

## Communication

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

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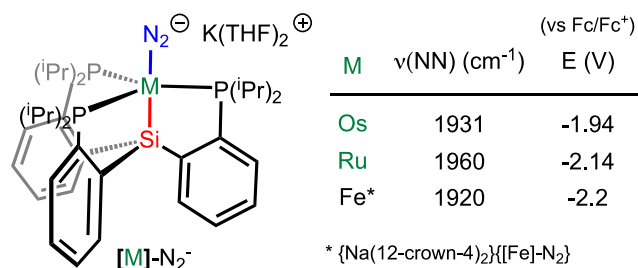
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**ABSTRACT:** Despite the critical role ruthenium and osmium complexes have played in the development of transition metal dinitrogen chemistry, they have not been previously shown to mediate catalytic N<sub>2</sub>-to-NH<sub>3</sub> conversion (N<sub>2</sub>RR), nor have M-N<sub>x</sub>H<sub>y</sub> complexes been derived from protonation of M-N<sub>2</sub> precursors (M = Ru, Os). To help delineate key factors for N<sub>2</sub>RR catalysis, we report on isostructural tris(phosphino)silyl Ru and Os complexes that mediate catalytic N<sub>2</sub>RR, and compare their activities with an isostructural Fe complex. The Os system is most active, and is demonstrated to liberate more than 120 equiv NH<sub>3</sub> per Os center in a single batch experiment using Cp\*<sub>2</sub>Co and [H<sub>2</sub>NPh<sub>2</sub>][OTf] as the reductant and acid source. Isostructural Ru and Fe complexes generate very little NH<sub>3</sub> under the same conditions. Protonation of an anionic Os-N<sub>2</sub><sup>-</sup> state affords a structurally characterized Os=NNH<sub>2</sub><sup>+</sup> hydrazido species that itself mediates NH<sub>3</sub> 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<sub>2</sub>-to-NH<sub>3</sub> conversion (N<sub>2</sub>RR).<sup>1,2</sup> 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.<sup>3</sup> In contrast, synthetic models based on metals other than Fe or Mo that display efficacy for catalytic N<sub>2</sub>RR are to date limited to two cobalt systems, both of which use a combination of strong acid and reductant in the form of [H(OEt<sub>2</sub>)<sub>2</sub>][BAR<sup>F</sup><sub>4</sub>] (HBA<sup>F</sup><sub>4</sub>, BA<sup>F</sup><sub>4</sub> = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) and KC<sub>8</sub>.<sup>4</sup>

The heavier group VIII elements Ru and Os have played a significant role in the history and development of ammonia synthesis and M-N<sub>2</sub> model chemistry. For example, a very active heterogeneous Ru catalyst is used in the industrial Kellogg Advanced Ammonia Process (KAAP),<sup>5</sup> and the first metal-dinitrogen complex to be discovered featured ruthenium ((NH<sub>3</sub>)<sub>5</sub>Ru-N<sub>2</sub><sup>2+</sup>).<sup>6</sup> Noteworthy achievements in Ru and Os model chemistry have included (1) the demonstration of terminal nitride (M≡N<sup>[2/3+]</sup>) coupling to form (isolable or transient) N<sub>2</sub>-bridged bimetallics of the type L<sub>n</sub>M-N<sub>2</sub>-ML<sub>n</sub><sup>[4/5/6+]</sup> (M = Ru or Os);<sup>7,8</sup> (2) photochemically induced homolytic N<sub>2</sub> cleavage to generate terminal Os≡N products;<sup>9</sup> (3) selective protonation and hydrogenation of terminal osmium nitrides to generate NH<sub>3</sub>;<sup>10</sup> and (4) step-wise NH<sub>3</sub> oxidation to N<sub>2</sub> via diimide (HN=NH) and hydrazine (N<sub>2</sub>H<sub>4</sub>) intermediates at cofacial Ru porphyrins.<sup>11</sup>

Despite these advances, there remain no examples of synthetic Ru or Os complexes that demonstrate step-wise protonation of M-N<sub>2</sub> to generate M-N<sub>x</sub>H<sub>y</sub> species, nor complexes featuring these metals that catalyze N<sub>2</sub>RR.<sup>12</sup> 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<sub>2</sub>RR catalyst design.



**Figure 1.** Ruthenium and osmium N<sub>2</sub>RR catalysts studied herein and pertinent physical data from references 14a and 18.

A limitation with respect to achieving N<sub>2</sub>RR catalysis by either Ru or Os is that low-valent redox states (< 2+) can be difficult to access for these metals.<sup>13</sup> 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<sup>7</sup> systems.<sup>14</sup> For M-N<sub>2</sub> species, this should in turn lead to a less activated, and thereby less readily functionalized, N<sub>2</sub> ligand. One notable exception in this context are the [M]-N<sub>2</sub><sup>[0/1-]</sup> 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 M<sup>I</sup> and M<sup>0</sup> terminal dinitrogen compounds.<sup>14a</sup> These species exhibit v(NN) stretching frequencies suggestive of highly activated, terminally bonded N<sub>2</sub> ligands. To our knowledge, K(THF)<sub>2</sub><sup>+</sup>[Os]-N<sub>2</sub><sup>-</sup> (abbreviated hereafter as [Os]-N<sub>2</sub><sup>-</sup>) exhibits the lowest v(NN) stretching frequency (1931 cm<sup>-1</sup>) known for a terminal N<sub>2</sub> adduct of Ru or Os (Figure 1).<sup>14a</sup>

Herein, we establish that both [Ru]-N<sub>2</sub><sup>-</sup> and [Os]-N<sub>2</sub><sup>-</sup> mediate catalytic N<sub>2</sub>RR. [Os]-N<sub>2</sub><sup>-</sup> is a particularly competent catalyst in the presence of Cp\*<sub>2</sub>Co and mild acids. Moreover, the N<sub>2</sub> ligand of [Os]-N<sub>2</sub><sup>-</sup> can be protonated to afford a structurally characterized [Os]=NNH<sub>2</sub><sup>+</sup> hydrazido complex, a likely intermediate by analogy to related [Fe]=NNH<sub>2</sub><sup>+</sup> species that have been implicated as intermediates of N<sub>2</sub>RR by our lab.<sup>15</sup> Catalytically inactive Os-hydride species are characterized that appear to form as thermodynamic sinks of the spent catalyst system.

The N<sub>2</sub>RR performance of [Ru]-N<sub>2</sub><sup>-</sup> and [Os]-N<sub>2</sub><sup>-</sup> was initially canvassed under conditions similar to those first studied in the context of N<sub>2</sub>RR by related iron systems (46 equiv HBAR<sup>F</sup><sub>4</sub>, 50 equiv KC<sub>8</sub>, 1 atm N<sub>2</sub>, Et<sub>2</sub>O, -78 °C).<sup>2a-d</sup> [Os]-N<sub>2</sub><sup>-</sup> affords 1.6 ± 0.3 equiv of NH<sub>3</sub> (Table 1, entry 1) under these conditions, exceeding that observed for [Na(12-crown-4)<sub>2</sub>][P<sub>3</sub><sup>Si</sup>Fe-N<sub>2</sub>] ([Fe]-N<sub>2</sub><sup>-</sup>; entry 2). [Ru]-N<sub>2</sub><sup>-</sup> performs better under these conditions (entry 3), affording 4.3 ± 0.3 equiv of NH<sub>3</sub> (28% selectivity for NH<sub>3</sub> based on H<sup>+</sup>), confirming that N<sub>2</sub>RR catalysis with Ru is viable. Related tripodal, tetra(phosphine) Ru<sup>0</sup>-N<sub>2</sub> complexes have not yet shown selective reactivity at the coordinated N<sub>2</sub> ligand; the weak acids canvassed (e.g., 2,6-lutidinium tetrafluoroborate) tend to react at the metal center to yield oxidized [Ru<sup>II</sup>(N<sub>2</sub>)(H)]<sup>+</sup> products, whereas stronger acids (e.g., HCl, HOTf) have been shown to protonate at the phosphine ligand.<sup>16</sup>

**Table 1. N<sub>2</sub>-to-NH<sub>3</sub> Conversion Mediated by [M]-N<sub>2</sub><sup>-</sup> Complexes<sup>a</sup>**

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

<sup>a</sup>The catalyst, acid, reductant, and Et<sub>2</sub>O were sealed in a Schlenk tube at -196 °C under an N<sub>2</sub> atmosphere, warmed to -78 °C and stirred. For runs utilizing HBAR<sup>F</sup><sub>4</sub>, 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. <sup>b</sup>From ref. 2a. <sup>c</sup>HBAR<sup>F</sup><sub>4</sub>. <sup>d</sup>KC<sub>8</sub>. <sup>e</sup>[H<sub>2</sub>NPh<sub>2</sub>][OTf]. <sup>f</sup>Cp\*<sub>2</sub>Co. <sup>g</sup>[H<sub>3</sub>NPh][OTf]. <sup>h</sup>[H<sub>3</sub>N-2,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>][OTf]. <sup>i</sup>[N-Me-H<sub>2</sub>NPh][OTf]. <sup>j</sup>[H<sub>2</sub>NPh<sub>2</sub>][BAR<sup>F</sup><sub>4</sub>]. <sup>k</sup>[H<sub>3</sub>NPh][BAR<sup>F</sup><sub>4</sub>]. <sup>l</sup>HOTf.

With the above results in hand, we next canvassed milder reagents.<sup>2f,17</sup> These reactions highlight the far superior N<sub>2</sub>RR activity of [Os]-N<sub>2</sub><sup>-</sup> by comparison to either [Ru]-N<sub>2</sub><sup>-</sup> or [Fe]-N<sub>2</sub><sup>-</sup>. Thus, treatment of a suspension of [Os]-N<sub>2</sub><sup>-</sup> in Et<sub>2</sub>O at -78 °C with 46 equiv of [H<sub>2</sub>NPh<sub>2</sub>][OTf] and 50 equiv of Cp\*<sub>2</sub>Co results in the generation of 7.1 ± 0.6 equiv of NH<sub>3</sub> per Os (Table 1, entry 6; 46% based on acid). An identical catalytic run performed under an <sup>14</sup>N<sub>2</sub> atmosphere using [H<sub>2</sub><sup>15</sup>NPh<sub>2</sub>][OTf] yields only [<sup>14</sup>NH<sub>4</sub>][Cl], confirming that the NH<sub>3</sub> formed is derived from the N<sub>2</sub> atmosphere. Attempts to use either [(η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)Os(Cl)(μ-Cl)]<sub>2</sub> or [Os]-Cl as the (pre)catalyst generates only < 0.1 and 2.5 equiv of NH<sub>3</sub>, respectively, underscoring a privileged role for

[Os]-N<sub>2</sub><sup>-</sup> as the catalyst. For comparison, [Fe]-N<sub>2</sub><sup>-</sup>, whose [Fe]-N<sub>2</sub><sup>0/1-</sup> redox couple (-2.2 V vs Fc/Fc<sup>+</sup>) is shifted ~220 mV cathodically from that of Cp\*<sub>2</sub>Co/Cp\*<sub>2</sub>Co<sup>+</sup>,<sup>18</sup> generates only stoichiometric quantities of NH<sub>3</sub> under analogous conditions (entry 4); likewise [Ru]-N<sub>2</sub><sup>-</sup> (*E* = -2.14 V vs Fc/Fc<sup>+</sup>, Figure 1)<sup>14a</sup> shows very poor N<sub>2</sub>RR performance (0.8 ± 0.5 equiv of NH<sub>3</sub>; entry 5).

Os-catalyzed N<sub>2</sub>RR was found to proceed in the presence of correspondingly weaker and stronger anilinium acids with unperturbed yields for NH<sub>3</sub> production. For example, replacing [H<sub>2</sub>NPh<sub>2</sub>][OTf] with either [H<sub>3</sub>NPh][OTf] or [H<sub>3</sub>N-2,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>][OTf] affords 7.9 equiv of NH<sub>3</sub> per Os, respectively (Table 1, entries 11 and 12). [N-Me-H<sub>2</sub>NPh][OTf] gives a slightly diminished yield (6.3 ± 0.5 equiv of NH<sub>3</sub> per Os; entry 13). These observations contrast the behavior of P<sub>3</sub><sup>B</sup>Fe-N<sub>2</sub><sup>-</sup>, where the selectivity for N<sub>2</sub>RR (vs HER) is substantially diminished when using [H<sub>3</sub>NPh][OTf] compared to [H<sub>2</sub>NPh<sub>2</sub>][OTf].<sup>2f</sup>

Attempts to replace Cp\*<sub>2</sub>Co with weaker metallocene reductants, such as cobaltocene (Cp<sub>2</sub>Co) or decamethylchromocene (Cp\*<sub>2</sub>Cr), did not yield any detectable NH<sub>3</sub>. Similarly, the Et<sub>2</sub>O soluble acids [H<sub>2</sub>NPh<sub>2</sub>][BAR<sup>F</sup><sub>4</sub>] and [H<sub>3</sub>NPh][BAR<sup>F</sup><sub>4</sub>] furnished much lower yields of NH<sub>3</sub> 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]-N<sub>2</sub><sup>-</sup>, we tested 150 equiv of [H<sub>2</sub>NPh<sub>2</sub>][OTf] and 180 equiv of Cp\*<sub>2</sub>Co and detected 18 ± 1 equiv of NH<sub>3</sub> per Os (Table 1, entry 7), only a modestly diminished yield (35% based on H<sup>+</sup>) relative to the lower loading. Increasing the substrate loading leads to further increases in the total yield of NH<sub>3</sub>, again with rather little impact on overall efficiency for NH<sub>3</sub> 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 NH<sub>3</sub>, 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 [H<sub>2</sub>NPh<sub>2</sub>][OTf] and 1800 equiv of Cp\*<sub>2</sub>Co, a yield of 120 ± 11 equiv of NH<sub>3</sub> per Os (24 ± 2% for NH<sub>3</sub>; entry 10) is observed. This total turnover number exceeds that of previously reported Fe catalysts, regardless of protocol,<sup>19</sup> and also exceeds TON data for most Mo catalysts.<sup>1</sup> Noteworthy exceptions concern recent Mo catalysts supported by pincer-phosphine ligands, which have been shown to be both very active and selective for NH<sub>3</sub> generation under certain conditions.<sup>1d,f</sup>

For a direct single-run comparison under the present conditions, we tested the best known Fe catalyst, [Na(12-crown-4)<sub>2</sub>][P<sub>3</sub><sup>B</sup>Fe-N<sub>2</sub>],<sup>2d,f</sup> at 1500 equiv of [H<sub>2</sub>NPh<sub>2</sub>][OTf] and 1800 equiv of Cp\*<sub>2</sub>Co; only 22 ± 5 equiv of NH<sub>3</sub> are produced (average of two runs). This P<sub>3</sub><sup>B</sup>Fe-N<sub>2</sub><sup>-</sup> catalyst performs more efficiently than [Os]-N<sub>2</sub><sup>-</sup> at lower substrate loading, however.<sup>2f</sup> The single-run TON value for [Os]-N<sub>2</sub><sup>-</sup> is hence noteworthy, despite its modest selectivity for NH<sub>3</sub> relative to H<sub>2</sub> overall.

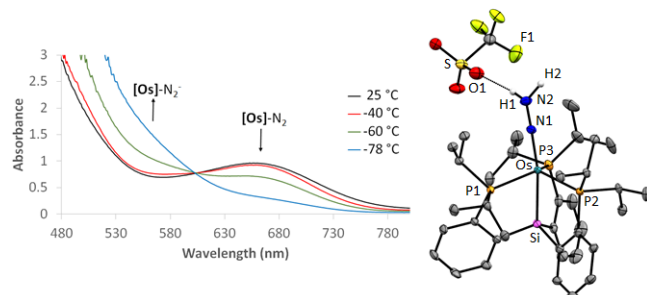
With respect to formation of inactive osmium hydrides, we comment for comparison that [Fe]-N<sub>2</sub><sup>-</sup> reacts with stoichiometric acid (e.g., HBAR<sup>F</sup><sub>4</sub>) to liberate 0.5 equiv of H<sub>2</sub> and its one-electron oxidized derivative, [Fe]-N<sub>2</sub>, presumably via a diazenido intermediate, [Fe]-N=NH, that releases H<sub>2</sub> bimolecularly;<sup>20</sup> none of the thermally stable, and catalytically inactive, hydride product, [Fe](N<sub>2</sub>)(H),<sup>21</sup> is observed. By contrast, exposing [Os]-N<sub>2</sub><sup>-</sup> to stoichiometric HBAR<sup>F</sup><sub>4</sub> in THF-*d*<sub>8</sub> solution at -78 °C affords a mixture of the hydride products [Os](N<sub>2</sub>)(H) (ma-

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or) and  $[\text{Os}]\text{H}_3$  (minor), as determined by variable temperature NMR spectroscopy (Scheme 1).<sup>22</sup> 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  $\text{LiEt}_3\text{BH}$ , or by exposing either  $[\text{Os}](\text{N}_2)(\text{H})$  or  $[\text{Os}]\text{-N}_2$  to an atmosphere of  $\text{H}_2$  (Scheme 1). Subjecting  $[\text{Os}](\text{N}_2)(\text{H})$  or  $[\text{Os}]\text{H}_3$  to 46 equiv of acid ( $\text{HBAr}^{\text{F}_4}$  or  $[\text{H}_2\text{NPh}_2][\text{OTf}]$ ) and 50 equiv of reductant ( $\text{KC}_8$  or  $\text{Cp}^*\text{Co}$ ; 1 atm  $\text{N}_2$ ,  $\text{Et}_2\text{O}$ ,  $-78^\circ\text{C}$ ) does not furnish any detectable  $\text{NH}_3$ . 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%;  $[\text{H}_2\text{NPh}_2][\text{OTf}]/\text{Cp}^*\text{Co}$ : 0%) and  $[\text{Os}]\text{H}_3$  ( $\text{HBAr}^{\text{F}_4}/\text{KC}_8$ : 48%;  $[\text{H}_2\text{NPh}_2][\text{OTf}]/\text{Cp}^*\text{Co}$ : 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  $\text{P}_3^{\text{E}}\text{Fe-N}_2$  catalyst system using  $[\text{H}_2\text{NPh}_2][\text{OTf}]/\text{Cp}^*\text{Co}$ , off-path hydrides are not observed;<sup>2f</sup> they are observed, however, when using  $\text{HBAr}^{\text{F}_4}/\text{KC}_8$ .<sup>2d</sup>

We hypothesized that access to zero-valent  $[\text{Os}]\text{-N}_2$  is critical for productive  $\text{N}_2$  functionalization, presumably proceeding via an initial  $[\text{Os}]\text{-N}=\text{NH}$  intermediate formed via the first protonation step. The  $[\text{Os}]\text{-N}_2^{0/1-}$  redox couple is  $-1.94\text{ V}$  (vs  $\text{Fc}/\text{Fc}^+$ , Figure 1),<sup>14a</sup> suggesting that  $\text{Cp}^*\text{Co}$  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  $\text{N}_2\text{RR}$  catalysis.<sup>2d,f</sup> Invoking  $[\text{Os}]\text{-N}_2$  as “on-path” for catalysis helps rationalize the poor  $\text{N}_2$ -to- $\text{NH}_3$  conversion exhibited by the osmium catalyst when  $\text{Cp}^*\text{Co}$  is replaced by either  $\text{Cp}_2\text{Co}$  ( $E = -1.33$  vs  $\text{Fc}/\text{Fc}^+$ , THF) or  $\text{Cp}^*\text{Cr}$  ( $E = -1.55$  vs  $\text{Fc}/\text{Fc}^+$ , THF); these reagents are not sufficiently reducing to regenerate  $[\text{Os}]\text{-N}_2$ .



**Figure 2.** Left: UV-visible absorbance spectra for the reaction of  $[\text{Os}]\text{-N}_2$  (1.2 mM) and 5 equiv of  $\text{Cp}^*\text{Co}$  (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.

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

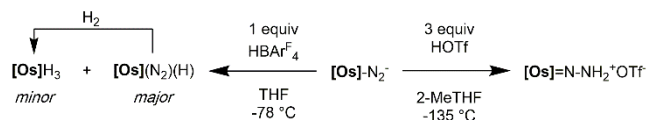
An analogous experiment, performed in  $\text{THF-}d_8$  and monitored by  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopies at room temperature, shows only unreacted  $[\text{Os}]\text{-N}_2$  and  $\text{Cp}^*\text{Co}$ . However, upon cooling this mixture to  $-78^\circ\text{C}$ , resonances consistent with the formation of  $[\text{Os}]\text{-N}_2$  appear.<sup>23</sup> 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  $\lambda = 670$

nm and  $\lambda = 1000$  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  $\lambda = 550$  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  $-78^\circ\text{C}$ ,  $\text{Cp}^*\text{Co}$  is sufficiently capable of reducing  $[\text{Os}]\text{-N}_2$  to  $[\text{Os}]\text{-N}_2$ , a step that may be entropically driven via formation of  $\{[\text{Os}]\text{-N}_2\}\{\text{Cp}^*\text{Co}\}$ . The VT optical data suggest that an observable population of  $[\text{Os}]\text{-N}_2$  can be generated at temperatures as high as  $-40^\circ\text{C}$ . Accordingly, a catalytic run carried-out at  $-40^\circ\text{C}$  (46 equiv  $[\text{H}_2\text{NPh}_2][\text{OTf}]$  and 50 equiv  $\text{Cp}^*\text{Co}$ ) produces 6.2 equiv  $\text{NH}_3$ .<sup>24</sup> By contrast, it appears that neither  $[\text{Ru}]\text{-N}_2$  nor  $[\text{Fe}]\text{-N}_2$  can be competently generated using  $\text{Cp}^*\text{Co}$ , 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 ( $\text{E} = \text{B}$ )<sup>15a</sup> and structurally characterized ( $\text{E} = \text{Si}$ ),<sup>15b</sup> 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 ( $-135^\circ\text{C}$ ) 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  $3232\text{ cm}^{-1}$  and a diagnostic  $^1\text{H}$  NMR resonance ( $\text{THF-}d_8$ ) at  $\delta = 10.0$  ppm. For comparison, the related resonance for  $\{[\text{Fe}]=\text{NNH}_2\}\{\text{OTf}\}$  is at 9.5 ppm.<sup>15b</sup>

### Scheme 1. Synthesis of Os-hydride and Os-hydrazido(2-) Complexes



X-ray diffraction analysis of  $\{[\text{Os}]=\text{NNH}_2\}\{\text{OTf}\}$  locates two protons bound to the  $\text{sp}^2$ -hybridized  $\beta$  N-atom ( $\text{N}_2$ ) with H-bonding to the triflate anion (Figure 2, right). The  $\text{Os-N-NH}_2$  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  $\text{Os-N}_1$  distance is short ( $1.815(3)\text{ \AA}$ ), in accord with a hydrazido(2-) featuring substantial  $\text{Os-N}$  multiple bond character. The  $\text{Os-N}$  and  $\text{N-N}$  distances in  $[\text{Os}]=\text{NNH}_2^+$  are within the range observed for previous structurally characterized linear and bent hydrazido(2-) complexes of osmium,<sup>25</sup> prepared by trapping  $\text{Os}^{\text{IV}}$ -imido intermediates<sup>26</sup> or by the reaction between Os-nitride complexes with secondary amines.<sup>27</sup> A related osmium-imide complex prepared by our lab,  $[\text{Os}]=\text{N-Ar}$  ( $\text{Ar} = p$ -trifluoromethylphenyl),<sup>14a</sup> displays remarkably similar structural parameters to  $[\text{Os}]=\text{NNH}_2^+$ , including comparable  $\text{Os-N}$  bond lengths,  $\text{Os-P}$  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  $\text{Os-N}_2$  species to be converted to a protonated  $\text{Os-N}_x\text{H}_y$  product.

To assess the possible intermedicity of  $[\text{Os}]=\text{NNH}_2^+$  in the Os-mediated  $\text{N}_2\text{RR}$  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  $\text{Cp}^*\text{Co}$  at low temperature, generating greater-than-stoichiometric quantities of  $\text{NH}_3$  (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  $\text{H}_2$ ) owing to very weak N-H bonds.<sup>2f,15c,20</sup> 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\*<sub>2</sub>Co can reduce [Os]-N<sub>2</sub> to [Os]-N<sub>2</sub><sup>-</sup> at low temperature, and that [Os]-N<sub>2</sub><sup>-</sup> can be protonated to yield [Os]=NNH<sub>2</sub><sup>+</sup>, the observation that [Os]=NNH<sub>2</sub><sup>+</sup> can facilitate NH<sub>3</sub> formation lends support to an ET-PT N<sub>2</sub>RR 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<sub>2</sub>RR 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\*<sub>2</sub>Co and [H<sub>2</sub>NPh<sub>2</sub>][OTf]. Access to zero-valent [Os]-N<sub>2</sub><sup>-</sup> appears to be critical for N<sub>2</sub> functionalization, and a bona fide [Os]=NNH<sub>2</sub><sup>+</sup> hydrazido complex can be generated via protonation of [Os]-N<sub>2</sub><sup>-</sup> and is shown to facilitate NH<sub>3</sub> generation; [Os]=NNH<sub>2</sub><sup>+</sup> is hence a plausible intermediate. Os-hydrides, including [Os](N<sub>2</sub>)(H) and [Os]H<sub>3</sub>, form during the catalysis as catalytically inactive states.

That a tris(phosphine)silyl ligand proves so effective for osmium-mediated N<sub>2</sub>RR catalysis, but is largely ineffective for the isostructural [Fe]-N<sub>2</sub><sup>-</sup> and [Ru]-N<sub>2</sub><sup>-</sup> systems using Cp\*<sub>2</sub>Co and [H<sub>2</sub>NPh<sub>2</sub>][OTf], underscores the value in comparatively exploring highly related systems for N<sub>2</sub>RR. In this case, the key [Os]-N<sub>2</sub><sup>[0/1-]</sup> redox couple is accessible with Cp\*<sub>2</sub>Co, but only at low

temperature, whereas a stronger reductant is needed to drive the [Fe]-N<sub>2</sub><sup>[0/1-]</sup> and [Ru]-N<sub>2</sub><sup>[0/1-]</sup> reductions. While other factors are most certainly at play, access to M-N<sub>2</sub><sup>-</sup> states is emerging as a common theme for N<sub>2</sub>RR catalysis by group VIII metals.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge via the Internet at <http://pubs.acs.org>. Experimental methods, synthetic details, additional experiments and data, Tables S1-S13, Figures S1-S62.

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