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Catalytic dinitrogen reduction to hydrazine and ammonia using $\text{Cr}(\text{N}_2)_2(\text{diphosphine})_2$ complexes†Charles H. Beasley,^a Olivia L. Duletski,^a Ksenia S. Stankevich,^a Navamoney Arulsamy,^b and Michael T. Mock^{*a}

The synthesis, characterization of *trans*- $[\text{Cr}(\text{N}_2)_2(\text{depe})_2]$ (**1**) is described. **1** and *trans*- $[\text{Cr}(\text{N}_2)_2(\text{dmpe})_2]$ (**2**) catalyze the reduction of N_2 to N_2H_4 and NH_3 in THF using SmI_2 and H_2O or ethylene glycol as proton sources. **2** produces the highest total fixed N for a molecular Cr catalyst to date.

Motivated by the desire to understand and control the challenging multi-proton, multi-electron reaction of N_2 reduction to NH_3 , researchers have intensely studied the reactivity of molecular transition metal dinitrogen complexes.¹ Well-defined molecular systems offer a high degree of electronic and structural control to regulate chemical reactivity of N_2 .² When combined with effective strategies to form N–H bonds, such as proton-coupled electron transfer (PCET) reagents,³ *i.e.* SmI_2 and a proton source, tens-of-thousands of equivalents of NH_3 can be generated.⁴ The valuable information obtained from these studies includes the identification of viable M– N_2H_y reaction intermediates from spectroscopic data that can be used to delineate the mechanistic steps of a putative catalytic cycle. Such studies can aid in the understanding of the mechanistically complex biological N_2 fixation processes carried out by nitrogenase enzymes,⁵ as well as heterogeneous Haber–Bosch catalysts.⁶

Group 6 N_2 complexes bearing monodentate phosphine ligands, especially with Mo and W, were among the first molecular systems to generate stoichiometric quantities of N_2 -derived NH_3 from protonolysis reactions with strong acids nearly 50 years ago.⁷ Recently, a renaissance of examining structurally similar $[\text{M}(\text{N}_2)_2(\text{P–P})_2]$, (M = Mo, W; P–P = diphosphine) systems has begun, elevating these simple complexes as catalysts for N_2 reduction to NH_3 , or other remarkable reac-

tions such as cleavage of the N_2 triple bond.⁸ Masuda and co-workers reported spontaneous $\text{N}\equiv\text{N}$ bond cleavage upon one-electron oxidation of *trans*- $[\text{Mo}(\text{N}_2)_2(\text{depe})_2]$ (depe = $\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$) to form $[\text{Mo}(\text{N})(\text{depe})_2]^+$.⁹ Chirik and co-workers developed a photocatalytic strategy to form NH_3 from $[\text{Mo}(\text{N})(\text{depe})_2]^+$ and H_2 .¹⁰ Electrocatalytic N_2 fixation with Mo and W-phosphine complexes was described by Peters and co-workers using a tandem catalysis approach.¹¹ Nishibayashi and co-workers showed simple Mo-phosphine complexes catalyzed N_2 reduction to NH_3 using SmI_2 and various proton sources.¹²

While these examples highlight new discoveries using $[\text{M}(\text{N}_2)_2(\text{P–P})_2]$ (M = Mo, W) complexes, catalytic N_2 reduction with analogous Cr compounds are limited. Recent reports highlighted the utility of molecular Cr complexes using a variety of ligand architectures for N_2 activation,^{8a,13} functionalization,¹⁴ or catalytic N_2 silylation.¹⁵ However, molecular Cr complexes that catalyze the direct reduction of N_2 to NH_3 are rare. In 2022, Nishibayashi and co-workers reported a Cr complex bearing a PCP pincer ligand that catalyzed direct N_2 reduction to NH_3 and N_2H_4 at -78°C to rt. KC_8 and phosphonium salts as H^+ sources were required for turnover, and this system was not catalytic using SmI_2 .¹⁶ Herein we prepared and characterized *trans*- $[\text{Cr}(\text{N}_2)_2(\text{depe})_2]$ (**1**), and report catalytic N_2 reduction to NH_3 and N_2H_4 with **1** and *trans*- $[\text{Cr}(\text{N}_2)_2(\text{dmpe})_2]$ ¹⁷ (**2**) (dmpe = $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$) at room temperature using SmI_2 and ethylene glycol or H_2O as proton sources.

Vigorous stirring of yellow *trans*- $[\text{CrCl}_2(\text{depe})_2]$ ¹⁸ (**1-Cl**) in THF with excess Mg powder under a N_2 atmosphere for 24 h furnished **1** as a dark red solid in 70% yield. Isolation of **1** allowed for a comparison of the structural and spectroscopic data with **2** that was reported in 1983.^{17a} The structure of **1**, determined by single crystal X-ray diffraction, shows Cr with four phosphorus atoms of the chelates on the equatorial plane and two axial end-on bound N_2 ligands, Fig. 1, panel a. The average Cr–N, Cr–P, and $\text{N}\equiv\text{N}$ bond distances are 1.904 ± 0.005 Å, 2.334 ± 0.007 Å, and 1.104 ± 0.004 Å, respectively. The corresponding Cr–N, and Cr–P, bond distances in **2** (see ESI†),

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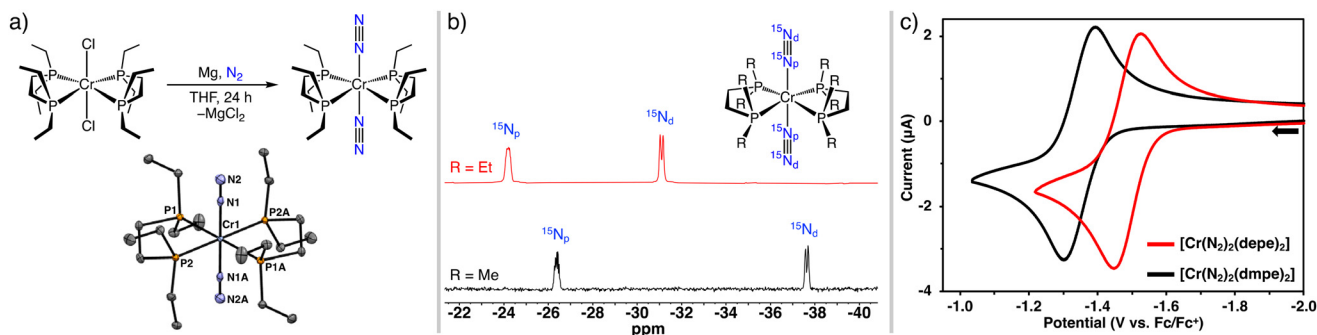


Fig. 1 (a) Synthesis and molecular structure of **1**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity. Crystals of **1** contain two molecules per asymmetric unit with comparable metric parameters; only one molecule is shown. Selected bond distances (Å) and angles (°): Cr1–N1 = 1.9081(10); N1–N2 = 1.1003(14); Cr–P1 = 2.3343(3); Cr–P2 = 2.3249(3). Cr2–N3 = 1.9008(10); N3–N4 = 1.1069(14); Cr–P3 = 2.3425(3); Cr–P4 = 2.3346(3). P1–Cr1–P2 = 81.650(9); P3–Cr2–P4 = 81.583(10); P1–Cr1–N1 = 89.25(3); P2–Cr1–N1 = 90.21(3); P3–Cr2–N3 = 89.29(3); P4–Cr2–N3 = 90.59(3). (b) $^{15}\text{N}\{^1\text{H}\}$ NMR spectra of ^{15}N (red) and $^{2^{15}\text{N}}$ (black) recorded at 25 °C in THF- d_8 . (c) Cyclic voltammograms of **1** and **2** in THF showing the $\text{Cr}^{\text{I}/0}$ wave.

are slightly shorter at 1.8862(17) Å, and 2.294 ± 0.005 Å, and the N≡N distance is 1.110(2) Å.¹⁹ The ligand bite angles for **1** and **2**, *i.e.* P1–Cr–P2, are 81.6° and 83.5°, respectively, and the P–Cr–N angles are near 90°.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** in THF- d_8 , displays a singlet at 79.9 ppm (68.8 ppm for **2**) consistent with four magnetically equivalent P atoms. Complexes **1** and **2** were characterized by ^{15}N NMR spectroscopy to augment the cumulative library of tabulated ^{15}N NMR data of phosphine-supported group 6 N_2 complexes.^{13h} The $^{15}\text{N}_2$ -labelled complexes $^{1^{15}\text{N}}$ and $^{2^{15}\text{N}}$, were prepared by mixing the respective Cr- N_2 complexes in THF- d_8 under 1 atm $^{15}\text{N}_2$. The ^{15}N NMR spectra were collected after mixing for 24 h. The $^{15}\text{N}\{^1\text{H}\}$ NMR spectra contain two resonances; a doublet ($J_{\text{NN}} = 7.0$ Hz) and a multiplet (~ 2.5 Hz ^{31}P coupling) ($^{1^{15}\text{N}}$: –31.1 ppm, –24.2 ppm, and $^{2^{15}\text{N}}$: –37.6 ppm, –26.4 ppm), assigned as the distal (N_d) and proximal (N_p) nitrogen atoms, respectively, (Fig. 1, panel b).¹³ⁱ

Cyclic voltammetry (CV) experiments established the redox behaviour of the Cr(0)- N_2 complexes. Voltammograms were recorded using a glassy carbon working electrode at 0.1 V s^{-1} in THF. The voltammogram for each complex displays a reversible, one-electron $\text{Cr}^{\text{I}/0}$ wave with the half-wave potential ($E_{1/2}$) of –1.49 V and –1.34 V (*vs.* Cp₂Fe^{+/0}) for **1** and **2**, respectively (Fig. 1, panel c). The electrochemically reversible $\text{Cr}^{\text{I}/0}$ couples indicate N_2 dissociation does not occur upon oxidation to Cr(I) during the CV experiments. The reversibility of the waves for **1** and **2** contrasts other *cis*- or *trans*-[Cr(N_2)₂(P₄)] complexes measured by CV that exhibit quasi-reversible or irreversible $\text{Cr}^{\text{I}/0}$ waves due to rapid N_2 loss upon oxidation.^{13b,c,i} In the current study, an irreversible anodic wave was assigned to the Cr^{II/I} redox feature at $E_{\text{pa}} = -0.48$ V and $E_{\text{pa}} = -0.63$ V, for **1** and **2**, respectively, due to N_2 dissociation at more positive potentials, (Fig. S17 and S18 ESI[†]). The CV results suggest a one-electron chemical oxidation to form *trans*-[Cr(N_2)₂(P-P)₂]⁺ should be possible; however, our attempts to isolate such a species have been unsuccessful. Owing to the more electron-rich metal centre of **1**, the ν_{NN} band in the infrared spectrum

at 1906 cm^{-1} (THF) appears at lower energy than the ν_{NN} band for **2** at 1917 cm^{-1} (THF).

Complexes **1** and **2** were examined as catalysts for the direct reduction of N_2 to NH_3 and N_2H_4 . The catalysis studies were performed in THF at room temperature using the PCET reagent SmI₂ and ethylene glycol and/or water as proton donors. A typical catalytic run used 583 equiv. SmI₂, 1166 equiv. ROH per Cr centre and was stirred for 48 h. Quantification of NH_3 , N_2H_4 and H_2 (see ESI for details[†]) products assessed the total fixed N generated in each reaction. Selected catalytic data are listed in Table 1 (see ESI for all tabulated results[†]).

Analysis of the catalysis results provides insights about the performance of **1** and **2** under identical reaction conditions. **2** afforded more total fixed N than **1** in all catalytic trials. For example, **1** generated up to 5 equiv. of NH_3 and 5 equiv. N_2H_4 per Cr center using ethylene glycol as the proton donor after >100 h. Under identical conditions, **2** produced up to 16 equiv. NH_3 and 10 equiv. N_2H_4 in 48 h. Furthermore, ethylene glycol worked more effectively as the proton donor affording higher total fixed N than using H_2O . The deleterious effect of H_2O on catalysis was noted in reactions with **2** using ethylene glycol as the primary proton source. As the amount of H_2O added to the reaction increased, NH_3 production declined, while the N_2H_4 formed stayed relatively constant. We postulate the Cr complexes may simply be more prone to degradation in the presence of H_2O . Separately, **2** was treated with 500 equiv. H_2O or ethylene glycol in THF- d_8 . Free dmpe from complex degradation appeared more rapidly using H_2O , as assessed by ^{31}P NMR spectroscopy. Catalysis performed with **2** under an atmosphere of $^{15}\text{N}_2$ afforded $^{15}\text{NH}_4^+$ as a doublet at 7.1 ppm ($J_{^{15}\text{N}-^1\text{H}} = 71$ Hz) in the ^1H NMR spectrum, identifying $^{15}\text{N}_2$ as the source of $^{15}\text{NH}_3$.

Catalytic trials using *trans*-[CrCl₂(dmpe)₂] (**2-Cl**) and ethylene glycol generated comparable amounts of NH_3 and N_2H_4 as using **2** as the precatalyst. **1-Cl** did not catalyze N_2 reduction, affording only 1 equiv. of NH_3 and N_2H_4 per Cr center. SmI₂

Table 1 Selected Cr-catalyzed N₂ reduction experiments
$$\text{N}_2 + \text{SmI}_2 + \text{ROH} \xrightarrow[\text{THF, rt}]{[\text{Cr}] \text{ cat.}} \text{NH}_3 + \text{N}_2\text{H}_4 + \text{H}_2$$

| Entry | Cr cat. | ROH | NH ₃ equiv./Cr ^a | N ₂ H ₄ equiv./Cr ^b | Total fixed N | Time (h) |
|-----------------|-------------|-----------------------------------|--|--|-------------------------|----------|
| 1 | None | (CH ₂ OH) ₂ | 0 | 0 | 0 | 48 |
| 2 | 1 | (CH ₂ OH) ₂ | 3.7 ± 0.9 | 1.4 ± 0.8 | 4.9 ^h ± 1.5 | 48 |
| 3 | 1 | (CH ₂ OH) ₂ | 4.6 ± 0.6 | 4.0 ± 1.7 | 8.6 ^h ± 2.1 | 100 |
| 4 ^c | 1 | H ₂ O | 1.4 | 0.7 | 2.1 | 48 |
| 5 ^d | 1 | H ₂ O | 3.2 | 0.6 | 3.8 | 28 |
| 6 | 1-Cl | (CH ₂ OH) ₂ | 1.2 | 0.9 | 2.1 | 48 |
| 7 | 2 | (CH ₂ OH) ₂ | 14.6 ± 1.6 | 5.9 ± 2.9 | 20.5 ^h ± 3.8 | 48 |
| 8 ^e | 2 | (CH ₂ OH) ₂ | 6.2 ± 0.5 | 6.4 ± 0.8 | 12.6 ^h ± 0.3 | 48 |
| 9 ^f | 2 | (CH ₂ OH) ₂ | 4.4 ± 0.9 | 6.6 ± 0.6 | 11 ^h ± 0.4 | 48 |
| 10 ^g | 2 | (CH ₂ OH) ₂ | 1.1 | 5.7 | 6.8 | 48 |
| 11 ^d | 2 | H ₂ O | 5.1 | 5.9 | 11 | 3 |
| 12 | 2-Cl | (CH ₂ OH) ₂ | 13.5 ± 2.8 | 5.9 ± 0.6 | 19.4 ^h ± 3.4 | 48 |

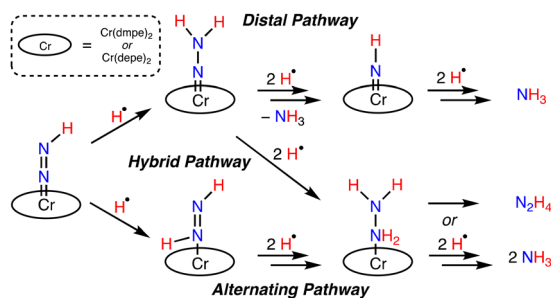
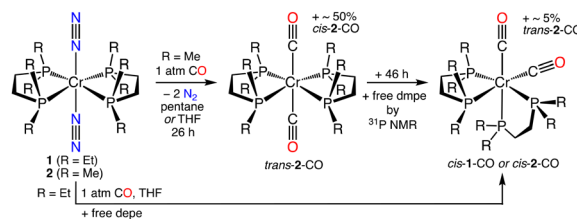
Experiments performed using 0.6 μmol catalyst in 15.0 mL THF at 25 °C under 1 atm N₂, with 583 equiv. of SmI₂, and with 1166 equiv. ROH unless otherwise specified. ^a Determined by acidification and NH₄⁺ quantification using ¹H NMR spectroscopy (see ESI[†]). ^b Determined by colorimetric *p*-dimethylaminobenzaldehyde method (see ESI[†]). ^c 1000 equiv. H₂O/Cr. ^d 10 000 equiv. H₂O/Cr. ^e 25 ppm of H₂O. ^f 250 ppm of H₂O. ^g 583 equiv. (CH₂OH)₂, 583 equiv. H₂O. ^h Average of two or more trials. H₂ quantification by gas chromatography, values are tabulated in ESI[†].

and ethylene glycol may be ineffective at reducing the Cr(II) center of **1-Cl** to Cr(0) where N₂ is strongly activated. Treatment of **2-Cl** with 2 equiv. SmI₂ and 2 equiv. ethylene glycol rapidly generated **2** (see ESI[†]). However, the same reaction of **1-Cl** and SmI₂ with ethylene glycol additive did not form **1** ($E_{1/2} = -1.49$ V, *vide supra*). **1** or **2** could not be generated from **1-Cl** or **2-Cl** using excess SmI₂(THF) alone (E° of SmI₂(THF) = -1.41 ± 0.08 V²⁰ vs. Fc/Fc⁺). A Cr(I) species could be accessible, but N₂ activation and subsequent functionalization steps may be moderated at Cr(I), limiting catalysis.

The mixed N₂ reduction selectivity to form NH₃ and N₂H₄ provides preliminary evidence for a catalytic cycle that follows, at least in part, an alternating N₂ reduction mechanism, Fig. 2, bottom. A purely distal N₂ reduction pathway, Fig. 2, top, would be selective for NH₃ formation. In a 1986 report, the reaction of **2** with CF₃SO₃H was postulated to form a Cr-hydrazido product, [Cr(NNH₂)(dmpe)₂][CF₃SO₃]₂.²¹ A recent study by Wei, Yi, Xi, and co-workers examining early stage N₂ functionalization of [Cp*Cr⁰(depe)(N₂)]⁻ (Cp* = η⁵-C₅(CH₃)₅) using a variety of electrophiles (H⁺, Me₃Si⁺, Me⁺) also revealed the selective formation of Cr-hydrazido products, consistent

with a distal pathway. Contrary to these reaction patterns, protonation studies of related *cis*- or *trans*-[Cr(N₂)₂(P₄)] complexes we examined using strong acids or H⁺/e⁻ reagents, as well as the catalytic Cr[PCP] system¹⁶ generated NH₃ and N₂H₄.^{13c,i,15a} Considering all these examples, and that N₂ reduction mechanisms are sensitive to reaction conditions, (*i.e.* identity of the H⁺ and e⁻ reagents, solvent, temperature), a hybrid N₂ reduction pathway²² where the third and fourth N–H bonds are formed at the proximal N atom of a Cr-hydrazido intermediate, Fig. 2, middle, cannot be excluded for the current systems. Further studies are warranted to understand the N₂ reduction pathways with Cr.

The proclivity for N₂ ligand substitution in **1** and **2** was evaluated as a metric that could reflect catalyst stability and influence catalytic performance. We examined reactions of **1** and **2** with CO to assess the rate of ligand exchange, Fig. 3. Ligand substitution in these six-coordinate complexes is expected to be a dissociative process; a result of Cr–N or Cr–P bond dissociation. Wilkinson, Hursthouse, and co-workers noted **2** did not react with 7 atm CO for several hours except under u.v. irradiation (in light petroleum) to form *cis*-[Cr(CO)₂(dmpe)₂] (*cis*-2-CO).^{17b} This account was surprising, and the unreactive nature toward N₂/CO exchange seemed uncharacteristic of a

**Fig. 2** Plausible N₂ reduction mechanisms for Cr mediated formation of hydrazine and ammonia.**Fig. 3** Ligand exchange reactions of **1** and **2** with CO display different reaction profiles.

complex with terminally bound N₂ ligands. We reacted **2** with 1 atm CO at 25 °C in pentane or THF without u.v. irradiation and monitored the reaction by *in situ* IR spectroscopy, or ³¹P NMR spectroscopy (see ESI†). In both solvents the reaction was slow, but **2** was not unreactive. In THF, after 26 h ~85% of **2** converted to a ~1:1 mixture of *cis*-**2**-CO and *trans*-[Cr(CO)₂(dmpe)₂] (*trans*-**2**-CO). *trans*-**2**-CO converts to ~95% *cis*-**2**-CO (and ~5% free dmpe) after additional 46 h by ³¹P NMR spectroscopy. In THF, **1** converts directly to *cis*-[Cr(CO)₂(depe)₂] *cis*-**1**-CO ($\nu_{\text{CO}} = 1829, 1768 \text{ cm}^{-1}$) in ~3 h by *in situ* IR spectroscopy (see ESI†). The vastly different rates of N₂/CO ligand exchange underscore the greater kinetic stability of **2** toward Cr–L dissociative processes that could ultimately curtail catalyst deactivation pathways (*i.e.* ligand loss) improving catalyst performance for N₂ reduction compared to **1**.

In conclusion, we present a contemporary advancement in the use of *trans*-[Cr(N₂)₂(P–P)₂] complexes (**1** and **2**) for direct catalytic reduction of N₂ to form NH₃ and N₂H₄ using the PCET reagent SmI₂ and H₂O and/or ethylene glycol as proton donors. A new complex, *trans*-[Cr(N₂)₂(depe)₂], was presented herein. Despite having similar electronic structures, we posit **2** is a better catalyst than **1** (using the presented conditions), due to a less negative Cr^{I/0} redox couple and greater kinetic stability from Cr–L dissociative processes.

Author contributions

C. Beasley, investigation, methodology, writing, editing; O. L. Duletski, investigation; K. S. Stankevich, investigation; N. Arulsamy, investigation, writing; M. T. Mock, conceptualization, methodology, supervision, writing, editing, funding acquisition.

Conflicts of interest

There are no conflicts of interest to declare.

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