

Homogeneous iron complexes for the conversion of dinitrogen into ammonia and hydrazine

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One of the most challenging problems in small molecule activation is the development of a homogeneous catalyst for converting dinitrogen into ammonia at ambient temperatures and atmospheric pressure. A catalytic cycle based on molybdenum that converts dinitrogen into ammonia has been reported. However, a well defined iron based system for the conversion of dinitrogen into ammonia or hydrazine has remained elusive, despite the relevance of iron to biological nitrogen fixation. In recent years several research groups have made significant progress towards this target. This *tutorial review* provides a brief historical perspective on attempts to develop iron based catalysts for dinitrogen functionalisation and then focuses on recent breakthroughs in the chemistry of coordinated dinitrogen, such as the generation of ammonia and hydrazine from coordinated dinitrogen, the isolation and characterisation of several proposed intermediates for ammonia generation and some preliminary mechanistic conclusions.

Introduction

The prospect of catalytically producing ammonia or hydrazine from dinitrogen at room temperature and ambient pressure has fascinated scientists for more than half a century.^{1–6} Nitrogen is found in many essential natural and synthetic compounds such as amino acids, fertilisers, explosives, synthetic fibres, polymers, resins and acrylics. The ultimate source of this nitrogen is dinitrogen. Although almost eighty percent of molecules in the atmosphere are dinitrogen, efficient conversion of these molecules into ammonia or other organo-nitrogen species is challenging due to their chemical inertness.

Dinitrogen molecules are non-polar, have a negative electron affinity, exhibit a high ionisation energy (15.58 eV), possess a low energy HOMO and a high energy LUMO and contain a triple bond that is extremely stable towards dissociation (the N≡N bond dissociation energy is approximately 945 kJ mol⁻¹). As a result, finding a method to catalytically convert atmospheric dinitrogen molecules into useful organic nitrogen containing species at mild reaction conditions remains an unsolved problem in modern day chemistry.

Currently the Haber–Bosch process is used to synthesise approximately 150 million tons of ammonia from dinitrogen and dihydrogen each year.⁷ The reaction conditions required to produce acceptable yields using only an iron catalyst are extreme, with temperatures of at least 400 °C and pressures of between 200 and 300 atmospheres required. Even the most advanced plants, which utilise a ruthenium catalyst in combination with traditional iron catalysts to perform the Kellogg Advanced Ammonia Process (KAAP), require pressures of approximately 90 atmospheres.⁷ In contrast biological nitrogen fixation, catalysed by the enzyme nitrogenase, occurs at ambient temperature and atmospheric pressure.⁸ Three distinct kinds of nitrogenase enzymes have been characterised to date. Their active sites contain either molybdenum and iron, vanadium and iron or iron with no other metal present. This has fuelled speculation that iron, not molybdenum or vanadium, is the crucial metal in the active site of nitrogenase. Over the last decade Hoffman and co-workers have performed extensive experiments using electron nuclear double resonance (ENDOR) and electron spin echo envelope modulation (ESEEM) spectroscopy, which suggest that an iron centre is the specific site of reactivity in iron–molybdenum nitrogenases.⁹ In addition they have utilized a combination of genetic and biochemical techniques to study intermediates relevant to dinitrogen reduction. However, despite these intensive and impressive research efforts the exact mechanism of enzymatic nitrogen fixation remains unclear.^{8,9}

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California Institute of Technology. He is currently an Assistant Professor in the Chemistry Department at Yale University, where his group focuses on developing homogeneous transition metal catalysts.

The discovery of the first dinitrogen complex $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ by Allen and Senoff in 1965¹⁰ prompted the belief that a transition metal mimic of nitrogenase would soon be developed. Indeed, dinitrogen-containing complexes have now been prepared for almost every transition metal even though the dinitrogen ligand is both a poorer σ -donor and a weaker π -acceptor than isoelectronic CO. Unfortunately, attempts to functionalise coordinated dinitrogen have not been as successful. Pioneering work was performed by Manriquez and Bercaw,¹¹ Chatt *et al.*,¹² Hidai¹ and Bazhenova and Shilov,¹³ who were all able to convert dinitrogen into functionalised products using early transition metals. This work provided the basis for Schrock and co-workers to develop a molybdenum catalyst that can convert dinitrogen into ammonia using protons and electrons.^{4,14} They used a molybdenum dinitrogen complex which contained an extremely bulky triamidoamine ligand as the catalyst (Fig. 1). When they treated this complex with thirty-six equivalents of CrCp^*e^- and forty-eight equivalents of $[\text{2,6-lutidinium}][\text{B}(\text{ArF})_4]$ ($\text{ArF} = 3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3$) under an atmosphere of N_2 , dinitrogen was reduced to ammonia and the catalyst regenerated. The slow addition of the proton source and reductant were critical for achieving high efficiency ($\sim 66\%$ in four turnovers), as side reactions such as dihydrogen production were minimised. Numerous X-ray studies, along with isolation and characterisation of eight proposed intermediates in the catalytic reaction under noncatalytic conditions, suggest that dinitrogen is reduced at a sterically protected, single molybdenum centre that cycles between Mo(III), Mo(IV), Mo(V) and Mo(VI) (Fig. 1).

This is consistent with a Chatt type mechanism in which consecutive protonation of dinitrogen and electron transfer was proposed to occur at a single metal centre.¹⁵ At the moment this catalyst is the only non-enzymatic system capable of reducing dinitrogen to ammonia using protons and electrons at room temperature and atmospheric pressure.

Whereas Schrock used protons and electrons to reduce dinitrogen, Chirik and co-workers demonstrated the direct reduction of zirconium dinitrogen complexes using dihydrogen (Scheme 1).^{6,16} They showed that the side-on bound dinitrogen complex $[(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{Zr}]_2(\mu_2, \eta^2, \eta^2\text{-N}_2)$ reacts with dihydrogen at room temperature to form the bridging diazenido complex $[(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{ZrH}]_2(\mu_2, \eta^2, \eta^2\text{-N}_2\text{H}_2)$. Incredibly, further reaction of the diazenido complex with dihydrogen at elevated temperature results in the formation of a monomeric zirconium dihydride and ammonia in low yield.

Despite these important advances in nitrogen fixation using early transition metals, there is considerable interest in developing iron based nitrogenase mimics, due to its biological relevance, relative cost and relationship to current Haber–Bosch catalysts. This review focuses on attempts to develop homogeneous iron complexes for the conversion of dinitrogen into ammonia and hydrazine. A brief description of the properties of iron dinitrogen complexes is followed by a more detailed discussion of recent developments in the field, such as the generation of ammonia and hydrazine from coordinated dinitrogen, the isolation and characterisation of several proposed intermediates for ammonia and hydrazine generation, and the preparation of high valent iron nitrido and imido complexes.

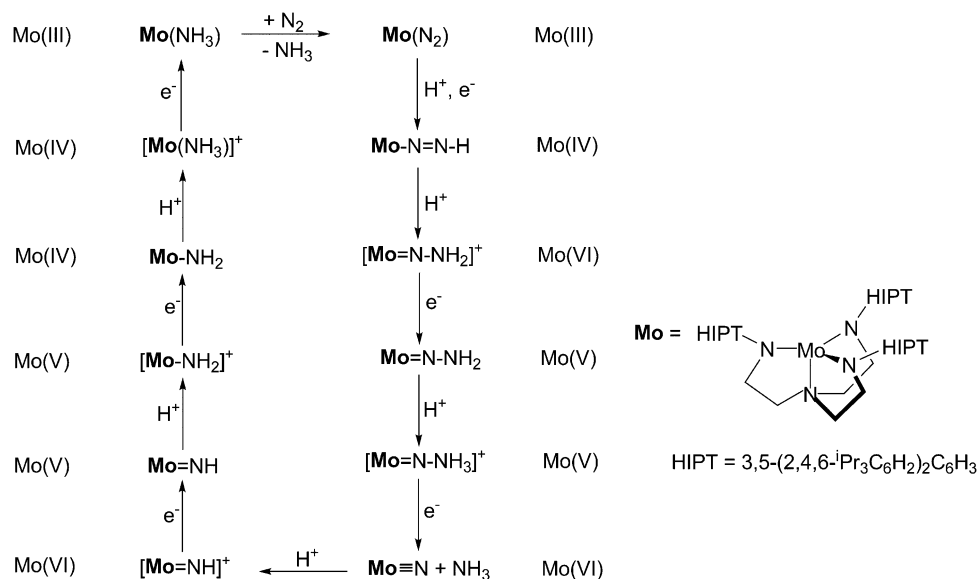
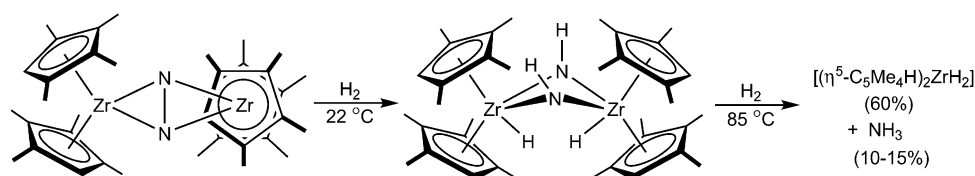


Fig. 1 Proposed intermediates in the reduction of dinitrogen at a $[\text{HIPTN}_3]\text{Mo}$ centre through the stepwise addition of protons and electrons.^{4,14}



Scheme 1

Iron dinitrogen complexes

The binding of dinitrogen to a metal centre is believed to be crucial for the functionalisation of dinitrogen as it weakens the strong $\text{N}\equiv\text{N}$ bond. The interaction between a metal centre and dinitrogen involves both σ and π components as shown in Fig. 2. The dinitrogen is able to bind as a Lewis base and donate electron density from the filled highest occupied molecular orbital (HOMO, $3\sigma_g$) into an empty metal d-orbital. This results in the formation of a σ -type bond. Furthermore, the empty lowest unoccupied molecular orbital (LUMO, $1\pi_g^*$) on the dinitrogen is able to act as a Lewis acid and accept electron density from a filled metal d-orbital of the correct symmetry. This results in the formation of a π back-bond. The bonding of dinitrogen to a metal can be measured by the ability of the metal centre(s) to reduce or 'activate' the $\text{N}\equiv\text{N}$ bond *via* donation of electron density into the π^* -orbitals of the dinitrogen moiety, which weakens the $\text{N}\equiv\text{N}$ bond. The extent of activation is proportional to the strength of the metal–nitrogen $d-\pi^*$ back-bonding interaction and the degree of this interaction has typically been inferred both from the increase of the $\text{N}\equiv\text{N}$ bond length and from the decrease of the $\text{N}\equiv\text{N}$ stretching frequency compared with the values for free dinitrogen. It should be noted that several controlled studies have demonstrated that there is not always a correlation between the degree of dinitrogen activation and the extent of reactivity.² For example less activated dinitrogen complexes can often be protonated more readily than activated dinitrogen species.

The first iron dinitrogen complex was prepared in 1968 by Sacco and Aresta.¹⁷ Since this discovery, numerous related dinitrogen complexes, featuring a variety of different ancillary ligands, have been prepared. In general, iron(II) dinitrogen complexes have been synthesised through ligand substitution of a halide ligand (typically chloride) with dinitrogen in a protic solvent (eqn (1)). Alternatively, both Leigh and Tyler have substituted a halide ligand with dihydrogen, and then replaced the exceptionally labile dihydrogen ligand with dinitrogen.^{18,19} One of the few iron(II) dinitrogen complexes

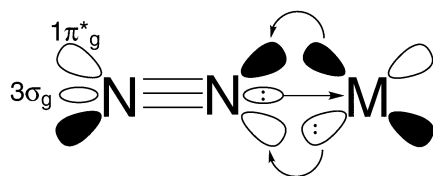
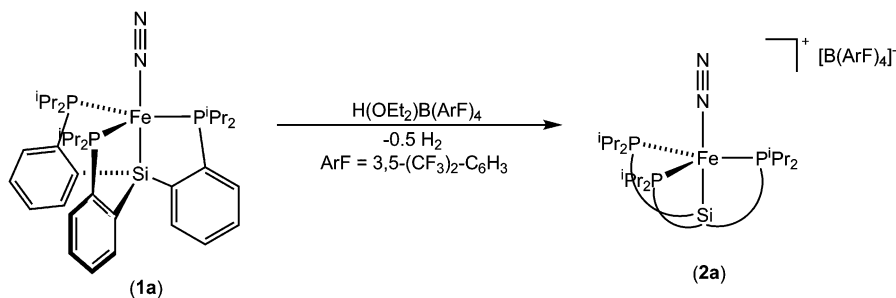
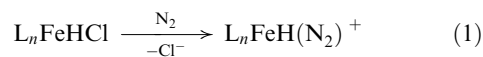


Fig. 2 Bonding between dinitrogen and a metal centre involves both σ and π components.



which was not prepared by ligand substitution is $[\text{Fe}(\text{SiP}^{\text{iPr}}_3)(\text{N}_2)][\text{B}(\text{ArF})_4]$ (**2a**) ($\text{SiP}^{\text{iPr}}_3 = [\text{Si}(2\text{-P}^{\text{iPr}}_2\text{C}_6\text{H}_4)_3]^-$), which was recently prepared by oxidation of the neutral iron(II) dinitrogen complex $[\text{Fe}(\text{SiP}^{\text{iPr}}_3)(\text{N}_2)]$ (**1a**) (eqn (2)).²⁰ Currently almost all known monomeric iron(II) species contain phosphine ligands and feature end-on bound dinitrogen (Table 1). There is little activation of dinitrogen in these systems and the $\text{N}\equiv\text{N}$ bond length and IR stretching frequency are similar to the values observed in free dinitrogen, which has an $\text{N}\equiv\text{N}$ distance of 1.0975 Å and a stretching frequency of 2331 cm^{-1} . The approximate range for $\nu(\text{N}\equiv\text{N})$ in divalent iron complexes is 2040–2145 cm^{-1} . Surprisingly a number of complexes have shorter $\text{N}\equiv\text{N}$ bond lengths than those observed in free dinitrogen even though the IR stretching frequency indicates a partial weakening of the $\text{N}\equiv\text{N}$ bond. The following factors can all contribute to this apparent shortening: (i) disorder, (ii) the presence of trace amounts of impurities in the crystal which are not factored into the crystallographic model, and (iii) the fact that X-ray diffraction locates electron density, not nuclei.^{20,21} In general the short $\text{N}\equiv\text{N}$ bond length is an artefact and should be ignored. The relatively small amount of dinitrogen activation in iron(II) species results from a weak metal–nitrogen bond and causes the dinitrogen ligand to be highly labile. This allows for the facile preparation of ^{15}N -labelled dinitrogen complexes through exchange between unlabelled coordinated dinitrogen and free ^{15}N -labelled dinitrogen.²² Despite this convenient synthetic route, the ^{15}N NMR chemical shifts for coordinated dinitrogen have only been reported for a small number of iron complexes and not enough data exist to assess if there is a correlation between the chemical shift and the degree of dinitrogen activation.



In contrast to iron(II) dinitrogen complexes, low valent iron(0) and iron(I) dinitrogen complexes were first prepared a little over twenty years ago and have only been structurally characterised in the last fifteen years.^{41–43} They are often prepared by reduction of iron(II) chloride complexes under dinitrogen (eqn (3)). In some cases iron(0) dinitrogen complexes may be prepared directly from iron(II) dinitrogen hydrido complexes through deprotonation (eqn (4)). Low valent iron activates dinitrogen to a greater extent than iron(II) due to increased back-bonding from the electron rich metal centre (Table 2). The $\nu(\text{N}\equiv\text{N})$ bands of end-on dinitrogen in zerovalent iron complexes range from 1950–2141 cm^{-1} . When a cation also coordinates to the bound dinitrogen the $\text{N}\equiv\text{N}$ stretching frequency is often lowered below 1950 cm^{-1} .

Table 1 Monomeric iron(II) dinitrogen compounds

Complex	$\nu(\text{N}\equiv\text{N})/\text{cm}^{-1}$	$\text{N}\equiv\text{N}$ distance/Å	$\delta^{15}\text{N}$ NMR ^a (ppm)	Ref.
[FeH(dmpe) ₂ (N ₂)] [BPh ₄]	2094	1.112(9)	-62.1, -39.2	18, 22
[FeH(depe) ₂ (N ₂)] [BPh ₄]	2091	1.070(12)	-60.7, -42.2	22–24
[FeH(dppe) ₂ (N ₂)] [BPh ₄]	2120, 2145 ^b		-63.2, -48.2	22, 25
[FeH(DMeOPrPE) ₂ (N ₂)] [BPh ₄]	2093	1.112(3)	-60.0, -40.0	19, 26
[FeH(hptpd)(N ₂)] [Br]	2130	1.076(15)		27
[FeH(P ⁱ Pr ₃)(N ₂)] [BPh ₄]	2095		-51.5, -19.5	28
[FeH(P ^{Me} ₃)(N ₂)] [BPh ₄]	2117		-63.7, -35.0	22, 29
[FeH(P ^{Ph} ₃)(N ₂)] [BPh ₄]	2100			30
[FeH(NP ^{Ph} ₃)(N ₂)] [BPh ₄]	2090	1.102(13)		31
[FeH(NP ⁱ Pr ₃)(N ₂)] [PF ₆]	2087	1.113(4)		32
[FeH ₂ (PPh ₃)(N ₂)]	2008			33
[FeH ₂ (PMePh ₂)(N ₂)]	2058			34
[FeH ₂ (PEtPh ₂)(N ₂)]	2055	1.136(7)		17, 34
[FeH ₂ (P ⁿ BuPh ₂)(N ₂)]	2074			34, 35
[FeCl(dmpe) ₂ (N ₂)] [BPh ₄]	2105			36
[FeBr(dmpe) ₂ (N ₂)] [BPh ₄]	2107			37
[FeCl(depe) ₂ (N ₂)] [BPh ₄]	2086	1.073(11)		23, 38
[FeBr(depe) ₂ (N ₂)] [BPh ₄]	2091			38
[Fe(η^5 -C ₅ H ₅)(dippe)(N ₂)] [BPh ₄]	2112	1.13(1)		39
[Fe(Si ⁱ Pr ₃)(N ₂)] [B(ArF) ₄]	2143	1.091(3)		20
2[Na][Fe(EDTA)(N ₂)]·H ₂ O	2040			40
2[Na][Fe(CDTA)(N ₂)]·H ₂ O	2060			40

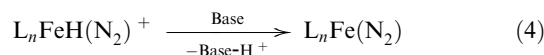
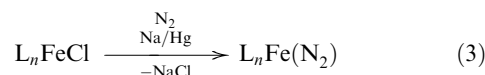
^a Chemical shifts are referenced to neat nitromethane at δ 0.00 ppm; first value is the chemical shift for N_α (adjacent to metal) and second is for N_β (terminal). ^b Both diamagnetic (singlet) and paramagnetic (triplet) complexes are observed which give different IR stretches. dmpe = Me₂PCH₂CH₂PMe₂; depe = Et₂PCH₂CH₂PEt₂; dppe = Ph₂PCH₂CH₂PPh₂; DMeOPrPE = (MeOCH₂CH₂CH₂)₂PCH₂CH₂P(CH₂CH₂-CH₂OMe)₂; hptpd = 3,6-diphenyl-4,8-bis(diphenylphosphino)-3,6-diphosphaoctane; PⁱPr₃ = P(CH₂CH₂PⁱPr₂)₃; P^{Me}₃ = P(CH₂CH₂PMe₂)₃; P^{Ph}₃ = P(CH₂CH₂PPh₂)₃; NP^{Ph}₃ = N(CH₂CH₂PPh₂)₃; NPⁱPr₃ = N(CH₂CH₂PⁱPr₂)₃; dippe = ⁱPr₂PCH₂CH₂PⁱPr₂; SiⁱPr₃ = [Si(2-ⁱPr₂C₆H₄)₃]⁻; B(ArF)₄ = B(3,5-(CF₃)₂-C₆H₃)₄; EDTA = ethylenediaminetetraacetate; CDTA = diaminocyclohexanetetraacetate.

Table 2 Monomeric iron(0) and iron(I) dinitrogen compounds

Complex	$\nu(\text{N}\equiv\text{N})/\text{cm}^{-1}$	$\text{N}\equiv\text{N}$ distance/Å	$\delta^{15}\text{N}$ NMR ^a (ppm)	Ref.
[Fe(dmpe) ₂ (N ₂)]	1975		-47.5, -42.6	18
[Fe(depe) ₂ (N ₂)]	1956	1.142(7)	-45.2, -40.5	42, 45
[Fe(dmpp) ₂ (N ₂)]	1950			46
[Fe(dppe) ₂ (N ₂)]	2068			47
[Fe(DMeOPrPE) ₂ (N ₂)]	1966		-47.5, -43.5	19
[Fe(P ⁱ Pr ₃)(N ₂)]	1985	1.1279(16)	-18.0, 18.1	28
[Fe(P ^{Me} ₃)(N ₂)]	2013			29
[Fe(NP ^{Ph} ₃)(N ₂)]	1967			31
[Fe(PEt ₃) ₂ (CO) ₂ (N ₂)]	2098	1.078(30)		43
[Fe(PO ⁱ Pr ₃) ₂ (CO) ₂ (N ₂)]	2141			43
[Fe(CNC)(N ₂) ₂]	2109, 2031, 2044 ^b	1.115(3)		48
[Fe(CNC)(C ₂ H ₄)(N ₂)]	2056	1.121(5)		48
[Fe(CNC)(PMe ₃)(N ₂)]	2032	1.129(4)		48
[Fe(CNC)(PCy ₃)(N ₂)]	2012			48
[Fe(ⁱ PrPDI)(N ₂) ₂]	2124, 2053	1.090(2), 1.104(3)		49
[Fe(ⁱ PrBPDI)(N ₂) ₂]	2138, 2086	1.106(6), 1.107(5)		50
[Fe(ⁱ PrPDI)(N ₂) ₂]	2036			49
[Fe(ⁱ PrBPDI)(N ₂) ₂]	2061			50
[Fe(ⁱ PrPDI-H)(N ₂) ₂]		1.136(12)		51
[Na(THF)][Fe(ⁱ PrPDI-H)(N ₂) ₂]	1912	1.090(5)		51
[Na(Et ₂ O) ₃][Fe(ⁱ PrPDI-H)(N ₂) ₂]	1965	1.154(6)		51
[MgCl(THF) ₂][Fe(PhBP ⁱ Pr ₃)(N ₂) ₂]	1830			52
0.5[Mg(18-C-6)][Fe(PhBP ⁱ Pr ₃)(N ₂) ₂]	1884			52
[Fe(Si ⁱ Pr ₃)(N ₂) ₂]	2003	1.1245(2)		20, 44, 53
[Fe(Si ^{Ph} ₃)(N ₂) ₂]	2041	1.106(3)		44
[Na(THF) ₃][Fe(Si ⁱ Pr ₃)(N ₂) ₂]	1891	1.147(4)		20
[Na(12-C-4)][Fe(Si ⁱ Pr ₃)(N ₂) ₂]	1920	1.132(4)		20
[Na(12-C-4)][Fe(Si ^{Ph} ₃)(N ₂) ₂]	1967			44

^a Chemical shifts are referenced to neat nitromethane at δ 0.00 ppm; first value is the chemical shift for N_α (adjacent to metal) and second is for N_β (terminal). ^b A mixture of two different isomers may give rise to the three N≡N bands. dmpp = Me₂PCH₂CH₂CH₂PMe₂; CNC = 2,6-bis(aryl-imidazol-2-ylidene)pyridine; aryl = 2,6-ⁱPr₂C₆H₃; ⁱPrPDI = 2,6-(2,6-ⁱPr₂C₆H₃N=CMe)₂C₅H₃N; ⁱPrBPDI = 2,6-(2,6-ⁱPr₂C₆H₃N=CPh)₂C₅H₃N; ⁱPrPDI-H = [2-(2,6-ⁱPr₂C₆H₃N=CMe)-6-(2,6-ⁱPr₂C₆H₃N=CCH₂)]C₅H₃N; PhBPⁱPr₃ = [PhB(CH₂PⁱPr₂)₃]⁻; 18-C-6 = 18-crown-6; Si^{Ph}₃ = [Si(2-PPh₂C₆H₄)₃]⁻; 12-C-4 = 12-crown-4.

Almost all crystallographically characterised iron(0) dinitrogen complexes are five coordinate with trigonal bipyramidal coordination geometries around iron. Only two monomeric iron(I) dinitrogen complexes⁴⁴ have been synthesised to date and complexes of this nature remain a target for synthetic inorganic chemists.



Dimeric species with bridging dinitrogen ligands are less common than monomeric complexes with terminal dinitrogen ligands; only symmetrical dimeric species have been prepared (Table 3). The N≡N stretching frequency is quantified using Raman spectroscopy as the N≡N stretch is not IR active in symmetrical dimeric species (stretching the N≡N bond does not change the overall dipole moment of the molecule). In all known cases, the dinitrogen ligand bridges through an η¹:η¹ end-on coordination mode, however, general synthetic routes into these species are yet to be developed. Recently, Chirik and co-workers prepared a series of dimeric complexes with both bridging and terminal dinitrogen ligands and ¹⁵N NMR spectroscopy suggests exchange between the different sites.⁵⁴ In general, the lability of coordinated dinitrogen in dimeric species has not been extensively probed but it is clear that the degree of dinitrogen activation can be increased by preparing bridging dinitrogen complexes with low coordination numbers. Holland and co-workers were able to prepare a family of three coordinate iron(I) dimers with a bridging dinitrogen ligand by using a bulky β-diketiminato ligand.⁵⁵ Originally these complexes were prepared by reduction of

chloride precursors under dinitrogen,⁵⁵ however, subsequently it was demonstrated that UV-irradiation of related hydride species under dinitrogen results in extrusion of dihydrogen and formation of the dinitrogen complexes.⁵⁶ The extraordinary degree of dinitrogen activation in these three coordinate species is greater than in any other iron dinitrogen complex and is attributed to the low coordination number. The degree of dinitrogen activation decreased when an additional ligand was added to each metal centre to generate four coordinate species.

Generation of ammonia and hydrazine from iron dinitrogen complexes

The reduction of coordinated dinitrogen into hydrazine at an iron centre was first reported by Shilov and co-workers in 1971.⁶¹ They demonstrated that the reaction of (Ph₃P)₂FeCl₃, ⁱPrMgCl, N₂ and gaseous HCl at low temperature resulted in a 10% yield of hydrazine. The binuclear mixed-valent complex **3** was tentatively proposed as the starting dinitrogen complex formed from (Ph₃P)₂FeCl₃, ⁱPrMgCl and N₂ and reaction of **3** with HCl is believed to generate hydrazine. The mechanism of this seminal reaction remains a mystery and there have been no further reports related to this chemistry. Schrauzer and Guth subsequently demonstrated that preparation of alkaline suspensions of Fe(OH)₂ under dinitrogen led to the formation of ammonia and hydrazine, albeit in low yields.⁶² Elemental iron, which precipitates as a result of the disproportionation of iron, is proposed to be the active species.

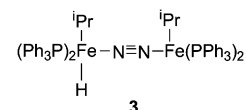
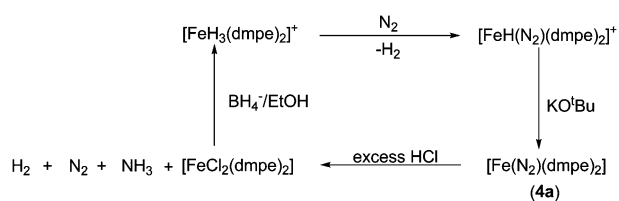


Table 3 Dimeric bridging dinitrogen compounds

Complex	$\nu(N \equiv N)/cm^{-1}$	N≡N distance/Å	Ref.
[FeH(PP ^{Me} ₃) ₂ (μ-N ₂) ₂][BPh ₄]	2060		29
[Fe(η ⁵ -C ₅ H ₅)(dmpe) ₂ (μ-N ₂) ₂][BF ₄]	2054		57
[Fe(η ⁵ -C ₅ H ₅)(dppe) ₂ (μ-N ₂) ₂][PF ₆]	2040		58
[Fe(^{Me} , ^{iPr} PDI)(N ₂)](μ-N ₂)	2099, 2084 ^b		54
[Fe(^{Et} PDI)(N ₂)](μ-N ₂)	2101, 2086 ^b	Bridging 1.137(3) and 1.124(3) ^c Terminal 1.098(3), 1.121(4) and 1.107(4), 1.114(4)	54
[Fe(^{Me} PDI)(N ₂)](μ-N ₂)	2102, 2085 ^b		54
[Fe(^{Me} BPDI)(N ₂)](μ-N ₂)	2120, 2109 ^b	Bridging 1.124(3) Terminal 1.102(2), 1.102(2) ^d	54
[(N ₂ P ₂)Fe] ₂ (μ-N ₂)	1760	1.166(3)	59
[Fe(PhBP ^{iPr} ₃) ₂ (μ-N ₂)		1.138(6)	52
[Na(THF) ₆][Fe(PhBP ^{iPr} ₃) ₂ (μ-N ₂)		1.171(4)	52
[Fe(^t Bu ₂ nacnac) ₂ (μ-N ₂)	1778	1.182(5)	55
[Fe(^{Me} ₂ nacnac) ₂ (μ-N ₂)	1810	1.18(1)	56
[Fe(^t Bu ₂ nacnac)(4- ^t Bu-pyridine)] ₂ (μ-N ₂)	1770	1.151(3)	56
[Fe(^{Me} ₂ nacnac)(4- ^t Bu-pyridine)] ₂ (μ-N ₂)		1.161(4)	56
2[K][Fe(^t Bu ₂ nacnac)] ₂ (μ-N ₂)	1589	1.233(6)	55
2[K][Fe(^{Me} ₂ nacnac)] ₂ (μ-N ₂)	1625	1.215(6)	56
[Fe(CO) ₂ (POMe ₃) ₂](μ-N ₂)		1.13(1)	60
[Fe(CO) ₂ (PEt ₃) ₂](μ-N ₂)		1.134(21)	43

^a Raman bands except where noted. ^b IR bands for terminal dinitrogen ligands. ^c Two independent molecules in unit cell. ^d Both terminal N–N bond distances the same by symmetry. ^{Me},^{iPr}PDI = 2,6-(2-ⁱPr₂,6-Me-C₆H₃N=CMe)₂C₅H₃N; ^{Et}PDI = 2,6-(2,6-Et₂C₆H₃N=CMe)₂C₅H₃N; ^{Me}PDI = 2,6-(2,6-Me₂C₆H₃N=CMe)₂C₅H₃N; ^{Me}BPDI = 2,6-(2,6-Me₂C₆H₃N=CPh)₂C₅H₃N; N₂P₂ = [BuNSiMe₂N(CH₂CH₂P^{Pr}₂)₂]⁻; ^tBu₂nacnac = [ArNC(^tBu)]₂CH⁻; aryl = 2,6-ⁱPr₂C₆H₃; ^{Me}₂nacnac = [ArNC(Me)]₂CH⁻.



Scheme 2

A major breakthrough in the fixation of nitrogen using iron occurred in 1991, when Leigh *et al.* developed a reaction cycle for the conversion of coordinated dinitrogen into ammonia (Scheme 2).^{18,41,63} The key steps involved *in situ* generation and subsequent protonation of the iron(0) species $[\text{Fe}(\text{N}_2)(\text{dmpe})_2]$ (**4a**), leading to the formation of ammonia (best yield of 20%) and the iron(II) complex $[\text{FeCl}_2(\text{dmpe})_2]$ (80%). As written in Scheme 2, the cycle cannot be correct as the stoichiometry does not balance (see comments in the mechanism section) and the difficult task of determining the nitrogen balance (dinitrogen plus ammonia) has not been achieved. At least three processes were believed to be occurring when **4a** was treated with acid: (i) loss of N_2 to yield $[\text{Fe}(\text{dmpe})_2]$, which subsequently decomposed, (ii) protonation of coordinated N_2 to generate ammonia and N_2 and (iii) protonation at iron to give $[\text{FeH}(\text{N}_2)(\text{dmpe})_2]^+$ which eventually formed dihydrogen and $[\text{FeCl}_2(\text{dmpe})_2]$. A variety of different bases and acids could be used for both the deprotonation of *trans*- $[\text{FeH}(\text{N}_2)(\text{depe})_2]^+$ and the protonation of $[\text{Fe}(\text{N}_2)(\text{dmpe})_2]$ (**4a**), but the iron product of the reaction was characterised only when KO^tBu was used as the base and HCl was the acid. Ammonia has also been generated when the products of the deprotonation of *trans*- $[\text{FeH}(\text{N}_2)(\text{depe})_2]^+$,¹⁸ water soluble *trans*- $[\text{FeH}(\text{N}_2)(\text{DMeOPrPE})]^+$,¹⁹ *cis*- $[\text{FeH}(\text{N}_2)\{\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}]^+$ ³¹ and *cis*- $[\text{FeH}(\text{N}_2)\{\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}]^+$ ¹⁸ were treated with acid. In contrast to Leigh's system the products of these deprotonation reactions have yet to be isolated or fully characterised.

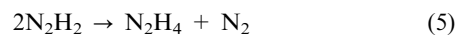
A limitation of the Leigh cycle and related systems is that the crucial iron(0) dinitrogen intermediates, which are relatively unstable, have not been isolated or structurally characterised. There remains the possibility that a mixed metal, iron/potassium complex or some other species related to an iron(0) dinitrogen compound may be forming. An observation which is consistent with the formation of mixed metal species is that treatment of isolated samples of $[\text{Fe}(\text{N}_2)(\text{depe})_2]$ (which has been crystallographically characterised)^{42,45} with HCl does not lead to the generation of detectable levels of ammonia.⁴² Instead the iron(II) species $[\text{FeCl}_2(\text{depe})_2]$ is formed, presumably along with dihydrogen.

In contrast to the systems described above, which are proposed to involve initial protonation of an iron(0) species, Peters and co-workers have shown that protonation of monomeric iron(I) dinitrogen complexes can generate hydrazine.⁴⁴ Treatment of $[\text{Fe}(\text{SiP}^{\text{Ph}}_3)(\text{N}_2)]$ (**1b**) ($\text{SiP}^{\text{Ph}}_3 = [\text{Si}(\text{2-PPh}_2\text{C}_6\text{H}_4)_3]^-$) with HCl or HBF_4 results in yields of hydrazine of 17% and 7% per equivalent of iron, respectively. The resulting iron complexes have not been characterised. Performing the protonation in the presence of a one-electron reductant such as CrX_2 ($\text{X} = \text{Cl}$ or Cp^*) increases the yield of hydrazine to almost

50% per equivalent of iron, the highest currently known. Lower yields of hydrazine (9% per equivalent of iron) are observed when the electron rich species $[\text{Fe}(\text{SiP}^{\text{iPr}}_3)(\text{N}_2)]$ (**1a**) is protonated, even in the presence of a reductant (although weaker acids such as $[\text{HN}^{\text{iPr}}_2\text{Et}][\text{BPh}_4]$ can be utilised). It is postulated that the lower hydrazine yields observed for **1a** occur as a result of competing processes: proton to dihydrogen reduction *versus* dinitrogen reduction. Interestingly, related low coordinate dimeric iron(I) systems such as $[\text{Fe}^{\text{tBu}}_2(\text{nacnac})_2(\mu\text{-N}_2)]$ or $[\text{Fe}(\text{PhBP}^{\text{iPr}}_3)_2(\mu\text{-N}_2)]$ (**5a**) do not generate ammonia or hydrazine upon treatment with acid and neither does the iron(0) complex $[\text{Na}(12\text{-C-4})\text{-}[\text{Fe}(\text{SiP}^{\text{Ph}}_3)(\text{N}_2)]$ (which has the same ligand set as **1**). It remains a challenge for the field to understand the unique reactivity of low coordinate monomeric iron(I) dinitrogen complexes.

Potential mechanisms for ammonia and hydrazine formation

Given the uncertainty about the structure of the coordinated dinitrogen starting materials in the reactive Shilov and Schrauzer systems, no detailed mechanisms have been proposed for these reactions. Hence, the following discussion will concentrate on the Leigh cycle (Scheme 2). As mentioned earlier even in this system the exact nature of the starting material is unclear but it is almost certainly an iron(0) dinitrogen complex of some form. A further complication is that to reduce coordinated dinitrogen into two molecules of ammonia, six electrons and six protons are required, and it is unlikely that a single iron centre could provide the reducing power to convert dinitrogen into ammonia. In the Leigh system no external reductant is added and presumably a certain proportion of iron(0) (or a later stage intermediate) is diverted from the ammonia forming pathway. The majority of the isolated iron is in the +2 oxidation state; thus four additional electrons (two additional iron(0) centres) are required for the formation of two equivalents of ammonia from the starting iron complex, which presumably provides two electrons. The maximum yield of ammonia per iron centre is therefore 66% (two molecules of ammonia for every three iron(0) complexes). In principle a mechanism involving disproportionation of diazene into hydrazine and dinitrogen (eqn (5)), followed by disproportionation of hydrazine into ammonia and dinitrogen (eqn (6)), could occur without electron transfer from iron(0). Density functional theory (DFT) calculations suggest that a pathway of this type is plausible for the formation of hydrazine if a strongly binding ion is present to displace coordinated hydrazine.⁶⁴ Given that a strongly binding anion is not always present in the Leigh system (for example when HBF_4 is used as the acid) this mechanism seems unlikely, but cannot be ruled out completely.



Perhaps the simplest pathway for dinitrogen reduction involves a Chatt type mechanism in which consecutive

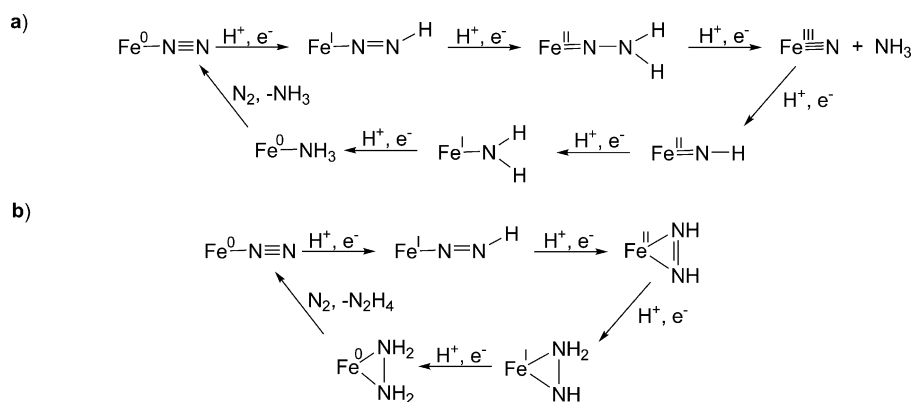


Fig. 3 Proposed pathway for Chatt type conversion of dinitrogen into ammonia: (a) asymmetric protonation; (b) symmetric protonation.

protonation of dinitrogen and electron transfer occurs at a single metal centre (Fig. 1 and 3).¹⁵ Protonation can occur in a symmetric fashion, where N_α and then N_β are successively protonated, or in an asymmetric fashion, where N_β is fully protonated before N_α reacts. Although hydrazine seems like a more reasonable product from symmetric protonation in some cases metal complexes have been shown to catalyse the disproportionation of hydrazine into ammonia and dinitrogen.⁶⁵ As described above, it is believed that Schrock's tris(amido)amine molybdenum catalyst for the conversion of dinitrogen into ammonia follows an asymmetric Chatt type pathway.^{4,14,66} In the Leigh system a Chatt type mechanism seems unlikely; such a mechanism would involve iron(0) which generally functions as a two electron reductant performing one electron chemistry. This mechanism does however seem more reasonable for the Peters system which utilises an iron(i) starting material.⁴⁴ The generation of hydrazine in this system suggests symmetric protonation, and the observation of increased yields when an external reductant is utilised is consistent with less of the iron(i) starting material being consumed as a sacrificial reductant. As more information is gathered about the nature of the final iron species in this system, it may be possible to

predict the modifications that are required to produce a catalytic reaction.

Tyler *et al.* have recently proposed several mechanisms, based on DFT calculations, for generating ammonia from iron(0) dinitrogen species where iron(0) functions as a two electron reductant (Fig. 4).⁶⁴ In these mechanisms two protonations are proposed to occur, either in a symmetric or asymmetric manner, before two electrons are transferred from iron(0). The addition of the first two protons to the same nitrogen (asymmetric protonation) is energetically favoured. However, there is subsequently a large thermodynamic barrier for either the transfer of two electrons from iron(0) or addition of a third proton to form an iron nitride and release ammonia without electron transfer. Symmetric protonation is therefore preferred despite the higher energy requirements of the first few steps. A disproportionation reaction is proposed to account for the formation of ammonia and dinitrogen from coordinated hydrazine. Only ground state energies were calculated for these mechanisms, so the barriers between intermediates are unclear.

A complication which others have previously recognised in regard to the Chatt and Tyler mechanisms relates to the

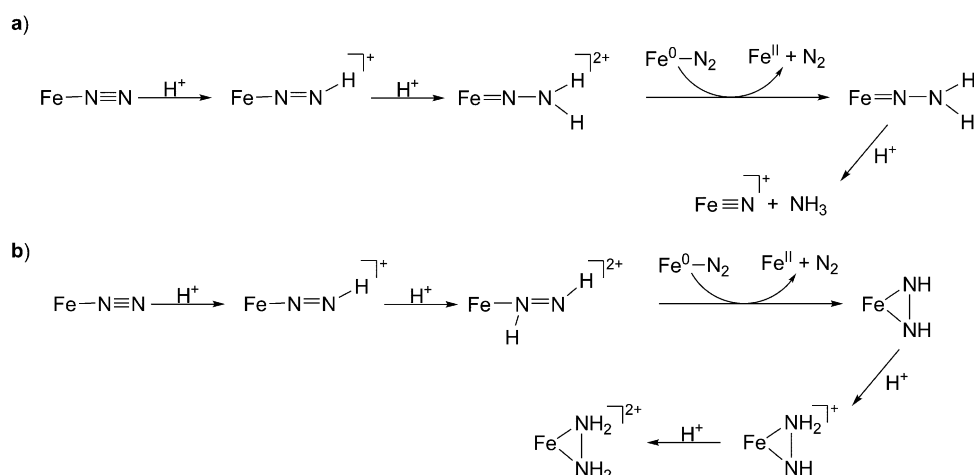


Fig. 4 Proposed pathway for conversion of dinitrogen into ammonia using iron(0) as a two electron reductant: (a) asymmetric protonation; (b) symmetric protonation.

regioselectivity of the first protonation of the iron(0) dinitrogen complex.^{42,64} Both experimental and computational observations suggest that protonation at iron (to generate an iron(II) hydrido dinitrogen complex) is thermodynamically favoured over protonation at the terminal nitrogen.^{42,64} It is possible that protonation at the terminal nitrogen is kinetically preferred or that other ions remaining in solution from the *in situ* preparation of the iron(0) dinitrogen complex may influence the regioselectivity. Furthermore, none of the proposed mechanisms consider the effect of K^+ or Li^+ on the stability of the reaction intermediates or selectivity of the reaction. In fact preliminary evidence suggests that the presence of ions is a crucial factor in the Leigh system but does not affect the Peters system.^{44,67} Experiments in which an isolated iron(0) dinitrogen complex, such as $Fe(N_2)(depe)_2$, is protonated in the presence of ions such as Li^+ or K^+ are yet to be performed and may prove to be informative.

An alternative pathway for dinitrogen reduction could involve bimetallic or multimetallic iron complexes. There are several examples of dinitrogen bridging between two iron(II) centres, two iron(I) centres, and two iron(0) centres.^{29,54–56,60,68,69} These species have not been shown to generate ammonia or hydrazine on protonation and in general appear to be relatively inert compared with monomeric dinitrogen complexes. DFT calculations by Tyler and co-workers suggest that dimerisation of $[Fe(N_2)(DMeOPrPE)_2]$ to form $[Fe_2(DMeOPrPE)_4(\mu-N_2)]$ and dinitrogen is thermodynamically unfavourable. However, this cannot be considered to be a general result as the steric bulk of the ancillary ligands may play a large role in determining whether dimerisation will occur.⁶⁴ Dimeric species are unlikely to play a major role in the first step of dinitrogen reduction, but the possibility of bimetallic or multimetallic intermediates cannot be ruled out even though there is no direct evidence for such compounds at this time.⁷⁰

Despite the impressive amount of research performed to date, a significant amount of further work is required to elucidate the mechanism of dinitrogen reduction at iron. The mechanisms described above are all somewhat limited and it is conceivable that key mechanistic pathways leading to the formation of ammonia have not yet been identified. There are many steps in the pathways presented where the reaction to produce ammonia could be halted or where there could be alternative competing reactions. The strength and concentration of the acid could also be key factors in determining the course of the reaction and only limited attention has been paid to examining their role. Additionally, in most cases investigated, ammonia precipitates out of the reaction in the form of NH_4^+ (similarly hydrazine is typically generated as $N_2H_5^+$). This may provide a driving force that pushes the reaction to completion. Performing detailed mechanistic studies on current systems is experimentally challenging and is complicated by the low yields of ammonia, large numbers of potential intermediates, competing side reactions, and difficulties in accurately measuring the dinitrogen or dihydrogen gas which is produced as a by-product. These obstacles may be overcome through the development of systems which can operate using external reductants and give higher yields of ammonia or hydrazine, as was demonstrated in the Peters system.

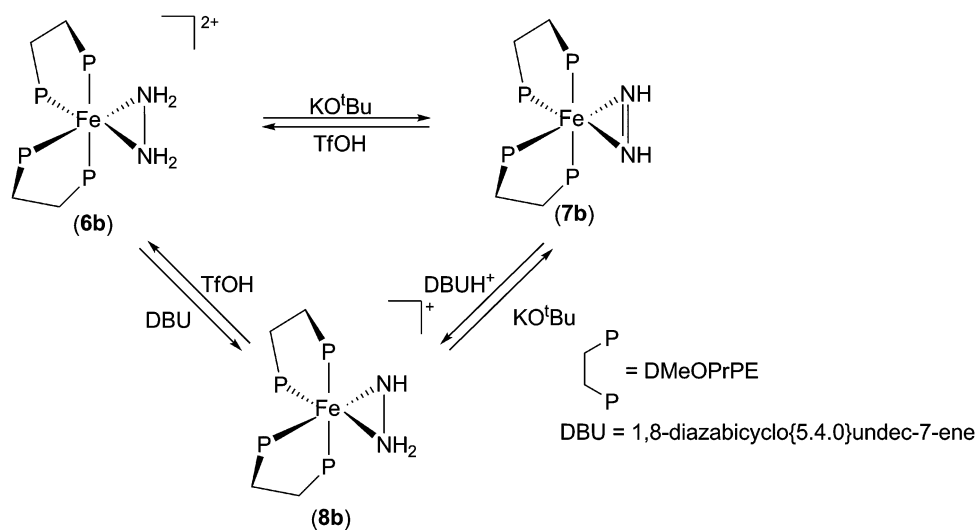
In the last decade a large amount of research has been directed towards finding potential intermediates in ammonia and hydrazine formation. This research will be discussed in the following sections.

Intermediates in the conversion of dinitrogen to ammonia and hydrazine

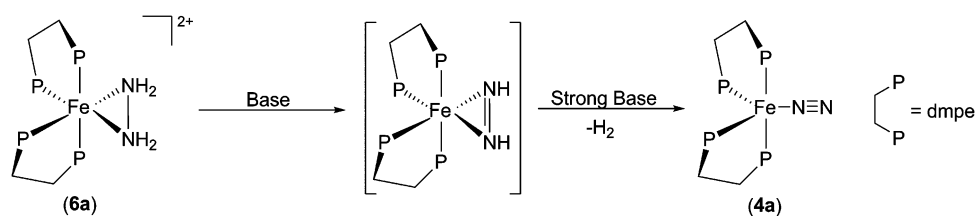
Ground-breaking work on the isolation and characterization of potential intermediates in the conversion of dinitrogen to ammonia was performed by Sellmann and Sutter almost twenty years ago.⁷⁰ Using sulfur based ligands a series of diazene, hydrazine and amine complexes were prepared. In some cases hydrogen bonding between the diazene or hydrazine ligand and the sulfur atoms stabilises the complexes thereby preventing deleterious side reactions. Perhaps the only limitation of this pioneering work is that iron dinitrogen complexes with sulfur based ligands are yet to be prepared and it is not clear if interconversion between the intermediates is possible. This work has been reviewed previously and will not be discussed further here.⁷⁰

The conversion of coordinated hydrazine complexes to coordinated diazene species using base has been recently studied by both Tyler and Field. Both groups initially prepared η^2 -side on hydrazine complexes through reaction of *cis*- $[FeCl_2(dmpe)_2]$ or *cis*- $[FeCl_2(DMeOPrPE)_2]$ with hydrazine.^{71,72} Subsequent treatment of *cis*- $[Fe(N_2H_4)(PP)_2]^{2+}$ (PP = dmpe (**6a**) or DMeOPrPE (**6b**)) with excess base resulted in the isolation of the η^2 -side on diazene species *cis*- $[Fe(N_2H_2)(PP)_2]$ (PP = dmpe (**7a**) or DMeOPrPE (**7b**)) (Scheme 3).^{73,74} The N–N bond length in **7a** (N–N = 1.427(7) Å and 1.398(8) Å from two independent molecules) is suggestive of an N–N single bond with significant back-donation from iron(0) to the diazene.⁷² Unfortunately, DFT calculations performed by both groups have led to divergent conclusions. One group suggests that the bonding is best represented as a donor–acceptor iron(0) π -complex, while the other suggests that a hydrazido(2-) fragment binding to an iron(II) metal centre is the more appropriate resonance form.^{64,72,74} Compound **7a** can also be prepared in low yield through the reduction of *cis*- $[Fe(N_2H_4)(dmpe)_2]^{2+}$ (**6a**) with KC_8 .⁷² The deprotonation of *cis*- $[Fe(N_2H_4)(PP)_2]^{2+}$ is believed to occur in a stepwise manner. Accordingly, treatment of $[Fe(N_2H_4)(DMeOPrPE)_2]^{2+}$ (**6b**) with a weak base resulted in the formation of the singly deprotonated intermediate *cis*- $[Fe(N_2H_3)(DMeOPrPE)_2]^+$ (**8b**), which was spectroscopically characterised (Scheme 3).

Importantly, the conversion of *cis*- $[Fe(N_2H_4)(PP)_2]^{2+}$ (**6**) to *cis*- $[Fe(N_2H_2)(PP)_2]$ (**7**) is reversible as treatment of **7** with acid regenerates the starting material. The transformation of the diazene species to the hydrazido complex with acid could be directly relevant to the mechanism for the conversion of N_2 to NH_3 and suggests that protonation of the coordinated dinitrogen containing species occurs in a symmetric fashion, where the two nitrogen atoms are protonated consecutively. In contrast protonation is proposed to occur asymmetrically in Schrock's Mo system, with N_β being fully protonated before N_α is protonated.^{14,66} Further protonation of *cis*- $[Fe(N_2H_4)(PP)_2]^{2+}$ (**6**) with triflic acid generates ammonia and hydrazine, where the ammonia is presumed to be formed through the



Scheme 3

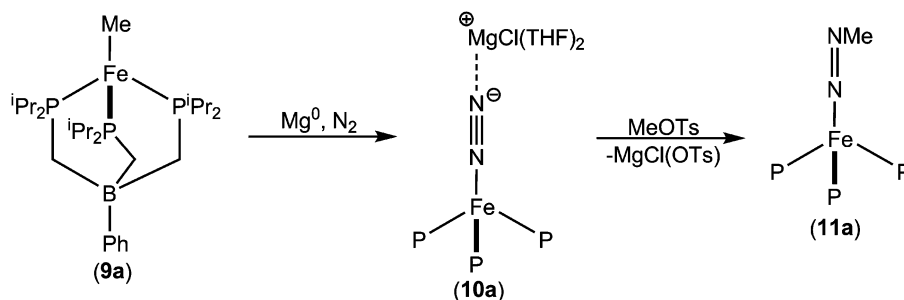


Scheme 4

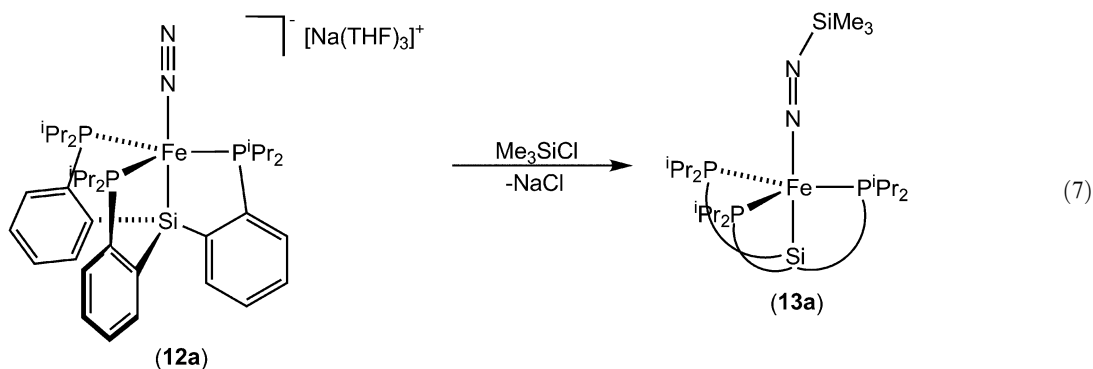
disproportionation of hydrazine into ammonia and dinitrogen but a metal mediated process has not been ruled out.^{71,74}

The formation of a well-defined diazene complex from an iron dinitrogen complex, which requires either dihydrogen or proton and electron equivalents (assuming an Fe(0) diazene is formed), has not been demonstrated with simple bidentate phosphines. (If an Fe(II) diazene is formed only an electrophile is required.) In studying the microscopic reverse, Field *et al.* have been able to deprotonate *cis*-[Fe(N₂H₄)(dmpe)₂]²⁺ (**6a**) with Schlosser's base (KO^tBu and ^tBuLi) to generate the end-on iron dinitrogen compound [Fe(N₂)(dmpe)₂] (**4a**) (Scheme 4).⁷⁴ The diazene complex [Fe(N₂H₂)(dmpe)₂]²⁺ (**7a**) is observed in small quantities but it is not clear if it is an intermediate or a by-product. In 2003, Betley and Peters described the first conversion of a coordinated dinitrogen complex to a coordinated diazenido species using a simple electrophile.⁵² They treated the iron(0)

complex [MgCl(THF)₂][Fe(PhBPⁱPr₃)(N₂)] (**10a**) (formed from [Fe(PhBPⁱPr₃)(Me)] (**9a**) with methyl tosylate to form the monodentate diazenido iron(II) species (**11a**) (Scheme 5). The observed change in ν_{NN} from 1830 cm⁻¹ in **10a** to 1597 cm⁻¹ in **11a** is consistent with a change in the N–N bond order with methylation occurring at the terminal nitrogen rather than at the iron centre. The *pseudo*-tetrahedral geometry of **11a** permits multiple bond character between the metal and coordinated diazenido moiety, thereby stabilising the product. The only other report of the formation of an iron diazenido species directly from coordinated dinitrogen involves attack of Me₃SiCl or Me₃SiOTf on the anionic iron(0) dinitrogen complex [Na(THF)₃][Fe(SiPⁱPr₃)(N₂)] (**12a**) to generate [Fe(SiPⁱPr₃)(N₂SiMe₃)] (**13a**) (eqn (7)).²⁰ The N–N stretching frequency of **13a** is 1748 cm⁻¹, which suggests that the degree of dinitrogen reduction is less than in **11a**.



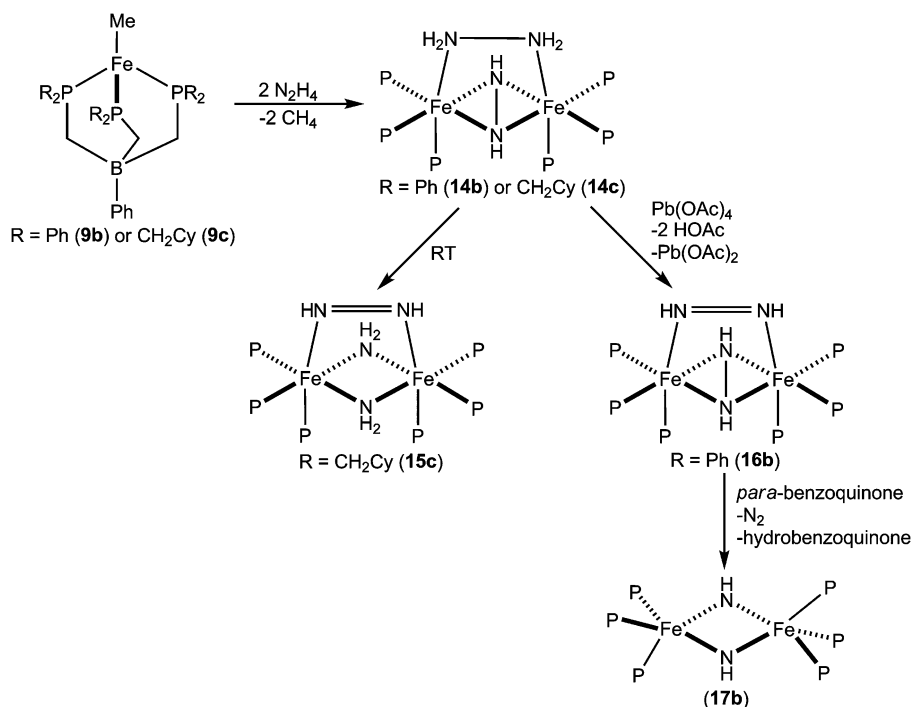
Scheme 5



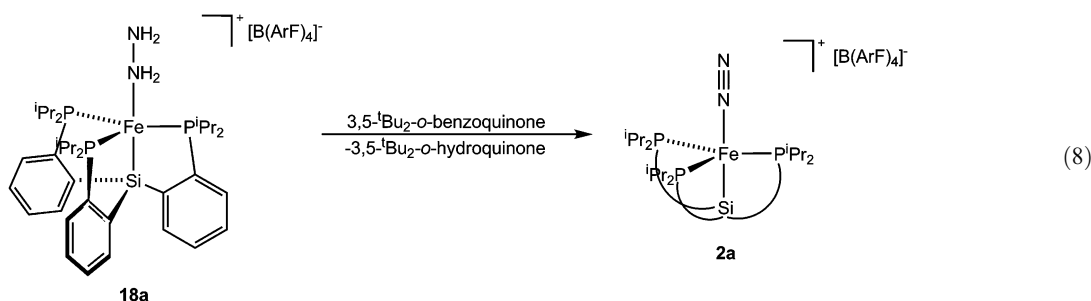
Recently, Peters and co-workers prepared an interesting series of diazene and hydrazido complexes using a tripodal phosphine ligand.⁷⁵ Reaction of the iron(II) alkyls $[\text{Fe}(\text{PhBP}^{\text{R}}_3)(\text{Me})]$ ($\text{R} = \text{Ph}$ (**9b**) or CH_2Cy (**9c**)) with one equivalent of hydrazine results in the release of methane and the formation of the diamagnetic iron(II) dimers (**14**) which contain both $\eta^1:\eta^1\text{-N}_2\text{H}_4$ and $\eta^2:\eta^2\text{-N}_2\text{H}_2^{2-}$ moieties (Scheme 6). The N–N bond distances of the N_2H_4 unit (1.465(3) Å) and the $\text{N}_2\text{H}_2^{2-}$ unit (1.429(3) Å) of **14b** are consistent with a structure containing two N–N single bonds. Compound **14c** is thermally unstable in solution and decomposes to give **15c**, a diamagnetic species with two bridging $\eta^1\text{-NH}_2$ ligands and a neutral $\eta^1:\eta^1\text{-N}_2\text{H}_2$ ligand. The N–N bond distance in the diazene unit of **15c** is 1.283(2) Å, indicative of a double bond. In contrast, **14b** is thermally stable at 60 °C but is readily oxidised by $\text{Pb}(\text{OAc})_4$ to form **16b**, a species with $\eta^1:\eta^1\text{-N}_2\text{H}_2$ and $\eta^2:\eta^2\text{-N}_2\text{H}_2^{2-}$ ligands. Subsequently, **16b** can be further oxidised with *p*-benzoquinone to release hydrobenzoquinone and dinitrogen to form **17b**. The relevance of these compounds to nitrogen fixation is not clear, but they clearly demonstrate that iron can

support a number of different coordination modes of both diazenes and hydrazides. The dimeric iron(II) bridging nitride $[\text{Fe}(\text{PhBP}^{\text{Ph}}_3)_2(\mu\text{-N})][\text{Na}(\text{THF})_3]$ has also been synthesised and reacts with three equivalents of hydrochloric acid to generate ammonia in almost 87% yield.⁷⁶ Thus, the tripodal phosphine ligand $\text{PhBP}^{\text{Ph}}_3$ can support low valent (iron(I) or iron(II)) complexes with dinitrogen, diazenido, hydrazido and nitrido ligands.

The $\text{SiP}^{\text{iPr}}_3$ and SiP^{Ph}_3 ligand systems which Peters and co-workers used to convert dinitrogen coordinated to iron(II) into hydrazine⁴⁴ can also support a number of potential intermediates for dinitrogen reduction.²⁰ Treatment of the dinitrogen complexes $[\text{Fe}(\text{SiP}^{\text{iPr}}_3)(\text{N}_2)][\text{B}(\text{ArF})_4]$ (**2a**) with hydrazine results in the formation of the unusual $\eta^1\text{-N}_2\text{H}_4$ complex $[\text{Fe}(\text{SiP}^{\text{iPr}}_3)(\text{N}_2\text{H}_4)][\text{B}(\text{ArF})_4]$ (**18a**). The related compound $[\text{Fe}(\text{SiP}^{\text{Ph}}_3)(\text{N}_2\text{H}_4)][\text{B}(\text{ArF})_4]$ (**18b**) can be prepared through the reaction of $[\text{Fe}(\text{SiP}^{\text{Ph}}_3)(\text{THF})][\text{B}(\text{ArF})_4]$ with hydrazine. Oxidation of **18a** with 3,5-*t*-Bu₂-*o*-benzoquinone regenerates the terminal iron(II) dinitrogen **2a**, although no diazene intermediates are detected (eqn (8)).²⁰ On the other



Scheme 6

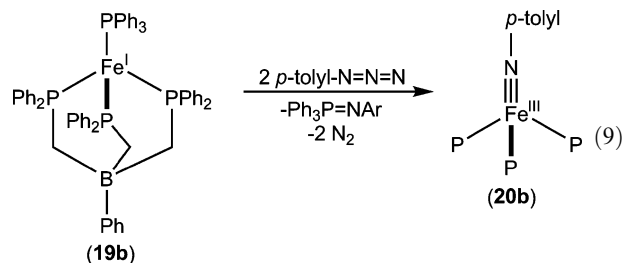


hand, reduction of **18a** and **18b** under an atmosphere of dinitrogen results in the formation of the iron(I) dinitrogen complexes $[\text{Fe}(\text{SiP}^{\text{R}}_3)(\text{N}_2)]$ ($\text{R} = \text{iPr}$ (**1a**) or $\text{R} = \text{Ph}$ (**1b**)) along with both hydrazine and ammonia by-products. The iron(II) ammonia adducts $[\text{Fe}(\text{SiP}^{\text{R}}_3)(\text{NH}_3)]$ can be generated by substitution of hydrazine in **18a** or **18b**. Reduction of the ammonia adduct $[\text{Fe}(\text{SiP}^{\text{iPr}}_3)(\text{NH}_3)]$ under dinitrogen results in the quantitative release of ammonia and the formation of the iron(I) dinitrogen complex **1a**. This is a particularly significant reaction because it demonstrates that it is possible to replace coordinated ammonia with dinitrogen which will almost certainly be a crucial step in any catalytic cycle for the conversion of dinitrogen into ammonia.

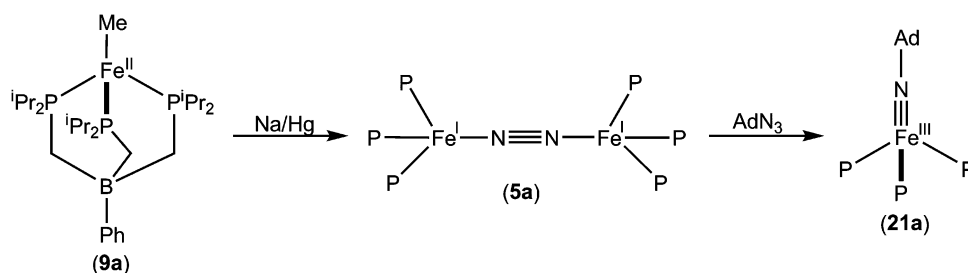
Potential intermediates with iron nitrogen multiple bonds

In the Chatt cycle for dinitrogen conversion into ammonia the same metal must be able to initially bind π -acidic N_2 in a low oxidation state and later bind a π -basic nitride or imide in a high oxidation state.¹⁵ For many years it was believed that iron would not be able to facilitate dinitrogen fixation using a Chatt type cycle, because there were no examples of high valent iron species which could support metal–ligand multiple bonds. Over the last ten years, seminal work by Peters and co-workers has demonstrated that tripodal anionic phosphine donor sets enable the preparation of high valent iron nitrido and imido complexes.^{52,68,77} Initially, Peters *et al.* prepared an iron(III) imide (**20b**) with an $S = \frac{1}{2}$ ground state through the oxidation of the iron(I) precursor (**19b**) with *p*-tolyl azide (eqn (9)).⁷⁷ It is conceivable that the parent NH version of **20b** could be an intermediate in ammonia formation from an iron nitride as shown in Fig. 2. Subsequently, the iron(III) imide (**21a**) was prepared directly from the dimeric iron(I) dinitrogen complex (**5a**) using adamantyl azide (Scheme 7).⁵² A similar reaction between azides and $[\text{Fe}(\text{iPrPDI})(\text{N}_2)_2]$ ($\text{iPrPDI} = 2,6\text{-}(2,6\text{-iPr}_2\text{C}_6\text{H}_3\text{N}=\text{CMe})_2\text{C}_5\text{H}_3\text{N}$) has been

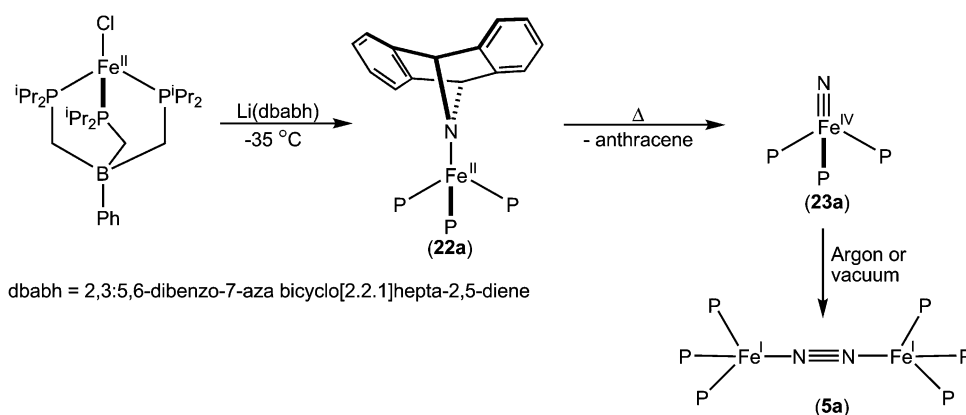
reported by Chirik and co-workers to give the four coordinate iron imide $[\text{Fe}(\text{iPrPDI})(\text{NAr})]$ ($\text{Ar} = \text{aryl}$).^{78,79} The exact oxidation state of Chirik's iron imides is unclear; the zero-field Mössbauer parameters are consistent with either iron(II) or iron(III). Arguably the most significant breakthrough in the development of high valent iron complexes with metal nitrogen multiple bonds was the synthesis of an iron(IV) nitride (**23a**) from the high spin iron(II) amide (**22a**), with concomitant loss of anthracene (Scheme 8).⁶⁸ Interestingly **23a** is unstable under vacuum or argon and readily decomposes into the bridging dinitrogen iron(I) dimer (**5a**). In this $\text{Fe}\equiv\text{N}$ coupling an incredible six electron redox process is mediated by two iron centres. It is proposed that one of the main reasons that **23a** is stable is the low coordination number and *pseudo*-tetrahedral geometry around iron.⁶⁸ This allows the iron centre to form one σ - and two π -bonds with the nitride.



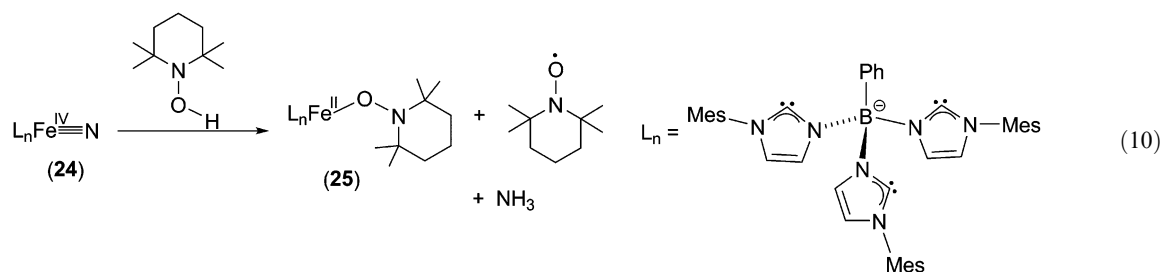
Confirmation that high oxidation state iron(IV) nitrido complexes can in fact generate ammonia was provided by both Betley and Peters and subsequently by Smith and co-workers.^{68,80} Betley and Peters showed that reaction of **23a** with three equivalents of both protons ($[\text{lutidinium}][\text{BPh}_4]$) and electrons (CoCp_2) generates ammonia in 41% yield at room temperature.⁶⁸ Later Smith *et al.* showed that treatment of $[\text{PhB}(\text{MesIm})_3\text{Fe}\equiv\text{N}]$ (**24**), where $\text{PhB}(\text{MesIm})_3^-$ is a triscarbene(borate)ligand, with excess TEMPO-H (TEMPO-H = 1-hydroxy-2,2,6,6-tetramethylpiperidine) results in the formation of high yields of ammonia (74% per equivalent of iron),



Scheme 7



Scheme 8



TEMPO (greater than 95%) and the iron(II) complex [PhB(MesIm)₃Fe(TEMPO)] (**25**) (eqn (10)). Whereas most systems for dinitrogen reduction typically utilise separate proton and electron sources, this reaction is unique in that the protons and electrons appear to come from a single source, TEMPO-H. Hydrogen atom transfer from TEMPO-H to **24** to form an iron(III) imide is proposed as the first step. The reaction of metal hydride [Co(dppe)₂H] with **24** also results in ammonia formation consistent with a single electron mechanism.

Conclusions and future outlook

In the last fifteen years a number of new and unusual iron dinitrogen complexes have been prepared. For example the first well characterised iron(I) dinitrogen complexes have been generated and three and four coordinate complexes which have an unprecedented degree of dinitrogen activation have been synthesised. It is now clear that both iron(0) and iron(I) centres can mediate the stoichiometric conversion of coordinated dinitrogen into ammonia or hydrazine, albeit with relatively low yields. Further work is required to elucidate the mechanism of this reaction and the optimisation of the yields of ammonia and hydrazine may assist in this process. Important work by a number of different groups has demonstrated that iron centres can stabilise a number of potential intermediates such as diazenido, hydrazido, imido and nitrido complexes and a Chatt type mechanism for the conversion of dinitrogen into ammonia in which iron is present in four oxidation states now seems plausible.

Unfortunately, at this stage on most occasions when coordinated dinitrogen is converted into ammonia or hydrazine the exact source of electrons is not clear and well characterised

iron products have not been recovered. Both of these problems represent major barriers to the development of catalytic systems and will need to be addressed. Additionally, a key feature in any potential catalytic cycles is being able to control the delivery of protons and electrons, so that the competing generation of dihydrogen is limited. Although there are still significant obstacles that need to be overcome, it seems likely that an iron based analogue to Schrock's molybdenum system for dinitrogen functionalisation will be discovered.

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