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Review

Iron–dinitrogen coordination chemistry: Dinitrogen activation and reactivity

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Contents

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ABSTRACT

Understanding the coordination of dinitrogen to iron is important for understanding biological nitrogen fixation as well as for designing synthetic systems that are capable of reducing N_2 to NH_3 under mild conditions. This review discusses recent advances in iron–dinitrogen coordination complexes and describes the factors that contribute to the degree of activation of the coordinated N_2. The reactivity of the N_2 ligand is also reviewed, with an emphasis on protonation reactions that yield ammonia and/or hydrazine. Coordination complexes containing N_2 reduction intermediates such as diazene (N_2H_2), hydrazido ($N_2H_2^{2-}$), hydrazine (N_2H_4), nitride (N^{3-}), imide (NH^{2-}), and amide (NH_2^-) are also discussed in the context of the mechanism of N_2 reduction to NH_3 mediated by iron coordination complexes.

1. Introduction

1.1. Overview

All life on earth depends on nitrogen fixation, the process by which atmospheric dinitrogen is reduced to ammonia. Because most organisms cannot directly incorporate dinitrogen into molecules such as proteins and nuclei acids, reduced forms of dinitrogen are needed for biomolecule synthesis. Although having a source of reduced N_2 is crucial for life to exist, the process of reducing N_2 is very energy intensive. The inertness of the dinitrogen molecule is partly due to its triple bond, as evidenced by a dissociation energy of 944 kJ/mol. However, this factor is not solely responsible for the inertness of N_2 because other triply bonded small molecules, notably CO, readily undergo a wide variety of chemical transformations. Rather, the inertness of N_2 arises from the lack of a dipole moment and the large gap between the HOMO and LUMO (22.9 eV), causing the molecule

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to be resistant to electron transfer and Lewis acid/base reactivity [1].

In spite of this inertness, both biological and industrial processes exist that reduce dinitrogen to ammonia, with each process accounting for roughly half of the global ammonia supply [2]. Because of the high energy requirements for the current industrial production of ammonia, a low-energy alternative is desirable. Since the discovery of the first dinitrogen complex in 1965 by Allen and Senoff [3], chemists have sought an alternative means to achieve this reduction using homogeneous catalysis. One feature common to both the biological and industrial routes to ammonia is the use of iron as the active metal. Coordination chemists have taken this inspiration and made significant advancements in the coordination chemistry of iron–dinitrogen complexes, as well as the reduction of dinitrogen using homogeneous iron complexes.

This review will briefly cover the biological and industrial production of ammonia and then delve into the coordination chemistry of homogeneous iron complexes with dinitrogen and reduced dinitrogen intermediates (i.e. N_2H_2, $N_2H_2^{2-}$, N_2H_4, N^{3-}, NH^{2-}, and NH_2^-). The transformations of coordinated N_2 will be explored, particularly the protonation of coordinated dinitrogen to yield ammonia and/or hydrazine. This review will focus on mono and binuclear iron complexes; the chemistry of iron clusters as related to nitrogen fixation will not be covered here [4,5]. The chemistry of simple iron salts and their ability to catalyze N_2 reduction in the presence of a strong reducing agent will also not be covered. The reader is instead directed to the literature [1,6–10].

1.2. Haber–Bosch process

The industrial production of ammonia is achieved using the Haber–Bosch process [11,12]. In this process, hydrogen gas, typically produced by steam reformation of natural gas or partial oxidation of hydrocarbons, is reacted with dinitrogen gas over a promoted iron catalyst (other metals, such as ruthenium are also commonly used) at high temperature (>200 °C) and pressure (>400 atm) (Eq. (1)).

$$N_2 + H_2 \xrightarrow[>400\,\text{atm}]{\text{Fe},\ >200\,^\circ\text{C}} 2NH_3 \quad (1)$$

The reaction of H_2 with N_2 to produce NH_3 is exothermic (−46 kJ/mol), but due to the significant activation barrier, high temperatures are needed to increase the rate of ammonia formation. However, as the temperature is increased the equilibrium of the reaction shifts toward the reactant gases, and thus increased pressure is needed to shift the equilibrium in favor of ammonia. Although this process requires large amounts of energy it must be mentioned that the process is actually quite energy efficient, with state-of-the-art Haber–Bosch plant efficiencies approaching the theoretical limit [12].

1.3. Biological N_2 reduction

Nature uses nitrogenase enzymes to convert atmospheric N_2 to NH_3 [13–16]. These enzymes, which are limited to certain bacterial species (100–200 species), are responsible for all biologically fixed nitrogen [2]. Nitrogenase enzymes catalyze the reduction and protonation of dinitrogen, and although the breaking of the dinitrogen bond is extremely energy intensive, these enzymes are able to perform the conversion at biological temperatures and atmospheric pressure (Eq. (2)).

$$N_2 + 8H^+ + 8e^- + 16\text{MgATP} \rightarrow 2NH_3 + H_2 + 16\text{MgADP} + 16\text{Pi} \quad (2)$$

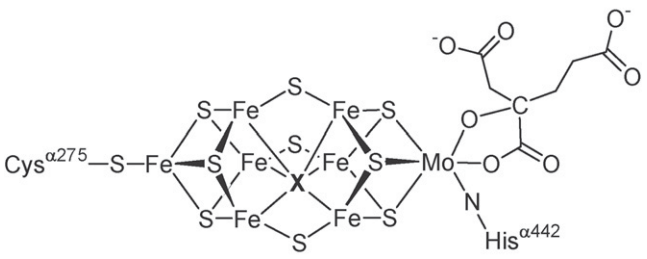


Fig. 1. Structure of the FeMo cofactor in nitrogenase [19]. The identity of X is currently unknown, but thought to be either C, N, or O.

There are three types of nitrogenase enzymes, which vary by the metal composition in the active site: iron and molybdenum, iron and vanadium, and iron only [17]. The three nitrogenases all have similar structures and reactivity, with the latter two types typically produced only under molybdenum deficient conditions [18]. The structure of the iron–molybdenum nitrogenase enzyme, which is the most efficient and commonly studied type, consists of two separate protein clusters: dinitrogenase reductase (an iron containing dimer) that supplies electrons for the reduction and dinitrogenase (an iron and molybdenum containing tetramer) where dinitrogen binding and reduction occur [18].

The active site of nitrogenase is the FeMo cofactor, which is located within the dinitrogenase protein cluster. The FeMo cofactor consists of seven iron atoms and one molybdenum atom bridged by nine sulfur atoms (Fig. 1). The FeMo cofactor is ligated to the protein structure through a cysteine residue (iron bound) and a histidine residue (molybdenum bound). A homocitrate ligand completes the coordination sphere of the molybdenum atom. Refined crystal structure data of the FeMo cofactor at 1.16 Å resolution revealed the existence of a central atom within the iron-sulfur cluster (Fig. 1) [19]. The identity of this central atom is still hotly debated, but from the electron density data it is expected to be either C, N, or O [20–29].

The FeMo cofactor is accepted to be the site of N_2 binding and reduction based on a wide variety of evidence [13]. In fact, recent site-directed mutagenesis studies have suggested that two of the "belt" iron atoms of the FeMo cofactor are the site of N_2 binding and reduction [30–33]. The exact mechanism of N_2 reduction mediated by nitrogenase remains unknown; however, growing biochemical evidence supports a mechanism that proceeds through diazene and hydrazine intermediates in route to ammonia formation [34–38]. This proposed mechanism is in contrast to the mechanisms detailed by Chatt [39] and Schrock [40] for synthetic Mo and W systems.

Because of the growing biochemical evidence suggesting that iron is responsible for the reduction of N_2 to ammonia in nitrogenase, understanding the coordination chemistry of iron with dinitrogen and reduced dinitrogen species, such as diazene and hydrazine, is becoming increasingly important.

2. Coordination of N_2 to iron

The coordination of dinitrogen to a transition metal is described by the Dewar–Chatt–Duncanson σ-donor/π-acceptor model of ligand bonding [1,41]. Despite the fact that dinitrogen is both a poor σ donor and a poor π acceptor (making it a very poor ligand) numerous iron–dinitrogen complexes have been synthesized with a variety of ancillary ligands (Tables 1 and 2). All iron–dinitrogen complexes display an η^1, or end-on, binding geometry (Table 1). The N_2 ligand is bridging between two metals in a small number of these complexes (Table 2), but the majority of the complexes have non-bridging N_2 ligands. Iron–dinitrogen complexes are typically

Table 1
Terminal dinitrogen iron complexes.

Complex	ν_{NN} (cm^{-1})	N–N bond length (Å)	Ref.
$[Fe(\eta^5\text{-}C_5H_5)(DIPPE)(N_2)][BPh_4]$	2112	1.13	[45]
$Fe(PEtPh_2)_3(N_2)(H)_2$	2055	–	[46]
$Fe(PBuPh_2)_3(N_2)(H)_2$	2060	–	[46]
$Fe(PEtPh_2)_2(N_2)(H)_2$	1989	–	[46]
$Fe(PPh_3)_3(N_2)(H)_2$	2074	–	[47]
$Fe(PMePh_2)_3(N_2)(H)_2$	2058	–	[48]
$[Fe(P(EtPPh_2)_3)(N_2)H][BPh_4]$	2100	–	[49]
$[Fe(N(EtPPh_2)_3)(N_2)H][BPh_4]$	2090	1.102	[49,50]
$Fe(N(EtPPh_2)_3)(N_2)$	1967	–	[49,50]
$[Fe(DPPE)_2(N_2)H][BPh_4]$	2130	–	[51]
$[Fe(DPPE)_2(N_2)]$	2068	–	[52]
$Fe(PhBP^iPr_3)(N_2)(MgCl\text{-}(THF)_2)$	1830	–	[53]
$[Fe(PhBP^iPr_3)(N_2)][Mg(18\text{-}C\text{-}6)]$	1884	–	[53]
$[Fe(N(EtP^iPr_2)_3)(N_2)(H)][PF_6]$	2090	1.113	[54]
$[Fe(DMeOPrPE)_2(N_2)H][BPh_4]$	2088	1.112	[55]
$[Fe(DMeOPrPE)_2(N_2)Cl][Cl]$	2094	–	[56]
$Fe(DMeOPrPE)_2(N_2)$	1966	–	[57]
$[Fe(DHBuPE)_2(N_2)H][Cl]$	2095	–	[56]
$[Fe(DMPE)_2(N_2)H]$	2094	1.13	[58]
$[Fe(DMPE)_2(N_2)]$	1975	–	[59]
$[Fe(DEPE)_2(N_2)H]$	2090	1.070	[60,61]
$[Fe(DEPE)_2(N_2)]$	1955	1.139	[62]
$[Fe(DEPE)_2(N_2)Cl][BPh_4]$	2088	1.073	[63]
$[Fe(DEPE)_2(N_2)Br][BPh_4]$	2091	–	[63]
$[Fe(DMPE)_2(N_2)Cl][BPh_4]$	2105	–	[58]
$[Fe(Ph_2PEtPPhEtPPhEtPh_2)(N_2)H][Br]$	2130	1.076	[64]
$[Fe(P(EtPMe_2)_3)(N_2)H][BPh_4]$	2117	–	[65]
$[Fe(P(EtP^iPr_2)_3)(N_2)][BPh_4]$	1985	1.1279	[66]
$[Fe(P(EtP^iPr_2)_3)(N_2)H][BF_4]$	2095	–	[66]
$[Fe(Si(o\text{-}C_6H_4PPh_2)_3)(N_2)]$	2041	1.106	[67,68]
$[Fe(Si(o\text{-}C_6H_4PPh_2)_3)(N_2)][Na([12]c\text{-}4)_2]$	1961	–	[67]
$[Fe(Si(o\text{-}C_6H_4P^iPr_2)_3)(N_2)]$	2008	1.065	[67,68]
$Fe(((2,6\text{-}HMe_2)_2C_6H_3N{=}CMe)_2C_5H_3N)_3(N_2)_2$	2124, 2053	1.090, 1.104	[69]
$Fe(((2,6\text{-}HMe_2)_2C_6H_3N{=}CPh)_2C_5H_3N)_3(N_2)_2$	2130, 2074	1.106, 1.107	[70]
$Fe(((2,6\text{-}HMe_2)_2C_6H_3N{=}CPh)_2C_5H_3N)_3(N_2)$	2061	–	[70]
$Fe((2,6\text{-}^iPr_2PCH_2)_2C_5H_3N)(N_2)(SiH_2Ph)H$	2032	1.120	[71]
$Fe((2,6\text{-}^iPr_2PCH_2)_2C_5H_3N)(N_2)H_2$	2016	–	[71]
$Fe(NHC)(N_2)_2$	2109, 2031	1.115	[72]
$Fe(NHC)(N_2)(C_2H_4)$	2056	–	[72]
$Fe(NHC)(N_2)(PMe_3)$	2032	–	[72]
$Fe(PEt_3)_2(CO)_2(N_2)$	2097	1.078	[73]
$Fe(PO^iPr_3)_2(CO)_2(N_2)$	2141	–	[73]

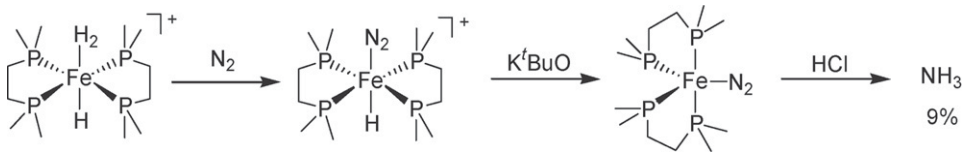
NHC = 2,6-bis((2,6-diisopropylbenzene)imidazol-2-ylidene)pyridine.

prepared by (i) displacement of a weakly bound ligand (such as H_2), (ii) abstraction of a halide ligand, (iii) addition of N_2 to a coordinatively unsaturated precursor, or (iv) reduction of a precursor complex under an N_2 atmosphere.

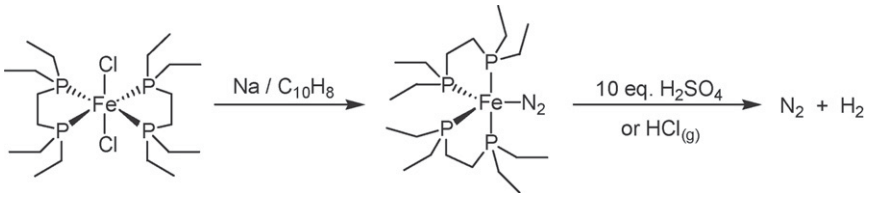
The extent of activation of the coordinated N_2 ligand in these complexes is measured by the N–N bond length in those molecules where a crystal structure has been obtained, or by IR or Raman spectroscopy (by examining the N–N stretching frequency) in those complexes without X-ray structural data. Tables 1 and 2 list the N–N bond lengths and/or N–N stretching frequencies for all the Fe–N_2 complexes synthesized to date. As can be seen from the N–N bond lengths and N–N stretching frequencies, most of the iron–dinitrogen complexes exhibit minimal activation of the N_2 ligand as compared with dinitrogen complexes of other metals [42–44]. It is important to note however that the term activation refers only to the lengthening of the N–N bond and the decrease in the N–N stretching frequency as compared with uncoordinated N_2; strong activation is not necessarily a requirement to observe

Table 2
Bridging dinitrogen iron complexes.

Complex	ν_{NN} (cm^{-1})	N–N bond length (Å)	Ref.
$[\{Fe(\eta^5\text{-}C_5H_5)(DPPE)\}_2(N_2)]^{2+}$	2040	–	[74]
$[\{Fe(\eta^5\text{-}C_5H_5)(DMPE)\}_2(N_2)]^{2+}$	2054	–	[75]
$[Fe(PPh_3)_2Et(\mu\text{-}N_2)]_2[Mg(THF)_4]$	1830	–	[76]
$\{Fe(PhBP^iPr_3)\}_2(\mu\text{-}N_2)$	–	1.138	[53,77]
$[\{Fe(PhBP^iPr_3)\}_2(\mu\text{-}N_2)][Na(THF)_6]$	–	1.171	[53]
$[\{FeCl(DEPE)_2\}_2(N_2)][BPh_4]_2$	2081	–	[78]
$\{Fe(PEt_3)_2(CO)_2\}_2(\mu\text{-}N_2)$	–	1.134	[73]
$\{Fe(POMe_3)_2(CO)_2\}_2(\mu\text{-}N_2)$	–	1.13	[79]
$\{Fe(MesNC^tBuCHC^tBuNMes)\}_2(\mu\text{-}N_2)$	1778	1.182	[80]
$[\{Fe(MesNC^tBuCHC^tBuNMes)\}_2(\mu\text{-}N_2)][K]_2$	1589, 1123	1.233	[80]
$\{Fe(MesNCMeCHCMeNMes)\}_2(\mu\text{-}N_2)$	1810	1.186	[81]
$[\{Fe(MesNCMeCHCMeNMes)\}_2(\mu\text{-}N_2)][K]_2$	1625, 1437	1.215	[81]
$\{Fe(MesNC^tBuCHC^tBuNMes)(^tBuC_5H_4N)\}_2(\mu\text{-}N_2)$	–	1.161	[81]
$\{Fe(MesNCMeCHCMeNMes)(^tBuC_5H_4N)\}_2(\mu\text{-}N_2)$	1770	1.151	[81]



Scheme 1.



Scheme 2.

reactivity of the coordinated N_2 molecule, as will be seen in the following section.

Nearly all iron–dinitrogen complexes contain phosphine ligands. An electron rich metal center is needed to coordinate N_2 (because π-backdonation is an important component of the bonding), and thus electron donating ligands such as phosphines are typically used. As expected, the oxidation state of the iron affects the degree of N_2 activation, with iron(0) N_2 complexes being among the most activated. Coordination number also has a large effect on the activation of N_2. The lower coordination numbers often show increased activation of the N_2 molecule, with the most activated N_2 complexes to date having a coordination number of only three.

3. Reactivity of N_2 coordinated to iron

Now that the coordination of dinitrogen to iron has been explored, the reactivity of the coordinated dinitrogen ligand will be discussed. The reactivity of Fe–N_2 complexes will be separated into three categories: displacement of N_2, protonation of N_2, and elongation of the N–N bond.

3.1. Displacement of N_2

The N_2 ligand is in general weakly coordinated to the iron center, and consequently the displacement of the dinitrogen ligand is a commonly observed reaction pathway. The ancillary ligands often dictate the binding strength of the N_2 ligand, with increased electron-donating ability increasing backdonation and stabilizing the coordinated N_2.

Dinitrogen ligands of iron complexes are typically substituted by CO and nitriles, e.g., MeCN and PhCN [51,55,57,59,82,83]. Some N_2 ligands can also be displaced by organic solvents. In *trans*-[Fe(DPPE)$_2$(N_2)H][BPh_4] the N_2 ligand can be displaced by pyridine, acetone, or THF [51]. Acetone also displaces the N_2 ligand of [Fe(η^5-C_5H_5)(N_2)(DPPE)][PF_6] [74]. Although organic solvents displace N_2, one of the few water-soluble N_2 complexes, *trans*-[Fe(DMeOPrPE)$_2$(N_2)H]$^+$ is inert to substitution by H_2O [82].

The substitution reactivity of N_2 in the five-coordinate Fe(DEPE)$_2$$N_2$ complex has been extensively studied. The N_2 ligand can be displaced by a wide variety of ligands including CO, CS_2, H_2, CO_2, and HCl [84,85]. The Fe(DEPE)$_2$$N_2$ complex also cleaves C–S, C–H, and N–H bonds of various heterocycles; however, this resulted in loss of the dinitrogen ligand without functionalization [86].

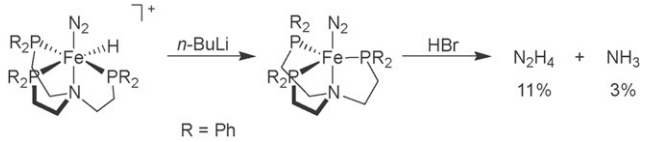
3.2. Protonation of Fe–N_2 complexes

The most common type of reactivity studied for iron–dinitrogen complexes is protonation of the coordinated N_2 [87]. This mode of reactivity is aimed at mimicking biological nitrogen fixation by using a proton source and the electrons of the iron to reduce dinitrogen to ammonia. Leigh and coworkers were the first to observe such reactivity in 1991. Using DMPE as the ancillary ligand, the *trans*-[Fe(DMPE)$_2$(N_2)H]$^+$ complex (Scheme 1), was synthesized by N_2 substitution of H_2 in *trans*-[Fe(DMPE)$_2$(H_2)H]$^+$ [59,88,89].

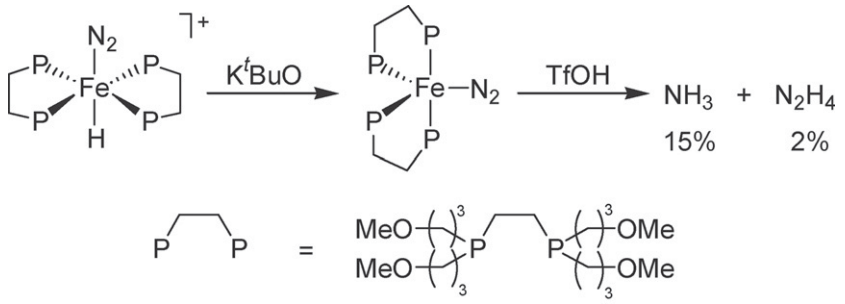
The dinitrogen ligand in *trans*-[Fe(DMPE)$_2$(N_2)H]$^+$ is minimally activated, as indicated by the N–N bond length of 1.13 Å and ν_{NN} = 2094 cm^{-1}. The complex produces trace amounts of ammonia (<4%) upon protonation with H_2SO_4 and no NH_3 upon exposure to HCl [88]. However, by deprotonating the hydride ligand to form Fe(DMPE)$_2$$N_2$, resulting in the formal reduction of the iron center from 2+ to 0, the activation of the dinitrogen ligand can be sufficiently increased (ν_{NN} = 1975 cm^{-1}) to allow reaction with a strong acid (Scheme 1). Optimized yields of ammonia produced from this five coordinate Fe–N_2 complex reached 20% using HCl at low temperatures [89]. Using HCl Leigh and coworkers also showed that the iron dichloride starting material, *trans*-Fe(DMPE)$_2$$Cl_2$, was regenerated, hinting at the possibility of a catalytic cycle [88]. The Fe(DMPE)$_2$$N_2$ complex was never isolated and assignment of this complex as the active ammonia producing species was thrown into question by work done on the analogous DEPE system, discussed next.

In contrast to the reactivity observed by Leigh, Komiya and coworkers were unable to detect any ammonia formation during the protonation of Fe(DEPE)$_2$$N_2$ (Scheme 2) [62,84]. Access to this complex was achieved by a different route than that described for the DMPE system. Fe(DEPE)$_2$$N_2$ was directly generated from *trans*-Fe(DEPE)$_2$$Cl_2$ and sodium metal under an atmosphere of N_2 (Scheme 2). This species was isolated and the crystal structure was obtained, confirming the proposed structure.

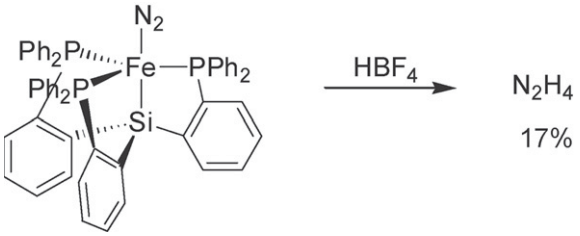
Upon protonation with HCl or H_2SO_4, neither NH_3 nor N_2H_4 were produced, and only N_2 and H_2 were observed (Scheme 2). This result is puzzling as both the Fe(DMPE)$_2$$N_2$ and Fe(DEPE)$_2$$N_2$ complexes display similar activation of the coordinated dinitrogen, ν_{NN} = 1975 cm^{-1} and ν_{NN} = 1955 cm^{-1}, respectively. Because Fe(DEPE)$_2$$N_2$ was isolated in pure form it threw into doubt that the Fe(DMPE)$_2$$N_2$ complex was in fact responsible for ammonia formation. However, continued work on the protonation of



Scheme 3.



Scheme 4.



Scheme 5.

iron N_2 phosphine complexes showed that the production of ammonia observed in the protonation of $Fe(DMPE)_2N_2$ was not unique.

Using a nitrogen phosphine tripodal ligand, $N(CH_2CH_2PPh_2)_3$, and following a similar synthetic strategy as that used by Leigh, George et al. were able to produce hydrazine and ammonia from the protonation of an iron–dinitrogen complex (Scheme 3) [50]. Starting from $[Fe(N(CH_2CH_2PPh_2)_3)(N_2)H][BPh_4]$, which had previously been synthesized by Sacconi, they were able to deprotonate the hydride ligand using *n*-BuLi to form the Fe(0) complex $Fe(N(CH_2CH_2PPh_2)_3)N_2$ (Scheme 3). This complex displayed similar N_2 activation to that of other Fe(0) complexes, with a $\nu_{NN} = 1967\ cm^{-1}$. Upon exposure to HBr, hydrazine (11%) and a small amount of ammonia (3%) were produced.

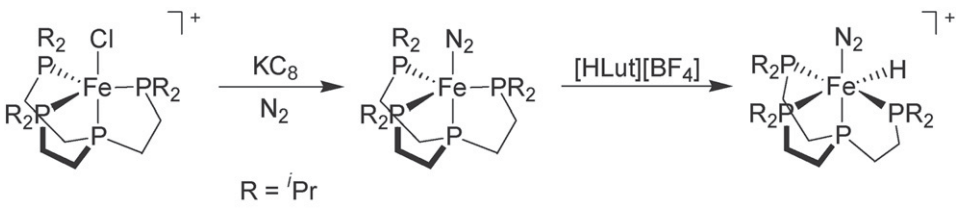
Following the work of Leigh, the Tyler group was also able to observe ammonia upon protonation of an iron(0) N_2 complex (Scheme 4) [57]. The dinitrogen hydride complex, *trans*-$[Fe(DMeOPrPE)_2(N_2)H]^+$ (DMeOPrPE = 1,2-(bis(dimethoxypropyl)phosphino)ethane), was again synthesized by substitution of N_2 for H_2 in *trans*-$[Fe(DMeOPrPE)_2(H_2)H]^+$. Of particular note is that this dihydrogen complex was generated directly from H_2 and *trans*-$Fe(DMeOPrPE)_2Cl_2$, instead of sodium borohydride. Thus, H_2 was the ultimate source of electrons for the reduction of N_2 to NH_3. Again, the N_2 ligand in the six-coordinate hydride species is minimally activated, N–N = 1.112 Å and $\nu_{NN} = 2088\ cm^{-1}$, and is unreactive toward protonation [55]. By deprotonating the hydride ligand to form $Fe(DMeOPrPE)_2N_2$, the activation of the N_2 is increased ($\nu_{NN} = 1966\ cm^{-1}$) and protonation of the complex with 1 M triflic acid produces 15% NH_3 and 2% N_2H_4 (Scheme 4) [57].

Recently, protonation of an iron N_2 complex utilizing a tripodal ligand system was revisited. Using a unique tripodal ligand, $Si(1,2\text{-}C_6H_4PPh_2)_3$, Peters and coworkers synthesized an iron(I)-N_2 complex that generated hydrazine on exposure to a strong acid (Scheme 5) [67]. The N_2 ligand seemed to be minimally activated ($\nu_{NN} = 2041\ cm^{-1}$). However, the complex produced 17% hydrazine on reaction with HBF_4. The yield of hydrazine was increased to 47% by addition of a one-electron reducing agent ($CrCl_2$). Interestingly, further reduction of the iron(I)-N_2 complex to the iron(0) N_2 complex resulted in increased activation of the N_2 ($\nu_{NN} = 1967\ cm^{-1}$), yet no reduction of N_2 was observed under the same protonation conditions. The authors hypothesized that the increased reducing ability of the iron(0) N_2 complex favored H^+ reduction over N_2 reduction.

Field and coworkers also recently utilized a tripodal ligand. $Fe(P(CH_2CH_2P^iPr_2)_3)N_2$ was synthesized by reducing the chloride precursor under an N_2 atmosphere (Scheme 6) [66]. Exposure of the complex to a weak acid, lutidinium tetrafluoroborate, resulted in protonation of the iron center to yield $[Fe(P(CH_2CH_2P^iPr_2)_3(N_2)H)]^+$ (Scheme 6). No ammonia or hydrazine was observed, although the protonation of this complex using strong acids was not reported.

As shown by the examples above, the protonation of iron–N_2 complexes is very inefficient, producing limited yields of ammonia and/or hydrazine. From the results of these protonation experiments, an important conclusion was made, namely that increasing the activation of the coordinated N_2 ligand does not necessarily lead to increased yields of NH_3 or N_2H_4. The absence of a correlation between N_2 activation and the yields results from the fact that increasing the reducing ability of the iron center favors H^+ reduction and protonation of the metal center rather than reduction and protonation of the dinitrogen ligand. DFT calculations have shown that, for the reaction of $Fe(DMPE)_2N_2$ with acid, protonation of the electron rich iron center is favored over protonation of the terminal nitrogen by 40 kcal/mol [90].

Another factor limiting the yields of N_2 reduction in these systems is that the only source of electrons is the iron center. Because these iron centers are transferring only two electrons in the reaction ($Fe^0 \rightarrow Fe^{II}$), three separate iron complexes must be used to fully reduce N_2 to NH_3 (a six electron process), thus limiting the theoretical yields. Note, however, that Peters has shown that addition of an external reducing reagent can increase the yield of N_2H_4 [67].



Scheme 6.

An interesting trend that can be observed from the examples discussed above is that systems using tripodal ligands favor the formation of hydrazine, while systems using bidentate ligands favor the formation of ammonia. This observation perhaps provides information about the mechanism of N_2 reduction is these systems. Thus, one speculation is that tripodal ligands may not be able to accommodate η^2 ligands, whereas accommodation of an η^2 ligand is possible with bidentate phosphine systems, as was shown recently in the syntheses and structural characterizations of *cis*-$[Fe(P_2)_2(\eta^2\text{-}N_2H_4)]^{2+}$, where P_2 = DMPE or DMeOPrPE [91,92]. Subsequent protonation of *cis*-$[Fe(DMeOPrPE)_2(\eta^2\text{-}N_2H_4)]^{2+}$ resulted in the disproportionation of hydrazine, yielding a mixture of ammonia and hydrazine [91]. Thus, for systems containing bidentate phosphine ligands, the disproportionation of hydrazine via an η^2-N_2H_4 intermediate may be responsible for the observed yields of ammonia. In systems containing tripodal ligands it may be that the η^2-N_2H_4 intermediate is not formed and the reduction of N_2 therefore stops at hydrazine. Another key difference between the two ligand geometries is that protonation of the iron center results in a *trans* hydride in complexes with bidentate phosphines and a *cis* hydride complex in the tripodal complexes. The strong *trans* influence of the hydride ligand in the bidentate systems could affect the stability of an intermediate complex, such as a coordinated η^1-N_2H_4 molecule, perhaps favoring cleavage of the N_2H_4 to NH_3. One speculation is that this could explain why ammonia is observed in bidentate phosphine systems but not in the tripodal ligand systems. Consistent with this conjecture is the Tyler group's unpublished observation that the *trans*-$[Fe(DMeOPrPE)_2(\eta^1\text{-}N_2H_4)(H)]^+$ complex is unstable and forms the *trans*-$[Fe(DMeOPrPE)_2(NH_3)(H)]^+$ complex without the addition of an acid.

3.3. Elongation of the N–N bond

Complete cleavage of dinitrogen yielding a nitride ligand has been observed for some group 5 and 6 metals [93–96]. However, no such reaction has yet been observed for iron–dinitrogen complexes. Toward this goal, recent progress has been made in elongating the N–N bond using unique ligand sets.

Peters and coworkers synthesized three Fe–N_2 complexes that show atypical activation of the coordinated N_2 ligand [53]. Reduction of a tris(phosphino)borate iron chloride complex with Mg^0 under a dinitrogen atmosphere resulted in formation of a terminally bonded N_2 complex (Scheme 7).

The complex shows a relatively low energy stretching frequency of 1830 cm^{-1}. This activated N_2 molecule can be functionalized by reaction with an electrophile such as methyl tosylate (Scheme 7). While this type of reactivity had been previously observed for Mo and W systems [97], this represents the first and only example of the direct conversion of an iron–coordinated N_2 molecule to a diazenido (N_2R^-) complex by addition of an electrophile.

If the iron halide precursor is reduced using Na/Hg amalgam, a bridged dinitrogen complex is obtained (Scheme 8). This dinuclear Fe(I)–N_2-bridged complex has an N–N bond length of 1.138 Å. Further reduction of this complex using Na/Hg amalgam resulted in a mixed valence Fe^IFe^0 N_2 complex, which lengthens the N–N bond to 1.171 Å.

Holland and coworkers have been able to achieve significant elongation of the N–N bond using low-coordinate iron complexes stabilized by bulky β-diketiminate ligands [80,81]. By reducing the chloride precursor with sodium naphthalenide or potassium/graphite they were able to synthesize bridged dinitrogen complexes with N–N bond lengths of ~1.18 Å (Scheme 9).

The stability of these complexes was explored in the presence of a variety of ligands (CO, PPh_3, C_6H_6), with reactivity resulting in loss of N_2 and coordination of the ligand. The stability of the bridged dinitrogen complex is affected by the steric bulk of the ligand, with the ^{t}Bu complex being more stable than the Me complex. Further reduction of these complexes resulted in increased activation of the N–N bond, with the N–N bond lengths reaching over 1.2 Å (Scheme 9). These N–N bond distances are the longest observed for any iron–dinitrogen complex. Even though the N_2 ligand in these complexes is quite activated, reaction with a variety of electrophiles yielded no evidence for successful functionalization of the N_2 molecule.

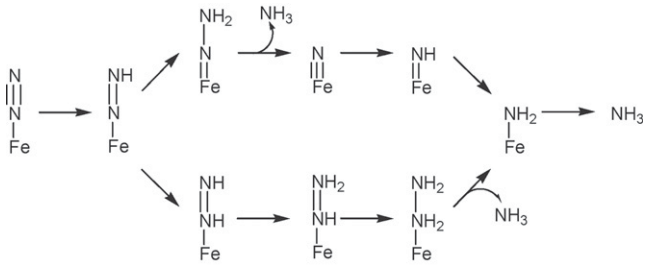


Fig. 2. Asymmetric/distal mechanism (top pathway) and symmetric/alternating (bottom pathway) mechanism for the reduction of Fe-coordinated N_2 to NH_3 [36].

4. Coordination chemistry of reduced dinitrogen species

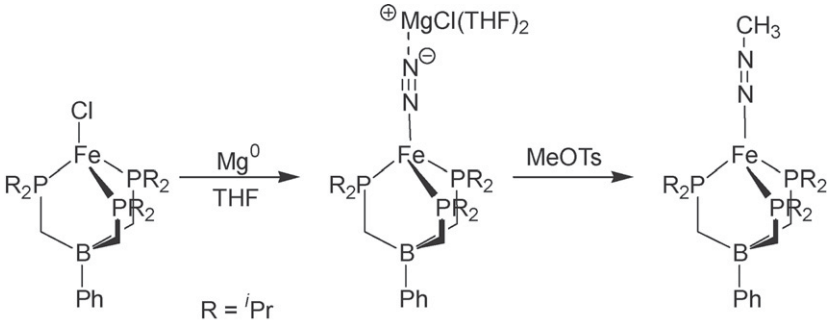
The sections above demonstrate: (i) iron readily binds dinitrogen, and (ii) some iron–dinitrogen complexes have the ability to reduce dinitrogen to ammonia, similar to the reactivity observed in nitrogenase enzymes. One remaining puzzle in both the synthetic ammonia-producing systems as well as in biological systems is the mechanism of N_2 reduction. There are two general reaction pathways that can be envisioned for the reduction of N_2 to ammonia: a symmetric (or alternating) pathway and an asymmetric (or distal) pathway (Fig. 2) [36]. In the symmetric pathway, protonation of the coordinated dinitrogen ligand occurs in an alternating fashion, with diazene (N_2H_2) and hydrazine (N_2H_4) intermediates being formed (Fig. 2, bottom pathway). In the asymmetric pathway, protonation occurs at the distal nitrogen atom of N_2, resulting in N–N bond cleavage to form a nitride intermediate (Fig. 2, top pathway). This next section will describe the coordination chemistry of iron with reduced dinitrogen species in the context of N_2 reduction mechanisms.

4.1. Symmetric N_2 reduction pathway

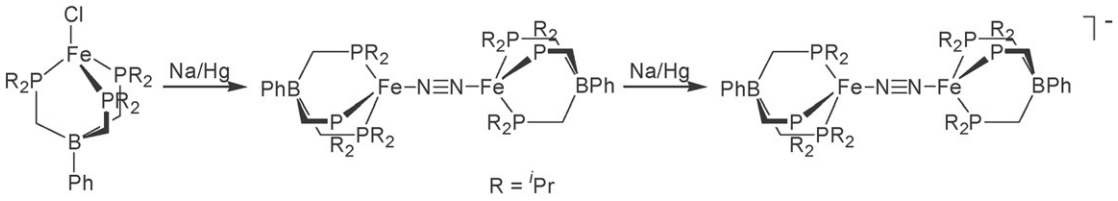
The symmetric N_2 reduction pathway, in which diazene and hydrazine intermediates are formed (the bottom pathway in Fig. 2), is currently the favored mechanism for nitrogenase [13,35]. Both diazene and hydrazine are substrates of nitrogenase, and spectroscopic data of trapped intermediates has been obtained [37,38]. Synthetic iron complexes containing parent diazene (N_2H_2), hydrazido ($N_2H_2^{2-}$), and hydrazine (N_2H_4) ligands could provide useful data to compare with that obtained for nitrogenase and these complexes will be discussed next. The coordination chemistry of aryl and alkyl substituted N_2 species (i.e. N_2R_2, N_2R_4, etc.) will not be included.

4.1.1. Iron diazene and hydrazido complexes

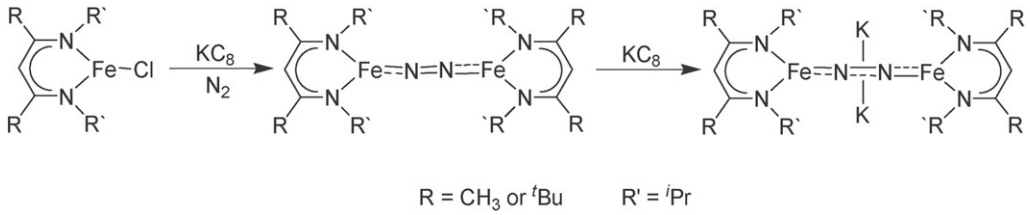
Diazene (N_2H_2) is formed by the addition of two electrons and two protons to dinitrogen and is thought to be an important intermediate during nitrogenase turnover [37]. Unfortunately, coordination complexes of diazene are rare [98,99], especially those containing iron. The lack of diazene complexes likely arises from the reactive nature of the diazene molecule. Uncoordinated diazene is very reactive and readily decomposes (Eq. (3))



Scheme 7.



Scheme 8.



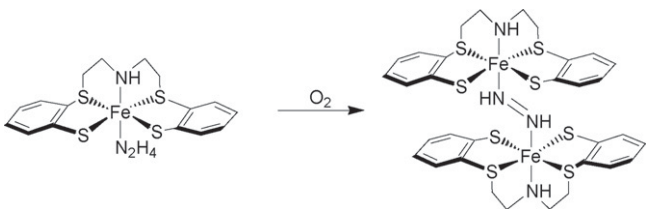
Scheme 9.

or disproportionates (Eq. (4)) within seconds [100,101]. However, coordination of diazene to a transition metal center can stabilize the molecule. Diazene complexes are primarily synthesized by oxidation of hydrazine, typically using $Pb(OAc)_4$, although other oxidizing reagents such as O_2 and $[FeCp]^+$ have been used successfully. This method of preparation circumvents the problem of having uncoordinated diazene in solution, although as will be discussed below, there are examples where diazene has been generated in solution and coordinated to an iron center.

$$N_2H_2 \rightarrow N_2 + H_2 \quad (3)$$

$$2N_2H_2 \rightarrow N_2H_4 + N_2 \quad (4)$$

Using a variety of iron sulfur scaffolds, Sellmann et al. successfully synthesized a number of bridging η^1 diazene complexes [102–105]. Starting with the iron hydrazine complex shown in Eq. (5), they were able to oxidize the terminal η^1-N_2H_4 ligand to a bridging η^1-N_2H_2 complex using air (Eq. (5)) [102]. The coordinated diazene has a *trans* geometry with a N–N bond distance of 1.30 Å.

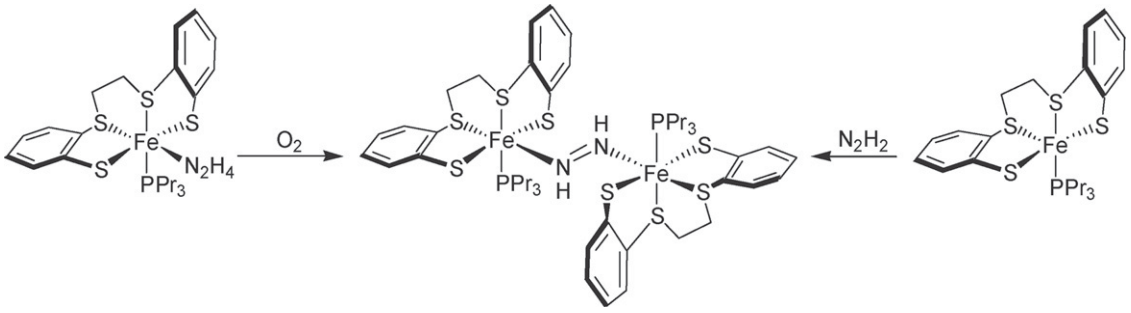


(5)

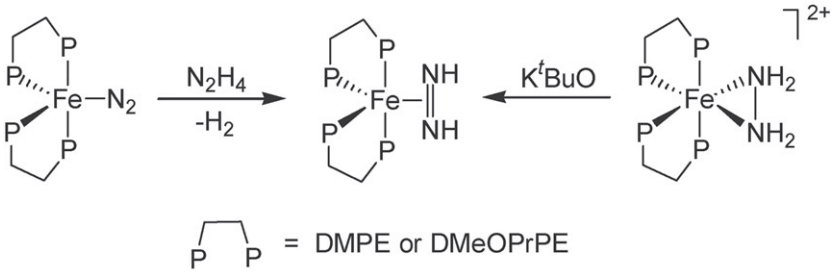
A related complex using an all-sulfur donor ligand was synthesized later by Sellmann. In this case, the bridging η^1 diazene complex could be prepared by either oxidation of the hydrazine complex [103] or by trapping diazene gas generated *in situ* (Scheme 10) [104]. The diazene ligand again coordinates in a *trans* geometry with a N–N bond distance of 1.288 Å. The diazene ligands in these bridged complexes are stabilized by steric shielding, strong π-bonds between the iron d-orbitals and the π system of diazene, and bifurcated hydrogen bonding between the diazene protons and the thiolate ligands.

Iron–phosphine scaffolds have also recently been used to stabilize diazene, although the assignment of the N_2H_2 ligands as true diazene complexes is unsettled. Reaction of $Fe(P_2)_2N_2$ (where P_2 = DMPE or DMeOPrPE) with hydrazine results in the formation of an iron(0) η^2 diazene complex and loss of H_2 (Scheme 11) [106,107]. The crystal structure of *cis*-$Fe(DMPE)_2(N_2H_2)$ was obtained and showed *trans*-diazene coordinated in an η^2 geometry. These iron(0)-diazene complexes can also be synthesized by an alternative route. Reaction of the $Fe(P_2)_2(\eta^2\text{-}N_2H_4)^{2+}$ complex with K^tBuO resulted in the deprotonation of the coordinated hydrazine to form the η^2-N_2H_2 complex (Scheme 11) [92,106]. These complexes can be represented by two resonance forms; an iron(0) diazene complex or an iron(II) hydrazido(2-) complex. Charge decomposition analysis calculations favor the iron(0) diazene resonance form, but the N–N bond length and chemical shifts of the nitrogen bound protons suggest the iron(II) hydrazido(2-) resonance form [92].

Interestingly, the hydrazine ligand of *cis*-$[Fe(DMPE)_2(N_2H_4)]^{2+}$ can be converted to N_2 using Schlosser's base (K^tBuO and ^tBuLi) [92]. The mechanism of this conversion is currently unknown; however, labeling studies have shown that the dinitrogen ligand comes



Scheme 10.



Scheme 11.

directly from the diazene ligand and not from an external dinitrogen source.

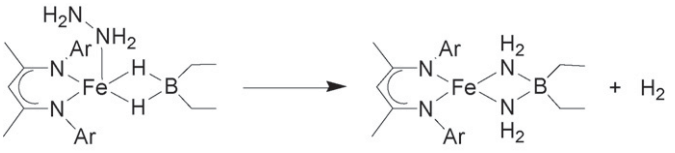
Peters and coworkers recently used a tris(phosphino)borate ligand to stabilize a series of dinuclear iron complexes containing hydrazine, diazene, amide, and imide ligands (Scheme 12) [108]. Addition of two equivalents of hydrazine to the starting material in Scheme 12 resulted in the formation of a dinuclear iron complex containing bridging hydrazine and hydrazido(2-) ligands. With electron donating groups (–CH_2Cy; Cy = C_6H_{11}) present on the tris(phosphino)borate ligand, the hydrazine and hydrazido(2-) ligands were converted to diazene and amide ligands after sitting at room temperature for 36 h. With less electron donating groups (-Ph) the complex is thermally stable. The conversion of the phenyl complex to a diazene hydrazido complex was achieved by oxidation using $Pb(OAc)_4$. These two bridged diazene complexes are unique in that they contain *cis*-diazene; all other examples of transition metal diazene complexes contain a *trans*-diazene ligand.

4.1.2. Iron hydrazine (N_2H_4) complexes

Hydrazine represents the addition of four electrons and four protons to dinitrogen and is also considered a likely intermediate in biological nitrogen fixation. Nearly all iron N_2H_4 complexes contain hydrazine bonded in a terminal [109–120] η^1 geometry or a bridging [108,116,121] η^1 geometry. Recently an η^2 coordination mode was observed using iron–phosphine scaffolds [91,92]. A representative selection of these iron hydrazine complexes will be highlighted here.

Sellmann and coworkers synthesized several iron hydrazine complexes using biologically relevant thiolate ligands. Most significantly, one iron thiolate system (the scaffold shown in Eq. (5)) stabilizes N_2H_2, N_2H_4, and NH_3 ligands. Unfortunately, the final ligand in the series, N_2, did not coordinate to the complex [112].

Holland's research group showed that an η^1-N_2H_4 complex of Fe undergoes N–N bond cleavage at elevated temperatures (60 °C) to yield a bridged –NH_2 complex (Eq. (6)) [120]. This represents a rare example of N–N bond cleavage among iron systems and demonstrates the utility of low-coordinate iron complexes in the discovery of novel reaction pathways.

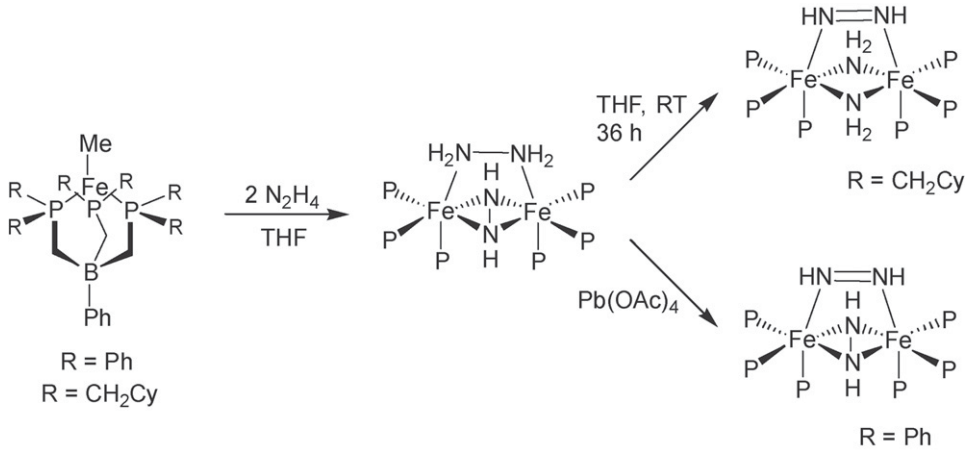


(6)

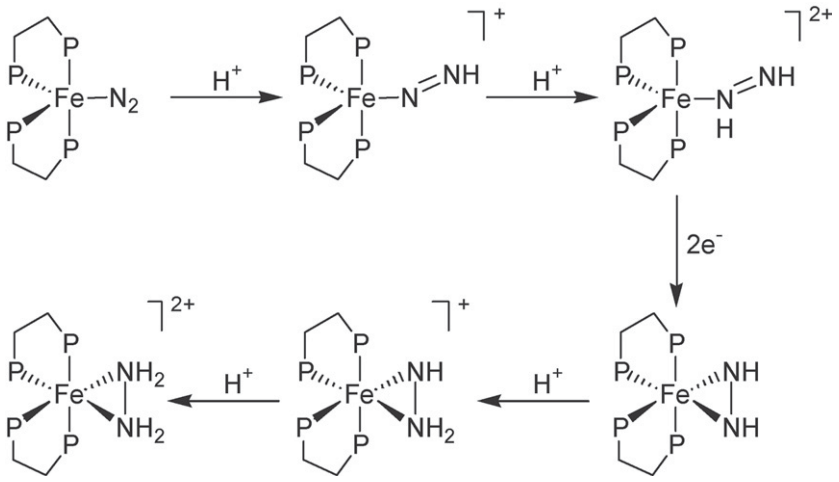
Tyler and coworkers recently synthesized a novel η^2-N_2H_4 complex and explored the acid base reactivity of the hydrazine ligand [91,106]. Addition of a strong acid (1 M TfOH) to a solution of *cis*-$[Fe(DMeOPrPE)_2(N_2H_4)]^{2+}$ resulted in the formation of ammonia (21%) via a disproportionation reaction. This reaction suggests that the hydrazine complex could be an intermediate in the reduction of N_2 to NH_3 in iron–phosphine systems. As described in the previous section, the η^2-N_2H_4 complex can also be deprotonated to yield η^2 diazene (N_2H_2) and hydrazido(1-) ($N_2H_3^-$) complexes. Notably, these deprotonation reactions are reversible by addition of acid. From this work, Tyler and coworkers proposed the mechanism shown in Scheme 13. This particular reaction pathway was examined by DFT calculations and was thermodynamically favorable, especially compared to an asymmetric N_2 reduction pathway. This work showed that diazene can be converted to hydrazine and then to ammonia by addition of protons. However, further work is needed, especially in the early stages of N_2 reduction to elucidate how N_2 is converted to diazene.

4.2. Asymmetric N_2 reduction pathway

As discussed above, biochemical studies on nitrogenase and reactivity studies of iron diazene complexes and iron hydrazine complexes suggest a symmetric pathway for the reduction of N_2. However, an asymmetric N_2 reduction pathway cannot be ruled out, especially because an asymmetric pathway has been observed in synthetic Mo and W systems that convert dinitrogen to ammonia. In the following section, potential intermediates in an asymmetric N_2 reduction pathway (top pathway, Fig. 2) will be explored, includ-



Scheme 12.



Scheme 13.

ing complexes with nitrido (N^{3-}), imido (NH^{2-}), and amido (NH_2^-) ligands.

4.2.1. Iron nitride complexes

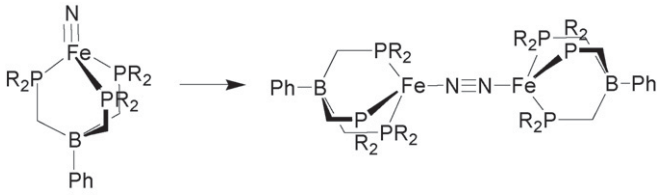
Several bridging and terminal nitride complexes of iron have been synthesized in a variety of oxidation states [53,77,123–128]. Even though iron forms nitride complexes, one problem limiting the validity of the asymmetric reaction pathway is that no iron nitride complex has yet been generated directly from N_2. Instead, these iron nitride complexes are typically generated by loss of N_2 from an iron azide precursor. In keeping with the theme of this review, only those iron nitrido complexes that exhibit reactivity related to nitrogen fixation will be highlighted here.

Smith and coworkers recently synthesized an iron nitride complex using the phenyltris(1-mesitylimidazol-2-ylidene)borate ligand (Scheme 14) [129]. Reaction of the chloride precursor with sodium azide followed by irradiation and loss of N_2 generates the four-coordinate iron nitrido complex.

Reaction of the nitride complex with TEMPO-H (TEMPO-H = 1-hydroxy-2,2,6,6-tetramethylpiperidine) resulted in yields of ammonia up to 74% (Scheme 14). It was proposed that the initial N–H bond forming step occurs through a hydrogen atom transfer. Metal hydrides can also act as hydrogen atom sources, although with significantly lower yields of ammonia. This reaction is unique among ammonia producing reactions using iron in that the protons and electrons come from the same source.

Peters and coworkers showed the utility of tris(phosphino)borate ligands in stabilizing many potential intermediates of nitrogen fixation [130]. Using these ancillary ligands, they were able to generate a low-oxidation state bridging nitride species [128]. The nitride complex is generated using sodium azide followed by reduction with sodium mercury amalgam (Scheme 15).

The nitride ligand was converted to ammonia in good yield (80–95%) upon exposure to three equivalents of HCl (Scheme 14). In an analogous system where the phenyl groups on the phosphines were replaced by isopropyl groups, they observed the coupling reaction of the terminal nitride species to produce a bridging dinitrogen complex (Eq. (7)) [53,77]. This nitride coupling reaction represents the microscopic reverse of the dinitrogen cleavage reaction; however, with this system they have yet been unable to achieve the N–N cleavage reaction.



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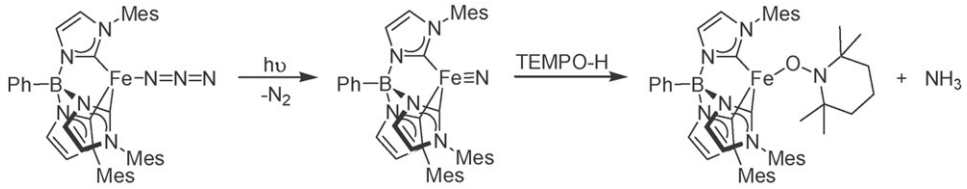
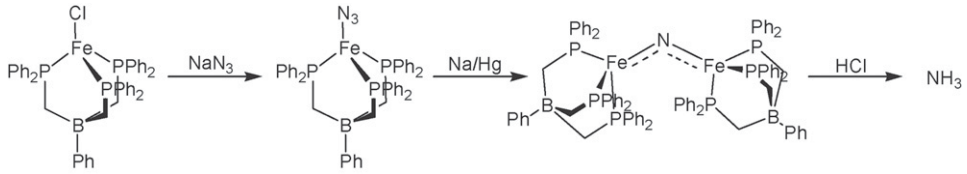
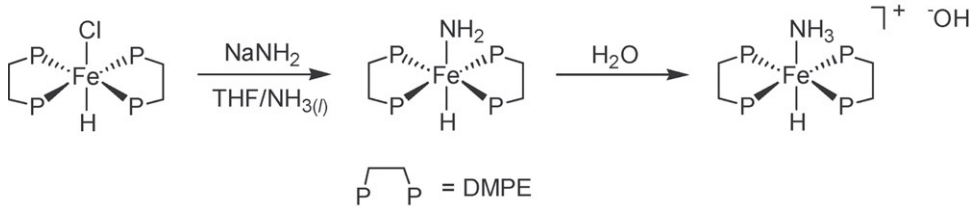


Scheme 14.



Scheme 15.



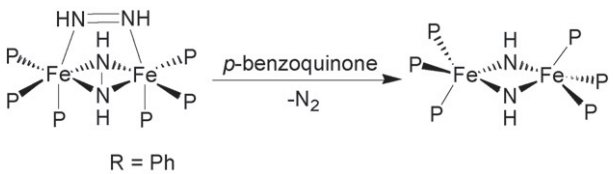
Scheme 16.

The examples above show the utility of low-coordinate iron to stabilize nitride ligands. These iron nitride complexes can then be converted to ammonia by addition of protons and electrons. While the conversion of the nitride ligand to ammonia is significant, the ultimate source of nitrogen for the ammonia is azide, not dinitrogen. However, the observation of the coupling of two iron nitride complexes to form a bridged dinitrogen complex may hint at the possibility of nitride formation directly from dinitrogen.

4.2.2. Iron imide and amide complexes

After formation of an iron nitride complex, further protonation and reduction would yield imide and amide complexes. Only a few iron imide and iron amide complexes have thus far been described in the literature. In one example, the Peters group, once again using the tris(phosphino)borate scaffold, observed imide [108,131] and amide [108] bridged dinuclear iron complexes.

Bridged μ-NH_2 and μ-NH complexes were also synthesized by Peters' group by thermal and oxidative transformations. The reactivity depended on the R group present on the tris(phosphino)borate ligand, $PhB(CH_2PR_2)_3^-$ [108]. With electron donating groups (R = CH_2Cy), the hydrazine hydrazido(2-) complex thermally decayed to give the diazene bis μ-NH_2 complex (top reaction, Scheme 12). With electron withdrawing groups (e.g., R = Ph), the hydrazine hydrazido(2-) complex is thermally stable but can be converted to a bis μ-NH complex by oxidation with Pb(OAc)4 (bottom reaction, Scheme 12), followed by further oxidation with *p*-benzoquinone (Eq. (8)). Particularly intriguing is the observation of N–N bond cleavage in a hydrazido(2-) ligand to yield a bis μ-NH_2 complex at room temperature. This work again highlights the ability of diiron complexes to mediate a wide variety of transformations.



(8)

In another example, Bergman's group synthesized a terminal amide complex via the addition of sodium amide to *trans*-$Fe(DMPE)_2(H)Cl$ (Scheme 16) [122]. The amide complex, which quickly isomerizes between *cis* and *trans* geometries, is strongly basic and can be protonated with a variety of weak carbon acids or water to form *trans*-$[Fe(DMPE)_2(NH_3)H]^+$.

There are relatively few iron complexes containing nitride, imide, or amide ligands. However, from the work reported thus far it is apparent that both nitride and amide complexes have the ability to produce ammonia by the addition of a proton or hydrogen atom source. Determining when the N–N bond is cleaved in these pathways remains an important unanswered question. Although direct cleavage of N_2 to form a nitride has not yet been observed with iron, the cleavage of hydrazine to form bridging imides and amides has been observed [108,120].

5. Summary

The coordination chemistry of dinitrogen and reduced dinitrogen species with iron has seen a growth spurt in the past ten years. The goals of research in this area are to shed light on the active mechanism in nitrogenase enzymes and to find synthetic systems capable of fixing atmospheric dinitrogen, either by forming ammonia or by incorporating dinitrogen into useful nitrogen-containing organic chemicals under mild reaction conditions.

More and more biochemical evidence implicates iron as the active metal in biological nitrogen fixation. Therefore, understanding how dinitrogen and reduced dinitrogen species interact with iron is becoming increasingly important. There are now numerous synthetic Fe–N_2 coordination complexes, all of which contain an end-on (η^1) bonded N_2. The activation of the coordinated N_2 is governed by the electronics of the ancillary ligands, with increased electron donation increasing activation. Coordination number and metal oxidation state also greatly influence the activation of dinitrogen, with iron(0) complexes and four-coordinate complexes displaying the highest degree on N–N bond activation. However, as shown by examples discussed above, increased activation does not necessarily lead to increased reactivity of the dinitrogen ligand.

The reactivity of iron–dinitrogen complexes can be separated into three categories: displacement, protonation, and elongation. Because dinitrogen is often weakly bound, a commonly observed reaction pathway is the displacement of the N_2 ligand. Numerous ligands displace N_2 including H_2, CO, acetonitrile, and acetone. The protonation of iron coordinated dinitrogen has been one of the most commonly studied reaction pathways. Dinitrogen can be successfully reduced to ammonia and/or hydrazine by addition of a strong acid to five-coordinate Fe–N_2 phosphine complexes. Although these complexes do not contain biologically relevant ancillary ligands, this class of compounds represents one of the few functional mimics of nitrogenase. Recently, progress has been made toward the goal of cleaving the N–N bond of dinitrogen to form nitrides, with low-coordinate iron–dinitrogen complexes showing the highest degree of N–N bond elongation.

Finally, it is noted that the iron coordination chemistry of diazene, hydrazine, nitride and other reduced dinitrogen species is growing more important and relevant because biochemical evidence suggests that these species are formed during nitrogen fixation in nitrogenase enzymes. Biological and theoretical evidence suggest that the mechanism of N_2 reduction mediated by iron proceeds through a symmetric protonation mechanism in which diazene and hydrazine intermediates are formed. The reactivity of iron coordination complexes of diazene and hydrazine also suggest that these intermediate can directly lead to ammonia. However, continued work is needed in this area to determine the actual N_2 reduction pathway. In particular, questions about the early stages of N_2 reduction, i.e. the conversion of dinitrogen to diazene and the N–N bond cleavage event, are important questions that remain unanswered.

Acknowledgment

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References

[1] T.A. Bazhenova, A.E. Shilov, Coord. Chem. Rev. 144 (1995) 69.
[2] J. Postgate, Nitrogen Fixation, 3rd ed., Cambridge University Press, Cambridge, UK, 1998.
[3] A.D. Allen, C.W. Senoff, Chem. Commun. (1965) 621.
[4] S.C. Lee, R.H. Holm, Chem. Rev. 104 (2004) 1135.
[5] P.L. Holland, in: J. McCleverty, T.J. Meyer (Eds.), Comprehensive Coordination Chemistry II, vol. 8, Elsevier, Oxford, 2004, p. 569.
[6] Y.G. Borodko, M.O. Broitman, L.M. Kachapina, A.E. Shilov, L.Y. Ukhin, J. Chem. Soc., Chem. Commun. (1971) 1185.
[7] A.E. Shilov, Russ. Chem. Rev. 43 (1974) 378.
[8] B. Tchoubar, A.E. Shilov, A.K. Shilova, Kinet. Katal. 16 (1975) 179.
[9] B. Jezowska-Trzebiatowska, P.J. Sobota, J. Organomet. Chem. 46 (1972) 339.
[10] A.E. Shilov, New J. Chem. 16 (1992) 213.
[11] J.R. Jennings, Catalytic Ammonia Synthesis, Plenum Press, New York, 1991.
[12] United Nations Industrial Development Organization (UNIDO), I.F.D.C.I Fertilizer Manual, 3rd ed., Kluwer Academic Publishers, The Netherlands, 1998.
[13] L.C. Seefeldt, B.M. Hoffman, D.R. Dean, Annu. Rev. Biochem. 78 (2009) 701.
[14] B.K. Burgess, D.J. Lowe, Chem. Rev. 96 (1996) 2983.
[15] J.B. Howard, D.C. Rees, Chem. Rev. 96 (1996) 2965.
[16] B.E. Smith, M.C. Durrant, S.A. Fairhurst, C.A. Gormal, K.L.C. Gronberg, R.A. Henderson, S.K. Ibrahim, T. Le Gall, C.J. Pickett, C. J. Coord. Chem. Rev. 185/186 (1999) 669.
[17] R.R. Eady, Chem. Rev. 96 (1996) 3013.
[18] L.M. Rubio, P.W. Ludden, J. Bacteriol. 187 (2005) 405.
[19] O. Einsle, A. Tezcan, S.L.A. Andrade, B. Schmid, M. Yoshida, J.B. Howard, D.C. Rees, Science 297 (2002) 1696.
[20] V. Vrajmasu, E. Munck, E.L. Bominaar, Inorg. Chem. 42 (2003) 5974.
[21] I. Dance, Chem. Commun. (2003) 324.
[22] I. Dance, Inorg. Chem. 45 (2006) 5084.
[23] B. Hinnemann, J.K. Nørskov, J. Am. Chem. Soc. 125 (2003) 1466.
[24] B. Hinnemann, J.K. Nørskov, J. Am. Chem. Soc. 126 (2004) 3920.
[25] V. Pelmenschikov, D.A. Case, L. Noodleman, Inorg. Chem. 47 (2008) 6162.
[26] T. Lovell, T. Liu, D.A. Case, L. Noodleman, J. Am. Chem. Soc. 125 (2003) 8377.
[27] H.I. Lee, P.M.C. Benton, M. Laryukhin, R.Y. Igarashi, D.R. Dean, L.C. Seefeldt, B.M. Hoffman, J. Am. Chem. Soc. 125 (2003) 5604.
[28] H.I. Lee, M. Sorlie, J. Christiansen, T.C. Yang, J.L. Shao, D.R. Dean, B.J. Hales, B.M. Hoffman, J. Am. Chem. Soc. 127 (2005) 15880.
[29] D. Lukoyanov, V. Pelmenschikov, N. Maeser, M. Laryukhin, T.-C. Yang, L. Noodleman, D.R. Dean, D.A. Case, L.C. Seefeldt, B.M. Hoffman, Inorg. Chem. 46 (2007) 11437.
[30] P.C. Dos Santos, R.Y. Igarashi, H.-I. Lee, B.M. Hoffman, L.C. Seefeldt, D.R. Dean, Acc. Chem. Res. 38 (2005) 208.
[31] B.M. Barney, R.Y. Igarashi, P.C. Dos Santos, D.R. Dean, L.C. Seefeldt, J. Biol. Chem. 279 (2004) 53621.
[32] L.C. Seefeldt, I.G. Dance, D.R. Dean, Biochemistry 43 (2004) 1401.
[33] P.C.C. Benton, M. Laryukhin, S.M. Mayer, B.M. Hoffman, D.R. Dean, L.C. Seefeldt, Biochemistry 42 (2003) 9102.
[34] B.M. Hoffman, D.R. Dean, L.C. Seefeldt, Acc. Chem. Res. 42 (2009) 609.
[35] B.M. Barney, H.-I. Lee, P.C. Dos Santos, B.M. Hoffman, D.R. Dean, L.C. Seefeldt, Dalton Trans. (2006) 2277.
[36] B.M. Barney, D. Lukoyanov, T.-C. Yang, D.R. Dean, B.M. Hoffman, L.C. Seefeldt, Proc. Natl. Acad. Sci. U.S.A. 103 (2006) 17113.
[37] B.M. Barney, J. McClead, D. Lukoyanov, M. Laryukhin, T.-C. Yang, D.R. Dean, B.M. Hoffman, L.C. Seefeldt, Biochemistry 46 (2007) 6784.
[38] B.M. Barney, T.-C. Yang, R.Y. Igarashi, P.C. Dos Santos, M. Laryukhin, H.-I. Lee, B.M. Hoffman, D.R. Dean, L.C. Seefeldt, J. Am. Chem. Soc. 127 (2005) 14960.
[39] J. Chatt, A.J. Pearman, R.L. Richards, J. Chem. Soc., Dalton Trans. (1977) 1852.
[40] R.R. Schrock, Angew. Chem. Int. Ed. 47 (2008) 5512.
[41] M.P. Shaver, M.D. Fryzuk, Adv. Synth. Catal. 345 (2003) 1061.
[42] F. Tuczek, N. Lehnert, Angew. Chem. Int. Ed. 37 (1998) 2636.
[43] G.J. Leigh, Science 268 (1995) 827.
[44] M.D. Fryzuk, S.A. Johnson, Coord. Chem. Rev. 200–202 (2000) 379.
[45] A.D. Leal, M. Jimenez-Tenorio, M.C. Puerta, P. Valerga, Organometallics 14 (1995) 3839.
[46] A. Sacco, M. Aresta, Chem. Commun. (1968) 1223.
[47] D.H. Gerlach, W.G. Peet, E.L. Muetterties, J. Am. Chem. Soc. 94 (1972) 4545.
[48] Y.G. Borodko, M.O. Broitman, L.M. Kachapina, A.K. Shilova, A.E. Shilov, Zh. Struct. Khim. 12 (1971) 545.
[49] P. Stoppioni, F. Mani, L. Sacconi, Inorg. Chim. Acta 11 (1974) 227.
[50] T.A. George, D.J. Rose, Y. Chang, Q. Chen, J. Zubieta, Inorg. Chem. 34 (1995) 1295.
[51] P. Giannoccaro, M. Rossi, A. Sacco, Coord. Chem. Rev. 8 (1972) 77.
[52] R.A. Cable, M. Green, R.E. Mackenzie, P.L. Timms, T.W. Turney, J. Chem. Soc., Chem. Commun. (1976) 270.
[53] T.A. Betley, J.C. Peters, J. Am. Chem. Soc. 125 (2003) 10782.
[54] C.E. MacBeth, S.B. Harkins, J.C. Peters, Can. J. Chem. 83 (2005) 332.
[55] J.L. Crossland, D.M. Young, L.N. Zakharov, D.R. Tyler, Dalton Trans. (2009) 9253.
[56] W.K. Miller, J.D. Gilbertson, C. Leiva-Paredes, P.R. Bernatis, T.J.R. Weakley, D.K. Lyon, D.R. Tyler, Inorg. Chem. 41 (2002) 5453.
[57] J.D. Gilbertson, N.K. Szymczak, D.R. Tyler, J. Am. Chem. Soc. 127 (2005) 10184.
[58] A. Hills, D.L. Hughes, M. Jimenez-Tenorio, G.J. Leigh, J. Organomet. Chem. 391 (1990) C41.
[59] A. Hills, D.L. Hughes, M. Jimenez-Tenorio, G.J. Leigh, A.T. Rowley, J. Chem. Soc., Dalton Trans. (1993) 3041.
[60] I.E. Buys, L.D. Field, T.W. Hambley, A.E.D. McQueen, Acta Crystallogr. Sect. C: Cryst. Struct. Commun. 49 (1993) 1056.
[61] G.M. Bancroft, M.J. Mays, B.E. Prater, J. Chem. Soc., Chem. Commun. (1969) 585.
[62] S. Komiya, M. Akita, A. Yoza, N. Kasuga, A. Fukuoka, Y. Kai, J. Chem. Soc., Chem. Commun. (1993) 787.
[63] B.E. Wiesler, N. Lehnert, F. Tuczek, J. Neuhausen, W. Tremel, Angew. Chem. Int. Ed. 37 (1998) 815.
[64] C.A. Ghilardi, S. Midollini, L. Sacconi, P. Stoppioni, J. Organomet. Chem. 205 (1981) 193.
[65] L.D. Field, B.A. Messerle, R.J. Smernik, Inorg. Chem. 36 (1997) 5984.
[66] L.D. Field, R.W. Guest, K.Q. Vuong, S.J. Dalgarno, P. Jensen, Inorg. Chem. 48 (2009) 2246.
[67] N.P. Mankad, M.T. Whited, J.C. Peters, Angew. Chem. Int. Ed. 46 (2007) 5768.
[68] M.T. Whited, N.P. Mankad, Y. Lee, P.F. Oblad, J.C. Peters, Inorg. Chem. 48 (2009) 2507.
[69] S.C. Bart, E. Lobkovsky, P.J. Chirik, J. Am. Chem. Soc. 126 (2004) 13794.
[70] A.M. Archer, M.W. Bouwkamp, M.-P. Cortez, E. Lobkovsky, P.J. Chirik, Organometallics 25 (2006) 4269.
[71] R.J. Trovitch, E. Lobkovsky, P.J. Chirik, Inorg. Chem. 45 (2006) 7252.
[72] A.A. Danopoulos, J.A. Wright, W.B. Motherwell, Chem. Commun. (2005) 784.
[73] H. Kandler, C. Gauss, W. Bidell, S. Rosenberger, T. Bürgi, I.L. Eremenko, D. Veghini, O. Orama, P. Burger, H. Berke, Chem. Eur. J. 1 (1995) 541.
[74] D. Sellmann, E. Kleinschmidt, Angew. Chem. Int. Ed. 14 (1975) 571.
[75] W.E. Silverthorn, J. Chem. Soc., Chem. Commun. (1971) 1310.
[76] A. Yamamoto, Y. Miura, T. Ito, H.L. Chen, K. Iri, F. Ozawa, K. Miki, T. Sei, N. Tanaka, N. Kasai, Organometallics 2 (1983) 1429.
[77] T.A. Betley, J.C. Peters, J. Am. Chem. Soc. 126 (2004) 6252.
[78] J.M. Bellerby, M.J. Mays, P.L. Sears, J. Chem. Soc., Dalton Trans. (1976) 1232.
[79] H. Berke, G. Huttner, W. Bankhardt, J. von Seyerl, L. Zsolnai, Chem. Ber. 114 (1981) 2754.
[80] J.M. Smith, R.J. Lachicotte, K.A. Pittard, T.R. Cundari, G. Lukat-Rodgers, K.R. Rodgers, P.L. Holland, J. Am. Chem. Soc. 123 (2001) 9222.
[81] J.M. Smith, A.R. Sadique, T.R. Cundari, K.R. Rodgers, G. Lukat-Rodgers, R.J. Lachicotte, C.J. Flaschenriem, J. Vela, P.L. Holland, J. Am. Chem. Soc. 128 (2006) 756.
[82] J.D. Gilbertson, N.K. Szymczak, J.L. Crossland, W.K. Miller, D.K. Lyon, B.M. Foxman, J. Davis, D.R. Tyler, Inorg. Chem. 46 (2007) 1205.
[83] R.A. Henderson, J. Chem. Soc., Dalton Trans. (1988) 515.

[84] M. Hirano, M. Akita, T. Morikita, H. Kubo, A. Fukuoka, S. Komiya, J. Chem. Soc., Dalton Trans. (1997) 3453.
[85] M. Hirano, M. Akita, K. Tani, K. Kumagai, N.C. Kasuga, A. Fukuoka, S. Komiya, Organometallics 16 (1997) 4206.
[86] T. Morikita, M. Hirano, A. Sasaki, S. Komiya, Inorg. Chim. Acta 291 (1999) 341.
[87] G.J. Leigh, Acc. Chem. Res. 25 (1992) 177.
[88] G.J. Leigh, M. Jimenez-Tenorio, J. Am. Chem. Soc. 113 (1991) 5862.
[89] D.A. Hall, G.J. Leigh, J. Chem. Soc., Dalton Trans. (1996) 3539.
[90] R.B. Yelle, J.L. Crossland, N.K. Szymczak, D.R. Tyler, Inorg. Chem. 48 (2009) 861.
[91] J.L. Crossland, L.N. Zakharov, D.R. Tyler, Inorg. Chem. 46 (2007) 10476.
[92] L.D. Field, H.L. Li, A.M. Magill, Inorg. Chem. 48 (2009) 5.
[93] A. Zanotti-Gerosa, E. Solari, L. Giannini, C. Floriani, A. Chiesi-Villa, C. Rizzoli, J. Am. Chem. Soc. 120 (1998) 437.
[94] A. Caselli, E. Solari, R. Scopelliti, C. Floriani, N. Re, C. Rizzoli, A. Chiesi-Villa, J. Am. Chem. Soc. 122 (2000) 3652.
[95] C.E. Laplaza, C.C. Cummins, Science 268 (1995) 861.
[96] C.E. Laplaza, M.J.A. Johnson, J. Peters, A.L. Odom, E. Kim, C.C. Cummins, G.N. George, I.J. Pickering, J. Am. Chem. Soc. 118 (1996) 8623.
[97] M. Hidai, Y. Mizobe, Chem. Rev. 95 (1995) 1115.
[98] D. Sutton, Chem. Rev. 93 (1993) 995.
[99] Y. Mizobe, Y. Ishii, M. Hidai, Coord. Chem. Rev. 139 (1995) 281.
[100] C.E. Miller, J. Chem. Educ. 42 (1965) 254.
[101] S. Hunig, H.R. Muller, W. Thier, Angew. Chem. Int. Ed. 4 (1965) 271.
[102] D. Sellmann, W. Soglowek, F. Knoch, M. Moll, Angew. Chem. Int. Ed. 28 (1989) 1271.
[103] D. Sellmann, H. Friedrich, F. Knoch, M. Moll, Z. Naturforsch. B 48 (1993) 76.
[104] D. Sellmann, A. Hennige, Angew. Chem. Int. Ed. 36 (1997) 276.
[105] D. Sellmann, D.C.F. Blum, F.W. Heinemann, Inorg. Chim. Acta 337 (2002) 1.
[106] J.L. Crossland, C.G. Balesdent, D.R. Tyler, Dalton Trans. (2009) 4420.
[107] L.D. Field, H.L. Li, S.J. Dalgarno, P. Turner, Chem. Commun. (2008) 1680.
[108] C.T. Saouma, P. Muller, J.C. Peters, J. Am. Chem. Soc. 131 (2009) 10358.
[109] V.L. Goedkin, S.-M. Peng, J.M. Norris, Y.J. Park, J. Am. Chem. Soc. 98 (1976) 8391.
[110] D. Sellmann, H. Friedrich, F. Knoch, Z. Naturforsch. B 49 (1994) 660.
[111] D. Sellmann, T. Becker, T. Hofmann, F. Knoch, M. Moll, Inorg. Chim. Acta 219 (1994) 75.
[112] D. Sellmann, W. Soglowek, F. Knoch, G. Ritter, J. Dengler, Inorg. Chem. 31 (1992) 3711.
[113] D. Sellmann, H. Kunstmann, F. Knoch, M. Moll, Inorg. Chem. 27 (1988) 4183.
[114] G. Albertin, S. Antoniutti, E. Bordignon, F. Chimisso, Inorg. Chem. Commun. 4 (2001) 402.
[115] G. Albertin, S. Antoniutti, E. Bordignon, S. Pattaro, J. Chem. Soc., Dalton Trans. (1997) 4445.
[116] M.J. Zdilla, A.K. Verma, S.C. Lee, Inorg. Chem. 47 (2008) 11382.
[117] D. Sellmann, S.Y. Shaban, F.W. Heinemann, Eur. J. Inorg. Chem. (2004) 4591.
[118] D. Sellmann, N. Blum, F.W. Heinemann, Z. Naturforsch. B 56 (2001) 581.
[119] S.P. Rath, M.M. Olmstead, A.L. Balch, Inorg. Chem. 43 (2004) 6357.
[120] Y. Yu, W.W. Brennessel, P.L. Holland, Organometallics 26 (2007) 3217.
[121] D. Sellmann, P. Kreutzer, G. Huttner, A. Frank, Z. Naturforsch. B 33 (1978) 1341.
[122] D.J. Fox, R.G. Bergman, Organometallics 23 (2004) 1656.
[123] J.J. Scepaniak, M.D. Fulton, R.P. Bontchev, E.N. Duesler, M.L. Kirk, J.M. Smith, J. Am. Chem. Soc. 130 (2008) 10515.
[124] C. Vogel, F.W. Heinemann, J. Sutter, C. Anthon, K. Meyer, Angew. Chem. Int. Ed. 47 (2008) 2681.
[125] J.F. Berry, E. Bill, E. Bothe, S. DeBeer George, B. Mienert, F. Neese, K. Wieghardt, Science 312 (2006) 1937.
[126] N. Aliaga-Alcalde, S. DeBeer George, B. Mienert, E. Bill, K. Wieghardt, F. Neese, Angew. Chem. Int. Ed. 44 (2005) 2908.
[127] T. Justel, M. Muller, T. Weyhermueller, C. Kressl, E. Bill, P. Hildebrandt, M. Lengen, M. Grodzicki, A.X. Trautwein, B. Nuber, K. Wieghardt, Chem. Eur. J. 5 (1999) 793.
[128] S.D. Brown, J.C. Peters, J. Am. Chem. Soc. 127 (2005) 1913.
[129] J.J. Scepaniak, J.A. Young, R.P. Bontchev, J.M. Smith, Angew. Chem. Int. Ed. 48 (2009) 3158.
[130] M.P. Hendrich, W. Gunderson, R.K. Behan, M.T. Green, M.P. Mehn, T.A. Betley, C.C. Lu, J.C. Peters, Proc. Natl. Acad. Sci. U.S.A. 103 (2006) 17107.
[131] S.D. Brown, M.P. Mehn, J.C. Peters, J. Am. Chem. Soc. 127 (2005) 13146.