[Os]-N ₂ [−]	46 ^g	50 ^f	7.9 ± 0.3	52 ± 2
12	[Os]-N ₂ [−]	46 ^h	50 ^f	7.9	52
13	[Os]-N ₂ [−]	46 ⁱ	50 ^f	6.3 ± 0.5	41 ± 3
14	[Os]-N ₂ [−]	46 ^j	50 ^f	0.1 ± 0.1	0.8 ± 0.2
15	[Os]-N ₂ [−]	46 ^k	50 ^f	1.2 ± 0.1	7.6 ± 0.8
16	[Os]-N ₂ [−]	46 ^l	50 ^f	0.7 ± 0.1	4.6 ± 0.7

^aThe catalyst, acid, reductant, and Et₂O were sealed in a Schlenk tube at −196 °C under an N₂ atmosphere, warmed to −78 °C and stirred. For runs utilizing HBARF₄, reactions were stirred at −78 °C for 1 hour, followed by stirring at room temperature for 45 minutes. For all other runs, reactions were allowed to stir and gradually warm to room temperature overnight. See Supporting Information for individual experiments.

^bFrom ref. 2a.

^cHBARF₄.

^dKC₈.

^e[H₂NPh₂][OTf].

^fCp*₂Co.

^g[H₃NPh][OTf].

^h[H₃N-2,5-Cl₂C₆H₃][OTf].

ⁱ[N-Me-H₂NPh][OTf].

^j[H₂NPh₂][BARF₄].

^k[H₃NPh][BARF₄].

^lHOTf.