Reactivity and Structure of Complexes of Small Molecules: Dinitrogen

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Introduction

- 1. Group 3 and actinide transition metal–dinitrogen complexes**
- 2. Group 4 transition metal–dinitrogen complexes**
- 3. Group 5 transition metal–dinitrogen complexes**
- 4. Group 6 transition metal–dinitrogen complexes**
- 5. Group 7 transition metal–dinitrogen complexes**
- 6. Group 8 transition metal–dinitrogen complexes**
- 7. Group 9 transition metal–dinitrogen complexes**
- 8. Group 10 transition metal–dinitrogen complexes**
- 9. Group 11 transition metal–dinitrogen complexes**

Conclusion and perspectives

References

Abstract

In this contribution, a comprehensive review of the coordination chemistry of dinitrogen since 2003 is presented. Tremendous advances have been achieved during this time frame on the activation and functionalization of dinitrogen, i.e. fixation, by metal centers. An emphasis is made on these cases. Mechanistic aspects pertaining to functionalization of N₂ are presented.

Keywords

Dinitrogen, reduction, N₂-to-NH₃ catalysis, N₂-to-N(SiMe₃)₃ catalysis, mechanisms

Introduction

This chapter, dedicated to the coordination chemistry of N₂ follows the one from Comprehensive Coordination Chemistry II, and aims to be comprehensive presenting the results obtained since 2003. However, the chapter written in CCCII mainly focused on “Nature’s solution to the nitrogen fixation problem, describing our understanding (up to the end of 2002) of the metal cluster of the nitrogenase enzymes”. We will therefore include in the present review some results that date back from before 2003, which were crucial for the subsequent developments of the N₂ coordination and functionalization.

1. Group 3 and actinide transition metal–dinitrogen complexes

In 1909, Haber patented uranium nitride as heterogeneous catalyst, active enough to be industrial candidates for the N₂-to-NH₃ process.^{1, 2} Bosch, Mittasch and co-workers patented later the use of Fe based catalysts and showed that Y, La, Ce, Th and U in combination with other metals were also active.³ In 1985, Evans reported the first N₂

complex of an f-block element [(Cp*₂Sm)₂(μ-η²:η²-N₂)]⁴, which crystal structure was obtained in 1988.⁵ In 1986, Shur showed that several lanthanide complexes reacted with N₂ (atm pressure, room temp) in the presence of excess of Na/naphthalenide, and that hydrolysis of the reaction medium would generate sub-stoichiometric amounts of NH₃.⁶ Since then, dozens of complexes of rare-earth or actinide N₂ complexes have been reported, with an increase in the number of reports in the past decade, yet their reactivity remains unexplored.

1.1. Preparation of Rare Earth (RE : group 3 and Lanthanides) metal–dinitrogen complexes

The overwhelming coordination mode of N₂ at rare earth metals is side-on between two metals. It is interesting to note that the chemistry of dinitrogen complexes of RE metals is intimately linked to the search for stable RE complexes at the +II oxidation state.⁷ Only a limited number of anionic ligands have been used successfully in this chemistry: Cp derivatives, N(SiMe₃)₂, bulky OAr, Tp (tris-pyrazolylborate) and calix[4]pyrrole.^{8,9} The most common synthetic procedure for the M(N₂) (M = RE) complexes involves reduction under atmospheric pressure of N₂ of a chosen precursor in the +III oxidation state with stoichiometric amounts of strong reducing agents (KC₈, NaK, Li, Na...). In these cases, THF is classically used as solvent, and its coordination in the final complex depends on the size of the M center.

Scheme 1

Following equation 1, scheme 1, [$\{(\text{Cp})_2\text{M}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)$] complexes have been obtained: $\text{M} = \text{Sc}$; “Cp” = Cp”; $\text{M} = \text{Y}$; “Cp” = Cp*; $\text{M} = \text{Nd}, \text{Lu}$; “Cp” = Cp^{tBu3}; $\text{M} = \text{Gd}, \text{Tb}, \text{Lu}$; “Cp” = Cp*; $\text{M} = \text{Lu}$; “Cp” = Cp*Cp”. With other combinations of “Cp” ligands and M, solvated complexes are formed, [$\{(\text{Cp})_2(\text{THF})\text{M}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)$]: $\text{M} =$

Y; “Cp” = Cp’, Cp”, Cp^{TMS}; **M** = **La**, **Ce**, **Pr**; “Cp” = Cp*, Cp”; **M** = **Tb**; “Cp” =, Cp”; **M** = **Dy**; “Cp” =, Cp”, Cp’; **M** = **Lu**; “Cp” =, Cp”.^{10,11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22}

With the bisilylamido ligand N(TMS)₂, [{(NTMS)₂(THF)**M**}]₂(μ-η²:η²-N₂) (**M** = **Y**,²³ **La**, **Nd**, **Tb**,²⁴ complexes were obtained following equation 2, scheme 1.

Bulky aryloxy complexes of [{(OAr)₂(THF)**M**}]₂(μ-η²:η²-N₂) (Ar = 2,6-di*t*BuPh, **M** = **Dy**, **Nd**) have been synthesized according to two different strategies. The first one is similar to the one presented above,²⁵ while the second relies on the accessibility to the M^{II}I₂ precursors (**M** = **Nd**, **Dy**), and substitution of I (Scheme 2).^{26, 27} In addition to these expected complexes, small amounts of one electron reduced complexes were formed (vide infra).

Scheme 2

In fact, this strategy precedes the one involving reduction of the M^{III} precursor for the synthesis of several of the bis amide complexes.²⁷ The group of Takats reported in 2008 the formation of a Tm^(III)-dinitrogen [(Tp’)**Tm**(NHR)](μ-η²:η²-N₂) (Tp’ = hydro-tris(3-*t*Bu-5-Me-pyrazolyl)borate, R = 2,5-*t*Bu₂-C₅H₃) complex while attempting to synthesize the primary imido derivative (Tp’)**Tm**^(III)(NHR).

A third strategy has been discovered in 2013. It is based on the observation that

$[(\text{Cp}^*)(\text{Cp}'')_2\text{Lu}]$ and $[(\text{Cp}^*)_2(\text{Cp}'')\text{Y}]$ react slowly with N₂ (3 weeks) to form the known $\{[(\text{Cp}^*)(\text{Cp}'')\text{Lu}]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)\}$ and $\{[(\text{Cp}^*)_2\text{Y}](\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)\}$. In the sterically crowded precursors the Cp'' ligand in fact coordinates as $(\eta^3\text{-C}_5\text{Me}_4\text{H})^-$ ligand, which elimination as the radical can be photoactivated, leaving an excited d1 metal fragment that can reduce N₂.^{28, 29}

All the dinitrogen ligands bridging two rare earth metals presented above contain the diazenido N₂²⁻ ligand, in light of the N-N bond distances measured between 1.17 and 1.31 Å (compare to N=N bond of trans-diazene 1.247 Å). These complexes thus feature a NN double bond.

As mentioned above Evans initially observed the formation of the one electron reduced derivatives $[\text{K}(\text{thf})_6][\{(2,6\text{-}t\text{Bu}_2\text{C}_6\text{H}_3\text{O})_2(\text{thf})\text{Dy}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)]$ and $[\{(2,6\text{-}t\text{Bu}_2\text{C}_6\text{H}_3\text{O})_2(\text{thf})\text{Dy}\}_2(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-N}_2)\text{K}(\text{thf})]$ as well as $[\text{K}(\text{thf})_6][\{(\text{NTMS}_2)_2(\text{THF})\text{Y}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)]$ and $[\{(\text{NTMS}_2)_2(\text{THF})\text{Y}\}_2(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-N}_2)\text{K}(\text{thf})]$ as byproducts. It was however a very significant discovery and the N-N bond distance of 1.40 Å, as well as EPR and Raman characterization showed that the N₂²⁻ moiety could be further reduced to the trianionic radical hydrazido(3-) ligand, N₂³⁻. Alternatively the $[\{(\text{NTMS}_2)_2(\text{THF})\text{M}\}_2(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-N}_2)\text{K}(\text{thf})]$ (M = Y, Gd, Tb, Dy) complexes could be synthesized by the one electron reduction of the corresponding $[\{(\text{NTMS}_2)_2(\text{THF})\text{M}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)]$ complexes.^{25, 30} In these complexes, the K is bound to the side-on N₂ moiety. This coordination can be prevented by using Na as reducing agent, cryptands of K, or if K(THF)₆⁺ is formed.²⁵ In terms of reactivity, the first successful example of protonation to form the (N₂H₂)²⁻ bridging ligand was given with the anionic Y complex (Scheme 3).³¹ Indeed, none of the neutral rare earth related

complexes (thus featuring N₂²⁻ bridging moiety) showed this type of reactivity, and rather released N₂ upon protonation. In this reaction, the radical N₂³⁻ apparently dismutates into N₂²⁻ and N₂⁴⁻, the latter being protonated. The related Gd (N₂H₂)²⁻ complex could be synthesized from the sequence involving reduction of the neutral [$\{(\text{NTMS})_2(\text{THF})\text{Gd}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)\text{] by KC}_8$, followed by treatment with NEt₃H⁺.³¹

Scheme 3

The chemistry of N₂³⁻ was subsequently developed with the Cp^{''} derivatives.^{32,33} Most notably, the use of the radical trianion of side-on N₂ ligand is shown to allow coupling between two lanthanide ions, promoting strong axial magnetic anisotropy leading to single molecule magnets.²⁰

Further reduction of N₂ to N₂⁴⁻ with rare earth metals was evidenced. Indeed, starting in 1994, Gambarotta reported the coordination of calix[4]pyrrolide(4-) ligand to Sm^(II) and Sm^(III). Coordination of N₂ to the Sm(II) complex formed a dimeric complex in which N₂ is surprisingly not reduced when the reaction is done in THF/hexane, while a trinuclear “Sm^(III)₃(N₂⁴⁻)” complex is formed in THF.⁸ They also used dipyrrolyl coordination to Sm(II) to promote electron transfer to N₂.^{34, 35, 36} In these cases dinitrogen bridged tetrasamarium complexes [$(\text{dipyr})_4\{(\text{THF})\text{Sm}\}_2\text{Sm}_2(\mu_4\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-N}_2)\text{] are formed, in which N}_2$ is coordinated to two Sm centers end-on and to the two others side-

on, with overall four Sm^{III} and N₂⁴⁻ moieties.

In 2017, *ca* almost 30 years after the first report of side-on bridging N₂ complexes of rare earth metals, Evans presented the first example of end-on N₂ coordination in $[\{(\text{NTMS})_2\text{Sc}\}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2)][\text{K}(\text{crypt})]_2$ (crypt = 2.2.2-cryptand) (Scheme 4). Although the $[\text{Sc}(\text{NTMS}_2)_3][\text{K}(\text{crypt})]$ complex does not appear to react with N₂ at room temperature, treatment at low temperature (-35°C) in the absence of light, allowed the synthesis of the bridging N₂ complex. DFT calculations of the paramagnetic complex shows two degenerate HOMOs mainly N₂ π^* in character but also with significant Sc-N₂-Sc π bonding character, and thus features a triplet N₂²⁻ ligand (N-N distance of 1.221(3)Å).³⁷ Irradiation of the complex under Ar liberates N₂ and reforms the $[\text{Sc}(\text{NTMS}_2)_3][\text{K}(\text{crypt})]$ starting species. It is proposed that the small size and high Lewis acidity of Sc³⁺ is responsible for the presence of three anionic amide ligands per metal, and therefore an important steric crowding at the metal favoring the unprecedented end-on coordination in bridging N₂ complexes of rare earth metals.

Scheme 4

In 2019, the group of Zhang and Xi reported a novel ligand platform at Sc to activate and functionalize N₂.³⁸ It involves Cp* and amidinate (Scheme 5). Reduction of the Sc^{III} precursor with stoichiometric amounts of K formed the N₂²⁻ side-on bridging

complex, while reduction with an excess of K in the presence of cryptand [2.2.2] formed the paramagnetic N₂³⁻ bridging complex featuring an elongated NN bond distance (1.3963(16) Å) (between single and double). Most interestingly, only the anionic complex reacted with MeOTf. In the latter complex, the (N₂Me₂)²⁻ fragment possesses a nucleophilic character, and several hydrazine derivatives were obtained in good yield upon reaction with activated electrophiles. Reaction with CO yielded an unsymmetrical dimer in excellent yield via N-C bond formation.

Scheme 5

1.2. Preparation of Uranium metal–dinitrogen complexes

In 1998, Roussel and Scott reported the first actinide-N₂ complex using a bulky trisamido-amine ligand.³⁹ Coordination of N₂, in side-on fashion, proved to be reversible

and the short NN bond distance (1.109(7) Å) suggests that the “U(NN’₃)” fragment acts as a potent Lewis acid, preventing back donation and formal N₂ reduction. The same year, Cummins reported the end-on coordination of N₂ between a U^{III} and a Mo^{III} tris-amide complexes.⁴⁰ A double electron transfer occurs to form the U^{IV}-(N₂²⁻)-Mo^{IV} complex. In 2002, Cloke and Hitchcock provided the second example of side-on bridging coordination of N₂ at U^{III}, using bulky Cp* and pentalene ligands.⁴¹ In that case, magnetic susceptibility and NN bond distance of 1.232(10) Å consistent with N₂²⁻, point to reduction of N₂ by the two U^{III} centers, leading to two U^{IV} centers. Despite the stronger activation of N₂ in this complex, N₂ is readily lost in the solid state or in solution. The same year, Gambarotta reported that the reduction of a U^{III} tetrapyrrole complex by potassium naphthalenide under N₂ resulted in the formation of the bridging dinitrido U^{IV}/U^V complex, in which the NN triple bond has been split.⁴² In 2003, the only mononuclear rare earth or actinide N₂ complex featuring end-on coordination was reported by Evans. Exposure of [UCp*₃] to *ca* 5 atm of N₂ afforded the U^{III}-N₂ complex, which readily releases N₂ upon lowering the pressure (Scheme 7; top).⁴³

It is worth noting here that Gambarotta evidenced the formation of parent amido NH₂ fragment upon the reduction of a Th complex under N₂, although an intermediate N₂ complex was not isolated.⁴⁴ This is the first and sole example of functionalization of N₂ into terminal amide NH₂ in rare earth and actinide complexes (Scheme 6).

Scheme 6

In 2011, Arnold reported the coordination of N₂ at U^{III} [U(OR)₃] complexes (R = 2,6-di-*tert*-butylphenoxide, 2,4,6-tri-*tert*-butylphenoxide, Si(Mes)₃, Scheme 7, bottom), and that the analytical data points the U^{IV}-N₂²⁻-U^{IV} structures.⁴⁵ The OSi(Mes)₃ dinitrogen complex is remarkably thermally stable.⁴⁶

Scheme 7

In 2013, Mazzanti showed that the [U{OSi(OtBu)₃}]₂[K(18-C-6)] reacted with organic azides to form the corresponding imido complexes. The reaction of [U(OSi(OtBu)₃)₂(μ-OSi(OtBu)₃)₂] with CsN₃ at low temperature resulted in the formation of the U^{IV}/U^{IV} bridging nitride Cs{(μ-N)[U(OSi(OtBu)₃)₃]}.⁴⁷ The reactivity of the latter complex was subsequently studied. Its reduction by KC₈ results in the formation of [K₃{[U(OR)₃]₂(μ-N)}] which does react with N₂ to form the [K₃(μ₄-η¹:η¹:η¹:η¹-N)(μ₃-η²:η²:η²-N₂)(U{OSi(OtBu)₃})₃]₂ complex, in which the side-on N₂ moiety is N₂⁴⁻ (Scheme 8).⁴⁸ Protonation of the complex under sub-stoichiometric conditions allowed isolation of the parent imido-dinitrogen complex, while with two equiv. of H⁺, the dinitrogen moiety is protonated to form the bis-bridging imido complex. Most interestingly, reaction with excess H⁺ source under H₂ resulted in 77% formation of NH₃, whereas without H₂ a lower yield of NH₃ is found.

Scheme 8

In 2019, the same group studied the reactivity of a diuranium $U^{III}-O-U^{III}$ complex toward N_2 (Scheme 9).⁴⁹ In this case also a bridging hydrazido 4- is formed, which strong nucleophilic character was evidenced by its reactivity toward excess CO . A cyanamido NCN^{2-} bridged complex is formed resulting from NC bond formation and CO bond breaking. Addition of excess CO to isolated cyanamide complex promotes a slow reduction of the diuranium(V) complex into a bis-oxo diuranium(IV) complex. Unfortunately, the fate of the N containing product could not be identified. Rather surprisingly, protonation of the hydrazido 4- moiety did not result in NH_3 formation but rather in N_2 liberation.

Scheme 9

In conclusion, rare earth and actinide complexes of dinitrogen have been reported quite recently, and their reactivity has not been studied extensively yet. However, first trends can be seen. In the rare earth complexes, it appears that the nucleophilic or basic character of the N atoms of the bridging N₂²⁻ is rather weak, and N₂ is typically liberated rather than functionalized. On the other hand, the one electron reduced species, featuring N₂³⁻ is readily protonated or alkylated, forming the corresponding (N₂H₂)²⁻ and (N₂Me₂)²⁻ bridging species, opening ways to further functionalize dinitrogen. Recent developments at U centers also evidenced the need for strongly reduced N₂⁴⁻ moiety for subsequent functionalization.

2. Group 4 transition metal–dinitrogen complexes

2.1. Ti complexes: synthesis and reactivity

Major developments of the coordination chemistry of N₂ obtained in the 2000s are based on the early works by Vol'pin and Shur, Shilov, and Bercaw. The latter group introduced the Cp* (pentamethylcyclopentadienyl) ligand in the titanocene chemistry, synthesized N₂ complexes and demonstrated reversible end-on coordination depending on the temperature (Scheme 10, top).^{50,51} Teuben, Mach and coworkers have used the less sterically demanding η^5 -C₅Me₄H ligand and reported that unlike the Cp* derivative, the Ti-H complex reacts instantaneously with N₂ to form the bridging end-on [$\{(\eta^5$ -Me₄C₅H)₂Ti₂(μ - η^1 : η^1 -N₂) $\}$].⁵² The group of Chirik studied the effect of systematic modification of the substitution pattern of the Cp ring. They observed changes in both the stability of the N₂ adducts (decreased stability with increasing bulk), and in its coordination mode. Indeed, if the end-on coordination is favored with bulky Cp rings and ansa derivative,⁵³ the side-on coordination is observed in [$\{(\eta^5$ -1,2,4-Me₃C₅H₂)₂Ti₂(μ - η^2 : η^2 -N₂) $\}$] (Scheme 10, middle).⁵³ This coordination results in a significant N-N bond elongation to 1.216(3) Å, indicating a two electron reduction to N₂²⁻. Reduction of the bond order was classically associated with increased reactivity at the N₂ fragment, yet reaction with H₂ liberated N₂ and formed the dihydride complex. When the steric bulk was reduced further, a trimetallic Ti complex was formed in which the N₂ binds in a μ_3 - η^1 : η^2 : η^1 fashion. It features the longest N-N bond in titanocene complexes (1.320(3) Å) (Scheme 10, bottom left).⁵⁴

Scheme 10

Reduction of Cp^*TiCl_3 under N_2 in the presence of fulvene derivatives resulted in the formation of related end-on complexes.⁵⁵

Simple bis-silylamide ligands were shown by Gambarotta to stabilize reduced Ti complexes bearing strongly activated N_2 moieties.⁵⁶ Indeed, N-N bonds of 1.379(21) Å and 1.263(7) Å are measured in the anionic mixed valent complex $[\text{Li}(\text{tmeda})][\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Ti}\}_2(\mu-\eta^2:\eta^2-\text{N}_2)_2]$ (Scheme 10, bottom right) and $[\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{TiCl}(\text{tmeda})\}_2(\mu-\eta^1:\eta^1-\text{N}_2)]$ respectively. The same group then reported the use of tridentate ligands featuring pyrrolide moieties. Reduction of a Ti^{III} precursor LTiCl ($\text{L}=2,5\text{-}\{(\text{C}_4\text{H}_3\text{N})\text{CPh}_2\}_2\text{C}_4\text{H}_2\text{N}(\text{Me})$) under N_2 with various amounts of Na/Hg in DME resulted in N-N bond splitting in the coordination sphere of Ti (Scheme 11). Using

THF as crystallization solvent resulted in protonation of one of the two bridging nitride moieties, and reaction with SiMe₃Cl yielded the imido complex [LTiNTMS].

Scheme 11

A bis-guanidinate titanium dichloride complex was reduced with Mg under N₂ to yield the end-on $\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2$ bridging complex. The N-N bond of 1.28(1) Å is significantly longer than in the related end-on Cp derivatives, which explains its stability under reduced pressure. The reported reactivity of the complex however shows facile displacement of N₂, and no functionalization at N.⁵⁷ The group of Liddle obtained a major achievement in 2018, using a tetradentate tris-amido-amine. The stepwise reduction of the Ti^{IV} precursor was studied, and the end-on [$\{(\text{Tren}^{\text{TMS}})\text{Ti}^{\text{III}}\}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2)$] and [$\{(\text{Tren}^{\text{TMS}})\text{Ti}^{\text{IV}}\}_2(\mu_4\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-N}_2\text{K}_2)$] complexes were thus synthesized (Scheme 12). In the latter complex, the K cations are bound to the N₂ moiety and the N-N bond is highly elongated to 1.315(3) Å compared to 1.121(6) Å in the Ti^{III} complex. Addition of cryptant resulted in charge separation and further N-N bond elongation

(1.461(7) Å), suggesting Ti-imido character. However, Raman stretch which is a better indicator of N₂ activation, suggests a reduced activation in the latter complex. Most interestingly, the authors showed that the $[(\text{Tren}^{\text{TMS}})\text{Ti}^{\text{IV}}]_2(\mu_4\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-N}_2\text{K}_2)$ complex catalyzes the production of up to 18 equivalents of NH₃, making this complex the only homogeneous Ti species competent for catalytic reduction of N₂ into NH₃.⁵⁸

Scheme 12

In 2019, the same group reported a Haber-Bosch like approach to stoichiometric N₂ functionalization.⁵⁹ Indeed, they evidenced a homogeneous reductive cleavage of N₂ to N³⁻ by a Ti-Mg complex, as well as conversion to NH₃ using H₂, split by a frustrated Lewis pair (FLP). Starting from the $[\text{Ti}(\text{Tren}^{\text{TMS}})\text{Cl}]$ complex, reduction by excess Mg over 3 days resulted in the formation of the bis-μ³-nitrido complex $[\{\text{Mg}(\text{Tren}^{\text{TMS}})\}_2\{(\mu_3\text{-N})_2(\text{Ti})_2\}]$ in 20% yield. Major ligand rearrangement is observed during this reaction. It is interesting to note that N₂ is reduced to the N³⁻ state in this case, whereas it was reduced to N₂⁴⁻ with KC₈, despite Mg ($E^\circ = -2.37$ V) being a weaker

reducing agent compared to K ($E^\circ = -2.92$ V). The authors suggest that the cooperative combination of Ti and Mg for the six electron reduction of N₂. Subsequent hydrolysis produced near quantitative amounts of NH₃, whereas treatment with D₂ and PtBu₃/BCF (6 equiv.) formed 0.29 equiv. of ND₃.

As an alternative strategy to activate and functionalize N₂, Hou and coworkers reacted the mixed valent Ti^{III}/Ti^{IV} bridging hydride trimetallic complex $[\{(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)\text{Ti}\}_3(\mu_3\text{-H})(\mu_2\text{-H})_6]$ with N₂. Several intermediates along the path of N₂ functionalization were characterized, proving the NH bond formation from both bridging nitride and hydride (Scheme 13, top).⁶⁰ In 2016, the same group reported the synthesis of a mixed amide/nitride tetranuclear Ti complex as well as the subsequent functionalization of the four N atoms with a variety of acid chlorides (alkyl and aryl) to yield nitrile derivatives in good to excellent yields (60 to 84%) (Scheme 13, middle).⁶¹ Hydrogenolysis of a (PNP)Ti(CH₂SiMe₃)₂ Ti^{III} complex under a mixture of H₂/N₂ afforded the binuclear $\{[(\text{PNP})\text{Ti}]_2(\mu_2, \eta^1, \eta^2\text{-N}_2)(\mu\text{-H})_2\}$ complex (Scheme 13, bottom). Subsequent hydrogenation under mild conditions (1 atm, 60°C), allowed N-H bond formation and NN bond splitting,⁶² a reactivity observed previously by Fryzuk et al. at Zr (vide infra).

Scheme 13

2.2. Zr and Hf complexes: synthesis and reactivity

The group of Fryzuk has studied for ca 30 years the polydentate (poly-)anionic ligands featuring phosphine and amido donors. The reduction of the [(PNP)ZrCl₃] under N₂ provided the first Zr side-on coordinated [{(PNP)ZrCl}₂(μ-η²:η²-N₂)] complex, featuring an activated N₂ unit, as shown by the very long N-N bond of 1.548(7)Å (Scheme 14).⁶³ This discovery was the starting point of their extensive work dealing with

N₂ activation and functionalization.⁶⁴ The PNP complex proved too reactive toward H₂ or silane, likely because of phosphine dissociation, which prompted the development of the macrocyclic P₂N₂ dianionic ligand. Reduction of the corresponding Zr^{IV} complex resulted in the formation of the bimetallic side-on bound N₂ complex [$\{(P_2N_2)Zr\}_2(\mu-\eta^2:\eta^2-N_2)$]. Hydrogenation of the side-on N₂ with H₂ resulted in the formation of [$\{(P_2N_2)Zr\}_2(\mu-\eta^2:\eta^2-N_2H)(\mu-H)$], while the addition of Si-H bond formed the related [$\{(P_2N_2)Zr\}_2(\mu-\eta^2:\eta^2-N_2SiH_2Bu)(\mu-H)$]. Most notably, the NH bond formation was the first case of hydrogenation of coordinated N₂.⁶⁵ CN bond formation was also demonstrated through alkyne addition. The reaction involves a [2+2] cycloaddition between Zr-N and the C≡C bond, followed by protonation of the Zr-C bond by the terminal alkyne.⁶⁶

Scheme 14

Because side-on coordination of N₂ in these complexes appeared key to its reactivity, the group of Chirik studied the effect of substitution pattern of Cp ligands in zirconocene and hafnocene complexes of N₂. Sodium amalgam reduction of $[(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{ZrCl}_2]$ under N₂ furnished the $[\{(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{Zr}\}_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-N}_2)]$ with side-on coordination (featuring N₂⁴⁻ moiety) (scheme 15).⁶⁷ The solution behavior however pointed equilibrium between the end-on and side-on complexes (10-15% of the end-on). Synthesis of the Hf congener revealed only side-on coordination.⁶⁸

Scheme 15

These activated N₂ complexes react with H₂ to form the corresponding dihydride diazenido derivatives $[\{(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{M(H)}\}_2(\mu\text{-}\eta^1\text{-}\eta^1\text{-N}_2\text{H}_2)]$, with the Hf complex being *ca* four times faster than the Zr analogue.⁶⁹ A detailed kinetic study, involving isotopic labeling, of the H₂ addition lead to a mechanistic proposal in which the H₂ 1,2-addition on Zr-N is rate determining. The corresponding transition state involves simultaneous H-H bond breaking and Zr-H and N-H bond formation.⁶⁷ DFT calculations supported this mechanism.⁷⁰ The outcome of thermolysis of the Zr and Hf $[\{(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{M(H)}\}_2(\mu\text{-}\eta^1\text{-}\eta^1\text{-N}_2\text{H}_2)]$ complexes differed drastically. Indeed, if H₂ loss was observed in both cases, N-N bond breaking occurred in the Zr complex, leading to μ -nitrido, μ -NH₂

moieties, whereas CH activation of the ligand was seen in the Hf complex.⁶⁸ If the thermal treatment of the Zr complex is done under H₂, formation of the Zr dihydride is observed together with the elimination of NH₃ from the coordination sphere of the Zr.⁷¹ The reactivity of the coordinated N₂⁴⁻ moiety toward various sources of protons was then studied. Protonation by H₂O or EtOH liberates hydrazine from the Zr, whereas addition of amines or terminal alkynes left “N₂H₂” moiety in the coordination sphere (scheme 16).⁷²

Scheme 16

When one cyclopentadienyl ligand was changed to an indenyl ligand, the presence of the arene ring resulted in markedly different N₂ complexes.⁷³ It is to be noted that at least two alkyl groups are to be present on the Cp moiety of the indenyl for the success of the

reduction of the Zr^{IV} precursor (scheme 17). Reduction under Ar leads to $\eta^5:\eta^4$ coordination of the indenyl at a single Zr center. When this species is exposed to an N₂ atmosphere, a bimetallic complex featuring a $\mu\text{-}\eta^1:\eta^1$ end on N₂ ligand is formed. On the other hand, when the reduction was performed under N₂, a bimetallic complex with a end-on side-on N₂ ligand is preferably formed. With two indenyl ligands, reduction of the Zr^{IV} precursor under N₂ resulted in the inclusion of one equivalent of the salt (NaX) per Zr center in addition to the expected coordination/reduction of N₂.⁷⁴ Most interestingly, hydrogenation of this complex resulted in the double NH bond formation, proving that end on coordinated N₂ could also undergo 1,2 additions of H₂.

Scheme 17

Finally, the N₂ coordinated ansa-zirconocene complex $[K\{Me_2Si(C_5Me_4)_2Zr(\mu-Cl-1\kappa,2\kappa)\}_2(\mu-\eta^1:\eta^1-N_2)]$ proved to undergo reversible end-on to side-on switch upon one electron redox process (scheme 18).⁷⁵

Scheme 18

The authors reinvestigated the coordination of N₂ in the complex resulting from the reduction of $[Cp_2Zr(CH_2(SiMe_3)_2)Cl]$. Lappert initially proposed the formation of the monomeric complex $[Cp_2Zr(CH_2(SiMe_3)_2)(N_2)]$ favoring a side-on rather than the end-on coordination. When the solid was kept under vacuum, dimerization occurred as shown by crystallization from toluene, and bridging end-on was proposed,^{76, 77} later proved by Chirik.

The same group further studied the reactivity of the Hf complex $[\{ (\eta^5-C_5Me_4H)_2Hf \}_2 (\mu-\eta^2:\eta^2-N_2)]$ toward polar electrophiles, such as CO₂ and PhNCO,⁷⁸ and observed N-C bond formations. Elimination of a hydrazine derivative could be achieved (scheme 19).⁷⁹

Scheme 19

Related chemistry involving cyclopentadienyl steric and electronic tuning was subsequently developed, and significant changes in the reactivity at N were observed proving the richness of this chemistry. The reactivity of the $[\{(\eta^5\text{-C}_5\text{Me}_3\text{H}_2)_2\text{Hf}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)]$ is particularly rich, showing successive N-C, N-B and N-Si⁸⁰ bond formations (scheme 20).⁸¹ The isocyanato μ -nitrido complex $[\{(\eta^5\text{-C}_5\text{Me}_3\text{H}_2)_2\text{Hf}\}_2(\mu\text{-N})(\text{NCO})]$ obtained upon reaction with CO⁸² demonstrated a versatile reactivity of the bridging nitride. Indeed, reactions with nitrile, isocyanate, CO₂ as well as allenes and activated alkyne was observed.⁸³

Scheme 20

The chemistry of ansa-hafnocene complex $[\{\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_3\text{tBu})\text{Zr}\}(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)]$ was studied simultaneously.⁸⁴ In this case, reaction with one equiv. of CO leads to NN splitting, as above, followed by CH activation of a tBu group of a ligand by the bridging nitride. Alternatively, double CO addition to form a $(\text{N}_2\text{C}_2\text{O}_2)^{4-}$ ligand was observed under 1 atm. of CO (scheme 21).

Scheme 21

3. Group 5 transition metal–dinitrogen complexes

Despite the fact that one type of nitrogenase enzyme contains a vanadium center, the dinitrogen chemistry of group 5 metals has been developed rather late compared to discoveries of M-N₂ complexes in the 60s. Indeed, the first dinitrogen complex of group 5, a Ta complex, was reported in 1980 by Schrock and co-workers.⁸⁵ Only a few reports precede 2003, and therefore will be included in this chapter for the sake of providing a historical perspective.

3.1. Vanadium complexes: synthesis and reactivity

The first vanadium N₂ complex was obtained in 1989 by Gambarotta more than twenty years after the discovery of the first Ru-N₂ complex by Allen and Senoff. It was obtained from the reaction between *trans*-(TMEDA)₂VCl₂ with two equivalents of an anionic ligand [o-(CH₃)₂NCH₂)C₆H₄]⁻Li under N₂. The bimetallic complex featured an

end-on bridging N₂ ligand, for which a NN bond distance of 1.228(4) Å was measured suggesting a reduced N₂²⁻ ligand. Magnetic susceptibility on the other hand supports two formal V^{II} centers, and thus marginally reduced N₂ ligand, also in accord with facile displacement by pyridine.⁸⁶ This example already points that in group 5, as in all other groups, the elongation of the NN bond distance compared to free N₂ is a poor indicator of NN bond reduction upon coordination, as well as a poor guide for N functionalization. Three years later, in 1992, Rehder reported the V anionic analogue [V(dppe)₂(N₂)₂][Na(THF)] of the extensively studied [Mo(dppe)₂(N₂)₂], synthesized in 1969. This complex is a rare example featuring a terminal end-on N₂ ligand at group 5 metals. It is obtained by reduction of VCl₃ with Na sand in the presence of dppe, under N₂.⁸⁷ The complex decomposes in solution within days and hydrolysis with excess HBr generates NH₄⁺ (one equiv. per complex). The dmpe analogue was reported in 1994.⁸⁸ In the following years, the group of Gambarotta studied N based ligands to obtain V-N₂ complexes, such as amide, polydentate amides⁸⁹ and amidinate.⁹⁰ In 1995, the same group synthesized an anionic V-nitride dimer [((SiMe₃)₂N)₂V(μ-N)]₂⁻ via hydrogenolysis of a vanadacyclobutane complex under N₂, N₂ being the source of the bridging nitride ligands.⁹¹ Few years later, in 1999, Cloke also observed direct N₂ cleavage upon reduction of a V^{III} complex featuring a tridentate diamidoamine ligand (scheme 22). Reduction by two electrons yielded the paramagnetic anionic complex with symmetrical V-μN bond distances. The 15 line EPR spectrum at 293K in toluene is consistent with the unpaired electron of the d1 V^V-V^{IV} dimer being delocalized in solution.⁹² Oxidation with Ag⁺ forms the doubly nitride-bridged V^(V)-V^(V) dimer, as a diamagnetic complex. The VN bond distances are unsymmetrical, 1.769(10) Å and 1.862(10) Å in this dimer.

Scheme 22

In 2005, Gambarotta showed that a tridentate [NNN] Pyridine-bis-imine ligand could be non-innocent and either accept or give electron from or to the metal center (scheme 23).⁹³ DFT calculations on simplified models (Me instead of 2,6-(*i*Pr₂)C₆H₃) point that $S = 0$ and $S = 1$ are close in energy and provide very similar geometries. In 2012, Chirik prepared a related bisimino-pyridine ligand (R = Ph), and observed a similar complex featuring a reduced dianionic tridentate ligand.⁹⁴ In 2006, Schrock reported the second example of monometallic terminal end-on N₂ complex of V, [V(HIPTN₃N)(N₂)]K supported by the very bulky tetrapodal, trianionic (HIPTN₃N)³⁻ ligand.⁹⁵ It was obtained by reduction of the [V(HIPTN₃N)(THF)] complex under N₂, and is stable at room temperature, although N₂ can reversibly dissociate under these conditions.

Scheme 23

In 2007, the dipyrroliide-pyrrole dianionic [NNN]²⁻ ligand was designed to provide variable σ and π donation. Reduction of the V^{III} precursor yielded the mononuclear V^{II} complex, and coordination of N₂ could only be achieved upon THF abstraction by AlMe₃ in toluene under N₂ (scheme 24). The magnetic moment measurement shows the two V centers in V^{II} oxidation state, in accord with modest NN bond distance elongation (1.248(5) Å), as well as easy displacement by THF. Interestingly, this complex could be reduced to induce NN bond cleavage. Thus, upon reaction with KC₈ (2 equiv.), the mixed-valent V^{III}, V^{IV} μ -nitrido was formed as primary product, following an unknown mechanism. Reaction with the ¹⁵N isotopomer nonetheless proved the nitride N atom to result from N₂ cleavage.⁹⁶

Scheme 24

Mindiola reported that an anionic tridentate [PNP][−] ligand supported the formation of the diamagnetic divanadium μ -N₂ complex, $[[\text{PNP}]\text{V}(\text{tBuCH})]_2(\mu\text{-}\eta^1:\eta^1\text{-N}_2)$, with a short NN bond distance of 1.246(6) Å, as well as short imide VN bond (1.757(3) Å).^{97, 98} The lack of N₂ displacement by tBuCN is consistent with the proposal of V^V centers. The same group later showed that N₂ can coordinate a V^{II} complex featuring bulky NacNac and ArO[−] ligands, leading to two antiferromagnetically coupled V^{III} centers bridged by the reduced end-on N₂ ligand (scheme 25). DFT calculations rationalize the reluctance of the dimer to split N₂ to form the corresponding V-nitride (barrier of > 80 kcal/mol).⁹⁹ Nocera reported the coordination of N₂ at V^{III} stabilized by a bulky alkoxy ligand (tBu)₂(CH₃)CO[−], following THF dissociation. Here also, the [V^{III}, V^{III}] bridging N₂ complex readily loses N₂ in solution.¹⁰⁰

Scheme 25

Cummins reported in 2014 the V-(μ-N₂)-Mo heterobimetallic complex to be formed by the reaction between [Mo(N(*t*Bu)-3,5-Me₂)C₆H₃)₃] and [V(N(*t*Bu)-2-(NMe₂)-5-(Me)C₆H₃)₂] under N₂. Unlike what is observed with the homobimetallic Mo complex, *vide infra*, this complex does not split N₂.¹⁰¹ Also in 2014, Kawaguchi synthesized the [[ONO]V(THF)] complex featuring a [ONO]³⁻ ligand, 2,6-(3-*t*Bu-5-Me-2-OC₆H₂CH₂)₂-4-*t*Bu-(*p*-tolyl)NC₆H₄)₂. Reaction with KH under N₂ resulted in H₂ elimination and formation of [[{ONO}V(μ-N)]{K(DME)}₂]₂, a paramagnetic [V^{IV},V^{IV}] bis (μ-N) complex (scheme 26). The absence of NN bond is evidenced by the NN distance of 2.550(3) Å for the V₂N₂ core. Two electron oxidation results in significant ligand reorganization, back to κ³ [ONO] coordination at V, forming the V^V nitride dimer, [[ONO]V(N)(μ-K(DME))]₂.¹⁰²

Scheme 26

Functionalization of the nitride was achieved with CO and CNXyl, leading to cyanate and carbodiimide complexes respectively. Most interestingly, addition of 2-butyne on the cyanate complex in toluene allowed for KNCO elimination (because of its precipitation in this solvent) from the coordination sphere and formation of the $[[\text{ONO}]\text{V}(\eta^2\text{-butyne})]$ complex. The alkyne can be displaced by THF, regenerating the starting complex. Unfortunately, elimination of KNCO by THF is not feasible because of its solubility in this solvent, which precluded development of a catalytic cycle.

3.2. Niobium dinitrogen complexes: synthesis, NN bond cleavage and functionalization

The first niobium N₂ complex was obtained in the mid-90s by Gambarotta. The diamagnetic $[\text{Nb}(\text{NCy}_2)_3]_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2)$ complex was obtained through reduction of the Nb^{IV} precursor under N₂ (scheme 27, top). The complex is thermally robust in solution, and N₂ was not readily displaced by classical strong σ donors.¹⁰³

Scheme 27

Cummins et al. synthesized a neutral, paramagnetic Nb-(μ -N₂)-Mo heterobimetallic complex in 2000 (scheme 27, bottom).¹⁰⁴ Electrochemistry suggested that the one electron reduction of the complex would result in NN bond splitting, which was confirmed chemically. When the anionic Nb nitride complex was oxidized, a cyclic trimer [Nb(N(iPr)Ar)₂(μ -N)]₃ was obtained. A complete synthetic cycle was achieved based on this system. Reaction of the anionic nitride intermediate with acylchlorides (R = tBu, Ph, Me, 1-adamantyl, vinyl) generates the desired nitriles and the [Nb(N(iPr)Ar)₂(O)] complex. Transformation into the bis-triflate followed by one electron reduction closes the synthetic cycle.¹⁰⁵

Scheme 28

Floriani reported the use of *p*-(*t*Bu)-calix[4]arene, “calix”, as precursor to tetraanionic O ligand. The reduction of the [(calix)NbCl]₂ dimer by four electron under Ar leads to the formation of [(calix)Nb]₂Na₂(THF)₆ which subsequently reacts with N₂ to form the [(calix)Nb]₂(μ-η¹:η¹-N₂)²⁻ dianion which crystal structure was obtained from diglyme as the ion pair with [Na(diglyme)₂]⁺ as counter ion (scheme 29).¹⁰⁶ In this complex, the remarkably long NN bond distance of 1.390(17)Å and the long NbN bond distance (1.748(12)Å) support the presence of N₂⁴⁻ hydrazido bridging moiety. It is to be noted that calculations were performed to explain this unusually long NN bond distance. Although all other metrical parameters were reproduced, the calculated NN bond distance fall within the range 1.26-1.30Å.¹⁰⁷ Anyhow, further reduction of the dimer by two electrons resulted in NN bond splitting and formation of the nitride dimer, featuring a planar Nb₂N₂ core with N...N separation of 2.598(8)Å.¹⁰⁸

Scheme 29

A related, tris-aryloxy [OOO]³⁻ trianionic ligand system was reported by Kawaguchi. The reaction of the [[OOO]NbCl₂]₂ precursor with LiBEt₃H under N₂ formed the [[OOO]Nb(μ-N)Li(thf)]₂ complex (scheme 30, top).¹⁰⁹ The ¹⁵N NMR spectrum of the complex synthesized under ¹⁵N₂ showed a signal at 312 ppm. The crystal structure showed the two bridging nitride to be arranged in an unsymmetrical fashion (Nb-N of 1.892(3) and 1.935(3) Å). In this case also, the N...N separation of 2.569(5) Å indicates full NN bond cleavage. With another tris-aryloxy [OOO]³⁻ trianionic ligand, the same group later reported that the tetrahydride complex [(CH(3,5-*t*Bu)₂-2-OC₆H₂)₃Nb(μ-H)₂]₂²⁻ 2[K(DME)]⁺ reacts with N₂ to form the corresponding dianionic [Nb^V, Nb^V] bis(μ-nitrido) complex, without the need for external reducing agent (scheme 30, bottom). Here also, the long NN distance of 2.589(5) Å indicates NN cleavage.¹¹⁰ The mechanisms of the NN bond cleavage in these two cases have been evaluated by DFT.¹¹¹ Alkylation of the nitrido was achieved with MeI. After reaction with pyridine, the

terminal methylimido complex was reacted with CO₂ to generate a mixture of bridging oxo and dianionic dimethylurea complexes.

Scheme 30

In 2015, the group of Mindiola used a very bulky aryloxy ligand to achieve NN bond splitting at Nb. Reduction of the $[(\text{ArO})_2\text{Nb}(\mu\text{-Cl})\text{Cl}_2]_2$ complex ($\text{ArO} = 4\text{-tBu-2,6-}(\text{CHPh}_2)_2\text{C}_6\text{H}_2\text{O}$) by six electrons under N₂ generates the formal $[\text{Nb}^{\text{V}}, \text{Nb}^{\text{V}}]$ bis(μ -nitrido) complex, $[(\text{ArO})_2\text{Nb}(\mu\text{-N})]_2$ (scheme 31). The mechanism involves formation of a low

valent Nb^{II} intermediate, which coordinates a N₂ molecule to which six electrons are transferred resulting in NN bond splitting (NN distance of 2.56 Å).¹¹² The bis(μ-N) complex can be reversibly reduced by one electron to form the formal mixed valent [Nb^{IV}, Nb^V]bis(μ-nitrido), which EPR spectrum at room temperature validates a delocalized electron over the Nb₂N₂ core. Treatment of both of these complexes with excess acid indicated stoichiometric NH₄⁺ production.

Scheme 31

In the late 90s, Fryzuk designed dianionic tripodal [NPN]²⁻ and tetrapodal [P₂N₂]²⁻ ligands for the stabilization of M-dinitrogen complexes. The first Nb complex, [(NPN)NbCl]₂(μ-η¹:η¹-N₂), reported in 2001, features a bridging N₂ with a solid state bond distance of 1.237(4) Å, and is proposed to formally have two Nb^V centers (scheme 32).¹¹³ The paramagnetic [(P^{Ph}₂N₂)Nb]₂(μ-η¹:η¹-N₂) complex was synthesized by reduction of the Nb^{III}Cl precursor with KC₈ under N₂. Variable temperature magnetic studies and EPR data concur to propose two Nb^{IV} centers coupled antiferromagnetically through the bridging hydrazido N₂⁴⁻ moiety.¹¹⁴ Thermolysis of this complex at 110°C results in NN bond cleavage and single bridging nitride formation. The second N atom appears to have inserted into the backbone of one of the [P₂N₂] ligand, provoking a

rearrangement. Methylation of the $[(P^R_2N_2)NbCl]$ ($R = Ph, Cy$) precursor induces reversible N₂ coordination and dimer formation.¹¹⁵

Scheme 32

In addition to the V complex, Mindiola reported the synthesis of $[[PNP]NbCl_2]_2(\mu-\eta^1:\eta^1-N_2)$ ($[PNP] = [N(2-P(iPr)_2-4-(CH_3)C_6H_3)_2]$) from the reduction of the $[[PNP]NbCl_3]$ precursor, forming the $[[PNP]NbCl_2]$ as intermediate.¹¹⁶ The short NbN and elongated NN bond distances ($1.851(3)\text{\AA}$ and $1.277(6)\text{\AA}$ respectively), together with DFT calculations point a bonding of the core between $Nb=N-N=Nb$ and $Nb=N=N=Nb$.

3.3 Tantalum dinitrogen complexes: synthesis and reactivity

The first tantalum N₂ complex was obtained as early as 1980 by Schrock.⁸⁵ Reduction of

the Ta^V alkylidene [Ta(PMe₃)₂(Me₃CCH)Cl₃] by Na/Hg under N₂ in the presence of additional PMe₃ yielded the [Ta(PMe₃)₂((CH₃)₃CCH₂)Cl]₂(μ-η¹:η¹-N₂). Presence of bridging N₂ was confirmed by reaction with HCl and acetone. Furthermore, alkylation of this complex with RLi (R = Np or Me) formed the corresponding [Ta(PMe₃)₂((CH₃)₃CCH₂)R]₂(μ-η¹:η¹-N₂) complexes, and crystal structure was obtained for R = Np). Diamagnetism, long NN bond (1.298(12)Å), relatively short TaN bond (1.840 av.) support the Ta=N-N=Ta structure with two Ta^V centers and N₂⁴⁺ bridge.¹¹⁷ A related bimetallic Ta^{III} (μ-η¹:η¹-N₂) complex is obtained by the reduction of [Ta(C₂H₄)(PMe₃)₃Cl₃] under N₂.¹¹⁷

In 1998, as stated by Fryzuk, they “serendipitously discovered a simple way to prepare a new dinitrogen complex”.¹¹⁸ It relied on the reaction of the bimetallic Ta^{IV},Ta^{IV} bridging tetrahydride complex [[NP^{Ph}N]Ta]₂(μ-H)₄ with N₂, which readily eliminated H₂ to yield the formal Ta^V,Ta^V end-on, side-on bridged N₂ complex [[NP^{Ph}N]Ta]₂(μ-η¹:η²-N₂)(μ-H)₂ (scheme 33).^{113, 119} This complex is remarkable because of the strongly elongated NN bond (1.319(6)Å) as well as by the end-on, side-on coordination, which disymmetrizes the NN fragment. In 2015, the same group developed a similar complex with the [NP^{Cy}N] ligand.¹²⁰ A wealth of reactivity has been discovered with this complex.¹²¹ Focusing on the reactivity of the bridging NN, the nucleophilic character of the “terminal” N is evidenced first by reaction with electrophiles such as PhCH₂Br¹¹³ or X=C=X’ (X, X’ = S or NPh).¹²²

Scheme 33

The complex also reacts with several E-H bonds (B-H, Si-H, Al-H) to form N-E and Ta-H bonds as initial steps, followed in general by H₂ elimination. This elimination is necessary for NN bond cleavage and subsequent functionalization, as it provides the required additional two electrons.¹²³ In the case of boranes R₂BH (9-BBN = 9-borobicyclononane, Cy₂BH, HB(C₆F₅)₂) or RBH₂ (thexylborane = H₂BCMe₂CHMe₂), several cases were observed (scheme 34).¹²⁴ In the case of 9-BBN the final bimetallic Ta

complex features a bridging nitride, an imide resulting from N functionalization by B, as well as a bridging imide resulting from ligand rearrangement.¹²⁵ Reaction with DIBAL (diisobutylaluminum hydride) also results in ligand rearrangement. One of the amide arm coordinates the Al center in the final complex, which features two bridging nitrides.¹²⁶

Scheme 34

Reaction with silanes were also very interesting.^{127, 128} The complexes resulting from the first Si-H bond addition across the TaN bond could be isolated. When an excess of

BuSiH₃ is reacted, the elimination of H₂ is seen, which results in NN bond splitting and subsequent functionalization of the intermediate bridging nitride. Finally, a second equivalent of H₂ is released to form the bis silylimide bridging complex.¹²⁸

Reaction with Schwartz reagent Cp₂ZrHCl was intriguing as neither H nor Cl were found in the final product. A much higher yield of the trimetallic “Ta₂Zr” complex was obtained when the zirconocene precursor Cp₂Zr(Py)(TMSCTMS) was used.¹²³

Cyclopentadienyl ligands have also been used to stabilize Ta-dinitrogen complexes. Thus, reduction of Cp*₂TaCl₂ by Na/Hg under N₂ in THF forms the [Cp*₂TaCl]₂(μ-η¹:η¹-N₂) with NN bond of 1.235(13) Å,¹²⁹ while the one of [(η⁵-C₅Me₄R)TaCl₄] forms [(η⁵-C₅Me₄R)TaCl₂]₂(μ-η¹:η¹-N₂) (R = Me, Et) with NN bond of 1.280(6) Å suggesting stronger reduction of the N₂ bridge in the latter (scheme 35, top).¹³⁰ The chloride ligands could be substituted to synthesize the amidate complexes, with elongated NN bond (1.292(4) Å).¹³¹ Alternatively, reduction of the Cp*TaCl₄ with an excess of KC₈ (5 equiv.) under N₂ in the presence of ArS-SAr provided the Ta^V,Ta^V complex [Cp*Ta(S-4-(MeC₆H₄)₂)]₂(μ-η¹:η¹-N₂) (*d*(NN) 1.281(7) Å) (scheme 35, bottom).¹³² The thiolate ligands were subsequently shown to act as bridging ligands between Ta and M (M = Cr, Mo) upon photolysis of M(CO)₆ in the presence of the N₂ complex. Prolonged photolysis was studied to promote NN bond cleavage, but rather resulted in elimination of one M(CO)₄ fragment.

Scheme 35

3.4. Cp*-amidinate group 5 dinitrogen complexes: synthesis and reactivity

The group of Sita has studied a family of dinitrogen complexes featuring the fragment Cp*/amidinate/M, M = group 4, 5 and 6 transition metal complexes. Thus, they have obtained a large number of isostructural $[(\eta^5\text{-C}_5\text{Me}_5)(\text{N}(\text{R}^1)\text{C}(\text{R}^2)\text{N}(\text{R}^1))\text{M}]_2(\mu\text{-}\eta^1:\eta^1\text{-N}_2)$ complexes (M = Ti, Zr, Hf, V, Nb, Ta, Mo, and W) which allow a meaningful comparison of the structure/ d^n electron count/reactivity at N₂ relationship.

Scheme 36

As shown, reduction of the V^{III} or Nb^V and Ta^V precursors led to the desired N₂ complexes (scheme 36).^{133, 134} The V dimer is obtained as a paramagnetic [V^{II}, V^{II}] complex, thermally stable in solution even at 120°C. It features a short NN bond distance of 1.225(2)Å. On the other hand, the Nb and Ta complexes are kinetically unstable in solution depending on the nature of the metal center and the R group of the amidinate ligand. Apart from the Nb complex with R = Me, all other complexes were crystallized and characterized in solution, below 0°C. The NN bond distances higher than 1.300Å (1.300(3)Å to 1.313(4)Å) in these complexes point to [M^{IV}, M^{IV}] (M = Nb, Ta) complexes, and thus a reduced N₂⁴⁻ bridging moiety. Interestingly, they evolve quantitatively to the diamagnetic [(η⁵-C₅Me₅)(N(R¹)C(R²)N(R¹))M(μ-N)]₂ complexes ([M^V, M^V] dimer). This thermal process is accompanied by a marked increase in the NN bond distance, now above 2.55Å, confirming the NN bond splitting. Kinetic data as well as crossover experiments support the rate-determining intramolecular μ-η¹:η¹-N₂ to μ-

$\eta^2:\eta^2$ -N₂ isomerization prior μ -nitride formation.

Scheme 37

commentaire

4. Group 6 transition metal–dinitrogen complexes

4.1. Cr complexes: synthesis and reactivity

After the reported activity of CrCl₃ as catalyst in the N(SiMe₃)₃ formation from N₂/SiMe₃Cl/Li by Shiina in 1972 followed by first syntheses of N₂ complexes of chromium in 1977, *i.e.* the thermally unstable [Cr(PMe₃)₄(N₂)₂]¹³⁵ complex and [Cr(dppe)₂]₂(μ-N₂)¹³⁶, little attention was paid to Cr for N₂ activation in the next thirty years. In 2007, Budzelaar proposed the use of a tridentate [NNN] pyridine-bis-imine (PDI) ligand to stabilize a bridged N₂ complex obtained via the one electron reduction of the (PDI^{•-})Cr^{II} precursor under N₂ (scheme 38).¹³⁷ Electron transfer from the *in situ* generated Cr⁰ to the end on bridging N₂ moiety results in N₂²⁻ formation (NN bond distance of 1.241(6)Å). Further addition of NaH allowed reduction and functionalization

of N₂ and NN splitting. Protonation of the anionic imido complex released ammonium. The electron acceptor capacity of the PDI ligand appears to be important in the sequence of reactions leading to N₂ functionalization. The same year, Theopold reported the synthesis of $[(i\text{-Pr}_2\text{Ph})_2\text{nacnac}]\text{Cr}]_2(\mu\text{-}\eta^2:\eta^2\text{-N}_2)$ by reduction of the corresponding Cr(II) precursor.¹³⁸ Changing the β -diketimate ligand by a tris-pyrazolylborate ligand favored the coordination of N₂ in an end-on fashion rather than side on. In these two cases, a significant N-N bond elongation is observed compared to free N₂ (1.249(5)Å and 1.213(5)Å) pointing a strong electron transfer from the Cr^I center to N₂.¹³⁹ Functionalization of the coordinated N₂ was nevertheless not attempted.

Scheme 38

Since 2011, the group of Mock has focused on low valent Cr dinitrogen complexes stabilized by neutral macrocyclic ligands “P_nN_n” (8-16 membered rings), for which the ligands are bound solely via the phosphines.¹⁴⁰ With the diphosphine P^{Ph}₂N^{Bn}₂, both the *cis* (ca 15% yield) and *trans* isomers could be obtained, depending on the reduction conditions of the Cr^{III} precursor (Scheme 39).¹⁴⁰

Scheme 39

In 2013, they showed that the macrocyclic diphosphine ligand $\text{P}^{\text{Ph}}_2\text{N}^{\text{Bn}}_2$ rearranges to the 12 ($\text{P}^{\text{Ph}}_3\text{N}^{\text{Bn}}_3$) and 16 ($\text{P}^{\text{Ph}}_4\text{N}^{\text{Bn}}_4$) membered macrocycles upon coordination to Cr^{II} . Reduction of $[(\text{P}^{\text{Ph}}_4\text{N}^{\text{Bn}}_4)\text{CrCl}_2]$ by Mg under N_2 formed the *trans* $[(\text{P}^{\text{Ph}}_4\text{N}^{\text{Bn}}_4)\text{Cr}(\text{N}_2)_2]$ in good yield (63%). X-ray diffraction and IR spectroscopy (strong and weak ν_{NN} bands at 1918 cm^{-1} and at 2072 cm^{-1} respectively) proved the *trans* geometry (scheme 40).¹⁴¹ Protonation at room temperature resulted in N_2 and phosphine loss and produced no reduced N_2 products. If phosphine loss is also observed at -50°C , protonation at N moieties to form hydrazinium N_2H_5^+ was observed as the major N containing species rather than NH_4^+ (traces). DFT calculations were carried out and suggest protonation of the ligand at the pending NBn , followed by transfer to the β N of N_2 . Note that the electrons needed for the reduction of N_2 are provided by the metal center in the absence of external electron source.

Scheme 40

In a subsequent study, in 2015, the reduction of $\text{fac}-(\text{P}^{\text{Ph}}_3\text{N}^{\text{Bn}}_3)\text{CrCl}_3$ by Mg under N_2 in the presence of dmpe was reported.¹⁴² Protonation of the electron rich Cr^0 complex was studied. Reaction with HBArF (12 equiv.) at -78°C resulted in immediate and quantitative protonation at Cr consistent with the formation of only traces of NH_4^+ in addition to free N_2 . In 2016, the same group reported a family of group 6 dinitrogen (Cr, Mo, W) complexes featuring bidentate phosphine ligands. They evidenced a strong metal dependence on the reduction of coordinated N_2 , and NH_4^+ (0.08 eq.) and N_2H_5^+ (0.22 eq.) were only observed with the Cr complex (scheme 41).¹⁴³

Scheme 41

In 2018, they reported a systematic study involving Cr complexes as catalysts of the N_2 -to- $\text{N}(\text{SiMe}_3)_3$ transformation.¹⁴⁴ Between 4.8 and 6.8 equiv. of $\text{N}(\text{SiMe}_3)_3$ were obtained for the Cr-dinitrogen complexes with bidentate and tridentate ligands (100 equiv. Na and SiMe_3Cl , 1 atm N_2 , 23°C , 16h, THF). The tetraphosphine “ P_4N_4 ” ligand,

featuring the 16 membered macrocycle provided the best results (10.6 equiv. NH₄⁺), and proved catalytically active after reloading (maximum 34.1 equiv. NH₄⁺), pointing resistance of the “P₄Cr” fragment to ligand dissociation and catalyst deactivation. Interestingly, reaction under 90 atm N₂ failed to increase the efficiency, suggesting that a five coordinate “P₄Cr⁰(N₂)” complex is a prerequisite for catalysis. Finally, in 2019, the group of Xi proposed a novel Cp-phosphine ligand capable of stabilizing low valent Cr N₂ complexes (neutral Cr^I and anionic Cr⁰) (scheme 42). They showed that even if the NN bond distance is very similar in the Cr^I (1.05 - 1.17 Å) and Cr⁰ (1.141 Å), the N-N stretching frequencies show much stronger activation for the reduced complexes. The best catalytic efficiency in the N₂-to-N(SiMe₃)₃ reaction was found to be 26.0 eq of NTMS₃ per Cr complex. Mechanistic investigation showed that the hydrazido complex Cr=N-N(SiMe₃)₃ could be formed from the anionic Cr⁰ complex.

Scheme 42

4.2. Mo and W complexes

Together with Fe, Mo is most intensively studied in the context of N₂ activation. This fact takes its origin in their presence in the most common as well as most efficient nitrogenase enzyme. Seminal works by Hidai and Chatt at the end of the 1960s and in the 1970s have focused on the synthesis of M⁰ bis-dinitrogen (M = Mo, W) with mono or bidentate phosphines and their subsequent reactivity.¹⁴⁵ A large body of work has

subsequently focused on phosphine variation with the long time goal of developing a catalytic process. Two synthetic strategies for the low valent metal complexes N₂ are classically used. A high valent precursor is reduced under N₂ in the presence of the chosen ligand, or the high valent ligand-metal complex is synthesized prior to its reduction under N₂. Monodentate phosphine displacement by bidentate ones has also been reported. In 2008, Nishibayashi reported a series of [M(PP)₂(N₂)₂] (M = Mo and W) where “PP” is a bidentate phosphine featuring a metallocene (ferrocenyl, ruthenocenyl, or chromobenzene) backbone (vide infra).^{146, 147, 148}

Tridentate ligands, [PEP] (with P = R₂P, R = Ar or alkyl; E= O, NH, S, PR) have also been used as platforms to stabilize low valent M-N₂ complexes. The stability of the complexes strongly depends on the nature of the “P” ligand. In the case of PPh₂, an additional donor ligand has to be added to stabilize the Mo⁰ oxidation state (Scheme 43, top).^{149, 150, 151} Similar requirements are found for [PNN] ligands.¹⁵² On the other hand, with P(alkyl)₂ moieties,¹⁵³ the Mo⁰ complex can be stable in the absence of additional phosphine and several complexes featuring bridging end-on N₂ ligand have been synthesized which have proved relevant to N₂ functionalization in recent years (vide infra) (Scheme 43, middle).^{154, 155, 156, 157, 158} Tripodal,^{159, 160} Tetradentate^{161, 162, 163} and pentadentate^{164, 165} phosphine ligands have been designed to favor coordination of either one or two N₂ ligands at the Mo⁰ center.

Tridentate [NNN] ligand pyridine-di-imine (PDI) has been used by Chirik to stabilize efficiently the [(PDI)Mo(N₂)₂](μ-N₂) complex (Scheme 43, bottom). Subsequent attempts of N₂ functionalization were unsuccessful, resulting in N₂ displacement by H₂, or C-N bond breaking in the ligand backbone (imine moiety) upon reaction with NH moieties.¹⁶⁶

Scheme 43

4.3. From end-on bridging complexes to NN bond splitting

As exemplified previously, formation of bridging N₂ complexes can result in significant electron transfer from the metal center to N₂, thereby potentially weakening the bond and favoring its subsequent functionalization. These complexes can be synthesized using two strategies. Firstly, a stable “M-N₂” complex can be used as a ligand for the second fragment, opening ways to heterobimetallic (or polymetallic)

complexes. Secondly, the bridging N₂ ligand can be installed upon reduction of a metal-halogen bond. The first strategy was reported as early as 1975 using [ReCl(PMe₂Ph)₄(N₂)] as a “ligand” for Mo^{IV} to form the N₂ bridging dimer [ReCl(PMe₂Ph)₄(μ-N₂)MoCl₄(MeOH)].¹⁶⁷ From 1997, Schrock used the “[N₃N]Mo-N=N⁻” anion of [[N₃N]Mo-N=N-Mg(THF)₂] as an X type ligand to generate the heteropolymetallic complexes [[N₃N]Mo(μ-η¹-η¹:N=N)}₃Fe], [[N₃N]Mo(μ-η¹-η¹:N=N)}₂VCl(THF)] and [[N₃N]Mo(μ-η¹-η¹:N=N)}₂ZrCl₂] (scheme 44, top).^{168, 169} At the same time, the [W(PMe₂Ph)₄(N₂)₂] complex was used by Hidai to synthesize the several examples of W-N₂-M (M = group 4 or 13 metal) complexes that result formally from the addition of M-Cl across the W-N₂ moiety (scheme 44, bottom), a reactivity reminiscent to other R-X additions (vide infra).^{170, 171}

Scheme 44

Schrock and coworkers also studied the activation of N₂ at high valent W and Mo complexes. Reduction of [W(Cp*)(Me)₃(OTf)] by one electron yields the bridging end-on N₂ W complexes [W(Cp*)(Me)₃]₂(μ-N₂), in which the NN Bond distance of *ca* 1.27 Å is consistent with a N₂²⁻ moiety.¹⁷² Functionalization of N₂ by acid was attempted but reactivity at M-CH₃ was only observed. The analogous homo-bimetallic [Mo(Cp*)(Me)₃]₂(μ-N₂) and hetero-bimetallic [W(Cp*)(Me)₃](μ-N₂)[Mo(Cp*)(Me)₃] were made.¹⁷³

Sita and co-workers studied the reduction under N₂ of related Mo^{IV}, Mo^V and W^V complexes featuring Cp* and amidinate (or guanidinate) ligands in 2010. The bridging

end-on complexes were obtained in excellent yields (scheme 45).¹⁷⁴

Scheme 45

In these end-on bridging complexes, although an activation of N₂ is observed, it is not sufficient to promote the splitting between the two metal centers. This requires the transfer of a total of six electrons into the π^* and σ^* manifold of N₂. Cummins and co-workers reported in 1995 that the coordinatively unsaturated Mo^{III} complex [Mo(N(R)Ar)₃] (R = C(CD₃)₂CH₃, Ar = 3,5-Me₂-C₆H₃) reacts with N₂ to eventually form the terminal nitrido complex [Mo(N)(N(R)Ar)₃].¹⁷⁵ Impressively, all the intermediates of the process have been observed. Thus, the [Mo(N(R)Ar)₃] complex forms first a monometallic complex at -35°C, which dimerizes to [Mo(N(R)Ar)₃](μ -N₂) (scheme 46). This latter complex evolves to the nitrido species at 30°C (½ life of 35 minutes at 30°C), via a zig-zag transition state, required for the electron flow from a π symmetry orbital (in the linear geometry) into the σ symmetry orbital (N-N antibonding, in the zig-zag geometry).¹⁷⁶ In a subsequent article, they showed that both the coordination of N₂ and

the splitting can be accelerated by addition of reducing agent.¹⁷⁷ Functionalization of the nitride moiety was then demonstrated (vide infra).

Scheme 46

This seminal study prompted several groups to search for conditions that favored N₂ splitting. In 2001, Floriani and co-workers reported the synthesis of [Mo(Mes)₃]₂(μ-N₂) by the reaction between MoCl₄.DME and MesMgBr under N₂. Although this complex is thermally stable, irradiation with UV light results in N₂ splitting, leading to the mixed valent nitrido dimer [{Mo(Mes)₃}(μ-N)]. The authors propose that the intermediate terminal nitrido complex is formed and reacts with the starting complex [Mo(Mes)₃]₂(μ-N₂) to generate a tetra Mo complex which breaks apart by N₂ elimination.¹⁷⁸

In 2012, Schrock and co-workers synthesized the [Mo[PCP](N)(I)]⁻ complex by the two electron reduction of the [Mo[PCP](I)₂] pincer complex ([PCP] = C₆H₃-1,3-[OP(*t*-Bu)₂]₂)

(scheme 47).¹⁷⁹ Protonation of the anionic nitrido complex did not yield the expected parent imido species but provide a rare example of a bridging H between Mo and P.

Scheme 47

In 2014, the group of Nishibayashi has used the depf, diethylphosphinoferrocene, ligand, in conjunction to the bulky Cp* ligand to study the activation of end-on bridging N₂ Mo complex depending on the oxidation state at the metal.^{180, 181} Irradiation of the neutral complex resulted in the NN splitting giving the Mo^{IV} nitride complex, although in low yield, which oxidation allowed NN reformation (scheme 48).

Scheme 48

Sita and co-workers reported in 2015 the photochemical N₂ splitting form [M(Cp*)(N(*i*Pr)C(CH₃)N(*i*Pr))]₂(μ-N₂) (M = Mo, W) complexes. In the case of Mo, a mixture of bridging nitrido complexes, the Mo^V-Mo^V [Mo(Cp*)(N(*i*Pr)C(CH₃)N(*i*Pr))]₂(μ-N) and the Mo^{III}-Mo^{IV} [Mo(Cp*)(N(*i*Pr)C(CH₃)N(*i*Pr))(μ-N)]₂ complexes was obtained (scheme 49).¹⁸² In the case of W, the reaction is slower but cleaner, forming the [W(Cp*)(N(*i*Pr)C(CH₃)N(*i*Pr))(μ-N)]₂ complex. In 2016, they showed that decreasing the steric crowding at the amidinate ligand (Me instead of *i*Pr) allowed the thermal N₂ splitting process forming the bridging nitrido complexes in excellent isolated yields (Mo = 80%; W = 77%), opening ways for further functionalization (vide infra).¹⁸³

Scheme 49

Also in 2016, Mézailles and co-workers studied the two electron reduction of the [Mo(P^{Cy}P^{Ph}P^{Cy})(Cl)₃] complex in the presence of NaI. The nitrido complex [Mo(P^{Cy}P^{Ph}P^{Cy})(N)(I)] is formed in good 60% yield (80% NMR) (Scheme 50) via the proposed splitting of N₂ between two equivalents of the unobserved unsaturated Mo^I intermediate.¹⁸⁴

Scheme 50

In 2017, Schneider and co-workers reported the reduction of $[\text{Mo}(\text{PNP})\text{Cl}_3]$ complex ($\text{PNP}=\text{N}(\text{CH}_2\text{CH}_2\text{P}^t\text{Bu}_2)_2$) by two electrons (Na/Hg) to form the thermally stable bridged dimer $[\text{Mo}(\text{PNP})]_2(\mu\text{-N}_2)$ in 70% yield (Scheme 51).¹⁸⁵ Double protonation at the amido N centers of the ligands triggered the N_2 cleavage, and the $[\text{Mo}(\text{PN}^{\text{H}}\text{P})(\text{N})(\text{Cl})]^+\text{X}^-$ ($\text{X} = \text{OTf}, \text{BAR}^{\text{F}}_4$) complex was obtained in 80% yield. The mechanism of the proton induced N_2 splitting was probed experimentally and by DFT calculations, and linked to changes in ground state multiplicity between the neutral, protonated and doubly protonated complexes.

Scheme 51

4.4 Stoichiometric reactions of M-N₂

It is important here to recall the seminal reports by Chatt and co-workers in the early 1970s who studied the protonation at Mo and W coordinated dinitrogen. They showed that protonation of the N_2 ligand occurs in a stepwise manner, accompanied by electron transfer from the metal center. Protonation with H_2SO_4 in MeOH provided the best results (90% of NH_3 for the $[\text{W}(\text{PMePh}_2)_4(\text{N}_2)_2]$ complex vs 36% for the Mo

complex).¹⁸⁶ Chatt has demonstrated that the sequence of N₂ reduction involves diazenido (MNNH), hydrazido(2-) (MNNH₂), hydrazinium (MNNH₃⁺)¹⁸⁷ and nitrido (MN) intermediates. These form the basis of the Chatt cycle of catalytic N₂-to-NH₃ process. The protonation of complexes featuring dppe classically stopped at the hydrazido(2-) stage (scheme 52),^{188,189,190,191} and further functionalization of the M=N-NH₂ proved very rewarding (vide infra). The protonation of the complexes by inorganic acids to release NH₄⁺ or N₂H₅⁺ is now used as a benchmark reaction.

Starting from 2012, Mock and Bullock have studied the influence of a N moiety as pendant ligand in bidentate phosphine ligands in the outcome of the protonation of the corresponding Mo-dinitrogen complexes (scheme 52, bottom).^{192,193,194} These studies highlighted the strong influence of electronics and sterics of the ligand on the site of protonation and the eventual efficiency of NH₄⁺ production. In addition, they found out that poor yields of ammonia were indirectly correlated to the stability of the hydrazido Mo=N-NH₂ complexes, showing that external source of electron is likely required to achieve further conversion of the hydrazido moiety.

Scheme 52

Functionalization of coordinated N₂ with H₂ was also envisaged. The bis dinitrogen complexes of Mo and W being stable toward H₂, the groups of Morris and Hidai relied on the acidic character of coordinated H₂ in [Ru(Cp)(PP)(H₂)]¹⁹⁵ and [Ru(dppp)(Cl)(η²-H₂)]X respectively to efficiently protonate *trans*-[W(dppe)₂(N₂)₂]¹⁹⁶ to form the corresponding hydrazido(2-) derivative. Starting with the *cis*-[W(PMe₂Ph)₄(N₂)₂] complex, the reaction leads to NH₃ formation (55% yield) (Scheme 53, top).¹⁹⁶ No reaction was observed with the analogous Mo complexes, in which the terminal N center is less basic. Hidai further extended this concept to the use of hydrosulfido complexes as sources of proton, which mimic the postulated mode of action of enzymes. These can be used directly or generated *in situ* from H₂. Thus, reaction

between *cis*-[W(PMe₂Ph)₄(N₂)₂] and 10 equiv. of [(CpMo)₂(μ-S₂CH₂)(μ-S)(μ-SH)][OTf] under H₂ produced ammonia in 38% yield. Starting from the corresponding hydrazido(2-) complex near quantitative yield of NH₃ is formed. With the dppe analogue, the hydrazido(2-) complex Mo=NNH₂⁺ is observed as the final species.¹⁹⁷ Subsequent work was dedicated to changing the bridging hydrosulfido complexes (Mo, Ru, Rh and Ir) as proton donors, with the Ir complex being the most efficient (78% yield of NH₃ per W).¹⁹⁸

Scheme 53

In 2017, Sivasankar used a frustrated Lewis Pair to activate H₂ into the corresponding pyridinium borohydride and efficiently doubly protonate terminal N₂ of *trans*-[W(dppe)₂(N₂)₂] to form the *trans*-[(H)W(dppe)₂(N₂H₂)][HB(C₆F₅)₃] complex (Scheme 53, bottom).¹⁹⁹

4.5 N₂-to-NH₃ Catalytic Transformation

In 2003, Yandulov and Schrock reported the first catalytic N₂ reduction to NH₃ involving well-defined molecular complex.²⁰⁰ The Mo^{III} precursor features a sterically highly demanding ligand [HIPTN₃N] ([HIPTN₃N] = {3,5-(2,4,6-iPr₃C₆H₂)₂C₆H₃)NCH₂CH₂}₃N³⁻), crucial as it prevents formation of bimetallic Mo-N₂-Mo complex as well as provides good solubility in nonpolar solvents. A careful

optimization of the nature of the proton source and reducing agent was done, resulting in the use of sparingly soluble in heptane [LutH][BAr^F₄] proton source, and decamethylcobaltocene Cp*₂Co (Cp* = η^5 -C₅Me₅) as reducing agent. Moreover, slow addition (via syringe pump) of the reducing agent was used to reduce the amount of H₂ formed. Under optimized conditions (48 equiv. of [LutH][BAr^F₄] and 36 equiv. of Cp*₂Co) *ca* 8 equiv of NH₃ (*ca* 65% efficiency) were obtained per equiv. of [[HIPTN₃N]Mo(N₂)] complex under an N₂ atmosphere. The mechanism of the transformation was evaluated by stepwise electron and proton additions, and several intermediates have been isolated (in black in the scheme). These have been subsequently shown to perform nearly identically in the catalytic process.^{201–205} The corresponding catalytic cycle was later also corroborated by DFT calculations (Scheme 54).^{206–209}

Scheme 54

Competitive protonation of the amide moiety of the ligand has been shown to be the cause of the limited activity of the catalyst as it leads to catalyst decomposition. Many efforts have been dedicated to catalyst improvement via ligand tuning (sterics and electronics), which were not successful.^{210–212} The group of Nishibayashi reported in

2011 the catalyst $[[P^{tBu}NP^{tBu}]Mo(N_2)_2](\mu-N_2)$ (with $[P^{tBu}NP^{tBu}] = 2,6\text{-bis}[(\text{di-}i\text{-tert-butylphosphino)methyl] \text{pyridine}$) bearing a less basic neutral tridentate ligand scaffold which led to improved yields (Scheme 55). Under optimized conditions (288 equiv. $[LutH][OTf]$ as poorly soluble proton source, 216 equiv. $CoCp_2$ as reducing agent under slow addition, 1 atm N₂), a maximum of 23 equiv. of ammonia were obtained.¹⁵⁴ The presence of both the bridging and terminal N₂ moieties is crucial for the catalytic process as the related complexes $[[P^{tBu}NP^{tBu}]Mo(CO)_2](\mu-N_2)$ or $[[P^{tBu}NP^{tBu}]Mo(PMe_2Ph)(N_2)_2]$, did only provide 0.4 and 0.2 equiv. of NH₃ under the same experimental conditions, whereas $[[P^{tBu}NP^{tBu}]MoCl_2](\mu-N_2)$ and $[[P^{tBu}NP^{tBu}]W(PMe_2Ph)(N_2)_2]$ did not give any NH₃.^{213, 157} In subsequent works, the authors attempted to improve the process by P^RNP^R (where R = Ph, ⁱPr, Ad and Cy) ligand tuning or using the softer $As^{tBu}NAs^{tBu}$ ligand.²¹⁴ Only the ligand with the bulky adamantyl moiety allowed a moderate improvement of the catalytic performance, while the others showed a drastic decrease (between 1 and 3 equiv. NH₃).²¹⁵ A series of Mo-nitrido complexes, postulated intermediates in the reduction process, were then synthesized and tested.²¹⁶ The $[[P^{tBu}NP^{tBu}]Mo(N)Cl] Mo^{IV}$ and cationic $[[P^{tBu}NP^{tBu}]Mo(N)Cl]^+ Mo^V$ complexes are as efficient as the Mo⁰ dinitrogen dimer (6.8-7.1 equiv. NH₃ vs 5.9). Rather surprisingly, $[[P^{tBu}NP^{tBu}]Mo(N)Cl_2]$ and $[[P^{Ad}NP^{Ad}]Mo(N)Cl]^+ Mo^V$ complexes performed poorly (1.2 and 1.8 equiv. NH₃ resp.). Other changes in the ligand backbone also resulted in drastic decrease in catalytic activity.

Scheme 55

DFT calculations rationalizing the experimental facts were carried out independently by Nishibayashi, Yoshizawa and co-workers and Batista and co-workers.^{216,217} The most important result is that although $[\text{P}^{\text{tBu}}\text{NP}^{\text{tBu}}]\text{Mo}(\text{N}_2)_2(\mu\text{-N}_2)$ and the monomer $[\text{P}^{\text{tBu}}\text{NP}^{\text{tBu}}]\text{Mo}(\text{N}_2)_3$ can be in equilibrium in solution, the double protonation at terminal N₂ to form the hydrazido intermediate is only exergonic for the former. It appears that in the dimer, the Mo fragment $[\text{PNP}]\text{Mo}(\text{N}_2)_3$ acts as intramolecular (via N₂ bridge) electron donor to stabilize the hydrazido fragment, and therefore provides a strong kinetic preference for the pathway involving the dimeric species. Addition of a H⁺ and an electron to the hydrazido derivative leads to the NN bond splitting and formation of the first equivalent of NH₃ together with the nitrido intermediate. Nishibayashi and Yoshizawa propose that the dimer splits into the Mo-nitrido complex and the monomeric Mo(N₂)₃ complex. Functionalization of monometallic nitrido then leads to the second equivalent of NH₃, in accord with the fact

that isolated monometallic nitrido complexes are as efficient as the Mo dinitrogen dimer.²¹⁶ Batista proposes that the integrity of the dimer is retained till the end of the functionalization.²¹⁷ Overall, a catalytic scheme consistent with the experiments can be proposed (scheme 56).

Scheme 56

Based on this precise mechanistic understanding, the group of Nishibayashi has evaluated experimentally the influence of the [PEP] (E = pyridine ring, phosphine, carbene moiety) neutral tridentate ligand on the efficiency of the catalysis. First, electron donating substituents at the para position of the pyridine increased the yield of NH₃ up to 34 equiv. (for R = OMe vs 23 for H).¹⁵⁵ Non innocent moieties (in a redox sense), such as ferrocene or ruthenocene moieties were tested and the ferrocene substituent was shown to

be the fastest catalyst (rate for the 1st hour) as well as slightly more efficient (conditions: N₂, 216 equiv. Cp₂Co and 288 equiv of LutHOTf in toluene for 20 h: TON 37 equiv. NH₃; max TON 53).²¹⁸ With the [P^{*t*Bu}P^{Ph}P^{*t*Bu}] tridentate phosphine ligand, the Mo⁰ dinitrogen dimer was not isolated because of a weak Mo-N₂-Mo bond, although it was clearly observed by IR. Alternatively, the Mo^V cationic nitrido complex [[P^{*t*Bu}P^{Ph}P^{*t*Bu}]Mo(N)Cl]⁺ as well as the [[P^{*t*Bu}P^{Ph}P^{*t*Bu}]MoCl₃] precursor were used as catalysts, and proved to be more efficient with a maximum of 63 equiv. of NH₃.¹⁵⁶ In 2017, the P-carbene-P ligand was developed and the corresponding catalyst provided up to 230 equiv. NH₃.¹⁵⁸ In 2017 also, Nishibayashi studied the catalytic behavior of the [Mo[PNP]I₃] complex in the N₂-to-NH₃ reaction. Most interestingly, starting from this precursor instead of the reduced Mo⁰ dinitrogen complex, the efficiency of the transformation is drastically improved, with 415 equiv. of NH₃ (2880 [ColH]OTf / 2160 CoCp*₂) (ColH is 2,4,6-Me₃C₅H₂NH) vs 23 equiv. at best for the dimer as well as very little H₂ formation. Also, dramatic halide effect was observed as only 12 equiv. NH₃ are formed with the [Mo[PNP]Cl₃] pre-catalyst under the same conditions.²¹⁹ They showed that the [Mo[PNP](N)X] nitrido complexes are key intermediates in this process and therefore proposed a novel catalytic cycle, corroborated by DFT calculations (scheme 57).

Scheme 57

In 2017, Schrock reported that Mo^{VI} nitrido complexes, $[[N_2N]Mo(N)X]$ where $[N_2N]$ is a diamido-pyridine ligand and X is an alkoxide or chloride ligand, were catalytically competent for the reduction of N₂ into NH₃, producing up to 10.3 equivalents of ammonia under optimized conditions (108 equiv. of Cp*₂Co and 140 equiv. of Ph₂NH₂OTf).²²⁰

In the catalyzed N₂ to NH₃ reaction, the optimization of the sources of reducing agent and proton has to be done for each complex. In 2019, Nishibayashi has shown for the first time that alcohols or even H₂O can be used as source of proton if SmI₂ is used as the reducing agent.²²¹ Under these conditions, several of their previously reported catalytically competent complexes performed much more efficiently.²²² They could even show that starting from a Mo-oxo complex was not detrimental to the reaction as the oxo is transformed into the nitrido upon reduction by SmI₂ under N₂. The yield of NH₃ reaches 92% in the best case, almost suppressing the side reaction making H₂. The

maximum TON of 4350 is truly impressive, and the best TOF of ca 117 min⁻¹ is similar to what is measured in nitrogenase enzymes (40-120 min⁻¹).

4.6 N-C bond formation

N-C bond formation studies have been initiated by the groups of Chatt and George in the 70s. The reactivity relies on the nucleophilic character of the terminal N atom of the coordinated N₂ ligand. It is thus limited to Mo and W complexes featuring bidentate phosphine and polydentate thioether ligands. With alkyl halides, the first N-C bond creation requires irradiation and is proposed to occur via C radical intermediate. The second N-C at the same N center involves S_N2 mechanism.^{223,224} In 1989, Yoshida and Hidai showed the Mo tetra-thioether complex to be much more reactive, without the need for irradiation, toward MeI, PhCH₂Br and even ArX.²²⁵ Subsequent functionalization of the dialkylhydrazido complexes, apart from hydrolysis to the hydrazine derivatives, has not been reported since. On the other hand, Hidai has studied to large extent the N-C bond formation from the M=N-NH₂ hydrazido derivatives, as the terminal NH₂ reacts similarly to amines in condensation reactions with carbonyl derivatives (scheme 58). Various nitrogen containing derivatives, such as pyrazoles and phthalimidines, have been synthesized in stoichiometric fashion from N₂.^{226, 227, 228, 229}

Scheme 58

More recently, Cummins has developed a synthetic method toward nitriles via functionalization of the N atom of the $[(\text{N}^*)_3\text{Mo}(\text{N})]$ Mo^{VI} complex ($\text{N}^* = \text{N}(\text{tBu})(3,5\text{-Me}_2\text{Ph})$) they obtained by N_2 splitting. They showed that the N atom is weakly nucleophilic, and could only react once with strongly activated substrates, such as $\text{RCO}(\text{OTf})$, SiMe_3OTf or MeI to yield the corresponding imido complexes (scheme 59).²³⁰

scheme 59

4.7 N-E bond formation: Stoichiometric and catalytic processes.

A large number of studies have been dedicated in the recent years on the creation of N-Si and N-B bonds. These have found grounds on seminal works by the group of Hidai who showed reactivity at terminal N of coordinated N₂ with Si-Cl moieties as well as BH bond. Here again, the nucleophilic character of the terminal N center of the *trans*-[M(N₂)₂(dppe)₂] and *cis*-[M(N₂)₂(PMe₂Ph)₄] is evidenced through silylation reactions to form the corresponding diazenido complexes *trans*-[M(I)(PMe₂Ph)₄(N₂SiR₃)] and *trans*-[M(I)(dppe)₂(N₂SiR₃)] (M = Mo, W).²³¹ The double N-Si bond formation can occur to form the hydrazido(2-) “M=N-N(SiR₃)₂” complex using the ClSiMe₂CH₂CH₂SiMe₂Cl/2NaI couple (Scheme 60). Most importantly, reduction of the diazenido complex *trans*-[M(I)(PMe₂Ph)₄(N₂SiR₃)] with Na was shown to give mixtures of silylamines, which was the basis for the first efficient catalytic process of N₂ reduction, N₂-to-N(SiMe₃)₃ (vide infra). With *cis*-[Mo(PMe₂Ph)₄(N₂)₂], they reported a TON of 24

(Na dispersion as reducing agent) for the silylamine, while the W analogue and *trans*-[Mo(dppe)₂(N₂)₂] only provided “stoichiometric” amounts of silylamine (3 and 1 equiv. resp.).²³²

Scheme 60

In 2011, Nishibayashi has reported the silylation of neutral and anionic dinitrogen complexes featuring depf ligand, yielding the silyldiazido complex (Scheme 60, bottom), the first intermediate in the N₂-to-N(SiMe₃)₃ catalytic process.^{180,233} The efficiency of the *trans*-[Mo(depfp)₂(N₂)₂] complex is impressive with up to 226 equiv. of N(SiMe₃)₃ produced.²³³ Other complexes featuring the same depf ligand, *trans*-[Mo(depfp)(PMe₂Ph)₂(N₂)₂] and *trans*-[W(depfp)₂(N₂)₂] were also competent catalysts (TON of 54 and 60 resp.). The same authors reported in 2014 that the anionic complex [Cp*Mo(μ-N₂){Na(15-crown-5)}(depfp)][−] was less efficient (TON = 22).²³⁴ DFT calculations have been used to propose a catalytic cycle consistent with experimental data (Scheme 61), postulating the active species to be SiMe₃ radical.

Scheme 61

A key feature of the depf-Mo system lies in the capacity of the ligand to adopt flexible bonding modes (mono and bidentate coordination) to Mo in addition to their bulkiness and electron richness. It is proposed that the N-N bond splitting occurs outside the coordination sphere.

In 2013, Masuda and co-workers have reported several Mo-N₂ complexes featuring various bidentate bis(diphenylphosphino)amine RN(PPh₂)₂ ligands, as well as their behavior in the same silylamine catalytic formation. Unfortunately, the performances of the catalysts were quite limited as 0.3–4.0 equiv. of N(SiMe₃)₃ were obtained (by GC/MS).²³⁵

In 2014, Mézailles studied the stepwise silylation/reduction of a terminal N₂ complex generated *in situ* by reduction of the Mo^{II} precursor, featuring a tetradentate phosphine [PP₃] ligand. They have isolated the silylhydrazido(2-) and imido complexes,

and showed them to be catalytically competent (200 equiv. K and SiMe₃Cl, 50°C, 2 days, TON 12-15) (Scheme 62).²³⁶

Scheme 62

In a subsequent study, the stepwise reduction of a mixture of [Mo[P^{Cy}P^{Ph}P^{Cy}](N₂)_x] (x = 2, 3) complexes allowed isolation of the silylhydrazido(2-), the nitrido and the silylimido complexes (Scheme 63).²³⁷ These complexes perform equally well in catalysis with TON of 33-39 (400 equiv. K, 200 equiv. (CH₂SiMe₂Cl)₂, 50°C, 2 days). In addition to being reactive toward Si-Cl bond, the nitrido complex reacted with Si-H bonds under mild conditions providing a synthesis of bis-silylamine.¹⁸⁴

Scheme 63

Using the mixed Cp*/amidinate complexes presented above, Sita and co-workers reported in 2015 a synthetic cycle to produce SiMe₃NCO,¹⁸² or (SiMe₃)₂NH²³⁸ based on the reactivity of the nitrido derivative. Photolytic or thermal N₂ splitting is followed by functionalization of the nitrido intermediate with SiMe₃Cl (scheme 64).

Scheme 64

In 1998, the reaction between RBH_2 and an anionic W^0 complex, activated by N_2 substitution by an electron donating NCS^- , was reported by Hidai.²³⁹ In 2017, Simonneau used BCF (tris-pentafluorophenyl borane) to activate coordinated N_2 toward BH functionalization with $\text{HB}(\text{C}_6\text{F}_5)_2$ (scheme 65).²⁴⁰ In 2019, the same group reported on the 1,3 addition of BH across the $\text{W-N}\equiv\text{N}$ moiety, to form $\text{H-W-N}=\text{NB}(\text{C}_6\text{F}_5)_2$ fragments.²⁴¹ In 2018, Mézailles showed that stepwise functionalization of the $[[\text{P}^{\text{Cy}}\text{P}^{\text{Ph}}\text{P}^{\text{Cy}}]\text{Mo}(\text{N})\text{I}]$ nitrido complex with PinBH does lead to borylamine formation, via borylamido-hydride and (bis-boryl)amido-bis-hydride intermediate complexes (scheme 66).

Scheme 65

Scheme 66

5. Group 7 transition metal–dinitrogen complexes

The chemistry of group 7 metals pertaining to N₂ is very limited compared to its direct group 6 and 8 neighbors. Early work has focused on the synthesis of the N₂ complexes via two different strategies, i.e. the classical reduction of the halide precursor and the degradation of benzyldiazenido complex (scheme 67).^{242, 243, 244}

Scheme 67

Since 2003, only a handful of publications, summarized below, have been

dedicated to these metal centers dinitrogen complexes. In 2006, Pombeiro showed that CO and Cl⁻ ligands can be displaced from a Re center while keeping the N₂ coordinated, leading to the formation of a picolinate Re-N₂ complex.²⁴⁵ The dNN at 1.169(4) Å is only marginally elongated from free N₂ (1.0976 Å). Following the known strategy based on benzoyldiazenido decomposition, the same group reported the synthesis of a water soluble Re-N₂ complex, using the 1,3,5-triaza-7-phosphaadamantane as ligand.²⁴⁶

Chatt showed as early as 1969 that Re-N₂ complexes could be used to synthesize bridged N₂ heterobimetallic complexes. In fact, they proposed such Re-NN-Mo complex as model to understand the function of Mo in nitrogenase enzyme.²⁴⁷ This strategy was followed in 2006 by Brown to obtain another Re-NN-Mo heterobimetallic complex (scheme 68).²⁴⁸ The goal was to probe the NN bond cleavage between two different metal centers. They therefore also prepared the corresponding nitrido complexes of both Re and Mo to evaluate the microscopic reverse NN bond forming process.

Scheme 68

Unfortunately, the NN bond cleavage could not be observed under various conditions, including reduction, heating or photolysis, which only led to Re-N₂ complex and/or

several unidentified complexes. The N₂ formation from the two nitride complexes did not occur either, but the reaction formed the “(N)Re-N-Mo” μ -nitrido complex instead. The authors conclude that kinetic factors rather than thermodynamic ones govern the stability of the N₂ bimetallic complex.

In 2007 and 2009, Arnold reported the use of an anionic [N₂P₂][−] ligand, acting as tridentate ligand, to form the [[N₂P₂]Mn]₂(μ - η^1 : η^1 -N₂) complex, although in poor yield. The solution magnetic moment (8.7 μ_B), being close to the spin only value for eight unpaired electrons, is consistent two Mn^I high spin centers (scheme 69).^{249,250}

Scheme 69

The most advanced system pertaining to N₂ functionalization with group 7 metals has been proposed by Schneider since 2014. In a first report, reduction of the [Re[PNP]Cl₂] complex (where [PNP] = N(CH₂CH₂PtBu₂)₂) by one electron (Na/Hg or Cp*₂Co) under N₂ led to isolation of the Re^V nitride complex [[PNP]Re(N)Cl] in excellent yield, resulting from N₂ cleavage (scheme 70).²⁵¹ In a subsequent study, the mechanism for this process was studied. Performing the reduction at lower temperature, they were able to characterize the bimetallic bridging N₂ complex, including by X-ray diffraction. In parallel, a very thorough electrochemical study of the reduction, coupled to DFT calculations was performed. The mechanism for the NN cleavage thus follows a EC^{N₂}C^{Cl}EC^{dim} pathway (E = electrochemical, C = chemical; C^{N₂}: N₂ coordination, C^{Cl}: Cl[−] dissociation, C^{dim}: dimerization). The rate determining step occurs after dimerization,

and implies an *in plane zigzag* transition state with a NN distance of 1.59 Å.

Scheme 70

Schneider's group then studied the functionalization of the nitrido complex.^{252,253} They devised a multistep process based on alkylation, deprotonation and subsequent oxidation to generate two nitrile derivatives, PhCN and MeCN. Interestingly, the $[[\text{PNP}]\text{Re}(\text{N})\text{Cl}]$ complex can be regenerated closing a synthetic cycle for nitrile synthesis from atmospheric N₂.

In 2019, they reported a modified platform that splits N₂ under photolytic conditions (scheme 71). The corresponding Re^V nitrido complex $[[\text{PNP}]\text{Re}(\text{N})\text{Cl}_2]$ further reacted with benzoylchloride to form mixtures of PhCONH₂ (30%), PhCN (64%) as well as PhCOOH (64%). This process necessitates the participation of the ligand as a 2e⁻/2H⁺ donor, forming an imine moiety. A subsequent reaction of this intermediate with hydride then proton sources regenerated the starting complex, closing a four step synthetic cycle. Finally, an electrochemical process was also presented for this synthetic cycle.²⁵⁴

Scheme 71

6. Preparation of group 8 transition metal–dinitrogen complexes

The vast majority of group 8 metal dinitrogen complexes are known with Fe. Thus, this chapter will be presented according to ligand classes instead of metal centers. A plethora of ligands have been shown to allow the synthesis of group 8 M–N₂ complexes, and most of them contain phosphine ligands. As will be seen below several complexes are efficient in the N₂ reduction processes (N₂-to-NH₃ and N₂-to-N(SiMe₃)₃).

6.1 Fe–N₂ complexes: synthesis and stoichiometric reactivity

6.1.1 P containing ligands

Most of the known Fe–N₂ complexes contain phosphine ligands. Following seminal work by Leigh,²⁵⁵ with donating bidentate phosphines, Tyler synthesized

$[[PP]_2Fe(H_2)(H)]^+$ ([PP] = 1,2-bis(bis-(methoxypropyl)phosphino)ethane, a water soluble ligand)²⁵⁶ and showed that H₂ could be displaced by N₂ to form $[[PP]_2Fe(N_2)(H)]^+$, featuring a minimally activated N₂ moiety (ν_{NN} of 2088 cm⁻¹, NN distance 1.112 Å) (scheme 72).^{257,258} Dinitrogen is readily displaced in this type of complexes. In particular, coordination of NH₃, NH₂NH₂ and NH=NH was studied in light of their possible intermediacy in the N₂ reduction process.²⁵⁹ Subsequent deprotonation of $[[PP]_2Fe(N_2)(H)]^+$ yields the Fe⁰ complex $[[PP]_2Fe(N_2)]$, showing increased N₂ activation (ν_{NN} of 1966 cm⁻¹), and NH₃ (15%) and N₂H₄ (2%) were both obtained upon acid treatment (triflic acid). DFT calculations were carried out to rationalize the formation of NH₃ and hydrazine.²⁶⁰ Notably, the analogous complex $[Fe(depe)_2(N_2)]$ did not yield any NH₃ upon protonation.²⁶¹ Field has demonstrated in 2015 that starting from isolated $[Fe(dmpe)_2(N_2)]$, no NH₃ is formed upon acid treatment,²⁶² in contrast with initial reports by Leigh (20% NH₃, protonation with HCl at low temp using crude mixture containing the Fe-N₂ complex). Rather, protonation at the Fe center was observed, leading to Fe^{II} hydride complex. For the synthesis of $[Fe(dmpe)_2(N_2)]$, Field followed the reduction procedure from the dichloride they developed to isolate the related $[Fe(dmpe)_2(NH=NH)]$ complex.²⁶³ Interestingly, deprotonation of the diazene derivative with strong base regenerates the $[Fe(dmpe)_2(N_2)]$ complex.²⁶⁴ Related chemistry was studied in parallel by Field with ruthenium.²⁶⁵

Scheme 72

In 2016, Ashley also studied the $[\text{PP}]_2\text{Fe}(\text{N}_2)$ complexes ($[\text{PP}] = \text{dmpe}$, depe),²⁶⁶ and showed that the dimeric $[\text{Fe}(\text{dmpe})_2]_2(\mu-\eta^1:\eta^1\text{N}_2)$ complex is obtained from the monomer upon vacuum treatment and crystallization. They also discovered that reaction with TfOH produced appreciable amounts of N_2H_4 and NH_3 , with depe complex (*ca* 20% N_2H_4 , 8% NH_3) being more efficient than dmpe one (*ca* 9% N_2H_4 , 0% NH_3). Moreover, the significant proportion of hydrazine *vs* NH_3 suggests that the latter may be generated from the intermediacy of the hydrazine complex. The authors have studied the catalytic functionalization (*vide infra*). In parallel, they have also evaluated the addition of Si electrophile on the N_2 in the $[\text{Fe}(\text{dmpe})_2(\text{N}_2)]$ and $[\text{Fe}(\text{depe})_2(\text{N}_2)]$ complexes. Thus, addition of TMSCl and a chloride abstractor allowed the first isolation of a silyldiazenido

derivative of Fe, showing an acute NNSi bond angle of *ca* 130°. ²⁶⁷ DFT calculations were carried out and confirm a significant FeN π interaction as well as population of a NN π^* orbital, consistent with the observed ν_{NN} stretches at 1732 and 1727 cm⁻¹ (depe and dmpe complexes respectively). In 2017, Szymczak showed that an increase in the NN bond polarization could favor protonation at N rather than at Fe. ²⁶⁸ This could be achieved by coordination of various Lewis acids to [Fe(depe)₂(N₂)] and the extent of N₂ activation evaluated by IR spectroscopy (decrease in the ν_{NN} frequency by 129 cm⁻¹, at 1830 cm⁻¹). The BCF adduct was crystallized, as well as the [Fe(depe)(N=NH(BCF))] ⁺ complex.

In 2013 and 2014, Mock reported the synthesis of Fe^{II}-hydride-dinitrogen complexes, featuring bidentate phosphines with a pendant amine moiety ([P^NP] ligand), and studied the effect of this pendant N ligand on the protonation/electron events (scheme 73). ²⁶⁹ In the case of the [[PNP]Fe(H)(N₂)] ⁺ complex, protonation reactions did not result in functionalization at N or at Fe, but at the pendant N moiety, leading ultimately to the tricationic species with two ammonium moieties. ²⁷⁰ Reduction then triggers a sequence of N₂ decoordination, intermolecular proton and electron transfers, to eventually favor again N₂ coordination at Fe^{II}.

Scheme 73

Bidentate phosphine ligands have been shown to support piano-stool Ru-N₂ complexes. ²⁷¹

Tridentate ligands featuring phosphines can be separated in two families, the neutral and anionic type ligands. Whittlesey has reported in 2010 the synthesis of $[[\text{POP}]\text{Ru}(\text{H})(\text{PPh}_3)(\text{N}_2)][\text{BAr}^{\text{F}}_4]$ complexes, with $[\text{POP}]$ being $(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{O}$, xanthphos and DPEphos, thus featuring an ether and two diphenylphosphino moieties.²⁷²

The neutral tridentate $[\text{PPP}]$ type ligands have been surprisingly studied only quite recently. Indeed, Peters reported in 2017 the synthesis of the $[[\text{PPP}]\text{Fe}(\text{H})]_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2)$ ($[\text{PPP}] = (\text{o-PiPr}_2\text{-phenyl})_2\text{-PPh}$) upon reaction of the Fe^{II} precursor with NaBEt_3H under N_2 (scheme 74, left).²⁷³ The complex is in equilibrium with the monomeric $[[\text{PPP}]\text{Fe}(\text{H})(\text{N}_2)]$ complex, present in minor amounts in solution. The $[[\text{PPP}]\text{Fe}(\text{H})_2(\text{N}_2)]$ complex could be obtained upon protonation/e transfer. Both the Fe^{I} dimer and the Fe^{II} complexes are active catalysts in the N_2 -to- NH_3 process with respectively up to 24.6 equiv of NH_3 (per Fe center) (3000 eq. HBar^{F}_4 , 3600 KC_8 , THF, -80°C , 1h) and 2.6 equiv of NH_3 (150 eq. HBar^{F}_4 , 180 KC_8 , THF, -80°C , 1h). The authors showed that photolysis during catalysis did provide more active intermediates, from the Fe^{I} dimer resulting in most significant improvement of the efficiency (up to 66.7 equiv. NH_3). In 2018, Mézailles reported the synthesis of the $[[\text{PPP}]\text{Fe}(\text{N}_2)_2]$ (ν_{NN} 2048, 1981 cm^{-1}) and $[[\text{PPP}]\text{Fe}(\text{N}_2)(\text{H})_2]$ (ν_{NN} 2092 cm^{-1}) complexes ($[\text{PPP}] = \text{RP}(\text{CH}_2\text{CH}_2\text{PCy}_2)_2$, $\text{R} = \text{Ph}$, $t\text{Bu}$) and their poor efficiency in the same N_2 -to- NH_3 catalysis (3.6 and 2.7 equiv. NH_3 respect.; 200 eq. HBar^{F}_4 , 200 KC_8 , THF, -80°C , 1h) (scheme 74, right).²⁷⁴ Interestingly, in sharp contrast with Peters' results, with these different $[\text{PPP}]$ ligands, the authors report the instability of the $[[\text{PPP}]\text{Fe}(\text{N}_2)(\text{H})]$ toward dismutation into the known Fe^{II} $[[\text{PPP}]\text{Fe}(\text{N}_2)(\text{H})_2]$ and unknown Fe^0 complexes. In a follow up study, Peters isolated the $[[\text{PPP}]\text{Fe}(\text{N}_2)_2]$ complex (ν_{NN} 2065, 2009 cm^{-1}) as well as its one electron and most

impressively the two electron reduction derivatives $[[\text{PPP}]\text{Fe}(\text{N}_2)_2][\text{K}(\text{18-C6})]$ (ν_{NN} 1872 cm^{-1}) and $[[\text{PPP}]\text{Fe}(\text{N}_2)_2][\text{K}_2(\text{THF})_3]$ (ν_{NN} 1677 cm^{-1}).²⁷⁵ Stoichiometric functionalization by H^+ and Si^+ was studied, showing that an anionic state of the system is required for effective functionalization at N.

Scheme 74

Prior to these neutral [PPP] ligands, Peters had reported the use of anionic [PPP] ligands, $([\text{BP}_3] = \text{PhB}(\text{CH}_2\text{PPh}_2)_3^-)$ to support Fe dinitrogen complexes. Thus, reduction of the $[\text{BP}_3]\text{FeCl}$ Fe^{II} precursor by Na/Hg resulted in the formation of the neutral Fe^{I} bridging dimer $[(\text{BP}_3)\text{Fe}]_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2)$ as well as the formal $\text{Fe}^{0.5}$ dimer $[(\text{BP}_3)\text{Fe}]_2(\mu\text{-}$

$\eta^1:\eta^1\text{-N}_2$)[Na(THF)₆] upon addition of a second equivalent of Na/Hg (scheme 75).²⁷⁶ Alternatively, the anionic Fe⁰ complex [[PhBP₃]Fe(N₂)] [MgCl(THF)₂] (ν_{NN} 1872 cm⁻¹) was obtained from the Mg reduction. Functionalization with MeOTf yielded the high spin diazenido [[BP₃]Fe(N₂Me)] with ν_{NN} (¹⁵N₂) vibration at 1597 (1538) cm⁻¹. Synthesis of the Fe^I dimer was subsequently shown to be achieved from the *in situ* generated Fe^{IV} nitride.²⁷⁷ Indeed, although stable and characterized at -35°C, this species cleanly evolved to the dinitrogen complex at room temperature.

Scheme 75

In 2011, the same group utilized a similar platform to study the coordination/interconversion of N_xH_y ligands at Fe.²⁷⁸ They discovered that the $\mu\text{-N}_2\text{H}_4$ and $\mu\text{-N}_2\text{H}_2$ complexes react with free hydrazine reducing the latter to NH₃ as the former is oxidized (scheme 76).

Scheme 76

This tripodal anionic [BP₃][−] ligand has led to the development of related families of tetrapodal neutral [BP₃] and anionic [CP₃][−] and [SiP₃][−] ligands by the group of Peters. Both the C[−] and Si[−] moieties exert a strong *trans* influence on the coordinated N₂. With the [SiP^R₃][−] ligand (P^R = PPh₂ and PiPr₂), the neutral Fe^I-N₂ complexes were synthesized (scheme 77).^{279,280} The [SiP^{iPr}₃][−] ligand being more electron rich than the corresponding [SiP^{Ph}₃][−] one, the NN stretch is logically found at lower energy. In the latter case, addition of excess H⁺ only resulted in the formation of sub-stoichiometric amounts of hydrazine (0.17 equiv.) while the addition of H⁺ and electrons increased the yield up to 0.47 equiv. The neutral Fe-N₂ complexes could be further reduced to the anionic Fe⁰-N₂ derivatives. Protonation of the [[SiP^{iPr}₃]Fe(N₂)][−] at -78°C did not result in NH bond formation but rather in reduction to the [[SiP^{iPr}₃]Fe(N₂)] complex, via competitive H₂ production. On the other hand, N-Si bond formation occurred efficiently yielding [[SiP^{iPr}₃]Fe(NNSiR₃)] (R = Me, Ph, *iPr*).²⁸¹ Mössbauer and DFT calculations concur to define the complex as a Fe⁰ center with strong back donation to the π* system of N₂SiR₃⁺. The [[SiP^{iPr}₃]Fe(N₂)]

complex was used as pre-catalyst for the catalytic NN coupling of azides into azoarene.²⁸²

The first step of the transformation involves N₂ displacement by arylazide prior to imide formation. In the absence of arylazide, under N₂, the imide evolves back to the Fe-N₂ complex via ArNNAr formation.

Scheme 77

In subsequent studies, conditions to favor NH bond formation related to catalytic NH₃ production as well as NC bond formation were evaluated. Protonation of the $[[\text{SiP}^{i\text{Pr}}_3]\text{Fe}(\text{N}_2)]\text{K}(\text{THF})_x$ at very low temperature (-135°C) with excess H⁺ sources was required to yield the desired $[[\text{SiP}^{i\text{Pr}}_3]\text{Fe}(=\text{NNH}_2)]^+$ complex while alkylation with

MeOTf to form $[[\text{SiP}^{i\text{Pr}}_3]\text{Fe}(=\text{NNMe}_2)]^+$ was successful at -78°C .²⁸³ Both complexes could be reduced by one electron to form the corresponding $[[\text{SiP}^{i\text{Pr}}_3]\text{Fe}(=\text{NNR}_2)]$ derivatives (R = H, Me). The $[[\text{SiP}^{i\text{Pr}}_3]\text{Fe}(=\text{NNH}_2)]$ complex, synthesized at -135°C and characterized at low temperature by EPR spectroscopy, reacts readily at -78°C with $[[\text{SiP}^{i\text{Pr}}_3]\text{Fe}(=\text{NNH}_2)]^+$ via $\text{H}^\circ/\text{H}^+$ transfer to form the $[[\text{SiP}^{i\text{Pr}}_3]\text{Fe}(\text{NH}_2\text{NH}_2)]^+$ hydrazine and $[[\text{SiP}^{i\text{Pr}}_3]\text{Fe}(\text{N}_2)]$ complexes. Overall, these studies provide a very precise understanding on the sequence of protonation/reduction of N₂ at the $[\text{SiP}^{i\text{Pr}}_3]\text{Fe}$ fragment, where a distal intermediate “Fe=NNH₂” is formed first, followed by reduction/disproportionation to an alternating derivative “Fe(NH₂NH₂)” that finally serves as a source of NH₃ via late stage NN bond cleavage.²⁸¹ Notably, the same ligand was studied in the frame of cyanide reduction, CN[−] being isoelectronic to N₂.^{284,285} In 2017, additional N donor moieties (amines) were incorporated in the “SiP₃” ligand in order to evaluate secondary-sphere interactions in the catalytic N₂ fixation. It did not prove efficient because of kinetically facile Fe-H formation.²⁸⁶ In parallel to studies dedicated to Fe, the coordination to Ru and Os was evaluated. Thus, the $[[\text{SiP}^{i\text{Pr}}_3]\text{M}(\text{N}_2)]$ (M = Ru, Os) M^I complexes were synthesized via the one electron reduction of the M^{II} precursor.²⁸⁷ They featured NN stretches at 2088 and 2052 cm^{−1}. The Ru complex could be oxidized and reduced by one electron to Ru^{II} and Ru⁰, while the Os could be reduced to Os⁰. The $[[\text{SiP}^{i\text{Pr}}_3]\text{Ru}(\text{N}_2)]$ complex is a catalyst in the N-N coupling of arylazides to form azoarenes.²⁸⁸ Mechanistic studies point a different pathway than with Fe, with formation of free arylnitrene during catalysis. The M⁰ $[[\text{SiP}^{i\text{Pr}}_3]\text{M}(\text{N}_2)]^-$ complexes were tested in 2017 in the N₂ reduction reaction. Using knowledge gained with the [BP₃] ligand system, vide infra, anilinium/Cp*₂Co couple was shown to be optimal and up to

120 equiv. of NH₃ per Os center were produced (1500 equiv. acid, 1800 equiv. reductant) exceeding the best results with Fe catalysts.²⁸⁹

The group of Peters also developed tetradentate [CP₃][−] to probe Fe-N₂ functionalization. With [C^{SiPh}P₃][−], the diamagnetic [[C^{SiPh}P₃]Fe(N₂)] [K(benzo-15-C-5)] complex (ν_{NN} 1927 cm^{−1}) was obtained from the reduction of the [[C^{SiPh}P₃]Fe] Fe^I complex (scheme 78). Functionalization of N₂ at the terminal position required the use of a highly encumbered silylating agent, Si(*i*Pr₃)OTf at −78 °C, resulting in one phosphine arm decoordination. The diazenido ligand features an elongated NN bond length of 1.203(2) Å.²⁹⁰ Similar chemistry was carried out with the C analogue of the [SiP₃][−] ligand. Thus, reduction of the [[CP^{*i*Pr}₃]FeCl] complex over Na mirror yielded the neutral [[CP^{*i*Pr}₃]Fe(N₂)] Fe^I complex, while reaction with an excess of KC₈ produced the Fe⁰ complex [[CP^{*i*Pr}₃]Fe(N₂)] [K(OEt₂)₃]. The silyl diazenido complex [[CP^{*i*Pr}₃]Fe(N₂SiMe₃)] was obtained by trapping of the anionic complex, and impressively, treatment of the same complex at −78°C with an excess of electron and proton sources (40 equiv KC₈ and 38 equiv [H(Et₂O)₂][BAR^F₄]) provided the second case of a catalytic N₂ reduction, with 4.6 equiv. of NH₃ produced.²⁹¹

Scheme 78

Modification of the ligand scaffold to replace the anionic Si or C moieties by neutral B center was achieved. The corresponding “[BP₃]Fe” system is probably the most studied in the frame of N₂ functionalization. Thus, in 2011, Moret and Peters reported the synthesis of the Fe^I complex [[BP₃]FeBr] and its reduction to the neutral and anionic N₂ complexes [[BP₃]Fe(N₂)] and [[BP₃]Fe(N₂)]Na (Scheme 79).^{292,293} The latter features a stretching band at 1879 cm⁻¹ in the solid state, while in solution a mixture of Na coordinated and ion pair species are seen (ν_{NN} at 1877 and 1918 cm⁻¹). Trapping of the anionic complex with SiMe₃Cl resulted in the formation of the silyldiazene derivative [[BP₃]Fe(NNSiMe₃)] which could be further reduced to [[BP₃]Fe(NNSiMe₃)]Na. In that case, decoordination of a phosphine moiety is evidenced. If the anion is reacted with a bis-chlorosilane, then the bis-silylhydrazido Fe^{II} derivative is synthesized. Notably, in that case, the FeB bond elongates significantly, which illustrates the flexibility of the ligand in terms of electron acceptor capacity. Upon addition of tBuNC, a phosphine arm

dissociates, which provokes a slow NN bond breaking process, resulting in N-B and N-P bond formation, as well as Fe-bissilylamido generation.

Scheme 79

In 2013, the same group discovered that the anionic Fe complex $[[BP_3]Fe(N_2)][Na(12\text{-crown-4})_2]$ is a catalyst for the reduction of N₂ into NH₃.²⁹⁴ The catalytic performance is very sensitive to the nature of proton source (HBAr^F₄ required), reducing agent (KC₈ required) as well as temperature (7.0 equiv. per Fe complex at -78°C). Most notably, the

complexes $[[BP_3]Fe]^+$, $[[BP_3]Fe(NH_3)]^+$ and $[[BP_3]Fe(N_2H_4)]^+$ all produce 6 equivalents of NH₃ under the same catalytic conditions, demonstrating that they are likely intermediates in the catalytic cycle of N₂ functionalization.²⁹⁵ Moreover, the complex $[[BP_3]Fe(NNH_2)]^+$, was characterized at low temperature (-135°C) from the double protonation of the anionic complex $[[BP_3]Fe(N_2)][Na(12-crown-4)_2]$.²⁹⁶ It was later shown that at least some of the catalyst $[[BP_3]Fe(N_2)][Na(12-crown-4)_2]$ was stable at low temperature, allowing significant increase of the NH₃ yield upon successive reloading of substrates (up to 64 equiv. NH₃ per Fe center at 1500 equiv. acid loading).²⁹⁷ Based on these results Peters presented a catalytic cycle for the N₂-to-NH₃ transformation using the “[BP₃]Fe” system (scheme 80).²⁹⁷ In 2018, the same group evaluated by DFT calculations the competitive HER (hydrogen evolution reaction) and N₂RR (nitrogen reduction reaction) with the three “[EP₃]Fe” (E = B,C, Si) systems.²⁹⁸ They conclude that the comparative stability of the $[EP_3]Fe(NNH_2)^{n+}$ intermediates is one of the important factors in determining the selectivity for the N₂RR versus HER. Recent developments have focused on improving the selectivity at lower driving force using other H⁺/electron sources.²⁹⁹ Anilinium/metallocenes provide PCET (proton coupled electron transfer) pathways whose efficiencies are linked to the pK_a of the acid.³⁰⁰

The group of Lu has introduced in 2011 a trisphosphino-(triamido)amine $[\text{NN}_3\text{P}_3]^{3-}$ ligand capable to enforce M-M' interaction. Coordination of “Altraphos” to Fe^{II} followed by reduction under N_2 allowed the synthesis of $\text{Fe}^0\text{-N}_2$ complex $[[\text{NN}_3\text{P}_3]\text{AlFe}(\text{N}_2)]$, in equilibrium with its dimeric form via N_2 bridging (scheme 81).³⁰¹ One electron reduction can be achieved, which further activates N_2 and trapping with a bis-chlorosilane results in the isolation of the diamagnetic, low-spin Fe^{II} disilyl-hydrazido complex, “ $\text{FeNN}(\text{SiMe}_2\text{CH}_2)_2$ ”.³⁰²

Ligands based on related scaffolds, designed to favor bimetallic systems and/or incorporate S binding moieties were developed by the group of Peters (scheme 82).^{303,304,305,306} If the desired Fe-N₂ complexes could be synthesized, the successes in functionalization was limited.

Scheme 82

Iron complexes of tridentate anionic $[\text{SiP}_2]^-$ ligand were studied in 2017 by Nishibayashi, in link with the possible involvement of $[(\text{THF})\text{Fe}(\text{SiMe}_3)_2(\text{N}_2)]$ as intermediate in the N_2

to N(SiMe₃)₃ reduction by Cp₂Fe or Fe(CO)₅.³⁰⁷ Thus, [[Si^RP₂]Fe(H)(PMe₃)(N₂)] complexes were synthesized and evaluated as catalysts (scheme 83).³⁰⁸

Scheme 83

Iron dinitrogen complexes of anionic tridentate ligands featuring both amido and phosphine moieties have been studied recently. In 2015, Mindiola reported that minor amounts of a heterobimetallic FeMg-N₂ complex are formed when an excess of EtMgCl is reacted with [[PNP]FeCl] under N₂ (scheme 84).

Scheme 84

In 2016, the group of Nishibayashi expanded the chemistry of [PNP] pincer ligands with a central pyrrolide moiety toward Fe (scheme 85).³⁰⁹ They obtained Fe^I-N₂ complex upon reduction of the [[PNP]FeCl] ([PN^RP] = 2,5-bis(di-*t*Bu-phosphinomethyl)pyrrolide), or by protonation of the hydride or methyl derivative followed by reduction. A ν_{NN} band at 1964 cm⁻¹ assignable to terminal N₂ was found in the IR spectrum. This complex is a competent catalyst in NH₃ synthesis only when [H(OEt)₂]₄BAR^F₄ and KC8 were used as proton source and reducing agent, at low temperature (-78°C). Under optimized conditions, up to 14.3 equivalents of NH₃ are formed together with 1.8 equivalent of

hydrazine. In a subsequent study, they evaluated the effect of the electronics of the pyrrolide ligand on the efficiency of the catalysis.³¹⁰ They found out that more electron rich ligand increased the yield of NH₃ by 50% (up to 22.7 equiv for dimethylpyrrolide vs 14.3 for pyrrolide). In light of the facile protonation at the pyrrolide moiety, the same authors modified the ligand structure to incorporate a carbazole ring.³¹¹ However, the corresponding Fe-N₂ complex did not prove efficient (0.5 equiv. NH₃). The corresponding [[PN^RP]FeMe] ([PN^RP] = 2,5-bis(di-*t*Bu-phosphinomethyl)(3,6-di-*t*Bu)carbazole) did produce up to 3.2 equiv. NH₃ (80 equiv. KC₈, 78 equiv. HBAr^F₄, -78°C, Et₂O)

Scheme 85

Caulton reported in 2007 the hydrogenation of N₂O by the [[PNP]Os(H)₃] ([PNP] = N(SiMe₂CH₂P^{*t*}Bu₂)₂) complex.³¹² In addition to water, the reaction yielded the [[PNP]Os(H)(N₂)] complex, characterized by a high field hydride (-34.8 ppm) in ¹H NMR, as well as a ν_{NN} stretch at 2003 cm⁻¹ in the IR spectrum.

Fryzuk, Masuda and coworkers developed an anionic [PNN] ligand that features an iminophosphorane unit (R₃P=N–R), an electron-rich phosphine, and an amide (scheme 86). They reported that the reduction of the corresponding Fe^{II} complex [[PNN]FeBr] under N₂ yielded the N₂ bridging dimer.³¹³ The NN bond distance is elongated to 1.184(6) Å and the ν_{NN} stretch is found at 1755 cm^{–1} in the Raman spectrum, at lower energy compared to the Nacnac complexes reported by Holland (vide infra). The solution-state magnetic moment indicates six unpaired electrons, while the Mössbauer is consistent with Fe^{II} centers. Together, these data support antiferromagnetic coupling between N₂^{2–} and the two Fe^{II} centers.

Scheme 86

The coordination chemistry of tetradentate phosphine based ligands, [NP₃] and [PP₃] toward group 8 metals date back to Sacconi's work in the mid 70s. In 2005, Peters has reported novel, bulky examples of [NP₃] ligands and their coordination to Fe^{II}. Following a similar route, the [[NP^{iPr}₃]Fe(N₂)(H)][PF₆] complex could be obtained.³¹⁴ Coordination of bulky tetradentate [PP₃] ligands to Fe^{II} and Ru^{II} centers was studied by Field, as well as their reduction under N₂ (scheme 87).³¹⁵ The diamagnetic, trigonal bipyramidal, [[PP^R₃]M(N₂)] complexes were fully characterized. Functionalization of N₂ was attempted with mildly acidic lutidinium, but the metal-hydride-N₂ complexes were observed instead. Deprotonation regenerated the M(0) complexes.³¹⁶ Deprotonation of

the cationic hydrazine complex $[[PP^{iPr}_3]Ru(NH_2NH_2)Cl]^+$ provides another synthetic pathway to the Ru^0-N_2 complex, although it generates stoichiometric amounts of the $Ru(H)_2$ derivative.³¹⁷ Notably, when the more bulky $[PP^{tBu}_3]$ ligand was used, only tridentate coordination was observed.³¹⁸

Scheme 87

In 2017, Dzik, de Bruin, Reetz and coworkers studied the coordination of a novel $[PP^{Ph}_3]$ ligand, based on indole ring, to Ru. Stepwise reduction of the $[[PP^{Ph}_3]RuCl_2]$ yielded the Ru^I and Ru^0-N_2 complexes, featuring a ν_{NN} at 2125 cm^{-1} .³¹⁹

Also in 2017, Mock reported a series of Fe complexes bearing a rigid tetraphosphine ligand $[P_4N_2]$, and in particular the first example of a square pyramidal complex $[[P_4N_2]Fe(N_2)]$ (ν_{NN} at 2003 cm^{-1}) (scheme 88).³²⁰ They quantified the affinity of N_2 coordination at the “ $[P_4N_2]Fe^{(x)}$ ” fragment, with very unfavorable coordination at Fe^{II} ($>30\text{ kcal/mol}$), favorable at Fe^0 (-7 kcal/mol) and reversible at Fe^I (0.4 kcal/mol). Under a high pressure of N_2 (100 atm), the $[[P_4N_2]Fe(N_2)]$ complex is a competent catalyst in the N_2 to $N(SiMe_3)_3$ transformation (up to 65 equiv. $N(SiMe_3)_3$).

Scheme 88

The use of monodentate phosphines for the stabilization of group 8-dinitrogen complexes has been seldom reported. In fact, phosphine stabilized “Fe₄” and “Fe₆” clusters featuring bridging hydrides have been reported to be impressive catalysts in the N₂ to N(SiMe₃)₃ transformation (up to 183 equiv. for the “Fe₆” cluster).³²¹ It is to be noted however that no intermediate with Fe-N₂ has been observed in these cases. Ruthenium complex [Ru(H)₂(PCy₃)₂(N₂)₂] has been used to achieve CH and CO activation under mild conditions, thanks to easy N₂ dissociation.³²²

6.1.2 N based ligands

The chemistry of Fe-N₂ complexes with “N based ligands” has been most extensively studied with two families, the neutral [NNN] and the anionic [NN][−] ligands. The neutral [NNN] pyridine-diimine (PDI) ligands have been reported to stabilize Fe-N₂ by Chirik in 2004. Thus, reduction of the [Fe(ⁱPrPDI)X₂] (ⁱPrPDI = 2,6-{MeC=N(2,6-*i*-Pr₂C₆H₃)}₂C₅H₃N) under N₂ resulted in the formation of the highly unusual paramagnetic formally Fe⁰ bis-N₂ complex [Fe(ⁱPrPDI)(N₂)₂] (scheme 89).³²³ The complex crystallized as distorted square based pyramid, and present minimal activation of the N₂ ligands (by NN bond distance measurement, 1.090(2) Å and 1.104(3) Å and position of the NN stretching bands in IR, at 2122 and 2058 cm^{−1}) by the d⁸ Fe center. Subsequent combined spectroscopic, structural, and computational studies have resulted in a comprehensive

picture of the electronic structure of the complex, involving reduction of the PDI ligand to a dianionic [PDI]²⁻ fragment complexed to an intermediate spin ferrous ion, Fe^{II}.³²⁴ In terms of reactivity, the two N₂ ligands are readily displaced and the [Fe(ⁱPrPDI)(N₂)₂] complex acts as a masked unsaturated “Fe(ⁱPrPDI)” fragment in many significant transformations.^{325, 326, 327, 328, 329, 330, 330, 331, 332, 333, 334, 335, 336, 337, 338, 339, 340} Budzelaar, Gambarotta and coworkers showed in 2008 that reaction of the same [Fe(ⁱPrPDI)Cl₂] complex with excess NaH did form several reduced Fe-N₂ complexes (scheme 89, bottom).³⁴¹

Scheme 89

At the same time Chirik reported the synthesis of the [Fe(ⁱPrPDI)(N₂)₂] complex, Danopoulos synthesized the related [[CNC]Fe(N₂)₂] complex ([CNC] is a pyridine-bis-

NHC ligand).³⁴² In this case, because of the presence of the two NHC ligands, the complex is diamagnetic, and the NN stretching frequencies are measured at slightly lower wavelengths as expected (2109 and 2031 cm⁻¹). Electronic and steric ligand tuning was achieved from 2012 by Chirik, and the corresponding [[CNC]Fe(N₂)₂] are extremely active hydrogenation pre-catalysts.^{333, 343} In 2017, the saturated version of the NHC ligand was reported, and the Fe-N₂ complex enables oxidative addition of H₂ to Fe⁰.³⁴⁴

High oxidation state “Os-Nitride” complexes of neutral [NNN] ([NNN] = terpy or tris-pyrrazolylmethane) have been studied by Meyer and Huynh from 1999 (scheme 90).³⁴⁵ N-N bond formation to form N₂ as ligand was demonstrated in a variety of reactions between the [[NNN]Os(Cl)₂(N)]⁺ complexes and hydroxylamines (H₂NOH and MeHNOH) and methoxylamines (H₂NOMe and MeHNOMe) in MeOH at room temperature.³⁴⁶ A four electron reduction of the metal center occurs in this transformation. Intermediates featuring NN bonds have been observed during the transformations. Although not using polydentate ligands, the studies by Vogler need to be presented at this point, as they are related to the NN bond cleavage/formation at Os. Indeed, photolytic splitting of N₂ in [(NH₃)₅Os(μ-N₂)Os(NH₃)₅]⁵⁺ was achieved in aqueous medium.³⁴⁷ The mechanism involves an intramolecular photoredox process.

Scheme 90

In 2014, dinitrogen has been shown to displace H₂ in dinuclear Ru^{II} polyhydride cationic

complexes featuring the neutral [NNN] ligand 1,4,7-trimethyl-1,4,7-triazacyclononane.³⁴⁸

The other class of N ligands extensively studied in the frame of N₂ fixation is the anionic [NN][−] ligand β-diketiminato ($L^{tBu,dipp} = CH\{C(t-Bu)N(2,6-i-Pr_2C_6H_3)\}_2^-$), also known as Nacnac ligands. In 2001, Holland reported the reduction of [Fe($L^{tBu,dipp}$)Cl] by one electron under N₂ yielded the bimetallic bridging end-on complex [$\{Fe(L^{tBu,dipp})\}_2(\mu-\eta^1:\eta^1-N_2)$] ($\nu_{NN}=1778\text{ cm}^{-1}$) shown to feature elongated NN bond (1.182(5) Å) (scheme 91).³⁴⁹ The N₂ ligand is readily displaced in these complexes.³⁵⁰ In particular, it can be used as precursor for CO₂ reduction into CO.³⁵¹ Reduction by two electrons per Fe center to the formal Fe(0) was also achieved, forming the [$\{Fe(L^{tBu,dipp})\}_2(\mu-\eta^1:\eta^1-N_2)]M_2$ (M = Na, K) ($\nu_{NN}=1589\text{ cm}^{-1}$, M = K).³⁴⁹ In that case, the NN bond distance is elongated to 1.24 Å, in the range of N₂^{2−} moieties. In subsequent studies, ligand electronics and sterics were modulated. With Me in place of t-Bu, similar Fe-N₂ complexes were obtained.³⁵² When the ligand $L^{Me,Me,dipp} = CMe\{C(Me)N(2,6-i-Pr_2C_6H_3)\}_2^-$ was used, full N₂ splitting was achieved upon reduction (scheme 92). DFT calculations rationalized the necessity of having both multiple Fe centers as well as K⁺ coordination to allow nitride formation.³⁵³

Scheme 91

The authors further evaluated the effect of counter ion, and showed that with the smaller Na⁺, a trimetallic complex, with bridging nitrides, is obtained.³⁵⁴ On the other hand, with

Cs⁺, N₂ is not split, and a trinuclear complex with two μ, η^1, η^1 -N₂ bridging is formed.³⁵⁵

Finally, when Mg was used as reducing agent, metastable complexes consistent with the formulation $[\{\text{Fe}(\text{L}^{\text{R,dipp}})\}_2(\mu\text{-}\eta^1:\eta^1\text{-N}_2)]_2[\text{Mg}(\text{THF})_4]$ were obtained.³⁵⁶ When 18-crown-6 was added to the tetranuclear Fe complex, K⁺ was sequestered which resulted in NH bond formation and CH bond activation of the ligand backbone, likely via the intermediacy of the anionic nitride complex.³⁵⁷

Scheme 92

Most significantly, protonation with excess HCl of the tetranuclear Fe bis nitride complex

resulted in the formation of 82% of NH₄Cl.³⁵⁸ In 2016, an exhaustive protonation study was done, revealing no link between the pK_a of the acid and the quantity of ammonia produced. In fact, high yields of ammonia are often found for weak acids, and even with water (96% yield).³⁵⁹ Stepwise functionalizations of the nitrido moieties by protons and electrons (stepwise or coupled proton/electron transfer) were achieved. Impressively, several intermediates were isolated and/or spectroscopically characterized (scheme 93). The bridging imido/nitrido (NH/N), amido/nitrido (NH₂/N), bis amido (NH₂/NH₂) complexes were isolated while anionic imido/nitrido (NH/N), and amido (NH₂) complexes were spectroscopically characterized. Despite the fact that the N₂ is fully split with this system, it appears that the reversible reaction is kinetically accessible. Indeed, addition of two electron donors CO, 2,6-(CH₃)₂C₆H₃CN, or catalytic pyridine in benzene induced N₂ elimination and efficient synthesis of the Fe^I complexes.³⁶⁰

Scheme 93

In 2015, Murray developed a tris- β -diketiminate, linked via aromatic rings.³⁶¹ This ligand favored trimetallic Fe^{II} complex formation. Subsequent reduction by six electrons under N₂ resulted in N $\equiv$ N splitting and protonation (scheme 94). Based on this ligand platform, this group reported in 2018 the Fe catalyzed N₂ conversion to N(SiMe₃)₃.³⁶² Several pre-catalysts [(Ligand)Fe₃X₃] (X = Br, Cl, F, H, O, S) and [(Ligand)Fe₃(Br)₂(μ ₃-N)] and [(Ligand)Fe₃(μ ₃-N)] were tested. The yields obtained (*i.e.* N(SiMe₃)₃/Fe₃) for a reaction between 500 equiv. KC₈ and SiMe₃Cl at room temperature for 24h are for most of them higher than 50, with the highest at 64 (X = F). If the reaction is performed at -34°C for 96h, the best yield is 83 (X = Br), which makes this system the most effective one for this transformation (50% yield based on reducing equivalents). Interestingly, the μ ₃-N

complexes are slightly less efficient, consistent with the fact that [(Ligand)Fe₃(μ₃-N)] is stable under reducing conditions.

Scheme 94

Also in the family of anionic N based ligands, one finds the weak field ligands tris-pyrazolylborates. In light of the weak field ligand sulfide found in nitrogenase, the Tp ligands are interesting models for N₂ coordination to high spin Fe. Harman reported in 2015 that reduction of the Fe^{II} precursors [(Tp^{R,Me})FeCl] (R = Ph, Ad) results in the formation of [(Tp^{Ph,Me})Fe]₂(μ-η¹:η¹-N₂) and [(Tp^{Ad,Me})Fe(N₂)], the latter being the first terminal high-spin Fe^(I)-N₂ complex (S = 3/2) as proved by EPR, magnetic measurements and substantiated by DFT calculations.³⁶³ With the slightly less bulky Tp^{tBu,Me} ligand, the bridging dimer [(Tp^{tBu,Me})Fe]₂(μ-η¹:η¹-N₂) was obtained.³⁶⁴

Neutral [NN] ligands of the type 4,5-diazafluorene can be deprotonated from [Ru(H)(Cl)(LH)(PPh₃)₂] (LH= 4,5-diazafluorene) under N₂ to form the [Ru(H)(L)(PPh₃)₂(N₂)] complex.³⁶⁵ This complex reacts with CO₂ reversibly via insertion in a CH bond of the ligand.³⁶⁶

Finally concerning the N based ligand, a Ru complex featuring a macrocyclic [NNNN] ligand was designed as sensor for N₂ in water at different pH. It is based on the

dissociation of OH⁻ from the complex at high pH.³⁶⁷

6.1.3 S based ligands

Prior to 2003, the group of Sellmann has studied many polydentate ligands featuring thiolate moieties to develop functional models of nitrogenase.³⁶⁸ Relevant to the more recent literature is the dianionic [SNNS]²⁻ ligand, 1,2-ethanediamine-N,N'-dimethyl-N,N'-bis(2-benzenethiolate)²⁻. In 2001, the corresponding [[SNNS]Ru(PiPr₃)(N₂)] terminal Ru^{II}-N₂ complex was synthesized.³⁶⁹ The [[SNNS]Ru(PiPr₃)(NH₃)] complex was later obtained and NH₃ shown to be labile and readily displaced by N₂ at room temperature (scheme 95).³⁷⁰ The viability of diazene and hydrazine complexes as intermediates in the N₂ reduction upon H⁺/e⁻ transfers was studied with this metal fragment. Interestingly, reaction with hydrazine resulted in the slow formation of the diazene complex following a dismutation process from the N₂H₄ intermediate.

Scheme 95

In 2015, Holland designed a bis-thiolate ligand $[SArS]^{2-}$ which offers only S and C coordination sites.³⁷¹ Reduction of the $[[SArS]Fe(THF)_2]$ complex by two electrons at low temperature under N_2 allowed the isolation of the thermally sensitive complex $[[SArS]Fe(N_2)]^{2-}$, in which the Fe center is pseudo-tetracoordinated. Infrared spectroscopy analysis of single crystals of the complex showed a N–N stretching band at 1880 cm^{-1} .

Scheme 96

In 2017, a bridging Fe^{II}-N₂ complex featuring an anionic thiolate-phosphine [SP][−] ligand was reported to act as catalyst in the hydroboration of arenes.³⁷² The mechanism implies N₂ displacement by the substrate.

6.1.4 C and Si based ligands

In 2010, Sunada reported the synthesis of a dinuclear Fe complex with bridging N₂.³⁷³ The reaction between [Fe(mesityl)₂] and 1,2-bis(dimethyl-silyl)benzene in aromatic solvents yielded [(η⁶-arene)Fe(Me₂SiC₆H₄SiMe₂)]₂(μ-η¹:η¹-N₂) (arene = benzene or toluene). In these complexes, the N₂ ligand is readily displaced by CO, PPh₃ or H₂.

Carbene ligands have been introduced in group 8-N₂ chemistry rather recently. Whittlesey, MacGregor and Pregosin reported in 2009 the [Ru(NHC)₄(H)(N₂)]BAr^F₄ complexes (NHC = *i*Pr₂Me₂, and IEt₂Me₂) with hydride and N₂ ligands in trans position.³⁷⁴ The N₂ ligand is weakly coordinated and here also readily displaced by CO. In the reaction between [(p-cymene)Ru(μ-Cl)₃RuCl(C₂H₄)(IMes)] and N₂O, Severin observed the formation of [(p-cymene)Ru(μ-Cl)₃RuCl(N₂)(IMes)] which gradually disappeared to the benefit of a complex featuring a μ-alkoxy ligand derived from

oxidation of one of the *o*-Me group of the IMes ligand.³⁷⁵ The coordination of Picolyl-NHC (Py-NHC) ligands at Fe and Ru has been studied by the groups of Puerta, Valerga and Song. A weak coordination of N₂ was observed at the “M(Py-NHC)(X)⁺” cationic fragment (M = Fe, Ru, X = Cp*,³⁷⁶ M = Ru, X = Tp³⁷⁷). In 2015, Peters reported that the two coordinate [Fe(CAAC)₂] does only bind N₂ at low temperature (<-80°C) to form the [Fe(CAAC)₂(N₂)] Fe⁰ complex (scheme 97).³⁷⁸ This complex can be reduced at -95°C by KC₈ in the presence of 18-crown-6 to form [Fe(CAAC)₂(N₂)] [K(18-crown-6)], which features a ν_{NN} stretch at 1850 cm⁻¹.

Scheme 97

At this temperature, these complexes are catalysts of the NH₃ synthesis (3.3 and 2.6 equiv. respectively) using HBar^F₄ and KC₈ (50 equiv.). The anionic complex was reacted with R₃SiCl (R = Me, Et), and the diazenido [(CAAC)₂Fe(N₂SiR₃)] isolated. The [Fe(CAAC)₂(N₂)] complex proved to be a competent catalyst for the formation of N(SiMe₃)₃ (24.4 equiv. for a reaction with 600 equiv. of SiMe₃Cl and KC₈, room temp).

Finally, dinitrogen complexes of Fe⁰, Fe^I and Fe^{II} have been reported by Deng, with a bulky NHC supporting ligand (ICy) (scheme 98).³⁷⁹ Thus, reduction of the [Fe(ICy)₃(N₂)]⁺ complex by KC₈ at very low temperature (from -118°C to -80°C) yielded the expected [Fe(ICy)₃(N₂)] Fe⁰ complex. They feature a strong ν_{NN} stretch at 1967 cm⁻¹ and two ν_{NN} stretches at 1853 and 1841 cm⁻¹ respectively. In solution, the Fe⁰ complex is in equilibrium with the Fe^{II}-hydride-dinitrogen complex that results from CH bond insertion into the Cy moiety of the ligand.

Scheme 98

7. Group 9 transition metal–dinitrogen complexes

7.1 Cobalt complexes

7.1.1 P containing ligands

The first Co-N₂ complex [Co(H)(PPh₃)₃(N₂)] was synthesized in 1967, and subsequent years have witnessed studies using monodentate phosphine ligands to stabilize such Co-N₂ moieties. Much like for other metal centers, it has been common

belief that “activation of N₂”, identified by NN bond lengthening and ν_{NN} stretching frequency lowering, would translate into enhanced reactivity at N, thereby eventually allowing for N incorporation into valuable molecules, i.e. NH₃, N(SiMe₃)₃. The recent efficient N₂ functionalization by selected Co complexes prove that the problem is much more complex, and that looking at the M-N₂ reagent does not tell much about the subsequent energy profile linked to N functionalization.

In an early important report, Yamamoto et al. showed that reduction of the [Co(H)(PPh₃)₃(N₂)] complex into [Co(PPh₃)₃(N₂)] [Li(solv)₃] (solv = Et₂O or THF), allowed NH₃ and/or hydrazine formation from N₂ upon hydrolysis (20-30% of initial N₂ ligand is reduced), while the rest of N₂ is liberated.³⁸⁰

Starting from 1985, polydentate ligands were used to synthesize Co-N₂ complexes.³⁸¹ In 2003, Peters reported the use of a tripodal anionic [BP₃]⁻ ([PhB(CH₂PiPr₂)₃]⁻) ligand for the stabilization of Co⁰ and Co^IN₂ complexes. Stepwise reduction of the Co^{II} precursor by Na/Hg in THF allowed isolation of the Co^I bridging dimer [([BP₃]Co)₂(μ-η¹:η¹-N₂)], as well as the formal Co^{0.5} dimer [([BP₃]Co)₂(μ-η¹:η¹-N₂)] [Na(THF)₆] (scheme 99).²⁷⁶ Alternatively, reduction by Mg formed the dianionic Co⁰ dimer [([BP₃]Co)₂(μ-η¹:η¹-N₂)] [Mg(THF)₄]. Functionalization of the bridging N₂ in the latter complex with either TMSCl or MeOTs was reported to yield the corresponding diazenido complexes (low spin Co^{II}).

Scheme 99

The same group then synthesized a series of CoN₂ complexes featuring tetrapodal [EP₃] ligands, where E = B, Si and C following the same strategy, i.e. reduction of the Co^I (E = B) and Co^{II} (E = Si, C) precursors (scheme 100). In these complexes, the ligand *trans* to N₂ differs, as well as the charge, which allowed a systematic comparison of the extent of N₂ activation.^{280, 382, 383}

Scheme 100

The [BP₃] ligand allowed both Co⁰ and Co^{-I}N₂ complexes to be made, the latter being diamagnetic. The neutral Co^I can be obtained for the [SiP₃] and [CP₃] derivatives, and the cationic Co^{II} for the latter. Measures of the ν_{NN} stretching frequencies in these complexes point that, as one expects, more electron rich Co center (low oxidation state, more negative charge) results in greater N₂ activation. The authors evaluated these complexes, as well as several others, in the N₂-to-NH₃ reduction. The standard conditions involve reaction at -78°C between suspension of [H(Et₂O)₂][BARF₄] (47 equiv) and KC₈ (60 equiv) for one hour. Only the complexes featuring the [BP₃] ligand proved active, with the anionic complex [[BP₃]Co(N₂)]⁻ yielding 2.4 equivalents of NH₃, while the neutral one [[BP₃]Co(N₂)] produced 0.8 equivalents. The Co^I precursors [[BP₃]CoBr] and [[BP₃]Co]⁺ yielded 0.7 and 1.6 equivalents respectively.

In a related approach, in 2011, the group of Lu reported the synthesis of a ligand trisphosphino-(triamido)amine [NN₃P₃]³⁻ capable to enforce M-M' interaction (scheme 101).³⁰¹ With this ligand, bimetallic M-Co complexes (M = Al, Co) were obtained.^{302, 384} In the case of M = Co, cyclic voltammetry showed an irreversible one electron reduction under N₂, which suggested coordination of N₂ upon reduction. Chemical reduction under N₂ with KC₈ in the presence of 2.2.2-cryptand allowed isolation of the expected [[NN₃P₃]CoCo(N₂)] [K(crypt-222)]. Similarly, reduction of the [[NN₃P₃]AlCo(N₂)] complex by one electron formed the [[NN₃P₃]AlCo(N₂)] [K(crypt-222)] species. Most interestingly, the reduction potential for the CoCo and AlCo complexes and the ν_{NN} stretching frequencies of the reduced MCoN₂⁻ complexes are nearly identical, although the M center is *trans* to N₂ and would be expected to have a significant influence. The three complexes [[NN₃P₃]AlCo(N₂)], [[NN₃P₃]CoCo] and [[NN₃P₃]CoCo(N₂)]⁻ were tested as catalysts in the N₂-to-NTMS₃ reduction (1 atm N₂, 2000 eq. TMSCl, 2000 KC₈, r.t, THF, 12h), and compared to other Co species. The “AlCo” complex did provide 30 equiv. of NTMS₃, which is less than what was obtained with [Co(PPh₃)₃Cl] (TON: 44) or derivatives obtained by mixing CoCl₂ and monophosphines (TON: *ca* 90 equiv.). On the other hand, the neutral and anionic “CoCo” complexes proved highly active, generating 195 and 178 equivalents of the silylamine respectively. Even more impressively, when a second batch of chlorosilane and KC₈ was added, a total of 326 equiv. of NTMS₃ was produced. In 2015, the same group further extended the family of [[NN₃P₃]MCo] complexes (M = Ti, V, Cr). Reduction of the VCo and CrCo complexes under N₂ also resulted in the formation of the anionic N₂ derivatives [[NN₃P₃]MCo(N₂)]⁻. A thorough DFT analysis revealed that the CoCo derivative is unique in the series. Indeed, the

(MCo)²⁺ core features a M^{III}Co^{-I} oxidation state for M = Al, Ti, V and Cr, while it is Co^{II}Co⁰ in the dicobalt anion.³⁸⁵

Scheme 101

The group of Peters also evaluated the tridentate [BP₂] ligand, and in this case, the Co center uses the BPh moiety as ligand (scheme 102).³⁸⁶ Reduction of the Co^{II} precursor lead to formation of the Co⁰-N₂ complex [[BP₂]Co(N₂)], as the major species in solution, as attested by the N₂ stretch at 2098 cm⁻¹. However, in the crystal, both the end-on and the bridging N₂ complexes are found. As mentioned above, each Co center is pentacoordinated because of the interaction with the ipso carbon of the phenyl ring.

Scheme 102

Starting from 2009, the group of Thomas has developed the use of phosphino-amide ligands to stabilize M-Co heterobimetallic (M = Zr, Hf) edifices.^{387, 388} Reduction of the

precursors under N₂ by an excess of Na/Hg resulted in the formation of “MCo-N₂” complexes in which N₂ is bound to Co (scheme 103). Depending on the nature of the substituents at P and N, the Na⁺ cation remains coordinated to either N₂ or the X-M fragment. Co and Zr K-edge XANES data indicates that the reduced ZrCoN₂ derivatives are best described as Zr^{IV}Co^{-I}.³⁸⁹ The Thomas group utilized the [(MesNP*i*Pr₂)₃ZrCoN₂] complex in a range of stoichiometric and catalytic transformations,^{390,391,392,393,394,395,396} all involving the Zr center, but did not report successful N₂ functionalization.

In 2015, successful synthesis of the related TiCoN₂ complex could be achieved with less sterically demanding ligand RNP*i*Pr₂ (R= 3,5-dimethylphenyl). In this case, the N₂ is so weakly bound to Co that it readily dissociates under vacuum or under Ar. This is corroborated by the high ν_{N2} stretch at 2084 cm⁻¹ (compared to 2045 cm⁻¹ for the Zr analogue) showing much poorer back donation from Co, linked to increased donation toward the more Lewis acidic center Ti.³⁹⁷ Most interestingly, the “TiCoN₂” complex catalyzes the disproportionation of hydrazine into NH₃ and N₂. Unfortunately, the complexes are decomposed in the presence of excess NH₃ which limits the catalyst efficiency.

Scheme 103

In 2012, this group also reported the synthesis of the M-Co-N₂ (M = Nb, Ta) complexes with the Ph₂PNiPr₂ ligand, following the same reductive strategy. In this case, the group 5 imido complexes are used as precursors.³⁹⁸

Bis-phosphino pyridine [PNP] ligands were also shown to stabilize Co-N₂ fragments.³⁹⁹ Thus, synthesis of [[PNP]Co(BPin)(N₂)] complexes ([PNP] = 2,6-(iPr₂PCH₂)₂-4-R-Py), R = H, Me, BPin, Pyrrole) was reported by Chirik in the frame of Co catalyzed borylation reactions. Only the complex with 4-pyrrole derivative is stable toward N₂ loss under vacuum. Catalysis involves N₂ dissociation to generate the active [[PNP]Co(BPin)] species.

7.1.2 N Based ligands

Bulky β -diketiminate ligands have been used in the Co-N₂ chemistry by Holland. Thus, reduction of the [Co(L^{tBu,dipp})Cl] (L^{tBu,dipp} = CH{C(*t*-Bu)N(2,6-*i*-Pr₂C₆H₃)}₂[−]) by one electron yielded the bimetallic bridging end-on complex [{Co(L^{tBu,dipp})}₂(μ-η¹:η¹-N₂)], shown to feature two Co^I centers, ferromagnetically coupled (scheme 104).⁴⁰⁰ Reduction by two electrons to the formal Co⁰ was also achieved, forming the [{Co(L^{tBu,dipp})}₂(μ-η¹:η¹-N₂)]M₂ (M = Na, K). In that case, the NN bond distance is elongated to 1.21-1.22 Å (vs 1.139(2) Å in the neutral complex), in the range of N₂^{2−} moieties (N=N double bond), also confirmed by the N–N vibration band at 1599 cm^{−1} in the Raman spectrum. DFT calculations revealed that the extent of bond lengthening is due both to the reduction and alkali metal coordination. Similar reactivity was recently observed by Scheer with the ligand L^{Me,dipp} = CH{C(Me)N(2,6-*i*-Pr₂C₆H₃)}₂[−].⁴⁰¹

Scheme 104

In 2001, Gibson synthesized the [Co(ⁱPrPDI)(N₂)]⁺ (ⁱPrPDI = 2,6-{MeC=N(2,6-*i*-Pr₂C₆H₃)}₂C₅H₃N) complex by abstraction of a CH₃ moiety under N₂. In 2010 and 2013,

Chirik reported the reduction of this complex by one and two electrons, and evidenced the non-innocence of the PDI ligands in the process. Thus, in the complexes, the Co center remains at the +I oxidation state and the N₂ is only moderately affected by the reduction as shown by ν_{NN} stretching frequencies (from 2184 to 2093 to 2046 cm⁻¹) (scheme 105).^{402,403}

Scheme 105

7.1.3 Carbon Based ligands: carbenes and isocyanides

Surprisingly, NHC ligands (N Heterocyclic Carbene) have only been used recently in the Co-N₂ chemistry. Deng reported in 2012 first studies using the IMes (1,3-dimesitylimidazol-2-ylidene) ligand. Despite being unsaturated, coordination of N₂ at the [Co(IMes)₂]⁺ complex was not evidenced. Reduction of the [Co(IMes)₂Cl] complex with Na/Hg resulted in the double CH bond insertion in the ligand, but reaction with MeLi did yield a [Co(IMes)(IMes')(N₂)] complex, concomitant with CH₄ elimination (scheme 106).⁴⁰⁴ The complex is thus a Co^I diamagnetic species. In a subsequent study, the same group studied the coordination of 1,3-dicyclohexylimidazol-2-ylidene (ICy).⁴⁰⁵ In this case, reduction of [Co(ICy)₃Cl] by KC₈ in THF yielded the Co⁰ complex [Co(ICy)₃(N₂)]. Cyclic voltammetry studies revealed that this complex could be reduced further at -2.10V vs SCE. Chemical reduction with M (M = K, Rb, Cs) was thus done, leading to

[Co(ICy)₂(N₂)₂]M complexes, featuring terminally bound N₂ to Co, while the interaction with M can be either η^1 or η^2 . Functionalization of the coordinated N₂ was then studied. Treatment of the [Co(ICy)₃(N₂)] and [Co(ICy)₂(N₂)₂][−] complexes with excess strong acid resulted in quantification of significant amounts of hydrazine (5% and 23-31% respectively). Addition of SiCl bonds to [Co(ICy)₂(N₂)₂][−] resulted in the formation of the disilyl diazene complex [Co(ICy)₂(η^2 -R₃SiNNSiR₃)₂]. The NN bond distance of 1.457(3)Å is consistent with a single bond. In light of the stoichiometric functionalization of N₂ with chlorosilane, the authors tested the catalyzed formation of N(SiMe₃)₃ using the neutral, anionic and diazene complexes. Thus, reaction of N₂ with 2000 equivalents of SiMe₃Cl and KC₈ per complex, in THF, yielded 103-125 equiv. of silylamine.

Scheme 106

In 2013, Chirik reported Co complexes featuring the pyridine-bis carbene ligand [CNC] in a study dedicated to catalytic hydrogenation (scheme 107).⁴⁰⁶ The sequence of Co-N₂ formation is quite unusual. It involves migration of a hydride ligand from the Co to the para position of the Py ligand, which therefore acts as a non-innocent ligand. If the reaction is carried out in the presence of 1,1-diphenylethylene, migration of the alkyl moiety formed after insertion is observed.

Scheme 107

A related tridentate ligand, [PNC] phosphine-pyridine-carbene, was reported in 2016 by Braunstein, Danopoulos and coworker.⁴⁰⁷ Reaction of the imidazolium precursor with [Co(NTMS₂)₂] formed the [[PNC]CoBr] Co^{II} complex featuring dearomatized anionic PNC ligand. Subsequent reduction of this complex by KC₈ yielded the diamagnetic Co^I-N₂ complex [[PNC]Co(N₂)]. In this complex, a NN bond distance of 0.987(3) Å was measured, shorter than the distance in free N₂ (1.098 Å), apparently incompatible with the

ν_{NN} at 2057 cm⁻¹ which shows some activation via back bonding, and thus which should lead to elongation.

Scheme 108

Bulky isocyanide ligands have enabled synthesis of $\text{Co}^{\text{I}}\text{-N}_2$ complexes. Starting from the $[\text{Co}(\text{CNAr}^{\text{Mes}_2})_3]^-$ anion, the $[\text{Co}(\text{CNAr}^{\text{Mes}_2})_3(\text{SiMe}_3)(\text{N}_2)]$ complex was obtained by Figueroa's group upon addition of SiMe_3Cl under N_2 (scheme 109).⁴⁰⁸ In this complex the N_2 moiety is trans to the SiMe_3 group. The presence of strong π acceptor isocyanide ligands deplete the Co^{I} center from electron density which translates to the highest vibrational band for NN at 2231 cm⁻¹. The same group then evaluated the addition of strong donor ligands, Cp derivatives.⁴⁰⁹ In the case of the $[\text{CpCo}(\text{CNAr}^{\text{Dipp}_2})\text{I}_2]$, reduction did not lead to formation of a Co-N_2 complex, but on dimerization. With the more donating and sterically encumbered, the desired $[\text{Cp}^*\text{Co}(\text{CNAr}^{\text{Dipp}_2})(\text{N}_2)]$ complex was obtained. However, it is not stable under vacuum, and ligand rearrangement was observed.

Scheme 109

7.1.4 Pincer ligands

A variety of pincer, tridentate anionic, ligands favoring meridional coordination at the metal center have been used to stabilize Co-N_2 fragments.

In 2006, the group of Mindiola studied the reduction of the $[[\text{PNP}]\text{CoCl}]$ complex where $[\text{PNP}]$ is $[\text{N}\{2\text{-PiPr}_2\text{-4-MeC}_6\text{H}_3\}_2]^-$ (scheme 110).⁴¹⁰ Under N_2 , reaction with $t\text{BuLi}$ formed the $\text{Co}^{\text{I}}\text{Co}^{\text{I}}$ dimer $[[\text{PNP}]\text{Co}]_2(\mu\text{-N}_2)$, featuring two square planar Co centers. At this oxidation state the N_2 binds reversibly to the Co center. Reduction with

an excess of Na/naphthalene yielded the diamagnetic dianionic Co⁻¹ complex $[[\text{PNP}]\text{Co}(\text{N}_2)]^{2-}$. The X-ray structure $[[\text{PNP}]\text{Co}(\mu\text{-N}_2)\text{Na}_2(\text{THF})_3]_2$ is rather complex, with highly distorted tetrahedral geometry at Co. Despite the formal highly reduced Co center, the ν_{NN} at 1784 cm⁻¹ indicates a moderate N₂ activation.

Scheme 110

Similar reversible coordination of N₂ was observed the same year by Caulton with another [PNP] pincer ligand, $(t\text{Bu}_2\text{PCH}_2\text{SiMe}_2)_2\text{N}^-$.⁴¹¹ The group of Arnold reported in 2013 the use of a stronger donor pincer ligand, $(i\text{Pr}_2\text{PCH}_2\text{CH}_2)_2\text{N}^-$.⁴¹² In that case, reduction of the CoCl precursor with KC₈ under N₂ yielded the desired $[[\text{PNP}]\text{Co}(\text{N}_2)]$ complex, as a diamagnetic species. As above, it readily loses N₂ even in the solid state in an N₂ filled glovebox. In 2016, the group of Nishibayashi further expanded the chemistry of [PNP] pincer ligands toward Co, with the pyrrolide derivative (scheme 111, top).⁴¹³ They also obtained diamagnetic Co^I-N₂ complexes upon reduction of the $[[\text{PNP}]\text{CoCl}]$ ([PNP] = 2,5-bis(dialkyl-phosphinomethyl)pyrrolide). Most interestingly, these

complexes are catalysts of the N₂-to-NH₃ reduction, using [H(OEt₂)₂][BAr^F₄] as proton source and KC₈ as reducing agent. Under carefully optimized conditions, *i.e.* -78°C, Et₂O as solvent, 1h, 200 eq. KC₈ and 184 eq. H⁺ source, up to 15.9 equivalents of NH₃ are formed together with 1.0 equivalent of hydrazine.

Scheme 111

A diazaborole [PBP] pincer ligand was reported by Peters to allow the formation of the [[PBP]Co(N₂)] complex upon reduction under N₂ with Na/Hg (scheme 111, bottom).⁴¹⁴ It appears that the strongly σ donor boryl and the π basic amido are similarly (poorly) effective in N₂ activation (ν_{NN} values of 2013 cm⁻¹ and 2024 to 1999 respectively).

The group of Fryzuk and Masuda developed a novel pincer [N^PNP]⁻ ligand which N^PN anionic part bears resemblance to β -diketiminato ligand.⁴¹⁵ Reduction of the Co^{II} precursor by KC₈ generated the paramagnetic (*S* = 1) complex [[N^PNP]Co], which exists in solution in equilibrium with a small amount of the dinitrogen complex [[N^PNP]Co(N₂)] (scheme 112). Crystals incorporating both complexes could be grown. Most interestingly, the mixture catalyzed the N₂-to-NTMS₃ reduction. Under optimized

conditions (-40°C, THF, 1500 KC₈, 2000 SiMe₃Cl, 10 days), 200 equiv. of N(SiMe₃)₃ were formed.

Scheme 112

Pincer [^RCCC]⁻ (R = Dipp, Mes) ligands featuring two carbenes and an aryl moiety was used by Fout to synthesize Co-N₂ complexes via reduction of the Co^{II} precursor at low temperature (scheme 113).^{416, 417} Like most of the Co^I-N₂ complexes, they are diamagnetic with a square planar geometry at Co and present a weakly activated N₂. Addition of a phosphine yielded the square base pyramid complexes, also diamagnetic, with N₂ in the equatorial plane. The [[^{Dipp}CCC]Co(N₂)] complex was used as catalyst in hydrosilylation of alkene reactions.⁴¹⁸

Scheme 113

The group of Deng synthesized a pincer [CSiC][−] anionic ligand featuring two carbene moieties in the coordination sphere of Co (scheme 114).⁴¹⁹ Subsequent reaction of the Co^{III} [[CSiC]Co(H)(OEt₂)] [BPh₄] complex with hydride source under N₂ resulted in the formation of the [[CSiC]Co(N₂)] species, which presents a strongly distorted square planar geometry at Co (SiCoN angle of 131°). Despite this, the complex is diamagnetic in solution. IR data collected both in solution and solid state show nearly identical frequencies (ν_{NN} : 2004 cm^{−1} for ¹⁴N complex in the solid, 1943 cm^{−1} and 1937 cm^{−1} for ¹⁵N complex in the solid and in solution respectively).

Scheme 114

7.2. Rh complexes

As will be seen below, no Rh and Ir complexes are known for N₂ functionalization, either in a stoichiometric or catalytic way. They thus differ markedly from Co complexes for which N-H and N-Si bond formations have been reported.

7.2.1 P and N containing neutral ligands

Even if the first crystal structure of a Rh-N₂ complex was obtained in 1976 using phosphine ligands, [Rh(H)(N₂)(P*t*Bu₂Ph)₂],⁴²⁰ little work has been reported since 2003 using such ligands. In a work related to studies on the formation of Rh-vinylidenes, Werner and coworkers studied the coordination of diazoalkanes to [Rh(P*i*Pr₃)₂Cl]₂.⁴²¹ In most cases, simple coordination via terminal N of the diazo occurs, without NC bond breaking, leading to [Rh(P*i*Pr₃)₂(R₂CN₂)Cl] complexes. Only in the case of CH(CO₂Et)N₂ does the [Rh(P*i*Pr₃)₂(N₂)Cl] complex forms. Neutral tridentate ligand featuring phosphines or phosphites, such as [PNP], where N is a pyridine moiety have been reported to stabilize square planar Rh^I-N₂ complexes.^{422, 423} Upon deprotonation, the ligand becomes [PNP]⁻ anionic, and metal-ligand cooperation has been reported.⁴²⁴

The group of Burger has used bis-(imino)pyridine [N^RNN^R] (R= Mes or Dipp) ligands to study the synthesis and reactivity of M≡N nitrido complexes (M =Rh, Ir) (scheme 115).⁴²⁵ In order to study the dimerization process, they independently synthesized the Rh-N₂ by reduction of the [[N^RNN^R]RhCl] precursors. In the case of R = Mes, a bridging N₂ complex is formed while the terminal end-on complex is obtained for the more bulky Dipp ligand. In fact, the N₂ complex does not form upon irradiation of the azide derivative [[N^{Dipp}NN^{Dipp}]Rh(N₃)] because of the high reactivity of the generated nitride [[N^{Dipp}NN^{Dipp}]Rh(N)]. Instead, multiple CH bond insertions into the ligand are observed.

Scheme 115

7.2.2 P and N containing anionic ligands

Anionic [PCP][−] ligands have been used to a large extent to provide robust platforms “M[PCP]” for many catalytic applications. Accordingly, coordination of N₂ at these fragments is sufficient to allow isolation of the 16 electron complexes, yet N₂ is readily displaced by many two electron donors en route to catalysis.^{426, 427} An equilibrium between terminal and bridging end-on complexes has been observed (scheme 116).⁴²⁸ Unlike what was presented above, reaction of PhCHN₂ formed a stable adduct only at low temperature. Above -30°C, the diazo is transformed into the carbene complex.

Scheme 116

Related properties have been observed with anionic [PNP]⁻ ligands, i.e. weak coordination of N₂ at Rh.^{429, 430} In 2013, Schneider, de Bruin and coworkers reported the synthesis of [[PNP]Rh(N₂)] and [[PNP]Rh](μ-N₂) ([PNP] = [N(CH=CH*t*Bu₂)₂]) via coupling of the unstable [[PNP]Rh(N)] Rh^{IV} nitride derivative (scheme 117).⁴³¹ Thus, irradiation of the azide precursor in frozen solution generated the nitride which was characterized by in situ IR and EPR spectroscopies. Upon warming, dimerization occurs followed by formation of the terminal N₂ complex.

Scheme 117

Yamashita, Nozaki and coworkers reported the use of [PBP]-diazaborolide/phosphine pincer ligand to stabilize unsaturated [[PBP]Rh] fragment.⁴³² Indeed, this T shaped fragment is only stabilized in the crystal structure by a σCH bond of the benzene moiety of another ligand. In solution, coordination of N₂ is favorable and leads to the expected square planar Rh^I derivative.

7.2.3 NHC ligands

The group of Crudden has studied the coordination of the bulky NHC ligands (IPr and SIPr) as alternative to phosphines. The [Rh(IPr)₂Cl(N₂)] and [Rh(SIPr)₂Cl(N₂)] complexes feature coordinated N₂ ligand, also readily displaced, even in the crystal by O₂ and CO.^{433,434}

7.3. Ir complexes

7.3.1 Neutral ligands

Using the bulky monodentate phosphine *PiPr*₂Ad, Figueroa observed the reversible N₂ coordination at [Ir(*PiPr*₂Ad)₂(H)(N₂)] and CH bond insertion into the ligand at room temperature (scheme 118).⁴³⁵

Scheme 118

Also in 2010, Aldridge reported the first example of a bis-N₂ complex of Ir, [Ir(IMes)₂(N₂)₂][BAr^F₄], in which the N₂ ligands are trans to each other.⁴³⁶ One of the N₂ ligand is readily displaced by THF. Here, as above, the NN bond distance of 1.109(8) Å shows minimal elongation compared to free N₂, although the IR stretch are found at *ca* 1985 cm⁻¹. The same group also prepared the [Ir(IMes)(Cl)(N₂)(COE)] complex, as precursor to [Ir(IMes)₂(Cl)(COE)].⁴³⁷

In 2013, Bohle and coworkers used the labile character of N₂ in [Ir(PPh₃)₂Cl(N₂)] to trap the azo form of the azo-triazole equilibrium (scheme 119).⁴³⁸

Scheme 119

7.3.1 Anionic ligands

In search for luminescent Ir complexes, the group of Zhang and Ding discovered serendipitously an Ir^{II}/Ir^{II} metal–metal-bonded complex featuring a single end-on N₂ ligand. The two metal centers are coordinated by three cyclometalated phenylquinolyl ligands in total.⁴³⁹

The tetradentate $[\text{SiP}_3]^-$ was utilized to stabilize trigonal bipyramidal Ir^I $[[\text{SiP}_3]\text{Ir}(\text{N}_2)]$, similarly to Co.²⁸⁰ The N₂ ligand, trans to the strong σ -donor silyl, is weakly coordinated and shows a stretching frequency at 2122 cm⁻¹, 59 cm⁻¹ higher than the Co analogue. It is readily removed under vacuum.

Like for the Rh complexes, anionic $[\text{PCP}]^-$ ligands have been used to provide robust platforms “Ir[PCP]” for catalytic applications,^{440, 441} such as alkane dehydrogenation.⁴⁴² In these cases, the N₂ complexes can inhibit the reactivity, but in general N₂ is readily displaced by even poor sigma donors. Brookhart has even showed that N₂ can be displaced and that reactions could subsequently occur in single crystals.⁴⁴³

Shimada reported the synthesis of a $[\text{PSiP}]^-$ pincer ligand by insertion of an Ir(I)

precursor into the SiH bond of the [PSiHP] ligand. Subsequent reaction of the [[PSiP]Ir(H)(Cl)] with hydride sources lead to *mer* (major, 85-90%) and *fac* (minor) dihydride complexes [[PSiP]Ir(H)₂(N₂)]. In the *mer* isomer, the N₂ ligand is trans to a hydride while in the *fac*, it is trans to Si with the N-N stretching frequencies are at 2091 cm⁻¹ and 1926 cm⁻¹ respectively.⁴⁴⁴

Tris-pyrazolyl borates have also been shown to support N₂ coordination at Ir. Carmona and coworkers irradiated the Ir(I) [(Tp^{tol})Ir(isoprene)] complex in C₆H₆ under N₂. The isoprene loss resulted in both intra (in the tolyl substituent) and inter (in C₆H₆) CH bond activations yielding an Ir(III)-N₂ complex.⁴⁴⁵

In 2004, Chirik showed that [Ir(L^{Me,dipp})(N₂)(COE)] (L^{Me,dipp} = CH{CMeN(2,6-*i*-Pr₂C₆H₃)₂}₂⁻) can be used as precursor for H₂ and CH bond activation.⁴⁴⁶

In 2008, Grubbs reported the use of a [[PNP]Ir(N₂)] complex as catalyst for the oxidation of *t*BuMeO by organic azide to produce HC=NR(*Ot*Bu) (scheme 120).⁴⁴⁷ The Ir-N₂ moiety is generated from the reaction between the Ir=CHO*t*Bu Fischer carbene intermediate and nucleophilic azide. The reaction requires the use of NBE (norbornene) as sacrificial H₂ acceptor.

Scheme 120

The groups of Schneider and de Bruin have studied in greatest details the chemistry of the “[PNP]Ir” fragment ([PNP] = (N(CHCHPtBu₂)₂), in parallel to the one of Rh presented above. They do bear some similarities. In particular, photolysis of the Ir^{II} azide precursor generates the nitride Ir^{IV} complex, unstable at room temperature which eventually leads to the bridging N₂ dimer (scheme 121). On the other hand, oxidation by one electron yields the stable Ir^V nitride cationic species.⁴⁴⁸ This is explained by the nitridyl N^o character of the neutral *vs* closed shell nature of the cation. Alternatively, the bridging N₂ dimer can be obtained upon one electron reduction of the cation and the mechanism was studied.⁴⁴⁹ Although the nitride is not obtained from N₂, understanding its functionalization is important.

Scheme 121

H atom transfer to form the amido complex was studied experimentally and computationally. Protonation of the amido finally generates the Ir-NH₃ complex.⁴⁵⁰

8. Group 10 and 11 transition metal–dinitrogen complexes

Jonas made a seminal report on the synthesis and structural characterization of the

Ni-N₂ complex [Ni(PCy₃)₂(N₂)] in 1968. An equilibrium between the mononuclear complex and the $\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2$ bridged dinuclear complex was evidenced. Johnson proposed a different synthetic approach to the [Ni(PiPr₃)₂]($\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2$) complex, relying on the reduction of the [Ni(PiPr₃)₂Cl] Ni^I precursor with Mg in THF (scheme 122).⁴⁵¹ Interestingly, the complex features a NN stretching frequency at 1908 cm⁻¹ in the Raman spectrum, a very low value compared to other Ni complexes, which can be linked to the geometry of the complex favoring the orbital overlap with the π^* orbitals of N₂.

Scheme 122

Waterman and Hillhouse reported the synthesis of the pseudo tetrahedral Ni⁰ complex [Ni(dtbpe)(PPh₃)(N₂)] from the reaction of [Ni(dtbpe)]₂($\mu,\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6$) with PPh₃ under N₂.⁴⁵² Starting from 2014 Lee and coworkers developed tridentate phosphine/Ni platforms that support N₂ coordination. In a first study, the neutral [[PPP]Ni(N₂)] Ni⁰ complex ([PPP] = PMe(2-PiPr₂-C₆H₄)₂) was reported (scheme 123).⁴⁵³ It is in equilibrium with the N₂ bridged dimer. N₂ is reversibly displaced by CO₂, pointing a weak coordination of both ligands to Ni.

Scheme 123

The same group found out that the related phosphide Ni^{II} complex reacted with alkoxide sources under N₂ to form the Ni⁰ [[PPP]Ni(N₂)] complexes via a formal reductive elimination of the P-OR' moiety.^{454, 455} If the reaction is carried out under Ar, the reduction of the Ni center does not occur, and the ligand remains the anionic [PPP]⁻ ligand featuring a central phosphide.

The groups of Balcells and Hazari observed a related reactivity with an anionic [PSiP]⁻ ligand ([PSiP] = SiMe(2-PCy₂-C₆H₄)₂). Thus, upon reaction of the [[PSiP]NiH] complex with N₂, reductive elimination of SiH was evidenced (scheme 124). The coordination sphere of the Ni⁰ formed is completed by an agostic interaction with the Si-H bond.⁴⁵⁶

Scheme 124

The group of Peters evidenced tridentate coordination of the neutral [BP₂] ligand, via the BPh moiety as well as phosphines, in the [[BP₂]Ni(N₂)] Ni⁰ complex, obtained by Na/Hg reduction of the Ni^I precursor (scheme 125).⁴⁵⁷ In the solid state structure, both the monomer and the end on N₂ bridging dimer are present. The complex reacts with H₂ to release N₂ and form first the dihydrogen adduct, followed by H-H cleavage and insertion into the NiB bond.

Scheme 125

Coordination of another tridentate neutral [PPP] ligand featuring a ferrocenyl moiety ([PPP] = [Fe(η⁵-C₅H₄PPh₂)(η⁵-C₅H₄P*i*Bu-2-PPh₂C₆H₄)]) to Ni⁰ under N₂ also yielded a binuclear complex with bridging dinitrogen [[PPP]Ni]₂(μ-η¹:η¹-N₂) (scheme 126).⁴⁵⁸ If the PPh₂ moiety is replaced by a BPh₂ moiety, its coordination is observed rather than N₂ coordination, much like for the [BP₂] ligand presented above.

Scheme 126

Tetrapodal ligands have also been used for the stabilization of Ni-N₂ complexes. Upon protonation of the $[[\text{SiP}_3]\text{Ni}(\text{CH}_3)]$ Ni^{II} complexes under N₂, Peters isolated the corresponding cationic N₂ complex $[[\text{SiP}_3]\text{Ni}(\text{N}_2)]^+$, in which the N₂ ligand is minimally activated, as attested by the NN bond distance and the very high stretching frequency (2223 and 2234 cm⁻¹ for the complexes with *i*Pr and Ph substituents at P) (scheme 127, top).⁴⁵⁹ Exposition of the bimetallic In^{III}-Ni⁰ complex supported by a [N₄P₃] ligand to N₂ allowed Lu to isolate the corresponding thermally stable $[[\text{N}_4\text{P}_3]\text{InNi}(\text{N}_2)]$ complex (scheme 127, bottom).⁴⁶⁰ Synthesis of the related Al^{III} and Ga^{III} $[[\text{N}_4\text{P}_3]\text{MNi}]$ analogues was done but these complexes do not coordinate N₂.³⁰¹

Scheme 127

Like for many other metal centers, beta diketiminates have permitted stabilization of Ni-N₂ complexes. Thus, as shown by Limberg, reduction of the $[(L^{tBu,dipp})NiBr]$ ($L^{tBu,dipp} = CH\{C(t-Bu)N(2,6-i-Pr_2C_6H_3)\}_2^-$) complex resulted in the formation of the Ni^I end-on N₂ dimer $[\{Ni(L^{tBu,dipp})\}_2(\mu-\eta^1:\eta^1-N_2)]$ via the proposed intermediate $[Ni(L^{tBu,dipp})H]_2$ (scheme 128).⁴⁶¹ Alternatively, the complex can be obtained by the KC₈ reduction. This complex, featuring two Ni centers in T shaped geometry, is a triplet of spin consistent with two uncoupled Ni^I ions. Most interestingly, upon further reductions by KC₈, both the mono and di-reduced complexes could be isolated and characterized. In these complexes, the K⁺ cations coordinate the aryl groups as well as the N₂ ligand in a side on fashion. X-ray structure analyses of the “Ni₂N₂”, “Ni₂N₂K” and “Ni₂N₂K₂” complexes evidenced stepwise reduction of the N₂ fragment (NN bond distances of 1.120(4), 1.143(8) and 1.185(8) Å respectively) also corroborated by the systematic decrease of the ν_{N-N} stretching frequencies from 2164 to 1825 to 1696 cm⁻¹ respectively. The same group reported the reduction of the “Ni₂N₂”, “Ni₂N₂K” complexes by Na instead of KC₈ to form the related “Ni₂N₂Na₂” and “Ni₂N₂KNa” complexes. A similar side on coordination of N₂ to Na was also evidenced.⁴⁶² Despite a formal reduction of the N₂ fragment in the Ni⁽⁰⁾ complexes, it is readily displaced by CO. The complex also reacts with extremely inert SF₆ gas first via redox process followed by S-F bond breaking.⁴⁶³

Scheme 128

Even if it does not concern molecular complexes, it is pertinent to cite here the work of Bordiga who has measured the adsorption enthalpy of N₂ on a five coordinate Ni^{II} site of the MOF CPO-27-Ni to be -17 kJ/mol.⁴⁶⁴ It is expectedly much weaker than coordination of both CO and NO (-50 and -90 kJ/mol respectively).

Finally, there are no Pd or Pt complexes of N₂ to date.

9. Group 11 transition metal–dinitrogen complexes

The first Cu complex of N₂ was isolated as recently as 2014 by the group of Murray. They carefully designed a macrocyclic tris(β-diketimine) ligand which upon deprotonation favors coordination of three Cu^I centers as well as a N₂ molecule, making a “Cu₃N₂³⁺” central core (scheme 129).⁴⁶⁵ In the crystal structure, the position of N₂ is disordered with a major component (75%) presenting a μ-η¹:η²:η¹-N₂ coordination and a distance of 1.0956(1) Å. In the minor component (25%) the N₂ ligand presents only η¹ coordination mode with the two N atoms acting as μ^{1,1} and μ^{1,2} bridging respectively. The NN stretching frequency in the Raman spectrum is found at 1952 cm⁻¹, pointing a relatively activated N₂ fragment. DFT calculations on truncated models reveal that subtle changes in the ligand have a large influence on the activation of N₂ in this environment. If the reaction is done with CuCl instead of CuOTf, the complex featuring a μ³-Cl is obtained.⁴⁶⁶

Scheme 129

Cundari, Warren and coworkers showed that the tris-pyrazolylborate ligand ⁱPr²Tp allows Cu^I-N₂-Cu^I formation.⁴⁶⁷ Thus, reaction of the [(ⁱPr²Tp)Cu^{II}(OH)]₂ precursor with two equivalents of Ph₃SiH at -20°C led to several color changes, ultimately forming colorless crystals of [(ⁱPr²Tp)Cu]₂(μ-η¹:η¹-N₂) in 38% yield. Impressively, the authors were able to isolate and crystallize a purple intermediate, only stable at low temperature (below -20°C) [(ⁱPr²Tp)Cu]₂(μ-H), a mixed valence dicopper hydride complex. The dinitrogen complex [(ⁱPr²Tp)Cu]₂(μ-η¹:η¹-N₂) presents modest thermal stability and N₂ is readily displaced by two electron donors, such as nitriles or isonitriles to form the corresponding monometallic Cu^I complexes.

Chen and coworkers studied the *in situ* generated formamidinate ligands coordination to Cu^{II}acetate under solvothermal conditions (scheme 130).⁴⁶⁸ The ligand (*N,N'*-bis(pyridine-*n*-ylmethyl)formamidinate), made from either 3 or 4-aminomethylpyridine, acts as building block for coordination polymers together with N₂. Presence of N₂ was evidenced by the differences in the IR spectra obtained using ¹⁴N₂ and ¹⁵N₂ gases. The NN stretching frequency at 1575 cm⁻¹ is consistent with a N₂⁻ moiety.

Scheme 130

There has been no report of molecular N₂ complexes of Ag and Au since 2003.

Conclusion and perspectives

It is quite obvious in light of the large body of works presented in this review that tremendous progresses have been made in the coordination chemistry of N₂ since 2003. In fact, the domain goes far beyond simple coordination of N₂ to metal fragments. It is well understood that functionalization of N₂ requires “activation”, *i.e.* electron transfer from the metal center to N₂. It has been a standard practice to evaluate such activation, or degree of N-N bond order reduction, by comparing crystallographically determined NN bond distance in a complex with the one of free N₂. As we now know a vast number of metal complexes of N₂, it appears that the NN bond distance is neither useful in terms of predicting complex stability, reactivity at N₂, nor helpful to assign oxidation state at metal within bimetallic complexes.

In terms of N₂ coordination, activation and functionalization, three cases can be put forward.

First, activation of N₂ between two metals is classically observed with metallic fragments featuring metal centers in low oxidation state. Multiple electron transfers from the metals to N₂ result in reduction to formal N₂^{x-} moiety. It would seem enough to transfer two electrons to N₂ to enhance nucleophilicity at N and enable functionalization under mild conditions. A representative example is given by recent work of Xi and Zhang. Indeed functionalization of a “Sc₂N₂” complex, featuring N₂²⁻ fragment, was not observed, while the one additional electron complex, featuring the reduced N₂³⁻ fragment, reacted with the strong electrophile MeOTf. Accordingly, most significant achievements have been witnessed with formal N₂⁴⁻ fragment stabilized by group 4 metals by the

groups of Fryzuk and Chirik. In particular, reactivity with H₂, silanes (Si-H), boranes (B-H) and CO have allowed N-E (E = H, Si, B, C) bond formation under neutral conditions.

A second case is found when enough electrons are found at metal centers to favor a six-electron transfer to π^* and σ^* orbitals of N₂. This transfer, also implying appropriate orbital symmetry overlap, results in N $\equiv$ N bond splitting and nitride (bridging or terminal) formation. Bridging nitrides are obtained for example from a Ti₃ hydride cluster or from two group 5 “M^{II}(amidinate)(Cp*)” fragments, or from two “Fe⁰(Nacnac)” fragments, while terminal nitride was first obtained by Cummins using a “Mo^{III}(amide)₃” fragment. Subsequent functionalization of the terminal nitride has led to stoichiometric synthesis of N derivatives (nitriles by Cummins and Schneider, silylamine by Sita, silylamine and borylamine by Mézailles, cyanate by Kawaguchi).

The third case concerns mid to late transition metals, for which terminal M-N₂ are classical, sometimes needing that bulky ligands are used to prevent end-on bridging dimer formation. In that case, functionalization of N₂ requires significant nucleophilic or basic character of the terminal N center, and competition with alkylation/protonation at the metal center can be a major issue. Seminal works by Chatt and Hidai in the seventies illustrate favorable reactivity at N for group 6 M⁰ centers, while many other M-N₂ metal complexes require reduction (by one or two electrons) prior to functionalization (works of Schrock, Peters to achieve NH bond formation, or Nishibayashi, Peters, Lu, Fryzuk and Masuda for N-Si bond formation).

Notably, these principles of N₂ activation/functionalization have been extended most recently to main group metals. Braunschweig reported in 2018 that the generation of an electron rich borylene fragment allowed the first trapping of N₂ between two B

centers,⁴⁶⁹ and in 2019 the coupling between two N₂ molecules.⁴⁷⁰ Subsequent protonation created two NH bonds. In 2019, Berben showed that controlled potential electrolysis (-1.16V vs SCE in THF) of a cationic Al^{III} complex under N₂, in the presence of a proton source yielded 21% of NH₃.⁴⁷¹ Although no N₂ complex was observed, isotope labelling demonstrated it to be the source of NH₃.

The studies dealing with stoichiometric functionalization of N₂ have allowed the development of the two known catalytic reductions of N₂: the N₂-to-N(SiMe₃)₃ and the N₂-to-NH₃ processes. Hidai reported in 1989 that a Mo⁰ complex is a competent catalyst

(TON ca 20) for the N₂-to-N(SiMe₃)₃ reaction, and catalysts based on Mo (Nishibayashi), Co (Lu, Masuda and Fryzuk) and Fe (Ashley) have been reported in the last decade to achieve TONs of ca 200, 200 and 120 respectively. This process is proposed to involve SiMe₃ radicals. Several complexes that are catalytic intermediates (hydrazido, nitrido, imido) have been isolated from stepwise functionalization of Mo-N₂ by Mézailles.

Schrock reported the first catalyzed N₂-to-NH₃ process in 2003, using a trisamido-amine Mo complex, and characterized many catalytic intermediates. Nishibayashi has presented several Mo complexes, among which a Mo-nitride, with improved efficiency and TONs (up to ca 400 equiv. NH₃). In 2019, this group reported the use of SmI₂ as reductant in combination with protic solvents, leading to unprecedented efficiency (91%), TON of 4350 equiv. of NH₃ (from 14400 equiv. SmI₂ and H₂O) and turnover frequency of 117 min⁻¹. Among the other metals active in this catalysis, Fe occupies an important place. Several catalysts have been developed by the groups of Peters and Nishibayashi. Most importantly, detailed mechanistic investigations have been carried out by Peters allowing characterization of many intermediates in N-H bond formation especially for their [BP₃]Fe system. Moreover, this group has recently demonstrated improved performance at lower driving force (*i.e.* use of [Ph₂NH₂]OTf/Cp*₂Co couple vs HBAR^F₄/KC₈), which highlights the importance of optimizing the proton source/reductant couple. In terms of mechanism, in addition to stepwise electron transfer (ET)-proton transfer (PT) or PT-ET pathways, PCET steps have been discussed in the past years.

To the catalytic systems involving these two metals, one needs to add the first examples of Ti by Liddle, V by Nishibayashi, Ru and Os by Peters, and Co by Peters and Nishibayashi in the past six years. These results demonstrate that catalysis for N₂

reduction is not limited to the metal complexes found in nitrogenase enzymes (especially Mo and Fe), and pave the way for further developments.

References

- (1) Haber, F. Verfahren Zur Herstellung von Ammoniak Durch Katalytische Vereinigung von Stickstoff Un Wasserstoff, Zwekmässig Unter Hohem Druck., 1909.
- (2) Haber, F. No Title. *Z. Angew. Chem* **1914**, 27, 473–477.
- (3) Mittasch, A.; Frankenburger, W. The Historical Development and Theory of Ammonia Synthesis. *J. Chem. Educ.* **1929**, 6 (12), 2097–2098.
<https://doi.org/10.1021/ed006p2097>.
- (4) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. Metal Vapor Synthesis of (C₅Me₅Sm(THF)₂ and (C₅Me₄Et)₂Sm(THF)₂ and Their Reactivity with Organomercurial Reagents. Synthesis and X-Ray Structural Analysis of (C₅Me₅Sm(C₆H₅)(THF). *Organometallics* **1985**, 4 (1), 112–119.
<https://doi.org/10.1021/om00120a019>.
- (5) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. Isolation and X-Ray Crystal Structure of the First Dinitrogen Complex of an f-Element Metal, [(C₅Me₅)₂Sm]N₂. *J. Am. Chem. Soc.* **1988**, 110 (20), 6877–6879. <https://doi.org/10.1021/ja00228a043>.
- (6) Bochkarev, M. N.; Trifonov, A. A.; Razuvaev, G. A.; Ilatovskaya, M. A.; Shur, V. B. FIXATION OF MOLECULAR NITROGEN BY RARE-EARTH METAL COMPOUNDS. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1986**, 35, 1726–1728.

- (7) Evans, W. J. Tutorial on the Role of Cyclopentadienyl Ligands in the Discovery of Molecular Complexes of the Rare-Earth and Actinide Metals in New Oxidation States^{136†}. *Organometallics* **2016**, *35* (18), 3088–3100.
<https://doi.org/10.1021/acs.organomet.6b00466>.
- (8) Guan, J.; Dube, T.; Gambarotta, S.; Yap, G. P. A. Dinitrogen Labile Coordination versus Four-Electron Reduction, THF Cleavage, and Fragmentation Promoted by a (Calix-Tetrapyrrole)Sm(II) Complex. *Organometallics* **2000**, *19* (23), 4820–4827.
<https://doi.org/10.1021/om000698p>.
- (9) Jubb, J.; Gambarotta, S. Dinitrogen Reduction Operated by a Samarium Macrocyclic Complex. Encapsulation of Dinitrogen into a Sm₂Li₄ Metallic Cage. *J. Am. Chem. Soc.* **1994**, *116* (10), 4477–4478.
<https://doi.org/10.1021/ja00089a047>.
- (10) Demir, S.; Siladke, N. A.; Ziller, J. W.; Evans, W. J. Scandium and Yttrium Metallocene Borohydride Complexes: Comparisons of (BH₄)¹⁻-vs. (BPh₄)¹⁻ Coordination and Reactivity. *Dalt. Trans.* **2012**, *41* (32), 9659–9666.
<https://doi.org/10.1039/c2dt30861d>.
- (11) Demir, S.; Lorenz, S. E.; Fang, M.; Furche, F.; Meyer, G.; Ziller, J. W.; Evans, W. J. Synthesis, Structure, and Density Functional Theory Analysis of a Scandium Dinitrogen Complex, [(C₅Me₄H)₂Sc]₂(μ-H₂: H₂-N₂). *J. Am. Chem. Soc.* **2010**, *132* (32), 11151–11158. <https://doi.org/10.1021/ja102681w>.
- (12) Mueller, T. J.; Fieser, M. E.; Ziller, J. W.; Evans, W. J. (C₅Me₄H)₁--Based Reduction of Dinitrogen by the Mixed Ligand Tris(Polyalkylcyclopentadienyl) Lutetium and Yttrium Complexes, (C₅Me₅)_{3-x}(C₅Me₄H)_xLn. *Chem. Sci.* **2011**,

- 2 (10), 1992–1996. <https://doi.org/10.1039/c1sc00139f>.
- (13) Schmiede, B. M.; Ziller, J. W.; Evans, W. J. Reduction of Dinitrogen with an Yttrium Metallocene Hydride Precursor, [(C₅Me₅)₂YH]₂. *Inorg. Chem.* **2010**, *49* (22), 10506–10511. <https://doi.org/10.1021/ic101558e>.
- (14) Fieser, M. E.; Woen, D. H.; Corbey, J. F.; Mueller, T. J.; Ziller, J. W.; Evans, W. J. Raman Spectroscopy of the N-N Bond in Rare Earth Dinitrogen Complexes. *Dalt. Trans.* **2016**, *45* (37), 14634–14644. <https://doi.org/10.1039/c5dt04547a>.
- (15) Lorenz, S. E.; Schmiede, B. M.; Lee, D. S.; Ziller, J. W.; Evans, W. J. Synthesis and Reactivity of Bis(Tetramethylcyclopentadienyl) Yttrium Metallocenes Including the Reduction of Me₃SiN₃ to [(Me₃Si)₂N] – with [(C₅Me₄H)₂Y(THF)]₂(μ-η²:η²-N₂). *Inorg. Chem.* **2010**, *49* (14), 6655–6663. <https://doi.org/10.1021/ic100682d>.
- (16) MacDonald, M. R.; Ziller, J. W.; Evans, W. J. Synthesis of a Crystalline Molecular Complex of Y₂⁺, [(18-Crown-6)K][(C₅H₄SiMe₃)₃Y]. *J. Am. Chem. Soc.* **2011**, *133* (40), 15914–15917. <https://doi.org/10.1021/ja207151y>.
- (17) Evans, W. J.; Lee, D. S.; Lie, C.; Ziller, J. W. Expanding the LnZ₃/Alkali-Metal Reduction System to Organometallic and Heteroleptic Precursors: Formation of Dinitrogen Derivatives of Lanthanum. *Angew. Chem. Int. Ed.* **2004**, *43* (41), 5517–5519. <https://doi.org/10.1002/anie.200461170>.
- (18) Evans, W. J.; Rego, D. B.; Ziller, J. W. Synthesis, Structure, and ¹⁵N NMR Studies of Paramagnetic Lanthanide Complexes Obtained by Reduction of Dinitrogen. *Inorg. Chem.* **2006**, *45* (26), 10790–10798. <https://doi.org/10.1021/ic061485g>.

- (19) Jaroschik, F.; Momin, A.; Nief, F.; Le Goff, X. F.; Deacon, G. B.; Junk, P. C.
Dinitrogen Reduction and C-H Activation by the Divalent Organoneodymium
Complex [(C₅H₂tBu₃)₂Nd(μ-I)K([18] Crown-6)]. *Angew. Chem. Int. Ed.* **2009**, *48*
(6), 1117–1121. <https://doi.org/10.1002/anie.200804934>.
- (20) Demir, S.; Gonzalez, M. I.; Darago, L. E.; Evans, W. J.; Long, J. R. Giant
Coercivity and High Magnetic Blocking Temperatures for N₂- Radical-Bridged
Dilanthanide Complexes upon Ligand Dissociation /639/638/263/406
/639/638/911 /639/638/298/920 Article. *Nat. Commun.* **2017**, *8* (1), 1–9.
<https://doi.org/10.1038/s41467-017-01553-w>.
- (21) Evans, W. J.; Allen, N. T.; Ziller, J. W. Expanding Divalent Organolanthanide
Chemistry: The First Organothulium(II) Complex and the in Situ
Organodysprosium(II) Reduction of Dinitrogen. *Angew. Chem. Int. Ed.* **2002**, *41*
(2), 359–361. [https://doi.org/10.1002/1521-3773\(20020118\)41:2<359::AID-ANIE359>3.0.CO;2-A](https://doi.org/10.1002/1521-3773(20020118)41:2<359::AID-ANIE359>3.0.CO;2-A).
- (22) Evans, W. J.; Lee, D. S.; Johnston, M. A.; Ziller, J. W. The Elusive (C₅Me₄H)
3Lu: Its Synthesis and LnZ₃/K/N₂ Reactivity. *Organometallics* **2005**, *24* (26),
6393–6397. <https://doi.org/10.1021/om050709k>.
- (23) Evans, W. J.; Lee, D. S.; Ziller, J. W. Reduction of Dinitrogen to Planar Bimetallic
M₂(N₂) Complexes of Y, Ho, Tm, and Lu Using the K/Ln[N(SiMe₃)₂]₃
Reduction System Evans, W. J., Lee, D. S., & Ziller, J. W. (2004). Reduction of
Dinitrogen to Planar Bimetallic M₂(N₂) Com. *J. Am. Chem. Soc.*
2004, *126* (2), 454–455. <https://doi.org/10.1021/ja036923m>.
- (24) Evans, W. J.; Lee, D. S.; Rego, D. B.; Perotti, J. M.; Kozimor, S. A.; Moore, E. K.;

- Ziller, J. W. Expanding Dinitrogen Reduction Chemistry to Trivalent Lanthanides via the LnZ3/Alkali Metal Reduction System: Evaluation of the Generality of Forming Ln₂(μ-H₂:H₂-N₂) Complexes via LnZ3/K. *J. Am. Chem. Soc.* **2004**, *126* (44), 14574–14582. <https://doi.org/10.1021/ja046047s>.
- (25) Fang, M.; Bates, J. E.; Lorenz, S. E.; Lee, D. S.; Rego, D. B.; Ziller, J. W.; Furche, F.; Evans, W. J. (N₂)₃- Radical Chemistry via Trivalent Lanthanide Salt/Alkali Metal Reduction of Dinitrogen: New Syntheses and Examples of (N₂)₂- and (N₂)₃- Complexes and Density Functional Theory Comparisons of Closed Shell Sc³⁺, Y³⁺, and Lu³⁺ versus 4f⁹ Dy³⁺. *Inorg. Chem.* **2011**, *50* (4), 1459–1469. <https://doi.org/10.1021/ic102016k>.
- (26) Evans, W. J.; Fang, M.; Zucchi, G. L.; Furche, F.; Ziller, J. W.; Hoekstra, R. M.; Zink, J. I. Isolation of Dysprosium and Yttrium Complexes of a Three-Electron Reduction Product in the Activation of Dinitrogen, the (N₂)₃- Radical. *J. Am. Chem. Soc.* **2009**, *131* (31), 11195–11202. <https://doi.org/10.1021/ja9036753>.
- (27) Evans, W. J.; Zucchi, G.; Ziller, J. W. Dinitrogen Reduction by Tm(II), Dy(II), and Nd(II) with Simple Amide and Aryloxide Ligands. *J. Am. Chem. Soc.* **2003**, *125* (1), 10–11. <https://doi.org/10.1021/ja0211712>.
- (28) Fieser, M. E.; Bates, J. E.; Ziller, J. W.; Furche, F.; Evans, W. J. Dinitrogen Reduction via Photochemical Activation of Heteroleptic Tris(Cyclopentadienyl) Rare-Earth Complexes. *J. Am. Chem. Soc.* **2013**, *135* (10), 3804–3807. <https://doi.org/10.1021/ja400664s>.
- (29) Fieser, M. E.; Johnson, C. W.; Bates, J. E.; Ziller, J. W.; Furche, F.; Evans, W. J. Dinitrogen Reduction, Sulfur Reduction, and Isoprene Polymerization via

Photochemical Activation of Trivalent Bis(Cyclopentadienyl) Rare-Earth-Metal Allyl Complexes. *Organometallics* **2015**, 34 (17), 4387–4393.

<https://doi.org/10.1021/acs.organomet.5b00613>.

- (30) Meihaus, K. R.; Corbey, J. F.; Fang, M.; Ziller, J. W.; Long, J. R.; Evans, W. J. Influence of an Inner-Sphere K⁺ Ion on the Magnetic Behavior of N₂³⁻ Radical-Bridged Dilanthanide Complexes Isolated Using an External Magnetic Field. *Inorg. Chem.* **2014**, 53 (6), 3099–3107. <https://doi.org/10.1021/ic4030102>.
- (31) Fang, M.; Lee, D. S.; Ziller, J. W.; Doedens, R. J.; Bates, J. E.; Furche, F.; Evans, W. J. Synthesis of the (N₂)₃⁻ Radical from Y²⁺ and Its Protonolysis Reactivity to Form (N₂H₂)₂⁻ via the Y[N(SiMe₃)₂]₃/K⁺ 8 Reduction System. *J. Am. Chem. Soc.* **2011**, 133 (11), 3784–3787. <https://doi.org/10.1021/ja1116827>.
- (32) Rinehart, J. D.; Fang, M.; Evans, W. J.; Long, J. R. Strong Exchange and Magnetic Blocking in N₂³⁻ Radical-Bridged Lanthanide Complexes. *Nat. Chem.* **2011**, 3 (7), 538–542. <https://doi.org/10.1038/nchem.1063>.
- (33) Rinehart, J. D.; Fang, M.; Evans, W. J.; Long, J. R. A N₂³⁻ Radical-Bridged Terbium Complex Exhibiting Magnetic Hysteresis at 14 K. *J. Am. Chem. Soc.* **2011**, 133 (36), 14236–14239. <https://doi.org/10.1021/ja206286h>.
- (34) Dubé, T.; Conoci, S.; Gambarotta, S.; Yap, G. P. A.; Vasapollo, G. Tetrametallic Reduction of Dinitrogen: Formation of a Tetranuclear Samarium Dinitrogen Complex. *Angew. Chem. Int. Ed.* **1999**, 38 (24), 3657–3659. [https://doi.org/10.1002/\(SICI\)1521-3773\(19991216\)38:24<3657::AID-ANIE3657>3.0.CO;2-A](https://doi.org/10.1002/(SICI)1521-3773(19991216)38:24<3657::AID-ANIE3657>3.0.CO;2-A).
- (35) Dube', T.; Ganesan, S.; Conoci, S.; Gambarotta, S.; Yap, G. P. A. Tetrametallic

- Divalent Samarium Cluster Hydride and Dinitrogen Complexes. *Organometallics* **2000**, *19* (18), 3716–3721. <https://doi.org/10.1021/om000502l>.
- (36) Ganesan, M.; Gambarotta, S.; Yap, G. P. A. Highly Reactive SmII Macrocyclic Clusters: Precursors to N₂ Reduction. *Angew. Chem. Int. Ed.* **2001**, *40* (4), 766–769. [https://doi.org/10.1002/1521-3773\(20010216\)40:4<766::AID-ANIE7660>3.0.CO;2-H](https://doi.org/10.1002/1521-3773(20010216)40:4<766::AID-ANIE7660>3.0.CO;2-H).
- (37) Woen, D. H.; Chen, G. P.; Ziller, J. W.; Boyle, T. J.; Furche, F.; Evans, W. J. End-On Bridging Dinitrogen Complex of Scandium. *J. Am. Chem. Soc.* **2017**, *139* (42), 14861–14864. <https://doi.org/10.1021/jacs.7b08456>.
- (38) Lv, Z. J.; Huang, Z.; Zhang, W. X.; Xi, Z. Scandium-Promoted Direct Conversion of Dinitrogen into Hydrazine Derivatives via N-C Bond Formation. *J. Am. Chem. Soc.* **2019**, *141* (22), 8773–8777. <https://doi.org/10.1021/jacs.9b04293>.
- (39) Roussel, P.; Scott, P. Complex of Dinitrogen with Trivalent Uranium. *J. Am. Chem. Soc.* **1998**, *120*, 1070–1071. <https://doi.org/10.1021/ja972933+>.
- (40) Odom, A. L.; Arnold, P. L.; Cummins, C. C. Heterodinuclear Uranium/Molybdenum Dinitrogen Complexes [16]. *J. Am. Chem. Soc.* **1998**, *120* (23), 5836–5837. <https://doi.org/10.1021/ja980095t>.
- (41) Cloke, F. G. N.; Hitchcock, P. B. Reversible Binding and Reduction of Dinitrogen by a Uranium(III) Pentalene Complex. *J. Am. Chem. Soc.* **2002**, *124* (32), 9352–9353. <https://doi.org/10.1021/ja027000e>.
- (42) Korobkov, I.; Gambarotta, S.; Yap, G. P. A. A Highly Reactive Uranium Complex Supported by the Calix[4]Tetrapyrrole Tetraanion Affording Dinitrogen Cleavage, Solvent Deoxygenation, and Polysilanol Depolymerization. *Angew. Chem. Int. Ed.*

2002, No. 18, 3433–3436.

- (43) Evans, W. J.; Kozimor, S. A.; Ziller, J. W. A Monometallic f Element Complex of Dinitrogen: (C⁵Me⁵)₃U(H¹-N₂). *J. Am. Chem. Soc.* **2003**, *125* (47), 14264–14265. <https://doi.org/10.1021/ja037647e>.
- (44) Korobkov, I.; Gambarotta, S.; Yap, G. P. A. Amide from Dinitrogen by In Situ Cleavage and Partial Hydrogenation Promoted by a Transient Zero-Valent Thorium Synthone. *Angew. Chem. Int. Ed.* **2003**, *42* (40), 4958–4961. <https://doi.org/10.1002/anie.200352205>.
- (45) Mansell, S. M.; Kaltsoyannis, N.; Arnold, P. L. Small Molecule Activation by Uranium Tris(Aryloxides): Experimental and Computational Studies of Binding of N₂, Coupling of CO, and Deoxygenation Insertion of CO₂ under Ambient Conditions. *J. Am. Chem. Soc.* **2011**, *133* (23), 9036–9051. <https://doi.org/10.1021/ja2019492>.
- (46) Mansell, S. M.; Farnaby, J. H.; Germeroth, A. I.; Arnold, P. L. Thermally Stable Uranium Dinitrogen Complex with Siloxide Supporting Ligands. *Organometallics* **2013**, *32* (15), 4214–4222. <https://doi.org/10.1021/om4003957>.
- (47) Camp, C.; Pécaut, J.; Mazzanti, M. Tuning Uranium-Nitrogen Multiple Bond Formation with Ancillary Siloxide Ligands. *J. Am. Chem. Soc.* **2013**, *135* (32), 12101–12111. <https://doi.org/10.1021/ja405815b>.
- (48) Falcone, M.; Chatelain, L.; Scopelliti, R.; Živković, I.; Mazzanti, M. Nitrogen Reduction and Functionalization by a Multimetallic Uranium Nitride Complex. *Nature* **2017**, *547* (7663), 332–335. <https://doi.org/10.1038/nature23279>.
- (49) Falcone, M.; Barluzzi, L.; Andrez, J.; Fadaei Tirani, F.; Živkovic, I.; Fabrizio, A.;

- Corminboeuf, C.; Severin, K.; Mazzanti, M. The Role of Bridging Ligands in Dinitrogen Reduction and Functionalization by Uranium Multimetallic Complexes. *Nat. Chem.* **2019**, *11* (2), 154–160. <https://doi.org/10.1038/s41557-018-0167-8>.
- (50) Bercaw, J. E.; Brintzinger, H. H. Bis(Pentamethylcyclopentadienyl)Titanium(II). Isolation and Reactions with Hydrogen, Nitrogen, and Carbon Monoxide. *J. Am. Chem. Soc.* **1971**, *93* (8), 2045–2046. <https://doi.org/10.1021/ja00737a033>.
- (51) Bercaw, J. E. Bis(Pentamethylcyclopentadienyl)Titanium(II) and Its Complexes with Molecular Nitrogen. *J. Am. Chem. Soc.* **1974**, *96* (16), 5087–5095. <https://doi.org/10.1021/ja00823a012>.
- (52) de Wolf, J. M.; Blaauw, R.; Meetsma, A.; Teuben, J. H.; Gyepes, R.; Varga, V.; Mach, K.; Veldman, N.; Spek, A. L. Bis(Tetramethylcyclopentadienyl)Titanium Chemistry. Molecular Structures of [(C₅HMe₄)(μ-η¹:η⁵-C₅Me₄)Ti]₂ and [(C₅HMe₄)₂Ti]₂N₂. *Organometallics* **1996**, *15* (23), 4977–4983. <https://doi.org/10.1021/om960509w>.
- (53) Hanna, T. E.; Bernskoetter, W. H.; Bouwkamp, M. W.; Lobkovsky, E.; Chirik, P. J. Bis(Cyclopentadienyl) Titanium Dinitrogen Chemistry: Synthesis and Characterization of a Side-on Bound Haptomer. *Organometallics* **2007**, *26* (9), 2431–2438. <https://doi.org/10.1021/om0611913>.
- (54) Semproni, S. P.; Milsmann, C.; Chirik, P. J. Side-on Dinitrogen Complexes of Titanocenes with Disubstituted Cyclopentadienyl Ligands: Synthesis, Structure, and Spectroscopic Characterization. *Organometallics* **2012**, *31* (9), 3672–3682.

<https://doi.org/10.1021/om300156z>.

- (55) Scherer, A.; Kollak, K.; Lützen, A.; Friedemann, M.; Haase, D.; Saak, W.; Beckhaus, R. Low-Valent Titanium-Pentafulvene Complexes - Formation of Dinuclear Titanium-Nitrogen Complexes. *Eur. J. Inorg. Chem.* **2005**, No. 6, 1003–1010. <https://doi.org/10.1002/ejic.200400938>.
- (56) Duchateau, R.; Gambarotta, S.; Beydoun, N.; Bensimon, C. Side-On versus End-On Coordination of Dinitrogen to Titanium (II) and Mixed-Valence Titanium(I)/Titanium(II) Amido Complexes. *J. Am. Chem. Soc.* **1991**, *113* (23), 8986–8988. <https://doi.org/10.1021/ja00023a080>.
- (57) Mullins, S. M.; Duncan, A. P.; Bergman, R. G.; Arnold, J. Reactivity of a Titanium Dinitrogen Complex Supported by Guanidinate Ligands: Investigation of Solution Behavior and a Novel Rearrangement of Guanidinate Ligands. *Inorg. Chem.* **2001**, *40* (27), 6952–6963. <https://doi.org/10.1021/ic010631+>.
- (58) Doyle, L. R.; Wooles, A. J.; Jenkins, L. C.; Tuna, F.; McInnes, E. J. L.; Liddle, S. T. Catalytic Dinitrogen Reduction to Ammonia at a Triamidoamine–Titanium Complex. *Angew. Chem. Int. Ed.* **2018**, *57* (21), 6314–6318. <https://doi.org/10.1002/anie.201802576>.
- (59) Doyle, L. R.; Wooles, A. J.; Liddle, S. T. Bimetallic Cooperative Cleavage of Dinitrogen to Nitride and Tandem Frustrated Lewis Pair Hydrogenation to Ammonia. *Angew. Chem. Int. Ed.* **2019**, *58* (20), 6674–6677. <https://doi.org/10.1002/anie.201902195>.
- (60) Shima, T.; Hu, S.; Luo, G.; Kang, X.; Luo, Y. Y.; Hou, Z. Dinitrogen Cleavage and Hydrogenation by a Trinuclear Titanium Polyhydride Complex. *Science* (80-.

-). **2013**, 340 (6140), 1549–1552. <https://doi.org/10.1126/science.1238663>.
- (61) Guru, M. M.; Shima, T.; Hou, Z. Conversion of Dinitrogen to Nitriles at a Multinuclear Titanium Framework. *Angew. Chem. Int. Ed.* **2016**, 55 (40), 12316–12320. <https://doi.org/10.1002/anie.201607426>.
- (62) Wang, B.; Luo, G.; Nishiura, M.; Hu, S.; Shima, T.; Luo, Y.; Hou, Z. Dinitrogen Activation by Dihydrogen and a PNP-Ligated Titanium Complex. *J. Am. Chem. Soc.* **2017**, 139 (5), 1818–1821. <https://doi.org/10.1021/jacs.6b13323>.
- (63) Fryzuk, M. D.; Haddad, T. S.; Rettig, S. J. Reduction of Dinitrogen by a Zirconium Phosphine Complex To Form a Side-On-Bridging N₂ Ligand. Crystal Structure of {[PrI₂PCH₂SiMe₂)₂N]ZrCl}₂(μ-H₂:H₂-N₂). *J. Am. Chem. Soc.* **1990**, 112 (22), 8185–8186. <https://doi.org/10.1021/ja00178a063>.
- (64) Burford, R. J.; Yeo, A.; Fryzuk, M. D. Dinitrogen Activation by Group 4 and Group 5 Metal Complexes Supported by Phosphine-Amido Containing Ligand Manifolds. *Coord. Chem. Rev.* **2017**, 334, 84–99. <https://doi.org/10.1016/j.ccr.2016.06.015>.
- (65) Fryzuk, M. D.; Love, J. B.; Rettig, S. J.; Young, V. G. Transformation of Coordinated Dinitrogen by Reaction with Dihydrogen and Primary Silanes. *Science* (80-.). **1997**, 275 (5305), 1445–1447. <https://doi.org/10.1126/science.275.5305.1445>.
- (66) Morello, L.; Love, J. B.; Patrick, B. O.; Fryzuk, M. D. Carbon-Nitrogen Bond Formation via the Reaction of Terminal Alkynes with a Dinuclear Side-on Dinitrogen Complex. *J. Am. Chem. Soc.* **2004**, 126 (31), 9480–9481. <https://doi.org/10.1021/ja049490b>.

- (67) Bernskoetter, W. H.; Lobkovsky, E.; Chirik, P. J. Kinetics and Mechanism of N₂ Hydrogenation in Bis(Cyclopentadienyl) Zirconium Complexes and Dinitrogen Functionalization by 1,2-Addition of a Saturated C-H Bond. *J. Am. Chem. Soc.* **2005**, *127* (40), 14051–14061. <https://doi.org/10.1021/ja0538841>.
- (68) Bernskoetter, W. H.; Olmos, A. V.; Lobkovsky, E.; Chirik, P. J. N₂ Hydrogenation Promoted by a Side-on Bound Hafnocene Dinitrogen Complex. *Organometallics* **2006**, *25* (4), 1021–1027. <https://doi.org/10.1021/om0509037>.
- (69) Pool, J. A.; Bernskoetter, W. H.; Chirik, P. J. On the Origin of Dinitrogen Hydrogenation Promoted by [(H⁵-C⁵Me₄H)₂Zr]₂(M₂, H₂, H₂-N₂). *J. Am. Chem. Soc.* **2004**, *126* (44), 14326–14327. <https://doi.org/10.1021/ja045566s>.
- (70) Miyachi, H.; Shigeta, Y.; Hirao, K. Theoretical Study of the Mechanism of Hydrogenation of Side-on Coordinated Dinitrogen Activated by Zr Binuclear Complexes ([(H⁵-C⁵Me₄H)₂Zr]₂(M₂, H₂, H₂-N₂)). *J. Phys. Chem. A* **2005**, *109* (39), 8800–8808. <https://doi.org/10.1021/jp053308r>.
- (71) Pool, J. A.; Lobkovsky, E.; Chirik, P. J. Hydrogenation and Cleavage of Dinitrogen to Ammonia with a Zirconium Complex. *Nature* **2004**, *427* (6974), 527–530. <https://doi.org/10.1038/nature02274>.
- (72) Bernskoetter, W. H.; Pool, J. A.; Lobkovsky, E.; Chirik, P. J. Dinitrogen Functionalization with Terminal Alkynes, Amines, and Hydrazines Promoted by [(H⁵-C⁵Me₄H)₂Zr]₂(M₂, H₂, H₂-N₂): Observation of Side-on and End-on Diazenido Complexes in the Reduction of N₂ to Hydrazine. *J. Am. Chem. Soc.* **2005**, *127* (21), 7901–7911. <https://doi.org/10.1021/ja050387b>.
- (73) Pun, D.; Lobkovsky, E.; Chirik, P. J. Indenyl Zirconium Dinitrogen Chemistry: N₂

- Coordination to an Isolated Zirconium Sandwich and Synthesis of Side-on, End-on Dinitrogen Compounds. *J. Am. Chem. Soc.* **2008**, *130* (18), 6047–6054.
<https://doi.org/10.1021/ja801021w>.
- (74) Pun, D.; Bradley, C. A.; Lobkovsky, E.; Keresztes, I.; Chirik, P. J. N₂ Hydrogenation from Activated End-on Bis(Indenyl) Zirconium Dinitrogen Complexes. *J. Am. Chem. Soc.* **2008**, *130* (43), 14046–14047.
<https://doi.org/10.1021/ja8048332>.
- (75) Semproni, S. P.; Knobloch, D. J.; Milsman, C.; Chirik, P. J. Redox-Induced N₂ Hapticity Switching in Zirconocene Dinitrogen Complexes. *Angew. Chem. Int. Ed.* **2013**, *52* (20), 5372–5376. <https://doi.org/10.1002/anie.201301800>.
- (76) Gynane, M. J. S.; Jeffery, J.; Lappert, M. F. Organozirconium(III)-Dinitrogen Complexes : Evidence for (Q²-N₂)-Metal Bonding in [Zr(q-C₅H₅), (N₂)(R)] [R = Me, Si, CH]. *J.C.S. Chem. Comm.* **1978**, 34–36.
- (77) Jeffery, J.; Lappert, M. F.; Riley, P. I. ORGANOZIRCONIUM DINITROGEN COMPLEXES [Zr(η-C₅H₅, R')₂(E₂-N₂)R] AND [{Zr(η-C₅H₄R')₂N₂R}] [R = (Me₂Si)₂CH, R' = H OR Me]. **1979**, *181*, 25–36.
- (78) Bernskoetter, W. H.; Olmos, A. V.; Pool, J. A.; Lobkovsky, E.; Chirik, P. J. N-C Bond Formation Promoted by a Hafnocene Dinitrogen Complex: Comparison of Zirconium and Hafnium Congeners. *J. Am. Chem. Soc.* **2006**, *128* (33), 10696–10697. <https://doi.org/10.1021/ja064163k>.
- (79) Bernskoetter, W. H.; Lobkovsky, E.; Chirik, P. J. Nitrogen-Carbon Bond Formation from N₂ and CO₂ Promoted by a Hafnocene Dinitrogen Complex Yields a Substituted Hydrazine. *Angew. Chem. Int. Ed.* **2007**, *46* (16), 2858–2861.

<https://doi.org/10.1002/anie.200604099>.

- (80) Semproni, S. P.; Lobkovsky, E.; Chirik, P. J. Dinitrogen Silylation and Cleavage with a Hafnocene Complex. *J. Am. Chem. Soc.* **2011**, *133* (27), 10406–10409.
<https://doi.org/10.1021/ja2042595>.
- (81) Semproni, S. P.; Chirik, P. J. Dinitrogen Borylation with Group 4 Metallocene Complexes. *Eur. J. Inorg. Chem.* **2013**, 2 (22–23), 3907–3915.
<https://doi.org/10.1002/ejic.201300046>.
- (82) Semproni, S. P.; Milsmann, C.; Chirik, P. J. Structure and Reactivity of a Hafnocene μ -Nitrido Prepared from Dinitrogen Cleavage. *Angew. Chem. Int. Ed.* **2012**, *51* (21), 5213–5216. <https://doi.org/10.1002/anie.201201361>.
- (83) Semproni, S. P.; Chirik, P. J. Synthesis of a Base-Free Hafnium Nitride from N₂ Cleavage: A Versatile Platform for Dinitrogen Functionalization. *J. Am. Chem. Soc.* **2013**, *135* (30), 11373–11383. <https://doi.org/10.1021/ja405477m>.
- (84) Knobloch, D. J.; Lobkovsky, E.; Chirik, P. J. Dinitrogen Cleavage and Functionalization by Carbon Monoxide Promoted by a Hafnium Complex. *Nat. Chem.* **2010**, 2 (1), 30–35. <https://doi.org/10.1038/nchem.477>.
- (85) Turner, H. W.; Fellmann, J. D.; Rocklage, S. M.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. Tantalum Complexes Containing Diimido Bridging Dinitrogen Ligands. *J. Am. Chem. Soc.* **1980**, *102* (26), 7809–7811.
<https://doi.org/10.1021/ja00546a044>.
- (86) Edema, J. J. H.; Meetsma, A.; Gambarotta, S. Divalent Vanadium and Dinitrogen Fixation: The Preparation and X-Ray Structure of $(\mu\text{-N}_2)\{[(\text{o-Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{V}(\text{Py})\}_2(\text{THF})_2$. *J. Am. Chem. Soc.* **1989**, *111* (17), 6878–

6880. <https://doi.org/10.1021/ja00199a079>.

- (87) Rehder, D.; Woitha, C.; Pribsch, W.; Gailus, H. Trans-[Na(Thf)][V(N₂)₂(Ph₂PCH₂CH₂PPh₂)₂] : Structural Characterization of a Dinitrogenvanadium Complex, a Functional Model for Vanadiumnitrogenase. *J.C.S. Chem. Comm.* **1992**, 28, 364–365.
- (88) Gailus, H.; Woitha, C.; Rehder, D. Dinitrogenvanadates(- I): Synthesis, Reactions and Conditions for Their Stability. *J. Chem. Soc. Dalt. Trans.* **1994**, 3471–3477.
- (89) Song, J. I.; Berno, P.; Gambarotta, S. Dinitrogen Fixation, Ligand Dehydrogenation, and Cyclometalation in the Chemistry of Vanadium(III) Amides. *J. Am. Chem. Soc.* **1994**, 116 (15), 6927–6928.
<https://doi.org/10.1021/ja00094a054>.
- (90) Desmangles, N.; Jenkins, H.; Rupp, K. B.; Gambarotta, S. Preparation and Characterization of a Vanadium (III) Dinitrogen Complex Supported by a Tripodal Anionic Amide Ligand. *Inorganica Chim. Acta* **1996**, 250 (1-2 PART I), 1–4.
- (91) Berno, P.; Gambarotta, S. Reaction of a Vanadium(Ir1) Amide with H₂ : Isolation and Characterization of a Polynuclear Mixed-Valence Polyhydrido -Nitrido Complex. **1995**, 34, 922–924.
- (92) Clentsmith, G. K. B.; Bates, V. M. E.; Hitchcock, P. B.; Cloke, F. G. N. Reductive Cleavage of Dinitrogen by a Vanadium Diamidoamine Complex: The Molecular Structures of [V(Me₃SiN{CH₂CH₂NSiMe₃}₂)(μ-N)]₂ and K[V(Me₃SiN{CH₂CH₂NSiMe₃}₂)(μ-N)]₂ [15]. *J. Am. Chem. Soc.* **1999**, 121 (44), 10444–10445. <https://doi.org/10.1021/ja9921219>.
- (93) Vidyaratne, I.; Gambarotta, S.; Korobkov, I.; Budzelaar, P. H. M. Dinitrogen

Partial Reduction by Formally Zero- and Divalent Vanadium Complexes

Supported by the Bis-Iminopyridine System. *Inorg. Chem.* **2005**, *44* (5), 1187–1189. <https://doi.org/10.1021/ic048358+>.

- (94) Milsman, C.; Semproni, S. P.; Chirik, P. J. N-N Bond Cleavage of 1,2-Diarylhydrazines and N-H Bond Formation via H-Atom Transfer in Vanadium Complexes Supported by a Redox-Active Ligand. *J. Am. Chem. Soc.* **2014**, *136* (34), 12099–12107. <https://doi.org/10.1021/ja5062196>.
- (95) Smythe, N. C.; Schrock, R. R.; Müller, P.; Weare, W. W. Synthesis of [(HIPTNCH₂)₃N]V Compounds (HIPT = 3,5-(2,4,6-*i*-Pr₃CH₂)₂C₆H₃) and an Evaluation of Vanadium for the Reduction of Dinitrogen to Ammonia. *Inorg. Chem.* **2006**, *45* (23), 9197–9205. <https://doi.org/10.1021/ic061554r>.
- (96) Vidyaratne, I.; Crewdson, P.; Lefebvre, E.; Gambarotta, S. Dinitrogen Coordination and Cleavage Promoted by a Vanadium Complex of a σ,π,σ -Donor Ligand. *Inorg. Chem.* **2007**, *46* (21), 8836–8842. <https://doi.org/10.1021/ic701219h>.
- (97) Kilgore, U. J.; Sengelaub, C. A.; Pink, M.; Fout, A. R.; Mindiola, D. J. A Transient VIII-Alkylidene Complex: Oxidation Chemistry Including the Activation of N₂ to Afford a Highly Porous Honeycomb-Like Framework. *Angew. Chem. Int. Ed.* **2008**, *47* (20), 3769–3772. <https://doi.org/10.1002/anie.200705931>.
- (98) Kilgore, U. J.; Sengelaub, C. A.; Fan, H.; Tomaszewski, J.; Karty, J. A.; Baik, M. H.; Mindiola, D. J. A Transient Vanadium(III) Neopentylidene Complex. Redox Chemistry and Reactivity of the V=CH TBu Functionality. *Organometallics* **2009**, *28* (3), 843–852. <https://doi.org/10.1021/om800800g>.

- (99) Tran, B. L.; Pinter, B.; Nichols, A. J.; Konopka, F. T.; Thompson, R.; Chen, C. H.; Krzystek, J.; Ozarowski, A.; Telser, J.; Baik, M. H.; et al. A Planar Three-Coordinate Vanadium(II) Complex and the Study of Terminal Vanadium Nitrides from N₂: A Kinetic or Thermodynamic Impediment to N-N Bond Cleavage? *J. Am. Chem. Soc.* **2012**, *134* (31), 13035–13045. <https://doi.org/10.1021/ja303360v>.
- (100) Groysman, S.; Villagrán, D.; Freedman, D. E.; Nocera, D. G. Dinitrogen Binding at Vanadium in a Tris(Alkoxide) Ligand Environment. *Chem. Commun.* **2011**, 47 (37), 10242–10244. <https://doi.org/10.1039/c1cc13645c>.
- (101) Cozzolino, A. F.; Silvia, J. S.; Lopez, N.; Cummins, C. C. Experimental and Computational Studies on the Formation of Cyanate from Early Metal Terminal Nitrido Ligands and Carbon Monoxide. *Dalt. Trans.* **2014**, 43 (12), 4639–4652. <https://doi.org/10.1039/c3dt52738g>.
- (102) Ishida, Y.; Kawaguchi, H. Nitrogen Atom Transfer from a Dinitrogen-Derived Vanadium Nitride Complex to Carbon Monoxide and Isocyanide. *J. Am. Chem. Soc.* **2014**, *136* (49), 16990–16993. <https://doi.org/10.1021/ja510317h>.
- (103) Berno, P.; Gambarotta, S. Formation of a Metallaaziridine Ring and Dinitrogen Fixation Promoted by a Niobium Amide Complex. *Organometallics* **1995**, *14* (5), 2159–2161. <https://doi.org/10.1021/om00005a012>.
- (104) Mindiola, D. J.; Meyer, K.; Cherry, J. P. F.; Baker, T. A.; Cummins, C. C. Dinitrogen Cleavage Stemming from a Heterodinuclear Niobium/Molybdenum N₂complex: New Nitridoniobium Systems Including a Niobazene Cyclic Trimer. *Organometallics* **2000**, *19* (9), 1622–1624. <https://doi.org/10.1021/om000159k>.
- (105) Figueroa, J. S.; Piro, N. A.; Clough, C. R.; Cummins, C. C. A Nitridoniobium(V)

Reagent That Effects Acid Chloride to Organic Nitrile Conversion: Synthesis via Heterodinuclear (Nb/Mo) Dinitrogen Cleavage, Mechanistic Insights, and Recycling. *J. Am. Chem. Soc.* **2006**, *128* (3), 940–950.

<https://doi.org/10.1021/ja056408j>.

- (106) Zanotti-Gerosa, A.; Solari, E.; Giannini, L.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. Stepwise Reduction of Dinitrogen to Nitride Assisted by Niobium Bonded to Oxygen Donor Atoms: The Potential of Reduced Forms of Niobium Calix[4]Arene. *J. Am. Chem. Soc.* **1998**, *120* (2), 437–438.
<https://doi.org/10.1021/ja9722584>.

- (107) Terrett, R.; Cavigliasso, G.; Stranger, R.; Yates, B. F. On the Unprecedented Level of Dinitrogen Activation in the Calix[4]Arene Complex of Nb(III). *Dalt. Trans.* **2011**, *40* (42), 11267. <https://doi.org/10.1039/c1dt11091h>.

- (108) Caselli, A.; Solari, E.; Scopelliti, R.; Floriani, C.; Re, N.; Rizzoli, C.; Chiesi-Villa, A. Dinitrogen Rearranging over a Metal–Oxo Surface and Cleaving to Nitride: From the End-On to the Side-On Bonding Mode, to the Stepwise Cleavage of the N:N Bonds Assisted by Nb III -Calix[4]Arene. *J. Am. Chem. Soc.* **2000**, *122* (15), 3652–3670. <https://doi.org/10.1021/ja9943288>.

- (109) Kawaguchi, H.; Matsuo, T. Dinitrogen-Bond Cleavage in a Niobium Complex Supported by a Tridentate Aryloxy Ligand. *Angew. Chem. Int. Ed.* **2002**, *41* (15), 2792–2794. [https://doi.org/10.1002/1521-3773\(20020802\)41:15<2792::AID-ANIE2792>3.0.CO;2-K](https://doi.org/10.1002/1521-3773(20020802)41:15<2792::AID-ANIE2792>3.0.CO;2-K).

- (110) Akagi, F.; Matsuo, T.; Kawaguchi, H. Dinitrogen Cleavage by a Dinioobium Tetrahydride Complex : Formation of a Nitride and Its Conversion into Imide

- Species **. **2007**, 8778–8781. <https://doi.org/10.1002/anie.200703336>.
- (111) Tanaka, H.; Shiota, Y.; Matsuo, T.; Kawaguchi, H.; Yoshizawa, K. DFT Study on N₂ Activation by a Hydride-Bridged Diniobium Complex. N≡N Bond Cleavage Accompanied by H₂ Evolution. *Inorg. Chem.* **2009**, 48 (8), 3875–3881. <https://doi.org/10.1021/ic802377p>.
- (112) Searles, K.; Carroll, P. J.; Chen, C. H.; Pink, M.; Mindiola, D. J. Niobium-Nitrides Derived from Nitrogen Splitting. *Chem. Commun.* **2015**, 51 (17), 3526–3528. <https://doi.org/10.1039/c4cc09563d>.
- (113) Fryzuk, M. D.; Johnson, S. A.; Patrick, B. O.; Albinati, A.; Mason, S. A.; Koetzle, T. F. New Mode of Coordination for the Dinitrogen Ligand: Formation, Bonding, and Reactivity of a Tantalum Complex with a Bridging N₂ Unit That Is Both Side-on and End-On. *J. Am. Chem. Soc.* **2001**, 123 (17), 3960–3973. <https://doi.org/10.1021/ja0041371>.
- (114) Fryzuk, M. D.; Kozak, C. M.; Bowdridge, M. R.; Patrick, B. O.; Rettig, S. J. Nitride Formation by Thermolysis of a Kinetically Stable Niobium Dinitrogen Complex. *J. Am. Chem. Soc.* **2002**, 124 (28), 8389–8397. <https://doi.org/10.1021/ja025997f>.
- (115) Fryzuk, M. D.; Kozak, C. M.; Patrick, B. O. Dinuclear Organometallic Dinitrogen Complexes of Niobium. *Inorganica Chim. Acta* **2003**, 345, 53–62. [https://doi.org/10.1016/S0020-1693\(02\)01305-1](https://doi.org/10.1016/S0020-1693(02)01305-1).
- (116) Kilgore, U. J.; Yang, X.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. Activation of Atmospheric Nitrogen and Azobenzene N=N Bond Cleavage by a Transient Nb(III) Complex. *Inorg. Chem.* **2006**, 45 (26), 10712–10721.

<https://doi.org/10.1021/ic061642b>.

- (117) Rocklage, S. M.; Turner, H. W.; Fellmann, J. D.; Schrock, R. R. Preparation of Tantalum μ -Dinitrogen Complexes from Molecular Nitrogen and Reduced Tantalum Complexes. *Organometallics* **1982**, *1* (5), 703–707.
<https://doi.org/10.1021/om00065a006>.
- (118) Fryzuk, M. D. Side-on End-on Bound Dinitrogen: An Activated Bonding Mode That Facilitates Functionalizing Molecular Nitrogen. *Acc. Chem. Res.* **2009**, *42* (1), 127–133. <https://doi.org/10.1021/ar800061g>.
- (119) Fryzuk, M. D.; Johnson, S. A.; Rettig, S. J. New Mode of Coordination for the Dinitrogen Ligand: A Dinuclear Tantalum Complex with a Bridging N₂ Unit That Is Both Side-on and End-on [25]. *J. Am. Chem. Soc.* **1998**, *120* (42), 11024–11025.
<https://doi.org/10.1021/ja982377z>.
- (120) Yeo, A.; Shaver, M. P.; Fryzuk, M. D. A New Side-on End-On Ditantalum Dinitrogen Complex and Its Reaction with BuSiH₃. *Zeitschrift für Anorg. und Allg. Chemie* **2015**, *641* (1), 123–127. <https://doi.org/10.1002/zaac.201400167>.
- (121) Shaver, M. P.; Johnson, S. A.; Fryzuk, M. D. Activation and Cleavage of Alkynes by the Dinuclear Tantalum Complexes ([NPN]Ta)₂(μ -H)₄ and ([NPN]Ta)₂(μ -H₁:H₂-N₂)(μ -H)₂ (Where NPN = PhP(CH₂SiMe₂NPh)₂). *Can. J. Chem.* **2005**, *83* (6–7), 652–660. <https://doi.org/10.1139/v05-034>.
- (122) Ballmann, J.; Yeo, A.; Patrick, B. O.; Fryzuk, M. D. Carbon-Nitrogen Bond Formation by the Reaction of 1,2-Cumulenes with a Ditantalum Complex Containing Side-on- and End-on-Bound Dinitrogen. *Angew. Chem. Int. Ed.* **2011**, *50* (2), 507–510. <https://doi.org/10.1002/anie.201005704>.

- (123) Spencer, L. P.; MacKay, B. A.; Patrick, B. O.; Fryzuk, M. D. Inner-Sphere Two-Electron Reduction Leads to Cleavage and Functionalization of Coordinated Dinitrogen. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103* (46), 17094–17098.
<https://doi.org/10.1073/pnas.0602132103>.
- (124) MacKay, B. A.; Johnson, S. A.; Patrick, B. O.; Fryzuk, M. D. Functionalization and Cleavage of Coordinated Dinitrogen via Hydroboration Using Primary and Secondary Boranes. *Can. J. Chem.* **2005**, *83* (4), 315–323.
<https://doi.org/10.1139/v04-161>.
- (125) Fryzuk, M. D.; MacKay, B. A.; Johnson, S. A.; Patrick, B. O. Hydroboration of Coordinated Dinitrogen: A New Reaction for the N₂ Ligand That Results in Its Functionalization and Cleavage. *Angew. Chem. Int. Ed.* **2002**, *41* (19), 3709–3712.
[https://doi.org/10.1002/1521-3773\(20021004\)41:19<3709::AID-ANIE3709>3.0.CO;2-U](https://doi.org/10.1002/1521-3773(20021004)41:19<3709::AID-ANIE3709>3.0.CO;2-U).
- (126) MacKay, B. A.; Patrick, B. O.; Fryzuk, M. D. Hydroalumination of a Dinuclear Tantalum Dinitrogen Complex: N–N Bond Cleavage and Ancillary Ligand Rearrangement. *Organometallics* **2005**, *24* (16), 3836–3841.
<https://doi.org/10.1021/om050208z>.
- (127) MacKay, B. A.; Munha, R. F.; Fryzuk, M. D. Substituent Effects in the Hydrosilylation of Coordinated Dinitrogen in a Ditantalum Complex: Cleavage and Functionalization of N₂. *J. Am. Chem. Soc.* **2006**, *128* (29), 9472–9483.
<https://doi.org/10.1021/ja061508q>.
- (128) Fryzuk, M. D.; MacKay, B. A.; Patrick, B. O. Hydrosilylation of a Dinuclear Tantalum Dinitrogen Complex: Cleavage of N₂ and Functionalization of Both

Nitrogen Atoms. *J. Am. Chem. Soc.* **2003**, *125* (11), 3234–3235.

<https://doi.org/10.1021/ja034303f>.

- (129) Bregel, D. C.; Oldham, S. M.; Lachicotte, R. J.; Eisenberg, R. A New Tantalum Dinitrogen Complex and a Parahydrogen-Induced Polarization Study of Its Reaction with Hydrogen. *Inorg. Chem.* **2002**, *41* (17), 4371–4377.

<https://doi.org/10.1021/ic025578j>.

- (130) Lee, T. Y.; Wooten, A. J.; Luci, J. J.; Swenson, D. C.; Messerle, L. Four-Electron Reduction of Dinitrogen during Solution Disproportionation of the Organodimetallic (η -C₅Me₄R)₂Ta₂(μ -Cl)₄ (R = Me, Et) to a New μ -H1, H1-N₂ Complex and Odd-Electron Organotrimetallic Cluster. *Chem. Commun.* **2005**, 2 (43), 5444–5446. <https://doi.org/10.1039/b508148c>.

- (131) Horrillo-Martinez, P.; Patrick, B. O.; Schafer, L. L.; Fryzuk, M. D. Oxygen Extrusion from Amidate Ligands to Generate Terminal TaO Units under Reducing Conditions. How to Successfully Use Amidate Ligands in Dinitrogen Coordination Chemistry. *Dalt. Trans.* **2012**, *41* (5), 1609–1616.

<https://doi.org/10.1039/c1dt11595b>.

- (132) Takada, R.; Hirotsu, M.; Nishioka, T.; Hashimoto, H.; Kinoshita, I. Sulfur-Bridged Ta-M (M = Mo, Cr) Multinuclear Complexes Bearing a Four-Electron-Reduced Dinitrogen Ligand. *Organometallics* **2011**, *30* (16), 4232–4235.

<https://doi.org/10.1021/om200596v>.

- (133) Hirotsu, M.; Fontaine, P. P.; Epshteyn, A.; Zavalij, P. Y.; Sita, L. R. Dinitrogen Activation at Ambient Temperatures: New Modes of H₂ and PhSiH₃ Additions for an “End-on-Bridged” [Ta(IV)]₂(μ -H1:H1-N₂) Complex and for the Bis(μ -

- Nitrido) [Ta(V)(μ -N)]₂ Product Derived from Facile N $\equiv$ N Bond Cleavage. *J. Am. Chem. Soc.* **2007**, *129* (30), 9284–9285. <https://doi.org/10.1021/ja072248v>.
- (134) Keane, A. J.; Yonke, B. L.; Hirotsu, M.; Zavalij, P. Y.; Sita, L. R. Fine-Tuning the Energy Barrier for Metal-Mediated Dinitrogen N $\equiv$ N Bond Cleavage. *J. Am. Chem. Soc.* **2014**, *136* (28), 9906–9909. <https://doi.org/10.1021/ja505309j>.
- (135) Karsch, H. H. CisBis(Dinitrogen)Tetrakis(Trimethylphosphane)Chromium. *Angew. Chem. Int. Ed. Engl.* **1977**, *16* (1), 56–56. <https://doi.org/10.1002/anie.197700561>.
- (136) Sobota, P.; Jezowska-Trzebiatowska, B. Fixation of Dinitrogen and Acetylene by the System CrCl₂Mg. Isolation and Properties of Chromium Complexes with Fixed N₂ and C₂H₂. *J. Organomet. Chem.* **1977**, *131* (3), 341–345. [https://doi.org/10.1016/S0022-328X\(00\)84409-5](https://doi.org/10.1016/S0022-328X(00)84409-5).
- (137) Vidyaratne, I.; Scott, J.; Gambarotta, S.; Budzelaar, P. H. M. Dinitrogen Activation, Partial Reduction, and Formation of Coordinated Imide Promoted by a Chromium Diiminepyridine Complex. *Inorg. Chem.* **2007**, *46* (17), 7040–7049. <https://doi.org/10.1021/ic700810f>.
- (138) Monillas, W. H.; Yap, G. P. A.; MacAdams, L. A.; Theopold, K. H. Binding and Activation of Small Molecules by Three-Coordinate Cr(I). *J. Am. Chem. Soc.* **2007**, *129* (26), 8090–8091. <https://doi.org/10.1021/ja0725549>.
- (139) Akturk, E. S.; Yap, G. P. A.; Theopold, K. H. Mechanism-Based Design of Labile Precursors for Chromium(i) Chemistry. *Chem. Commun.* **2015**, *51* (84), 15402–15405. <https://doi.org/10.1039/c5cc05993c>.
- (140) Mock, M. T.; Chen, S.; Rousseau, R.; O'Hagan, M. J.; Dougherty, W. G.; Kassel,

- W. S.; DuBois, D. L.; Bullock, R. M. A Rare Terminal Dinitrogen Complex of Chromium. *Chem. Commun.* **2011**, 47 (44), 12212.
<https://doi.org/10.1039/c1cc15430c>.
- (141) Mock, M. T.; Chen, S.; O'Hagan, M.; Rousseau, R.; Dougherty, W. G.; Kassel, W. S.; Bullock, R. M. Dinitrogen Reduction by a Chromium(0) Complex Supported by a 16-Membered Phosphorus Macrocyclic. *J. Am. Chem. Soc.* **2013**, 135 (31), 11493–11496. <https://doi.org/10.1021/ja405668u>.
- (142) Mock, M. T.; Pierpont, A. W.; Egbert, J. D.; O'Hagan, M.; Chen, S.; Bullock, R. M.; Dougherty, W. G.; Kassel, W. S.; Rousseau, R. Protonation Studies of a Mono-Dinitrogen Complex of Chromium Supported by a 12-Membered Phosphorus Macrocyclic Containing Pendant Amines. *Inorg. Chem.* **2015**, 54 (10), 4827–4839. <https://doi.org/10.1021/acs.inorgchem.5b00351>.
- (143) Egbert, J. D.; O'Hagan, M.; Wiedner, E. S.; Bullock, R. M.; Piro, N. A.; Kassel, W. S.; Mock, M. T. Putting Chromium on the Map for N₂ Reduction: Production of Hydrazine and Ammonia. A Study of: Cis -M(N₂)₂ (M = Cr, Mo, W) Bis(Diphosphine) Complexes. *Chem. Commun.* **2016**, 52 (60), 9343–9346.
<https://doi.org/10.1039/c6cc03449g>.
- (144) Kendall, A. J.; Johnson, S. I.; Bullock, R. M.; Mock, M. T. Catalytic Silylation of N₂ and Synthesis of NH₃ and N₂H₄ by Net Hydrogen Atom Transfer Reactions Using a Chromium P₄ Macrocyclic. *J. Am. Chem. Soc.* **2018**, 140 (7), 2528–2536. <https://doi.org/10.1021/jacs.7b11132>.
- (145) Hidai, M.; Tominari, K.; Uchida, Y.; Misono, A. A Trans-Dinitrogen Complex of Molybdenum. *J. Chem. Soc. D Chem. Commun.* **1969**, No. 23, 1392.

<https://doi.org/10.1039/C29690001392>.

- (146) Yuki, M.; Miyake, Y.; Nishibayashi, Y.; Wakiji, I.; Hidai, M. Synthesis and Reactivity of Tungsten– and Molybdenum–Dinitrogen Complexes Bearing Ferrocenyldiphosphines toward Protonolysis. *Organometallics* **2008**, 27 (15), 3947–3953. <https://doi.org/10.1021/om800327j>.
- (147) Yuki, M.; Midorikawa, T.; Miyake, Y.; Nishibayashi, Y. Synthesis and Protonolysis of Tungsten– and Molybdenum–Dinitrogen Complexes Bearing Ruthenocenyldiphosphines. *Organometallics* **2009**, 28 (16), 4741–4746. <https://doi.org/10.1021/om900298g>.
- (148) Yuki, M.; Miyake, Y.; Nishibayashi, Y. Preparation and Protonation of Tungsten- and Molybdenum-Dinitrogen Complexes Bearing Bis(Dialkylphosphinobenzene)Chromiums as Auxiliary Ligands. *Organometallics* **2009**, 28 (19), 5821–5827. <https://doi.org/10.1021/om9006467>.
- (149) Broda, H.; Hinrichsen, S.; Tuzek, F. Molybdenum(0) Dinitrogen Complexes with Polydentate Phosphine Ligands for Synthetic Nitrogen Fixation: Geometric and Electronic Structure Contributions to Reactivity. *Coord. Chem. Rev.* **2013**, 257 (2), 587–598. <https://doi.org/10.1016/j.ccr.2012.05.010>.
- (150) Hinrichsen, S.; Schnoor, A. C.; Grund, K.; Flöser, B.; Schlimm, A.; Näther, C.; Krahmer, J.; Tuzek, F. Molybdenum Dinitrogen Complexes Facially Coordinated by Linear Tridentate PEP Ligands (E = N or P): Impact of the Central e Donor in: Trans -Position to N₂. *Dalt. Trans.* **2016**, 45 (37), 14801–14813. <https://doi.org/10.1039/c6dt02316a>.
- (151) Hanna, B. S.; Macintosh, A. D.; Ahn, S.; Tyler, B. T.; Palmore, G. T. R.; Williard,

- P. G.; Bernskoetter, W. H. Ancillary Ligand Effects on Carbon Dioxide-Ethylene Coupling at Zerovalent Molybdenum. *Organometallics* **2014**, *33* (13), 3425–3432. <https://doi.org/10.1021/om500324h>.
- (152) Arashiba, K.; Nakajima, K.; Nishibayashi, Y. Synthesis and Reactivity of Molybdenum-Dinitrogen Complexes Bearing PNN-Type Pincer Ligand. *Zeitschrift fur Anorg. und Allg. Chemie* **2015**, *641* (1), 100–104. <https://doi.org/10.1002/zaac.201400117>.
- (153) Dahlenbourg, L.; Pietsch, B. Mono- Und Bis(Distickstoffmolybden(0)-Komplexe Des Dreizahnigen Chelat- Phosphans MeP(CH₂CH₂CH₂PMe₂)₂: Synthesen, Strukturen Und Reaktionen Mit Kohlendioxid. *Chem. Berichte* **1989**, *122*, 2085–2090.
- (154) Arashiba, K.; Miyake, Y.; Nishibayashi, Y. A Molybdenum Complex Bearing PNP-Type Pincer Ligands Leads to the Catalytic Reduction of Dinitrogen into Ammonia. *Nat. Chem.* **2011**, *3* (2), 120–125. <https://doi.org/10.1038/nchem.906>.
- (155) Kuriyama, S.; Arashiba, K.; Nakajima, K.; Tanaka, H.; Kamaru, N.; Yoshizawa, K.; Nishibayashi, Y. Catalytic Formation of Ammonia from Molecular Dinitrogen by Use of Dinitrogen-Bridged Dimolybdenum–Dinitrogen Complexes Bearing PNP-Pincer Ligands: Remarkable Effect of Substituent at PNP-Pincer Ligand. *J. Am. Chem. Soc.* **2014**, *136* (27), 9719–9731. <https://doi.org/10.1021/ja5044243>.
- (156) Arashiba, K.; Kinoshita, E.; Kuriyama, S.; Eizawa, A.; Nakajima, K.; Tanaka, H.; Yoshizawa, K.; Nishibayashi, Y. Catalytic Reduction of Dinitrogen to Ammonia by Use of Molybdenum-Nitride Complexes Bearing a Tridentate Triphosphine as Catalysts. *J. Am. Chem. Soc.* **2015**, *137* (17), 5666–5669.

<https://doi.org/10.1021/jacs.5b02579>.

- (157) Arashiba, K.; Sasaki, K.; Kuriyama, S.; Miyake, Y.; Nakanishi, H.; Nishibayashi, Y. Synthesis and Protonation of Molybdenum-and Tungsten-Dinitrogen Complexes Bearing PNP-Type Pincer Ligands. *Organometallics* **2012**, *31* (5), 2035–2041. <https://doi.org/10.1021/om300011z>.
- (158) Eizawa, A.; Arashiba, K.; Tanaka, H.; Kuriyama, S.; Matsuo, Y.; Nakajima, K.; Yoshizawa, K.; Nishibayashi, Y. Remarkable Catalytic Activity of Dinitrogen-Bridged Dimolybdenum Complexes Bearing NHC-Based PCP-Pincer Ligands toward Nitrogen Fixation. *Nat. Commun.* **2017**, *8*, 1–12. <https://doi.org/10.1038/ncomms14874>.
- (159) Broda, H.; Hinrichsen, S.; Krahmer, J.; Näther, C.; Tucek, F. Molybdenum Dinitrogen Complexes Supported by a Silicon-Centred Tripod Ligand and Dppm or Dmpm: Tuning the Activation of N₂. *Dalton Trans.* **2014**, *43* (5), 2007–2012. <https://doi.org/10.1039/c3dt52965g>.
- (160) Söncksen, L.; Gradert, C.; Krahmer, J.; Näther, C.; Tucek, F. Bonding and Activation of N₂ in Mo(0) Complexes Supported by Hybrid Tripod Ligands with Mixed Dialkylphosphine/Diarylphosphine Donor Groups: Interplay of Steric and Electronic Factors. *Inorg. Chem.* **2013**, *52* (11), 6576–6589. <https://doi.org/10.1021/ic400582v>.
- (161) George, T. A.; Rose, D. J.; Chang, Y.; Chen, Q.; Zubieta, J. Reduction of Dinitrogen to Ammonia and Hydrazine in Iron(0) and Molybdenum(0) Complexes Containing the N(CH₂CH₂PPh₂)₃ Ligand. Crystal Structures of [FeH(L)(N(CH₂CH₂PPh₂)₃)] [BPh₄] (L = N₂, CO). *Inorg. Chem.* **1995**, *34* (5),

- 1295–1298. <https://doi.org/10.1021/ic00109a046>.
- (162) Römer, R.; Stephan, G.; Habeck, C.; Hoberg, C.; Peters, G.; Näther, C.; Tucek, F. Stereoselective Synthesis of the First Chatt-Type Bis(Dinitrogen)- Molybdenum(0) Complex with a Tetrphosphane Ligand. *Eur. J. Inorg. Chem.* **2008**, No. 21, 3258–3263. <https://doi.org/10.1002/ejic.200800417>.
- (163) Römer, R.; Gradert, C.; Bannwarth, A.; Peters, G.; Näther, C.; Tucek, F. One-Step Synthesis of Mo(0) and W(0) Bis(Dinitrogen) Complexes with the Linear Tetrphosphine Ligand PrP4: Stereoselective Formation of Cis-[M(N₂)₂(Rac-PrP₄)] and Trans-[M(N₂)₂(Meso-PrP₄)]; M = Mo, W. *Dalt. Trans.* **2011**, 40 (13), 3229. <https://doi.org/10.1039/c0dt01646b>.
- (164) Stephan, G. C.; Peters, G.; Lehnert, N.; Habeck, G. M.; Näther, C.; Tucek, F. Bonding, Activation, and Protonation of Dinitrogen on a Molybdenum Pentaphosphine Complex - Comparison to Trans-Bis(Dinitrogen) and -Nitrile - Dinitrogen Complexes with Tetrphosphine Coordination. *Can. J. Chem.* **2005**, 83 (4), 385–402. <https://doi.org/10.1139/v05-015>.
- (165) Hinrichsen, S.; Kindjajev, A.; Adomeit, S.; Krahmer, J.; Näther, C.; Tucek, F. Molybdenum(0) Dinitrogen Complexes Supported by Pentadentate Tetrapodal Phosphine Ligands: Structure, Synthesis, and Reactivity toward Acids. *Inorg. Chem.* **2016**, 55 (17), 8712–8722. <https://doi.org/10.1021/acs.inorgchem.6b01255>.
- (166) Margulieux, G. W.; Turner, Z. R.; Chirik, P. J. Synthesis and Ligand Modification Chemistry of a Molybdenum Dinitrogen Complex: Redox and Chemical Activity of a Bis-(Imino)Pyridine Ligand. *Angew. Chem. Int. Ed.* **2014**, 53 (51), 14211–14215. <https://doi.org/10.1002/anie.201408725>.

- (167) Cradwick, P. D.; Chatt, J.; Crabtree, R. H.; Richards, R. L. Preparation and X-Ray Structure of a Trinuclear Dinitrogen-Bridged Complex, Trans-[MoCl₄{(N₂)ReCl(PMe₂Ph)₄}₂]. *J. Chem. Soc. Chem. Commun.* **1975**, No. 9, 351–352. <https://doi.org/10.1039/C39750000351>.
- (168) Mösch-Zanetti, N. C.; Schrock, R. R.; Davis, W. M.; Wanninger, K.; Seidel, S. W.; O'Donoghue, M. B. Triamidoamine Complexes of Molybdenum and Tungsten That Contain Metal-E (E = N, P, and as) Single, Double, or Triple Bonds. *J. Am. Chem. Soc.* **1997**, *119* (45), 11037–11048. <https://doi.org/10.1021/ja971727z>.
- (169) O'Donoghue, M. B.; Davis, W. M.; Schrock, R. R.; Reiff, W. M. Heterobimetallic Dinitrogen Complexes That Contain the {[N₃N]Mo–NN} - Ligand. *Inorg. Chem.* **1999**, *38* (2), 243–252. <https://doi.org/10.1021/ic9811188>.
- (170) Takagahara, K.; Ishino, H.; Ishii, Y.; Hidai, M. Synthesis and Molecular Structure of Tetranuclear Tungsten-Gallium Complexes with Bridging Dinitrogen Ligands. *Chemistry Letters*. 1998, pp 897–898. <https://doi.org/10.1246/cl.1998.897>.
- (171) Ishino, H.; Nagano, T.; Kuwata, S.; Yokobayashi, Y.; Ishii, Y.; Hidai, M.; Mizobe, Y. Syntheses, Structures, and Reactivities of Heterobimetallic Bridging Dinitrogen Complexes Containing Group 6 and Group 4 or 5 Transition Metals 1. *Organometallics* **2001**, *20* (1), 188–198. <https://doi.org/10.1021/om000684j>.
- (172) O'Regan, M. B.; Liu, A. H.; Finch, W. C.; Schrock, R. R.; Davis, W. M. A Study of High-Oxidation-State Complexes of the Type [W(.Eta.⁵-C₅Me₅)Me₂X]₂(.Mu.-N₂), Including x-Ray Structures of [W(.Eta.⁵-C₅Me₅)Me₂(OC₆F₅)]₂(.Mu.-N₂) and [W(.Eta.⁵-C₅Me₅)Me₂(S-2,4,6-C₆H₂Me₃)]₂(.Mu.-N₂). *J. Am. Chem. Soc.* **1990**, *112* (11), 4331–4338. <https://doi.org/10.1021/ja00167a033>.

- (173) Schrock, R. R.; Kolodziej, R. M.; Liu, A. H.; Davis, W. M.; Vale, M. G.
Preparation and Characterization of Two High Oxidation State Molybdenum
Dinitrogen Complexes: [MoCp*Me₃]₂(μ-N₂) and [MoCp*Me₃](μ-N₂)[WCp*Me₃]. *J. Am. Chem. Soc.* **1990**, *112* (11), 4338–4345.
<https://doi.org/10.1021/ja00167a034>.
- (174) Fontaine, P. P.; Yonke, B. L.; Zavalij, P. Y.; Sita, L. R. Dinitrogen Complexation
and Extent of NtN Activation within the Group 6 “End-On-Bridged” Dinuclear
Complexes, {(H⁵-C⁵Me₅)M[N(i-Pr)C(Me)N(i-Pr)]}₂(μ-H¹:H¹-N₂)(M = Mo and
W). **2010**, *20* (June), 159–161.
- (175) Laplaza, C. E.; Cummins, C. C. Dinitrogen Cleavage by a Three-Coordinate
Molybdenum(III) Complex. *Science* (80-.). **1995**, *268* (5212), 861–863.
<https://doi.org/10.1126/science.268.5212.861>.
- (176) Laplaza, C. E.; Johnson, M. J. A.; Peters, J. C.; Odom, A. L.; Kim, E.; Cummins,
C. C.; George, G. N.; Pickering, I. J. Dinitrogen Cleavage by Three-Coordinate
Molybdenum(III) Complexes: Mechanistic and Structural Data 1. *J. Am. Chem.
Soc.* **1996**, *118* (36), 8623–8638. <https://doi.org/10.1021/ja960574x>.
- (177) Peters, J. C.; Cherry, J. P. F.; Thomas, J. C.; Baraldo, L.; Mindiola, D. J.; Davis,
W. M.; Cummins, C. C. Redox-Catalyzed Binding of Dinitrogen by Molybdenum
N-Tert- Hydrocarbylanilide Complexes: Implications for Dinitrogen
Functionalization and Reductive Cleavage. *J. Am. Chem. Soc.* **1999**, *121* (43),
10053–10067. <https://doi.org/10.1021/ja991435t>.
- (178) Solari, E.; Da Silva, C.; Iacono, B.; Hesschenbrouck, J.; Rizzoli, C.; Scopelliti, R.;
Floriani, C. Photochemical Activation of the N N Bond in Formation of a

Molybdenum Nitride **. *Angew. Chem. Int. Ed.* **2001**, *40*, 3907–3909.

[https://doi.org/10.1002/1521-3773\(20011015\)40:20<3907::AID-ANIE3907>3.0.CO;2-#](https://doi.org/10.1002/1521-3773(20011015)40:20<3907::AID-ANIE3907>3.0.CO;2-#).

(179) Hebden, T. J.; Schrock, R. R.; Takase, M. K.; Müller, P. Cleavage of Dinitrogen to Yield a (t-BuPOCOP)Molybdenum(Iv) Nitride. *Chem. Commun.* **2012**, *48* (13), 1851. <https://doi.org/10.1039/c2cc17634c>.

(180) Miyazaki, T.; Tanabe, Y.; Yuki, M.; Miyake, Y.; Nakajima, K.; Nishibayashi, Y. Design and Preparation of Molybdenum-Dinitrogen Complexes with Ferrocenyldiphosphine and Pentamethylcyclopentadienyl Moieties as Auxiliary Ligands. *Chem. - A Eur. J.* **2013**, *19* (36), 11874–11877. <https://doi.org/10.1002/chem.201302700>.

(181) Miyazaki, T.; Tanaka, H.; Tanabe, Y.; Yuki, M.; Nakajima, K.; Yoshizawa, K.; Nishibayashi, Y. Cleavage and Formation of Molecular Dinitrogen in a Single System Assisted by Molybdenum Complexes Bearing Ferrocenyldiphosphine. *Angew. Chem. Int. Ed.* **2014**, *53* (43), 11488–11492. <https://doi.org/10.1002/anie.201405673>.

(182) Keane, A. J.; Farrell, W. S.; Yonke, B. L.; Zavalij, P. Y.; Sita, L. R. Metal-Mediated Production of Isocyanates, R₃EN≡C≡O from Dinitrogen, Carbon Dioxide, and R₃ECl. *Angew. Chem. Int. Ed.* **2015**, *54* (35), 10220–10224. <https://doi.org/10.1002/anie.201502293>.

(183) Duman, L. M.; Farrell, W. S.; Zavalij, P. Y.; Sita, L. R. Steric Switching from Photochemical to Thermal Reaction Pathways for Enhanced Efficiency in Metal-Mediated Nitrogen Fixation. *J. Am. Chem. Soc.* **2016**, *138* (45), 14856–14859.

<https://doi.org/10.1021/jacs.6b09789>.

- (184) Liao, Q.; Cavaillé, A.; Saffon-Merceron, N.; Mézailles, N. Direct Synthesis of Silylamine from N₂ and a Silane: Mediated by a Tridentate Phosphine Molybdenum Fragment. *Angew. Chem. Int. Ed.* **2016**, 55 (37), 11212–11216.
<https://doi.org/10.1002/anie.201604812>.
- (185) Silantyev, G. A.; Förster, M.; Schluschaß, B.; Abbenseth, J.; Würtele, C.; Volkmann, C.; Holthausen, M. C.; Schneider, S. Dinitrogen Splitting Coupled to Protonation. *Angew. Chem. Int. Ed.* **2017**, 56 (21), 5872–5876.
<https://doi.org/10.1002/anie.201701504>.
- (186) Chatt, J.; Pearman, A. J.; Richards, R. L. The Reduction of Mono-Coordinated Molecular Nitrogen to Ammonia in a Protic Environment. *Nature* **1975**, 253 (39).
- (187) Galindo, A.; Hills, A.; Hughes, D. L.; Richards, R. L.; Hughes, M.; Mason, J. Protonation Reactions of Dinitrogen Complexes of Molybdenum and Tungsten with PMe₃ as Co-Ligand. X-Ray Structure of the Hydrazidium Complex [WCl(NNH₃)(PMe₃)₄] Cl₂. *J. Chem. Soc. Dalt. Trans.* **1990**, No. 1, 283–288.
<https://doi.org/10.1039/DT9900000283>.
- (188) Chatt, J.; Heath, G. A.; Richards, R. L. Diazene-N-(Di-Imide) and Hydrazido-(2–)N-(Aminoimido) Complexes: The Addition of Acids to Dinitrogen Complexes. *J. Chem. Soc., Dalt. Trans.* **1974**, No. 19, 2074–2082.
<https://doi.org/10.1039/DT9740002074>.
- (189) Chatt, J.; Heath, G. A.; Richards, R. L. The Reduction of Ligating Dinitrogen to Yield a Ligating N₂H₂ Moiety. *J. Chem. Soc. Chem. Commun.* **1972**, No. 18, 1010–1011. <https://doi.org/10.1039/C39720001010>.

- (190) Heath, G. A.; Mason, R.; Thomas, K. M. Reduction of Coordinated Dinitrogen to the Coordinated Hydrazido Dianion. The Structural Characterization of the 1- η -Hydrazido(2-)-Chlorobis[1,2-Bis(Diphenylphosphino)Ethane]Tungsten(IV) Cation. *J. Am. Chem. Soc.* **1974**, 96 (1), 259–260.
<https://doi.org/10.1021/ja00808a048>.
- (191) Hidai, M.; Kodama, T.; Sato, M.; Harakawa, M.; Uchida, Y. Preparation and Properties of Dinitrogen-Molybdenum Complexes. 3.1 Preparation and Molecular Structure of 1-(η -Hydrazido(2-))Fluorobis[1,2-Bis(Diphenylphosphino)Ethane]Molybdenum Tetrafluoroborate-Dichloromethane Solvate, [Mo(N₂H₂)F(Ph₂PCH₂CH₂PPh₂)₂] [BF₄]. *Inorg. Chem.* **1976**, 15 (11), 2694–2697. <https://doi.org/10.1021/ic50165a025>.
- (192) Labios, L. A.; Heiden, Z. M.; Mock, M. T. Electronic and Steric Influences of Pendant Amine Groups on the Protonation of Molybdenum Bis(Dinitrogen) Complexes. *Inorg. Chem.* **2015**, 54 (9), 4409–4422.
<https://doi.org/10.1021/acs.inorgchem.5b00209>.
- (193) Weiss, C. J.; Groves, A. N.; Mock, M. T.; Dougherty, W. G.; Kassel, W. S.; Helm, M. L.; DuBois, D. L.; Bullock, R. M. Synthesis and Reactivity of Molybdenum and Tungsten Bis(Dinitrogen) Complexes Supported by Diphosphine Chelates Containing Pendant Amines. *Dalt. Trans.* **2012**, 41 (15), 4517.
<https://doi.org/10.1039/c2dt12224c>.
- (194) Labios, L. A.; Weiss, C. J.; Egbert, J. D.; Lense, S.; Bullock, R. M.; Dougherty, W. G.; Kassel, W. S.; Mock, M. T. Synthesis and Protonation Studies of Molybdenum(0) Bis(Dinitrogen) Complexes Supported by Diphosphine Ligands

- Containing Pendant Amines. *Zeitschrift fur Anorg. und Allg. Chemie* **2015**, 641 (1), 105–117. <https://doi.org/10.1002/zaac.201400119>.
- (195) Jia, G.; Morris, R. H.; Schweitzer, C. T. An Acidic H₂-Dihydrogen Complex Protonating Coordinated Dinitrogen. *Inorg. Chem.* **1991**, 30 (4), 593–594. <https://doi.org/10.1021/ic00004a001>.
- (196) Nishibayashi, Y. Bimetallic System for Nitrogen Fixation: Ruthenium-Assisted Protonation of Coordinated N₂ on Tungsten with H₂. *Science* (80-.). **1998**, 279 (5350), 540–542. <https://doi.org/10.1126/science.279.5350.540>.
- (197) Nishibayashi, Y.; Wakiji, I.; Hirata, K.; DuBois, M. R.; Hidai, M. Protonation of Coordinated N₂ on Tungsten with H₂ Mediated by Sulfido-Bridged Dinuclear Molybdenum Complexes. *Inorg. Chem.* **2001**, 40 (3), 578–580. <https://doi.org/10.1021/ic000716v>.
- (198) Nishibayashi, Y.; Iwai, S.; Hidai, M. A Model for Protonation of Dinitrogen by Nitrogenase: Protonation of Coordinated Dinitrogen on Tungsten with Hydrosulfido-Bridged Dinuclear Complexes [9]. *J. Am. Chem. Soc.* **1998**, 120 (40), 10559–10560. <https://doi.org/10.1021/ja981223g>.
- (199) Tamizmani, M.; Sivasankar, C. Protonation of Coordinated Dinitrogen Using Protons Generated from Molecular Hydrogen. *Eur. J. Inorg. Chem.* **2017**, 2017 (37), 4239–4245. <https://doi.org/10.1002/ejic.201700784>.
- (200) Yandulov, D. V.; Schrock, R. R. Catalytic Reduction of Dinitrogen to Ammonia at a Single Molybdenum Center. *Science* (80-.). **2003**, 301 (5629), 76–78. <https://doi.org/10.1126/science.1085326>.
- (201) Yandulov, D. V.; Schrock, R. R. Reduction of Dinitrogen to Ammonia at a Well-

- Protected Reaction Site in a Molybdenum Triamidoamine Complex. *J. Am. Chem. Soc.* **2002**, *124* (22), 6252–6253. <https://doi.org/10.1021/ja020186x>.
- (202) Weare, W. W.; Dai, X.; Byrnes, M. J.; Chin, J. M.; Schrock, R. R.; Müller, P. Catalytic Reduction of Dinitrogen to Ammonia at a Single Molybdenum Center. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103* (46), 17099–17106. <https://doi.org/10.1073/pnas.0602778103>.
- (203) Yandulov, D. V.; Schrock, R. R. Studies Relevant to Catalytic Reduction of Dinitrogen to Ammonia by Molybdenum Triamidoamine Complexes. *Inorg. Chem.* **2005**, *44* (4), 1103–1117. <https://doi.org/10.1021/ic040095w>.
- (204) Hetterscheid, D. G. H.; Hanna, B. S.; Schrock, R. R. Molybdenum Triamidoamine Systems. Reactions Involving Dihydrogen Relevant to Catalytic Reduction of Dinitrogen. *Inorg. Chem.* **2009**, *48* (17), 8569–8577. <https://doi.org/10.1021/ic900468n>.
- (205) Kinney, R. A.; McNaughton, R. L.; Chin, J. M.; Schrock, R. R.; Hoffman, B. M. Protonation of the Dinitrogen-Reduction Catalyst [HIPTN₃N] Mo^{III} Investigated by ENDOR Spectroscopy. *Inorg. Chem.* **2011**, *50* (2), 418–420. <https://doi.org/10.1021/ic102127v>.
- (206) Schrock, R. R. Catalytic Reduction of Dinitrogen to Ammonia by Molybdenum: Theory versus Experiment. *Angew. Chem. Int. Ed.* **2008**, *47* (30), 5512–5522. <https://doi.org/10.1002/anie.200705246>.
- (207) Schenk, S.; Guennic, B. Le; Kirchner, B.; Reiher, M.; Schenk, S.; Guennic, B. Le; Kirchner, B.; Reiher, M. First-Principles Investigation of the Schrock Mechanism of Dinitrogen Reduction Employing the Full HIPTN N Ligand First-Principles

Investigation of the Schrock Mechanism of Dinitrogen Reduction Employing the Full HIPTN 3 N Ligand. **2008**, 47 (9), 3634–3650.

<https://doi.org/10.1021/ic702083p>.

- (208) Schenk, S.; Kirchner, B.; Reiher, M. A Stable Six-Coordinate Intermediate in Ammonia-Dinitrogen Exchange at Schrock's Molybdenum Catalyst. *Chem. - A Eur. J.* **2009**, 15 (20), 5073–5082. <https://doi.org/10.1002/chem.200802438>.
- (209) Thimm, W.; Gradert, C.; Broda, H.; Wennmohs, F.; Neese, F.; Tuczek, F. Free Reaction Enthalpy Profile of the Schrock Cycle Derived from Density Functional Theory Calculations on the Full [Mo^{HIPT}N₃] Catalyst. *Inorg. Chem.* **2015**, 54 (19), 9248–9255. <https://doi.org/10.1021/acs.inorgchem.5b00787>.
- (210) Ritleng, V.; Yandulov, D. V.; Weare, W. W.; Schrock, R. R.; Hock, A. S.; Davis, W. M. Molybdenum Triamidoamine Complexes That Contain Hexa-Tert-Butylterphenyl, Hexamethylterphenyl, or p-Bromohexaisopropylterphenyl Substituents. An Examination of Some Catalyst Variations for the Catalytic Reduction of Dinitrogen. *J. Am. Chem. Soc.* **2004**, 126 (19), 6150–6163. <https://doi.org/10.1021/ja0306415>.
- (211) Weare, W. W.; Schrock, R. R.; Hock, A. S.; Müller, P. Synthesis of Molybdenum Complexes That Contain “Hybrid” Triamidoamine Ligands, [(Hexaisopropylterphenyl-NCH₂CH₂)₂NCH₂CH₂N-Aryl]³⁻, and Studies Relevant to Catalytic Reduction of Dinitrogen. *Inorg. Chem.* **2006**, 45 (23), 9185–9196. <https://doi.org/10.1021/ic0613457>.
- (212) Reithofer, M. R.; Schrock, R. R.; Müller, P. Synthesis of [(DPPNCH₂CH₂)₃N]³⁻ Molybdenum Complexes (DPP = 3,5-(2,5-Diisopropylpyrrolyl)₂C₆H₃) and

- Studies Relevant to Catalytic Reduction of Dinitrogen. *J. Am. Chem. Soc.* **2010**, *132* (24), 8349–8358. <https://doi.org/10.1021/ja1008213>.
- (213) Arashiba, K.; Kuriyama, S.; Nakajima, K.; Nishibayashi, Y. Preparation and Reactivity of a Dinitrogen-Bridged Dimolybdenum-Tetrachloride Complex. *Chem. Commun.* **2013**, 49 (95), 11215–11217. <https://doi.org/10.1039/c3cc46946h>.
- (214) Kinoshita, E.; Arashiba, K.; Kuriyama, S.; Miyake, Y.; Shimazaki, R.; Nakanishi, H.; Nishibayashi, Y. Synthesis and Catalytic Activity of Molybdenum–Dinitrogen Complexes Bearing Unsymmetric PNP-Type Pincer Ligands. *Organometallics* **2012**, *31* (23), 8437–8443. <https://doi.org/10.1021/om301046t>.
- (215) Tanabe, Y.; Kuriyama, S.; Arashiba, K.; Miyake, Y.; Nakajima, K.; Nishibayashi, Y. Preparation and Reactivity of Molybdenum–Dinitrogen Complexes Bearing an Arsenic-Containing ANA-Type Pincer Ligand. *Chem. Commun.* **2013**, 49 (81), 9290–9292. <https://doi.org/10.1039/c3cc45228j>.
- (216) Tanaka, H.; Arashiba, K.; Kuriyama, S.; Sasada, A.; Nakajima, K.; Yoshizawa, K.; Nishibayashi, Y. Unique Behaviour of Dinitrogen-Bridged Dimolybdenum Complexes Bearing Pincer Ligand towards Catalytic Formation of Ammonia. *Nat. Commun.* **2014**, *5*, 3737. <https://doi.org/10.1038/ncomms4737>.
- (217) Tian, Y. H.; Pierpont, A. W.; Batista, E. R. How Does Nishibayashi's Molybdenum Complex Catalyze Dinitrogen Reduction to Ammonia? *Inorg. Chem.* **2014**, *53* (8), 4177–4183. <https://doi.org/10.1021/ic500221n>.
- (218) Kuriyama, S.; Arashiba, K.; Nakajima, K.; Tanaka, H.; Yoshizawa, K.; Nishibayashi, Y. Nitrogen Fixation Catalyzed by Ferrocene-Substituted Dinitrogen-Bridged Dimolybdenum–Dinitrogen Complexes: Unique Behavior of

Ferrocene Moiety as Redox Active Site. *Chem. Sci.* **2015**, 6 (7), 3940–3951.

<https://doi.org/10.1039/C5SC00545K>.

- (219) Arashiba, K.; Eizawa, A.; Tanaka, H.; Nakajima, K.; Yoshizawa, K.; Nishibayashi, Y. Catalytic Nitrogen Fixation via Direct Cleavage of Nitrogen-Nitrogen Triple Bond of Molecular Dinitrogen under Ambient Reaction Conditions. *Bull. Chem. Soc. Jpn.* **2017**, 90 (10), 1111–1118. <https://doi.org/10.1246/bcsj.20170197>.
- (220) Wickramasinghe, L. A.; Ogawa, T.; Schrock, R. R.; Müller, P. Reduction of Dinitrogen to Ammonia Catalyzed by Molybdenum Diamido Complexes. *J. Am. Chem. Soc.* **2017**, 139 (27), 9132–9135. <https://doi.org/10.1021/jacs.7b04800>.
- (221) Ashida, Y.; Arashiba, K.; Nakajima, K.; Nishibayashi, Y. Molybdenum-Catalysed Ammonia Production with Samarium Diiodide and Alcohols or Water. *Nature* **2019**, 568 (7753), 536–540. <https://doi.org/10.1038/s41586-019-1134-2>.
- (222) Ashida, Y.; Arashiba, K.; Tanaka, H.; Egi, A.; Nakajima, K.; Yoshizawa, K.; Nishibayashi, Y. Molybdenum-Catalyzed Ammonia Formation Using Simple Monodentate and Bidentate Phosphines as Auxiliary Ligands. *Inorg. Chem.* **2019**, 58 (14), 8927–8932. <https://doi.org/10.1021/acs.inorgchem.9b01340>.
- (223) Bossard, G. E.; Busby, D. C.; Chang, M.; George, T. A.; Iske, S. D. A. Reactions of Coordinated Dinitrogen. 4. Reactions of Bromoalkanes with Bis(Dinitrogen)Bis[Ethylenebis(Diphenylphosphine)]Molybdenum. Formation of Ammonia and Amines. *J. Am. Chem. Soc.* **1980**, 102 (3), 1001–1008. <https://doi.org/10.1021/ja00523a016>.
- (224) Hussain, W.; Leigh, G. J.; Modh-Ali, H.; Pickett, C. J. Mechanism of Alkylation of Alkyldiazenido-Complexes of Molybdenum(II) and Tungsten(II): Influence of

- Metal and Co-Ligands on the Nucleophilicity of a Diazenido-Group. *J. Chem. Soc. Dalt. Trans.* **1986**, No. 7, 1473. <https://doi.org/10.1039/dt9860001473>.
- (225) Yoshida, T.; Adachi, T.; Ueda, T.; Kaminaka, M.; Sasaki, N.; Higuchi, T.; Aoshima, T.; Mega, I.; Mizobe, Y.; Hidai, M. N-Arylation And N,N-Dibenzylation of Coordinated N₂ with Organic Halides; Differences in the Reactivity Of trans-[Mo(N₂)₂(Me₈[16]AneS₄)] and Its Phosphane Analogues. *Angew. Chem. Int. Ed. Engl.* **1989**, 28 (8), 1040–1042. <https://doi.org/10.1002/anie.198910401>.
- (226) Hidai, M.; Mizobe, Y. Recent Advances in the Chemistry of Dinitrogen Complexes. *Chem. Rev.* **1995**, 95 (4), 1115–1133. <https://doi.org/10.1021/cr00036a008>.
- (227) Aoshima, T.; Tamura, T.; Mizobe, Y.; Hidai, M. Preparation and Properties of Molybdenum and Tungsten Dinitrogen Complexes. *J. Organomet. Chem.* **1992**, 435 (1–2), 85–99. [https://doi.org/10.1016/0022-328X\(92\)83462-Q](https://doi.org/10.1016/0022-328X(92)83462-Q).
- (228) Harada, Y.; Mizobe, Y.; Ishii, Y.; Hidai, M. Syntheses of Tungsten Diazoalkane Complexes from a Dinitrogen Complex and Diketones. Conversion of Molecular Nitrogen into Pyrazoles via the Diazoalkane Complexes as Intermediates. *Bull. Chem. Soc. Jpn.* **1998**, 71 (11), 2701–2708. <https://doi.org/10.1246/bcsj.71.2701>.
- (229) Seino, H.; Ishii, Y.; Hidai, M. Synthesis and Structure Determinations of Complexes Containing a Five-Membered Lactam Structure Based on Organohydrazido(2–) Ligands. *Inorg. Chem.* **1997**, 36 (2), 161–171. <https://doi.org/10.1021/ic960778e>.
- (230) Curley, J. J.; Sceats, E. L.; Cummins, C. C. A Cycle for Organic Nitrile Synthesis via Dinitrogen Cleavage. *J. Am. Chem. Soc.* **2006**, 128 (43), 14036–14037.

<https://doi.org/10.1021/ja066090a>.

- (231) Hidai, M.; Komori, K.; Kodama, T.; Jin, D.-M.; Takahashi, T.; Sugiura, S.; Uchida, Y.; Mizobe, Y. Preparation and Properties of Molybdenum and Tungsten Dinitrogen Complexes. *J. Organomet. Chem.* **1984**, 272 (2), 155–167.
[https://doi.org/10.1016/0022-328X\(84\)80463-5](https://doi.org/10.1016/0022-328X(84)80463-5).
- (232) Komori, K.; Oshita, H.; Mizobe, Y.; Hidai, M. Catalytic Conversion of Molecular Nitrogen into Silylamines Using Molybdenum and Tungsten Dinitrogen Complexes. *J. Am. Chem. Soc.* **1989**, 111 (5), 1939–1940.
<https://doi.org/10.1021/ja00187a092>.
- (233) Tanaka, H.; Sasada, A.; Kouno, T.; Yuki, M.; Miyake, Y.; Nakanishi, H.; Nishibayashi, Y.; Yoshizawa, K. Molybdenum-Catalyzed Transformation of Molecular Dinitrogen into Silylamine: Experimental and DFT Study on the Remarkable Role of Ferrocenyldiphosphine Ligands. *J. Am. Chem. Soc.* **2011**, 133 (10), 3498–3506. <https://doi.org/10.1021/ja109181n>.
- (234) Tanabe, Y.; Nishibayashi, Y. Catalytic Dinitrogen Fixation to Form Ammonia at Ambient Reaction Conditions Using Transition Metal-Dinitrogen Complexes. *Chem. Rec.* **2016**, 1549–1577. <https://doi.org/10.1002/tcr.201600025>.
- (235) Ogawa, T.; Kajita, Y.; Wasada-Tsutsui, Y.; Wasada, H.; Masuda, H. Preparation, Characterization, and Reactivity of Dinitrogen Molybdenum Complexes with Bis(Diphenylphosphino)Amine Derivative Ligands That Form a Unique 4-Membered P-N-P Chelate Ring. *Inorg. Chem.* **2013**, 52 (1), 182–195.
<https://doi.org/10.1021/ic301577a>.
- (236) Liao, Q.; Saffon-Merceron, N.; Mézailles, N. Catalytic Dinitrogen Reduction at the

Molybdenum Center Promoted by a Bulky Tetradentate Phosphine Ligand. *Angew. Chem. Int. Ed.* **2014**, 53 (51), 14206–14210.

<https://doi.org/10.1002/anie.201408664>.

- (237) Liao, Q.; Saffon-Merceron, N.; Mézailles, N. N₂ Reduction into Silylamine at Tridentate Phosphine/Mo Center: Catalysis and Mechanistic Study. *ACS Catal.* **2015**, 5 (11), 6902–6906. <https://doi.org/10.1021/acscatal.5b01626>.
- (238) Duman, L. M.; Sita, L. R. Closing the Loop on Transition-Metal-Mediated Nitrogen Fixation: Chemoselective Production of HN(SiMe₃)₂ from N₂, Me₃SiCl, and X—OH (X = R, R₃Si, or Silica Gel). *J. Am. Chem. Soc.* **2017**, 139 (48), 17241–17244. <https://doi.org/10.1021/jacs.7b08859>.
- (239) Ishino, H.; Ishii, Y.; Hidai, M. Synthesis of Boryldiazenido Complexes from Tungsten Dinitrogen Complexes. *Chemistry Letters*. 1998, pp 677–678. <https://doi.org/10.1246/cl.1998.677>.
- (240) Simonneau, A.; Turrel, R.; Vendier, L.; Etienne, M. Group 6 Transition-Metal/Boron Frustrated Lewis Pair Templates Activate N₂ and Allow Its Facile Borylation and Silylation. *Angew. Chem. Int. Ed.* **2017**, 56 (40), 12268–12272. <https://doi.org/10.1002/anie.201706226>.
- (241) Coffinet, A.; Specklin, D.; Vendier, L.; Etienne, M.; Simonneau, A. Frustrated Lewis Pair Chemistry Enables N₂ Borylation by Formal 1,3-Addition of a B–H Bond in the Coordination Sphere of Tungsten. *Chem. - A Eur. J.* **2019**, 1–5. <https://doi.org/10.1002/chem.201904084>.
- (242) Chatt, J.; Crabtree, R. H.; Jeffery, E. A.; Richards, R. L. The Basic Strengths of Some Dinitrogen Complexes of Molybdenum(o), Tungsten(o), Rhenium(I), and

- Osmium(II). *Dalt. Trans.* **1973**, 1167.
- (243) Chatt, J.; Dilworth, J. R.; Leigh, G. J. Dinitrogen Complexes of Rhenium(I) and Rhenium(II). *J.C.S. Dalt.* **1973**, No. 612.
- (244) Mösch-Zanetti, N. C.; Köpke, S.; Herbst-Irmer, R.; Hewitt, M. Unsymmetrical Tren-Based Ligands: Synthesis and Reactivity of Rhenium Complexes. *Inorg. Chem.* **2002**, *41* (13), 3513–3520. <https://doi.org/10.1021/ic025572u>.
- (245) Kirillov, A. M.; Haukka, M.; Guedes da Silva, M. F. C.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. A Picolinate-N₂ Complex of Rhenium, the First Dinitrogen Complex Bearing a Carboxylate or a N,O-Ligand. *J. Organomet. Chem.* **2006**, *691* (19), 4153–4158. <https://doi.org/10.1016/j.jorganchem.2006.06.015>.
- (246) Smoleński, P.; Pombeiro, A. J. L. Water-Soluble and Stable Dinitrogen Phosphine Complexes Trans-[ReCl(N₂)(PTA-H)_n(PTA)_{4-n}]⁺ (n = 0–4), the First with 1,3,5-Triaza-7-Phosphaadamantane. *Dalt. Trans.* **2008**, No. 1, 87–91. <https://doi.org/10.1039/b712360d>.
- (247) Chatt, J.; Dilworth, J. R.; Richards, R. L.; Sanders, J. R. Chemical Evidence Concerning the Function of Molybdenum in Nitrogenase [13]. *Nature* **1969**, *224* (5225), 1201–1202. <https://doi.org/10.1038/2241201a0>.
- (248) Seymore, S. B.; Brown, S. N. Kinetic Effects in Heterometallic Dinitrogen Cleavage. *Inorg. Chem.* **2006**, *45* (23), 9540–9550. <https://doi.org/10.1021/ic061153b>.
- (249) Chomitz, W. A.; Arnold, J. Transition Metal Dinitrogen Complexes Supported by a Versatile Monoanionic [N₂P₂] Ligand. *Chem. Commun.* **2007**, No. 45, 4797–4799. <https://doi.org/10.1039/b709763h>.

- (250) Chomitz, W. A.; Arnold, J. Synthesis and Characterization of Manganese and Iron Complexes Supported by Multidentate [N₂P₂] Ligands. *J. Chem. Soc. Dalt. Trans.* **2009**, No. 10, 1714–1720. <https://doi.org/10.1039/b821954k>.
- (251) Klopsch, I.; Finger, M.; Würtele, C.; Milde, B.; Werz, D. B.; Schneider, S. Dinitrogen Splitting and Functionalization in the Coordination Sphere of Rhenium. *J. Am. Chem. Soc.* **2014**, *136* (19), 6881–6883. <https://doi.org/10.1021/ja502759d>.
- (252) Klopsch, I.; Kinauer, M.; Finger, M.; Würtele, C.; Schneider, S. Conversion of Dinitrogen into Acetonitrile under Ambient Conditions. *Angew. Chem. Int. Ed.* **2016**, *55* (15), 4786–4789. <https://doi.org/10.1002/anie.201600790>.
- (253) Klopsch, I.; Schendzielorz, F.; Volkmann, C.; Würtele, C.; Schneider, S. Synthesis of Benzonitrile from Dinitrogen. *Zeitschrift für Anorg. und Allg. Chemie* **2018**, *644* (17), 916–919. <https://doi.org/10.1002/zaac.201800181>.
- (254) Schendzielorz, F.; Finger, M.; Abbenseth, J.; Würtele, C.; Krewald, V.; Schneider, S. Metal-Ligand Cooperative Synthesis of Benzonitrile by Electrochemical Reduction and Photolytic Splitting of Dinitrogen. *Angew. Chem. Int. Ed.* **2019**, *58* (3), 830–834. <https://doi.org/10.1002/anie.201812125>.
- (255) Leigh, G. J.; Jimenez-Tenorio, M. Exchange of Dinitrogen between Iron and Molybdenum Centers and the Reduction of Dinitrogen Bound to Iron: Implications for the Chemistry of Nitrogenases. *J. Am. Chem. Soc.* **1991**, *113* (15), 5862–5863. <https://doi.org/10.1021/ja00015a050>.
- (256) Gilbertson, J. D.; Szymczak, N. K.; Tyler, D. R. H₂ Activation in Aqueous Solution: Formation of Trans-[Fe(DMeOPrPE)₂H(H₂)]⁺ via the Heterolysis of H₂ in Water. *Inorg. Chem.* **2004**, *43* (11), 3341–3343.

<https://doi.org/10.1021/ic0498642>.

- (257) Gilbertson, J. D.; Szymczak, N. K.; Tyler, D. R. Reduction of N₂ to Ammonia and Hydrazine Utilizing H₂ as the Reductant. *J. Am. Chem. Soc.* **2005**, *127* (29), 10184–10185. <https://doi.org/10.1021/ja053030g>.
- (258) Gilbertson, J. D.; Szymczak, N. K.; Crossland, J. L.; Miller, W. K.; Lyon, D. K.; Foxman, B. M.; Davis, J.; Tyler, D. R. Coordination Chemistry of H₂ and N₂ in Aqueous Solution. Reactivity and Mechanistic Studies Using Trans-FeII(P₂)₂X₂-Type Complexes (P₂ = a Chelating, Water-Solubilizing Phosphine). *Inorg. Chem.* **2007**, *46* (4), 1205–1214. <https://doi.org/10.1021/ic061570o>.
- (259) Crossland, J. L.; Balesdent, C. G.; Tyler, D. R. Coordination of a Complete Series of N₂ Reduction Intermediates (N₂H₂, N₂H₄, and NH₃) to an Iron Phosphine Scaffold. *Inorg. Chem.* **2012**, *51* (1), 439–445. <https://doi.org/10.1021/ic201873a>.
- (260) Yelle, R. B.; Crossland, J. L.; Szymczak, N. K.; Tyler, D. R. Theoretical Studies of N₂ Reduction to Ammonia in Fe(Dmpe)₂N₂. *Inorg. Chem.* **2009**, *48* (3), 861–871. <https://doi.org/10.1021/ic800930t>.
- (261) Hirano, M.; Akita, M.; Morikita, T.; Kubo, H.; Fukuoka, A.; Komiya, S. Results and Discussion. *J. Chem. Soc., Dalt. Trans.* **1997**, *2*, 3453–3458.
- (262) Field, L. D.; Hazari, N.; Li, H. L. Nitrogen Fixation Revisited on Iron(0) Dinitrogen Phosphine Complexes. *Inorg. Chem.* **2015**, *54* (10), 4768–4776. <https://doi.org/10.1021/acs.inorgchem.5b00211>.
- (263) Field, L. D.; Li, H. L.; Dalgarno, S. J.; Turner, P. The First Side-on Bound Metal Complex of Diazene, HN=NH. *Chem. Commun.* **2008**, *33* (14), 1680–1682. <https://doi.org/10.1039/b802039f>.

- (264) Field, L. D.; Li, H. L.; Magill, A. M. Base-Mediated Conversion of Hydrazine to Diazene and Dinitrogen at an Iron Center. *Inorg. Chem.* **2009**, *48* (1), 5–7.
<https://doi.org/10.1021/ic801856q>.
- (265) Field, L. D.; Li, H. L.; Dalgarno, S. J. Side-on Bound Diazene and Hydrazine Complexes of Ruthenium. *Inorg. Chem.* **2010**, *49* (13), 6214–6221.
<https://doi.org/10.1021/ic100821u>.
- (266) Doyle, L. R.; Hill, P. J.; Wildgoose, G. G.; Ashley, A. E. Teaching Old Compounds New Tricks: Efficient N₂ Fixation by Simple Fe(N₂)(Diphosphine)₂ Complexes. *Dalt. Trans.* **2016**, *45* (18), 7550–7554.
<https://doi.org/10.1039/c6dt00884d>.
- (267) Piascik, A. D.; Hill, P. J.; Crawford, A. D.; Doyle, L. R.; Green, J. C.; Ashley, A. E. Cationic Silyldiazenido Complexes of the Fe(Diphosphine)₂(N₂) Platform: Structural and Electronic Models for an Elusive First Intermediate in N₂ Fixation. *Chem. Commun.* **2017**, *53* (54), 7657–7660. <https://doi.org/10.1039/c7cc04188h>.
- (268) Geri, J. B.; Shanahan, J. P.; Szymczak, N. K. Testing the Push-Pull Hypothesis: Lewis Acid Augmented N₂ Activation at Iron. *J. Am. Chem. Soc.* **2017**, *139* (16), 5952–5956. <https://doi.org/10.1021/jacs.7b01982>.
- (269) Heiden, Z. M.; Chen, S.; Mock, M. T.; Dougherty, W. G.; Kassel, W. S.; Rousseau, R.; Bullock, R. M. Protonation of Ferrous Dinitrogen Complexes Containing a Diphosphine Ligand with a Pendent Amine. *Inorg. Chem.* **2013**, *52* (7), 4026–4039. <https://doi.org/10.1021/ic4000704>.
- (270) Heiden, Z. M.; Chen, S.; Labios, L. A.; Bullock, R. M.; Walter, E. D.; Tyson, E. L.; Mock, M. T. Proton and Electron Additions to Iron(II) Dinitrogen Complexes

Containing Pendant Amines. *Organometallics* **2014**, 33 (6), 1333–1336.

<https://doi.org/10.1021/om401089d>.

- (271) Beach, M. T.; Walker, J. M.; Wang, R.; Spivak, G. J. Ruthenium Piano-Stool Complexes Containing Mono- or Bidentate Pyrrolidinylalkylphosphines and Their Reactions with Small Molecules. *J. Organomet. Chem.* **2011**, 696 (20), 3198–3205. <https://doi.org/10.1016/j.jorganchem.2011.06.037>.
- (272) Ledger, A. E. W.; Moreno, A.; Ellul, C. E.; Mahon, M. F.; Pregosin, P. S.; Whittlesey, M. K.; Williams, J. M. J. Pincer Phosphine Complexes of Ruthenium: Formation of Ru(P-O-P)(PPh₃)HCl (P-O-P = Xantphos, DPEphos, (Ph₂PCH₂CH₂)₂O) and Ru(Dppf)(PPh₃)HCl and Characterization of Cationic Dioxygen, Dihydrogen, Dinitrogen, and Arene Coordinated Phosphine Products. *Inorg. Chem.* **2010**, 49 (16), 7244–7256. <https://doi.org/10.1021/ic100438d>.
- (273) Buscagan, T. M.; Oyala, P. H.; Peters, J. C. N₂-to-NH₃ Conversion by a Triphos–Iron Catalyst and Enhanced Turnover under Photolysis. *Angew. Chem. Int. Ed.* **2017**, 56 (24), 6921–6926. <https://doi.org/10.1002/anie.201703244>.
- (274) Cavaillé, A.; Joyeux, B.; Saffon-Merceron, N.; Nebra, N.; Fustier-Boutignon, M.; Mézailles, N. Triphos-Fe Dinitrogen and Dinitrogen-Hydride Complexes: Relevance to Catalytic N₂ Reduction. *Chem. Commun.* **2018**, 54 (84), 11953–11956. <https://doi.org/10.1039/c8cc07466f>.
- (275) Schild, D. J.; Peters, J. C. Light Enhanced Fe-Mediated Nitrogen Fixation: Mechanistic Insights Regarding H₂ Elimination, HER, and NH₃ Generation. *ACS Catal.* **2019**, 9 (5), 4286–4295. <https://doi.org/10.1021/acscatal.9b00523>.
- (276) Betley, T. A.; Peters, J. C. Dinitrogen Chemistry from Trigonal Coordinated Iron

and Cobalt Platforms. *J. Am. Chem. Soc.* **2003**, *125* (36), 10782–10783.

<https://doi.org/10.1021/ja036687f>.

- (277) Betley, T. A.; Peters, J. C. A Tetrahedrally Coordinated L₃ Fe-N_x Platform That Accommodates Terminal Nitride and Dinitrogen Ligands. *J. Am. Chem. Soc.* **2004**, *126*, 6252.
- (278) Saouma, C. T.; Moore, C. E.; Rheingold, A. L.; Peters, J. C. A Five-Coordinate Phosphino / Acetate Iron (II) Scaffold That Binds N₂ ., *Inorg. Chem.* **2011**, *50* (11), 11285–11287.
- (279) Mankad, N. P.; Whited, M. T.; Peters, J. C. Terminal FeI-N₂ and FeII···H-C Interactions Supported by Tris(Phosphino)Silyl Ligands. *Angew. Chem. Int. Ed.* **2007**, *46* (30), 5768–5771. <https://doi.org/10.1002/anie.200701188>.
- (280) Whited, M. T.; Mankad, N. P.; Lee, Y.; Oblad, P. F.; Peters, J. C. Dinitrogen Complexes Supported by Tris(Phosphino)Silyl Ligands. *Inorg. Chem.* **2009**, *48* (6), 2507–2517. <https://doi.org/10.1021/ic801855y>.
- (281) Lee, Y.; Mankad, N. P.; Peters, J. C. Triggering N₂ Uptake via Redox-Induced Expulsion of Coordinated NH₃ and N₂ Silylation at Trigonal Bipyramidal Iron. *Nat. Chem.* **2010**, *2* (7), 558–565. <https://doi.org/10.1038/nchem.660>.
- (282) Mankad, N. P.; Müller, P.; Peters, J. C. Catalytic N-N Coupling of Aryl Azides to Yield Azoarenes via Trigonal Bipyramid Iron-Nitrene Intermediates. *J. Am. Chem. Soc.* **2010**, *132* (12), 4083–4085. <https://doi.org/10.1021/ja910224c>.
- (283) Rittle, J.; Peters, J. C. An Fe-N₂ Complex That Generates Hydrazine and Ammonia via Fe=NNH₂: Demonstrating a Hybrid Distal-to-Alternating Pathway for N₂ Reduction. *J. Am. Chem. Soc.* **2016**, *138* (12), 4243–4248.

<https://doi.org/10.1021/jacs.6b01230>.

- (284) Rittle, J.; Peters, J. C. Proton-Coupled Reduction of an Iron Cyanide Complex to Methane and Ammonia. *Angew. Chem. Int. Ed.* **2016**, *55* (40), 12262–12265.

<https://doi.org/10.1002/anie.201606366>.

- (285) Rittle, J.; Peters, J. C. N-H Bond Dissociation Enthalpies and Facile H Atom Transfers for Early Intermediates of Fe-N₂ and Fe-CN Reductions. *J. Am. Chem. Soc.* **2017**, *139* (8), 3161–3170. <https://doi.org/10.1021/jacs.6b12861>.

- (286) Creutz, S. E.; Peters, J. C. Exploring Secondary-Sphere Interactions in Fe-N_xH_y Complexes Relevant to N₂ Fixation. *Chem. Sci.* **2017**, *8* (3), 2321–2328.

<https://doi.org/10.1039/c6sc04805f>.

- (287) Takaoka, A.; Gerber, L. C. H.; Peters, J. C. Access to Well-Defined Ruthenium(I) and Osmium(I) Metalloradicals. *Angew. Chem. Int. Ed.* **2010**, *49* (24), 4088–4091.

<https://doi.org/10.1002/anie.201001199>.

- (288) Takaoka, A.; Moret, M. E.; Peters, J. C. A Ru(I) Metalloradical That Catalyzes Nitrene Coupling to Azoarenes from Arylazides. *J. Am. Chem. Soc.* **2012**, *134* (15), 6695–6706. <https://doi.org/10.1021/ja211603f>.

- (289) Fajardo, J.; Peters, J. C. Catalytic Nitrogen-to-Ammonia Conversion by Osmium and Ruthenium Complexes. *J. Am. Chem. Soc.* **2017**, *139* (45), 16105–16108.

<https://doi.org/10.1021/jacs.7b10204>.

- (290) Rittle, J.; Peters, J. C. Fe- N₂/CO Complexes That Model a Possible Role for the Interstitial C Atom of FeMo-Cofactor (FeMoco). *Proc. Natl. Acad. Sci. U. S. A.*

2013, *110* (40), 15898–15903. <https://doi.org/10.1073/pnas.1310153110>.

- (291) Creutz, S. E.; Peters, J. C. Catalytic Reduction of N₂ to NH₃ by an Fe-N₂

- Complex Featuring a C-Atom Anchor. *J. Am. Chem. Soc.* **2014**, *136* (3), 1105–1115. <https://doi.org/10.1021/ja4114962>.
- (292) Moret, M. E.; Peters, J. C. Terminal Iron Dinitrogen and Iron Imide Complexes Supported by a Tris(Phosphino)Borane Ligand. *Angew. Chem. Int. Ed.* **2011**, *50* (9), 2063–2067. <https://doi.org/10.1002/anie.201006918>.
- (293) Moret, M. E.; Peters, J. C. N₂ Functionalization at Iron Metallaboratranes. *J. Am. Chem. Soc.* **2011**, *133* (45), 18118–18121. <https://doi.org/10.1021/ja208675p>.
- (294) Anderson, J. S.; Rittle, J.; Peters, J. C. Catalytic Conversion of Nitrogen to Ammonia by an Iron Model Complex. *Nature* **2013**, *501* (7465), 84–87. <https://doi.org/10.1038/nature12435>.
- (295) Anderson, J. S.; Moret, M.-E.; Peters, J. C. Conversion of Fe–NH₂ to Fe–N₂ with Release of NH₃. *J. Am. Chem. Soc.* **2013**, *135* (2), 534–537. <https://doi.org/10.1021/ja307714m>.
- (296) Anderson, J. S.; Cutsail, G. E.; Rittle, J.; Connor, B. A.; Gunderson, W. A.; Zhang, L.; Hoffman, B. M.; Peters, J. C. Characterization of an Fe≡N–NH₂ Intermediate Relevant to Catalytic N₂ Reduction to NH₃. *J. Am. Chem. Soc.* **2015**, *137* (24), 7803–7809. <https://doi.org/10.1021/jacs.5b03432>.
- (297) Del Castillo, T. J.; Thompson, N. B.; Peters, J. C. A Synthetic Single-Site Fe Nitrogenase: High Turnover, Freeze-Quench ⁵⁷Fe Mössbauer Data, and a Hydride Resting State. *J. Am. Chem. Soc.* **2016**, *138* (16), 5341–5350. <https://doi.org/10.1021/jacs.6b01706>.
- (298) Matson, B. D.; Peters, J. C. Fe-Mediated HER vs N₂RR: Exploring Factors That Contribute to Selectivity in P₃EF_e(N₂) (E = B, Si, C) Catalyst Model Systems.

- ACS Catal.* **2018**, 8 (2), 1448–1455. <https://doi.org/10.1021/acscatal.7b03068>.
- (299) Chalkley, M. J.; Del Castillo, T. J.; Matson, B. D.; Roddy, J. P.; Peters, J. C. Catalytic N₂-to-NH₃ Conversion by Fe at Lower Driving Force: A Proposed Role for Metallocene-Mediated PCET. *ACS Cent. Sci.* **2017**, 3 (3), 217–223. <https://doi.org/10.1021/acscentsci.7b00014>.
- (300) Chalkley, M. J.; Del Castillo, T. J.; Matson, B. D.; Peters, J. C. Fe-Mediated Nitrogen Fixation with a Metallocene Mediator: Exploring p K_a Effects and Demonstrating Electrocatalysis. *J. Am. Chem. Soc.* **2018**, 140 (19), 6122–6129. <https://doi.org/10.1021/jacs.8b02335>.
- (301) Rudd, P. A.; Liu, S.; Gagliardi, L.; Young, V. G.; Lu, C. C. Metal–Alane Adducts with Zero-Valent Nickel, Cobalt, and Iron. *J. Am. Chem. Soc.* **2011**, 133 (51), 20724–20727. <https://doi.org/10.1021/ja2099744>.
- (302) Rudd, P. A.; Planas, N.; Bill, E.; Gagliardi, L.; Lu, C. C. Dinitrogen Activation at Iron and Cobalt Metallalumatrane. *Eur. J. Inorg. Chem.* **2013**, 2013 (22–23), 3898–3906. <https://doi.org/10.1002/ejic.201300272>.
- (303) Rittle, J.; McCrory, C. C. L.; Peters, J. C. A 106-Fold Enhancement in N₂-Binding Affinity of an Fe₂(μ-H)₂core upon Reduction to a Mixed-Valence Fe^{II}Fe^Istate. *J. Am. Chem. Soc.* **2014**, 136 (39), 13853–13862. <https://doi.org/10.1021/ja507217v>.
- (304) Creutz, S. E.; Peters, J. C. Diiron Bridged-Thiolate Complexes That Bind N₂ at the Fe^{II}Fe^{II}, Fe^{II}Fe^I, and Fe^IFe^I Redox States. *J. Am. Chem. Soc.* **2015**, 137 (23), 7310–7313. <https://doi.org/10.1021/jacs.5b04738>.
- (305) Takaoka, A.; Mankad, N. P.; Peters, J. C. Dinitrogen Complexes of Sulfur-Ligated Iron. *J. Am. Chem. Soc.* **2011**, 133 (22), 8440–8443.

<https://doi.org/10.1021/ja2020907>.

- (306) Gu, N. X.; Oyala, P. H.; Peters, J. C. An $S = 1/2$ Iron Complex Featuring N₂, Thiolate, and Hydride Ligands: Reductive Elimination of H₂ and Relevant Thermochemical Fe-H Parameters. *J. Am. Chem. Soc.* **2018**, *140* (20), 6374–6382. <https://doi.org/10.1021/jacs.8b02603>.
- (307) Yuki, M.; Tanaka, H.; Sasaki, K.; Miyake, Y.; Yoshizawa, K.; Nishibayashi, Y. Iron-Catalysed Transformation of Molecular Dinitrogen into Silylamine under Ambient Conditions. *Nat. Commun.* **2012**, *3*, 1254–1256. <https://doi.org/10.1038/ncomms2264>.
- (308) Imayoshi, R.; Nakajima, K.; Takaya, J.; Iwasawa, N.; Nishibayashi, Y. Synthesis and Reactivity of Iron- and Cobalt-Dinitrogen Complexes Bearing PSiP-Type Pincer Ligands toward Nitrogen Fixation. *Eur. J. Inorg. Chem.* **2017**, *2017* (32), 3769–3778. <https://doi.org/10.1002/ejic.201700569>.
- (309) Kuriyama, S.; Arashiba, K.; Nakajima, K.; Matsuo, Y.; Tanaka, H.; Ishii, K.; Yoshizawa, K.; Nishibayashi, Y. Catalytic Transformation of Dinitrogen into Ammonia and Hydrazine by Iron-Dinitrogen Complexes Bearing Pincer Ligand. *Nat. Commun.* **2016**, *7*, 1–9. <https://doi.org/10.1038/ncomms12181>.
- (310) Sekiguchi, Y.; Kuriyama, S.; Eizawa, A.; Arashiba, K.; Nakajima, K.; Nishibayashi, Y. Bearing Anionic Methyl- and Phenyl-Substituted Catalytic Nitrogen Fixation †. *Chem. Commun.* **2017**, *53*, 12040–12043. <https://doi.org/10.1039/C7CC06987A>.
- (311) Higuchi, J.; Kuriyama, S.; Eizawa, A.; Arashiba, K.; Nakajima, K.; Nishibayashi, Y. Preparation and Reactivity of Iron Complexes Bearing Anionic Carbazole-

- Based PNP-Type Pincer Ligands toward Catalytic Nitrogen Fixation. *Dalt. Trans.* **2018**, 47 (Chart 1), 1117–1121. <https://doi.org/10.1039/c7dt04327a>.
- (312) Lee, J. H.; Pink, M.; Tomaszewski, J.; Fan, H.; Caulton, K. G. Facile Hydrogenation of N₂O by an Operationally Unsaturated Osmium Polyhydride. *J. Am. Chem. Soc.* **2007**, 129 (28), 8706–8707. <https://doi.org/10.1021/ja071452f>.
- (313) Suzuki, T.; Wasada-Tsutsui, Y.; Ogawa, T.; Inomata, T.; Ozawa, T.; Sakai, Y.; Fryzuk, M. D.; Masuda, H. N₂ Activation by an Iron Complex with a Strong Electron-Donating Iminophosphorane Ligand. *Inorg. Chem.* **2015**, 54 (19), 9271–9281. <https://doi.org/10.1021/acs.inorgchem.5b00536>.
- (314) MacBeth, C. E.; Harkins, S. B.; Peters, J. C. Synthesis and Characterization of Cationic Iron Complexes Supported by the Neutral Ligands NPi-Pr₃, NArPi-Pr₃, and NSt-Bu₃. *Can. J. Chem.* **2005**, 83 (4), 332–340. <https://doi.org/10.1139/v05-017>.
- (315) Field, L. D.; Guest, R. W.; Vuong, K. Q.; Dalgarno, S. J.; Jensen, P. Iron(0) and Ruthenium(0) Complexes of Dinitrogen. *Inorg. Chem.* **2009**, 48 (5), 2246–2253. <https://doi.org/10.1021/ic8019827>.
- (316) Gilbert-Wilson, R.; Field, L. D.; Colbran, S. B.; Bhadbhade, M. M. Low Oxidation State Iron(0), Iron(I), and Ruthenium(0) Dinitrogen Complexes with a Very Bulky Neutral Phosphine Ligand. *Inorg. Chem.* **2013**, 52 (6), 3043–3053. <https://doi.org/10.1021/ic3024953>.
- (317) Field, L. D.; Li, H. L.; Dalgarno, S. J.; McIntosh, R. D. Base-Induced Dehydrogenation of Ruthenium Hydrazine Complexes. *Inorg. Chem.* **2013**, 52 (3), 1570–1583. <https://doi.org/10.1021/ic302449n>.

- (318) Gilbert-Wilson, R.; Field, L. D.; Bhadbhade, M. Ruthenium Hydrides Containing the Superhindered Polydentate Polyphosphine Ligand P(CH₂CH₂PtBu₂)₃. *Inorg. Chem.* **2014**, *53* (23), 12469–12479. <https://doi.org/10.1021/ic501895s>.
- (319) van de Watering, F. F.; van der Vlugt, J. I.; Dzik, W. I.; de Bruin, B.; Reek, J. N. H. Metalloradical Reactivity of Ru^I and Ru⁰ Stabilized by an Indole-Based Tripodal Tetrakisphosphine Ligand. *Chem. - A Eur. J.* **2017**, *23* (52), 12709–12713. <https://doi.org/10.1002/chem.201702727>.
- (320) Prokopchuk, D. E.; Wiedner, E. S.; Walter, E. D.; Popescu, C. V.; Piro, N. A.; Kassel, W. S.; Bullock, R. M.; Mock, M. T. Catalytic N₂ Reduction to Silylamines and Thermodynamics of N₂ Binding at Square Planar Fe. *J. Am. Chem. Soc.* **2017**, *139* (27), 9291–9301. <https://doi.org/10.1021/jacs.7b04552>.
- (321) Araake, R.; Sakadani, K.; Tada, M.; Sakai, Y.; Ohki, Y. [Fe₄] and [Fe₆] Hydride Clusters Supported by Phosphines: Synthesis, Characterization, and Application in N₂ Reduction. *J. Am. Chem. Soc.* **2017**, *139* (15), 5596–5606. <https://doi.org/10.1021/jacs.7b01965>.
- (322) Lau, S.; Ward, B.; Zhou, X.; White, A. J. P.; Casely, I. J.; MacGregor, S. A.; Crimmin, M. R. Mild Sp²Carbon-Oxygen Bond Activation by an Isolable Ruthenium(II) Bis(Dinitrogen) Complex: Experiment and Theory. *Organometallics* **2017**, *36* (18), 3654–3663. <https://doi.org/10.1021/acs.organomet.7b00632>.
- (323) Bart, S. C.; Lobkovsky, E.; Chirik, P. J. Preparation and Molecular and Electronic Structures of Iron(0) Dinitrogen and Silane Complexes and Their Application to Catalytic Hydrogenation and Hydrosilation. *J. Am. Chem. Soc.* **2004**, *126* (42),

13794–13807. <https://doi.org/10.1021/ja046753t>.

- (324) Bart, S. C.; Chłopek, K.; Bill, E.; Bouwkamp, M. W.; Lobkovsky, E.; Neese, F.; Wieghardt, K.; Chirik, P. J. Electronic Structure of Bis(Imino)Pyridine Iron Dichloride, Monochloride, and Neutral Ligand Complexes: A Combined Structural, Spectroscopic, and Computational Study. *J. Am. Chem. Soc.* **2006**, *128* (42), 13901–13912. <https://doi.org/10.1021/ja064557b>.
- (325) Bart, S. C.; Lobkovsky, E.; Bill, E.; Chirik, P. J. Synthesis and Hydrogenation of Bis(Imino)Pyridine Iron Imides. *J. Am. Chem. Soc.* **2006**, *128* (16), 5302–5303. <https://doi.org/10.1021/ja057165y>.
- (326) Bart, S. C.; Bowman, A. C.; Lobkovsky, E.; Chirik, P. J. Iron Diazoalkane Chemistry: N-N Bond Hydrogenation and Intramolecular C-H Activation. *J. Am. Chem. Soc.* **2007**, *129* (23), 7212–7213. <https://doi.org/10.1021/ja070056u>.
- (327) Bart, S. C.; Lobkovsky, E.; Bill, E.; Wieghardt, K.; Chirik, P. J. Neutral-Ligand Complexes of Bis(Imino)Pyridine Iron: Synthesis, Structure, and Spectroscopy. *Inorg. Chem.* **2007**, *46* (17), 7055–7063. <https://doi.org/10.1021/ic700869h>.
- (328) Trovitch, R. J.; Lobkovsky, E.; Bill, E.; Chirik, P. J. Functional Group Tolerance and Substrate Scope in Bis(Imino)Pyridine Iron Catalyzed Alkene Hydrogenation. *Organometallics* **2008**, *27* (7), 1470–1478. <https://doi.org/10.1021/om701091z>.
- (329) Sylvester, K. T.; Chirik, P. J. Iron-Catalyzed, Hydrogen-Mediated Reductive Cyclization of 1,6-Enynes and Diynes: Evidence for Bis(Imino)Pyridine Ligand Participation. *J. Am. Chem. Soc.* **2009**, *131* (25), 8772–8774. <https://doi.org/10.1021/ja902478p>.
- (330) Bowman, A. C.; Bart, S. C.; Heinemann, F. W.; Meyer, K.; Chirik, P. J. Synthesis

of Bis(Imino)Pyridine Iron Amide and Ammonia Compounds from an N-H
Transfer Agent. *Inorg. Chem.* **2009**, *48* (13), 5587–5589.

<https://doi.org/10.1021/ic9003017>.

- (331) Russell, S. K.; Lobkovsky, E.; Chirik, P. J. Iron-Catalyzed Intermolecular $[2\pi + 2\pi]$ Cycloaddition. *J. Am. Chem. Soc.* **2011**, *133* (23), 8858–8861.

<https://doi.org/10.1021/ja202992p>.

- (332) Stieber, S. C. E.; Milsmann, C.; Hoyt, J. M.; Turner, Z. R.; Finkelstein, K. D.; Wieghardt, K.; Debeer, S.; Chirik, P. J. Bis(Imino)Pyridine Iron Dinitrogen Compounds Revisited: Differences in Electronic Structure between Four- and Five-Coordinate Derivatives. *Inorg. Chem.* **2012**, *51* (6), 3770–3785.

<https://doi.org/10.1021/ic202750n>.

- (333) Yu, R. P.; Darmon, J. M.; Hoyt, J. M.; Margulieux, G. W.; Turner, Z. R.; Chirik, P. J. High-Activity Iron Catalysts for the Hydrogenation of Hindered, Unfunctionalized Alkenes. *ACS Catal.* **2012**, *2* (8), 1760–1764.

<https://doi.org/10.1021/cs300358m>.

- (334) Darmon, J. M.; Stieber, S. C. E.; Sylvester, K. T.; Fernández, I.; Lobkovsky, E.; Semproni, S. P.; Bill, E.; Wieghardt, K.; Debeer, S.; Chirik, P. J. Oxidative Addition of Carbon-Carbon Bonds with a Redox-Active Bis(Imino)Pyridine Iron Complex. *J. Am. Chem. Soc.* **2012**, *134* (41), 17125–17137.

<https://doi.org/10.1021/ja306526d>.

- (335) Atienza, C. C. H.; Tondreau, A. M.; Weller, K. J.; Lewis, K. M.; Cruse, R. W.; Nye, S. A.; Boyer, J. L.; Delis, J. G. P.; Chirik, P. J. High-Selectivity Bis(Imino)Pyridine Iron Catalysts for the Hydrosilylation of 1,2,4-

- Trivinylcyclohexane. *ACS Catal.* **2012**, 2 (10), 2169–2172.
<https://doi.org/10.1021/cs300584b>.
- (336) Tondreau, A. M.; Atienza, C. C. H.; Weller, K. J.; Nye, S. A.; Lewis, K. M.; Delis, J. G. P.; Chirik, P. J. Iron Catalysts for Selective Anti-Markovnikov Alkene Hydrosilylation Using Tertiary Silanes. *Science* (80-.). **2012**, 335 (6068), 567–570. <https://doi.org/10.1126/science.1214451>.
- (337) Hoyt, J. M.; Sylvester, K. T.; Semproni, S. P.; Chirik, P. J. Synthesis and Electronic Structure of Bis(Imino)Pyridine Iron Metallacyclic Intermediates in Iron-Catalyzed Cyclization Reactions. *J. Am. Chem. Soc.* **2013**, 135 (12), 4862–4877. <https://doi.org/10.1021/ja400895j>.
- (338) Obligacion, J. V.; Chirik, P. J. Highly Selective Bis(Imino)Pyridine Iron-Catalyzed Alkene Hydroboration. *Org. Lett.* **2013**, 15 (11), 2680–2683.
<https://doi.org/10.1021/ol400990u>.
- (339) Hoyt, J. M.; Schmidt, V. A.; Tondreau, A. M.; Chirik, P. J. Iron-Catalyzed Intermolecular [2+2] Cycloadditions of Unactivated Alkenes. *Science* (80-.). **2015**, 349 (6251), 960–963. <https://doi.org/10.1126/science.aac7440>.
- (340) Pony Yu, R.; Hesk, D.; Rivera, N.; Pelczar, I.; Chirik, P. J. Iron-Catalysed Tritiation of Pharmaceuticals. *Nature* **2016**, 529 (7585), 195–199.
<https://doi.org/10.1038/nature16464>.
- (341) Scott, J.; Vidyaratne, I.; Korobkov, I.; Gambarotta, S.; Budzelaar, P. H. M. Multiple Pathways for Dinitrogen Activation during the Reduction of an Fe Bis(Iminepyridine) Complex. *Inorg. Chem.* **2008**, 47 (3), 896–911.
<https://doi.org/10.1021/ic701643d>.

- (342) Danopoulos, A. A.; Wright, J. A.; Motherwell, W. B. Molecular N₂ Complexes of Iron Stabilised by N-Heterocyclic “pincer” Dicarbene Ligands. *Chem. Commun.* **2005**, No. 6, 784–786. <https://doi.org/10.1039/b415562a>.
- (343) Darmon, J. M.; Yu, R. P.; Semproni, S. P.; Turner, Z. R.; Stieber, S. C. E.; Debeer, S.; Chirik, P. J. Electronic Structure Determination of Pyridine N-Heterocyclic Carbene Iron Dinitrogen Complexes and Neutral Ligand Derivatives. *Organometallics* **2014**, 33 (19), 5423–5433. <https://doi.org/10.1021/om500727t>.
- (344) Yu, R. P.; Darmon, J. M.; Semproni, S. P.; Turner, Z. R.; Chirik, P. J. Synthesis of Iron Hydride Complexes Relevant to Hydrogen Isotope Exchange in Pharmaceuticals. *Organometallics* **2017**, 36 (22), 4341–4343. <https://doi.org/10.1021/acs.organomet.7b00398>.
- (345) Huynh, M. H. V.; El-Samanody, E. S.; Demadis, K. D.; Meyer, T. J.; White, P. S. Oxo-like Reactivity of High Oxidation State Osmium Hydrazido Complexes [13]. *J. Am. Chem. Soc.* **1999**, 121 (6), 1403–1404. <https://doi.org/10.1021/ja983290g>.
- (346) Huynh, M. H. V.; Meyer, T. J.; Hiskey, M. A.; Jameson, D. L. Os(II)-Nitrosyl and Os(II)-Dinitrogen Complexes from Reactions between Os(VI)-Nitrido and Hydroxylamines and Methoxylamines. *J. Am. Chem. Soc.* **2004**, 126 (11), 3608–3615. <https://doi.org/10.1021/ja030574e>.
- (347) Kunkely, H.; Vogler, A. Photolysis of Aqueous [(NH₃)₅Os(η²-N₂)Os(NH₃)₅]⁵⁺: Cleavage of Dinitrogen by an Intramolecular Photoredox Reaction. *Angew. Chem. Int. Ed.* **2010**, 49 (9), 1591–1593. <https://doi.org/10.1002/anie.200905026>.
- (348) Namura, K.; Suzuki, H. Synthesis, Structure, and Reactivity of Mixed-Ligand Dinuclear Ruthenium Polyhydrido Complexes Supported by 1,4,7-Trimethyl-

- 1,4,7-Triazacyclononane and Bulky Phosphine Ligands. *Organometallics* **2014**, *33* (12), 2968–2983. <https://doi.org/10.1021/om500018j>.
- (349) Smith, J. M.; Lachicotte, R. J.; Pittard, K. A.; Cundari, T. R.; Lukat-Rodgers, G.; Rodgers, K. R.; Holland, P. L. Stepwise Reduction of Dinitrogen Bond Order by a Low-Coordinate Iron Complex [5]. *J. Am. Chem. Soc.* **2001**, *123* (37), 9222–9223. <https://doi.org/10.1021/ja016094+>.
- (350) Eckert, N. A.; Vaddadi, S.; Stoian, S.; Lachicotte, R. J.; Cundari, T. R.; Holland, P. L. Coordination-Number Dependence of Reactivity in an Imidoiron(III) Complex. *Angew. Chem. Int. Ed.* **2006**, *45* (41), 6868–6871. <https://doi.org/10.1002/anie.200601927>.
- (351) Sadique, A. R.; Brennessel, W. W.; Holland, P. L. Reduction of CO₂ to CO Using Low-Coordinate Iron: Formation of a Four-Coordinate Iron Dicarbonyl Complex and a Bridging Carbonate Complex. *Inorg. Chem.* **2008**, *47* (3), 784–786. <https://doi.org/10.1021/ic701914m>.
- (352) Smith, J. M.; Sadique, A. R.; Cundari, T. R.; Rodgers, K. R.; Lukat-Rodgers, G.; Lachicotte, R. J.; Flaschenriem, C. J.; Vela, J.; Holland, P. L. Studies of Low-Coordinate Iron Dinitrogen Complexes. *J. Am. Chem. Soc.* **2006**, *128* (3), 756–769. <https://doi.org/10.1021/ja052707x>.
- (353) Figg, T. M.; Holland, P. L.; Cundari, T. R. Cooperativity between Low-Valent Iron and Potassium Promoters in Dinitrogen Fixation. *Inorg. Chem.* **2012**, *51* (14), 7546–7550. <https://doi.org/10.1021/ic300150u>.
- (354) Grubel, K.; Brennessel, W. W.; Mercado, B. Q.; Holland, P. L. Alkali Metal Control over N–N Cleavage in Iron Complexes. *J. Am. Chem. Soc.* **2014**, *136* (48),

16807–16816. <https://doi.org/10.1021/ja507442b>.

- (355) McWilliams, S. F.; Rodgers, K. R.; Lukat-Rodgers, G.; Mercado, B. Q.; Grubel, K.; Holland, P. L. Alkali Metal Variation and Twisting of the FeNNFe Core in Bridging Diiron Dinitrogen Complexes. *Inorg. Chem.* **2016**, 55 (6), 2960–2968. <https://doi.org/10.1021/acs.inorgchem.5b02841>.
- (356) Dugan, T. R.; Macleod, K. C.; Brennessel, W. W.; Holland, P. L. Cobalt-Magnesium and Iron-Magnesium Complexes with Weakened Dinitrogen Bridges. *Eur. J. Inorg. Chem.* **2013**, No. 22–23, 3891–3897. <https://doi.org/10.1002/ejic.201300187>.
- (357) MacLeod, K. C.; Menges, F. S.; McWilliams, S. F.; Craig, S. M.; Mercado, B. Q.; Johnson, M. A.; Holland, P. L. Alkali-Controlled C-H Cleavage or N-C Bond Formation by N₂-Derived Iron Nitrides and Imides. *J. Am. Chem. Soc.* **2016**, 138 (35), 11185–11191. <https://doi.org/10.1021/jacs.6b04984>.
- (358) Rodriguez, M. M.; Bill, E.; Brennessel, W. W.; Holland, P. L. N₂ Reduction and Hydrogenation to Ammonia by a Molecular Iron-Potassium Complex. *Science* (80-.). **2011**, 334 (6057), 780–783. <https://doi.org/10.1126/science.1211906>.
- (359) MacLeod, K. C.; McWilliams, S. F.; Mercado, B. Q.; Holland, P. L. Stepwise N-H Bond Formation from N₂-Derived Iron Nitride, Imide and Amide Intermediates to Ammonia. *Chem. Sci.* **2016**, 7 (9), 5736–5746. <https://doi.org/10.1039/c6sc00423g>.
- (360) MacLeod, K. C.; Vinyard, D. J.; Holland, P. L. A Multi-Iron System Capable of Rapid N₂ Formation and N₂ Cleavage. *J. Am. Chem. Soc.* **2014**, 136 (29), 10226–10229. <https://doi.org/10.1021/ja505193z>.

- (361) Lee, Y.; Sloane, F. T.; Blondin, G.; Abboud, K. A.; García-Serres, R.; Murray, L. J. Dinitrogen Activation upon Reduction of a Triiron(II) Complex. *Angew. Chem. Int. Ed.* **2015**, *54* (5), 1499–1503. <https://doi.org/10.1002/anie.201409676>.
- (362) Ferreira, R. B.; Cook, B. J.; Knight, B. J.; Catalano, V. J.; García-Serres, R.; Murray, L. J. Catalytic Silylation of Dinitrogen by a Family of Triiron Complexes. *ACS Catal.* **2018**, *8* (8), 7208–7212. <https://doi.org/10.1021/acscatal.8b02021>.
- (363) Mcskimming, A.; Harman, W. H. A Terminal N₂ Complex of High-Spin Iron(I) in a Weak, Trigonal Ligand Field. *J. Am. Chem. Soc.* **2015**, *137* (28), 8940–8943. <https://doi.org/10.1021/jacs.5b06337>.
- (364) Cummins, D. C.; Yap, G. P. A.; Theopold, K. H. Scorpionates of the “Tetrahedral Enforcer” Variety as Ancillary Ligands for Dinitrogen Complexes of First Row Transition Metals (Cr–Co). *Eur. J. Inorg. Chem.* **2016**, *2016* (15–16), 2349–2356. <https://doi.org/10.1002/ejic.201501326>.
- (365) Stepowska, E.; Jiang, H.; Song, D. Reversible H₂ Splitting between Ru(II) and a Remote Carbanion in a Zwitterionic Compound. *Chem. Commun.* **2010**, *46* (4), 556–558. <https://doi.org/10.1039/b919606d>.
- (366) Annibale, V. T.; Song, D. Reversible Formal Insertion of CO₂ into a Remote C–H Bond of a Ligand in a Ru(II) Complex at Room Temperature. *Chem. Commun.* **2012**, *48* (44), 5416–5418. <https://doi.org/10.1039/c2cc17933d>.
- (367) Kizaki, T.; Matsumoto, T.; Ogo, S. Dissolved N₂ Sensing by PH-Dependent Ru Complexes. *Dalt. Trans.* **2010**, *39* (5), 1339–1344. <https://doi.org/10.1039/b918940h>.
- (368) Sellmann, D.; Sutter, J. In Quest of Competitive Catalysts for Nitrogenases and

Other Metal Sulfur Enzymes. *Acc. Chem. Res.* **1997**, *30* (11), 460–469.

<https://doi.org/10.1021/ar960158h>.

- (369) Sellmann, D.; Hautsch, B.; Rösler, A.; Heinemann, F. W. [Ru(N₂)(PiPr₃)(N₂Me₂S
2')]: Coordination of Molecular N₂ to Metal Thiolate Cores under Mild

Conditions. *Angew. Chem. Int. Ed.* **2001**, *40* (8), 1505–1507.

[https://doi.org/10.1002/1521-3773\(20010417\)40:8<1505::AID-](https://doi.org/10.1002/1521-3773(20010417)40:8<1505::AID-)

[ANIE1505>3.0.CO;2-2](https://doi.org/10.1002/1521-3773(20010417)40:8<1505::AID-).

- (370) Sellmann, D.; Hille, A.; Rösler, A.; Heinemann, F. W.; Moll, M.; Brehm, G.;
Schneider, S.; Reiher, M.; Hess, B. A.; Bauer, W. Binding N₂, N₂H₂, N₂H₄, and
NH₃ to Transition-Metal Sulfur Sites: Modeling Potential Intermediates of
Biological N₂ Fixation. *Chem. - A Eur. J.* **2004**, *10* (4), 819–830.

<https://doi.org/10.1002/chem.200305499>.

- (371) Čorić, I.; Mercado, B. Q.; Bill, E.; Vinyard, D. J.; Holland, P. L. Binding of
Dinitrogen to an Iron-Sulfur-Carbon Site. *Nature* **2015**, *526* (7571), 96–99.

<https://doi.org/10.1038/nature15246>.

- (372) Zhang, F.; Song, H.; Zhuang, X.; Tung, C. H.; Wang, W. Iron-Catalyzed 1,2-
Selective Hydroboration of N-Heteroarenes. *J. Am. Chem. Soc.* **2017**, *139* (49),

17775–17778. <https://doi.org/10.1021/jacs.7b11416>.

- (373) Sunada, Y.; Imaoka, T.; Nagashima, H. Half-Sandwich (H₆-Arene)Iron(II)
Dinitrogen Complexes Bearing a Disilaferracycle Skeleton as a Precursor for
Double Silylation of Ethylene and Alkynes. *Organometallics* **2010**, *29* (23), 6157–

6160. <https://doi.org/10.1021/om100889w>.

- (374) Burling, S.; Häller, L. J. L.; Mas-Marzá, E.; Moreno, A.; Macgregor, S. A.;

- Mahon, M. F.; Pregosin, P. S.; Whittlesey, M. K. The Influence of N-Heterocyclic Carbenes (NHC) on the Reactivity of [Ru(NHC)₄H]⁺ with H₂, N₂, CO and O₂. *Chem. - A Eur. J.* **2009**, *15* (41), 10912–10923.
<https://doi.org/10.1002/chem.200901736>.
- (375) Tskhovrebov, A. G.; Solari, E.; Scopelliti, R.; Severin, K. Activation of Nitrous Oxide by Dinuclear Ruthenium Complexes. *Organometallics* **2012**, *31* (20), 7235–7240. <https://doi.org/10.1021/om300786f>.
- (376) Liang, Q.; Song, D. Reactivity of Fe and Ru Complexes of Picolyl-Substituted N-Heterocyclic Carbene Ligand: Diverse Coordination Modes and Small Molecule Binding. *Inorg. Chem.* **2017**, *56* (19), 11956–11970.
<https://doi.org/10.1021/acs.inorgchem.7b01918>.
- (377) Fernández, F. E.; Puerta, M. C.; Valerga, P. Picolyl-NHC Hydrotris(Pyrazolyl)Borate Ruthenium(II) Complexes: Synthesis, Characterization, and Reactivity with Small Molecules. *Inorg. Chem.* **2013**, *52* (8), 4396–4410. <https://doi.org/10.1021/ic302553z>.
- (378) Ung, G.; Peters, J. C. Low-Temperature N₂ Binding to Two-Coordinate L₂Fe⁰ Enables Reductive Trapping of L₂FeN₂⁻ and NH₃ Generation. *Angew. Chem. Int. Ed.* **2015**, *54* (2), 532–535. <https://doi.org/10.1002/anie.201409454>.
- (379) Ouyang, Z.; Cheng, J.; Li, L.; Bao, X.; Deng, L. High-Spin Iron(I) and Iron(0) Dinitrogen Complexes Supported by N-Heterocyclic Carbene Ligands. *Chem. - A Eur. J.* **2016**, *22* (40), 14162–14165. <https://doi.org/10.1002/chem.201603390>.
- (380) Yamamoto, A.; Miura, Y.; Ito, T.; Chen, H. L.; Iri, K.; Ozawa, F.; Miki, K.; Kasai, N.; Sei, T.; Tanaka, N. Preparation, X-Ray Molecular Structure Determination,

- and Chemical Properties of Dinitrogen-Coordinated Cobalt Complexes Containing Triphenylphosphine Ligands and Alkali Metal or Magnesium. Protonation of the Coordinated Dinitrogen to Ammonia and Hydrazine. *Organometallics* **1983**, 2 (10), 1429–1436. <https://doi.org/10.1021/om50004a032>.
- (381) Cecconi, F. Synthesis, Characterization, and Crystal Structure of the Dimeric, Paramagnetic Cobalt(0) Complex $\{ [M \sim C(CH_3)_3PPPh_3]_2 \}$. **1985**, No. 1, 731–733.
- (382) Suess, D. L. M.; Tsay, C.; Peters, J. C. Dihydrogen Binding to Isostructural $S = 1/2$ and $S = 0$ Cobalt Complexes. *J. Am. Chem. Soc.* **2012**, 134 (34), 14158–14164. <https://doi.org/10.1021/ja305248f>.
- (383) Del Castillo, T. J.; Thompson, N. B.; Suess, D. L. M.; Ung, G.; Peters, J. C. Evaluating Molecular Cobalt Complexes for the Conversion of N₂ to NH₃. *Inorg. Chem.* **2015**, 54 (19), 9256–9262. <https://doi.org/10.1021/acs.inorgchem.5b00645>.
- (384) Siedschlag, R. B.; Bernales, V.; Vogiatzis, K. D.; Planas, N.; Clouston, L. J.; Bill, E.; Gagliardi, L.; Lu, C. C. Catalytic Silylation of Dinitrogen with a Dicobalt Complex. *J. Am. Chem. Soc.* **2015**, 137 (14), 4638–4641. <https://doi.org/10.1021/jacs.5b01445>.
- (385) Clouston, L. J.; Bernales, V.; Carlson, R. K.; Gagliardi, L.; Lu, C. C. Bimetallic Cobalt-Dinitrogen Complexes: Impact of the Supporting Metal on N₂ Activation. *Inorg. Chem.* **2015**, 54 (19), 9263–9270. <https://doi.org/10.1021/acs.inorgchem.5b00983>.
- (386) Nesbit, M. A.; Suess, D. L. M.; Peters, J. C. E-H Bond Activations and Hydrosilylation Catalysis with Iron and Cobalt Metalloboranes. *Organometallics*

- 2015**, 34 (19), 4741–4752. <https://doi.org/10.1021/acs.organomet.5b00530>.
- (387) Greenwood, B. P.; Forman, S. I.; Rowe, G. T.; Chen, C. H.; Foxman, B. M.; Thomas, C. M. Multielectron Redox Activity Facilitated by Metal - Metal Interactions in Early/Late Heterobimetallics: Co/Zr Complexes Supported by Phosphinoamide Ligands. *Inorg. Chem.* **2009**, 48 (13), 6251–6260. <https://doi.org/10.1021/ic900552b>.
- (388) Setty, V. N.; Zhou, W.; Foxman, B. M.; Thomas, C. M. Subtle Differences between Zr and Hf in Early/Late Heterobimetallic Complexes with Cobalt. *Inorg. Chem.* **2011**, 50 (10), 4647–4655. <https://doi.org/10.1021/ic200445x>.
- (389) Krogman, J. P.; Gallagher, J. R.; Zhang, G.; Hock, A. S.; Miller, J. T.; Thomas, C. M. Assignment of the Oxidation States of Zr and Co in a Highly Reactive Heterobimetallic Zr/Co Complex Using X-Ray Absorption Spectroscopy (XANES). *Dalt. Trans.* **2014**, 43 (37), 13852–13857. <https://doi.org/10.1039/c4dt01534g>.
- (390) Zhou, W.; Saper, N. I.; Krogman, J. P.; Foxman, B. M.; Thomas, C. M. Effect of Ligand Modification on the Reactivity of Phosphinoamide-Bridged Heterobimetallic Zr/Co Complexes. *Dalt. Trans.* **2014**, 43 (5), 1984–1989. <https://doi.org/10.1039/c3dt52133h>.
- (391) Zhou, W.; Marquard, S. L.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. Catalytic Hydrosilylation of Ketones Using a Co/Zr Heterobimetallic Complex: Evidence for an Unusual Mechanism Involving Ketyl Radicals. *Organometallics* **2013**, 32 (6), 1766–1772. <https://doi.org/10.1021/om301194g>.
- (392) Wesley Napoline, J.; Krogman, J. P.; Shi, R.; Kuppuswamy, S.; Bezpalko, M. W.;

- Foxman, B. M.; Thomas, C. M. Activation of E-H and E-E (E = S, O) Bonds by Heterobimetallic Zr/Co Complexes: Evidence for Both One- and Two-Electron Processes. *Eur. J. Inorg. Chem.* **2013**, 2 (22–23), 3874–3882.
<https://doi.org/10.1002/ejic.201300122>.
- (393) Marquard, S. L.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. Stoichiometric C=O Bond Oxidative Addition of Benzophenone by a Discrete Radical Intermediate to Form a Cobalt(I) Carbene. *J. Am. Chem. Soc.* **2013**, 135 (16), 6018–6021. <https://doi.org/10.1021/ja4022683>.
- (394) Zhou, W.; Napoline, J. W.; Thomas, C. M. A Catalytic Application of Co/Zr Heterobimetallic Complexes: Kumada Coupling of Unactivated Alkyl Halides with Alkyl Grignard Reagents. *Eur. J. Inorg. Chem.* **2011**, No. 13, 2029–2033.
<https://doi.org/10.1002/ejic.201100109>.
- (395) Napoline, J. W.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. N-H Activation of Hydrazines by a Heterobimetallic Zr-Co Complex: Promotion of One-Electron Chemistry at Zr. *Chem. Commun.* **2013**, 49 (39), 4388–4390.
<https://doi.org/10.1039/c2cc35594a>.
- (396) Krogman, J. P.; Foxman, B. M.; Thomas, C. M. Formation and Subsequent Reactivity of a N₂-Stabilized Cobalt-Hydride Complex. *Organometallics* **2015**, 34 (13), 3159–3166. <https://doi.org/10.1021/acs.organomet.5b00182>.
- (397) Wu, B.; Gramigna, K. M.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. Heterobimetallic Ti/Co Complexes That Promote Catalytic N-N Bond Cleavage. *Inorg. Chem.* **2015**, 54 (22), 10909–10917.
<https://doi.org/10.1021/acs.inorgchem.5b01962>.

- (398) Evers, D. A.; Bluestein, A. H.; Foxman, B. M.; Thomas, C. M. Synthesis and Investigation of the Metal–Metal Interactions in Early/Late Heterobimetallic Complexes Linking Group 5 Imido Fragments to Co(I). *Dalt. Trans.* **2012**, 41 (26), 8111. <https://doi.org/10.1039/c2dt00034b>.
- (399) Obligacion, J. V.; Semproni, S. P.; Pappas, I.; Chirik, P. J. Cobalt-Catalyzed C(Sp²)-H Borylation: Mechanistic Insights Inspire Catalyst Design. *J. Am. Chem. Soc.* **2016**, 138 (33), 10645–10653. <https://doi.org/10.1021/jacs.6b06144>.
- (400) Ding, K.; Pierpont, A. W.; Brennessel, W. W.; Lukat-Rodgers, G.; Rodgers, K. R.; Cundari, T. R.; Bill, E.; Holland, P. L. Cobalt-Dinitrogen Complexes with Weakened N-N Bonds. *J. Am. Chem. Soc.* **2009**, 131 (27), 9471–9472. <https://doi.org/10.1021/ja808783u>.
- (401) Spitzer, F.; Graßl, C.; Balázs, G.; Mädl, E.; Keilwerth, M.; Zolnhofer, E. M.; Meyer, K.; Scheer, M. Nacnac-Cobalt-Mediated P₄Transformations. *Chem. - A Eur. J.* **2017**, 23 (11), 2716–2721. <https://doi.org/10.1002/chem.201605451>.
- (402) Hojilla Atienza, C. C.; Milsmann, C.; Semproni, S. P.; Turner, Z. R.; Chirik, P. J. Reversible Carbon-Carbon Bond Formation Induced by Oxidation and Reduction at a Redox-Active Cobalt Complex. *Inorg. Chem.* **2013**, 52 (9), 5403–5417. <https://doi.org/10.1021/ic400352r>.
- (403) Bowman, A. C.; Milsmann, C.; Atienza, C. C. H.; Lobkovsky, E.; Wieghardt, K.; Chirik, P. J. Synthesis and Molecular and Electronic Structures of Reduced Bis(Imino)Pyridine Cobalt Dinitrogen Complexes: Ligand versus Metal Reduction. *J. Am. Chem. Soc.* **2010**, 132 (5), 1676–1684. <https://doi.org/10.1021/ja908955t>.

- (404) Mo, Z.; Chen, D.; Leng, X.; Deng, L. Intramolecular C(Sp³)-H Bond Activation Reactions of Low-Valent Cobalt Complexes with Coordination Unsaturation. *Organometallics* **2012**, *31* (20), 7040–7043. <https://doi.org/10.1021/om300804a>.
- (405) Gao, Y.; Li, G.; Deng, L. Bis(Dinitrogen)Cobalt(-1) Complexes with NHC Ligation: Synthesis, Characterization, and Their Dinitrogen Functionalization Reactions Affording Side-on Bound Diazene Complexes. *J. Am. Chem. Soc.* **2018**, *140* (6), 2239–2250. <https://doi.org/10.1021/jacs.7b11660>.
- (406) Yu, R. P.; Darmon, J. M.; Milsman, C.; Margulieux, G. W.; Stieber, S. C. E.; Debeer, S.; Chirik, P. J. Catalytic Hydrogenation Activity and Electronic Structure Determination of Bis(Arylimidazol-2-Ylidene)Pyridine Cobalt Alkyl and Hydride Complexes. *J. Am. Chem. Soc.* **2013**, *135* (35), 13168–13184. <https://doi.org/10.1021/ja406608u>.
- (407) Simler, T.; Braunstein, P.; Danopoulos, A. A. Cobalt PNCNHC “Pincers”: Ligand Dearomatisation, Formation of Dinuclear and N₂ Complexes and Promotion of C-H Activation. *Chem. Commun.* **2016**, *52* (13), 2717–2720. <https://doi.org/10.1039/c5cc10121b>.
- (408) Carpenter, A. E.; Margulieux, G. W.; Millard, M. D.; Moore, C. E.; Weidemann, N.; Rheingold, A. L.; Figueroa, J. S. Zwitterionic Stabilization of a Reactive Cobalt Tris-Isocyanide Monoanion by Cation Coordination. *Angew. Chem. Int. Ed.* **2012**, *51* (37), 9412–9416. <https://doi.org/10.1002/anie.201205058>.
- (409) Mokhtarzadeh, C. C.; Rheingold, A. L.; Figueroa, J. S. Dinitrogen Binding, P₄-Activation and Aza-Büchner Ring Expansions Mediated by an Isocyano Analogue of the CpCo(CO) Fragment. *Dalt. Trans.* **2016**, *45* (37), 14561–14569.

<https://doi.org/10.1039/c6dt02789j>.

- (410) Fout, A. R.; Basuli, F.; Fan, H.; Tomaszewski, J.; Huffman, J. C.; Baik, M. H.;

Mindiola, D. J. A Co₂N₂ Diamond-Core Resting State of Cobalt(I): A Three-Coordinate CoI Synthon Invoking an Unusual Pincer-Type Rearrangement.

Angew. Chem. Int. Ed. **2006**, 45 (20), 3291–3295.

<https://doi.org/10.1002/anie.200504343>.

- (411) Ingleson, M.; Fan, H.; Pink, M.; Tomaszewski, J.; Caulton, K. G. Three-

Coordinate Co(I) Provides Access to Unsaturated Dihydrido-Co(III) and Seven-Coordinate Co(V). *J. Am. Chem. Soc.* **2006**, 128 (6), 1804–1805.

<https://doi.org/10.1021/ja0572452>.

- (412) Rozenel, S. S.; Padilla, R.; Arnold, J. Chemistry of Reduced Monomeric and

Dimeric Cobalt Complexes Supported by a PNP Pincer Ligand. *Inorg. Chem.*

2013, 52 (19), 11544–11550. <https://doi.org/10.1021/ic4018882>.

- (413) Kuriyama, S.; Arashiba, K.; Tanaka, H.; Matsuo, Y.; Nakajima, K.; Yoshizawa,

K.; Nishibayashi, Y. Direct Transformation of Molecular Dinitrogen into

Ammonia Catalyzed by Cobalt Dinitrogen Complexes Bearing Anionic PNP

Pincer Ligands. *Angew. Chem. Int. Ed.* **2016**, 55 (46), 14291–14295.

<https://doi.org/10.1002/anie.201606090>.

- (414) Lin, T. P.; Peters, J. C. Boryl-Mediated Reversible H₂ Activation at Cobalt:

Catalytic Hydrogenation, Dehydrogenation, and Transfer Hydrogenation. *J. Am.*

Chem. Soc. **2013**, 135 (41), 15310–15313. <https://doi.org/10.1021/ja408397v>.

- (415) Suzuki, T.; Fujimoto, K.; Takemoto, Y.; Wasada-tsutsui, Y.; Ozawa, T. Efficient

Catalytic Conversion of Dinitrogen to N(SiMe₃)₃ Using a Homogeneous

- Mononuclear Cobalt Complex. **2018**. <https://doi.org/10.1021/acscatal.7b04351>.
- (416) Ibrahim, A. D.; Tokmic, K.; Brennan, M. R.; Kim, D.; Matson, E. M.; Nilges, M. J.; Bertke, J. A.; Fout, A. R. Monoanionic Bis(Carbene) Pincer Complexes Featuring Cobalt(I-III) Oxidation States. *Dalt. Trans.* **2016**, 45 (24), 9805–9811. <https://doi.org/10.1039/c5dt04723d>.
- (417) Tokmic, K.; Markus, C. R.; Zhu, L.; Fout, A. R. Well-Defined Cobalt(I) Dihydrogen Catalyst: Experimental Evidence for a Co(I)/Co(III) Redox Process in Olefin Hydrogenation. *J. Am. Chem. Soc.* **2016**, 138 (36), 11907–11913. <https://doi.org/10.1021/jacs.6b07066>.
- (418) Ibrahim, A. D.; Entsminger, S. W.; Zhu, L.; Fout, A. R. A Highly Chemoselective Cobalt Catalyst for the Hydrosilylation of Alkenes Using Tertiary Silanes and Hydrosiloxanes. *ACS Catal.* **2016**, 6 (6), 3589–3593. <https://doi.org/10.1021/acscatal.6b01091>.
- (419) Sun, J.; Luo, L.; Luo, Y.; Deng, L. An NHC–Silyl–NHC Pincer Ligand for the Oxidative Addition of C–H, N–H, and O–H Bonds to Cobalt(I) Complexes. *Angew. Chem. Int. Ed.* **2017**, 56 (10), 2720–2724. <https://doi.org/10.1002/anie.201611162>.
- (420) Hoffman, P. R.; Yoshida, T.; Okano, T.; Otsuka, S.; Ibers, J. A. Crystal and Molecular Structure of Hydrido(Dinitrogen)Bis[Phenyl(Di-Tert-Butyl)Phosphine]-Rhodium(I). *Inorg. Chem.* **1976**, 15 (10), 2462–2466. <https://doi.org/10.1021/ic50164a030>.
- (421) Werner, H.; Mahr, N.; Wolf, J.; Fries, A.; Laubender, M.; Bleuel, E.; Garde, R.; Lahuerta, P. Synthesis, Molecular Structure, and Reactivity of Rhodium(I)

- Complexes with Diazoalkanes and Related Substrates as Ligands. *Organometallics* **2003**, 22 (17), 3566–3576. <https://doi.org/10.1021/om0302037>.
- (422) Hanson, S. K.; Heinekey, D. M.; Goldberg, K. I. C-H Bond Activation by Rhodium(I) Phenoxide and Acetate Complexes: Mechanism of H-D Exchange between Arenes and Water. *Organometallics* **2008**, 27 (7), 1454–1463. <https://doi.org/10.1021/om7012259>.
- (423) Adams, G. M.; Chadwick, F. M.; Pike, S. D.; Weller, A. S. A CH₂Cl₂ Complex of a [Rh(Pincer)]⁺ Cation. *Dalt. Trans.* **2015**, 44 (14), 6340–6342. <https://doi.org/10.1039/c5dt00481k>.
- (424) Feller, M.; Diskin-Posner, Y.; Shimon, L. J. W.; Ben-Ari, E.; Milstein, D. N-H Activation by Rh(I) via Metal-Ligand Cooperation. *Organometallics* **2012**, 31 (11), 4083–4101. <https://doi.org/10.1021/om300248r>.
- (425) Schöffel, J.; Šušnjar, N.; Nüchel, S.; Sieh, D.; Burger, P. 4d vs. 5d - Reactivity and Fate of Terminal Nitrido Complexes of Rhodium and Iridium. *Eur. J. Inorg. Chem.* **2010**, No. 31, 4911–4915. <https://doi.org/10.1002/ejic.201000899>.
- (426) Salem, H.; Ben-David, Y.; Shimon, L. J. W.; Milstein, D. Exclusive C-C Activation and an Apparent α -H Elimination with a Rhodium Phosphinite Pincer Complex. *Organometallics* **2006**, 25 (9), 2292–2300. <https://doi.org/10.1021/om060005q>.
- (427) Cohen, R.; Rybtchinski, B.; Gandelman, M.; Shimon, L. J. W.; Martin, J. M. L.; Milstein, D. Novel Azine Reactivity: Facile N-N Bond Cleavage, C-H Activation, and N-N Coupling Mediated by RhI. *Angew. Chem. Int. Ed.* **2003**, 42 (17), 1949–1952. <https://doi.org/10.1002/anie.200250571>.

- (428) Cohen, R.; Rybtchinski, B.; Gandelman, M.; Rozenberg, H.; Martin, J. M. L.; Milstein, D. Metallocarbenes from Diazoalkanes: An Experimental and Computational Study of the Reaction Mechanism. *J. Am. Chem. Soc.* **2003**, *125* (21), 6532–6546. <https://doi.org/10.1021/ja028923c>.
- (429) Gatard, S.; Guo, C.; Foxman, B. M.; Ozerov, O. V. Thioether, Dinitrogen, and Olefin Complexes of (PNP)Rh: Kinetics and Thermodynamics of Exchange and Oxidative Addition Reactions. *Organometallics* **2007**, *26* (25), 6066–6075. <https://doi.org/10.1021/om700563k>.
- (430) Verat, A. Y.; Pink, M.; Fan, H.; Tomaszewski, J.; Caulton, K. G. [(T Bu₂ PCH₂ SiMe₂)₂ N]Rh I? Rapidly Reversible H–C(Sp³) and H–C(Sp²) Bond Cleavage by Rhodium(I). *Organometallics* **2008**, *27* (2), 166–168. <https://doi.org/10.1021/om701165n>.
- (431) Scheibel, M. G.; Wu, Y.; Stückl, A. C.; Krause, L.; Carl, E.; Stalke, D.; De Bruin, B.; Schneider, S. Synthesis and Reactivity of a Transient, Terminal Nitrido Complex of Rhodium. *J. Am. Chem. Soc.* **2013**, *135* (47), 17719–17722. <https://doi.org/10.1021/ja409764j>.
- (432) Hasegawa, M.; Segawa, Y.; Yamashita, M.; Nozaki, K. Isolation of a PBP-Pincer Rhodium Complex Stabilized by an Intermolecular C–H σ Coordination as the Fourth Ligand. *Angew. Chem. Int. Ed.* **2012**, *51* (28), 6956–6960. <https://doi.org/10.1002/anie.201201916>.
- (433) Zenkina, O. V.; Keske, E. C.; Wang, R.; Crudden, C. M. Double Single-Crystal-to-Single-Crystal Transformation and Small-Molecule Activation in Rhodium NHC Complexes. *Angew. Chem. Int. Ed.* **2011**, *50* (35), 8100–8104.

<https://doi.org/10.1002/anie.201103316>.

- (434) Praetorius, J. M.; Wang, R.; Crudden, C. M. Structure and Reactivity of Dinitrogen Rhodium Complexes Containing N-Heterocyclic Carbene Ligands. *Eur. J. Inorg. Chem.* **2009**, No. 13 SPEC. ISS., 1746–1751.

<https://doi.org/10.1002/ejic.200801191>.

- (435) Millard, M. D.; Moore, C. E.; Rheingold, A. L.; Figueroa, J. S. Four-Coordinate Iridium(I) Monohydrides: Reversible Dinitrogen Binding, Bond Activations, and Deprotonations. *J. Am. Chem. Soc.* **2010**, *132* (26), 8921–8923.

<https://doi.org/10.1021/ja1037808>.

- (436) Tang, C. Y.; Thompson, A. L.; Aldridge, S. Dehydrogenation of Saturated CC and BN Bonds at Cationic N-Heterocyclic Carbene Stabilized M(III) Centers (M = Rh, Ir). *J. Am. Chem. Soc.* **2010**, *132* (30), 10578–10591.

<https://doi.org/10.1021/ja1043787>.

- (437) Tang, C. Y.; Smith, W.; Thompson, A. L.; Vidovic, D.; Aldridge, S. Iridium-Mediated Borylation of Benzylic C-H Bonds by Borohydride. *Angew. Chem. Int. Ed.* **2011**, *50* (6), 1359–1362. <https://doi.org/10.1002/anie.201006320>.

- (438) Bohle, D. S.; Chua, Z.; Perepichka, I. Facile N-N Activation in Benzotriazole: Capturing the Dimroth Azo/Triazole Intermediate by Complexation to Iridium. *Chempluschem* **2013**, *78* (10), 1304–1310.

<https://doi.org/10.1002/cplu.201300245>.

- (439) Yang, W.; Zhang, S.; Ding, Y.; Shi, L.; Song, Q. A Photoluminescent Dinuclear Phenylquinolyl Ir(II)-Ir(II) Complex Featuring a μ -H1:H2-Phenylquinolyl Bridge and an End-on Dinitrogen Ligand. *Chem. Commun.* **2011**, *47* (18), 5310–5312.

<https://doi.org/10.1039/c1cc11254f>.

- (440) Ghosh, R.; Kanzelberger, M.; Emge, T. J.; Hall, G. S.; Goldman, A. S. Dinitrogen Complexes of Pincer-Ligated Iridium. *Organometallics* **2006**, 25 (23), 5668–5671. <https://doi.org/10.1021/om0607043>.
- (441) Arunachalampillai, A.; Olsson, D.; Wendt, O. F. Synthesis and Characterisation of PCsp³P Phosphine and Phosphinite Iridium Complexes. Cyclometallation and Dehydrogenation of a Cyclohexyl Ring. *Dalt. Trans.* **2009**, No. 40, 8626–8630. <https://doi.org/10.1039/b910798c>.
- (442) Göttker-Schnetmann, I.; White, P. S.; Brookhart, M. Synthesis and Properties of Iridium Bis(Phosphinite) Pincer Complexes (p-XPCP)IrH₂, (p-XPCP)Ir(CO), (p-XPCP)Ir(H)(Aryl), and {(p-XPCP)Ir}₂{μ-N₂} and Their Relevance in Alkane Transfer Dehydrogenation. *Organometallics* **2004**, 23 (8), 1766–1776. <https://doi.org/10.1021/om030670o>.
- (443) Huang, Z.; White, P. S.; Brookhart, M. Ligand Exchanges and Selective Catalytic Hydrogenation in Molecular Single Crystals. *Nature* **2010**, 465 (7298), 598–601. <https://doi.org/10.1038/nature09085>.
- (444) Fang, H.; Choe, Y. K.; Li, Y.; Shimada, S. Synthesis, Structure, and Reactivity of Hydrido-iridium Complexes Bearing a Pincer-Type PSiP Ligand. *Chem. - An Asian J.* **2011**, 6 (9), 2512–2521. <https://doi.org/10.1002/asia.201100085>.
- (445) Conejero, S.; Esqueda, A. C.; Valpuesta, J. E. V.; Álvarez, E.; Maya, C.; Carmona, E. Different Coordination Modes of an Aryl-Substituted Hydrotris(Pyrazolyl) Borate Ligand in Rhodium and Iridium Complexes. *Inorganica Chim. Acta* **2011**, 369 (1), 165–172. <https://doi.org/10.1016/j.ica.2010.12.031>.

- (446) Bernskoetter, W. H.; Lobkovsky, E.; Chirik, P. J. Synthesis of a β -Diiminate Iridium Tetrahydride for Arene C–H Bond Activation. *Chem. Commun.* **2004**, 4 (7), 764–765. <https://doi.org/10.1039/b315817a>.
- (447) Whited, M. T.; Grubbs, R. H. A Catalytic Cycle for Oxidation of Tert-Butyl Methyl Ether by a Double C-H Activation-Group Transfer Process. *J. Am. Chem. Soc.* **2008**, 130 (49), 16476–16477. <https://doi.org/10.1021/ja8071385>.
- (448) Scheibel, M. G.; Askevold, B.; Heinemann, F. W.; Reijerse, E. J.; De Bruin, B.; Schneider, S. Closed-Shell and Open-Shell Square-Planar Iridium Nitrido Complexes. *Nat. Chem.* **2012**, 4 (7), 552–558. <https://doi.org/10.1038/nchem.1368>.
- (449) Abbenseth, J.; Finger, M.; Würtele, C.; Kasanmascheff, M.; Schneider, S. Coupling of Terminal Iridium Nitrido Complexes. *Inorg. Chem. Front.* **2016**, 3 (4), 469–477. <https://doi.org/10.1039/c5qi00267b>.
- (450) Scheibel, M. G.; Abbenseth, J.; Kinauer, M.; Heinemann, F. W.; Würtele, C.; De Bruin, B.; Schneider, S. Homolytic N-H Activation of Ammonia: Hydrogen Transfer of Parent Iridium Ammine, Amide, Imide, and Nitride Species. *Inorg. Chem.* **2015**, 54 (19), 9290–9302. <https://doi.org/10.1021/acs.inorgchem.5b00829>.
- (451) Beck, R.; Shoshani, M.; Krasinkiewicz, J.; Hatnean, J. A.; Johnson, S. A. Synthesis and Chemistry of Bis(Triisopropylphosphine) Nickel(i) and Nickel(0) Precursors. *J. Chem. Soc. Dalt. Trans.* **2013**, 42 (2), 1461–1475. <https://doi.org/10.1039/c2dt32008h>.
- (452) Waterman, R.; Hillhouse, G. L. Synthesis and Structure of a Terminal Dinitrogen Complex of Nickel. *Can. J. Chem.* **2005**, 83 (4), 328–331. <https://doi.org/10.1139/v05-011>.

- (453) Kim, Y. E.; Kim, J.; Lee, Y. Formation of a Nickel Carbon Dioxide Adduct and Its Transformation Mediated by a Lewis Acid. *Chem. Commun.* **2014**, 50 (78), 11458–11461. <https://doi.org/10.1039/c4cc04800h>.
- (454) Kim, Y. E.; Oh, S.; Kim, S.; Kim, O.; Kim, J.; Han, S. W.; Lee, Y. Phosphinite-Ni(0) Mediated Formation of a Phosphide-Ni(II)-OCOOME Species via Uncommon Metal-Ligand Cooperation. *J. Am. Chem. Soc.* **2015**, 137 (13), 4280–4283. <https://doi.org/10.1021/ja513112r>.
- (455) Oh, S.; Kim, S.; Lee, D.; Gwak, J.; Lee, Y. Alkoxide Migration at a Nickel(II) Center Induced by a π -Acidic Ligand: Migratory Insertion versus Metal-Ligand Cooperation. *Inorg. Chem.* **2016**, 55 (24), 12863–12871. <https://doi.org/10.1021/acs.inorgchem.6b02226>.
- (456) Charboneau, D. J.; Balcells, D.; Hazari, N.; Lant, H. M. C.; Mayer, J. M.; Melvin, P. R.; Mercado, B. Q.; Morris, W. D.; Repisky, M.; Suh, H. W. Dinitrogen-Facilitated Reversible Formation of a Si-H Bond in a Pincer-Supported Ni Complex. *Organometallics* **2016**, 35 (18), 3154–3162. <https://doi.org/10.1021/acs.organomet.6b00514>.
- (457) Harman, W. H.; Lin, T. P.; Peters, J. C. A D₁₀ Ni-(H₂) Adduct as an Intermediate in H-H Oxidative Addition across a Ni-B Bond. *Angew. Chem. Int. Ed.* **2014**, 53 (4), 1081–1086. <https://doi.org/10.1002/anie.201308175>.
- (458) Cowie, B. E.; Emslie, D. J. H. Nickel and Palladium Complexes of Ferrocene-Backbone Bisphosphine-Borane and Trisphosphine Ligands. *Organometallics* **2015**, 34 (16), 4093–4101. <https://doi.org/10.1021/acs.organomet.5b00539>.
- (459) Tsay, C.; Peters, J. C. Thermally Stable N₂ and H₂ Adducts of Cationic Nickel(II).

- Chem. Sci.* **2012**, 3 (4), 1313–1318. <https://doi.org/10.1039/c2sc01033j>.
- (460) Cammarota, R. C.; Lu, C. C. Tuning Nickel with Lewis Acidic Group 13 Metalloligands for Catalytic Olefin Hydrogenation. *J. Am. Chem. Soc.* **2015**, 137 (39), 12486–12489. <https://doi.org/10.1021/jacs.5b08313>.
- (461) Pfirrmann, S.; Limberg, C.; Herwig, C.; Stöber, R.; Ziemer, B. A Dinuclear Nickel(i) Dinitrogen Complex and Its Reduction in Single- Electron Steps. *Angew. Chem. Int. Ed.* **2009**, 48 (18), 3357–3361. <https://doi.org/10.1002/anie.200805862>.
- (462) Horn, B.; Pfirrmann, S.; Limberg, C.; Herwig, C.; Braun, B.; Mebs, S.; Metzinger, R. N₂ Activation in NiI-NN-NiI Units: The Influence of Alkali Metal Cations and CO Reactivity. *Zeitschrift für Anorg. und Allg. Chemie* **2011**, 637 (9), 1169–1174. <https://doi.org/10.1002/zaac.201100140>.
- (463) Holze, P.; Horn, B.; Limberg, C.; Matlachowski, C.; Mebs, S. The Activation of Sulfur Hexafluoride at Highly Reduced Low-Coordinate Nickel Dinitrogen Complexes. *Angew. Chem. Int. Ed.* **2014**, 53 (10), 2750–2753. <https://doi.org/10.1002/anie.201308270>.
- (464) Chavan, S.; Bonino, F.; Vitillo, J. G.; Groppo, E.; Lamberti, C.; Dietzel, P. D. C.; Zecchina, A.; Bordiga, S. Response of CPO-27-Ni towards CO, N₂ and C₂H₄. *Phys. Chem. Chem. Phys.* **2009**, 11 (42), 9811–9822. <https://doi.org/10.1039/b907258f>.
- (465) Murray, L. J.; Weare, W. W.; Shearer, J.; Mitchell, A. D.; Abboud, K. A. Isolation of a (Dinitrogen)Tricopper(I) Complex. *J. Am. Chem. Soc.* **2014**, 136 (39), 13502–13505. <https://doi.org/10.1021/ja506445d>.
- (466) Di Francesco, G. N.; Gaillard, A.; Ghiviriga, I.; Abboud, K. A.; Murray, L. J.

- Modeling Biological Copper Clusters: Synthesis of a Tricopper Complex, and Its Chloride- and Sulfide-Bridged Congeners. *Inorg. Chem.* **2014**, *53* (9), 4647–4654.
<https://doi.org/10.1021/ic500333p>.
- (467) Zhang, S.; Fallah, H.; Gardner, E. J.; Kundu, S.; Bertke, J. A.; Cundari, T. R.; Warren, T. H. A Dinitrogen Dicopper(I) Complex via a Mixed-Valence Dicopper Hydride. *Angew. Chem. Int. Ed.* **2016**, *55* (34), 9927–9931.
<https://doi.org/10.1002/anie.201603970>.
- (468) Hsu, W.; Thapa, K. B.; Yang, X. K.; Chen, K. T.; Chang, H. Y.; Chen, J. Der. Dinitrogen-Supported Coordination Polymers. *CrystEngComm* **2016**, *18* (3), 390–393. <https://doi.org/10.1039/c5ce02127h>.
- (469) Welz, E.; Krummenacher, I.; Engels, B.; Braunschweig, H. Reduction At Boron. *Science (80-.)*. **2018**, *900* (February), 896–900.
- (470) Légaré, M. A.; Rang, M.; Bélanger-Chabot, G.; Schweizer, J. I.; Krummenacher, I.; Bertermann, R.; Arrowsmith, M.; Holthausen, M. C.; Braunschweig, H. The Reductive Coupling of Dinitrogen. *Science (80-.)*. **2019**, *363* (6433), 1329–1332.
<https://doi.org/10.1126/science.aav9593>.
- (471) Sherbow, T. J.; Thompson, E. J.; Arnold, A.; Sayler, R. I.; Britt, R. D.; Berben, L. A. Electrochemical Reduction of N₂ to NH₃ at Low Potential by a Molecular Aluminum Complex. *Chem. - A Eur. J.* **2019**, *25* (2), 454–458.
<https://doi.org/10.1002/chem.201804454>.