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## Recent Developments in Homogeneous Dinitrogen Reduction by Molybdenum and Iron

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### Abstract

The reduction of gaseous nitrogen ( $N_2$ ) is a challenge for industrial, biological and synthetic chemists, who want to understand the formation of ammonia ( $NH_3$ ) for agriculture and also want to form N-C and N-Si bonds for fine chemical synthesis. The iron-molybdenum active site of nitrogenase has inspired chemists to explore the ability of iron and molybdenum complexes to bring about transformations related to  $N_2$  reduction. This area of research has gained significant momentum, and the last two years have witnessed a number of significant advances in synthetic Fe- $N_2$  and Mo- $N_2$  chemistry. In addition, the identities of all atoms in the iron-molybdenum cofactor of nitrogenase have finally been elucidated, and the discovery of a carbide has generated new questions and targets for coordination chemists. This Perspective summarizes the recent work on iron and molybdenum complexes, and highlights the opportunities for continued research.

Dinitrogen ( $N_2$ ) is one of the most plentiful molecules around us, but ironically it is one of the most difficult to use for chemical processes. Its thermodynamic stability and nonpolar nature make it unreactive, and it is often used as an “inert gas.” However, since the nitrogen atoms from  $N_2$  are essential for agriculture, chemical reactions that transform  $N_2$  into more versatile molecules are necessary. Ammonia ( $NH_3$ ) is the most common product of these reduction reactions, and the synthesis of value-added organic molecules from  $N_2$  would also be worthwhile. In addition to these practical targets, chemists are also motivated by the challenge of activating the strong N-N triple bond through controllable and/or catalytic reactions. For these reasons, there is a long history of research in  $N_2$  reduction by transition-metal complexes.<sup>1,2,3</sup>

This article examines recent research progress on molybdenum and iron complexes that are capable of  $N_2$  reduction. Because of space limitations, and to avoid treading the same ground as earlier reviews,<sup>4,5</sup> we will focus on  $N_2$ -reducing complexes of Mo and Fe reported in the last two years. Mo and Fe have received the most attention because of their presence in Mo-dependent nitrogenase, for which the active site is a cluster called the iron-molybdenum cofactor or FeMoco. Chemists’ understanding of Mo-dependent nitrogenase itself has also benefitted from recent revelations, and these will be described near the end of the Perspective. We refer the reader to earlier reviews (and the papers cited therein) for discussions of  $N_2$  reduction chemistry with a broader coverage of synthetic chemistry with other metals.<sup>1,2,3</sup>

### Dinitrogen reduction and functionalization at Mo

Historically, molybdenum has been the most successful metal for homogeneous  $N_2$  reduction reactions. In prominent examples, Chatt described stoichiometric  $N_2$  reduction reactions with protons,<sup>6,7</sup> Shilov and Schrock reported catalytic reductions to ammonia,<sup>8,9</sup>

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and Shiina, Hidai, and Mizobe reported catalytic reduction of  $N_2$  to silylamines and organonitrogen compounds.<sup>3,10</sup> Research reported in the last two years has built upon these seminal discoveries.

One strategy, pioneered by Shiina<sup>10</sup> and further developed by Hidai,<sup>11</sup> is to functionalise dinitrogen using a silyl chloride and an alkali metal reductant. Nishibayashi recently described research that evaluated the idea that electron flow into the catalytic metal could be facilitated by the one-electron redox couple in ferrocene.<sup>12</sup> A Mo- $N_2$  complex featuring two depf (depf = 1,1'-bis(diethylphosphino)ferrocene) ligands, *trans*-[Mo( $N_2$ )<sub>2</sub>(depf)<sub>2</sub>], catalysed the transformation of  $N_2$  into tris(trimethylsilyl)amine [N(SiMe<sub>3</sub>)<sub>3</sub>] in the presence of chlorotrimethylsilane (Me<sub>3</sub>SiCl) and Na metal as a stoichiometric reductant (Figure 1a). This reaction gave up to 226 equivalents of N(SiMe<sub>3</sub>)<sub>3</sub> per mole of Mo catalyst, much more than the catalyst lacking the ferrocene substituents.<sup>11</sup> The authors also found that reaction of Mo( $N_2$ )<sub>2</sub>(depf)<sub>2</sub> with Me<sub>3</sub>SiOTf (OTf = trifluoromethanesulfonate) produced the potential intermediate Mo(depff)<sub>2</sub>(OTf)(NNSiMe<sub>3</sub>). On the basis of DFT calculations, the authors proposed the formation of Me<sub>3</sub>Si• radicals, which would react with the Mo( $N_2$ )<sub>2</sub>(depf)<sub>2</sub> catalyst to form Mo(depff)<sub>2</sub>(NNSiMe<sub>3</sub>), followed by a series of additional radical reactions to produce N(SiMe<sub>3</sub>)<sub>3</sub>. Additional studies are necessary to gain experimental support for this mechanism. Though the ferrocenes were introduced as a potential electron-transfer pathway, there was no clear evidence that the redox activity of the ferrocene substituents played a role in the catalytic efficiency. Nevertheless, these results serve as a strong motivation to incorporate redox-active ligands into other  $N_2$  reduction systems in the future.

A series of other reports have utilised tridentate pincer ligands for controlling the reactivity of Mo. One used the molybdenum(0) complex [PNP]Mo(PMe<sub>2</sub>Ph)( $N_2$ )<sub>2</sub>, where PNP = 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine.<sup>13</sup> When treated with an excess of H<sub>2</sub>SO<sub>4</sub> at room temperature, it produced significant amounts of NH<sub>3</sub> (1.4 equiv per Mo), as shown in Figure 1b. By comparison, the previously reported *trans*-[Mo( $N_2$ )<sub>2</sub>(triphos)(PPh<sub>3</sub>)], where triphos = PhP(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>, reacted with HBr to provide 0.9 equiv of NH<sub>3</sub>,<sup>14</sup> and *cis*-[M( $N_2$ )<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>4</sub>] provided 0.7 (M = Mo) or 2.0 (M = W) equiv of NH<sub>3</sub> upon treatment with H<sub>2</sub>SO<sub>4</sub>.<sup>6</sup> In contrast, the W- $N_2$  complex [PNP]W(PMe<sub>2</sub>Ph)( $N_2$ )<sub>2</sub> produced hydrazine (0.6 equiv) as the major product upon treatment with H<sub>2</sub>SO<sub>4</sub> under the same reaction conditions as the Mo- $N_2$  analogue (Figure 1b).<sup>13</sup> The different  $N_2$  reduction products for Mo vs. W suggest that there are different relative rates for reduction vs. protonation of a hydrazido intermediate. This is an interesting difference from earlier systems where the W complex was postulated to be more efficient than Mo because of its more electron-rich metal center.<sup>14</sup> Better understanding of the mechanisms is expected to elucidate how the product distribution may be controlled.

These stoichiometric reactions were extended to catalytic  $N_2$  reduction, using the related bimetallic molybdenum(0)- $N_2$  species {[PNP]Mo( $N_2$ )<sub>2</sub>}<sub>2</sub>( $\mu$ - $N_2$ ) (Figure 1c).<sup>15</sup> This complex catalysed the conversion of  $N_2$  to ammonia under one atmosphere of  $N_2$  at room temperature using conditions similar to those of Schrock,<sup>8</sup> with lutidinium triflate as the proton source and cobaltocene as a stoichiometric reductant. This reaction produced 12 moles of ammonia per mole of Mo.

In the proposed mechanism of ammonia formation, the bimetallic molybdenum species first breaks apart to form a monometallic tris(dinitrogen) species, which then undergoes a series of proton and electron transfers to convert the bound  $N_2$  into ammonia. This mechanistic proposal is consistent with the observed decrease in catalyst activity toward ammonia formation with the use of smaller PNP ligands,<sup>16</sup> because the greater steric pressure of the larger PNP ligands is expected to favour formation of the reactive monometallic tris(dinitrogen) species. Interestingly, the monometallic species [PNP]Mo(PMe<sub>2</sub>Ph)( $N_2$ )<sub>2</sub>,

discussed in the previous paragraph, did not catalytically reduce  $N_2$  under the same reaction conditions. A bimetallic carbonyl analogue,  $\{[PNP]Mo(CO)_2\}_2(\mu-N_2)$ , was also ineffective for catalytic ammonia production. These results suggest that incorporation of strongly-binding monodentate ligands reduces the reactivity of the complex toward ammonia formation. The number of turnovers from the PNP-supported Mo complex compares favourably to the results from Schrock's Mo complex supported by a tetradentate triamidoamine ligand.<sup>8</sup> Therefore, the new work shows that both triamidoamine and PNP are each appropriate scaffolds for  $N_2$  reduction by protons and electrons, despite the different coordinating geometries.

In another ligand variation, Schrock and co-workers reported the Mo chemistry of a tridentate POCOP ligand framework (POCOP =  $C_6H_3-1,3-[OP(t-Bu)_2]_2$ ) that replaced the coordinating nitrogen in the above PNP ligand with an anionic carbon, and had oxygens in place of the methylene bridges (Figure 1d).<sup>17</sup> In the POCOP system, reduction of  $N_2$  by a transient molybdenum(II) species gave a terminal nitride complex from cleavage of  $N_2$ . However, this nitride complex was not protonated at nitrogen. Accordingly, this POCOP-Mo system was not capable of catalytic  $N_2$  reduction. It is possible that the "dead-end" nitride complex was unsuitable as a Brønsted base, that the presence of an iodide ligand inhibited the catalytic reaction (by analogy to the CO and phosphine inhibition discussed above), or that ligand flexibility makes possible an undesired side reaction.

Cummins has made a recent contribution that builds upon his Mo-mediated reduction of  $N_2$  to nitride,<sup>18</sup> by demonstrating the conversion of this nitride into a cyanide group.<sup>19</sup> The initial C–N bond was formed by attack of the nitride on  $MeOCH_2I$ , which forms a cationic  $[N(t-Bu)Ar]_3Mo(NCH_2OMe)^+$  species, followed by deprotonation to give a methoxyketimide  $[N(t-Bu)Ar]_3Mo[NC(H)OMe]$ . Addition of  $SnCl_2$  and excess  $Me_2NSiMe_3$  gave the cyanide product  $[N(t-Bu)Ar]_3Mo(CN)$ . After this impressive demonstration of the ability to build  $CN^-$  from  $N_2$  stoichiometrically, the next challenge is to produce this C–N bond catalytically.

## Dinitrogen reduction and functionalization at Fe

Until 2011, there were no examples of complete stoichiometric  $N_2$  reduction by Fe complexes.<sup>4,5</sup> Nevertheless, researchers have studied N-containing Fe species that are part of *hypothetical* cycles for  $N_2$  reduction at Fe.<sup>20</sup> These hypothetical cycles are modeled after Mo chemistry, and typically involve terminal nitride complexes of iron (even though no terminal nitrides have come from direct cleavage of dinitrogen yet in iron chemistry). In the most thoroughly studied example, Smith has created a terminal iron(IV)-nitride complex that is supported by a tris(carbene)borate ligand (Figure 2a). Reaction of this Fe nitride species with excess TEMPO-H (1-hydroxy-2,2,6,6-tetramethylpiperidine) afforded ammonia in 74% yield.<sup>21</sup> Consideration of the relevant redox potentials and  $pK_a$  values indicated that the initial N–H bond formation proceeded by direct H-atom transfer from TEMPO-H to the Fe nitride through proton-coupled electron transfer. In support of radical-transfer ability of the nitride, reaction of the iron(IV) nitride with  $Ph_3C\cdot$  gave a new  $NCPH_3$  ligand. C–N bond formation was also observed upon treatment of this Fe-nitride species with CO and with *tert*-butyl isocyanide (Figure 2a).<sup>22</sup> These latter reactions indicate that the iron(IV) nitride can be electrophilic. Similarly, an iron(V)-nitride species reacts with water and cobaltocene to give ammonia, suggesting the formation of a Brønsted base *in situ*.<sup>23</sup> The active species in this ammonia formation is not the iron(IV)-nitride described above, because independent reactions show that it is inert to water. The reaction pathways that lead to N–H, N–C, and N–P bond formation in this system are clearly ripe for further study.

Other series of papers have described the interconversions of “nitrogenous” ligands consisting of nitrogen and hydrogen atoms, which are related to N<sub>2</sub> reduction chemistry. Tyler,<sup>24</sup> Field,<sup>25</sup> and Peters<sup>26,27</sup> have reported diazene (N<sub>2</sub>H<sub>2</sub>), hydrazine (N<sub>2</sub>H<sub>4</sub>), and ammonia complexes of iron that lie along a hypothetical “alternating” reduction mechanism for N<sub>2</sub> reduction by Fe.<sup>28</sup> The essential displacement of NH<sub>3</sub> by N<sub>2</sub> on iron was demonstrated by Peters, in research where reduction of an Fe center in an (SiP<sub>3</sub>)Fe complex (SiP<sub>3</sub> = Si(*o*-C<sub>6</sub>H<sub>4</sub>PR<sub>2</sub>)<sub>3</sub> with R = Ph or *i*-Pr) improved its ability to  $\pi$  backbond, causing preferential binding of N<sub>2</sub> over NH<sub>3</sub>.<sup>29</sup> However, these systems still lacked a key precedent: demonstration that iron complexes can stoichiometrically cleave the N-N bond of N<sub>2</sub>. This goal was achieved and reported in two different papers in 2011, each of which used a novel strategy that suggests future research directions.

One strategy, explored by Peters, has been the use of a flexible chelating ligand, tris[2-(diisopropylphosphino)phenyl]borane (TPB) (Figure 2b), in which the B can be viewed as a zero-electron neutral ligand (electron pair donated from metal to boron), as a two-electron dianionic ligand (electron pair donated from boron to metal), or as a resonance structure between these two limiting forms. Below, we use “formal” oxidation states that assume a neutral borane, though it should be understood that the oxidation level of iron would be more positive if the boron were assigned a negative charge. Reduction of (TPB)FeBr with 1 equivalent of Na-naphthalide provided the formally iron(0)-dinitrogen complex (TPB)Fe(N<sub>2</sub>) (Figure 2b), which had an *S* = 1 ground state.<sup>30</sup> Reduction with additional Na gave the anionic *S* = 1/2 complex Na[(TPB)Fe(N<sub>2</sub>)]. The N-N stretching band in this formally iron(-I) compound was significantly lower than that in the neutral analogues as a result of stronger  $\pi$ -backbonding.

Reaction of Na[(TPB)Fe(N<sub>2</sub>)] with silyl chloride electrophiles produced new N-Si bonds in silyldiazene (N<sub>2</sub>SiMe<sub>3</sub>) and disilylhydrazine (N<sub>2</sub>[Me<sub>2</sub>SiCH<sub>2</sub>CH<sub>2</sub>SiMe<sub>2</sub>]) products (Figure 2b).<sup>31</sup> The former type of N-Si bond formation at Fe was preceded only in other recent work from Peters.<sup>29</sup> Formation of a disilylhydrazide ligand from M-N<sub>2</sub> complexes is known with M = Mo and W,<sup>32</sup> but this new work was the first time this was observed in an Fe complex. Treatment of the disilylhydrazide complex with *tert*-butyl isocyanide caused substitution of the isocyanide for one phosphine of the TPB ligand. Upon standing at room temperature, the isocyanide compound spontaneously cleaved the N-N bond (Figure 2b): one N atom of N<sub>2</sub> was now part of a disilylamide ligand, with the other N atom attached to B and P atoms of the supporting ligand. Therefore, this reaction sequence led to complete cleavage of the N-N bond of N<sub>2</sub>, and the energetic cost was paid by formation of new N-Si, N-P, and N-B bonds. This metal-ligand cooperativity shows significant potential for forming new bonds to the N fragments remaining from N<sub>2</sub> cleavage, though the modification of the supporting ligand in the product is incompatible with expansion of this reaction into a catalytic N<sub>2</sub> reduction.

In a different strategy, the first example of an Fe-nitride complex derived from N<sub>2</sub> was reported recently by our research group.<sup>33</sup> Reduction of a  $\beta$ -diketiminato-supported iron(II) chloride complex with potassium-graphite (one molar equivalent of K per Fe) under an atmosphere of N<sub>2</sub> resulted in formation of an Fe bis(nitride) compound. This cluster contained four  $\beta$ -diketiminato Fe fragments with two bridging nitride ligands derived from N<sub>2</sub> (Figure 3). This six-electron redox reaction oxidised the four iron(I) sites to two iron(III) (the two Fe atoms bridging the nitride ligands) and two iron(II) (the remaining two Fe atoms). The K<sup>+</sup> ions in the product provided structural stabilisation of the bis(nitride) structure through cation  $\pi$  interactions. The use of multiple iron atoms together with potassium to cleave the N-N bond of nitrogen is reminiscent of the Mittasch catalyst for the Haber-Bosch process, which has a low-valent iron surface “promoted” with potassium additives. The structure of the Mittasch catalyst has surface and subsurface nitrides and

oxides embedded in a defect-rich surface, and cleaves  $N_2$  to nitrides in the limiting step of the catalytic reaction.<sup>34</sup> Therefore, the molecular iron-nitride compound is significant because it gives chemists a structurally confirmed complex from  $N_2$  cleavage by Fe and K ions.<sup>35</sup>

This reaction also serves as an example of how changes in the size of the supporting ligands can greatly influence  $N_2$  reactivity. Earlier work on closely related iron-diketimate complexes showed products in which the N-N bond was weakened and lengthened, but not cleaved.<sup>36</sup> In the earlier complexes, one iron atom bound to each end of the  $N_2$  molecule, but the bulky ligands prevented approach of additional iron centers to the coordinated  $N_2$ . The use of smaller diketimate ligands may enable approach of more metals to the  $N_2$  molecule, culminating in cooperative N-N bond cleavage. This hypothesis is supported by the fact that the product has the nitride remnants of  $N_2$  bound directly to *three* iron atoms. Computational investigation (using simplified ligands) suggested that three diketimate-bound iron(I) centers,  $K^+$ , and an additional electron can approach the  $N_2$  molecule in a side-on/side-on/end-on geometry from which N-N cleavage is favourable.<sup>37</sup> These pieces of evidence fit together into an overall model where simultaneous attack of more iron atoms is beneficial for  $N_2$  activation. The strategic reduction of ligand size to give side-on  $N_2$  and N-N cleavage finds precedent in the work of Chirik on cyclopentadienyl-supported zirconium complexes that cleave  $N_2$ .<sup>38</sup>

Treatment of the tetrairon bis(nitride) complex with an excess of anhydrous HCl produced ammonium chloride in 82% yield. This report marked the first example of high-yielding  $N_2$  conversion to  $NH_3$  with an Fe based system. However, the reaction is not catalytic, as the excess acid degrades the iron-containing products. Current work focuses on the use of other acids and acid stoichiometries, in order to better control this reaction and understand the intermediates.

The use of milder sources of H is another important goal in the conversion of  $N_2$  to  $NH_3$ , because these are more conducive to eventual *catalytic*  $N_2$  reduction at Fe. For example, the hydrogenation of a ruthenium nitrido complex with  $H_2$  was recently described.<sup>39</sup> In the diketimate-iron chemistry, it was reported that the bis(nitrido)tetrairon complex reacted with excess  $H_2$  to give a diiron(II) bis( $\mu$ -hydride) complex and a 40% yield of ammonia.<sup>33</sup> Though the production of the hydride complex from  $H_2$  has been reproducible, further experiments (not yet reported in detail) show that the ammonia observed in the  $H_2$  reaction comes from  $H^+$  in the workup rather than from the reaction with  $H_2$ . Thus, addition of  $H_2$  to this nitride complex does not actually produce  $NH_3$ , and the full reaction stoichiometry for the  $H_2$  reaction is a topic of current inquiry.

Though catalytic reduction of  $N_2$  to  $NH_3$  by molecular iron complexes is not yet known, Nishibayashi has recently discovered the first example of catalytic  $N_2$  reduction into  $N(SiMe_3)_3$  by a solution iron complex.<sup>40</sup> The catalytic reduction was catalyzed by  $Fe(CO)_5$  and by cyclopentadienyl-Fe compounds, in analogy to the Mo-catalyzed process in the previous section (Figure 1a).<sup>12</sup> In these reactions, mixtures of the catalysts with  $Me_3SiCl$  and Na metal under one atmosphere of  $N_2$  provided up to 34 equivalents of  $N(SiMe_3)_3$  per mole of Fe. A combination of computational and experimental results suggest that disilyliron(II) fragments may be the catalyst formed in situ. It is difficult to rule out the intermediacy of iron nanoparticles or small clusters in these catalytic reactions; note that the mercury drop test is ineffective for Fe because it is not amalgamated by mercury. Although further studies will be required to elucidate the mechanism involved in this process, analogy can be drawn to the well-characterized N-Si bond formation reported by Peters using well-defined Fe complexes, silyl chlorides, and Na (Figure 2b).<sup>31</sup> Incorporation of other

supporting ligands may lead to Fe complexes where experimental characterization of the mechanism is feasible.

## New structural revelations in the nitrogenase FeMoco

The most active nitrogenase enzyme has a catalytic cofactor called the iron-molybdenum cofactor (FeMoco). Chemists' view of the FeMoco for the last ten years has been informed by a 2002 crystal structure at 1.16 Å, which showed seven Fe, one Mo, nine bridging S, and a central atom whose identity was unknown.<sup>41</sup> In 2011, simultaneous papers by DeBeer and by Einsle finally demonstrated that the central atom is a carbon (Figure 4).<sup>42,43</sup> Three methods were used: (a) new crystallographic data to 1.0 Å resolution, (b) Electron Spin Echo Envelope Modulation (ESEEM) spectroscopy on fully <sup>13</sup>C-labeled protein, which showed a signal due to coupling of the <sup>13</sup>C nucleus to the ground-state spin, and (c) iron X-ray emission spectroscopy (XES), which gives valence-to-core emission signals that differ greatly depending on the atoms attached to iron. The identification as carbon was also supported in computations.<sup>44</sup>

It is surprising to learn that the FeMoco is an organometallic cluster, and that a formal carbide (C<sup>4-</sup>) is present in a biological system. However, exceptional stability of an iron-carbide cluster should not be shocking, because solid-state iron carbide materials are strong (*e.g.* cast iron and steel). The source of the carbon atom in the FeMoco is *S*-adenosylmethionine (SAM), as shown by <sup>14</sup>C tracer studies by Ribbe.<sup>45</sup> The insertion of carbon is brought about by the enzyme NifB, which reduces the sulfonium cation of SAM to transfer a methyl group to the nascent FeMoco. In the proposed mechanism, abstraction of another hydrogen atom from the methyl group forms an alkylidene intermediate, eventually culminating in a carbide product. In addition to the pressing mechanistic questions, the novel intermediates postulated in the FeMoco biosynthesis pose an added challenge to the inorganic chemistry community. In particular, chemists have never prepared any iron-sulfide cluster containing a metal-bound alkyl, alkylidene, alkylidyne, or carbide.

There are numerous other targets for synthetic chemists that would also help to understand the formation, structure, stability, and mechanism of the FeMoco. For example, no synthetic iron-sulfide compound has ever been observed to bind or reduce N<sub>2</sub>. Another active area of research will continue to address synthetic compounds that demonstrate fundamental mechanisms through which H can be added and removed from iron-bound carbon and nitrogen atoms. For example, a very recent report described the interconversion of NH<sub>2</sub> and NH<sub>3</sub> groups on a tris(phosphino)borane-supported iron complex.<sup>46</sup> These studies are likely to assist in the growing understanding of N<sub>2</sub> reduction intermediates in iron-molybdenum nitrogenase.<sup>47</sup>

## The future of iron and molybdenum dinitrogen chemistry

In addition to spectacular examples of new reactions, new mechanisms, and new bonding modes, these new research papers point toward the next series of targets for chemists interested in N<sub>2</sub> reduction by Mo and Fe. In Mo chemistry, catalytic reduction of N<sub>2</sub> to NH<sub>3</sub> has been achieved, although the number of turnovers is limited. Therefore, the main goals in this area should be to increase the efficiency of this process, and to extend the catalytic chemistry to the formation of more valuable nitrogen-containing products. In Fe chemistry, one of the key goals is to find well-characterised molecular complexes that catalytically reduce N<sub>2</sub>. Considering that iron is used in both surface and biological N<sub>2</sub> reduction, coordination chemists should also seek relevant supporting ligation on the Fe atom, including nitrides, oxides, and potassium (which are present in the technical Haber-Bosch

catalyst) and also carbide and sulfide ligation (which are present in the FeMoco of nitrogenase).

Much of the recent work on  $N_2$  reduction has focused on the production of  $NH_3$ . Although it is sometimes claimed that a homogeneous route for catalytic ammonia synthesis would be preferable to the high-temperature Haber-Bosch process, the presence of a solvent would create separation problems, and current Haber-Bosch technology already has an impressive 70% energy efficiency.<sup>34</sup> Biocatalytic  $N_2$  reduction based on nitrogenase seems intuitively appealing because of the lower temperature and pressure, but is unattractive on a large scale because nitrogenase is not energy-efficient, hydrolyzing at least 16 molecules of ATP per molecule of  $N_2$  reduced.<sup>48</sup> Thus, the promise of small-molecule or enzymatic catalysts for large-scale ammonia production is limited. Rather, the primary impact of synthetic complexes that reduce  $N_2$  to ammonia is that they provide well-characterised structures and systematic studies that teach chemists about the fundamental mechanisms of  $N_2$  reduction, and about analogies to enzyme and surface catalysts where the atomic-level mechanisms remain unknown. Additionally, chemists should strive to expand the range of products that can be derived from coordinated  $N_2$ . In early transition metal chemistry, stoichiometric  $N_2$  functionalisation now includes a range of N-C bond formation reactions, particularly through discoveries by Fryzuk<sup>49</sup> and Chirik.<sup>50,51,52,53,54,55,56</sup> Thus, a current challenge is to make these N-C bond forming reactions catalytic, possibly by using middle (Mo) and late (Fe) transition metals like those described above. Because these reactions can construct value-added chemical compounds, there is significantly more promise for commercialization for fine chemicals than for ammonia synthesis.

How do the recent discoveries guide future work in coordination chemistry? One emerging theme is the importance of the supporting ligand. Comparison of the PNP vs. POCOP chemistry of Mo, and of the SiP<sub>3</sub> and TBP ligands of Fe, highlights the major influence that the supporting ligand can exert through changing a coordinating atom and/or changing the charge.

The spin state and coordination number of the metal are other important factors that differentiate many of the above compounds, and it is important to systematically understand their influences. There are not yet clear general trends that enable chemists to guide the choice of supporting ligands; this may be due to the multitude of possible rate- and turnover-limiting steps, and the relative rates of decomposition pathways are also likely to be important. Therefore, mechanistic studies are urgently needed. A second emerging theme is that cooperative attack on  $N_2$  by multiple metals may be important; in these cases, steric effects may have a negative influence by preventing multiple metals from simultaneously approaching  $N_2$ . However, other systems use monometallic M- $N_2$  chemistry, and in these cases extremely bulky ligands are indispensable. A third emerging theme is alkali metal binding: in both the TBP and diketiminate complexes of Fe that cleave  $N_2$ , key intermediates have side-on interactions of  $N_2$  with a sodium or potassium ion. The alkali metal cations can stabilise reduced  $N_2$  species through Coulomb attractions, and may enforce key transition-state geometries for control over regiochemistry. Thus, there is a compelling case for incorporating alkali metal components into future molecular  $N_2$  reduction systems. Overall, the rapid progress in both Mo and Fe chemistry suggests that the future is bright for transition-metal catalyzed  $N_2$  reduction.

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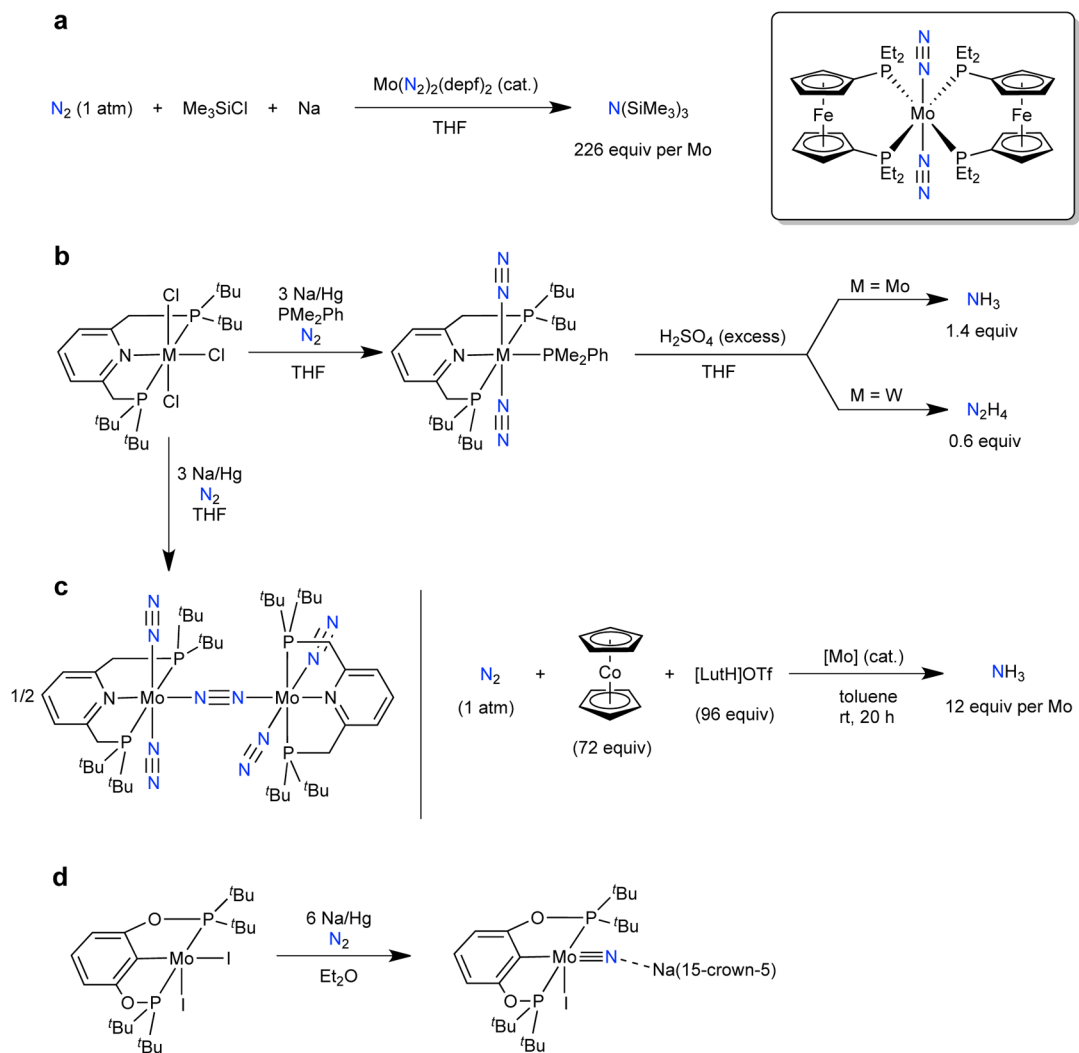
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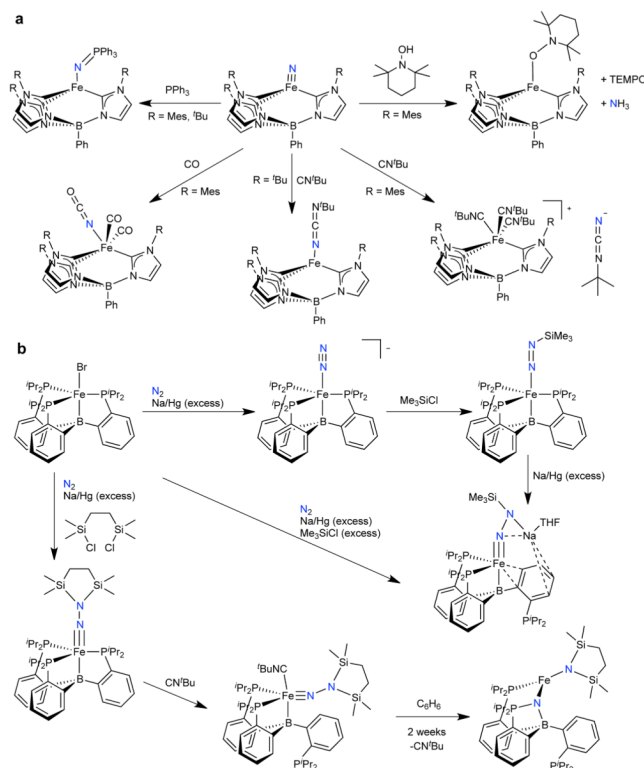


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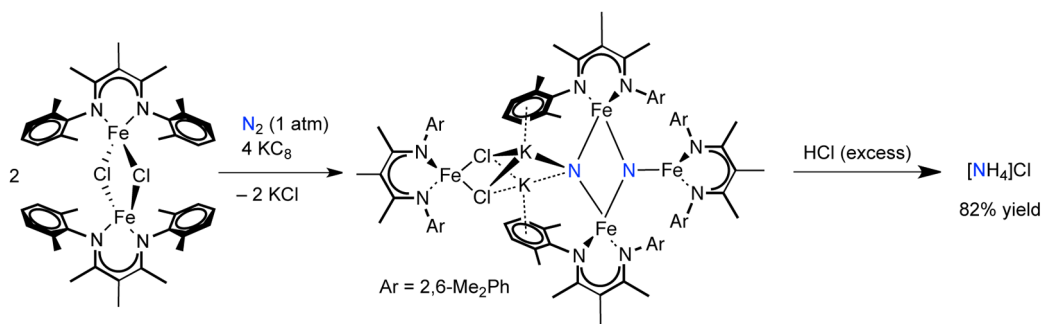
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**Figure 1.**

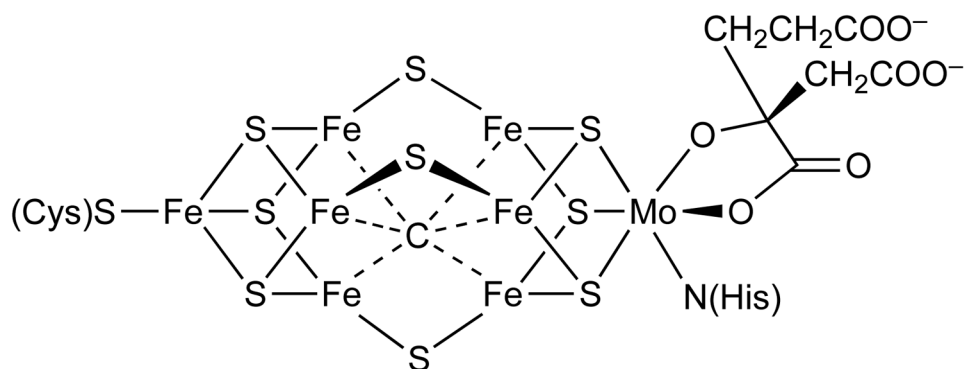
Key developments in molybdenum- $\text{N}_2$  chemistry. (a) Catalytic conversion of dinitrogen to tris(trimethylsilyl)amine by a depf-supported Mo complex (right). (b) Synthesis and stoichiometric reactions of PNP-supported Mo and W dinitrogen compounds. (c) Catalytic formation of ammonia with  $\{[\text{PNP}]\text{Mo}(\text{N}_2)_2\}_2(\mu\text{-N}_2)$  as catalyst. (d) Stoichiometric  $\text{N}_2$  reduction by a POCOP-supported Mo complex.

**Figure 2.**

Recent monometallic iron-based transformations of  $N_2$  or nitride. (a) Functionalization of terminal iron-nitride complexes. The reactions with triphenylphosphine ( $\text{PPh}_3$ ), carbon monoxide ( $\text{CO}$ ), and *tert*-butyl isocyanide ( $\text{CN}^t\text{Bu}$ ) demonstrate electrophilic reactivity at N, while the reaction with TEMPO-H on the right demonstrates abstraction of a hydrogen atom. (b) Dinitrogen activation and cleavage in a tris(phosphino)borate-iron system. The series of reactions along the top show addition of an electrophilic silyl group to coordinated  $N_2$ . Addition of two silyl groups in the bottom pathway gives a product that leads to eventual N-N bond cleavage.



**Figure 3.** Reduction of a diiron(II) dimer (using one equivalent of potassium graphite per iron atom) gives spontaneous cleavage of the N-N bond to form a bis(nitride) product. The nitride complex may be treated with acid to give a high yield of ammonia.



**Figure 4.** Spectroscopic, crystallographic, and <sup>14</sup>C tracer studies recently elucidated the final details of the atomic structure of the FeMoco of molybdenum-dependent nitrogenase, demonstrating that the cluster has a carbide core. This carbide is hypervalent, and has bonding interactions with six of the seven iron atoms in the cluster.