Exploring the Role of Pendant Amines in Transition Metal Complexes for the Reduction of N₂ to Hydrazine and Ammonia

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Abstract

This review examines the synthesis, properties, and acid reactivity of transition metal dinitrogen complexes bearing phosphine ligands containing pendant amine groups in the second coordination sphere. We have synthesized non-precious metal dinitrogen complexes containing bidentate, tridentate, and tetradentate phosphine ligands, some of which generate N₂ derived

ammonia and/or hydrazine in the presence of excess acid. The metal identity, metal oxidation state, ligand denticity, and functional groups on phosphorus/nitrogen all play a role in controlling the site of protonation (at the metal, pendant amine, or coordinated dinitrogen) with the addition of exogenous acid.

1. Introduction

Humans are experts in the controlled release of energy from non-renewable carbon-based resources [1]. In contrast, combining protons and electrons together in an environmentally responsible manner to generate “on-demand” fuels is not widely utilized. In order to avoid exacerbating the effects already observed as a result of climate change, an important criterion of responsible fuel consumption would be to use renewable and abundant fuel sources while selecting abundant materials and elements to catalyze their production [2]. One fuel candidate that meets these requirements is ammonia (NH₃) [3-5], which could be produced directly from dinitrogen (N₂) (eq 1), or first to hydrazine (N₂H₄) and then ammonia (NH₃) (eq 2 and 3) in the presence of protons, electrons, and a catalyst:

To further fulfill the requirements of using renewable and abundant resources for these transformations, the proton and electron source for the forward reaction can be dihydrogen (H₂)

ultimately derived from water [6] (H_2O) and the catalyst should contain abundant metal(s) (Ti, V, Cr, Mo, W, Mn, Fe, Co, Ni), ideally coupled with solar energy to drive these reactions [7, 8].

The approach described above to reduce N_2 mimics the process nitrogenase enzymes use to convert dinitrogen to ammonia, which sequentially add protons and electrons to a multi-metallic cofactor containing non-precious metals (Fe, Mo, V) under ambient conditions [9-13]. In stark contrast, current industrial standards rely on modern variants of the century old Haber-Bosch process to convert N_2 to NH_3 , which requires high H_2 pressures (150-350 atm) and temperatures (350-550 °C), using solid supported Fe catalysts [14]. This results in an overall high energy consumption, and operates by a different N_2 reduction mechanism under these demanding reaction conditions [15, 16].

In the last decade, diphosphine ligands containing non-coordinating pendant amines in the second coordination sphere have received considerable attention due to their ability to enhance the performance of molecular electrocatalysts [17]. The inclusion of pendant amines is inspired by naturally occurring catalysts such as [FeFe]-hydrogenase, whose non-coordinating pendant amine functions as a proton relay during catalysis [18]. For example, in the development of nickel-based bis(diphosphine) electrocatalysts for the oxidation of hydrogen, DuBois and coworkers found that utilizing the $\text{P}^{\text{R}}\text{N}^{\text{R}'}\text{P}^{\text{R}}$ ligand platform ($\text{P}^{\text{R}}\text{N}^{\text{R}'}\text{P}^{\text{R}} = \text{R}_2\text{PCH}_2\text{N}(\text{R}')\text{CH}_2\text{PR}_2$) in $[\text{Ni}(\text{P}^{\text{Et}}\text{N}^{\text{Me}}\text{P}^{\text{Et}})_2]^{2+}$ resulted in a 0.70 V decrease in the overpotential compared to a Ni complex bearing two diphosphine ligands without pendant amine groups such as $[\text{Ni}(\text{depp})_2]^{2+}$ (depp = $\text{Et}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PEt}_2$) [19]. Furthermore, employing the $\text{P}^{\text{R}_2}\text{N}^{\text{R}'_2}$ ligand ($\text{P}^{\text{R}_2}\text{N}^{\text{R}'_2}$ = substituted 1,5-diaza-3,7-diphosphacyclooctanes), containing a bio-inspired positioned pendant amine [20, 21] i.e. $[\text{Ni}(\text{P}^{\text{Cy}_2}\text{N}^{\text{tBu}_2})_2]^{2+}$ afforded a 100-fold enhancement in catalytic rate [17].

Building on the concept of second coordination sphere effects to control proton movement, we are interested in understanding whether diphosphines containing pendant amines can facilitate proton movement in the electrocatalytic conversion of dinitrogen to ammonia under mild conditions. To date, there are few known homogeneous transition metal complexes that catalyze the conversion of N_2 to NH_3 [22-27] and there are many reports that give a broad overview of recent developments in the field of N_2 reduction chemistry, which go beyond the scope of this review [28-34]. Instead, we will highlight the progress made in our lab toward the synthesis and reactivity of dinitrogen complexes containing diphosphine ligands with pendant amines in the second coordination sphere. In particular, we have examined Cr, Mo, W, Fe and V complexes, and will emphasize the effects of pendant amines on the reactivity with protons and/or electrons.

2. Chromium N_2 complexes

The synthesis and acid reactivity of low-valent mono- or bis(dinitrogen) complexes of Mo and W supported by monodentate, bidentate, or tridentate phosphine ligands have been rigorously examined over the last four decades [35-39]. In contrast, the chemistry of Cr- N_2 complexes of this structure type is remarkably undeveloped. Contributing to limited progress in this area is the scarcity of Cr- N_2 complexes, perhaps due to limited success obtaining stable Cr complexes with terminally bound N_2 ligands [40-42]. Prior to our contributions with Cr, to the best of our knowledge, there were only two reported Cr complexes supported by phosphine ligands with terminally bound N_2 ligands, i.e. *cis*-[Cr(N_2)₂(PMe₃)₄] [43] and *trans*-[Cr(N_2)₂(dmpe)₂] [44-46]. Given that N_2 appears to interact differently with Cr as compared to

Mo and W counterparts, we reasoned that if N₂ coordination could be achieved, the resulting Cr-N₂ complexes might also exhibit atypical N₂ reactivity patterns with acid. Furthermore, we were interested in understanding if pendant amines influenced the stability of N₂ binding in these uncommon Cr systems. Our studies described below were initiated with the synthesis of a Cr-N₂ complex containing the cyclic 8-membered P^{Ph}₂N^{Bn}₂ ligand and were followed by studies of Cr-N₂ complexes containing novel tridentate and tetradentate phosphine ligands.

2.1 Cr–N₂ complexes with the P^{Ph}₂N^{Bn}₂ ligand

Entry into Cr chemistry with the P^{Ph}₂N^{Bn}₂ ligand begins with the reaction of CrCl₃(THF)₃ and 1 equiv of the diphosphine, affording the distorted octahedral complex (κ³-P^{Ph}₂N^{Bn}₂)CrCl₃ (**1**). In addition to the phosphorus atoms, a pendant amine substituent is coordinated to Cr, (Cr–N = 2.206(2) Å) which was the first structurally characterized example of a κ³ binding mode in the P^R₂N^{R'}₂ class of ligands [47]. Since this initial report, other examples of pendant amine-containing diphosphine ligands (i.e. P^RN^{R'}P^R and P^{Ph}₂N^{Bn}₂) have been structurally characterized revealing a κ³-coordinate mode, including complexes of Mn [48] and Mo [49]. Employing **1** as synthon, treatment with Mg powder in THF in the presence of 1 equiv of P^{Ph}₂N^{Bn}₂ for 18 h, afforded *cis*-[Cr(N₂)₂(P^{Ph}₂N^{Bn}₂)₂] (**2**) in a reproducible but low (ca. 15 %) yield (Scheme 1). At the time of this report, this was only the second example of a “Chatt-type” ((P–P)₂M(N₂)₂, P–P = diphosphine ligand.)

Scheme 1. Mg reduction of **1** in THF to form **2**. Treatment of **2** with CO affords **3**. L = $\text{P}^{\text{Ph}_2\text{N}^{\text{Bn}_2}}$ ligand [47].

Cr–N₂ complex containing terminally bound N₂ ligands that was stable toward N₂ loss at room temperature. The infrared spectrum contained two ν_{NN} bands at 2009 and 1937 cm⁻¹ that shift to 1942 and 1873 cm⁻¹, respectively, when prepared under ¹⁵N₂ gas. The complex *cis*-[Cr(¹⁵N₂)₂(P^{Ph₂N^{Bn₂})₂] (**2**^{15N}) was characterized by ¹⁵N NMR spectroscopy, affording a doublet at δ -2.4 and a broad resonance at δ -13.4 for the distal and proximal nitrogen atoms of the N₂ ligands, respectively [50]. Additionally, the cyclic voltammetry revealed an irreversible wave (at all scan rates up to 5 V/s) corresponding to the Cr^{I/0} couple at -1.11 V (versus Cp₂Fe⁺⁰), suggesting the oxidized complex *cis*-[Cr(N₂)₂(P^{Ph₂N^{Bn₂})₂]⁺ is unstable, likely due to N₂ loss upon Cr oxidation. Treatment of a THF solution of **2** with CO afforded *cis*-[Cr(CO)₂(P^{Ph₂N^{Bn₂})₂] (**3**), which exhibits two ν_{CO} bands at 1837 and 1777 cm⁻¹ [47]. The molecular structures of **2** and **3**, shown in Fig. 1, are nearly identical, revealing the *cis* stereochemistry of the N₂ and CO ligands. Complex **2** exhibits an N–N bond distance of 1.133(3) Å, which is slightly elongated upon binding to Cr compared to free N₂ at 1.0975 Å.}}}

Fig. 1. Molecular structures of **2** (left) and **3** (right). Thermal ellipsoids drawn at 30% probability. Symmetry equivalent atom labels are not shown. Hydrogen atoms are omitted for clarity [47].

While reduction of **1** with Mg powder afforded only the *cis*-dinitrogen complex **2**, reduction with potassium graphite (KC₈) generates a mixture of **2** and *trans*-[Cr(N₂)₂(P^{Ph}₂N^{Bn}₂)₂] (*trans*-**2**) in a reaction that was complete in 4 h (Scheme 2).

Scheme 2. Formation of **2** and *trans*-**2** by KC₈ reduction in THF. L = P^{Ph}₂N^{Bn}₂ ligand [47].

The IR spectrum of *trans*-**2** exhibits a single ν_{NN} band at 2007 cm⁻¹ (hexanes), shifting to 1941 cm⁻¹ when prepared under an atmosphere of ¹⁵N₂ gas. The exact reason for the difference in *cis* and *trans* product formation based on the reductant identity is unclear. One possible cause for the contrasting product distribution is the more rapid reduction rate with KC₈, which may favor the

formation of the *trans* isomer as the kinetic product. Isomerization to the *cis* isomer may slowly occur over the longer reduction times required with Mg powder. The *trans* isomer was unstable over the course of several days in solution at room temperature, in contrast to the *cis* isomer that was stable for weeks in solution [47].

Computational analysis was employed to corroborate the observed difference in stability of the **2** and *trans*-**2** isomers and to examine the nature of the Cr–N₂ interaction [47]. These studies suggested the Cr–N₂ interaction is best described by strong electronic polarization of the N₂ ligands by the large amount of negative charge buildup at the Cr center, as NBO analysis found virtually no net metal-to-ligand charge transfer to N₂. Based on this electrostatic interpretation of the Cr–N₂ bonding, the pendant amine groups were found to play a decisive role in the stability of the *cis* and *trans* isomers. Specifically, the N₂••• pendant amine interactions were found to be repulsive; therefore, close interactions of the pendant amines destabilize N₂ binding by depolarizing the N₂ ligands. For this reason, the *cis* isomer was predicted by DFT to be lowest in energy and the thermodynamically preferred geometric isomer because the boat-chair conformation of the P^{Ph}₂N^{Bn}₂ ligand in a *cis* configuration minimizes direct interactions of the pendant amine groups with the N₂ ligands. In contrast, the boat-chair conformation of the P^{Ph}₂N^{Bn}₂ ligand for the *trans* isomer results in at least one interaction of the pendant amine groups with the N₂ ligands, making it less stable by up to 6 kcal mol⁻¹.

2.2 Chromium complexes containing P^{Ph}₃N^{Bn}₃ and P^{Ph}₄N^{Bn}₄ ligands

The low yield of **2** when prepared by the Mg reduction of **1** motivated us to explore other potential Cr precursors to prepare **2** in a greater yield. The synthesis of the complex CrCl₂(P^{Ph}₂N^{Bn}₂)₂ was considered an appropriate target as dihalide precursors such as

$\text{CrCl}_2(\text{dmpe})_2$ [51] and $\text{CrCl}_2(\text{depe})_2$ [52] have been reported by the addition of $\text{CrCl}_2(\text{THF})$ and the 2 equiv of the appropriate diphosphine ligand. Following an analogous procedure, the addition of $\text{CrCl}_2(\text{THF})$ to a stirring THF solution containing 2 equiv of $\text{P}^{\text{Ph}}_2\text{N}^{\text{Bn}}_2$ resulted in a bright green solution which slowly turned brown after stirring for several hours. The desired $\text{CrCl}_2(\text{P}^{\text{Ph}}_2\text{N}^{\text{Bn}}_2)_2$ complex was never isolated from this reaction; instead, two Cr-containing products containing larger phosphorus macrocycle ligands were formed (Fig. 2) [53]. X-ray crystallographic analysis identified yellow crystals (isolated in 5 % yield) as the Cr^{II} complex *trans*- $[\text{CrCl}_2(\text{P}^{\text{Ph}}_4\text{N}^{\text{Bn}}_4)]$ (**4**) that contained a 16-membered phosphorus macrocycle. Additionally, dark blue crystals were identified as the Cr^{III} complex $(\text{P}^{\text{Ph}}_3\text{N}^{\text{Bn}}_3)\text{CrCl}_3$ (**5**) 25 % yield, bearing a smaller facially coordinating 12-membered phosphorus macrocycle.

Fig. 2. Formation of $[\text{12}]\text{-P}^{\text{Ph}}_3\text{N}^{\text{Bn}}_3$ and $[\text{16}]\text{-P}^{\text{Ph}}_4\text{N}^{\text{Bn}}_4$ ligands isolated on Cr (complexes **4** and **5**). Thermal ellipsoids drawn at 30% probability. Hydrogen atoms are omitted for clarity [53].

The 12- and 16-membered macrocycle ligands were isolated as the Cr coordination complexes, and have not been isolated independently as free ligands. The mechanism leading to the formation of the larger P–N macrocycles starting from the Cr^{II} salt remains unclear, however these novel 12- and 16-membered ligands were utilized to prepare the desired Cr–N₂ complexes.

Complex **4** was reduced in THF with Mg powder to yield the bis(dinitrogen) complex *trans*-[Cr(N₂)₂(P^{Ph}₄N^{Bn}₄)] (**6**), in 63 % yield (Fig. 3) [53]. Complex **6** was characterized by X-ray crystallography revealing the *trans*-disposed N₂ ligands bound to Cr. The N₂ ligand residing within the pocket of four electron-rich phenyl groups exhibits a Cr–N bond length of 1.930(2) Å. The opposing N₂ ligand outside the phenyl pocket has a shorter Cr–N bond length of 1.884(2) Å.

Fig. 3. Mg reduction of **4** to form the Cr-dinitrogen complex **6**. Thermal ellipsoids drawn at 30% probability. Hydrogen atoms are omitted for clarity [53].

In accord with the observed variance of Cr–N bond distances, DFT calculations predicted the environment of the phenyl pocket destabilizes the Cr–N binding energy by 7 kcal/mol compared to that of the opposing N₂ ligand. The N–N bond distance of the N₂ ligand residing in the pocket is 1.112(3) Å, while the opposing N₂ ligand N–N distance is 1.120(3) Å. The IR spectrum recorded in THF indicates that the N₂ ligands are moderately activated as a strong ν_{NN} band was observed at 1918 cm⁻¹ and a weak intensity band at 2072 cm⁻¹ for the antisymmetric and symmetric N₂ stretching modes. The assignment of the ν_{NN} bands was further corroborated by the Raman spectrum of a microcrystalline sample of **6**. Furthermore, the cyclic voltammogram of **6** in THF at a scan rate of 0.1 V/s displays an irreversible Cr^{I/0} wave at $E_{\text{pa}} = -1.18$ V, which became quasi-reversible at faster scan rates (ca. 5 V/s) [53].

Protonation studies with triflic acid (HOTf) were carried out at -50 °C with samples of **6** prepared with ¹⁵N₂ gas so the reaction could be followed by ¹⁵N NMR spectroscopy [53]. Acid addition at low temperature was necessary as immediate bleaching of the orange solution occurred at room temperature due to N₂ dissociation from Cr. Treatment of **6** with 3 equiv of HOTf initially formed products containing protonated pendant amine groups such as **7**, shown in Scheme 3, that were assigned on the basis of ³¹P and ¹⁵N NMR spectroscopic data. In addition, a cross peak observed in a ¹H-¹⁵N HSQC experiment with a ¹⁵N signal at -181.0 ppm and a ¹H signal at 12.1 ppm was tentatively assigned as a diazenido (Cr–N–N–H) species based on known ¹⁵N chemical shifts in this region of the NMR spectrum [54-56]. The reaction was kept at -50 °C and hydrazinium (¹⁵N₂H₅⁺) was first observed in the ¹⁵N NMR spectrum after 27 h.

Scheme 3. Protonation of **6** affording **7**, N_2H_5^+ , and NH_4^+ from reduction of the N_2 ligands. N_2 ligands are derived from $^{15}\text{N}_2$ [53].

Treatment with an additional 5 equiv of HOTf resulted in an increase of the $^{15}\text{N}_2\text{H}_5^+$ peak in the ^{15}N NMR spectrum as well as the appearance of a new ^{15}N resonance at -364 ppm corresponding to the formation of ammonium ($^{15}\text{NH}_4^+$) in solution.

Computational studies were performed to examine the protonation mechanism leading to hydrazine formation [53]. DFT calculations predicted that protonation of the pendant amine groups lowers the dissociation energy of the N_2 ligand residing in the pocket of the phenyl rings. The dissociation of one of the N_2 ligands increases the proton affinity of the remaining N_2 ligand by 12 kcal/mol, thus N_2 loss is a critical step to initiate the protonation of the coordinated N_2 to form the diazenido species. Further DFT results suggested protonation of the diazenido ligand at the distal N atom to form a hydrazido ($\text{Cr}-\text{N}=\text{NH}_2$) intermediate was favored by ~ 7.5 kcal/mol over protonation at the proximal N atom affording a diazene ($\text{Cr}-\text{NHNH}$) species; each occurring with a concomitant spin-state change of Cr from a singlet to a triplet. Notably, the DFT simulations also predicted a bent Cr-hydrazido species ($\text{Cr}-\text{N}-\text{N} = 144^\circ$) that contrasts the linear hydrazido structures typically found in Mo and W complexes due to the formation of

metal-nitrogen multiple bonds. Subsequent protonation steps were envisaged to occur at the proximal N atom, and thus the lack of Cr–N multiple bonding was implicated to be a principle factor leading to the formation of hydrazine as the predominant N₂ reduction product.

Complex **5**, bearing the facially coordinating [12]-P^{Ph}₃N^{Bn}₃ ligand, was reduced with Mg powder in the presence of 1 equiv dmpe (dmpe = Me₂PCH₂CH₂PMe₂) to form Cr(N₂)(dmpe)(P^{Ph}₃N^{Bn}₃) (**8**) in 80 % yield (Fig. 4) [57]. To the best of our knowledge, complex **8** was the first example of a mono-dinitrogen complex of Cr in a pentaphosphorus coordination environment. The five phosphorus donors resulted in a very electron-rich Cr center, as supported by the ν_{NN} band in the IR at 1918 cm⁻¹ and the N–N bond distance of 1.132(3) Å as determined by X-ray crystallography. Notably, the N₂ vibrational frequency of **8** is lower than similar Mo–N₂ complexes with a pentaphosphorus coordination environment bearing only alkyl substituents on the phosphorus atoms. For example, Tuzek and co-workers prepared numerous examples of Mo mono-dinitrogen complexes [58-63] bearing a combination of tridentate and bidentate phosphine ligands; the complex Mo(N₂)(SiP^{Me}₂P^{iPr})(dmpm) [63], (SiP^{Me}₂P^{iPr} = [(diisopropylphosphino)methyl)-bis[(dimethylphosphino)methyl](methylsilane); dmpm =

Fig. 4. The reduction of **5** with Mg in the presence of dmpe to form **8**. Thermal ellipsoids drawn at 30% probability. Hydrogen atoms are omitted for clarity [57].

Me₂PCH₂PMe₂) containing only alkyl substituted phosphines, exhibits the lowest ν_{NN} band at 1932 cm⁻¹. The lower N₂ vibrational frequency for **8** is noteworthy given the expected periodic trend of increased basicity descending the group [64, 65]. Indeed, periodic trends influencing N₂ vibrational frequencies and acid reactivity for *all* the group 6 metals are not clearly established, mainly due to the lack of comparable complexes bearing identical ligands. This is a subject we recently addressed in a study that examined an isostructural series of Cr, Mo, and W-N₂ complexes [66]. .

The cyclic voltammogram of **8** recorded in THF (0.1 V/s) exhibits two one-electron redox processes [57]. The half-wave potential for the Cr^{I/0} couple appears as a reversible wave at $E_{1/2} = -1.50$ V, and an irreversible Cr^{II/I} oxidation wave appears at $E_{\text{pa}} = -0.77$ V. The reversible Cr^{I/0}

couple suggests that the $\text{Cr}^{\text{I}}\text{-N}_2$ cation may exhibit modest stability in solution, however chemical oxidation was not investigated. Compared to **2** and **6**, the pentaphosphine ligand environment of **8** displays a $\text{Cr}^{\text{I}/0}$ oxidation wave that is ~ 0.35 V more negative than the bis(dinitrogen) counterparts and likely helps stabilize the $\text{Cr}^{\text{I}}\text{-N}_2$ complex from ligand loss upon metal oxidation.

The acid reactivity of **8** was examined at low temperature with both HOTf and $[\text{H}(\text{OEt}_2)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ [57]. Monitoring the reaction by in situ IR spectroscopy, treatment of **8** with 1 equiv of $[\text{H}(\text{OEt}_2)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ in THF at -78 °C afforded a 7-coordinate $\text{Cr}\text{-N}_2$ hydride complex $[\text{Cr}(\text{H})(\text{N}_2)(\text{dmpe})(\text{P}^{\text{Ph}}_3\text{N}^{\text{Bn}}_3)]^+$ (**9**) (Scheme 4), based on a shift of the ν_{NN} band from 1918 cm^{-1} to 2006 cm^{-1} . Complex **9** was further characterized by variable-temperature ^{31}P NMR spectroscopy and ^{15}N NMR spectroscopy in samples prepared using $^{15}\text{N}_2$. **9** was found to be thermally unstable and N_2 loss occurred in solution at above -30 °C. To investigate the stoichiometric formation of NH_3 and hydrazine, 12 equiv of HOTf was added to **8** (a sample prepared with $^{15}\text{N}_2$ gas) at -78 °C and the reaction monitored by ^{15}N NMR spectroscopy. After 24 h at -50 °C, only a trace amount of $^{15}\text{NH}_4^+$ was formed, and $^{15}\text{N}_2\text{H}_5^+$ was not observed.

Scheme 4. Top: Protonation of **8** with 1 equiv acid to form **9**. Bottom: reaction of **8** with excess acid forming a trace amount of NH_4^+ . N_2 ligands are derived from $^{15}\text{N}_2$ gas. $\text{H}^+ = [\text{H}(\text{OEt}_2)_2][\text{B}(\text{C}_6\text{F}_5)_4]$.

In order to rationalize the acid reactivity of complexes **6** and **8** leading to the formation of $^{15}\text{N}_2$ derived $^{15}\text{N}_2\text{H}_5^+$ and $^{15}\text{NH}_4^+$ products, a comprehensive computational study was employed [57]. The main differences in N_2 reactivity predicted by DFT suggested that the electron-rich Cr center in **8** helps to stabilize $\text{Cr-N}_x\text{H}_y$ intermediates that contain Cr-N multiple bonds, such as a linear hydrazido species ($\text{Cr}=\text{N}=\text{NH}_2$). Thus, in contrast to the DFT results described above for **6**, an “alternating” N_2 reduction pathway would be favored to form NH_3 over hydrazine in this case. However, due to the high basicity of Cr, there is a strong thermodynamic preference to protonate the metal center, which is a competing reaction with N_2 protonation.

3. Molybdenum Complexes

To catalyze the reduction of dinitrogen to ammonia, group 6 transition metal dinitrogen complexes, especially those of molybdenum, have been of greatest interest to many research groups, partly because Mo is present in the iron-molybdenum cofactor (FeMoco) in nitrogenase [12]. Despite an extensive effort over 40 years, there have been only a few examples of homogeneous systems of Mo, notably from the research groups of Schrock and Nishibayashi, which catalyze the reduction of dinitrogen to ammonia with protons and electrons [22, 23, 27, 67]. Given the well-documented acid reactivity patterns of Mo-N_2 complexes supported by traditional phosphine ligands, our efforts focused on designing Mo-N_2 complexes with pendant amines in the secondary coordination sphere to assess the influence of the pendant bases on the

acid reactivity patterns, and ultimately to develop electrocatalytic systems to carry out this multi-proton, multi-electron transformation.

3.1 Mo-N₂ complexes with P^RN^{R'}P^R ligands

In contrast to the coordination chemistry of the cyclic 8-membered P^{Ph}₂N^{Bn}₂ ligand described above with chromium (e.g. complexes **2** and *trans*-**2**), our efforts to prepare similar Mo (or W) dinitrogen complexes of the type *cis*- or *trans*-[Mo(N₂)₂(P^R₂N^{R'}₂)₂] by following well-established synthetic procedures [68] that employed traditional diphosphine ligands were unsuccessful. Despite the challenges with the P^R₂N^{R'}₂ class of ligands, we could readily synthesize a series of molybdenum bis(dinitrogen) complexes supported with two P^RN^{R'}P^R diphosphine ligands, P^RN^{R'}P^R = (R₂PCH₂)₂N(R'), R = Et, Ph; R' = Me, Bn [69]. The synthesis was carried out in a one pot procedure for the ligands with ethyl substituents on phosphorous P^{Et}N^{R'}P^{Et} (R' = Me, Bn) by reduction of MoBr₃(THF)₃ with Mg powder in the presence of 2 equiv P^RN^{R'}P^R (Scheme 5). The *cis* isomer, *cis*-[Mo(N₂)₂(P^{Et}N^{R'}P^{Et})₂] (R = Et, R' = Bn (**10**); R = Et, R' = Me (**11**)) is the kinetic product of this reaction, and was isolated after 2.5 h of starting the reduction with only a minor amount of the *trans* isomer being formed after this time. Extended reaction stirring in THF for 48 – 60 h at room temperature resulted in the *cis* products isomerizing to >85% yield of the *trans* isomer, *trans*-[Mo(N₂)₂(P^{Et}N^{R'}P^{Et})₂] (R' = Bn (**12**); R' = Me (**13**)). Alternatively, a stepwise reductive route could also be followed by first treating MoBr₃(THF)₃ with Zn flakes in the presence of 2 equiv of P^RN^{R'}P^R ligand to afford MoBr₂(P^{Ph}N^{R'}P^{Ph})₂ (R' = Bn (**14**); R' = Me (**15**)). Reduction of **14** and **15** with Mg powder under N₂ atmosphere formed *trans*-[Mo(N₂)₂(P^{Ph}N^{R'}P^{Ph})₂] (R' = Bn (**16**); R' = Me (**17**)) (Scheme 5).

When $\text{MoBr}_3(\text{THF})_3$ was reduced using Mg in presence of 2 equiv of $\text{P}^{\text{Ph}}\text{N}^{\text{R}'}\text{P}^{\text{Ph}}$ ligands, **16** and **17** were obtained; the *cis* isomer was not observed. Unexpectedly, the desired Mo-N₂ complexes could not be obtained from Mg reduction of commonly used Mo starting materials, such as, MoCl_5 , $\text{MoCl}_4(\text{Et}_2\text{O})$, and $\text{MoCl}_3(\text{THF})_3$.

Scheme 5. Synthesis of Mo complexes containing PNP ligands [69].

The reactivity of **10**, **12** and **17** was carried out with CO gas [69]. When a mixture of **10** and **12** was exposed to 1 atm CO gas, **10** converts to *cis*-[Mo(CO)₂(P^{Et}N^{Bn}P^{Et})₂] within 5 min, whereas **12** requires 40 h to convert to >90 % *trans*-[Mo(CO)₂(P^{Et}N^{Bn}P^{Et})₂]. Under identical reaction conditions when a THF solution of **17** was exposed to a CO environment the ³¹P{¹H} NMR spectrum showed **17** and *trans*-[Mo(CO)₂(P^{Ph}N^{Me}P^{Ph})₂] in a 1:1 mixture. After 24 h,

[Mo(CO)₂(P^{Ph}N^{Me}P^{Ph})₂] was observed in 2:1 *cis-trans* ratio. However, loss of PNP ligand was also observed after this time.

Cyclic voltammetry experiments were performed on these Mo–N₂ complexes and the results are summarized in Table 1. As expected, the half-wave potentials of Mo^{I/0} couple are in accordance with the electron-donating ability of the substituents on the phosphorous atoms [70].

Table 1

Redox couples (V vs. Cp₂Fe^{+/0}) for Mo PNP complexes performed in THF 0.2 M [Bu₄N] [B(C₆F₅)₄] at 0.1 V s⁻¹ [69].

Complexes	Mo ^{I/0} (<i>E</i> _{1/2})	Mo ^{II/I} (<i>E</i> _{pa})
<i>trans</i> -[Mo(N ₂) ₂ (P ^{Et} N ^{Bn} P ^{Et}) ₂] (12)	-1.06	0.02
<i>trans</i> -[Mo(N ₂) ₂ (P ^{Et} N ^{Me} P ^{Et}) ₂] (13)	-1.07	0.01
<i>trans</i> -[Mo(N ₂) ₂ (P ^{Ph} N ^{Bn} P ^{Ph}) ₂] (16)	-0.81	0.23
<i>trans</i> -[Mo(N ₂) ₂ (P ^{Ph} N ^{Me} P ^{Ph}) ₂] (17)	-0.82	0.18

Complexes **12** and **13**, which contain with electron-donating ethyl groups, display more negative half-wave potentials (ca. 0.30 V) when compared to **16** and **17**, which contain electron-withdrawing phenyl substituents. All of these Mo complexes exhibit an irreversible wave for the Mo^{II/I} couple. Upon scanning through both the Mo^{I/0} and the Mo^{II/I} waves, loss of current was observed for the Mo^{I/0} couple in the returning cathodic scan resulting a quasi-reversible Mo^{I/0} wave. However, when the scan was stopped before reaching the Mo^{II/I} couple, the Mo^{I/0} wave is reversible. This suggests that at higher oxidation states, one or both of the N₂ ligands may dissociate from the metal center.

In addition to the alkyl substituted Mo–N₂ complexes, a new series of *trans*-[Mo(N₂)₂(P^{Et}N^RP^{Et})₂] complexes (R = Ph (**18**), 2,6-difluorobenzyl (**19**); 3,5-difluorobenzyl (**20**); CH₂CH₂NMe₂ (**21**); CH₂-o-Py (**22**)) were prepared to examine their reactivity with acid [71]. These complexes were synthesized following a similar method as shown in Scheme 5. Although formation of *cis*-products were observed early in the reaction (ca. 2 h), the reactions were stirred >20 h in order to obtain exclusively the *trans* isomer. As expected, the identity of the pendant amine groups has a minimal effect on N₂ ligand activation due to its distance from the metal center. Similar ν_{NN} bands in the IR spectra and similar N–N bond distances in X-ray crystal structures further supported this trend.

Protonation studies were carried out with complexes **18–22** in order to understand the influence of pendant amines on the reactivity of these complexes [71]. Prior to this study, Tuzek and co-workers reported the reactivity *trans*-[Mo(N₂)₂(dppe)(pyNP₂)] [72], (dppe = 1,2-bis(diphenylphosphino)ethane, pyNP₂ = *N,N*-bis(diphenylphosphinomethyl)-2-amino-pyridine) with 3 equiv of HBF₄·Et₂O and observed protonation at the dinitrogen ligand to form the Mo–hydrazido complex, as well as protonation of the pyridine nitrogen of the ligand [73]. In addition, literature reports on protonation reactions of Mo-bis(dinitrogen) complexes with traditional bidentate phosphine ligands [35] and metallocene containing disphosphine ligands [74, 75], with strong acids (e.g. HCl, HOTf, HBF₄·Et₂O etc.) afforded protonation at the dinitrogen ligand to generate hydrazido products [36, 76–79]. In our system, addition of 1 equiv of HOTf to a 10 mM solution of **18** in THF-*d*₈ at -40 °C generated ca. 25% of a 7-coordinate

Scheme 6. Stepwise protonation of **18** with HOTf [71].

molybdenum bis(dinitrogen) hydride, *trans*-[Mo(H)(N₂)₂(P^{Et}N^{Ph}P^{Et})₂]⁺ (**23**), and 50% Mo-hydrazido triflate complex, *trans*-[Mo(NNH₂)(OTf)(P^{Et}N^{Ph}P^{Et})₂]⁺ (**24**), and 25% of unreacted complex **18** (Scheme 6). Monitoring this reaction by *in situ* IR spectroscopy in THF at -40 °C showed an immediate shift of the ν_{NN} band from 1942 to 2022 cm⁻¹, indicating the formation of a Mo-H complex. Addition of a second equiv of HOTf resulted in a further shift of the ν_{NN} band to 2051 cm⁻¹, which indicates protonation at the pendant amine site to generate [Mo(H)(N₂)₂(P^{Et}N^{Ph}(H)P^{Et})(P^{Et}N^{Ph}P^{Et})]²⁺ (**25**). Addition of more than 2 equiv of HOTf did not lead to further change in the position of the ν_{NN} band, suggesting no further protonation at the pendant amine sites.

For protonation studies with HOTf, ¹⁵N₂ labeled isotopologues of these complexes were prepared so that ¹⁵N NMR spectroscopy could be used to analyze the products [71]. In the ¹⁵N

NMR spectrum of **18** at -40 °C, the proximal (N_p) and distal (N_d) nitrogen atoms appear at -40.8 and -42.5 ppm, respectively. Upon addition of 1 equiv of HOTf, resonances for three products were observed in the ^{15}N NMR spectrum. A new set of distal and proximal nitrogen resonances were formed at -37.2 and -54.3 ppm, which were assigned to **23** ^{15}N , based on ^1H - ^{15}N HMBC NMR data. The other product was assigned as **24** ^{15}N based on multiplicity, chemical shifts, and ^1H - ^{15}N HMBC data. Consistent with the *in situ* IR experiment, addition of a second equiv of HOTf protonates the pendant amine site to generate **25** ^{15}N as evidenced by four ^{15}N resonances resulting from two magnetically inequivalent $^{15}\text{N}_2$ ligands. Warming the solution to 25 °C results in loss of ^{15}N signals for **25** ^{15}N and release of $^{15}\text{N}_2$. However, the hydrazido product **24** ^{15}N persisted in solution. Addition of more HOTf did not further protonate the nitrogen ligand site of **24** ^{15}N ; instead, the pendant amine was protonated forming complex **26** ^{15}N . Even though electron-withdrawing phenyl substituent on nitrogen was present in complex **18**, protonation at the pendant amine site was preferred over nitrogen ligand sites in **24**.

With an understanding of the distribution of protonated products from HOTf addition to **18**, we also investigated the reactivity of complexes **19** and **20**, which contained more basic pendant amine substituents [71]. Similar to reactions with **18**, the ^1H NMR and *in situ* IR data indicated the addition of 1 equiv of HOTf to complexes **19** and **20** formed a mixture of the Mo-hydrazido complexes, **27** and **28**, and the 7-coordinate Mo-H products, **29** and **30**, respectively. Notably, due to the higher basicity of the benzylamine groups, compared to the phenyl amines of **18**, the addition of two additional equiv of HOTf resulted in protonation of both of the pendant amine sites, affording the tricationic Mo-H complexes **31** and **32**, respectively (Scheme 7). Monitoring the *in situ* IR spectrum at -40 °C readily identified the formation of the tricationic

complexes **31** and **32**, that display ν_{NN} bands at 2069 and 2063 cm^{-1} , respectively.

Complexes **21** and **22**, which contain two protonation sites per pendant amine group, similarly afforded a Mo-H species upon addition of 1 equiv of HOTf [71]. Unfortunately, the protonated products that were formed upon the addition of two or more equiv of HOTf could not be readily characterized in THF due to poor solubility of these charged complexes.

Protonolysis of these Mo(N₂) complexes to produce ammonia were also carried out with 100 equiv of HOTf. However, in case of **18**, **19**, and **21**, only a trace amount of NH₃ was detected and there was no evidence for N₂H₄ formation in these reactions.

Scheme 7. Acid reactivity of complexes **19** and **20** showing the formation of a tricationic Mo-H species [71].

3.2 Mo-N₂ complexes with P^{Et}P^{NRR'} ligands

Since the general acid reactivity patterns of the Mo-N₂ complexes containing the PNP ligands resulted in Mo-H formation as the major product, a new series of bidentate phosphine ligands containing flexible pendant amine groups were designed so that the steric and electronic

parameters of the pendant bases could be easily tuned to control the protonation site of the molecule, e.g. at the N₂ ligand, pendant amine, or the metal center. In this new series of Mo-N₂ complexes the pendant amines were not incorporated into the ligand backbone, rather the P^{Et}P^{NRR'} ligand contained the pendant bases as terminal substituents on the phosphorus atom [80]. Synthesis of the desired Mo-N₂ complexes was accomplished by ligand substitution reactions, treating the zero-valent complex *trans*-[Mo(N₂)₂(PMePh₂)₄] with 1 equiv of the P^{Et}P^{NRR'} ligand (Scheme 8).

Scheme 8. Synthesis of Mo-N₂ complexes with P^{Et}P^{NRR'} ligands [80].

The substituents on pendant amine were carefully chosen to span a range of p*K*_a values and to more closely match the protonated amines p*K*_a with the dinitrogen ligands. Since both are kinetically favored sites for protonation, p*K*_a matching is crucial for protonation at the dinitrogen ligand rather than at the pendant amine site or the metal center. Apart from tuning the electronic nature of the ligands, it is also important to modulate the steric profile of the ligand to inhibit intermolecular proton transfer to the metal center. Complexes **35** and **36**, which contain bulky phenyl and ⁱPr substituents on nitrogen (but have contrasting amine basicity), were synthesized

to fulfill this criterion [80]. However, the most notable structural difference of the $\text{P}^{\text{Et}}\text{P}^{\text{NRR}'}$ motif from the previously described ligands is the flexibility of the pendant amines. Since the amine groups are not part of the chelate ring, they exhibit greater flexibility, which could potentially improve intramolecular proton delivery to the N_2 ligand.

Protonation of these Mo complexes with HOTf were studied using multinuclear NMR and *in situ* IR spectroscopy. Treatment of **33** and **34** at $-40\text{ }^\circ\text{C}$ in THF with 1 equiv of HOTf afforded a seven-coordinate Mo-H complex, as seen previously with $\text{Mo}(\text{N}_2)(\text{PNP})_2$ complexes. Addition of a second equiv of HOTf resulted in protonation of the amine site (Scheme 9).

Scheme 9. Protonation reactions of **33** and **34** with 2 equiv HOTf [80].

Under similar reaction conditions, complex **35** does not form a Mo-hydride complex, and instead the Mo-hydrazido complex *trans*- $[\text{Mo}(\text{NNH}_2)(\text{OTf})(\text{PMePh}_2)_2(\text{P}^{\text{Et}}\text{P}^{\text{N(Ph)}_2})](\text{OTf})$ (**39**) formed (ca. 50 %) when 1 equiv HOTf was added. A second equiv of HOTf was necessary for the reaction to go to completion (Fig. 5). Complex **39** was characterized by ^1H , ^{31}P , and ^{15}N NMR spectroscopy and by X-ray crystallography [80]. Notably, from the crystal structure of **39**, an elongated N-N bond distance of $1.308(2)\text{ \AA}$ is consistent with formation of the hydrazido ligand. In addition, the diphenylamine substituents are positioned *exo* with respect to the axial hydrazido ligand. This

result is encouraging since protonation at the metal center was completely circumvented. The steric environment around the pendant amine might play an important role for such reactivity. Furthermore, phenyl groups might provide pK_a matching to prevent protonation at the amine site.

Fig. 5. Protonation of **35** to form the Mo-hydrazido complex **39**. Thermal ellipsoids drawn at 30% probability. Hydrogen atoms are omitted for clarity, except for the protons of the hydrazido ligands are shown [80].

Accordingly, stepwise protonation experiments were performed with complex **36**, which contains both sterically bulky and most basic pendant amine groups of this series. Addition of up to 2 equiv HOTf at -40°C forms monocationic complex **40** where one pendant amine site is protonated (Scheme 10) [80]. There was no evidence of protonation at the metal center. In all our previous cases, the metal hydride always formed prior to protonation at the amine site. This suggests that steric bulk and basicity of the amine group impedes the formation of the Mo-H product. Interestingly, addition of another 2 equiv of HOTf did not cause protonation to the other

pendant amine site. This is also unprecedented in our previous systems, as highly basic amines were typically protonated at both amine sites in presence of excess acid. The close proximity of the amines in the same ligand is one plausible explanation for this unexpected result.

Scheme 10. Acid addition to **36** forms **40** containing a protonated pendant amine as the major product and a trace amount of **41** [80].

In addition to **40**, two molybdenum hydrazido complexes, presumably isomers of *trans*-[Mo(NNH₂)(OTf)(PMePh₂)₂(P^{Et}₂P^{N(iPr)}₂(H))](OTf)₂ (**41**) (Scheme 10) were generated in small amounts, where with the protonated pendant amine is positioned near either the NNH₂ or OTf ligand. Complex **40** loses N₂ at room temperature; however **41** persists in solution at room temperature as observed by ¹H and ³¹P NMR spectroscopy [80].

To compare the effect of pendant amines in the presence of exogeneous protons, structurally similar Mo dinitrogen complexes without the pendant amine **42** were also synthesized (Scheme 11). Treatment of **42** with 2 equiv of HOTf, cleanly forms *trans*-

[Mo(NNH₂)(OTf)(PMePh₂)₂(depe)](OTf) (**43**). This finding was revealing because complex **33** and **34** both are structurally similar to **42**, all providing very little steric protection around the metal center. However, acid addition to **33** and **34** formed Mo-H products with stoichiometric amounts of HOTf. It seems clear that the pendant amines likely play an important role in delivering a proton to the metal center.

Scheme 11. Protonation of **42** to form the Mo-hydrazido complex **43** [80].

Reactions to produce ammonia from complex **33**, **35**, and **42** in presence of excess HOTf generated only 0.02-0.04 equiv of NH₃ per Mo atom. Particularly, in case of **35** and **42**, the stability of the intermediates **39** and **43** is a major obstacle, as these intermediates do not appear to react further with acid to produce NH₃ [80].

4. Tungsten N₂ complexes with P^RN^{R'}P^R ligands

Continuing our efforts into the acid reactivity of group six metal complexes featuring chelating phosphine ligands with pendant amine groups in the secondary coordination sphere, a variety of low-valent W-dinitrogen complexes were prepared and compared with our previously described Mo systems [69]. Related to complexes **10-17**, complexes containing one or two

$\text{P}^{\text{R}}\text{N}^{\text{R}'}\text{P}^{\text{R}}$ ligands, ($\text{R} = \text{Et}$, $\text{R}' = \text{Me}$; $\text{R} = \text{Ph}$, $\text{R}' = \text{Me}$) were synthesized using the known starting materials $\text{WCl}_4(\text{PPh}_3)_2$ and $\text{WCl}_4(\text{dppe})$ [68]. The complexes *trans*- $[\text{W}(\text{N}_2)_2(\text{dppe})(\text{P}^{\text{Et}}\text{N}^{\text{Me}}\text{P}^{\text{Et}})]$ (**44**) and *trans*- $[\text{W}(\text{N}_2)_2(\text{dppe})(\text{P}^{\text{Ph}}\text{N}^{\text{Me}}\text{P}^{\text{Ph}})]$ (**45**), and the corresponding complexes without a pendant amine, *trans*- $[\text{W}(\text{N}_2)_2(\text{dppe})(\text{dppp})]$ (**46**), ($\text{dppp} = 1,3\text{-bis(diphenylphosphino)propane}$) and *trans*- $[\text{W}(\text{N}_2)_2(\text{dppe})(\text{depp})]$ (**47**) ($\text{depp} = 1,3\text{-bis(diethylphosphino)propane}$) were synthesized following a similar procedure reported by Tuzek and co-workers (Scheme 12, top) [81]. Likewise, W-N_2 complexes containing two PNP ligands were synthesized by treating $\text{WCl}_4(\text{PPh}_3)_2$ with 2 equiv of PNP ligand in presence of excess Mg powder under a nitrogen atmosphere (Scheme 12, bottom). Depending on the substituents on phosphorous, either a *cis* or *trans* isomer was formed. For example, when the $\text{P}^{\text{Et}}\text{N}^{\text{Me}}\text{P}^{\text{Et}}$ ligand was used, *cis*- $[\text{W}(\text{N}_2)_2(\text{P}^{\text{Et}}\text{N}^{\text{Me}}\text{P}^{\text{Et}})_2]$ (**48**) was formed, whereas in case of $\text{P}^{\text{Ph}}\text{N}^{\text{Me}}\text{P}^{\text{Ph}}$, *trans*- $[\text{W}(\text{N}_2)_2(\text{P}^{\text{Ph}}\text{N}^{\text{Me}}\text{P}^{\text{Ph}})_2]$ (**49**), was obtained.

Scheme 12. Preparation of W-N₂ complexes with one PNP ligand (top) and two PNP ligands (bottom) [69, 82].

The electrochemistry of complexes **44** and **45** are similar to the Mo(PNP) complexes **12**, **13**, **16**, and **17**. In general, they exhibit a quasi-reversible W^{I/0} couple and an irreversible W^{II/I} couple. However, complex **46** shows a quasi-reversible M^{II/I} couple, which becomes reversible at higher scan rates. This may suggest that pendant amine could facilitate loss of N₂ ligand by interacting with the metal center in the higher W oxidation states.

Initial studies examining stoichiometric protonation reactions focused on **44** with only

one PNP ligand. For direct comparison, the structurally and electronically analogous complex **47** was also examined [82]. The products from the addition of 3 equiv of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ in CD_2Cl_2 were sensitive to temperature; when the solution temperature was kept rigorously low (-78 to -40 $^\circ\text{C}$), formation of W-H complex **50** was identified by a characteristic hydride signal in the proton NMR spectrum, along with four inequivalent ^{31}P NMR signals. When this solution was warmed to 5 $^\circ\text{C}$ for a few minutes, the dicationic complex **51** with a protonated pendant amine was observed (Scheme 13). Warming this solution to room temperature liberated N_2 , and unidentified paramagnetic products were formed.

Scheme 13. Protonation and deprotonation behavior of **44** with 3 equiv of HBF_4 in CD_2Cl_2 when the reaction temperature was kept at -40 $^\circ\text{C}$ leading to formation of **50**, then briefly warmed to 5 $^\circ\text{C}$ [82].

The protonation of the metal center as well as at the pendant amine can be reversed by addition of Et_3N . For instance, treatment of **51** with 20 equiv of Et_3N at -35 $^\circ\text{C}$ that rapidly deprotonated the pendant amine site and regenerated complex **50**. When the solution was warmed to room

temperature in presence of 20 equiv of Et_3N , the metal center was also deprotonated to regenerate **44**. However, **44** was not stable in presence of HNEt_3^+ , but when in presence of 100 equiv NEt_3 , was found to persist in solution for ~ 24 h at room temperature [82].

When the protonation of **44** was quickly warmed to room temperature for few minutes instead of being kept cold, a minor W-hydrazido product (**52**) (ca. 15%) was also observed in addition to **51** (ca. 85%, Scheme 14).

Scheme 14. Protonation of **44** with 3 equiv of HBF_4 in CD_2Cl_2 when the reaction was warmed briefly at room temperature before returning to -35°C for analysis [82].

In addition to protonation reactions with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$, **44** was also treated with HOTf to determine if the counter anion effected the distribution of the products. The addition of 6 equiv of HOTf at -78°C and keeping the solution at -40°C during NMR experiments, $\sim 81\%$ conversion to **51** and 18% conversion to **53** was observed (Scheme 15). Treatment of the product mixture of **51** and **53** with NEt_3 at -40°C resulted in formation of **44** and **50**, however N_2 loss

occurs at room temperature resulting in a paramagnetic product, based on the loss of ^{31}P NMR signals [82].

Scheme 15. Protonation of **44** with 6 equiv HOTf [82].

To compare the products formed in the protonation **44**, the analogue without the pendant amine was examined under the same reaction conditions. Complex **47** was treated with 3 equiv of HBF₄·Et₂O, or HOTf at -78 °C and then warmed to -40 °C to collect NMR data, (Scheme 16). In the case of both acids, protonation occurred at the N₂ ligand cleanly forming the hydrazido product [W(NNH₂)(X)(dppe)(depp)][X'], (X = F, X' = BF₄ (**54**); X = X' = OTf (**55**)). Unlike **44**, protonation at the metal center to generate the seven-coordinate W-H complex did not occur, suggesting that in **44** protonation of the pendant amine site may enable intra- or intermolecular proton transfer to the basic metal center [82].

Scheme 16. Protonation of **47** with forming Mo-hydrazido complexes **54** and **55**. H⁺ = HBF₄·Et₂O (**54**, X = F) or HOTf (**55**, X = OTf) [82].

With complexes **44** and **47** in hand, we examined whether the pendant amine-containing complex would lead to an enhancement of stoichiometric production of hydrazine or ammonia upon the addition of a large excess of acid. Treatment of complex **44** and **47** with 100 equiv of HOTf in CH₂Cl₂ at room temperature produced ammonia that was quantified by the indophenol method [83, 84]. Complex **44** formed twice the amount of NH₄⁺ per W center compared to **47** without pendant amine; i.e. 0.81 equiv of NH₄⁺, and 0.40 equiv of NH₄⁺, respectively, (Scheme 17) [82]. Reactions using isotopically labeled ¹⁵N₂ gas confirmed that the NH₄⁺ generated in these reactions was derived from the ¹⁵N₂ ligands. This encouraging result illustrated that minor changes in the second-coordination sphere can have a dramatic effect in reactivity patterns of these W-N₂ complexes with protic reagents. Specifically, in the N₂ reduction pathway, the pendant amine may play a role in promoting the formation of protonated N₂ intermediates past the W-hydrazido species, which was a stable intermediate formed in the stoichiometric acid additions noted above.

Scheme 17. Stoichiometric NH_4^+ formation by **44** and **47** [82].

Analysis of the products from the reaction of **44** in Scheme 17, showed the hydrazido intermediate was absent; however, complex **55** persisted in the reaction mixture after HOTf addition to **47**. In the case of protonation of **44**, the hydrazido intermediate, **53** would have a higher positive charge due to protonated pendant amine, which in turn could promote intermolecular electron transfer by shifting the reduction potential to a more positive value. Proton transfer to the $\text{W}=\text{NNH}_2$ species could follow this step or occur concomitantly with electron transfer. Although metal hydrides are generally believed to play an important role in reduction of dinitrogen to ammonia, it is unclear in this case whether preferential formation of W-H during the protonation reaction of **44** plays a role in producing greater amounts of NH_4^+ .

5. Iron N₂ complexes with $\text{P}^{\text{R}}\text{N}^{\text{R}'}\text{P}^{\text{R}}$ ligands

In addition to the extensive studies we performed with Group 6 metals, renewed interest in well-defined iron-dinitrogen complexes [28-31, 34, 85] tailored for the reduction of N_2 to NH_3 [24-26, 86-89] motivated us to investigate the synthesis and reactivity of iron-diphosphine complexes containing pendant amines. Recently, we synthesized octahedral iron(II) dinitrogen complexes with the general formula $\text{trans-}[\text{Fe}(\text{X})(\text{N}_2)(\text{PEtN}^{\text{Me}}\text{PEt})(\text{dmpm})]^+$ ($\text{X} = \text{H, Cl, Br}$; $\text{dmpm} = 1,1$ -

dimethylphosphinomethane) [90]. In particular, *trans*-[Fe(H)(N₂)(P^{Et}N^{Me}P^{Et})(dmpm)][BPh₄] (**56**) was reacted under a variety of conditions relevant to N₂ reduction (Scheme 18). In the presence of 1 equiv of strong acid (HOTf or [H(OEt₂)₂][B(C₆F₅)₄]) at -40 °C, **56** is protonated at the pendant amine nitrogen to generate a mixture of *endo/exo* isomers **57**, which were characterized in solution by IR and NMR spectroscopy. The ³¹P NMR spectrum and ¹⁵N NMR spectrum of isotopically enriched ¹⁵N₂-**57** both revealed that the ratio of *endo/exo* isomers in solution is approximately 3:1. Protonation of the ligand on going from **56** to **57** increases the N₂ stretching frequency by 25 cm⁻¹, going from 2114 cm⁻¹ to 2139 cm⁻¹, respectively. Furthermore, **57** can be cleanly deprotonated with NEt₃ to regenerate **56**, whose reaction can be monitored by in situ IR spectroscopy. Complex **56** reversibly binds H₂ to generate **58** [91] and also binds NH₃ with the concomitant release of N₂ to form **59**, in which the latter was characterized by NMR spectroscopy and X-ray crystallography [90]. Treatment of **56** with excess acid (50 equiv H₂SO₄) did not generate a detectable amount of ammonia.

Electrochemical analysis on **56** (-24 °C, CH₂Cl₂) reveals an irreversible Fe^{II/I} reduction wave at -2.58 V (vs. Fc^{0/+}). Low temperature electrochemical analysis of **57** results in a shift of the onset of the irreversible Fe^{II/I} reduction wave by +0.33 V, which is expected due to the increase in overall charge [90].

Scheme 18. Reactions of **56** with acid, hydrogen, and ammonia [90].

Computational analysis on the reactivity of **56** provided some insight into the energetics of N_2 binding and protonation. The binding affinity of N_2 to **56** is favorable by 10.1 kcal/mol, while by comparison the CO binding affinity for the isoelectronic complex *trans*- $[\text{Fe}(\text{H})(\text{CO})(\text{P}^{\text{Et}}\text{N}^{\text{Me}}\text{P}^{\text{Et}})(\text{dmpm})]^+$ is much stronger (36.0 kcal/mol). Protonation to form *endo-57* was found to be 43.5 kcal/mol more favorable than protonation at the distal nitrogen atom of coordinated N_2 , indicating that the dinitrogen ligand is 31.9 pK_a units more acidic [90]. This agrees with the experimental observations of **57** and suggests that a less basic pendant amine, in combination with a more activated N_2 ligand, should bias the N_2 ligand more towards protonation upon the addition of acid.

In order to access more electron-rich iron dinitrogen complexes, attempts were made to synthesize the five-coordinate $\text{Fe}(0)$ complex $\text{Fe}(\text{N}_2)(\text{P}^{\text{Et}}\text{N}^{\text{Me}}\text{P}^{\text{Et}})(\text{dmpm})$ from complex **56** [90]. However, each approach led to dmpm ligand loss and the formation of the crystallographically

characterized iron hydride complex $\text{HFe}(\text{Et}_2\text{PC}(\text{H})\text{N}(\text{Me})\text{CH}_2\text{PEt}_2)(\text{P}^{\text{Et}}\text{N}^{\text{Me}}\text{P}^{\text{Et}})$ (**60**) which contains a three-membered Fe-C-P metallacycle and a second $\text{P}^{\text{Et}}\text{N}^{\text{Me}}\text{P}^{\text{Et}}$ ligand (Fig. 6) [90].

The most direct and convenient method for synthesizing **60** was by mixing FeCl_2 and two

Fig. 6. Molecular structures of **60** (left) and the cation **61** (right). Thermal ellipsoids drawn at 30% probability. Hydrogen atoms are omitted for clarity except for the hydrogen atoms bound to Fe [90, 92].

equivalents of free ligand $\text{P}^{\text{Et}}\text{N}^{\text{Me}}\text{P}^{\text{Et}}$ in the presence of excess magnesium powder, leading to isolated yields of 39% after crystallization. In this case, it is possible that the target $\text{Fe}(0)$ complex is formed as a transient intermediate that then undergoes ligand C-H activation.

Detailed experimental and computational investigations involving proton/electron additions to **60** were conducted [92]. The overall reaction (Scheme 19) involves the addition of

Scheme 19. Investigation of proton and electron additions to complex **60** [92].

three protons followed by two electrons, resulting in expulsion of H_2 and uptake of N_2 in the final steps, relevant to the proposed “ E_4 ” state in active site of iron-molybdenum cofactor of nitrogenase after the uptake of four protons and electrons [11, 12, 93]. Beginning with complex **60**, the reactions can be conveniently followed by *in situ* IR analysis of the N_2 stretching band (Fig. 7). After the addition of 1 equiv acid ($[\text{H}(\text{OEt}_2)_2][\text{B}(\text{C}_6\text{F}_5)_4]$), the metallacyclic carbon atom in **60** is protonated with concomitant uptake of N_2 , generating the cationic *cis*- $[\text{Fe}(\text{H})(\text{N}_2)(\text{PEtN}^{\text{Me}}\text{PEt})_2]^+$ complex **61** ($\nu_{\text{NN}} = 2122 \text{ cm}^{-1}$), which was structurally characterized [92]. Next, **61** can be protonated further with two sequential additions of 1 equiv of acid, generating complex **62** and **63**, and shifting the observed ν_{NN} band by $+16$ and $+23 \text{ cm}^{-1}$ after each protonation, respectively. As in the case of complexes **56** and **57**, deprotonation with base

regenerates **61**. Addition of a one electron reductant (Cp_2Co) to **63** yields the proposed Fe(I) complex **64**, which was characterized by X-band EPR spectroscopy. This reduction also results in a cascade of reactions, supported by DFT calculations, involving intermolecular proton and electron rearrangements, ultimately yielding the proposed Fe(II) intermediates **65** and **66**. The formation of **65** was also supported by its independent synthesis from **60** with hydrogen gas, followed by the addition of 2 equiv of acid. Finally, the uptake of N_2 by **66** and/or the liberation of H_2 from **65** with subsequent N_2 uptake generated complex **67**. Computational analysis slightly favors the latter scenario, which is lower in energy by 2.4 kcal/mol [92].

Fig. 7. In Situ IR spectra recorded at $-78\text{ }^{\circ}\text{C}$ in THF of the sequential addition of protons and electrons to **61**. Figure was adapted from ref. [89], with permission of the copyright holders. (Z.M. Heiden, S. Chen, L.A. Labios, R.M. Bullock, E.D. Walter, E.L. Tyson, M.T. Mock, *Organometallics* 33 (2014) 1333-1336.). Copyright 2014 American Chemical Society [92].

6. Vanadium halide complexes with $\text{P}^{\text{R}}\text{N}^{\text{R}'}\text{P}^{\text{R}}$ and $\text{P}\text{R}_2\text{N}^{\text{R}'}_2$ ligands

In addition to the group 6 complexes described above, recent efforts investigated the coordination chemistry of organometallic vanadium complexes containing $\text{P}^{\text{R}}\text{N}^{\text{R}'}\text{P}^{\text{R}}$, and $\text{P}^{\text{R}_2}\text{N}^{\text{R}'_2}$ ligands. Vanadium complexes bearing traditional phosphine ligands have been shown to coordinate N_2 [94] and in some cases produce ammonia and hydrazine upon treatment with acid [95-97]. These results motivated our studies to explore vanadium complexes containing pendant amines. We recently synthesized a series of vanadium halide complexes containing diphosphines and pendant amines, according to Scheme 20 [98].

Scheme 20. Synthesis of vanadium complexes containing pendant amines [98].

Using the precursor Cp_2VI_2 , which is crucial to prevent undesirable disproportionation reactions [99], piano-stool complexes **68-70** was synthesized in two steps by first isolating the diiodide complexes $\text{Cp}_2\text{VI}_2(\text{P}^{\text{R}}\text{N}^{\text{R}'}\text{P}^{\text{R}})$ followed by reduction with excess zinc powder (Scheme 20, top). In

contrast, complex **71** was isolated using a one pot synthetic protocol. Furthermore, using 2 equiv of $\text{P}^{\text{R}}\text{N}^{\text{R}'}\text{P}^{\text{R}}$ ligand and $\text{VCl}_3(\text{THF})_3$ under reducing conditions produces the octahedral complexes $\text{VCl}_2(\text{P}^{\text{R}}\text{N}^{\text{R}'}\text{P}^{\text{R}})_2$ (**72-73**) (Scheme 20, bottom). In all cases, the complexes are paramagnetic and all but **72** were structurally characterized. Despite the complexes being coordinatively unsaturated 15-electron compounds, the PNP and P_2N_2 ligands coordinate in a κ^2 -binding mode, this was particularly surprising for complex **71** in which the boat-chair conformation of the P_2N_2 ligand can adopt a geometry that positions the amine group in close proximity to the metal center.

There electrochemical behavior of **68**, **69**, **71** and **73** was also investigated (25 °C, THF). Complexes **68** and **69** exhibit reversible $\text{V}^{\text{III/II}}$ redox waves at -0.85 and -0.81 V, respectively; compounds **71** and **73** exhibit quasi-reversible $\text{V}^{\text{III/II}}$ waves at -0.85 and -0.87 V, respectively [98]. These vanadium complexes are the first examples of complexes containing pendant amines with a group 5 metal, and represent possible entry points for N_2 fixation chemistry, as well as systems for electrocatalytic H_2 oxidation.

Conclusions and Outlook

With the specific objective of controlling proton transfers for the multi-proton, multi-electron reduction of N_2 to N_2H_4 and/or NH_3 , these studies have advanced our understanding of how pendant amine bases in second coordination sphere of transition metal dinitrogen complexes can affect reactivity with protons. Indeed, we have demonstrated that phosphine ligands with pendant amine bases can support a variety of inexpensive transition metal dinitrogen complexes. In particular, the synthesis, characterization, and reduction of N_2 by phosphine-supported Cr-N_2

complexes represents an emergent area where significant advancements by our group have been made. Reactivity studies of the Cr–N₂ complexes *trans*-[Cr(N₂)₂(PPh₄N^{Bn}₄)] (**6**) and *cis*-[Cr(N₂)₂(P^{Et}N^RP^{Et})₂] (R = 2,6-difluorobenzyl) [66] with triflic acid at low temperatures produced hydrazine as the main N₂ reduction product, while ammonia was formed in lesser amounts. The addition of triflic acid at low temperature to Cr(N₂)(dmpe)(PPh₃N^{Bn}₃) (**8**) produced only trace amounts of ammonia.

Broadly, the acid reactivity studies of Mo and W–N₂ complexes containing PNP ligands with amines in the ligand backbone revealed that the amines may be responsible for facilitating intramolecular proton movement to the thermodynamically favored metal center, compared to analogous complexes without the amines that resulted in protonation exclusively at the N₂ ligand. It is clear that a judicious choice of metal, as well as the steric and electronic properties of the pendant amine, must be considered to control the site of protonation and ultimately form M–N_xH_y intermediates along the N₂ reduction pathway. Our recent progress in ligand design of Mo–N₂ complexes incorporating pendant amines as the terminal substituents on the phosphines (P^{Et}P^{NRR'} ligand) underscores the importance of these variables as selective protonation at the metal, pendant amine, or N₂ ligand was achieved using this ligand platform.

An Fe(II) system containing dmpm and P^{Et}N^{Me}P^{Et} ligands was employed to examine N₂, H₂, and NH₃ ligand binding to the metal. Protonation studies of provided insights on the effect of amine protonation on redox potential of the Fe–N₂ complex and N₂ stretching frequency, resulting in the onset of the Fe^{II/I} reduction wave to shift by +0.33 V and the N₂ stretching frequency to increase by 25 cm⁻¹. Access to Fe(0)–N₂ complexes was not achieved with the P^{Et}N^{Me}P^{Et} ligand platform due to C-H activation at the PNP methylene groups affording

$\text{HFe}(\text{Et}_2\text{PC}(\text{H})\text{N}(\text{Me})\text{CH}_2\text{PEt}_2)(\text{PEtN}^{\text{Me}}\text{PEt})$ (**60**). Formation of **60** was energetically preferred over N_2 binding, however, acid addition showed that one equiv of protons resulted in N_2 binding in *cis*- $[\text{Fe}(\text{H})(\text{N}_2)(\text{PEtN}^{\text{Me}}\text{PEt})_2]^+$ (**61**), which can be protonated further at both pendant amine sites to form a tricationic $\text{HFe}(\text{II})\text{-N}_2$ complex. Reactions with Cp_2Co resulted in N_2 loss, H_2 formation, and N_2 uptake in the cooresponding $\text{HFe}(\text{II})\text{-N}_2$ complex of with 1+ lower overall charge.

With the goal of preparing well-defined transition metal complexes capable of catalyzing the electrochemical conversion of dinitrogen to ammonia and/or hydrazine with protons and electrons in mind, a continued effort to match the $\text{p}K_{\text{a}}$ of a pendant base and the dinitrogen ligand(s) by utilizing experimental and computational methods to obtain N–H bond energies, will be essential in the design of molecular complexes for N_2 reduction. In this regard, present efforts in our group are focused on synthesizing metal-dinitrogen complexes with multi-dentate phosphine ligands containing pendant amines. The studies described in this review represent a foundation for further optimization in ligand design to test the reactivity of these new systems with exogenous proton and electron sources, and develop molecular electrocatalytic systems for N_2 reduction. In addition, we aim to further exploit second coordination sphere pendant amine groups, for the reverse reaction; the six-proton, six-electron electrochemical oxidation of ammonia to N_2 . Efforts are currently underway to utilize the basicity and close proximity of amine groups to coordinated NH_3 ligands to facilitate the cleavage of N–H bonds. This work will complement the N_2 reduction studies by providing thermodynamic information on N–H bond energies that will be critical to aid catalyst design, and will further our ability to predict and control proton movement for making or breaking N–H bonds.

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References

[1] N.S. Lewis, D.G. Nocera, *Proc. Natl. Acad. Sci. U.S.A.* 103 (2006) 15729-15735.

- [2] "Catalysis without Precious Metals," R.M. Bullock, Ed. Wiley-VCH, Weinheim, 2010.
- [3] F. Schüth, R. Palkovits, R. Schlögl, D.S. Su, *Energy Environ. Sci.* 5 (2012) 6278-6289.
- [4] W.I. David, J.W. Makepeace, S.K. Callear, H.M. Hunter, J.D. Taylor, T.J. Wood, M.O. Jones, *J. Am. Chem. Soc.* 136 (2014) 13082-13085.
- [5] N.V. Rees, R.G. Compton, *Energy Environ. Sci.* 4 (2011) 1255-1260.
- [6] V.S. Thoi, Y. Sun, J.R. Long, C.J. Chang, *Chem. Soc. Rev.* 42 (2013) 2388-2400.
- [7] D.G. Nocera, *Inorg. Chem.* 48 (2009) 10001-10017.
- [8] T.R. Cook, D.K. Dogutan, S.Y. Reece, Y. Surendranath, T.S. Teets, D.G. Nocera, *Chem. Rev.* 110 (2010) 6474-6502.
- [9] B.M. Hoffman, D.R. Dean, L.C. Seefeldt, *Acc. Chem. Res.* 42 (2009) 609-619.
- [10] D. Lukoyanov, Z.-Y. Yang, B.M. Barney, D.R. Dean, L.C. Seefeldt, B.M. Hoffman, *Proc. Natl. Acad. Sci. U. S. A.* 109 (2012) 5583-5587.
- [11] B.M. Hoffman, D. Lukoyanov, D.R. Dean, L.C. Seefeldt, *Acc. Chem. Res.* 46 (2013) 587-595.
- [12] B.M. Hoffman, D. Lukoyanov, Z.Y. Yang, D.R. Dean, L.C. Seefeldt, *Chem. Rev.* 114 (2014) 4041-4062.
- [13] J.B. Howard, D.C. Rees, *Chem. Rev.* 96 (1996) 2965-2982.
- [14] V. Smil, *Enriching the Earth: Fritz Haber, Carl Bosch, and the Transformation of World Food Production*, MIT Press, Cambridge, MA, 2001.
- [15] R. Schlögl, *Handbook of Heterogeneous Catalysis*, 2nd ed., Wiley-VCH, Weinheim, 2008.
- [16] R. Schlögl, *Angew. Chem. Int. Ed.* 42 (2003) 2004-2008.
- [17] D.L. DuBois, *Inorg. Chem.* 53 (2014) 3935-3960.
- [18] Y. Nicolet, J.C. Fontecilla-Camps, *J. Biol. Chem.* 287 (2012) 13532-13540.
- [19] C.J. Curtis, A. Miedaner, R. Ciancanelli, W.W. Ellis, B.C. Noll, M. Rakowski DuBois, D.L. DuBois, *Inorg. Chem.* 42 (2003) 216-227.
- [20] J. Yang, S. Chen, W.G. Dougherty, W.S. Kassel, R.M. Bullock, D. DuBois, S. Raagei, R. Rousseau, M. Dupuis, M. Rakowski DuBois, *Chem. Commun.* 46 (2010) 8618-8620.
- [21] J.Y. Yang, S.E. Smith, T. Liu, W.G. Dougherty, W.A. Hoffert, W.S. Kassel, M. Rakowski DuBois, D.L. DuBois, R.M. Bullock, *J. Am. Chem. Soc.* 135 (2013) 9700-9712.
- [22] D.V. Yandulov, R.R. Schrock, *Science* 301 (2003) 76-78.
- [23] K. Arashiba, Y. Miyake, Y. Nishibayashi, *Nat. Chem.* 3 (2011) 120-125.
- [24] J.S. Anderson, J. Rittle, J.C. Peters, *Nature* 501 (2013) 84-87.
- [25] G. Ung, J.C. Peters, *Angew. Chem. Int. Ed.* 54 (2014) 532-535.
- [26] S.E. Creutz, J.C. Peters, *J. Am. Chem. Soc.* 136 (2014) 1105-1115.
- [27] K. Arashiba, E. Kinoshita, S. Kuriyama, A. Eizawa, K. Nakajima, H. Tanaka, K. Yoshizawa, Y. Nishibayashi, *J. Am. Chem. Soc.* 137 (2015) 5666-5669.
- [28] Y. Nishibayashi, *Inorg. Chem.* 54 (2015) 9234-9247.
- [29] N. Khoenkhon, B. de Bruin, J.N.H. Reek, W.I. Dzik, *Eur. J. Inorg. Chem.* 2015 (2015) 567-598.
- [30] Y. Tanabe, Y. Nishibayashi, *Coord. Chem. Rev.* 257 (2013) 2551-2564.
- [31] K.C. MacLeod, P.L. Holland, *Nat. Chem.* 5 (2013) 559-565.
- [32] S. Hinrichsen, H. Broda, C. Gradert, L. Soncksen, F. Tuczek, *Annu. Rep. Prog. Chem., Sect. A* 108 (2012) 17-47.

- [33] J.L. Crossland, D.R. Tyler, *Coord. Chem. Rev.* 254 (2010) 1883-1894.
- [34] N. Hazari, *Chem. Soc. Rev.* 39 (2010) 4044-4056.
- [35] J. Chatt, J.R. Dilworth, R.L. Richards, *Chem. Rev.* 78 (1978) 589-625.
- [36] M. Hidai, Y. Mizobe, *Chem. Rev.* 95 (1995) 1115-1133.
- [37] M. Hidai, *Coord. Chem. Rev.* 186 (1999) 99-108.
- [38] B.A. MacKay, M.D. Fryzuk, *Chem. Rev.* 104 (2004) 385-401.
- [39] H. Broda, S. Hinrichsen, F. Tuczek, *Coord. Chem. Rev.* 257 (2013) 587-598.
- [40] L.A. Berben, S.A. Kozimor, *Inorg. Chem.* 47 (2008) 4639-4647.
- [41] I. Vidyaratne, J. Scott, S. Gambarotta, P.H.M. Budzelaar, *Inorg. Chem.* 46 (2007) 7040-7049.
- [42] P. Sobota, B. Jezowska-Trzebiatowska, *J. Organomet. Chem.* 131 (1977) 341-345.
- [43] H.H. Karsch, *Angew. Chem. Int. Ed.* 16 (1977) 56-57.
- [44] G.S. Girolami, J.E. Salt, G. Wilkinson, M. Thornton-Pett, M.B. Hursthouse, *J. Am. Chem. Soc.* 105 (1983) 5954-5956.
- [45] J.E. Salt, G.S. Girolami, G. Wilkinson, M. Motevalli, M. Thornton-Pett, M.B. Hursthouse, *J. Chem. Soc. Dalton Trans.* (1985) 685-692.
- [46] J.E. Salt, G. Wilkinson, M. Motevalli, M.B. Hursthouse, *J. Chem. Soc. Dalton Trans.* (1986) 1141-1154.
- [47] M.T. Mock, S. Chen, R. Rousseau, M.J. O'Hagan, W.G. Dougherty, W.S. Kassel, D.L. DuBois, R.M. Bullock, *Chem. Commun.* 47 (2011) 12212-12214.
- [48] E.B. Hulley, M.L. Helm, R.M. Bullock, *Chem. Sci.* 5 (2014) 4729-4741.
- [49] S. Zhang, R.M. Bullock, *Inorg. Chem.* 54 (2015) 6397-6409.
- [50] Revised ¹⁵N chemical shift values for **2**, correcting the original report.
- [51] G.S. Girolami, G. Wilkinson, A.M.R. Galas, M. Thornton-Pett, M.B. Hursthouse, *J. Chem. Soc. Dalton Trans.* (1985) 1339-1348.
- [52] G. Ricci, A. Forni, A. Boglia, M. Sonzogni, *Organometallics* 23 (2004) 3727-3732.
- [53] M.T. Mock, S. Chen, M. O'Hagan, R. Rousseau, W.G. Dougherty, W.S. Kassel, R.M. Bullock, *J. Am. Chem. Soc.* 135 (2013) 11493-11496.
- [54] J.R. Dilworth, S. Donovan-Mtunzi, C.T. Kan, R.L. Richards, J. Mason, *Inorg. Chim. Acta* 53 (1981) L161-L162.
- [55] J. Chatt, R.L. Richards, *J. Organomet. Chem.* 239 (1982) 65-77.
- [56] J. Chatt, A.J. Pearman, R.L. Richards, *J. Chem. Soc. Dalton Trans.* (1976) 1520-1524.
- [57] M.T. Mock, A.W. Pierpont, J.D. Egbert, M. O'Hagan, S. Chen, R.M. Bullock, W.G. Dougherty, W.S. Kassel, R. Rousseau, *Inorg. Chem.* 54 (2015) 4827-4839.
- [58] J. Krahmer, H. Broda, C. Näther, G. Peters, W. Thimm, F. Tuczek, *Eur. J. Inorg. Chem.* 2011 (2011) 4377-4386.
- [59] K. Klatt, G. Stephan, G. Peters, F. Tuczek, *Inorg. Chem.* 47 (2008) 6541-6550.
- [60] G.C. Stephan, G. Peters, N. Lehnert, C.M. Habeck, C. Näther, F. Tuczek, *Can. J. Chem.* 83 (2005) 385-402.
- [61] L. Söncksen, C. Gradert, J. Krahmer, C. Nather, F. Tuczek, *Inorg. Chem.* 52 (2013) 6576-6589.
- [62] H. Broda, S. Hinrichsen, J. Krahmer, C. Nather, F. Tuczek, *Dalton Trans.* 43 (2014) 2007-2012.

- [63] H. Broda, J. Krahmer, F. Tuczek, *Eur. J. Inorg. Chem.* 2014 (2014) 3564-3571.
- [64] D.F. Shriver, *Acc. Chem. Res.* 3 (1970) 231-238.
- [65] F. Tuczek, K.H. Horn, N. Lehnert, *Coord. Chem. Rev.* 245 (2003) 107-120.
- [66] Note added during revisions: We recently reported the spectroscopic characteristics and acid reactivity of an isostructural series of Group 6 N₂ complexes, *cis*-[M(N₂)₂(P^{Et}N^RP^{Et})₂] (M = Cr, Mo, W; R = 2,6-difluorobenzyl). Protonolysis experiments showed that only Cr produced N₂H₅⁺ and NH₄⁺ from reduction of the N₂ ligands: J. D. Egbert, M. O'Hagan, E. S. Wiedner, R. M. Bullock, N. A. Piro, W. S. Kassel, M. T. Mock, *Chem. Commun.* (2016) DOI: 10.1039/c6cc03449g.
- [67] S. Kuriyama, K. Arashiba, K. Nakajima, H. Tanaka, N. Kamaru, K. Yoshizawa, Y. Nishibayashi, *J. Am. Chem. Soc.* 136 (2014) 9719-9731.
- [68] J.R. Dilworth, R. Richards, *Inorg. Synth.* 28 (2007) 33-43.
- [69] C.J. Weiss, A.N. Groves, M.T. Mock, W.G. Dougherty, W.S. Kassel, M.L. Helm, D.L. DuBois, R.M. Bullock, *Dalton Trans.* 41 (2012) 4517-4529.
- [70] W. Hussain, G.J. Leigh, H.M. Ali, C.J. Pickett, D.A. Rankin, *J. Chem. Soc., Dalton Trans.* (1984) 1703-1708.
- [71] L.A. Labios, C.J. Weiss, J.D. Egbert, S. Lense, R.M. Bullock, W.G. Dougherty, W.S. Kassel, M.T. Mock, *Z. Anorg. Allg. Chem.* 641 (2015) 105-117.
- [72] G.C. Stephan, C. Nather, C. Sivasankar, F. Tuczek, *Inorg. Chim. Acta* 361 (2008) 1008–1019.
- [73] G. Stephan, C. Nather, F. Tuczek, *Acta Crystallogr., Sect. E: Struct. Rep. Online* E64 (2008) m629.
- [74] M. Yuki, Y. Miyake, Y. Nishibayashi, I. Wakiji, M. Hidai, *Organometallics* 27 (2008) 3947-3953.
- [75] M. Yuki, Y. Miyake, Y. Nishibayashi, *Organometallics* 28 (2009) 5821-5827.
- [76] M. Hidai, T. Kodama, M. Sato, M. Harakawa, Y. Uchida, *Inorg. Chem.* 15 (1976) 2694-2697.
- [77] T.A. George, L. Ma, S.N. Shailh, R.C. Tisdale, J. Zubieta, *Inorg. Chem.* 29 (1990) 4789-4796.
- [78] K. Gebreyes, J. Zubieta, T.A. George, L.M. Koczon, R.C. Tisdale, *Inorg. Chem.* 25 (1986) 405-407.
- [79] R.A. Henderson, *J. Chem. Soc., Dalton Trans.* (1984) 2259-2163.
- [80] L.A. Labios, Z.M. Heiden, M.T. Mock, *Inorg. Chem.* 54 (2015) 4409-4422.
- [81] G.C. Stephan, C. Nther, C. Sivasankar, F. Tuczek, *Inorg. Chim. Acta* 361 (2008) 1008-1019.
- [82] C.J. Weiss, J.D. Egbert, S. Chen, M.L. Helm, R.M. Bullock, M.T. Mock, *Organometallics* 33 (2014) 2189-2200.
- [83] A.L. Chaney, E.P. Marbach, *Clin. Chem.* 8 (1962) 130-132.
- [84] M.W. Weatherburn, *Anal. Chem.* 39 (1967) 971-974.
- [85] S.F. McWilliams, P.L. Holland, *Acc. Chem. Res.* 48 (2015) 2059-2065.
- [86] J.S. Anderson, G.E. Cutsail, 3rd, J. Rittle, B.A. Connor, W.A. Gunderson, L. Zhang, B.M. Hoffman, J.C. Peters, *J. Am. Chem. Soc.* 137 (2015) 7803-7809.
- [87] J.D. Gilbertson, N.K. Szymczak, D.R. Tyler, *J. Am. Chem. Soc.* 127 (2005) 10184-10185.

- [88] C.G. Balesdent, J.L. Crossland, D.T. Regan, C.T. Lopez, D.R. Tyler, *Inorg. Chem.* 52 (2013) 14178-14187.
- [89] L.D. Field, N. Hazari, H.L. Li, *Inorg. Chem.* 54 (2015) 4768-4776.
- [90] Z.M. Heiden, S. Chen, M.T. Mock, W.G. Dougherty, W.S. Kassel, R. Rousseau, R.M. Bullock, *Inorg. Chem.* 52 (2013) 4026-4039.
- [91] R.M. Henry, R.K. Shoemaker, R.H. Newell, G.M. Jacobsen, D.L. DuBois, M.R. DuBois, *Organometallics* 24 (2005) 2481-2491.
- [92] Z.M. Heiden, S. Chen, L.A. Labios, R.M. Bullock, E.D. Walter, E.L. Tyson, M.T. Mock, *Organometallics* 33 (2014) 1333-1336.
- [93] Z.Y. Yang, N. Khadka, D. Lukoyanov, B.M. Hoffman, D.R. Dean, L.C. Seefeldt, *Proc. Natl. Acad. Sci. U. S. A.* 110 (2013) 16327-16332.
- [94] G. Liu, X. Liang, A. Meetsma, B. Hessen, *Dalton Trans.* 39 (2010) 7891-7893.
- [95] C. Woitha, D. Rehder, *Angew. Chem. Int. Ed.* 29 (1990) 1438-1440.
- [96] D. Rehder, C. Woitha, W. Pribsch, H. Gailus, *J. Chem. Soc. Chem. Commun.* (1992) 364-365.
- [97] H. Gailus, C. Woitha, D. Rehder, *J. Chem. Soc. Dalton Trans.* (1994) 3471-3477.
- [98] J.D. Egbert, L.A. Labios, J.M. Darmon, N.A. Piro, W. Scott Kassel, M.T. Mock, *Eur. J. Inorg. Chem* 2016 (2016) 1293-1299.
- [99] J. Nieman, J.H. Teuben, J.C. Huffman, K.G. Caulton, *J. Organomet. Chem.* 255 (1983) 193-204.