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Activation of Dinitrogen by Polynuclear Metal Complexes

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ABSTRACT: Activation of dinitrogen plays an important role in daily anthropogenic life, and the processes by which this fixation occurs have been a longstanding and significant research focus within the community. One of the major fields of dinitrogen activation research is the use of multimetallic compounds to reduce and/or activate N₂ into a more useful nitrogen-atom source, such as ammonia. Here we report a comprehensive review of multimetallic-dinitrogen complexes and their utility toward N_2 activation, beginning with the d-block metals from Group 4 to Group 11, then extending to Group 13 (which is exclusively populated by B complexes), and finally the rare-earth and actinide species. The review considers all polynuclear metal aggregates containing two or more metal centers in



which dinitrogen is coordinated or activated (i.e., partial or complete cleavage of the N_2 triple bond in the observed product). Our survey includes complexes in which mononuclear N2 complexes are used as building blocks to generate homo- or heteromultimetallic dinitrogen species, which allow one to evaluate the potential of heterometallic species for dinitrogen activation. We highlight some of the common trends throughout the periodic table, such as the differences between coordination modes as it relates to N₂ activation and potential functionalization and the effect of polarizing the bridging N₂ ligand by employing different metal ions of differing Lewis acidities. By providing this comprehensive treatment of polynuclear metal dinitrogen species, this Review aims to outline the past and provide potential future directions for continued research in this area.

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1. INTRODUCTION

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Dinitrogen activation has attracted substantial research interest for more than a half-century,^{1,2} arising from both the societal import of N₂ fixation and the fundamental understanding of the design criteria needed to activate small-molecule substrates. As evidenced by its common use as an inert gas in chemistry, the N₂ molecule is challenging to activate and functionalize, which is attributed to the lack of a dipole moment in the diatomic and the strong π - and σ -bonding interactions prevalent for the second row *p*-block atoms.³ Notably, the hydrogenation of dinitrogen is spontaneous under standard conditions with $\Delta G_f^o(NH_3) = -16.48$ kJ/mol, and the sixelectron, six-proton reduction of N₂ to ammonia is moderately endergonic (Scheme 1).⁴ It is evident, therefore, that the

Scheme	1.	Reduction	Potentials	for	N_2	vs NHE	
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$N_2 + e^ N_2^-$	<i>E</i> ^o = -4.16 V
$N_2 + H^+ + e^- $	$E^{\rm o}$ = -3.20 V
$N_2 + 2H^+ + 2e^- \longrightarrow N_2H_2$	<i>E</i> ^o = -1.10 V
$N_2 + 4H^+ + 4e^- \longrightarrow N_2H_4$	$E^{\rm o}$ = -0.33 V
$N_2 + 6H^+ + 6e^ 2 NH_3$	<i>E</i> ^o = -0.148 V

challenge associated with dinitrogen activation is one of kinetics rather than spontaneity. To highlight this point, the bond dissociation free energy (BDFE) for carbon monoxide (viz. 1072 kJ/mol) exceeds that for N₂ (viz. 947 kJ/mol). However, CO functionalization has strong precedent (e.g., CO insertion, hydroformylation, Fischer–Tropsch reaction, Water–Gas shift reaction), whereas analogous reactions for dinitrogen remain rare. This difference can be attributed to the superior σ -donor and π -acceptor properties of CO versus N₂.

There are several factors that make N_2 reduction kinetically difficult, with the major hurdle being the large HOMO– LUMO gap of 10.82 eV.⁵ Consequently, direct reduction of N_2 is energetically expensive—note the very unfavorable oneelectron reduction of N_2 (Scheme 1). Additionally, the low proton affinity and high ionization potential of dinitrogen make direct protonation or oxidative activation of N_2 challenging under standard conditions.⁶ The predominant approach for surmounting this kinetic challenge in activating N_2 is to coordinate dinitrogen to unsaturated centers dinitrogen adducts are known for *p*-, *d*-, and *f*-block elements—followed by intramolecular charge transfer and downstream functionalization of the N_2 fragment. Within this coordination paradigm, however, the lack of a dipole moment and relatively high energy π^* orbitals result in N_2 being a poor σ -donor and π -acceptor. Thus, the N \equiv N bond is not only strong and direct reduction kinetically difficult, but the interactions with a potential reactive atom (e.g., transition metal ion) are also weak.

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For mononuclear systems, circumventing these problems typically relies on employing reducing metal centers (e.g., formal Fe⁰ centers). An alternative strategy, however, is to coordinate N₂ to multiple metal ions to leverage the combined reducing power of the aggregate to activate the bound N₂ molecule. One can use this strategy to effect (*i*) N \equiv N bond scission to afford diazenido-, hydrazido-, or nitrido-metal species (Scheme 2) or (*ii*) sequential reduction and

Scheme 2. Proposed Dimetallic N₂ Scission Mechanism



protonation or hydrogenation of a coordinated N₂ in a proton-coupled electron transfer or PCET (Scheme 3). In the former case, the metal centers backbond into the N₂ fragment to generate a formally reduced N₂ derived ligand; in some cases, the systems are best described as charge transfer from the reduced metal centers to the N₂ ligand. The seminal example of multimetallic cleavage of N₂ to metal nitrides is from Cummins and co-workers in which 2 equiv of a tris(amido)-molybdenum(III) complex react with 1 equiv of N₂ to afford the corresponding Mo^{VI}≡N complex.⁷⁻⁹ Coupling (*i*) to (*ii*) has also been effective, that is, partial activation of N₂ followed by reduction and functionalization to complete dinitrogen bond cleavage.¹⁰

The PCET approach can operate under two limiting scenarios: a distal or an alternating pathway. The former occurs with protonation of the distal N atom of the bound N₂ with reduction ultimately leading to the metal nitride and 1 equiv of ammonia. The latter pathway involves alternating protonation of the distal and proximal N atoms to generate diazenide and hydrazide complexes with N–N cleavage resulting in ammonia and metal-amide or ammine products. Yandulov and Schrock reported the first catalytic N₂ to NH₃ conversion on a monometallic Mo complex by the distal pathway,^{11–13} and later work by Peters and co-workers extended such catalysis to monometallic iron complexes.^{10,14–22}

Scheme 3. Possible PCET Pathways for N_2 to NH_3 Conversion^{*a*}



^aNote: The scheme does not define the number of metal centers nor the coordination mode of N_{2} .

Our focus is on multimetallic dinitrogen activation by molecular systems, and specifically, we consider systems in which the dinitrogen-derived bridging ligand(s) coordinated to multiple redox-active centers has been validated experimentally (e.g., X-ray diffraction or absorption spectroscopic methods). Although a number of the compounds presented in this review have been covered by prior reviews by Hidai, Gambarotta, and Fryzuk, these reviews have limited scope (e.g., early transition metals) or have placed particular emphasis on functionalization of the coordinated N_2 .²³⁻²⁸ Contrastingly, our goal here is to be comprehensive with respect to known multimetallicdinitrogen species and to avoid-where reasonably possiblediscussing the downstream reactivity of the coordinated N₂. Complementing our efforts here is a review by Chirik and coworkers, which focus on N₂ functionalization and is a part of this special issue. Our discussion will begin with the prevalent modes of dinitrogen coordination and highlight the electronic effects necessary to bind and activate the $N \equiv N$ bond. Subsequently, we will summarize the reported compounds up to 2019 in order of the *d*-, *p*-, and then *f*-block compounds. In each grouping, we highlight compounds of novel structure types or strategies, such as seminal examples of specific coordination modes. For those examples in which vibrational data are the exclusive criterion for discussion (i.e., structural novelty or proof of concept is not demonstrated), we consider the formally N_2^{2-} oxidation level as our benchmark, while acknowledging that the extent of activation is a sliding scale and any potential limiting criteria can be viewed as arbitrary.²¹ If vibrational data are lacking for a specific compound, we default to using the imperfect approach of comparing the N-N bond distances to gauge N₂ activation.

2. DINITROGEN COORDINATION TO MULTIPLE METAL CENTERS

The first example of dinitrogen coordination is the report of the family of $[Ru(N_2)(NH_3)_5]X_2$ complexes $(X = Br^{-}, I^{-}, I^{$ BF_4^- , and PF_6^-) in 1965 by Allen and Senoff.³⁰ The infrared spectrum of these complexes evidenced a N-N stretching vibration at $\sim 200 \text{ cm}^{-1}$ below that of free dinitrogen (i.e., 2170-2115 cm⁻¹ for the complexes vs 2359 cm⁻¹ for N₂). Shortly thereafter, Taube reported that this rutheniumdinitrogen adduct reacts with the aqua precursor [Ru- $(NH_3)_{s}(OH_2)^{2+}$ to afford a (μ -1,2-dinitrogen)diruthenium species, $[Ru(NH_3)_5]_2(\mu$ -1,2-N₂), providing the first example of a dimetallic dinitrogen complex.³¹ The N–N stretching mode was assigned to a weak absorption at $\sim 2060 \text{ cm}^{-1}$ for the tetrafluoroborate salt, lower than that for the monometallic complex. Indeed, this trend of greater extent of activation of the N₂ ligand based on vibrational spectroscopy is generally observed for multimetallic species. A similar trend is well documented for metal carbonyl complexes wherein bridging modes result in markedly lower C≡O vibrational frequencies, but do not correlate with substantially elongated C≡O bond lengths in solid state structures. Thus, the aggregate effects greater overall activation of N2, although each metaldinitrogen interaction in the multimetallic is on average weaker than many comparable monometallic species.

Since that initial report of the μ -1,2 mode for dinitrogen coordination, a number of compounds containing up to four metal centers have been isolated and characterized with the growing body of work suggesting preferred coordination modes of dinitrogen in multimetallic systems.^{23,28} Coordination modes observed hitherto are depicted in Figure 1.



Figure 1. Binding modes of N_2 . The dinitrogen ligand is depicted as $N \equiv N$ for simplicity as the extent of activation varies depending on metal ion type and oxidation state. Associated s-block elements (e.g., Li+, K+) are not included in this treatment.

To simplify our analysis of coordination modes, we exclude *s*-block metals in our description of multimetallic coordination modes and consider only the connectivity of the redox active centers (e.g., *d*-block metal) and dinitrogen donor. Given the requirement for π -backbonding interactions to stabilize the metal-dinitrogen adduct, almost all reported examples employ low-valent metal centers and greater N₂ activation is typically observed for the more electropositive early transition metals as compared to the late transition metals.

Beginning with the simplest scenario, two commonly observed coordination modes for dinuclear-dinitrogen adducts are the μ -1,2 or μ - η^2 : η^2 modes (Figure 2). The



Figure 2. Bonding interactions for end-on/end-on and side-on/sideon dinitrogen complexes wherein the interactions of only one metal center with dinitrogen are depicted.

former, also known as an end-on/end-on bridging mode, results in near linear M-N-N-M units for the d-block elements as such an arrangement maximizes the π -backbonding interaction between the metal d_{π} and N₂ π^* orbitals. The second common dimetallic-dinitrogen coordination mode, viz. the μ - η^2 : η^2 or side-on/side-on, has not been reported for molecular complexes comprising late transition metals but rather is only observed for the early transition metals and for f-block compounds. Similar M-N₂ π -backbonding interactions as for the μ -1,2 mode are present here with the planar M-N₂-M favored as compared to the butterfly geometry (Figure 1). The primary difference that arises from the dinitrogen orbitals involved in the M–N₂ σ interaction is that the highest energy filled $\sigma_{\rm g}^{\;+}$ orbital of N $_2$ acts as the σ donor for the linear arrangement, whereas a π bonding orbital for the side-on/side-on mode. The preference for the μ -1,2 vs μ - η^2 : η^2 modes depends on steric effects enforced by the supporting ligand, metal-ion type, formal oxidation state, and coordination number; the latter three influence the energies of the metal orbitals needed to constitute the σ - and π -bonds for the M-N₂ unit.³² Finally, the rarest dimetallic coordination mode for N₂ is the μ - η^1 : η^2 mode, which has only been reported for Ti, Zr, and Ta. DFT calculations on Ta complexes of this type evidence π -backbonding interactions between the metal d_{π} orbitals and the N₂ π^* and the σ -bonding from the $3\sigma_{\rm g}$ orbital of N₂ and one Ta center (η^1) and the filled π -bond of the N₂ to the other Ta center (η^2).³³ As one might predict, this coordination mode polarizes the N2 ligand, allowing for facile asymmetric functionalization by electrophiles.

Few examples of μ_3 - and μ_4 -dinitrogen complexes have been reported as compared to the dimetallic cases. One can consider these coordination modes as extensions of the dinuclear cases; indeed, in almost all cases related dinuclear fragments have been reported. Homonuclear trimetallic examples are only reported for Ta, Ti, and Cu as well as a handful of heterometallic M_2M' compounds (M' = Group 13 center) for which the formally redox-neutral Group 13 electrophile functionalizes a precursor μ - η^1 : η^2 complex. The μ_3 - η^2 : η^2 : η^2 dinitrogen is only known for Sm wherein the Sm₃N₂ core is pseudo- C_{2v} symmetric with a near planar Sm₂(μ - η^2 : η^2 -N₂) fragment. Lastly, the μ_4 - η^1 : η^2 : η^1 mode is only reported thus far for two tetrasamarium complexes. A number of examples of this bridging mode are, however, known if one substitutes one of the redox active metal centers for an *s*-block metal ion. In this mode, the M_4N_2 core is approximately planar with a near linear $M_2(\mu$ -1,2- N_2) fragment as one might anticipate from our discussion of the μ - η^2 : η^2 and the μ -1,2 coordination modes.

3. DINITROGEN ACTIVATION BY MULTIMETALLIC COMPLEXES

As noted above, the report by Taube and co-workers of the μ -1,2-dinitrogen diruthenium complex was the first example of multimetallic dinitrogen activation. Our survey below begins with the *d*-block metals starting with Group 4 and ending with Group 11, followed by considering N2 activation by boron compounds, which is the only representative from Group 13. Lastly, we review the literature on complexes of the rare earth elements and actinides. We consider cases in which the metal centers are redox-active and the N2 fragment is derived from atmospheric dinitrogen; thus, complexes in which a monometallic-dinitrogen species is capped by a borane, alane, or other Lewis acid are omitted. One observes the following. First, greater activation of the N₂ unit for the second and third row transition metal complexes as compared to the analogous first row compounds in the early d-block with that trend eroding as one moves to the later transition metals. Second, greater activation of bound N2 for the earlier more electropositive metals as compared to the late transition metals. This latter trend is consistent with the greater reducing strength and stability of higher oxidation states of early vs late metals, leading to greater charge transfer to the dinitrogen ligand. The trend is consistent with the classical ligand field picture wherein the metal is considered as the Lewis acid and the ligand as Lewis base (i.e., metal orbitals are significantly higher in energy than the ligand orbitals); greater covalency is observed for the late transition metals as a consequence of the closer energy match between the metal and ligand valence orbitals. Finally, access to the metal center as dictated by the ligand sterics tunes the complex nuclearity, allowing for isolation of discrete mono- and multimetallic dinitrogen adducts, and also the extent of N₂ bond activation.

3.1. Group 4: Ti, Zr, Hf

In this section, we begin with dinitrogen adducts of bis(cyclopentadienyl)metal complexes as these complexes constitute the most well explored and largest family of metal—dinitrogen species in Group 4. That discussion is followed by the monocyclopentadienyl compounds, then the tetra- and tridentate PN ligand systems—many of which have both Ti and Zr complexes reported—and then complete our survey with the ligands for which only titanium examples have been reported.

3.1.1. Metallocene, *ansa*-Metallocene, and Related Complexes. In the 1960s, van Tamelen and co-workers first proposed that divalent titanium complexes were capable of binding dinitrogen reversibly and able to effect N₂ fixation to N₂H₄ and NH₃ and organic amines.³⁴ Shortly thereafter, Britzinger and co-workers proposed that a metastable [bis(η^{5} -cyclopentadienyl)titanium(II)] (μ -dinitrogen) or (Cp₂Ti)₂(μ -N₂) was accessible from the related monometallic hydride species;^{35,36} however, *sp*² C–H activation by the low valent Ti center limits the stability of this species. Bercaw and co-workers substituted C–H for C–CH₃ on the Cp⁻ ring, which limited degradation and sufficiently stabilized the dinitrogen

adduct to allow for its characterization. Reaction of bis(η^5 -pentamethylcyclopentadienyl)titanium(II) or decamethyltitanocene (Cp*₂Ti) with N₂ affords (Cp*₂Ti)₂(μ -1,2-N₂), 1-**Cp***.³⁷ The solid state structure evidences a μ -1,2-dinitrogen ligand with a N–N bond length of 1.165 Å and Ti–N distance of 2.005–2.016 Å³⁸ (Figure 3). The former metric is lengthened relative to free N₂ and comparable to that for



 θ : Angle between the planes defined by the centroid-M-centroid of the metallocene unit

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	Namo	CnR	$u(\mathbf{N}-\mathbf{N})$	θ
	Name	Ср	(A)	0
	1-Cp*	Ŕ	1.165	ave. ~90°
	1 - Cp'	Ŕ	1.170(4)	0°
1-	-Cp ^{Me4,Xyl}	$R = 3,5-Me_2-C_6H_3$	1.1574(11)	85.9°
1-C] 1-C]	p ^{Me12iPr4} p ^{Me12tBu4}	$R = {}^{i}Pr \text{ or } {}^{i}Bu$	1.168(3)	0 ⁰
1-0	Ср ^{тмs13}	SiMe ₃	1.164(5)	9.6°
2	2-(<i>p</i> -tol) ₂ 2-(Ad)	$ \begin{array}{c} $	1.216(3) 1.216(5)	3.2° 19.1°

Figure 3. Type A complexes: the $(\mu$ -1,2-dinitrogen)bis(titanocene) compounds.

 N_2^{2-} , implying significant charge transfer and formal reduction of the dinitrogen ligand. In the years since this initial report for titanium, numerous other dinitrogen-metallocene compounds employing Group 4 metal ions have been reported with many notable examples reported by Chirik and co-workers. These complexes can be divided into three categories: the $(\mu-1,2$ dinitrogen)bis(metallocene) species or type A (Figure 3), the $(\mu - (\eta^2 : \eta^2) - \text{dinitrogen})$ bis(metallocene) compounds or type B (Figure 5), and the $(\mu$ -1,2-dinitrogen)bis(metallocene) species supported by additional terminal, monodentate L- or X-type donors or type C (Figure 8 and Figure 9). As one might predict, these categories are closely related with minor changes in ligand sterics resulting in a transition from A to B, or by addition of exogeneous ligands to A- or B-type compounds yielding the related type C complex. In addition, ansametallocene complexes related to A-C are also known.

Extending the work of Bercaw and Teuben and their respective co-workers, Hanna and Chirik reported a series of $(\mu$ -1,2-dinitrogen)bis(titanocene) adducts in which the sterics of the Cp⁻ ring are systematically varied. Across the series, one notes comparable N–N bond distances for the μ -1,2dinitrogen complexes supported by cyclopentadienyl donors, with values ranging from 1.157(1) in 1-Cp^{Me4,Xyl} to 1.170(4) Å in 1-Cp' (Figure 3).^{39–42} Similar N–N bond distances are also observed for the $(\mu$ -1,2-dinitrogen)bis[$(\eta^{5}$ -fulvene) $(\eta^{5}$ cyclopentadienyl)titanium] complexes 2-(p-tol)2 and 2-Ad (1.216(3) and 1.216(5) Å, respectively) in which the substituent on the fulvene varies.43,44 The comparable distances across the series reflect the constant formal oxidation states of the titanium centers as well as the dinitrogen coordination mode. Reducing the sterics on the cyclopentadienyl ring results in a change to the μ - η^2 : η^2 coordination mode for the dinitrogen ligand in the titanium complexes. For example, substituting one methyl group on each Cp⁻ ring in 1-**Cp**' for an H atom yields the μ - η^2 : η^2 -dinitrogen complex in 1- Cp^{Me124} (Figure 5).⁴⁰ A similar structure is observed for 1- $Cp^{Me1iPr3}$ and 1- Cp^{iPr13} , and all three examples have comparable N–N bond lengths of ~1.21 Å.⁴⁵ Reducing the sterics from $1-Cp^{Me124}$ by employing 1,3-dimethylcyclopentadienyl yields instead a trimetallic complex $1-Cp^{Me13}$ in which C-H activation and C-C bond formation afford a dianionic fulvalenide ligand (Figure 4).⁴⁵ Notably, the three Ti centers in 1-Cp^{Me13} result in one of the longest N-N bond distances for a titanocene type dinitrogen complex at 1.320(3) Å.



Figure 4. Titanocene complexes (1-Cp^{Me13} and 1-Cp) featuring a μ_3 -dinitrogen coordination mode.

Compound 1-Cp^{Me13} bears similarity to the previously reported tetratitanium complex, 1-Cp, from Pez and coworkers. Similar to 1-Cp^{Me13}, C–H activation is observed during the reaction of $(\mu - \eta^1: \eta^5$ -cyclopentadienyl)(tris- η^5 cyclopentadienyl)dititanium with dinitrogen to afford $[(\eta^5: \eta^5-C_{10}H_8)(\eta^5-Cp)_2Ti_2][\mu - \eta^1: \eta^5-C_5H_4)(\eta^5-Cp)_3Ti_2]-(\mu_3 - \eta^1: \eta^2: \eta^1-N_2)$, 1-Cp, from (Figure 4).⁴⁶ This reaction may proceed through the metastable blue (Cp₂Ti)₂(μ -N₂) species with C– H activation and H₂ elimination leading to C–C coupling to afford 1-Cp, although detailed mechanistic studies have not been communicated.

Given the sensitivity of the coordination mode on cyclopentadienyl substitution, the Zr and Hf congeners of the $(\mu$ -1,2-dinitrogen)bis(metallocenes) have not been observed; the larger ionic radii of Zr and Hf as compared to Ti counterpoise the steric constraints imposed by the cyclopentadienyl donors. The $(Cp_{2}^{R}M)_{2}(\mu-\eta^{2}:\eta^{2}-N_{2})$ complexes (M = Zr or Hf) are exclusively observed for the monodinitrogen species. The Group 4 bis(metallocene)-dinitrogen adducts show increasing formal reduction of the N2 ligand as one transitions from Ti to Zr and Hf. Magnetic susceptibilities of 2.7(2) $\mu_{\rm B}$ and 2.2(2) $\mu_{\rm B}$ in the solid phase and benzene solution for 1-Cp^{Me124}, respectively, suggest two d^1 Ti(III) centers and consequently a formally diazenide ligand in line with the N-N bond distance (1.216(3) Å) and are further supported by the N–N stretching frequencies of 1742 and 1747 cm⁻¹ for 1-Cp^{MeliPr3} and 1-Cp^{iPr13}, respectively (N–N $(N-N)^{-1}$ stretching frequency was not reported for 1-Cp^{Mé124}).47,48 These data contrast the longer N–N bond distances (1.377(3))Å for 3-Cp' and 1.423(11) Å for 4-Cp') for the Zr and Hf congeners and much lower ν_{N-N} of 922 cm⁻¹ for 3-Cp' pointing toward hydrazide level of reduction.⁴⁹⁻⁵¹ One notes that the Zr and Hf compounds have similar N-N bond distances that range from $\hat{1.377}(3)$ Å for 3-Cp' to 1.47(3) Å for 3-Cp^{TMS13} and 1.423(11) Å for 4-Cp' to 1.457(7) Å for 4-Cp^{Me124} (Figure 5).⁵¹⁻⁵⁴ Unlike other bis(metallocene)dinitrogen complexes prepared by chemical reduction of a metallocene halide precursor under an N₂ atmosphere, 3-Cp' has also been synthesized by reductive elimination of the aryl groups in $(\eta^5 - Cp')_2 Zr(Ar)_2$ (Ar = 4-Me-C₆H₄, C₆H₅, 4-Et- C_6H_4 , 4-Ph- C_6H_4) under photochemical conditions.⁵

A comparison of the structures of the $(\mu - \eta^2 : \eta^2 - \text{dinitrogen})$ bis(metallocene) for titanium, zirconium, and hafnium evidences two notable differences: First, the angle between the two centroid-metal-centroid planes of each metallocene unit (θ) , or the angle between the wedges of each metallocene, is close to zero for the Ti compounds, but >49° for the Zr and Hf congeners except $3-Cp^{TMS13}$. Second, the dihedral angle between the M2N2 plane and the centroid-metal-centroid planes of each metallocene is nearly perpendicular for Ti, but more acute for the Zr and Hf analogs (Figure 5). DFT calculations reveal the consequence of the twists observed in the Zr and Hf congeners as compared to the Ti analogs (i.e., the two noted dihedral angles are nonzero): a π -bonding interaction between the out of phase linear combination of the frontier $1a_1$ orbitals on each metallocene fragment and the π^* orbital on N₂ leads to a metal-imide type bonding picture in Zr and Hf, whereas the coplanar wedges and the perpendicular relationship to the Ti₂N₂ plane lead to minimal-if anymultiple bonding character between the metal centers and the N_2 atoms.⁵⁶

The *ansa*-metallocenes accentuate the mixing of the metallocene frontier orbitals to favor interactions with the

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 θ : Angle between the planes defined by the centroid-M-centroid of the metallocene unit



Figure 5. Type B complexes: the $(\mu - (\eta^2 : \eta^2) - \text{dinitrogen})$ bis-(metallocene) compounds.

noncyclopentadienyl ligands. Consequently, one might anticipate that transitioning from the metallocene to the *ansa*-bridged congeners will favor π -backbonding into the N₂ bridge. Despite the expected electronic benefit, the greater steric constraints in the reported *ansa*-metallocene compounds prevents a faithful comparison. For example, only a minimal increase in the N–N distance is observed for the μ -1,2-dinitrogen dititanium complexes 5-1 and 5-2 (Figure 6) with values of 1.174(3) Å and 1.165(3) Å as compared to the non-*ansa* congeners 1-Cp^R.⁴⁰ Similarly, the side-on/side-on



θ: Angle between the planes defined by the centroid-Mcentroid of the metallocene unit



Figure 6. (μ -1,2-Dinitrogen)bis(ansa-titanocene) compounds (5).

dinitrogen-bridged bis(*ansa*-zirconocene) and bis(*ansa*-hafnocene) compounds demonstrate a comparable extent of N–N bond lengthening with values of 1.406(4) Å in 6-2 for Zr and 1.457(5) Å in 7 for Hf (Figure 7), which are within the range for the non-*ansa*-metallocene compounds.^{57,58} Of particular note is the more sterically encumbered bis(*ansa*-zircono-



 θ : Angle between the planes defined by the centroid-Mcentroid of the metallocene unit



Figure 7. $(\mu - (\eta^2 : \eta^2) - \text{Dinitrogen})$ bis(*ansa*-metallocene) compounds (6 and 7).

cene)-dinitrogen compound 6-1, in which a short d(N-N) of 1.241(3) Å is observed for the N₂ ligand.⁵⁹

Two general trends for Group 4 dinitrogen compounds are that (i) coordination of a terminal X or L type donor on each metal ion in the bis(metallocene)-dinitrogen adducts affords the μ -1,2-dinitrogen complexes and (*ii*) increasing donor strength of the terminal X or L type ligand leads to greater activation of the μ -1,2-dinitrogen. The coordination isomerization and donor strength effect are most apparent from the following cases. First, similar d(N-N) values are observed for the formally Ti^{II} complexes 1-Cp^R to the formally Ti^{III} complex 8-Cp,p-tolylide (1.162 Å) and bond lengthening for 8-Cp,PMe₃ (1.191 Å) (Figure 9). 60,61 Second, the ansatitanocene in 8-ansa comprises has a slightly contracted bond distance as compared to the 5-1 and 5-2 as a consequence of the weak π -acidity of the terminal N₂ donors (Figure 10).⁴⁰ Third, the formally Zr^{II} complex 9-Cp^{*} and the formally Zr^{III} complex 9-Cp,X and the mixed-valent congener Na[9-Cp,X] where X = bis(trimethylsilyl)methyl also have comparable bond lengths (Figure 8 and Figure 9).⁶² Chirik



Figure 8. Type C complexes: the (μ -1,2-dinitrogen)bis(metallocene) compounds.

and co-workers demonstrated through isotopic labeling studies that **3-Cp'** can coordinate additional dinitrogen donors to generate the Cp' congener for **9-Cp***, evidencing the sensitivity of the coordination mode to the presence of an ancillary donor.⁵³ One notes that the minimal change in bond length upon reduction of **9-Cp,X** to **Na**[**9-Cp,X**] suggests zirconium-centered reduction rather than dinitrogen-based.

G



Figure 9. Additional type C complexes: $(\mu$ -1,2-dinitrogen)bis-(metallocene) compounds containing X-type donor ligands.



Figure 10. An ansa-titanocene type C complex (8-ansa).

Related to these Zr complexes is **10-A** (Scheme 4) in which the terminal chloride donors do not result in a change in coordination mode.⁶² However, one-electron reduction of **10-A** results in a change in mode—which is reversible upon oxidation—to the μ -1,2 mode with close Cl…K⁺ and N₂…K⁺ contacts (**10-B**). A related dihydride congener of **10-A** (^tBu instead of Ad) has also been reported and the N–N bond length of 1.243 Å is substantially shorter than that for **6-2**, highlighting both the oxidation state change as well as electronic structure changes resulting from having two ligands in the equatorial plane of the *ansa*-metallocene.

Fourth, the Hf analog 4-Cp' undergoes coordination isomerization of the N₂ donor upon dimetallic oxidative addition. Reaction of 4-Cp' with alkyl halides, R-X (X = Cl, Br, I), initially affords the corresponding μ -1,2-dinitrogen complexes 11-R/X with the R and X coordinated to different Hf centers; disproportionation of these products yields 4-Cp' and the monometallic Cp'₂Hf(R)(X) species.⁶³ The oxidative addition has radical character based on reaction with radical clock substrates wherein the ring opened or cyclized products Scheme 4. Conversion of 10-A to 10-B



are observed in $11\mbox{-}R/X$ (Scheme 5). Oxidative addition of MeOTf is unique relative to the alkyl halides as ethane is

Scheme 5. Reaction of 4-Cp' with Radical Clock Substrates



produced and 11-OTf₂ is the major complex product.⁶⁴ The bond distances across the 11 series of complexes are comparable. Finally, the bis(hafnocene)–dinitrogen species 4-Cp^{Me124} reacts with 4-(dimethylamino)pyridine (DMAP) to yield the mono(DMAP) adduct 12 (Figure 11). Isomerization is not observed and the N–N distance contracts substantially relative to 4-Cp^{Me124}. The absence of isomerization and the N–N contraction are proposed to arise from the less steric encumbrance of the Cp^{Me124}, as compared to the other bis(hafnocene) compounds, and the lengthening of the Hf…Hf distance upon coordination of DMA from 3.8527(3) Å in 4-Cp^{Me124} to 3.9406(13) Å in 12, respectively.



Figure 11. μ - η^2 : η^2 -N₂-bis(hafnocene) DMAP-adduct.

The mixed indenyl–cyclopentadienyl zirconium complexes also allow access to dimetallic–dinitrogen species. In these complexes, the expanded donor properties of the 10 π -electron indenyl allow access to μ -indenyl species with closer metal– metal contacts. Two reduction outcomes were reported for the Cp*(η^{5} -Ind^{R1,R2})ZrCl₂ complexes (R¹/R² = Me/Me, iPr/Me, tBu/Me; Scheme 6).⁶⁵ Reduction under Ar occurs with

Scheme 6. Reduction of 13-R¹/R²-Cl₂



chloride loss and generates the $(\eta^9 \text{-Ind}^{\text{R1},\text{R2}})\text{Cp}^*\text{Zr}^{\text{II}}$ complexes, **13-R**¹/**R**². Exposure of **13-R**¹/**R**² to dinitrogen yields the *cis-µ*-1,2-dinitrogen complexes $(\eta^5:\eta^2 \text{-Ind}^{\text{R1},\text{R2}})_2(\text{Cp}^*\text{Zr})_2(\mu\text{-1},2\text{-N}_2)$, **13N**₂-**R**¹/**R**², with Zr–N–N bond angles of ~144° and a N–N bond distance of 1.197(3) Å $(\nu_{\text{N-N}} = 1563 \text{ cm}^{-1})$; this coordination mode is rare in dinitrogen coordination chemistry. The second outcome arises from reduction of the dichloride species in the presence of dinitrogen, which yields the chloride- and dinitrogen-bridged complexes $[\text{Cp}^*\text{Zr}]_2(\eta^4:\eta^5\text{-Ind}^{\text{R1},\text{R2}})(\mu-\eta^1:\eta^2\text{-N}_2)(\mu\text{-Cl})$, **14-R**¹/**R**² (Scheme 6). The disposition of the indenyl substituents relative to the chloride and dinitrogen ligands affords two isomers, which evidence nominally different crystallographic

parameters: the N–N distances are 1.196(4) Å and 1.220(10) Å for the *syn* and *anti* isomers of **14-iPr/Me**, respectively.

The bis(η^5 -indenyl)zirconium complexes are also competent for N₂ activation. Addition of excess sodium-mercury amalgam (Na/Hg) to the dihalide complexes affords the dinitrogen-bridged dizirconium complexes 15-Na₂X₂ of which the chloride and the iodide congeners were structurally characterized (Scheme 7).⁶⁶ The N-N bond distances in

Scheme 7. Reduction of $15-X_2$ under N_2 to Yield $15-Na_2X_2$



15-Na₂X₂ (1.352(5) Å and 1.316(5) Å for Cl and I, respectively) are comparable to that in the μ - η^2 : η^2 -dinitrogen complex 9-Cp', albeit with 15-Na₂X₂ being two electrons more reduced than 9-Cp'. Compared to 13N₂-R¹/R² and 14-R¹/R², the absence of π -backbonding from Zr to the benzo unit of the indenyl donor in 15-Na₂X₂ affords more electron-rich metal centers, leading to greater activation of the μ -1,2-dinitrogen.

A few examples of Group 4 monocyclopentadienyl complexes supported by additional ancillary ligands have also been reported to coordinate dinitrogen. The chemistry of a family of *trans* bis(Cp*-amidinato/guadinato-metal)-dinitrogen complexes, **16** and **17**, has been advanced by Sita and coworkers (Figures 12 and 13).^{67,68} The bond metrics and angles



Figure 12. Bis[Cp*(amidinato)titanium]-dinitrogen complex, 16.

for 16 bear a strong resemblance to the related β -diketiminate complex from Bai et al. (18, Figure 14), as one might anticipate from a similar donor atom set.⁶⁹ An end-on/end-on mode is observed for 16 whereas a side-on/side-on mode is observed for the zirconium and hafnium analogs, 17, consistent with the observations for the bis-metallocene compounds. The N–N bond distance increases from the lighter metal to the heavier counterparts with the hafnium congeners showing the longest N–N bond lengths reported of any Group 4 metal dinitrogen complex. In contrast to the bis-metallocene complexes, the M₂N₂ core is bent in a butterfly orientation rather than planar, with dihedral angles ranging from 20.0° in 17-C to the two largest values of 31.3° and 33.3° in 17-E and 17-D, respectively. This bending is correlated with π backdonation from each metal center to orthogonal π^* orbitals



Figure 13. Bis[Cp*(amidinato or guanidinato)-zirconium or -hafnium)-N₂ compounds (17-Zr and 17-A-E) featuring side-on/ side-on N₂ coordination mode.



Figure 14. Piano stool bis $[(Cp)(\beta$ -diketiminato)tititanium $](\mu$ -1,2-N₂) complex, **18**.

on the N₂ fragment. These complexes boast the longest N–N distances in a dimetallic complex with values almost 0.2 Å greater than that in hydrazine.^{47,49} Impressively, the N atoms in **17-D** and **17-E** can be alkylated with alkyl bromides—the first such example for any N₂ derived complex. A side-product containing a bromide bonded to each hafnium center $\{Cp^*Hf(Br)[N(Et)C(Me)N(Et)]\}_2(\mu-\eta^2:\eta^2-N_2)$ was observed for reaction of **17-E** with alkyl bromides.

In addition to the Sita and Stephan examples above, Nishibayashi and Hou have reported the remaining examples of monocyclopentadienyl complexes. Nishibayashi and coworkers accessed *cis-µ*-1,2-dinitrogen complexes of titanium and zirconium supported by a PNP pincer ligand and cyclopentadienyl (Figure 15).⁷⁰ Here, the PNP pincer ligand coordinates in a $\kappa^2 NP$ fashion in the case of Ti (19-Ti) affording a three-legged piano stool geometry with one dangling phosphine arm whereas the pincer coordinates $\kappa^3 PNP$ for the Zr congener (19-Zr) resulting in a fourlegged-piano-stool geometry. The M_2N_2 core deviates



Figure 15. Three- and four-legged piano stool dinuclear Ti- or Zr- μ -1,2-N₂-bridged complexes, **19-Ti** and **19-Zr**.

significantly from linearity with Ti–N–N angles of 158.9° and 159.6° for **19-Ti** and 163.7° for **19-Zr**, and the N–N bond distances are comparable to previously discussed μ -1,2-dinitrogen compounds with values of 1.247(3) Å and 1.287(4) Å for **19-Ti** and **19-Zr**, respectively.

As noted above, one expects a linear $M_2(\mu-1,2-N_2)$ unit to maximize π -backbonding to the bound N_2 in these complexes. The deviations from linearity observed for a number of Group 4 complexes with elongated N–N bonds hint at charge transfer and decreased covalency for Ti, Zr, and Hf as compared to the late transition metals.

Notable among the previously discussed monocyclopentadienyl compounds is the example from Hou and co-workers, which is the first example of complete scission of N₂ by a titanium hydride complex.⁷¹ Hydrogenolysis of (η^{5} - $C_{5}Me_{4}SiMe_{3}$)Ti(CH₂SiMe₃)₃ (**20-alk**₃) with H₂ affords heptahydride **20-H**₇, which readily cleaves N₂ to yield trititanium complexes with μ_{3} -nitride, μ -imide, and μ -hydride donors (Scheme 8). Cotreatment of **20-alk**₃ with H₂ and N₂





instead generates a tetratitanium complex with a cubane-like cluster containing two μ_3 -imides arising from N₂ bond scission. ¹⁵N NMR kinetic studies at low temperature suggested a hydrazide intermediate; further characterization of this temperature-sensitive transient, however, has yet to be reported.

3.1.2. Tetra- and Tridentate PN and Related Ligand Complexes. In addition to the Cp-ligated titanium centers, other supporting ligands have been utilized for coordination and activation of dinitrogen. A common aspect, however, remains the use of reducing titanium(II) or (III) species either generated *in situ* or first isolated.

Fryzuk and co-workers have utilized a tetranucleating $P^{Ph}_{2}N_{2}$ ligand to support dimetallic Ti and Zr dinitrogen complexes generated by reduction of the dichloride precursor with KC₈ (Figure 16)^{72,73} In a theme repeated from the metallocene examples, the Ti₂ complex **21** is an end-on/end-on complex, whereas the Zr₂ analog is a μ - η^{2} : η^{2} - dinitrogen complex. In both complexes the N–N bond is quite elongated; the bond is of the order of hydrazide for **22-N**₂ and the value in **21** is on par with those reported by Sita and co-workers (viz. **16**). Compound **22-N**₂ reacts with dihydrogen in toluene to afford **22-N**₂H/H in which N–H and Zr–H bonds are formed—the first example of Haber–Bosch-like reactivity in a molecular



21 d(N–N): 1.255(7) Å

Figure 16. Titanium-dinitrogen complex 21 supported by a tetranucleating $P^{Ph}_{2}N_{2}$ ligand.

system (Scheme 9). The N–N bond contracts from 22-N₂ to 22-N₂H/H (1.389 Å), suggesting oxidation of the N₂ ligand in 22-N₂ to facilitate Zr–H bond formation. A theoretical study on P_2N_2 –Zr complexes shows a preference for folding the

Scheme 9. Reaction of 22-N₂ with H₂



 Zr_2N_2 core as the system becomes less sterically encumbered.⁷⁴ The electronic rationale for the bending in the absence of steric conflicts is that bending leads to more uniform distribution of electron density between the Zr centers and N₂ and enhances π bonding from the amide lone-pairs to Zr.⁷⁵

Removal of a phosphine donor arm in **21** (viz. from $P^{Ph}_{2}N_2$ to $P^{Ph}N^{Ph}_{2}$) results in a dramatic change in the reduction outcome in the case of titanium: complete scission of the N–N bond and insertion of N atoms into the Ti–P bonds is observed.⁷³ The reaction is proposed to proceed with initial N₂ cleavage to the di(μ -nitride) followed by N atom insertion to yield the observed product, **23** (Scheme 10). Contrastingly,

Scheme 10. Proposed Mechanism for Formation of 23



the side-on/side-on bridged dizirconium complex 24 is isolable and is analogous to $22-N_2$ if one accounts for substitution of a THF donor for the second phosphine arm (Figure 17).



Figure 17. Side-on/side-on dizirconium-N₂ complex 24 supported by a diamido phosphine ligand $(P^{Ph}N^{Ph}_{2})$.

Although a titanium analog has not been reported, the $P^{tol}N^{Mes}_2$ ligand stabilizes a similar $Zr_2(\mu \cdot \eta^2 : \eta^2 \cdot N_2)$ species, 25-2THF, in which THF coordinates to the metal center as in 24 (Figure 18). The solvent molecules in 25-2THF can be readily substituted for pyridine or PhPMe₂ to afford the 25-2py and 25-PR₃, respectively, and with comparable N–N bond distances to that in 25-2THF. In 25-PR₃, only one PhPMe₂ is coordinated to the dimetallic, presumably because of steric crowding of the mesityl substituents. For 24 and the 25 series, the ZrN₂ plane contains the P-donor atom of the P^RN^R₂ ligand with the two zirconium-amide bonds lying perpendicular to that plane, likely arising from the favorable interactions from the π -donating amides. The similar N–N bond distances for 24 and the 25 series are noted despite the planar Zr₂N₂ unit in 24 vs the slightly bent one in 25 (12.3°-15.4°). Similar H₂



Figure 18. Side-on/side-on dizirconium–dinitrogen complex 25-2THF employing a diamidophosphine chelate $(P^{tol}N^{Mes}_{2})$.

activation is observed for $25\text{-}PR_3$ as for $22\text{-}N_2$ with formation of a Zr–H and N–H bonds.

Arnold and co-workers reported the dititanium and dizirconium dinitrogen complexes bearing the tripodal $P_2^{Me2}N_2^{tBu}$ ligand (Figure 19).⁷⁶ In spite of the four pnictogen





donor atoms afforded by the ligand, dinitrogen complexes **26**-**Ti/CH₂SiMe₃** and **26-Zr** retain only $\kappa^3 NNP$ coordination to the metal centers with a halide or alkyl completing the metal coordination sphere. In the solid-state structure of these complexes, each metal center is pentacoordinate with one noncoordinated phosphine arm, likely due to steric congestion around the metal centers. The μ - η^2 : η^2 mode is observed for **26-Zr**, and the N–N distance is the longest reported for any dizirconium dinitrogen complex. The purported chloride analog **26-Ti/Cl** has an IR absorption at 1300 cm⁻¹ attributed to the N–N stretching mode, comparable to that for **26-Ti/ CH₂SiMe₃** (1270 cm⁻¹), implying that both complexes adopt a similar coordination mode.

Completing the combination of tridentate PN donor ligands are the PNP pincer type complexes reported by Hou (Ti, 27) and Fryzuk (Zr, 28-X) and their respective co-workers (Figure 20). The hydrogenation of a PNP-ligated organotitanium complex with H_2 yields the related titanium tetrahydride compound, which undergoes reductive elimination in the



Figure 20. Dititanium– and dizirconium–dinitrogen compounds (27 and **28-Cl**, respectively) supported by amidodiphosphine (PNP) pincer type ligands. Complex **27** exhibits a rare μ - η^1 : η^2 -dinitrogen mode.

presence of N₂ to form {[$(N^{ph}P^{iPr}_{2})Ti$]₂(μ - η^{1} : η^{2} -N₂)(μ -H)₂}, 27.⁷⁷ The N–N bond at 1.301(3) Å is one of the longest reported for any titanium complex, only exceeded by those distances in the titanotrane complexes (*vide infra*). As noted by van Tamelen,³⁴ a broad range of Ti complexes are competent for the partial or complete cleavage of N₂ to generate hydrogenated N₂ derived species and 27 is no exception; further reaction of 27 with H₂ effects N₂ cleavage and formation of a dititanium(IV) complex comprising N₂-derived μ -imide and μ -nitride ligands.

A related meridionally coordinating ligand to that in 27 is the diarylether-dianilide pincer-type ligand that provides access to the μ -1,2-dinitrogen adduct, $[(^{iPr}NON)Ti-(PMe_3)_2]_2(\mu$ -1,2-N₂) (29, Figure 21).⁷⁸ The synthesis



Figure 21. Complex $[({}^{iPr}NON)Ti(PMe_3)_2]_2(\mu-1,2-N_2)$, 29.

proceeds through a proposed decomposition of (${}^{Pr}NON$)Ti-(CH₂CHMe₂)₂ in the presence of PMe₃ through β -hydride elimination, followed by H₂ reductive elimination and then N₂ coordination. The N–N bond distance of 1.264(8) Å in **29** is expectedly shorter than that in **27** given the weaker donor strength of the ethereal oxygen atom.

Rettig et al. reported the PNP pincer ligated Zr_2N_2 complex **28-Cl**,⁷⁹ which is conceptually related to **22-N**₂ by removal of N donor; in fact, the N₂P ligands in **24** and **28-X** are conceptual deconstructions of the N₂P₂ macrocycle in **22-N**₂. The N–N bond length observed in the solid-state structure of **28-Cl** is 1.548(7) Å, which is one of the longest distances

reported for any dinitrogen complex to date. Replacing the chloride with Cp⁻ results in the formation of an end-on/endon dinitrogen complex **28-Cp** as Cp⁻ competes for metal π backbonding interactions as well as introducing steric repulsions between Zr fragments.³² To further highlight the electronic effects, the related aryloxide complexes **28-OAr** (ArO⁻ instead of Cl⁻) also afford the side-on/side-on complex {[(Prⁱ₂PCH₂SiMe₂)₂N]Zr(OAr)}₂(μ - η ²: η ²-N₂) with a similar N–N bond length (1.528(7) Å) to the chloride congener.⁸⁰

A few examples of ligands have been used in which only titanium-centered complexes are reported. Gambarotta and coworkers reported the first example of a titanium dinitrogen species without using cyclopentadienyl donors: $[Ti(TMEDA)-(N(Me_3Si)_2)Cl]_2(\mu-1,2-N_2)$, **30** (Figure 22).⁸¹ This complex



Figure 22. Compounds $[Ti(TMEDA)(N(Me_3Si)_2)Cl]_2(\mu-1,2-N_2)$ (30) and $[Li(TMEDA)_2][\{[(Me_3Si)_2N]_2Ti\}_2(\mu-\eta^2:\eta^2-N_2)_2]$ (31).

was isolated from reaction of 1 equiv of LiHMDS with *trans*-Ti(TMEDA)₂Cl₂ and displayed an elongated N–N bond and short Ti–N(N₂) bonds with distances of 1.289(9) and 1.762(5) Å, respectively, consistent with a diazenide (N₂²⁻) complex. Contrastingly, upon addition of 2 equiv of LiHMDS to Ti(TMEDA)₂Cl₂, the formally dititanium(I/II) bis(μ - η^2 : η^2 dinitrogen) complex, [Li(TMEDA)₂][{[(Me₃Si)₂N]₂Ti}₂(μ - η^2 : η^2 -N₂)₂], is isolated (**31**, Figure 22).⁸¹ The N–N bond length (1.379(21) Å) is longer than the end-on/end-on complex as one might anticipate and suggests a formally N₂^{3-/4}ligand with Ti^{III} centers.

Despite extensive precedent for N₂ transformation to NH₃ and N₂H₄ by protonolysis or hydrogenation of dinitrogen adducts from late transition metals, examples of catalytic dinitrogen fixation employing titanium—or more broadly, any metal complex preceding Group 6-were unknown until recently. Doyle et al. provided the first such example based on titanatrane complex 32, [(tren^{TMS})Ti]₂(μ -1,2-N₂) (tren^{TMS} = $[N(CH_2CH_2NSiMe_3)_3]^{3-}$ (Scheme 11).⁸² The short N–N distance of 1.121(6) Å, observed X-band EPR signals, and solution magnetic susceptibility data agree with formally $\mathrm{Ti}^{\mathrm{III}}$ centers in 32. Data on the related two-electron reduced complexes $K_2\{[(tren^{TMS})Ti]_2(\mu-1,2-N_2)\}$ or 32-red, and $[K(benzo-15-crown-5)]_2\{[(tren^{TMS})Ti]_2(\mu-1,2-N_2)\}$ or 32crown provide evidence for the significant N₂ π^* character in the LUMO of 32. Briefly, the \sim 0.2 Å increase in the N–N bond length, shorter $Ti-N(N_2)$ distances, decreased N–N stretching frequency (1701 cm⁻¹ vs 1201/1246 cm⁻¹ for 32 vs 32-red/30-crown), and calculated Mayer bond orders for the $Ti-N(N_2)$ and N-N bonds are all consistent with reduction of 32 populating an orbital with significant N₂ π^* character (Scheme 11). Notably, encapsulation of the K^+ ions in **32-red**

Scheme 11. Two-electron reduction of 32



to afford **32-crown** leads to an increase in the N–N stretching frequency, suggesting an electrostatic contribution from the close association of the K⁺ cations with the N₂ ligand in **32-red**. Protonolysis of **32-red** affords predominantly N₂H₄ (0.88 equiv) together with a smaller amount of NH₃ (0.13 equiv). Complex **32-red** is competent for atmospheric N₂ fixation to ammonia, using $[Cy_3PH][I]$ and KC_8 as the proton and electron source, respectively, with the optimized conditions affording 18 equiv of NH₃ per **32-red**.

A bis(titanatrane) dinitrogen complex **33**, $[[K(THF)_2]-[K_2(\mu-THF)]\{([O_3C]Ti)_2(\mu-1,2-N_2)\}]^-$, from Nakanishi et al. bears structural similarity to **32-red** $([O_3C]^{4-} = [(3,5^{-t}Bu_2-2-O-C_6H_2)_3C]^{4-}$, Figure 23).⁸³ The N–N bond length



d(N–N): 1.320(5) Å, v_{N-N} : 1265 cm⁻¹

Figure 23. Bis(titanatrane)-N₂ complex 33, $[[K(THF)_2][K_2(\mu-THF)]\{([O_3C]Ti)_2(\mu-1,2-N_2)\}]^-$.

(1.320(5) Å), short Ti–N bond distances (1.797(4)– 1.802(4) Å), and the N–N stretching frequency (1265 cm⁻¹) support Ti–N multiple bond character and a $N_2^{2^{-/4-}}$ formalism and are comparable to those values reported for **32-red**. The reduced dinitrogen fragment in **33** reacts in a nucleophilic fashion with CO₂, *tert*-butylisocyanate and phenylallene to generate the C–N bonded product.

One other complex has been reported in which approximate 3-fold rotational symmetry about the Ti atoms is enforced.

Reduction of the subsite-differentiated heterocubane cluster $Cp^*{}_3Mo_3(\mu_3-S)_4TiCl_2$ or $(Mo_3TiS_4)Cl_2$ with 4 equiv of KC_8 under a dinitrogen atmosphere yields an octanuclear complex in which dinitrogen bridges two cubanes, viz. [K-(THF)]_2[(Mo_3TiS_4)_2(\mu-1,2-N_2)], 34-K_2 (Figure 24).⁸⁴ As







d(N–N): 1.293(5) Å

Figure 24. Subsite-differentiated heterocubane Mo_3Ti clusters 34- K_2 and 34- K_3 bridged by a linear N_2 donor.

observed in the bis-titanatrane complexes **32-red** and **33**, K⁺ cations are in close contact with the bridging N₂ ligand in **34-K**₂. The elongated N–N bond (1.294(7) Å) and low energy for the N–N stretching mode from resonance Raman spectra (1240 cm⁻¹) indicate a strong back bonding interaction from the Ti centers to the N₂ donor, with the latter formally between diazenide and hydrazide. Addition of 6–10 equiv of KC₈ to **34-K**₂ affords trace amounts of $[K_3(THF)_5]$ - $[(Mo_3TiS_4)_2(\mu$ -1,2-N₂)] (**34-K**₃). X-ray diffraction analysis showed a similar N–N bond length and elongation of the Ti-Mo and Mo–Mo distances as compared to those in **34-K**₂, suggesting a metal-based reduction instead of the bridging N₂ unit.

Using amidinates and guanidinates, Arnold and co-workers accessed a series of μ -1,2-dinitrogen-dititanium compounds of the type $[(XC(NR)_2)_2Ti]_2(\mu$ -1,2-N₂), **35-X/R** (Figure 25).⁸⁵ The N–N and Ti–N(N₂) bond metrics across the series suggest double bond character in the Ti–N(N₂) bond. Coordination of pyridine to **35-Ph/SiMe**₃ results in a shortening of the N–N bond and lengthening of the Ti–N(N₂) bonds; for **35-Ph/SiMe**₃/**py**, the N–N and Ti–N(N₂) bond length is 1.264(5) Å and ~1.800 Å, respectively.

Mindiola and co-workers reported a $[(P^{iPr}N^{tol})_2Ti]_2(\mu-1,2-N_2)$ (36, Figure 26) and investigated possible scission of dinitrogen to the terminal-nitride complex.⁸⁶ The crystallo-



Figure 25. [Bis(amidinato or guanidinato)titanium](μ -1,2-N₂) complexes, 35-X/R.



Figure 26. Complex $[(P^{iPr}N^{tol})_2Ti]_2(\mu-1,2-N_2)$, 36.

graphically observed N–N bond length of 1.252(8) Å agrees well with other titanium complexes supported by ligands bearing pnictogen donor atoms (e.g., 21-32, 35-X/R). N–N cleavage was, however, not observed upon further reduction of 36, which contrasts the result reported by Fryzuk for 23 and is attributed to the rigidity of the P^{iPr}N^{tol} ligand.

The final titanium example is that from Kawaguchi and coworkers who reported (μ -1,2-dinitrogen)dititanium complexes bearing bulky *p*-terphenoxide ligands (denoted OO²⁻) (Figure 27). In the series of complexes [(OO)Ti(L)]₂(μ -1,2-N₂) (37-L), the large bite angle of OO²⁻ enforces a pseudosquare pyramidal coordination environment about the Ti centers with the bridging N₂ occupying the axial site.⁸⁷ The energy of the N–N stretching mode for 37-DME and 37-Py of 1394 and



Figure 27. Compounds $[(OO)Ti(L)]_2(\mu-1,2-N_2)$ bearing bidentate *p*-terphenoxide ligands, 37-L.

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1362 cm⁻¹, respectively, suggests substantial backbonding from titanium to N_2 .

3.2. Group 5: V, Nb, and Ta

The reported dinitrogen complexes of the Group 5 metals are exclusively dimetallic with the μ -1,2 coordination mode predominating. Churchill and Schrock reported alkylidene complexes of the type $[Ta(R)Cl(PMe_3)_2]_2(\mu$ -1,2-N₂), **38-1** (R = neopentylidene or Np^{ene}) and **38-2** (R = ethylene or Et^{ene}), synthesized by reduction of TaCl₃(R)(PMe₃)₂ in the presence of excess PMe₃ under a dinitrogen atmosphere.⁸⁸ Substitution of the chloride ligand in **38-1** can be effected using neopentyllithium or methyllithium to generate $[Ta(Np^{ene})-(R')(PMe_3)_2]_2(\mu$ -1,2-N₂), R = Me **38-3** and R = Np **38-4** (Figure 28). Complex **38-3** was the first crystallographically



Figure 28. Organometallic ditantalum-N2 complexes 38-3 and 38-4.

characterized multimetallic dinitrogen species of Group 5 metal. The observed N–N and M– $N(N_2)$ bond distances, ¹⁵N NMR chemical shifts, and $\nu_{\rm N-N}$ at 847 cm⁻¹ strongly indicate metal-imide character and substantial charge transfer to the N2 ligand. Such activation of the N2 ligand is common for Group 5 metal complexes with a formal N_2^{4-} or a diimide ligand and metal ions in the +4 or +5 oxidation states typically invoked. Building from this seminal report, more than fifty-five Group 5 dimetallic-dinitrogen complexes have been reported with various supporting ligands, including cyclopentadienyl, chelating ligands with pnictogen or chalcogen donor atoms, and other organometallic ligands (e.g., mesityl). Our survey begins with complexes that are part of the isostructural series for different metal ion types (e.g., isostructural V₂ and Ta₂ complexes) and then ends with compounds of only one metal ion type (e.g., only V complex known). For both sections, we begin with aromatic or closely related ligands (e.g., Cp) and subsequently consider other supporting ligands in decreasing ligand denticity.

3.2.1. Dinitrogen Complexes of Group 5 Metals Using Common Supporting Ligands. The cyclopentadienylamidinate/guanidinate supported dimetallic dinitrogen species 39-M/R (M = V, Nb, Ta and R = Me, Ph, and NMe₂) constitute the only isostructural series with representatives from each of the Group 5 metals (Figure 29).^{89,90} These complexes are typically synthesized by chemical reduction of the pentavalent precursors. For example, reduction of Cp*- $[N(Pr)C(Me)N(Pr)]TaCl_3$ with 4 equiv of KC₈ yielded $\{Cp^*Ta[N(^{i}Pr)C(Me)N(^{i}Pr)]\}_2(\mu-1,2-N_2)$ (39-Ta/Me). Across the 39 series, the dinitrogen ligand is coordinated in a μ -1,2 fashion even for the Nb and Ta congeners, contrasting the transition from the μ -1,2 in Ti to the μ - η^2 : η^2 mode observed for the analogous Zr and Hf analogs. Consistently then, one notes that the N-N bond distances for 39 (Figure 29), with values from 1.225(2) Å for 39-V/Me and ~1.31 Å for 39-Ta/Ph and 39-Ta/NMe2, are comparable to 16 (1.270(2) Å) and decidedly shorter as compared to those of 17, for which the values range from 1.518 Å for 17-Zr to 1.635(5) Å for 17-E (Figure 13). Isomerization of the μ -1,2 isomers of 39 to the side-on/side-on coordination mode is



Figure 29. Bis[Cp*(amidinato or guanidinato)metal)-dinitrogen compounds 39-M/R where <math>M = V, Nb, and Ta.

likely thermally accessible, making it a plausible transition state for the observed N-N bond homolysis for **39-Nb/R** and **39-Ta/R** complexes (Scheme 12). Additional support for this

Scheme 12. Proposed N₂ Scission via μ -1,2 to μ - η^2 : η^2 Isomerization



isomerization is provided by the observed product (40-R) from the reaction of 39-Ta/R with N₂O, in which a side-on/ side-on hydrazide ligand is observed (Scheme 13).^{91,92} The ligand sterics strongly influence the stability of the N₂ complex primarily through changes in ΔS^{\ddagger} for conversion of the μ -1,2dinitrogen species to the di(μ -nitride) isomer. Complex 39-Ta/Me readily reacts with H₂, phenylsilane, and diphenylsul-

Scheme 13. Reaction of 39-Ta/R with N_2O





fide; for example, reaction with phenylsilane affords {Cp*Ta-(R')[N(ⁱPr)C(Me)N(ⁱPr)]}(μ -1,2-N₂){Cp*TaR[N(ⁱPr)C-(Me)N(ⁱPr)]} (41-R/R', R = SiH₂Ph, R' = H; Figure 30).⁹³



41-R/R', R = R' = H, d(N–N): 1.307(6) Å **41-R**/R', R = SiH₂Ph, R' = H, d(N–N): 1.284(4) Å **41-R**/R', R = R' = SPh, d(N–N): 1.297(3) Å

Figure 30. $Bis[Cp*(amidinato)tantalum](\mu-1,2-dinitrogen)$ compounds (41-R/R').

These reactions result from a bimetallic oxidative addition with retention of the bridging N₂ ligand and minimal changes to the N–N bond distances. These products of oxidative addition are structurally related to the dichloride complex *rac*-{Cp*Ta-(Cl)[N(ⁱPr)C(Me)N(ⁱPr)]}₂(μ -1,2-N₂) or **41-Cl/Cl** (Figure 31), which is accessed by reduction of Cp*[N(ⁱPr)C(Me)N-



Figure 31. Bis[Cp*(amidinato)tantalum](μ -1,2-N₂) compound, 41-Cl/Cl.

(ⁱPr)]TaCl₃ with 2.5 equiv of KC₈. The N–N bond (1.29(1) Å) is elongated in this compound relative to free N₂, but the value is comparable to that of **39-Ta/Me**, suggesting a metalcentered reduction as one transitions from the formally moreoxidized Ta centers in the dichloride compared to those in **39-Ta/Me**. Although analogous complexes of V and Nb are not reported, we consider the tantalum amidate complexes **42-**R/ **R'** (Figure 32) here insofar as the comparison to the amidinate



Figure 32. Bis[Cp*(amidato)tantalum](μ -1,2-dinitrogen) compounds, 42-R/R'.

complex **41** is worthwhile.⁹⁴ Of the two synthesized examples, the only solid state structure reported was that for **42-Xyl**/^t**Bu** in which a primary coordination sphere is strongly similar to that in **41** with the amidinate in **41** substituted to an amidate to afford **42-Xyl**/^t**Bu**. Consistently then, the N–N distance of 1.292(4) Å is determined for **42-Xyl**/^t**Bu**, which is within error of the value determined for **41**.

The remaining examples comprise complexes in which the same ligand has been used for only two of the possible three metals. Mindiola and co-workers reported the V and Nb complexes, **43-V/N** and **43-Nb**, of closely related PNP ligands derived from diphenylamine (Figure 33 and Figure 34).^{95–98}



Figure 33. Compounds 43-V/Np and 43-V/X supported by meridional PNP pincer ligands.



Figure 34. Diniobium-dinitrogen complex 43-Nb.

The metal coordination sphere is completed by chloride (43-Nb) or an imide or alkylidene (43-V/N or /Np, respectively). The N–N bond distances nominally increase as one moves from imide to alkylidene and then from V to Nb with values ranging from 1.222(4) Å to 1.277(6) Å for 43-V/N to 43-V/Nb. The calculated Mayer bond orders for 43-V/Nb are consistent with the bond metrics, with values of 1.3 and 1.5 for the Nb–N(N₂) and N–N bonds, respectively.

In contrast to the monoanionic PNP ligand based on diphenylamine, the Fryzuk group developed a dianionic diamide-phosphine ligand, NPN^{Ph}, for which the Ph superscript refers to the substituent on the amide N atoms. Complexes of Nb and Ta are known for this ligand set; the chemistry of the Ta congener has been reported to a greater extent. The ligand does not adopt the meridional orientation of a typical pincer ligand but rather coordinates in a facial geometry, as noted for the Nb₂(μ -1,2-N₂) complex **44-Nb** (Figure 35).³³ The extent of activation of the N₂ fragment in



Figure 35. Complex 44-Nb in which a dianionic diamidophosphine ligand, NPN^{Ph}, adopts a *fac* coordination mode.

this complex (d(N-N) = 1.237(4) Å) is comparable to that of the example from Mindiola **43-Nb**, in agreement with analogous formally $[Nb_2(N_2)]^{6+}$ fragments and the μ -1,2-dinitrogen coordination mode observed in both.

In contrast to 44-Nb in which reduction of the metal halide precursor was used to access the N₂ adduct, the hydride route was used for the related Ta complex: the ditantalum tetra(μ hydride) complex 44-Ta/4H reacts readily with dinitrogen to generate $(NPN^{Ph}Ta)_2(\mu-H)_2(\mu-\eta^{1}:\eta^2-N_2)$, 44-Ta/2H,N₂ (Scheme 14).⁹⁹ As noted previously, the side-on/end-on coordination mode is uncommon in dinitrogen chemistry and, here, the steric constraints placed on the metal-metal distance as a consequence of the small bridging hydrides precludes access to the end-on/end-on bridging mode. Such a comparison is reminiscent of the short metal-metal separations enforced in the indenyl dizirconium complex 14- $\mathbf{R}^{1}/\mathbf{R}^{2}$ in which a similar μ - η^{1} : η^{2} interaction is observed. Indeed, insertion of propene into $44-Ta/2H_{1}N_{2}$ affords the terminal dipropyl complex $(NPN^{Ph}Ta(nPr))_2(\mu-1,2-N_2)$ relaxing the short metal-metal separation (albeit introducing new conflicts between the ligand and the propyl groups).

The last category of isostructural complexes comprises the monodentate amide and RO⁻ ligands. For the amides, examples in which the R substituents are identical have been reported. These compounds are the (μ -1,2-dinitrogen)-bis-[tris(dialkylamido)vanadium/niobium] complexes **45-M/R** in which M/R = V/iPr, V/Cy, and Nb/Cy (Figure 36).^{95,100} Access to the tris(amide) and μ -1,2-dinitrogen complexes for V and Nb contrasts the bis(amide) and side-on/side-on N₂ ligands in **31**, reflecting the greater extent of reduction of the metal centers and the sterics of the R group in **31** as compared to **45**. The reported values for d(N–N) of 1.27(1) Å and 1.34(1) for the V and Nb congeners of **45** agree with the

Scheme 14. Synthesis of 44-Ta/2H₂N₂

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Figure 36. Bis[tris(dialkylamido)-vanadium or -niobium](μ -1,2-dinitrogen) complexes 45-V/R and 45-Nb/Cy.

observed trend of greater activation by the heavier *d*-block metal. By comparison, ^tBu₂MeCO⁻ and ^tBu₃SiO⁻ were employed for V (**46-V**) and Nb (**46-Nb**), respectively, to generate complexes with approximate D_{3d} symmetry for the (RO)₆M₂(μ -1,2-N₂) core (Figure 37).^{101,102} Complex **46-V** is



Figure 37. Bis[tris(alkoxy)vanadium] and bis[tris(siloxy)niobium] dinitrogen complexes 46-M.

the only example of a vanadium dinitrogen complex supported by alkoxide donors. The N–N bond distances and V–N bond distances (longest values of 1.232(3) Å and 1.773(2) Å, respectively) agree with the expected change in the donor properties from amide to alkoxide. Complex **46-Nb** has a singlet ground state, it is generated from the S = 1Nb(OSi⁶Bu₃)₃(PMe₃) complex with catalytic amounts of reductant under an N₂ atmosphere. This orbital symmetry forbidden reaction begins with initial formation of an S = 1/2 $[(^{t}Bu_{3}SiO)_{3}NbN_{2}]^{-}$ transient, which subsequently displaces PMe₃ on an unreacted Nb(OSi^fBu₃)₃(PMe₃) to afford the oneelectron reduced form of **46-Nb**. Oxidation of this anionic species by 1 equiv of Nb(OSi^tBu₃)₃(PMe₃) restarts the substitution process to ultimately afford **46-Nb** as the observed major product. As for the **45-V/R** and **46-V**, the N–N bond distances for the siloxide complex **46-Nb** are slightly shorter than that of the **45-Nb** (1.310(4) Å vs 1.34(1) Å).

3.2.2. Ligand Systems Unique to Vanadium–Dinitrogen Complexes. Only two examples of dinitrogenbridged cyclopentadienyl-vanadium fragments have been reported thus far. The first is the amidinate complex **39-V**/ **Me** from Sita and co-workers which was discussed above as part of the amidinate–cyclopentadienyl series.⁸⁹ The other example is **47**, which was reported by Liang and Liu (Figure **38**).¹⁰³ Here, the short N–N bond distance of 1.212(8) Å is



Figure 38. Piano stool divanadium-dinitrogen complex, 47.

consistent with competing π -backbonding interactions between the V center and the cyclopentadienyl and alkyne, which deplete the electron density at the metal center available for π bonding to N₂.

Transitioning to all N atom donor ligands, the tetradentate tris(aminoethyl)amine derived (or tren^{3–}) ligands and the tridentate 1,1,1-tris(isopropylaminomethyl)ethane afford μ -1,2-dinitrogen divandium complexes with comparable structures (Figure 39).^{104,105} For example, tren^{3–} complexes **48-X**



48-1 (R = ^{*i*}Bu), d(N–N): 1.203(4) Å **48-2** (R = EtBu), d(N–N): 1.221(4) Å **48-3** (R = 3,5-^{*i*}Pr-Bn), d(N–N): 1.200(5) Å



Figure 39. Dinitrogen-bridged bis(triamidovanadium) complexes 48-X and 49.

adopt approximate D_{3d} symmetry as does **49** and exhibit similar N–N and V–N(N₂) bond distances across the four compounds. The $\nu_{\rm NN}$ energies for **48-X** range from 1399 to 1402 cm⁻¹ and are in good agreement with the observed crystallographic N–N distances. The slight elongation of the N–N bond in **49** as compared to **48–1** or **-2** is consistent with the expected weaker V–N₂ σ interaction. Using a dianionic N₃ tripodal chelate related to the triamide in **49**, Clentsmith et al. demonstrated complete cleavage of dinitrogen at vanadium centers—the first example of N_2 to two nitrides on V (Scheme 15).¹⁰⁶ One-electron reduction of the bis(amido)amine-ligated

Scheme 15. Synthesis of $Di(\mu$ -nitride) 50



vanadium(III) chloride yields the di(μ -nitrido)divanadium(V) complex **50**, for which the crystallographic μ -N··· μ -N distance of 2.50(2) Å far exceeds that for hydrazine (cf. 1.45 Å).^{49,107} One electron reduction of **50** yields the anionic mixed-valent V^{IV/V}₂ complex, which is structurally unremarkable compared with **50** in the context of N₂ activation.

A few meridional, chelating ligands have been exploited in vanadium dinitrogen chemistry. Starting with all N chelates, Vidyaratne and Gambarotta (51-1 and -2) and Milsmann and Chirik (51-3) reported the synthesis of divanadium–dinitrogen adducts supported by redox active pyridine diimine chelates (Figure 40).^{108,109} The comparable ligand field for



Figure 40. Dinitrogen-bridged bis[bis(imino)pyridine-vanadium] complexes 51.

these complexes translates into analogous N–N and V–N(N₂) bond distances with values ranging from 1.232(3)-1.259(6) Å for the former and 1.777(2)-1.798(2) Å for the latter metrics. The M–N–N angles slightly deviate from linearity with values ranging from 162.4(2) to 167.2(1)° and likely arise from the steric effects of the near interdigitated diisopropylphenyl groups. The bond metrics for the pyridine diimine chelates in **S1-1** and -**2** imply a reduced ligand.

Somewhat related to the N₃ mer-chelates in **51** is the (μ -1,2dinitrogen)divanadium complex **52** from Vidyaratne et al. wherein the metal coordinates to the central *N*-methylpyrrole ring in an η^5 manner.¹¹⁰ The N–N and V–N(N₂) bond lengths (viz. 1.248(5) Å and 1.752(6) Å, respectively) compare favorably to those in **48**, **49**, and **51**, suggesting a formal V oxidation state of +3 or greater in **52** and contradicting the solution magnetic moment of 3.52 μ_B /per V atom. Surprisingly, reduction of **52** affords the (μ -nitrido)- divanadium(III/IV) complex (Scheme 16) as well as other unidentified byproducts, implying the N–N bond cleavage with possible intermediacy of mononuclear vanadium nitride species.





Nishibayashi and co-workers used the diphosphinopyrrolide ligand in **19** to synthesize the related divanadium complex **53** (Figure 41) in which the π -donating phenoxide completes the



Figure 41. Divanadium- μ -1,2-dinitrogen complex **53** wherein each V is ligated by a diphosphinopyrrolide pincer ligand and a phenoxide.

coordination sphere. Complexes **43-V/R** have related ligand fields arising from a comparable PNP pincer ligand and ancillary π -donating ligands (i.e., RHC²⁻, RN²⁻, and RO⁻). From the analogous N–N and V–N(N₂) bond distances across the series, one infers similar formal charges of the N₂ ligand (i.e., diazenide), suggesting V oxidation states of +4 in **43-V/R** and +3 in **53**.¹¹¹ Compound **53** is a competent catalyst for N₂ fixation to NH₃, albeit less effective based on turnovers than examples to be presented later, with highest reported turnovers of 12 equiv of NH₃ and 1.8 equiv of N₂H₄ per complex.

The final two examples of compounds with all pnictogen donor atoms are the amidinate (54) and the β -diketiminate (55) complexes. The bis[bis(amidinato)vanadium] μ -1,2-dinitrogen complexes [(RNC(R')NR)₂V](μ -1,2-N₂), 54-1 or -2 (R/R' = SiMe₃/Ph for 54-1 and Cy/Me for 54-2) (Figure 42), are accessed by reduction of the respective monometallic V^{III} chloride precursor using NaHBEt₃.¹¹² Only 54-2 was characterized by X-ray crystallography; the reported N–N and V–N(N₂) distances of 1.235(6) Å and 1.756(5) Å, respectively, are analogous to the examples mentioned above



Figure 42. Bis[bis(amidinato)vanadium](µ-1,2-dinitrogen) 54.

both in metrics and in the formal oxidation state assignments for the V_2N_2 fragment.

Complex 55 synthesized by exposure of $(^{Me}NacNac^{DIPP})$ - $V^{II}(OAr)$ was the first example of dinitrogen coordination by a three coordinate vanadium(II) species (Figure 43).¹¹³



Figure 43. Bis[(β -diketiminato)(phenoxy)vanadium](μ -1,2-N₂) compound 55.

Although structural data are not available, the N₂ stretching mode observed at 1374 cm⁻¹ by resonance Raman spectroscopy together with computational studies is consistent with antiferromagnetically coupled formally V^{III} centers and a N₂²⁻ bridge. Completing the examples with bidentate ligand is complex **56**, which was reported by Gambarotta and coworkers and was the first structurally characterized example of a polynuclear vanadium dinitrogen complex (Figure 44).¹¹⁴



Figure 44. Divanadium-dinitrogen complex 56.

The observed d(N–N) of 1.228(4) Å and a short V–N(N₂) distance of 1.833(3) Å suggest considerable reduction of the dinitrogen with substantial contribution from the diazenide (N_2^{2-}) resonance form.

Lastly, we consider the examples employing monodentate ligands. Previously, we considered the amido and alkoxide examples; here, we consider the alkyl and aryl complexes for which only V examples are known. Buijink and Teuben reported the (μ -1,2-dinitrogen)bis(tris(neopentyl)vanadium) **57**, synthesized by metathesis between LiCH₂(CH₃)₃ and VCl₃(THF)₃ (Figure 45).¹¹⁵ The N–N bond length of 1.250(3) Å is comparable somewhat unexpectedly to that of



Figure 45. Bis[tris(neopentyl)vanadium](dinitrogen), 57.

46-V but may arise from the different steric demands of the ligand. Floriani's redox series of $(\mu$ -1,2-dinitrogen)bis-[(trimesityl)vanadium] complexes **58** wherein the formal charge of the $[V_2N_2]^{n+}$ core varies (n = 4–6) evidences comparable metal–N₂ and N–N bond distances (Scheme 17).¹¹⁶ Magnetic susceptibility data and theoretical methods





suggest reduction of the N₂ ligand, however, which is consistent with protonation of **58-K** or **58-K**₂ to yield N₂H₄ (20% and 38%, respectively) and NH₃ (7% and 21%, respectively). One may then conclude that d(N–N) is not a reliable reporter for N₂ activation in metal–dinitrogen complexes, although the modest yield of hydrogenated-N₂ products could suggest more complex reaction pathways involving redistribution of reducing equivalents. Indeed, the long bond distance observed in **58-Na**₂ vs **58-K** and **58-K**₂ highlights the strongly activating effect of the Lewis acidic center proximal to the N₂ ligand.¹¹⁷

3.2.3. Ligand Systems Unique to Niobium–Dinitrogen Complexes. Only three niobium only examples have been reported to date: the $P^{Ph}_2N_2$ macrocyclic ligand from Fryzuk's group, the calix[4]arene complexes by Floriani and co-workers, and the (μ -1,2-dinitrogen)-bis[tris-(dithiocarbonato)niobium] complexes from Henderson et al.

Fryzuk and co-workers used their P^{Ph}₂N₂ macrocyclic ligand (see prior Ti and Zr examples **21** and **22**) to synthesize the corresponding μ -1,2-dinitrogen adduct **59-1** (Figure 46). The bond metrics are comparable to those of the diniobium compounds discussed above, with N–N and Nb–N(N₂) distances of 1.272(5) Å and 1.869(5)–1.840(6) Å, respectively.⁹² EPR spectroscopic data recorded at 300 K reveal a decet of triplets ($I = {}^{9}/{}_{2} {}^{93}$ Nb and I = ${}^{1}/{}_{2} {}^{31}$ P nuclei) at g =1.975 indicating local d^{1} character at each Nb, and variabletemperature magnetic susceptibility measurements could be well modeled assuming two antiferromagnetically coupled S = ${}^{1}/{}_{2}$ centers mediated by the N–N bridge. Notably, the dinitrogen ligand in the zirconium analog **22** adopts a μ - η^{2} : η^{2} coordination mode rather than the μ -1,2 mode observed in **59**. In the side-on/side-on mode, the two π^* orbitals of N₂ give rise to SALCs of π -type and δ -type symmetry, whereas the end-





Figure 46. Diniobium- μ -1,2-N₂ complexes 59.

on/end-on orientation affords two orbitals of M–N π -symmetry. The preference for the respective bridging mode then lies in the relative occupation of the respective orbitals, with the formally d^1 Nb^{IV} and the N₂^{4–} affording weaker δ -interactions destabilizing the δ -bond, whereas this metal-based δ -type orbital is unoccupied for Zr^{IV}. Related to **59-1** are **59-2** and **-3** for which the N–N bond lengths of 1.280(7) Å and 1.250(3) Å and Nb–N(N₂) bond lengths of 1.869(5)–1.840(6) Å for **59-2** and 1.868(2)–1.875(2) Å for **59-3** are within error of those for **59-1**.¹¹⁸ The compensatory effect of the strongly donating alkyl ligand on the crystallographic measure of N₂ activation is reminiscent of the similarities between **1-Cp*** and **8-Cp**,*p*-C₆H₄CH₃.

Rizzoli and co-workers reported complex **60**-N₂ in which a μ -1,2-dinitrogen links two monoanionic niobium-calixarene species (Scheme 18). The N–N (1.39(2) Å) and Nb–N (1.75(1) Å) bond distances are indicative of Nb–N multiple bond character and N–N single bond character; this formalism is consistent with the Wittig-like reactivity observed for **60**-N₂ with benzaldehyde, which yields the azine (PhCH=N–N=CHPh) and the corresponding niobium oxide species.¹¹⁹ Two-electron reduction of **60**-N₂ results in N–N bond cleavage affording the di(μ -nitrido)diniobium(V) complex **60-2N**.

The transition from the μ -1,2 mode for the N₂ fragment in 60-N₂ to the di(μ -nitride) in 60-2N could suggest intermediacy of two terminal nitrides or isomerization from a μ -1,2 to a μ - η^2 : η^2 (or μ - η^2 : η^1) coordination mode. Reduction of the THF solvate 60-N₂' in dimethoxyethane (DME) affords 61, in which the N₂ ligand now adopts a μ - η^2 : η^2 mode with contraction of the Nb–Nb distance (4.8847(18) in 60-N₂ vs 2.635(1) Å in 61) and minimal change to the N–N bond distance (Scheme 19). These structural changes suggest that reduction of 60-N₂' is initially metal-based rather than N₂based.⁹¹ Thermolysis of the N–N and Nb–Nb bonds in 61 can be effected in pyridine to generate di(μ -nitride) complex 62.

The final Nb example is that from Henderson et al., who reported the μ -1,2-dinitrogen diniobium complex $[(\text{NEt}_2\text{CS}_2)_3\text{Nb}]_2(\mu$ -1,2-N₂) (63, Figure 47).¹²⁰ The N–N

Scheme 18. Reduction of 60-N₂



Scheme 19. Reduction of the THF Solvate $60-N_2$



Figure 47. Bis[tris(dithiocarbamatoniobium)](μ -1,2-dinitrogen) complex **63**.

bond lengths of 1.25(2) Å are contracted as compared to many of the discussed Nb_2N_2 complexes, suggesting Nb(IV) centers in the $Nb(S_2CNEt_2)_3$ fragment. Here, the Nb-N-N bond angles of 166.8(9)° and 163.1(9)° reflect a slightly bent coordination mode in a nominal *cis* orientation.

3.2.4. Ligands Systems Unique to Tantalum–Dinitrogen Complexes. Starting with the cyclopentadienyl complexes, Bregel and Eisenberg reported $(Cp*_2TaCl)_2(\mu$ -1,2-N₂) (Figure 48), 64,¹²¹ which bears structural homology to 8-Cp,p-CH₃C₆H₄ (Figure 9) albeit with a slightly longer N–N bond length of 1.24(1) Å as compared to the Zr congener.



Figure 48. Bis[chloro-bis(Cp*)-tantalum](μ -1,2-N₂), 64.

Disproportionation of $(C_5Me_4R)_2Ta(\mu-Cl)_4$ under a dinitrogen atmosphere affords $[(C_5Me_4R)_3Ta_3(\mu-Cl)_6]$ - $[(C_5Me_4R)TaCl_4]$ as one product, and $[(C_5Me_4R)-TaCl_2]_2(\mu-1,2-N_2)$, **65-R**, where R = Me or Et (Figure 49).¹²² Structural characterization by X-ray crystallography of



Figure 49. Half-sandwich ditantalum-dinitrogen complexes 65-Me and 65-Et.

65-Et evidence a zigzag Ta₂N₂ core with a Ta-N-N angle of 166.3(4)°, a N–N distance of 1.280(6) Å, and a short Ta–N distance of 1.804(3) Å. Extending to pseudohalides, Takada and Kinoshita reported $[Cp*Ta(SC_6H_4Me)_2](\mu-1,2-N_2)$, 66, which was synthesized in a one pot reaction containing $Cp*TaCl_4$, di-*p*-tolyl disulfide, and KC_8 .¹²³ As expected given the similarities of the monodentate ligands in 65 and 66, the bond metrics and the zigzag conformation of the Ta_2N_2 core are comparable; for example, the N-N bond distance in 66 is 1.281(7) Å. To explore the effect of heterometals on the extent of N_2 activation, 66 was reacted with $M(CO)_6$ sources under UV irradiation to generate the tetrametallic complexes 66-2M (M = Cr, Mo) and 66-M (M = Cr, Mo) (Scheme 20). The thiolate donors bridge the Ta and Group 6 metal centers, with no direct interaction between the Cr or Mo and the N₂ ligand. DFT calculations and experimentally determined bond distances evidence minimal change to the Ta-N2 bonding interactions upon coordination of the Group 6 metal.

Related to these monocyclopentadienyl complexes is the borrolide species 67 report by Sperry and Bazan (Figure 50).¹²⁴ The mononuclear precursor is nominally Ta^{II} , assuming a borrolide oxidation state formalism, and expectedly affords a dinitrogen complex with strong $Ta-N(N_2)$ π -

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Scheme 20. Synthesis of 66-2M (M = Cr, Mo) and 66-M (M = Cr, Mo)



Figure 50. Ditantalum-dinitrogen with an η^5 -borrolide analog of Cp coordinated to each Ta center (67).

backbonding interactions. The N–N and Ta–N bond lengths are 1.309(9) Å and 1.838(7) Å, respectively, and well within the range of the monocyclopentadienyl compounds discussed above.

Schrock and co-workers reported a rare example of a dimetallic dinitrogen complex supported by thiolate ligands. Treating $[TaCl_3(THF)_2](\mu$ -1,2-N₂) with 6 equiv of LiDIPT (DIPT = S-2,6-C₆H₃-ⁱPr₂) affords $[Ta(DIPT)_3(THF)]_2(\mu$ -1,2-N₂), **68-1** (Figure 51).¹²⁵ Unfortunately, the solid state



Figure 51. Ditantalum- μ -1,2-N₂ complexes 68 with thiophenolates or phenolates as ancillary ligands.

structure of **68-1** is of sufficient quality to only validate connectivity, which is as depicted in Figure 51. The phenoxide analog **68-2** reported by the same authors afforded crystals of sufficient quality to allow determination of the lengths of the N–N bond (1.32(1) Å) and Ta–N(N₂) bonds (1.796 (5) Å); these metrics are reminiscent of other Ta₂N₂ fragments discussed above, such as **41-Ta/R** and **44-Ta/2H,N**₂.

3.3. Group 6: Cr, Mo, and W

Molybdenum is one of the most studied metals with respect to dinitrogen activation stemming in part from the initial reports of the molybdenum-dependent nitrogenases from *Azotobacter*. Unsurprisingly then, the dinitrogen chemistry of Group 6 is dominated by molybdenum compounds.^{126,127} Our survey begins with molybdenum dinitrogen complexes and includes closely related dinitrogen complexes of Cr and W where appropriate. Subsequently, we consider the singular examples for Cr and then those for W.

3.3.1. Molybdenum Complexes and Related Cr and W Compounds. The first example of a multinuclear molybdenum dinitrogen complex is $[Mo(dmpe)(\eta^6-mesitylene)]_2(\mu-$ 1,2-N₂), **69**, from Forder and Prout for which d(N-N) = 1.14Å and d(Mo-N) = 2.04 Å (Figure 52).¹²⁸ Related to this



Figure 52. $[Mo(dmpe)(\eta^6-mesitylene)]_2(\mu-1,2-N_2)$, 69.

arene complex is the dinuclear tungsten piano stool complex 70 in which each metal is ligated by a dmpe and Cp⁻ with a μ -1,2-dinitrogen completing the metal coordination spheres (Figure 53).¹²⁹ Despite the differences in the formal metal



Figure 53. Dinuclear tungsten end-on/end-on dinitrogen piano stool complex, 70.

charges for **69** and **70**, the N–N bond distance increases from **69** to **70** (d(N-N) = 1.22(1) Å), reflecting the difference in metal–ligand bonding and the donor properties of the aromatic ligand.

Other dimolybdenum dinitrogen complexes bearing aromatic ligands include the η^6 -arene complex from Agapie and co-workers (Figure 54) and the η^5 -Cp complexes from the



Figure 54. Bis(diphosphino- $(\eta^6$ -arene)-molybdenum)(μ -1,2-N₂) complex, 71.

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groups of Nishibayashi (Figure 55) and Sita (Figure 56 and Figure 57). 67,130,131 For the former, protonation of the



Figure 55. Dinitrogen adduct of [Cp*(dpef)Mo], 72.



Figure 56. Dinitrogen-bridged bis[Cp*(amidinato or guanidinato)metal] compounds of Mo and W, 73-M/N^R,X.



Figure 57. Bis[Cp*(amidinato)molybdenum](µ-dinitrogen), 74.

tris(pentafluorophenyl)borane adduct of the complex $(C_6H_4(C_6H_4-P^iPr_2)_2)Mo(CO)_2$ with $H(OEt_2)BAr^F_4$ (BAr^F_4 = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) in the presence of N₂ affords a mixture of products from which 71 is one of the major products. The structural parameters for 71 are expectedly comparable to those reported by Forder and Prout; for example, the N–N distance is 1.174 Å compared to 1.14 Å in **69**.

Using 1,1'-bis(diethylphosphino)ferrocene (depf), Nishibayashi and co-workers synthesized the redox series of $[Cp*Mo(depf)]_2(\mu-1,2-N_2)$, 72, wherein the overall charge ranges from 0 to +2.¹³¹ The N–N bond lengthens from 1.182(5) Å in 72 to 1.256(9) Å in 72²⁺ and an inverse trend is noted for the Mo–N bonds, indicating that the HOMO is N– N π -bonding rather than metal centered. Complex 72¹⁺ undergoes photoinduced N–N bond cleavage to liberate the corresponding nitride (depf)Cp*Mo \equiv N; oxidation of this mononuclear nitride complex results in dimerization to 72^{2+} .

Similar to their efforts with Group 5 metals, Sita and coworkers reported the isostructural molybdenum and tungsten congeners of **39**, viz. {Cp*[N(R)C(X)N(ⁱPr)]M}₂(μ -1,2-N₂), **73-M/N^R,X** (Figure 56).⁶⁷ The observed N–N bond lengths are comparable independent of metal ion type and substituent R and X; for example, the N–N bond length for **73-Mo/** N^{iPr},**NMe**₂ of 1.267(2) Å and for **73-W/N^{iPr}**,**Me** of 1.277(8) Å are within error. Complexes **73-M/N^{iPr}**,**Me** are thermally robust but convert to the di(μ -nitride) by photolysis (Scheme 21).¹³² In contrast, **73-M/N^{EF}**,**Ph** effects N–N cleavage above



25 °C.¹³³ These results correlate ligand sterics in these complexes with longer N–N bond lengths and the thermal stability of the dinitrogen adduct toward di(μ -nitride) formation. Related to 73-Mo/N^{iPr},Me is the *meso*-{Cp*[N-(ⁱPr)C(Me)N(ⁱPr)]Mo(H)}₂(μ -1,2-N₂), 74, which is synthesized by reaction of (Cp*[N(ⁱPr)C(Me)N(ⁱPr)])MoCl₂ with 2 equiv of *n*-BuLi.⁶⁷ The longer Mo–N(N₂) and shorter N–N bond distances are consistent with a higher metal oxidation state in 74 as compared to 73-Mo.

M = Mo or W

Related to 74 are the stereoisomers of $\{Cp^*[N({}^{i}Pr)C(Me)-N({}^{i}Pr)]W(Cl)\}_2(\mu-1,2-N_2)$, 75, accessed either by reduction of $Cp^*[N({}^{i}Pr)C(Me)N({}^{i}Pr)]WCl_3$ with 2.5 equiv of KC₈ or reaction of 73-W/N^{iPr},Me with excess PbCl₂. The isomers have comparable solid state structural metrics with d(N–N) values of 1.206(9) Å and 1.192(3) Å for the *rac* and *meso* isomers, respectively; the N–N bond lengths in 75 are shorter than in 73-W/N^{iPr},Me consistent with a decrease in electron density at the metal center.

A seminal contribution in dinitrogen activation independent of metal ion is the report by Laplaza et al. on the scission of N₂ upon exposure of a tris(anilido)molybdenum(III) complex to a dinitrogen atmosphere (Scheme 22).⁹ A transient purple (μ -dinitrogen)dimolybdenum species 76 prior to N₂ bond activation is supported by X-ray absorption data, resonance Raman spectra ($\nu_{(N-N)} = 1630 \text{ cm}^{-1}$), solid state magnetometry, and X-ray crystallography.⁸ These data evidence an elongated N–N and contracted Mo–N(N₂) bonds with values of 1.212(2) Å and 1.868(1) Å, respectively. The linear μ -1,2-dinitrogen complex is proposed to isomerize to a zigzag transition state prior to N₂ cleavage and formation of the molybdenum nitride products (Scheme 22).^{8,134}

In the redox series generated by oxidation of 76 (i.e., $[76]^{n+}$ where n = 1 or 2), one observes that the N–N bond lengthens with oxidation from 1.212(2) Å in 76 to 1.265(5) Å in $[76]^{2+}$

Scheme 22. Proposed N₂ Cleavage Mechanism for Cummins' Tris(anilido)molybdenum(III) Complex



together with a contraction of the Mo–N(N₂) bonds (1.868(1) Å in 76 to 1.798(2) Å in [76]²⁺). These changes arise from the relative energy of the N–N π bonding orbitals as compared to the Mo–N(N₂) bonding molecular orbitals; the LUMO in [76]²⁺ is N–N π bonding whereas the HOMO is metal(d_{π})–N₂(π^*) backbonding nature. This lowering of the energy of metal-based orbitals relative to the N₂ bonding orbitals is a direct consequence of the gradual transition from more electropositive early to more electronegative late transition metals.

A putative monometallic Mo-N₂ adduct or potential scrambling of metal ions within the dimetallic are possible mechanistic considerations for formation of 76, which are evidenced by access to a series of heterodimetallic complexes 76-M (M = Ti, Nb, and U).¹³⁴⁻¹³⁷ The 76-M complexes are isostructural with 76 from the perspective of the tris(anilido)molybdenum-dinitrogen fragment and the linear μ -1,2 coordination of N2. The N-N bond distances and energies of the $\nu_{\rm N-N}$ stretching mode are similar over the series, with the N₂ fragment nominally more activated when the heterometal is more reducing than the Mo center (Figure 58). A related compound 76-V, obtained as shown in Scheme 23, results in a lower activation of μ -N₂ as compared to the compounds in the 76-M series and is attributed to the less donating ligand environment around the V ion for the former.¹

The $(\mu$ -1,2-dinitrogen)bis(tris(mesityl)molybdenum), 77-Mo, reported by Floriani and co-workers from the reaction of mesityl magnesium bromide with MoCl₄ is structurally analogous to the tris-anilide congener 76.¹³⁹ The N–N bond is longer and Mo-N bonds shorter in 77-Mo than those in 76, consistent with the difference in donor properties of the supporting ligands. In comparison to 76 which readily converts to the mononuclear molybdenum nitride, 77-Mo is stable in benzene at reflux with no conditions reported to afford the Mo≡N species. However, exposure of 77-Mo dissolved in benzene to UV irradiation effects N₂ cleavage—a rare example of photolytic N₂ cleavage in a bimetallic system-to yield $[Mo(Mes)_3]_2(\mu$ -N) (Scheme 24). This reaction is proposed to initially form the monometallic nitride $Mo(Mes)_3(N)$ followed by reaction with unreacted 77-Mo. In addition to 77-Mo, Floriani and co-workers also synthesized a related ditungsten species (μ -1,2-dinitrogen)bis[chlorotri(mesityl)tungsten], 77-WCl.¹⁴⁰ Reduction of 77-WCl with Mg metal does not result



Figure 58. Heterodimetallic- μ -1,2-dinitrogen complexes (76-M) utilizing the tris(anilido)molybdenum-dinitrogen fragment.

Scheme 23. Synthesis of 76-V



in the loss of chloride only, but reductive aggregation is observed to afford the tri- and tetratungsten chainlike complexes 77- W_3 and 77- W_4 (Scheme 25). Across this series of W complexes, the N–N bond is shortest for 77-WCl (1.180(16) Å) and, on average, the longest of 77- W_3 (1.272 Å average).

The tren^{3–} presents a similar trigonal triamide coordination environment to that observed in 76; inclusion of an amine as an axial donor can aid in destabilizing a potential metal-nitride

Scheme 24. UV Irradiation of 77-Mo







bond to favor reduction and protonation to imide or amide species. Expectedly then, Mo_2N_2 and heterometallic complexes analogous to 76 and 76-M are also accessible with this ligand platform with various substituents on the tren³⁻ secondary amine N atoms (78, Figure 59).^{141–143} In the three reported cases, dinitrogen bridges two formally Mo^{III} centers (considering N_2 as a neutral bridge for simplicity) in a linear fashion and with N–N and Mo–N bond distances comparable to 76. For 78-3, no further reduction chemistry was observed in contrast to the two-electron reduction of the [(4-^tBuC₆H₄–



Figure 59. Tren³⁻ ligated dinuclear molybdenum or tungsten dinitrogen complexes, 78.

NCH₂CH₂)₃N]MoCl precursor, which yields the monomeric diazenide complex. Scheer et al. also reported the dinitrogen complex 78-4 as a side product in the synthesis of $[(NpNCH_2CH_2)_3N]WCl$ (Np = neopentyl).¹⁴⁴ The N–N bond length of 1.39(2) Å in 78-4 is remarkably long and is among the longest known for a μ -1,2-dinitrogen complex, being shorter than only the diniobium calixarene complexes **60-N₂**.

A series of heteronuclear metal complexes containing trenMoN₂ fragments, **79-M/Mo**_n (M = Zr, V, Fe, and n = 1, 2, or 3), were reported by O'Donoghue et al.¹⁴⁵ Spectroscopic data indicate Mo^{IV} centers with the μ -1,2-dinitrogen ligands best described as diazenide donors. Although the N–N bond distances are comparable across the series, the energy of the N–N stretching mode increases as complex nuclearity increases. For example, this mode is observed at 1515 cm⁻¹ in **79-Zr/Mo**₁, 1556 cm⁻¹ in **79-Zr/Mo**₂, and 1576 cm⁻¹ in **79-Zr/Mo**₃ (Figure 60). For the vanadium analogs, an



Figure 60. Heteronuclear Mo_nZr dinitrogen complexes, 79-M/Mo_n.

equilibrium between 79-V/Mo₂ and 79-V/Mo₃ is observed due to ligand exchange with THF (Scheme 26). The last example is 79-Fe/Mo₃ (Figure 61), which is the only example of an iron-molybdenum dinitrogen complex. The Fe centers in 79-Fe/Mo₃ adopt an unusual trigonal planar coordination environment surrounded by the three [((Me₃Si-NCH₂CH₂)₃N)Mo(N₂)]⁻ units. The μ -1,2-dinitrogen bridges are approximately linear with one being slightly bent with an \angle Fe-N-N = 156(2)°. This bending is proposed to arise from steric interactions rather than electronic effects. The N-N bond distances are comparable (1.20–1.27 Å) to the other pubs.acs.org/CR

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Figure 61. Heteronuclear Mo₃Fe dinitrogen complex, 79-Fe/Mo₃.

heterometallics, although IR spectra ($\nu_{N-N} = 1703 \text{ cm}^{-1}$) suggest a significantly less activated N₂.

Meridionally coordinating tridentate chelates have also been utilized in molybdenum-dinitrogen chemistry. Starting with all N-donor chelates, Cr (80) (Scheme 27) and Mo (81-N₂ and 81-diene) (Figure 62) complexes of pyridine(diimine) ligand were reported by Gambarotta and Chirik and their co-workers, respectively.¹⁴⁶⁻¹⁴⁸ The N-N bond distances with values of 1.241(6) Å for 80 and 1.246(4) Å for $81\text{-}N_2$ are elongated compared to other Cr and Mo complexes, which, together with the $M-N(N_2)$ distances of 1.781(3) Å for 80 and 1.819(3)-1.823(3) Å for 81-N₂, suggests appreciable backbonding from the metal to the bound N₂. For complex 80diene, the π -acidity of the butadiene results in less activation of the N–N bond (1.145(4) Å) based on the solid state structure, reinforcing the need for weakly π acidic ligands to favor N₂ bond lengthening. Reaction of 80 with 2 equiv of NaH gives 80-Na₂ (Scheme 27), in which the one hydride deprotonates the bis(imino)pyridine and the second is accepted by the N_2 ligand. The N atoms derived originally from N₂ are significantly pyramidalized in 80-Na2. Taken together,





Figure 62. Compounds 81-N₂ and 81-diene.

deprotonation of the bis(imino)pyridine to the more donating anionic ene-amide ligand and the proximal alkali cations leads to a charge redistribution with formal reduction of the N_2 ligand.

The other example utilizing an all N-donor meridional chelate is the phenyl-substituted terpyridine complex $[82]^{2+}$ (Figure 63), in which the coordination sphere of each Mo center is completed by a methyldiphenylphosphine ligand.¹⁴⁹ The values of d(N–N) and ν_{N-N} of 1.203(3) Å and 1563 cm⁻¹ are consistent with the reduced nature of this complex, and DFT calculations indicate that the HOMO comprises a mixture of N–N π bonding and Mo–N₂ π^* . Examining the five-electron redox series $[82]^{n+}$ (n = 0, 1, 2, 3, or 4) by Raman and EPR spectroscopy corroborates these computational findings: ν_{N-N} decreases from 1563 to 1477 cm⁻¹ with

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[82]²⁺, d(N–N): 1.203(3) Å

Figure 63. Dinuclear molybdenum-dinitrogen complex with redoxactive phenyl-substituted terpyridine ligands, $[82]^{2+}$.

increasing values of *n* from 2 to 4, and EPR spectra of $[82]^{3+}$ indicate that the SOMO is comprised of a metal d_{π} orbital.

For the mixed pnictogen pincer type complexes reported by Nishibayashi and co-workers, the Mo centers adopt pseudooctahedral geometries each comprising a meridionally ligated pincer ligand, two terminal η^1 -dinitrogen donors, and a μ -1,2-dinitrogen. With the exception of 83^{Cy} -H, 83^{iPr} -H, and bis-arsine 84 complexes, the common structure type is the *trans-trans* configuration of the μ -1,2-dinitrogen and the pyridyl N donor of the pincer ligands with a dihedral angle greater than 60° between each MoE₃ plane (E = donor atoms on pincer ligands) (Figure 64). For 83^{Cy} -H, 83^{iPr} -H, and 84,



Figure 64. Dinuclear molybdenum- μ -1,2-dinitrogen complexes (83^R- \mathbf{R}') chelated by [PNP] pincer-type ligands with *trans-trans* stereochemistry.

dubbed as *trans*-*cis* isomers, the MoE₃ planes are orthogonal and only one of the terminal N₂ ligands is *trans* to the μ dinitrogen (Figure 65). The bridging and terminal N–N bond distances vary slightly as a function of substituents; however, a strong correlation is observed between the IR-active N–N stretching mode for the *terminal* N₂ and the reduction potential of the complex.¹⁵⁰ In the series **83**^{*t*Bu}-**R**^{*i*} where R^{*i*}



83^{*m*}-**H**, d(N–N): 1.148(4) A **84**, L = As, R = ^{*t*}Bu, d(N–N): 1.142(6) Å, $v_{N-N}(\mu$ -N₂): 1904 cm⁻¹



is H, Ph, SiMe₃, ^tBu, Me, or OMe, the yield of ammonia produced under catalytic conditions using CoCp₂ and lutidinium triflate ([LutH]OTf) increases with greater electron donation from the substituent with 52 and 44 equiv for R' =OMe and H, respectively.¹⁵¹ Computational studies suggest that the terminal N2 ligands undergo reduction and protonation and that the bridging N2 functions as an electron transfer pathway with one Mo center acting as an electron reservoir.¹⁵² However, the *trans-cis* complexes exhibit minimal catalytic N₂ fixation, suggesting that a near equivalent electronic structure at each Mo center is important for N₂ fixation. In addition, steric effects of the phosphine substituents influence the number of turnovers with 83^{Ph} -H (2 NH₃ equiv) being a poor catalyst in comparison to $83^{A\dot{d}}$ -H (14 NH₃ equiv).¹⁵³ Related to 83^{tBu} -H are 83^{tBu} -4Cl and 83^{tBu} -4CO, in which the two terminal N₂ ligands on each Mo center are replaced by chloride or CO. The former has been structurally characterized and the observed N–N bond length (1.169(3))Å) is comparable to that of the *trans-trans* complexes.¹⁵⁴ In contrast, 83^{tBu}-4CO was characterized only by vibrational spectroscopy, which evidenced a N-N stretching mode of similar energy (1893 cm⁻¹) to that of 83^{tBu}-H (1890 cm⁻¹).

Substituting the pyridyl donor for imidazolyl in the pincer architectures yields the related *trans-trans* PCP-ligated $Mo_2(\mu-1,2-N_2)$ complexes **85** (Figure 66).¹⁵⁵ The N–N bonds in these complexes are on par with those for the PNP pincer compounds, such as **83**^{tBu}-H, with the stronger donating imidazolyl in **85-3** correlated with the longer N–N bond distance. These complexes are some of the most effective molecular catalysts for dinitrogen fixation to ammonia with **85**-1 affording up to 230 equiv of NH₃ using CrCp*₂ and [LutH]OTf.¹⁵⁵ Recently, Ashida et al. utilized a combination of SmI₂ and alcohols or water as a proton-coupled electron transfer reagent and recorded yields of 4350 equiv of NH₃ using the precursor {(^{tBu}P₂C)MoCl₃} of **85-1** as the catalyst.¹⁵⁶ The turnover frequency (117.0 min⁻¹) rivals that of the molybdenum-dependent nitrogenase (40–120 min⁻¹),¹⁵⁷ albeit with the more reducing SmI₂(OH₂) instead of NADH.

The bis(phosphinoethyl)amine and the bis-(phosphinoethyl)phenylphosphine ligands provide a more flexible tripnictogen chelate as compared to the ligands in 80-85. In the PNP system, coordinated amide is susceptible to protonation, providing a route to manage protons during chemical transformations. Silantyev et al. reported the dinitrogen dimolybdenum complex [N-





85-3, d(N-N): 1.154(4) Å

Figure 66. PCP-ligated $Mo_2(\mu-1,2-N_2)$ complexes, 85.

(CH₂CH₂P^tBu₂)₂ClMo]₂(μ -1,2-N₂), **86**, displaying a long N– N bond at 1.258(9) Å and low $\nu_{\rm NN}$ stretching frequency of 1343 cm^{-1.158} Indeed, protonation of two amide donors in **86** afforded the daughter molybdenum nitride complexes (Scheme 28). DFT calculations point to an increase in the Mo–N₂ σ -interaction as a result of the weaker Mo–amine vs Mo–amide bonds.

Scheme 28. Synthesis of and H⁺-Triggered N₂ Scission by 86



Arashiba et al. and Liao et al. reported complexes 87^{tBu} and 87^{Cy} , respectively, using the all P donor atoms ligand (Figure 67).^{159,160} From the solid state structure of 87^{Cy} , a similar extent of N–N bond elongation as observed for the 83 complexes is seen. Vibrational data were used to infer the





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structure of 87^{tBu} . In a follow-up article to the report of catalytic silvlation effected by 87^{Cy} , Liao et al. showed that the reduction of the molybdenum trichloride precursor with 3 equiv of Na/Hg in the presence of sodium iodide affords a Mo(IV) nitride complex with hypothesized intermediacy of a μ -1,2-dinitrogen transient 87^{Cy} -2I (Scheme 29).¹⁶¹ Shortly

Scheme 29. N₂ Cleavage via Proposed Transient 87^{Cy}-2I



thereafter, Nishibayashi and co-workers demonstrated that $({}^{tBu}P_2N)MoI_3$ (where ${}^{tBu}P_2N = 2,6$ -bis[(di-*tert*butylphoshpino)methyl]pyridine) is an effective precatalyst for N₂ fixation to ammonia with yields, turnover frequency, and turnover numbers greater than those for 83^{tBu}-H.¹⁶² Given that the terminal nitride (${}^{tBu}P_2N$)MoI(N) was observed in the reaction mixtures, the proposed mechanism invokes N₂ triple bond scission from a transient [(${}^{tBu}P_2N$)MoI]₂(μ -1,2-N₂), which precedes ammonia formation from the daughter monometallic nitrides by a proton-coupled electron transfer pathway.¹⁵² The same mechanism is proposed for (${}^{tBu}P_2C$)-MoCl₃ (where ${}^{tBu}P_2C = 2,6$ -bis[(di-*tert*-butylphoshpino)methyl]benzimidazolyl) reduction with SmI₂(OH₂) to yield 4350 equiv of NH₃.¹⁵⁶

Hexacoordinate bis(phosphine) complexes of chromium and molybdenum (88-M/R, Figure 68 and Figure 69) were also reported in addition to the half-sandwich complexes (69 and 70) discussed above. Berben and Kozimor reported the dichromium-dinitrogen complex supported by bis-(dimethylphosphino)ethane and trimethysilyl acetylide, 88-Cr/SiMe₃.¹⁶³ From modeling of variable-temperature magnetic susceptibility data recorded on a solid sample of 88-Cr/



Name	d(Cr–N) (Å)	d(N-N) (Å)	ν_{N-N} (cm ⁻¹)
88-Cr/SiMe ₃	1.870(10)	1.177(10)	-
88-Cr/Ph	1.885	1.177	1685
[88-Cr/Si ⁱ Pr ₃] ⁰	1.881(2)	1.187(5)	1680
[88-Cr/Si ⁱ Pr ₃] ¹⁺	1.857(7)	1.195(5)	-
[88-Cr/Si ⁱ Pr ₃] ²⁺	1.88(1)	1.181(8)	1710

Figure 68. Bis(dimethylphosphino)ethane ligated chromium complexes 88-M/R.



Figure 69. Complex 88-Mo/CO.

SiMe₃, the determined $\chi_{\rm MT}$ (0.96 cm³K/mol) is consistent with two magnetically isolated $S = {}^{1}/{}_{2}{\rm Cr}^{\rm I}$ centers. Formalisms then suggest a neutral and minimally activated N₂ ligand. Curiously, electronic structure calculations on a simplified model of 88 [(dmpe)_2Cr(CCH)]_2(μ -1,2-N₂) (dmpe = bis-(dimethylphosphino)ethane) proposed that the two SOMOs are M–N antibonding and N–N bonding in character, implying what would be an unusual oxidative enhancement of N–N bond activation.

To test this hypothesis, Shores and co-workers studied the series $[88-Cr/Si^{i}Pr_{3}]^{n+}$ in which n = 0, 1, and 2.¹⁶⁴ Magnetic susceptibility data evidence S = 1 and 2 ground states for [88- $Cr/Si^{i}Pr_{3}$ ^{0/2+}, and a quartet-to-doublet spin equilibrium for $[88-Cr/Si^{P}r_{3}]^{1+}$ below 16 K. Despite the prior calculations, N-N bond lengths are within error and vibrational data indicate a marginal increase in N-N bond strength as one increases the metal formal oxidation state across the series. This trend suggests that oxidation is of a metal nonbonding d_{δ} orbital rather than the M–N₂ or N–N π^* orbital (Figure 68). The Mo analog, $[(depe)(CO)Mo]_2(\mu-1,2-N_2)$ or 88-Mo/CO, features a short N-N bond length of 1.127(5) Å due to the *trans* influence of the CO, recapitulating the trend of π -acidic ligands disfavoring N2 activation.¹⁶⁵ Masuda and co-workers identified the dimetallic complex without the CO ligands, $[((depe)_2Mo)_2(\mu-N_2)]^{2+}$, by Raman spectra collected on mixtures for one-electron oxidation of trans-(depe)₂Mo(η^1 - N_2)₂.¹⁶⁶ The ν_{N-N} of 1292 cm⁻¹ is intermediate between that of hydrazine and diazene, evidencing the substantially greater activation despite the formally more oxidized Mo center as compared to 88-Mo/CO. This transient species from Masuda ultimately affords 2 equiv of the mononuclear nitride $[(depe)_2 MoN]^+$.

3.3.2. Multimetallic Chromium–Dinitrogen Complexes. Sellman and Maisel reported the first example of a multinuclear chromium dinitrogen complex, $[Cr(\eta^{6}\text{-arene})-(CO)_{2}](\mu-1,2-N_{2})$ where the arene is either hexamethylbenzene or mesitylene (89-HMB and 89-Mes, respectively), from photolysis reactions of the related piano stool complex $Cr(\eta^{6}\text{-arene})(CO)_{3}$ under a N₂ atmosphere.¹⁶⁷ Solid state structures were not reported for 89-HMB or 89-Mes; however, Hunter and co-workers subsequently synthesized and crystallized the hexaethylbenzene congener, $[Cr(\eta^{6}\text{-}C_{6}\text{Et}_{6})(CO)_{2}]_{2}(\mu-1,2-N_{2})$ or 89-HEB (Figure 70).¹⁶⁸ The N–N and Cr–N distances of



Figure 70. Compound 89-HEB, $[Cr(\eta^{6}-arene)(CO)_{2}](\mu-1,2-N_{2})$.

1.110(18) Å and 1.917(9) Å, respectively, in **89-HEB** agree with weaker metal-dinitrogen π -backbonding from competition with π -acidic CO and the arene ligand.

Yin et al. recently reported the di- and trinuclear chromiumdinitrogen complexes 90- Cr_n/R (n/R = 2/Cy, 3/Ph), generated by reduction of the monometallic chloride precursor with KBEt₃H under a dinitrogen atmosphere.¹⁶⁹ The substituents on phosphine donor dictate the product, with larger cone angle of Cy resulting in the dimetallic whereas Ph yields the trimetallic (Figure 71). The extent of activation of



Figure 71. Polynuclear chromium-dinitrogen adducts, 90-Cr_n/R.

the μ -1,2-dinitrogen ligands is moderate with N–N bond lengths of 1.169 and 1.176 Å for 90-Cr₂/Cy and 90-Cr₃/Ph, respectively, consistent with the ν_{N-N} energies of 1751 and 1962 cm⁻¹ (90-Cr₂/Cy) and 1739 and 1981 cm⁻¹ (90-Cr₃/ Ph). The higher energy vibration of each pair corresponds to the terminal N₂ donors in the complex. Reduction of 90-Cr₂/ Cy with excess K, Rb, or Cs yields the first examples of monometallic anionic Cr⁰–N₂ compounds 91-M where M = K, Rb, or Cs. Compound 91-K reacts with trimethylsilyl chloride to produce the monometallic hydrazide complex—the first example of a chromium hydrazide—and the monochromium(II) chloride complex.

With respect to the lighter pnictogen, Theopold and coworkers synthesized a number of N-donor atom supported dinitrogen-bridged multichromium complexes (Figure 72), including the only example of η^2 -coordination of N₂ to chromium.¹⁷⁰ Using the 2,6-diisopropylphenyl-substituted β diketiminate, [^{Me}NacNac^{DIPP}]⁻, metalation with Cr^{II} followed by reduction affords the [^{Me}NacNac^{DIPP}Cr]₂(μ - η^2 : η^2 -N₂), 92– **2Cr**, in which the N–N bond distance of 1.249(5) Å is one of the longest in any chromium dinitrogen compound. The dinitrogen ligand is labile, being readily replaced by stronger π acid ligands (e.g., CO). Using the less encumbering 2,6dimethylphenyl β -diketiminate [^{Me}NacNac^{Xyl}]⁻ affords a mixture of products when the Cr(II)-hydride dimeric precursor is exposed to trimethylsilyl-diazomethane, from which the tri- and tetrachromium dinitrogen 92-3Cr and 92-



Figure 72. (β -Diketiminatochromium)-dinitrogen complexes of varying nuclearities, 92-nCr. The side-on/side-on coordination mode observed for 92-2Cr is rare for Gp 6 complexes.

4Cr, respectively, were isolated.¹⁷¹ The solid state structures reveal the exclusive μ -1,2 coordination mode of the dinitrogen molecules in **92-nCr** (n = 3 and 4) with N–N bond lengths of 1.162 and 1.173 Å, and vibrational spectroscopy evidences N–N stretching frequencies of 2124–2244 and 2063 cm⁻¹, respectively. Repeating the theme noted thus far, the change of coordination mode from μ - η^2 : η^2 to μ -1,2 is accompanied by a shortening of the N–N bond distances.

In addition to the β -diketiminate complexes, Akturk et al. also reported a family of 4-coordinated dichromium dinitrogen complexes 93-R₁/R₂ in which the substituents on the supporting tris(pyrazolylborate) ligand, [^{R1,R2}Tp]⁻, vary (Figure 73).¹⁷² In all cases, the chromium centers are in a



Figure 73. Tris(pyrazolylborate)-supported dinuclear chromium-µ-1,2-dinitrogen complexes, 93

pseudotetrahedral geometry with a μ -1,2-dinitrogen bridge and N–N and Cr–N(N₂) bond lengths in the range of 1.213(5)–1.214(4) Å and 1.773(2)–1.838(3) Å, respectively. These bond distances are longer than the comparable tri- and tetrachromium complexes **92-nCr**.

3.3.3. Multinuclear Tungsten-Dinitrogen Compounds. Fewer dinitrogen adducts have been reported for tungsten as compared to Mo and Cr with all examples comprising a μ -1,2-dinitrogen. Homo- or heterodimetallic complexes predominate; the sole tri- and tetrametallic examples, complexes $77-W_3$ and $77-W_4$, adopt chainlike topologies and were discussed above.

The first example of $W_2(\mu-1,2-N_2)$ complex was $[(Et_2PhP)_3W(\eta^1-N_2)]_2(\mu-1,2-N_2)$, 94-Et, followed shortly thereafter by the report of the PⁿPr₂Ph analog 94-ⁿPr, which were synthesized by reduction of WCl₆ with Mg in the presence of the respective phosphine (Figure 74).^{173,174} The



Figure 74. Compounds $[(R_2PhP)_3W(\eta^1-N_2)]_2(\mu-1,2-N_2)$, 94-R.

structural solution was only able to confirm connectivity of the complex; the complex adopts a configuration analogous to that of the molybdenum PPP pincer complexes **87**. The IR spectra of **94-Et** suggest a comparable N–N vibration for the bridging and terminal N₂ ligands due to the observed signals at 1890 and 1895 cm⁻¹. Subsequent to these reports, the bis (dichlorotungsten) analog $[WCl_2(PMe_3)_3]_2(\mu$ -1,2-N₂), **95-2Cl**, the bis(trichlorotungsten) $[WCl_3(PMe_3)_2]_2(\mu$ -1,2-N₂), **95-3Cl**, the bis(tricarbonyltungsten) $[W(CO)_3(P^iPr_3)_2]_2(\mu$ -1,2-N₂), **95-CO**, and $[(PhN)Cl_2(PMe_3)_2W]_2(\mu$ -N₂), **95-NPh**, were obtained (Figure 75). The first two were reported by



Figure 75. $[W(CO)_3(P^iPr_3)_2]_2(\mu\text{-}1,2\text{-}N_2)$ (95-CO) and $[(PhN)\text{-}Cl_2(PMe_3)_2W]_2(\mu\text{-}1,2\text{-}N_2)$ (95-NPh).

Harvey et al., the carbonyl complex from Kubas and workers, and the imide by Harlan et al.^{175–177} The long N–N bonds observed in **95-2Cl** (1.279(4) Å) and **95-3Cl** (1.24(2) Å) as compared to **95-CO** (1.136(6) Å with $\nu_{\rm NN}$ = 1939 cm⁻¹) bear strong resemblance with the greater N–N bond activation observed upon removal of CO ligand from **88-Mo/CO**. The N–N bond in **95-NPh** (1.19(2) Å) is of comparable length to that of **95-CO**, highlighting again the discounting effect of ancillary π -acids on N₂ activation. Indeed, this series of W complexes highlights the need to adopt a holistic electronic structure treatment of the metal fragment rather than overly relying on metal oxidation state.

A number of heterodimetallic compounds of W and a metal either from Group 4 or 5 have been reported by Hidai and coworkers (Figure 76).^{178–180} Generally, these complexes have comparable W fragments with four P donor atoms in the square plane and an X-type donor *trans* to μ -1,2-dinitrogen. The heterometal fragment is variable as noted in Figure 76.





Routes to these complexes typically arise from reaction of a bis- or mono(dinitrogen) tungsten complex and a heterometal complex. As an example, reaction of $cis-[W(PMe_2Ph)_4(\eta^1 N_2$)₂] with titanocene dichloride and sodium iodide affords $[Cl(PMe_2Ph)_4W(\mu-1,2)TiCp_2Cl]$, 96-1. In these complexes, the frequency of the N-N stretching mode is substantially lower than that of free N_2 , ranging from 1408 to 1545 cm⁻¹ and in agreement with the formally low valent W center, the strong ligand field, and the push-pull effect of the W center and electropositive early transition metal. A related push-pull effect is proposed for N₂ fixation by nitrogenases in which the acidic amino acid side chains polarize the cofactor-bound dinitrogen ligand.^{181,182} Here, the proximal Lewis acidic groups and the cofactor pull and push electron density, respectively, into the bound dinitrogen. Similar effects are noted in the 96 series of compounds with the protic Lewis acid replaced by the Gp 4 or 5 metal center. Protonolysis of 96-1 and $[I(PMe_2Ph)_4W(u-N2)ZrCp_2Cl]$, 96-2, with excess sulfuric acid yields 0.86 mol of NH3 and 0.08 mol of N2H4 per mole of 96-1 and 0.33 mol of NH₃ and 0.16 mol of N₂H₄ per mole 96-2 with no observable N₂ evolution in either case. Further derivatization of these complexes is possible; treatment of 96-2 with excess pyridine substitutes one of the phosphine ligands to yield 96-2Py in which the bond metrics are comparable to those in 96-2.

Comparisons between ligand field and the consequences on N2 activation across the 96 series follows the trend that decreased π -acidity and increased electron donating ability of the ancillary ligands enhances N₂ activation. For [Cl- $(PMe_2Ph)_4W(\mu-1,2)TiCpCl_2]$, 96-3, vs 96-1 in which the heterometal fragment is a CpTiCl₂ instead of Cp₂TiCl, one notes greater activation of the N–N bond (viz. ν_{N-N} = 1468 and 1408 cm⁻¹ in 96-1 and 96-3, respectively). Similarly, the energy of the N–N stretching mode for $[NCS(dppe)_2W(\mu 1,2-N_2$)TiCp'Cl₂] (Cp'= Cp for 96-4, Cp* for 96-5), is greater for 96-4 vs 96-5 (1441 cm⁻¹ vs 1433 cm⁻¹). One also notes greater activation of the N2 ligand for the Ta and Nb heterometallic complexes.

Reduction of $(\eta^5 - Cp^*)W(Me)_3Cl$ with sodium-mercury amalgam in THF gave the first organometallic ditungsten dinitrogen complex 97-Me (Figure 77).¹⁸³ This complex is

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Figure 77. Bis $[Cp^*(Me)_3W](\mu$ -1,2-N₂), 97-Me.

analogous to reported dimolybdenum and heterodimetallic molybdenum-tungsten complexes for which the metal coordination environments are comparable. However, 97-Me arises from incorporation of atmospheric N₂ whereas the Mo₂ and MoW compounds utilize hydrazine or the hydrazide complex in their syntheses. The N–N bond of 1.334(26) Å in 97-Me is one of the longest reported for a μ -1,2-dinitrogen complex and longer than that of the Mo₂ and MoW analogs.¹ Building on this report, O'Regan et al. developed a general methodology to replace methyl ligands in 97-Me without dissolution of dimetallic.¹⁸⁵ Reaction of 97-Me with 2 equiv of HX (X = Cl, OTf, $O_2CC_6F_{5}$, OC_6F_{5} , and SC_6F_5) affords a series of 97-X, with the exchange of one methyl group per W center. Use of HBF₄ in the presence of acetonitrile instead of an acid with a coordinating conjugate base gives the dicationic solvent-adduct [97-ACN]²⁺. Loss of the strongly donating methyl ligand results in a decrease in the N-N bond distance as evidenced in 97-OC₆ F_5 with a N–N bond length of 1.26(2) Å. Reaction of 97-Me with 6 equiv of HOTf or tetrabromocatechol leads to loss of two methyl groups per W center (98-OTf and 98-Br₄Cat, respectively), with the tetrakis(triflate) complex providing a useful starting material to further derivatization. For example, thiolates can be incorporated into 98-OTf to generate the corresponding [Cp*W- $(Me)_2(SR)]_2(\mu-1,2-N_2)$ (R = 2,4,6-Me₃C₆H₂ and 2,4,6-ⁱ $Pr_3C_6H_2$) complexes, which are inaccessible from 97-Me with the respective thiol. As noted already, substitution of methyl leads to decreased π -backbonding from the W center to the N₂ ligand as reflected in the N–N bond distance.

3.4. Group 7: Mn, Tc, and Re

The dinitrogen coordination chemistry of Group 7 metals is substantially less than that of the neighboring groups; arguably, the radioactivity of Tc has limited greater exploration of its coordination chemistry and the s-block like coordination chemistry of Mn (particularly Mn^{II}) has similarly contributed to its limited investigation in this arena by comparison to other mid-to-late first row transition metals. Consequently, the dinitrogen-related chemistry is dominated by that of Re for this group with few examples for Mn.

3.4.1. Manganese and Technetium Complexes. The first example of a N2-bridged dimanganese complex did not arise from coordination of atmospheric dinitrogen but rather from a diazoalkane. In 1976, Ziegler et al. reported that addition of 2,2,2-trifluorodiazoethane to $[(C_5H_4R)-$ (CO)₂(THF)Mn] afforded the N₂ bridged complex $[(C_{5}H_{4}R)(CO)_{2}Mn]_{2}(\mu-1,2-N_{2})$ (R = H, Me).¹⁸⁶ These compounds exhibit IR absorptions attributable to the N2 stretching mode at 1971–1975 cm⁻¹, which are consistent with the crystallographic N-N bond distance of 1.118(7) Å and the inclusion of π acidic CO ancillary ligands in the complex. In 1979, Sellman and co-workers reported the related MnCr heterodimetallic $[(C_5H_5)(CO)_2Mn](\mu-1,2-N_2)[Cr-$ $(CO)_5$] utilizing $(C_5H_5)(CO)_2Mn(\eta^{1}-N_2)$ and $[Cr-(CO)_5(THF)]$; the latter is formally a N₂ complex although generated by oxidation of the hydrazide precursor.¹⁸⁷

The first multimanganese-dinitrogen complex arising from capture of atmospheric dinitrogen was $[N_2P_2]_2Mn(\mu-1,2-N_2)$ (99), which was synthesized by sodium naphthalenide reduction of the monometallic manganese chloride precursor (Figure 78).^{76,188} Each Mn center in this complex adopts a



Figure 78. First dimanganese- μ -1,2-N₂ complex (99) synthesized from atmospheric N₂.

pseudotetrahedral coordination sphere with the N–N bond length of 1.208(6) Å and ν_{N-N} stretching band from IR data at 1685 cm⁻¹. An analogous μ -1,2-dinitrogen complex with pseudotetrahedral metal centers was reported by Theopold and co-workers. Chemical reduction of tBu,Me TpMnCl under a dinitrogen atmosphere afforded the corresponding end-on/ end-on bridged dimetallic (tBu,Me TpMn)₂(μ -1,2-N₂), **100-Mn** (Figure 79).¹⁸⁹ The bond metrics are comparable to that of **99** with a d(N–N) of 1.196(5) Å.



Figure 79. Bis(TpMn)(*µ*-1,2-N₂), **100-Mn**.

Ziegler and co-workers obtained the only known example of a dinitrogen-bridged ditechnetium complex by photolysis of $[Tp'(CO)_3Tc]$ (Tp' = tris(3,5-dimethyl-1-pyrazolyl)borate) in THF under N₂ (100-Tc, Figure 80).¹⁹⁰ The complex bears similarity to the Mn analog 100-Mn. Given the presence of two CO donors per Tc center, the N–N bond distance (1.160(3) Å) is expectedly shorter than that for the Mn congener. We note here for comparison that Gunnoe et al. reported the rhenium congener, $[Tp(CO)_2Re](\mu-1,2-N_2)$, 100-Re (Figure 80).¹⁹¹ The bond metrics for this complex are comparable to that of 100-Tc with M–N and N–N bond lengths of 1.98(1) Å and 1.15(2) Å, respectively.

3.4.2. Rhenium Complexes. The earliest examples of multimetallic-dinitrogen complexes containing Re were a series of heteronuclear complexes in which $(PhMe_2P)_4Re(N_2)Cl$ was used as a building block, ^{192–195} and a number of similar complexes have since been reported (Figure 81 and Scheme 30).^{196–199} The general trend across the series is as noted for the heteronuclear molybdenum complexes from Schrock and co-workers; that is, higher nuclearity (1.154(29) for 101-Re₂Mo to 1.18(3) for 101-ReMo-1) results in decreased



Figure 80. Tp-ligated dimetallic Tc- and Re-µ-1,2- dinitrogen complexes, 100-Tc/Re.



Figure 81. Heterometallic TiRe and TiRe₂ dinitrogen compounds, 101-ReTi and 101-ReTi₂.

activation of the μ -1,2-dinitrogen donors whereas multiple Lewis acidic centers interacting with one N₂ donor lower the energy of the N–N stretching mode (1805 cm⁻¹ for **101-ReTi-1** to 1622 cm⁻¹ **101-ReTi**₂). Relatedly, heavier d^0 heterometals correlate with higher N–N stretching frequency as compared to their lighter counterparts, which again is related to the changes to Lewis acidity.

Schneider and co-workers have reported that reduction of a bis(phosphine)-amido (or $P^{(CH2)2}N^{(CH2)2}p^{tBu}$) rhenium dichloride, $(P^{(CH2)2}N^{(CH2)2}p^{tBu})$ ReCl₂, by one electron with Na/ Hg or CoCp*₂ under a N₂ atmosphere affords a mononuclear rhenium nitride product.²⁰⁰ A dinitrogen-bridged dirhenium complex was the proposed intermediate with the reaction traversing a mechanism similar to that proposed for Cummins' tris(anilido)molybdenum(III). Subsequently, the complex [$(P^{(CH2)2}N^{(CH2)2}p^{tBu})$ ReCl]₂(μ -1,2-N₂) (102) was isolated and characterized (Figure 82).²⁰¹ X-ray data reveal a N–N bond distance of 1.202(10) Å and short Re–N(N₂) bonds of 1.861(6) and 1.886(8) Å, consistent with the N–N stretching mode observed in resonance Raman experiments at 1771 cm⁻¹. Recently, the same group reported a slightly different system, (HPNP^{iPr})ReCl₃, which effects the photochemical



Scheme 30. Heterometallic Complexes Containing $Re(PMe_2Ph)_4(N_2)Cl$

Figure 82. Dirhenium complex 102 supported by a bis(phosphine)-amido ligand, $[P^{(CH2)2}N^{(CH2)2}P^{tBu}]^{-}$.

cleavage of N₂ to yield the corresponding nitride species.²⁰² The analogous (μ -1,2-dinitrogen)dirhenium complex, **103**, could be synthesized by one-electron reduction of (HPNP^{iPr})-ReCl₃ with CoCp*₂ in the presence of N₂ (Figure 83). In





contrast to **102**, the pincer N-atoms are *trans* to the N₂ bridge in the solid-state structure of $[(HPNP^{iPr})ReCl_2]_2(\mu-1,2-N_2)$. All metrics indicate less activation of the N–N bond in **103** as compared to **102**; the N–N bond length and ν_{N-N} are 1.169(5) Å and 1733 cm⁻¹, respectively. These protondependent differences in N₂ activation are analogous to that for Mo complex **86**.

3.5. Group 8: Fe, Ru, and Os

The dinitrogen coordination chemistry of the Group 8 metals has primarily focused on iron-based complexes, owing in large part to the use of Fe in the Mittasch catalyst and as the common metal type across all forms of the nitrogenase enzymes. The reported compounds presented below are primarily dimetallic complexes, with rare instances of higher nuclearity complexes. The discussion below begins with arene and cyclopentadienyl complexes and subsequently treats examples with descending denticity of the supporting ligand.

3.5.1. Arene and Cyclopentadienyl Complexes. Few complexes of the Group 8 metals bearing arene or cyclopentadienyl moieties have been reported compared to other ancillary ligands. Of these examples of Cp- (or Cp*) bearing dimetallic N_2 complexes, the osmium compounds were accessed by methods beyond the scope of this review and will not be discussed.^{203,204}

The first crystallographically characterized Fe–N₂ complex bearing a Cp* ligand was reported in 2008 by Tatsumi and coworkers, **104** (Figure 84).²⁰⁵ The experimentally determined N–N bond length of 1.132 Å and ν_{N-N} stretching frequency of 2126 cm⁻¹ are comparable to that of many of the reported mononuclear Fe^{II}–(η^{1} :N₂) compounds supported by phosphine or related strong-field ligands (*vide infra*). Solutionphase UV/visible and ¹H NMR data evidence an equilibrium between the diiron species **104** and the related monoiron– dinitrogen species.

Recently, Zhang et al. reported a unique example of a dinitrogen bridged diiron compound **105** (Figure 84), which utilizes a bidentate phosphinothiolate as an ancillary ligand.²⁰⁶ The complex displays typical structural and spectroscopic parameters for end-on/end-on Fe^{II} $-N_2$ complexes with a N-N bond length of 1.130 Å and N₂ stretching frequency of 2016 cm⁻¹.

A mixed phosphorus chalcogenide chelate was also reported for Ru; that is, the two (k^2 -P,O-1-PⁱPr₂-2-indanone)Cp*Ru fragments bridged by N₂ in **106** (Figure 84).²⁰⁷ The N–N bond length of 1.131(8) Å and the resonance Raman active ν_{N-N} band observed at 2042 cm⁻¹ are comparable to the data for **105**, which is somewhat surprising given the general trend noted up to this point. One observes similar bond metrics and vibrational data for the $[(Cp(P)_2Ru)_2(\mu-1,2-N_2)])][BAr^4_F]_2$ $((P)_2 = dippe, (PEt_3)_2, (PMe^iPr_2)_2, (PPh_3)_2),$ **107** (Figure 84).^{208,209} Specifically, the d(N–N) values vary from 1.114(5) Å for the bis-PEt₃ complex to 1.123 Å for bis-PPh₃ with the N–N stretching mode observed at 2050 cm⁻¹ (dippe), 2062 cm⁻¹ (PPh₃), and 2064 cm⁻¹ (PEt₃) in resonance Raman spectra. No Raman data nor crystal structure were obtained for the bis-PMeⁱPr₂ ligated derivative.

Moving to complexes with η^6 -arene ligands, an amidinato diiron-dinitrogen complex {[(Dipp)NC(^tBu)N(η^6 -Dipp)-Fe]₂(μ -1,2-N₂)}, **108**, was obtained from magnesium reduction of the diiron di(μ -bromide) precursor under N₂ (Figure 85).²¹⁰ The N–N and Fe–N(N₂) bond distances of 1.124(6) and 1.834(3) Å, respectively, are consistent with the vibrational data ($\nu_{N-N} = 2005 \text{ cm}^{-1}$) and as one might anticipate for a formally lower valent Fe center as compared to **105**. Complex **108** can also be accessed by displacement of a η^6 -toluene ligand by N₂ in a monometallic precursor.

The last arene examples are from Sunada and co-workers. The pair of half-sandwich bis-silyl diiron(II) dinitrogen complexes $[(\eta^6-C_6H_5R)Fe(Me_2SiC_6H_4SiMe_2)]_2(\mu-1,2-N_2)$ (109-R; R = H, Me) derived from reaction of $[Fe(mesityl)_2]_2$



Figure 84. Group 8 dimetallic-µ-1,2-N₂ complexes 104–107.

with 1,2-bis(dimethylsilyl)benzene in benzene or toluene (Figure 85).²¹¹ Again, we note that the N–N bond distances are unremarkable from the vantage of N₂ activation and functionalization with d(N–N) values of 1.119(3) Å and 1.126(3) Å for **109-H** and **109-Me**, respectively, which agree with the ~300 cm⁻¹ bathochromic shift for the N–N vibration vs free N₂ (i.e., $\nu_{N-N} = 2035$ and 2022 cm⁻¹ for R = H and Me, respectively). The dinitrogen ligand is readily displaced in this system by ligands, such as CO or PPh₃, and oxidative addition of H₂ is also reported.

3.5.2. Tetradentate Ligands. Collman et al. reported the earliest example of a complex in which a designed pocket was constructed to bind dinitrogen: the diruthenium(II) μ -1,2-dinitrogen complex, **110**, supported by a cofacial diporphyrin ligand (Figure 86).²¹² The N–N distance of 1.1 Å in a partially refined structure is expected given the energy of the observed



Figure 85. Coordination of N $_2$ by $\eta^6\text{-arene-bound}$ Fe centers in complexes 108 and 109-R.





 $\nu_{\rm N-N}$ stretching mode at 2112 cm⁻¹, and both reflect the relatively weak π -backbonding afforded by the Ru^{II} centers.

Related to this report by Collman is that from Floriani and co-workers of a tetrapyrrolide diruthenium dinitrogen complex by utilizing a meso-octaalkylporphyrinogen tetraanion. Occupation of the fifth coordination site on the mononuclear Ru precursors by NaCCH affords $Na_6\{[(Me_8N_4)Ru]_2(\mu-1,2 N_2$ N_2 for which solvent results in differences to the acetylide moiety. When crystallized from DME the complex 111 is best described as containing an acetylide ligand with Ru-C and C-C distances of 1.875(3) Å and 1.185(4) Å. respectively, whereas the THF solvate, 111-THF, evidences more vinylidene character with a contracted Ru-C (1.807(9) Å) and elongated C–C distances (1.31(1) Å) as compared with 111 (Figure 87). In both structures, however, the Ru_2N_2 core with d(N-N) = 1.28(1) Å is common with the end-on/ end-on N2 unit bridging the two ruthenium centers and interacting with four sodium cations. This bond length is the longest observed for a late transition metal with an end-on dinitrogen ligand. Notably, the $Ru-N(N_2)$ distance of 2.251(8) Å in 111-THF is the longest of any dinuclear ruthenium dinitrogen complex, highlighting the effect of the Lewis acid interactions on N₂ activation.

Tetradentate ligands capable of imposing a trigonal coordination environment in analogous fashion to the previously discussed tren systems for Ti and Mo have also been employed for Group 8 metals. Beginning with the all phosphine examples, the dinuclear iron(II) dihydride dinitrogen complex [((PP₃)HFe)₂(μ -1,2-N₂)][BAr^F₄]₂, **112-2H**, and the related mono- (**112-1H**) and dideprotonated (**112-noH**) complexes were reported by Field and co-workers (Figure 88).²¹⁴ Although the N–N distances remain within

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Figure 87. Bis(*meso*-octaalkylporphyrinatoruthenium) complexes 111 and 111-THF.



Figure 88. Diiron-dinitrogen complexes 112.

error (1.129(4) Å for 112-2H vs 1.127(2) Å for 112-1H) across the series, the Fe–N(N₂) markedly contracts with values of 1.905(2) Å and 1.798(2) Å for 112-2H and 112-1H, respectively, as anticipated for greater π -backdonation from the formally more reduced metal centers (Figure 88).

Building from the trigonal triphosphine ligands developed by their group (*vide infra*), Peters and co-workers developed a family of ligands wherein the apical unique P donor in **112** is replaced by a variety of donor atoms. Although these P₃X ligands do not afford multimetallic N₂ complexes, a subsequent iteration of this ligand design in which two of the meridional P donor atoms are replaced with thioether groups and the axial P donor substituted for a silicide allowed access to the diiron complex **113** by the one-electron reduction of the monometallic precursor under N₂ (Figure 89).²¹⁵ The structure was proposed based on vibration spectroscopic methods; ν_{N-N} stretching mode observed at 1881 cm⁻¹ for **113** suggests a dimetallic system.

Related to **112** and the ligands developed by the Peters group is the alane-based system (Altraphos) from Lu and coworkers in which a tren-like pocket binds Al^{III} with a phosphine rimmed upper cavity for binding a second metal ion (Figure 90). The formally iron(0) complex of this alatrane binds N₂ in an end-on/end-on fashion to yield **114**,²¹⁶ with IR spectra with the ν_{N-N} for the N–N stretching mode observed at 2010 cm⁻¹ and an X-ray diffraction determined d(N–N) value of 1.146(7) Å. The lesser extent of activation of the N₂



Figure 89. Diiron-dinitrogen complex (113) employing a bisthioether tripodal ligand.





ligand in **114** as compared to **112** and **113** can be attributed to the σ acidity of the Al^{III} center *trans* to the N₂ donor.

The final two tetradentate examples are the diruthenium polyamine complexes in which the metal centers are six-coordinate: The water-soluble dinitrogen-bridged diruthenium(II) polyamine complex **115** from Yoshimoto et al. and the N_2S_2 -supported diruthenium compound **116** from Sellman and co-workers (Figure 91).^{217,218} Both complexes



Figure 91. Tetraamine and diamine-dithiolate ligated dirutheniumdinitrogen adducts, 115 and 116, respectively.

exhibit similar N–N bond distances with values of 1.126(3) Å and 1.120(6) Å for **115** and **116**, respectively, and comparable to that for the Taube complex $\{[(NH_3)_5Ru](\mu-1,2-N_2)\}^{4+,21}$ The ν_{N-N} stretch is observed by resonance Raman spectroscopy at 1994 cm⁻¹ for **115** and is lower than the reported energy for this vibration in **116** (viz. 2047 cm⁻¹).

3.5.3. Tridentate Ligands: Meridional Chelates. The bis(imino)pyridine (PDI) derivatives are the only meridional chelating or pincer ligand for which N_2 complexes of more

than one Group 8 metal have been reported. A number of iron examples have been reported by Chirik and co-workers of the general type $[(^{R1,R2}PDI)Fe(N_2)]_2(\mu-1,2 -N_2)$ with $R_1/R_2 = Me/Me$, Et/Et, or $Me/^iPr$ (**117-R**₁,**R**₂) or a bis(arylimidazol-2-ylidene)pyridine (^{Me}CNC), $[(^{Me}CNC)Fe(N_2)]_2(\mu-1,2-N_2)$, **117-2** (Figure 92).^{219,220} In all cases, the bridging N_2 ligands



Figure 92. PDI and bis(NHC)-pyridine diiron-dinitrogen complexes, 117.

are minimally activated based on spectroscopic data and singlecrystal X-ray diffraction structures; for example, the N–N bond distances for the bridging N₂ in **117-Me,Me** and **-Et,Et** are 1.137 and 1.123(3) Å, respectively, and Mößbauer data are consistent with formally iron(II) centers and reduced pincer ligands, rather than zerovalent metal centers.^{221,222} Insofar as the bis(imino)pyridine ligand has an accessible LUMO, one anticipates such ligand-based reduction rather than population of N₂ π^* orbitals.

Related to 117 are ruthenium complexes 118 in which a similar PDI chelate is employed with minor differences to substituents on the pyridine ring and the aryl groups on the imine N atoms (Figure 93).^{219,220,223,224} The long N–N bond distance, such as the 1.161(5) Å value determined for 118-1, is



Figure 93. Diruthenium-dinitrogen complexes utilizing PDI chelates, 118.

consistent with more electron rich Ru centers as compared to the previously discussed complexes and suggests Ru(I) or Ru(0) character for these compounds. ¹H NMR spectroscopic data and computational methods suggest that the ground state is an admixture of an S = 0 state and low-lying electronic states of higher-spin multiplicities; this result was interpreted as reflecting the ligand noninnocence of the PDI chelate. **118-2** readily reacts with H₂ to afford the hydride derivative **118-2H**; the contraction of the N–N distance to 1.132(6) Å agrees with a more oxidized Ru center. One notes that the extent of activation of the N₂ ligand based on structural metrics and vibrational data is comparable for Fe and Ru in analogous ligand sets.

Derivatives of the PDI architecture in which the imine arms are saturated have also been explored in the context of ruthenium dinitrogen coordination chemistry. Generally, the ligands utilized employ a pyridyl or phenylide ring with saturated pnictogen donor atoms in the flanking arms. One such series comprises the pincers bearing two dimethylamine arms, two di(*tert*-butyl)phosphine arms, and two di(*tert*butyl)arsine arms as well as the NNP pincer in which one arm is a di(*tert*-butyl)phosphine and the other a dimethylamine (**119-X**, where **X** = **2N** for bis(dimethylamine), **NP** for (dimethylamine)(di(*tert*-butyl)phosphine), **2P** for bis(di(*tert*butyl)phosphine), or **2As** for bis(di(*tert*-butyl)arsine)) (Figure 94).²²⁵⁻²²⁸ For these complexes, two chloride ligands



Figure 94. ENE-type (E = N, P, or As) pincer diruthenium-dinitrogen complexes 119-X.

complete the coordination sphere on each metal and the N₂ fragment adopts a μ -1,2 coordination mode with the two pyridyl planes being orthogonal, implying that each metal backbonds into a different dinitrogen π^* orbital. The N–N distances are comparable across the series with values of 1.110(3) Å, 1.119(4) Å, 1.121(6) Å, and 1.108(5) Å for 119-2N, -2P, -NP, and -2As, respectively. The trend matches that of donor strength, although the observed changes are minimal. The crystallographic bond distances are consistent with the vibrational data where reported (e.g., $\nu_{N-N} = 2099 \text{ cm}^{-1}$ for 119-2N).

A diruthenium complex **120** ligated by a phenylide congener of **119-2P** was reported by Antipin and co-workers (Figure 95), although direct comparison to **119-2P** cannot be readily made as the ancillary ligands differ (viz. hydride and dinitrogen in **120** vs two chlorides in **119-2P**).²²⁹ The N–N bond



Figure 95. PCP pincer-type diruthenium-dinitrogen complex 120.

distance of 1.134(6) Å in the solid state structure of **120** is comparable to that of the **119** complexes and provides a consistent picture of minimal backbonding in these ruthenium pincer complexes. Members of these pincer complexes with saturated arms are in equilibrium with monometallic species, evidenced in some cases by NMR and vibrational spectroscopies.

Nishibayashi and co-workers reported a diiron dinitrogen complex of a related NP₂ pincer ligand (121) as the pyridyl systems; however, the anionic carbazole N atom provides a stronger donor than that of the pyridyl discussed above (Figure 96).²³⁰ In contrast to the planar pyridine-based PNP-pincer



Figure 96. Diiron-dinitrogen complex 121 in which the PNP pincer ligand employs a carbazole backbone.

Mo analogs $(83^{R}-R')$, the metal centers in 121 adopt a distorted tetrahedral geometry about the Fe center with solution magnetometry measurements indicating high spin d^7 metal centers. The observed spin state and geometry are attributed to the size and rigidity of the chelate ring of the complex as the greater rigidity of pyrrole-based complexes favors the square-planar geometry whereas the more flexible six-membered chelate rings of the carbazole complex allow access to the less-strained tetrahedral arrangement. Catalytic N₂ fixation to NH₃ was investigated; however, only minimal amounts of ammonia (0.5 equiv) were obtained.

Expanding beyond the more typical pincer architectures, Suzuki et al. used a tridentate iminophosphorane ligand to synthesize the diiron-dinitrogen complex **122** (Figure 97).²³¹ X-ray crystallography evidences each iron center in a distorted trigonal monopyramidal geometry ($\tau = 0.64$ and 0.65) with d(N-N) = 1.184(6) Å being comparable with other diiron systems discussed above. The Fe-N(N₂) distances of 1.800(4) and 1.814(4) Å, N-N stretching frequency of 1755 cm⁻¹, Mössbauer data with $\delta = 0.73$ mm/s and $\Delta E_Q = 1.83$ mm/s, and DFT calculations are all consistent with substantial activation of the N₂ donor.

The final example of a Group 8 diiron-dinitrogen species employing a pincer ligand is the dinitrogen-bridged di-(hydridoiron) complex **123** from Peters and co-workers (Figure 98).¹⁷ Complex **123** was synthesized by reduction of the mononuclear iron(II) dibromide precursor with NaHBEt₃. The complex exhibits a singlet ground state arising from the



Figure 97. Diiron-*µ*-1,2-dinitrogen complex **122** in which each Fe center is coordinated to an iminophospharane ligand.



Figure 98. DPB-based diiron- μ -1,2-N₂ complex (123).

antiferromagnetic coupling between the two S = 1/2 iron centers, which is consistent with the strong ligand field on each metal center. Complex **123** is competent toward catalytic NH₃ formation from N₂ under photolytic conditions, despite a weakly activated N₂ ligand.

3.5.4. Tridentate Ligands: Pseudo- C_{3v} or *fac* Chelates. The tris(pyrazolyl)borate ligand family is the only *fac* ligand for which both iron and ruthenium dinitrogen species have been reported. Valerga, Puerta, and co-workers reported the dinuclear Ru complexes 124-1/R (R = Me, iPr, and Ph; Figure 99) and 124-2 (Figure 100), in which the unsubstituted



 v_{N-N} : 2091 cm⁻¹ (Me), 2093 cm⁻¹ (ⁱPr)

Figure 99. Diruthenium–dinitrogen complex **124-1**/**R** in which both chelating pyridyl-carbenes and Tp ligands are employed.

tris(pyrazolyl)borate is bound in a *fac* mode and an additional bidentate ligand and a μ -1,2-N₂ occupy the remaining three



Figure 100. Diruthenium-dinitrogen complex 124-2 in which both chelating bisNHC and Tp ligands are employed.

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sites on each metal center.^{232,233} The N-N bond distance is longer for 124-1/Me as compared to 124-1/Ph but statistically equivalent to 124-2 (i.e., 1.124(5) vs 1.103(6) and 1.117(7) Å, respectively). The observed crystallographic changes in the $Ru-N(N_2)$ distances (viz. 1.971(6) and 1.884(6) for $R = Me_1$ and 1.941 and 1.925 Å for 124-1/Ph and 124-2, respectively) suggest, however, that N_2 activation is increased in 124-1/Me. For 124-1/Me vs 124-1/Ph, the increased steric conflicts imposed by the Ph vs Me substituents result in a hindered approach of the two metal fragments disfavoring greater metal-dinitrogen π -backbonding and consequent N₂ activation: however, one notes that vibrational data indicate no major differences between the compounds with $\nu_{\rm N-N}$ = 2091 cm⁻¹ for 124-1/Me and 2093 cm⁻¹ for 124-1/iPr. No N-N stretching band was observed for R = Ph due to the thermal decomposition of the complex by the laser.

One notable difference between Ru examples 124-1 and 124-2 and the iron congeners is that the latter complexes employ more sterically encumbering substituents on the pyrazolate donors, thereby enforcing four coordinate Fe centers. The first report of such an iron species was by McSkimming et al. of the dinuclear Fe–N₂ complex $(Tp^{Ph,Me}Fe)_2(\mu$ -1,2-N₂), 125-1 (Figure 101).²³⁴ X-ray crystal-



Figure 101. Tp-based diiron- μ -1,2-dinitrogen complexes (125).

lographic values for d(N-N) of 1.180(2) Å and the short Fe- $N(N_2)$ distance of 1.790 Å and the observed N–N stretching mode at 1779 cm^{-1} in resonance Raman spectra evidence the strong π -back-donation from the iron(I) center to the dinitrogen ligand and suggest a Fe^{II}-(N₂²⁻)-Fe^{II} formalism. The pyrazolate donors provide a weaker ligand field as compared to the phosphine donors from Peters (vide infra and to be discussed shortly), affording a solution magnetic moment of $\mu_{\rm eff}$ = 6.9 ± 0.2 $\mu_{\rm B}$ attributed to ferrimagnetism from two S = 2 Fe^{II} centers antiferromagnetically coupled with the bridging S = 1 diazenide. Shortly following the report of 125-1, Theopold and co-workers reported the dinculear iron-dinitrogen complex 125-2, which is isostructural to 93-^tBu/Me and 100-Mn (vide supra) and synthesized by reduction of the iron(II) iodide precursor with KC8.¹⁶⁶ The N-N bond length reported is within error of 125-1 as one might anticipate given the comparable ligand fields are the observed ground spin state for these complexes.

An asymmetric diiron-N₂ complex was prepared when $i^{Pr2}TpFe(II)Cl$ was combined with $(depe)_2FeN_2$ resulting in the complex $[(depe)_2Fe](\mu$ -1,2-N₂)[FeTp $i^{Pr,iPr}$]BAr^F₄ (**126**) for which the IVCT band at 910 nm (ε = 1700 M⁻¹cm⁻¹) suggests the charge localization with formal Fe(0) and Fe(II) centers on the method time scales (Scheme 31).²³⁵ The effect



of adding an oxidized iron center instead of a reduced iron center is apparent when comparing the d(N-N) and N-N stretching frequency of **126** with that of **127**, which was reported by Ashley and co-workers.²³⁶ The N–N bond distance is shorter and the N–N stretching mode observed at higher energy for **127** as compared to **126**. Thus, implying a push–pull effect wherein the more Lewis acidic Fe^{II} center aids in activation of the N₂ fragment. In the context of FeMoco, spatially resolved anomalous dispersion refinement (SpReAD) reported by Einsle and co-workers suggested unequal electron distribution within the resting state $S = \frac{3}{2}$ of the cofactor. Should similar disparities in electron distribution be manifested in the E₄ state of the cofactor, which binds N₂, a similar push–pull effect may operate if dinitrogen coordinates in a bridging mode.^{181,237,238}

Two mixed-ligand dinuclear clusters $(Cn^*Ru)(\mu_2-H)_2(RuH-(PR_3)_2)$ were bridged together by a dinitrogen bridge forming $[\{RuCn^*(\mu_2-H)_2RuH(PR_3)_2\}_2(\mu-1,2-N_2)](PF_6)_2$, **128-R**, where $Cn^* = 1,4,7$ -trimethyl-1,4,7-triazacyclononane and $\mathbf{R} = iPr$ and Cyp or cyclopentyl (Figure 102).²³⁹ The cyclopentyl congener was structurally characterized with the observed distances of 1.135(5) Å and 1.937(3) Å for the N–N and Ru– $N(N_2)$ bonds, respectively, being comparable to other dinuclear ruthenium dinitrogen complexes.

Continuing the theme of trigonal ligands, the metallo-ligand ruthenium dinitrogen complex [(CpCo{P(O)(OEt)₂}₃)-bpyRu](μ -1,2-N₂) **129** was structurally characterized with N–N and Ru–N(N₂) bond distances of 1.130(6), and 1.890(5)–1.916(6) Å, respectively (Figure 103).²⁴⁰ Together with resonance Raman data, which show the ν_{N-N} stretching band at 2000 cm⁻¹, **129** is one of the most activated diRu^{II}-dinitrogen complexes to date.



Figure 102. Complex **128-Cyp** featuring two $(Cn^*Ru)(\mu_2 \cdot H)_2(RuH-(PR_3)_2)$ units bridged together by an end-on/end-on N₂.



Figure 103. Diruthenium-dinitrogen complex 129 bearing Co-based metalloligand.

In 2003, Peters and co-workers synthesized a dimetallic fourcoordinate iron complex by utilizing a tripodal, triphosphinoborate ligand [PhB(CH₂CH₂PⁱPr₂)₃]⁻. On treating [PhBP^{iPr}₃]⁻ FeCl with 1 equiv of Na/Hg, a dinuclear iron complex with end-on bound dinitrogen, ([PhB(PⁱPr)₃]Fe)₂(μ -1,2-N₂) (130; Figure 104), was formed.²⁴¹ This complex can also be prepared



Figure 104. Triphosphinoborate-coordinated diiron-µ-1,2-dinitrogen complexes 130 and 130-red.

by reductive coupling between two Fe(IV) nitrides reminiscent of the high valent ruthenium and osmium complexes (*vide infra*).²⁴² The N–N and Fe–N(N₂) distances are 1.138(6) Å and 1.811(5)–1.818(5) Å, respectively, evidencing minimally activated N₂. The one-electron reduced mixed-valent congener is also accessible by reduction with Na/Hg (130-red). The N– N bond length increases to 1.171(4) Å as compared to 130, as might be predicted given the more reducing nature of the metal ions.

Chomitz and Arnold reported the dinitrogen-diiron complex bearing a N_2P_2 ligand (131), which is structurally analogous to

the tren ligands, but this ligand coordinates κ^3 with the apical N not coordinated to the metal centers (Figure 105).⁷⁶



Figure 105. $[N_2P_2]_2Fe(\mu-1,2-N_2)$, 131.

Substituting a neutral phosphine in **130** for a more basic amide donor in **131** results in an elongation of the N–N distance (1.166(3) Å for 131), which agrees with the energy for the N–N stretching mode (1760 cm^{-1}) .

The dinitrogen-bridged diiron complex using the cyclohexylsubstituted derivative of the $[PhBP^{iPr}_3]^-$ scaffold (132) was prepared by Saouma *et al.* (Figure 106). In contrast to the four



Figure 106. Triphosphinoborate diiron- μ -1,2-dinitrogen or hydrazine complexes 132-N₂ and 132-N₂H₂.

coordinate Fe centers in 130, the iron centers in 132 are six coordinate with a κ^2 -acetate as a coligand. The μ -1,2dinitrogen complex is in equilibrium with the dinitrogen-free monoiron species upon warming; together with the N–N bond length of 1.120 Å and a stretching frequency at 2083 cm⁻¹, this observation points to minimal activation of the N₂ donor. A series of related species to 132 were also reported, including the hydrazide, diazenide, and ammonia adducts; although the reactivity and interconversion of these species bears relevance to N₂ activation, such details are beyond our defined scope here.²⁴³

Peters and co-workers have developed a pair of tridentate ligand scaffolds redolent of their triphosphinoborane system in which the tridentate diphosphinoborane (or DPB) ligand has sufficient flexibility to adopt a facial coordination mode rather than the meridional mode of the typical pincer ligand family. Reduction of the isopropyl-substituted (DPB)FeBr complex with 1 equiv of Na/Hg yields the diiron-(μ -1,2-N₂) complex, **133** (Figure 107).²² The solid-state structure of the compound displays the two Fe centers in pseudotetrahedral coordination geometries, with one Fe center interacting with the *ipso*-C of



Figure 107. Dinitrogen adduct of (DPB)Fe, 133.

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the phenyl substituent on B and the other Fe ion bound η^2 to the *ortho*- and *ipso*-C of the phenyl substituent; this Fe-BC interaction is highly flexible, however, as the ¹H NMR spectrum indicates the two Fe centers are equivalent. The N–N bond distance of 1.17 Å is comparable to that for **131** and elongated with respect to **130**; the latter comparison is complicated by the metal–B interaction which could be considered as a formal borane, boryl, or boride with an iron center in either the zero-, mono-, or divalent oxidation states.

3.5.5. Bidentate Ligands. *β*-Diketiminates have been the most utilized with respect to iron-dinitrogen chemistry. The first such example was the three coordinate end-on/end-on dinitrogen complex $[(^{Dipp}NacNac^{tBu})Fe]_2(\mu$ -1,2-N₂), **134**-^t**Bu**, reported by Holland and co-workers, followed later by the two-electron reduced congeners M₂{ $[(^{Dipp}NacNac^{tBu})Fe]_2(\mu$ -1,2-N₂)}, **134**-^t**Bu**/2M (Figure 108).²⁴⁴ Prior to reduction, the



Figure 108. $Bis(\beta$ -diketiminatoiron)(μ -1,2-dinitrogen) complexes, 134.

N–N bond is ~0.1 Å longer than that in free N₂ for 134-^tBu with a value of 1.182(5) Å, and reduction to 134-^tBu/2M activates the bound N₂ with the bond distance elongated to 1.239(4) and 1.233(6) Å, for M = Na and K, respectively. Consistent with greater extent of π -backbonding, one notes that the Fe–N(N₂) shortens from 1.770(5)–1.779(5) Å to 1.763(6)–1.765(6) Å in 134-^tBu/2K as well as a decrease in the energy of the N–N stretching mode from 1778 cm⁻¹ in 134-^tBu to 1583 and 1589 cm⁻¹ for 134-^tBu/2Na and

134-^tBu/2K, respectively. Indeed, the same trend is observed for the N–N and Fe– $N(N_2)$ bond distances and the energy of the N-N vibration for the analogous methyl substituted congener: $[(^{Dipp}NacNac^{Me})Fe]_2(\mu-1,2-N_2)$ or **134-Me**; the one-electron reduced analog 134-Me/K, wherein the K cation is chelated by a crown ether;²⁴⁵ and the two-electron reduced complexes 134-Me/2M (M = Na, K, Cs, Rb). Across these series of complexes, one notes that the N–N and Fe– $N(N_2)$ bond distances and the energies for the N-N stretching modes exhibit minimal sensitivity to the alkali cation identity (Figure 108); encapsulation of that cation, however, affords structural metrics within error of that in 134-Me, evidencing the added effect of the cation-N₂ interaction toward favoring π backbonding. Taken together, the bonding picture evidenced from the structural and vibrational data are recapitulated in the magnetic, Mößbauer, and DFT results: 134-R ($\mathbf{R} = {}^{t}Bu$, Me) is best described as being a ferrimagnet due to antiferromagnetic coupling between each Fe^{II} center and a triplet N_2^{2-} . A similar electronic structure was later proposed for the tris(pyrazolyl)borate complex 125, mentioned above. Addition of pyridines to 134-R increases the coordination number on each Fe center to yield 134-R/X (Figure 109). Reaction of 134-tBu with 4-



Figure 109. NacNac-ligated diiron-dinitrogen complexes 143-R/X.

tert-butylpyridine results in lengthening of the Fe–N(N₂) bond to 1.794(2)–1.804(2) Å and nominal contraction of the N–N bond distance to 1.161(4) Å.²⁴⁶ The decreased π backbonding upon increasing the coordination number of the Fe center is more clearly noted in the methyl congener, viz. [(^{Dipp}NacNac^{Me})Fe(^tBuPy)]₂(μ -1,2-N₂), for which these bond metrics are 1.816(2) and 1.151(3) Å, respectively. This correlation of reduced coordination number with N₂ activation on low valent iron centers is consistent with prior computational studies by Smith et al.²⁴⁶

Reduction of the diiron di(μ -chloride) complex for which the sterics of the β -diketiminate are reduced (specifically, the 2,6-diisopropylphenyl groups are replaced by 2,6-dimethylphenyl, and the backbone C–H of the chelate is replaced by a C–CH₃) results in cleavage of N₂ to give the tetrairon di(μ nitride) complex 135 (Scheme 32).²⁴⁷ The large d(N–N) value of 2.799(2) Å in the solid-state structure agrees with a di(μ -nitride) formulation, as do the metal–ligand bond Scheme 32. Synthesis of $Di(\mu$ -nitride) 135



distances and the oxidation states (assigned from Mößbauer spectral simulations) of the iron centers. Each potassium cation interacts with one of the nitrides, with two chlorides, and with an aryl group of one of the β -diketiminate ligands. DFT calculations provide insight into the reasons for the bifurcation in reactivity away from μ -1,2 coordination of N₂ as in the 134 series of complexes and toward N2 scission. The reduced ligand sterics allow for approach of a third formally Fe^I center, resulting in a transient μ - η^1 : η^2 : η^1 -dinitrogen ligand.²⁴⁸ The minimum requirement for three iron centers to cleave N2 was supported by the products arising from reduction of $\{[(^{DMePh}NacNac^{Me3})Fe]_2\}(\mu_2-Cl)_2$ with different alkali metal reductants (Na and MC_8 , where M = K, Rb and Cs).²⁴⁹ In the case of Na⁺, K⁺, and Rb⁺, complete cleavage of N₂ was observed to generate analogous tetra- or tri-iron di(μ -nitride) products, whereas reduction with cesium yields $\{Cs_2[(^{DMePh}NacNac^{Me3})Fe(\mu_2-Cl)(\mu-1,2-N_2)_2]\}$ (136-2N₂, Figure 110). These results are rationalized based on the alkali cation facilitating or templating the iron-dinitrogen interactions and allowing access to the reactive transient triirondinitrogen adduct; that is, the larger Cs⁺ sterically precludes the close approach of the iron fragments. Upon increasing the number of reducing equivalents from two as in the instances above to four, the triiron tri(μ -1,2-dinitrogen) complexes 136- $3N_2$ (M = K, Rb, and Cs; Figure 110) are instead isolated, suggesting that the rate of reduction vs aggregation or N2 scission must be balanced appropriately.

Employing a variation on the β -diketiminate architecture, Fryzuk and co-workers reported the μ -1,2-dinitrogen diiron complex of an enamido-phosphinimine ligand 137-R (R = Mes or DIPP, Figure 111).²⁵⁰ The electronic asymmetry of the



Figure 110. Trimetallic iron-dinitrogen complexes utilizing β -diketiminate ligands.



Figure 111. Diiron-dinitrogen complexes 137-R supported by enamido-phosphinimine donors.

chelate was reasoned to limit the delocalization of charge as compared to the β -diketiminate, consequently affecting the extent of N₂ activation in the reduced polynuclear iron complexes. This hypothesis was later questioned based on comparable bond metrics within the ligand backbone of the iron(II) bromide complex of this enamido-phosphinimine ligand and that of (^{Dipp}NacNac^{tBu})FeCl. As one might anticipate then, the N–N bond distances in 137-R of 1.186(3) and 1.183(6) Å for R = DIPP and Mes, respectively, are comparable to those observed in 134-R as are the Fe–N(N₂) distances (1.776(2) and 1.764(3) Å for R = DIPP and Mes, respectively).

Although the N,N-chelates mentioned above have yet to be explored on Ru in the context of N₂ coordination and activation, acetylacetonate (acac) has been used and allows access to the μ -1,2-dinitrogen bis[bis(acac)-(triisopropylphosphine)ruthenium] complex, **138** (Figure 112).²⁵¹ Two isomers are observed in solution spectra: the homochiral ($\Delta\Delta/\Lambda\Lambda$) and the heterochiral ($\Delta\Lambda/\Lambda\Delta$)



Figure 112. Diruthenium-dinitrogen complex 138.

isomers. The solid-state structure evidences a short N–N distance of 1.135(8) Å and a Ru–N(N₂) distance of 1.919(4) Å. These values, together with the ν_{N-N} stretching frequency of 2089 cm⁻¹, are comparable to others reported for formally Ru^{II} complexes.

3.5.6. Monodentate Ligands. As noted in the introduction, Allen and Senoff's report of the $[Ru(NH_3)_5(N_2)]^{2+}$ —the first transition-metal dinitrogen complex reported—was quickly followed by Taube's communication of the first dinitrogen-bridged dimetallic complex $[(Ru(NH_3)_5)_2(\mu-1,2-N_2)]^{4+}$ (139; Figure 113).^{30,31} The product was characterized by UV/vis spectroscopy, but one predicts similarly short N–N bond distances as compared to the other diruthenium(II)-dinitrogen complexes.



Figure 113. Complex $[(Ru(NH_3)_5)_2(\mu-1,2-N_2)]^{4+}$ (139).

In contrast to the other Group 8 metals, osmium has few examples of multimetallic N₂ complexes, but related ammonialigated complexes such as **139** were reported by Magnuson and Taube in 1972.²⁵² Heating $[(NH_3)_5Os(N_2)]^{2+}$ with *cis*- $[(NH_3)_4Os(N_2)_2]^{2+}$ followed by an acid workup and aerial oxidation afforded $[H_2O(NH_3)_4Os(\mu-1,2-N_2)Os(NH_3)_5]^{5+}$, **140-1**, and $[Cl(NH_3)_4Os(\mu-1,2-N_2)Os(NH_3)_5]^{4+}$, **140-2** (Figure 114).²⁵² $[\{Cl(NH_3)_4Os\}_2(\mu-1,2-N_2)]^{3+}$, **140-3**, was also prepared using a similar protocol. Raman bands assigned as the ν_{N-N} stretching modes were observed at 1995 and 1999 cm⁻¹ for **140-2** and **140-3**, respectively, with spectroscopic data not reported for aqua-complex **140-1**.



Figure 114. Dimetallic osmium-dinitrogen complexes, 140.

The first example of a dinuclear iron-dinitrogen complex was reported in 1981 by Berke and co-workers, who reported the diiron- μ -1,2-N₂ complex **141** by irradiation of Fe(CO)₃(P-(OMe)₃)₂ complex in diethyl ether at -80 °C under a N₂ atmosphere (Figure 115).²⁵³ The presence of two π -acidic carbonyl ligands on each iron center in this complex diminishes iron to N₂ π -backbonding, which results in a N–N bond distance of 1.13 Å.



Figure 115. Bis(dicarbonyl-bis(phosphite)iron)-dinitrogen complex 141.

Our final species from Group 8 is **142**, which is bis(dihydridoruthenium)-dinitrogen complex supported by tris(isopropyl)phosphines (Figure 116).²⁵⁴ Compound **142** is



Figure 116. Dinitrogen-bridged ruthenium dihydride complex 142.

derived from reaction of the Kubas-type complex Ru-(H)₂(H₂)₂(PⁱPr₃)₂ with N₂ in solution and exists in equilibrium with the monomeric congener (ⁱPr₃)₂P-(H)₂(N₂)₂Ru.²⁵⁵ Once again, one notes that the N–N bond distance is unremarkable in comparison to free N₂ with a value of 1.113(2) Å and the Ru–N(N₂) distances are expectedly long ranging from 2.051(1) to 2.049(1) Å. Indeed, an overall theme from Group 8 is that low valence provides the greatest extent of observed π -backbonding to N₂ and points to an inversion of the trend from earlier *d*-block metals in which the heavier and more reducing members of the group demonstrated greater proclivity to activate and cleave N₂.

3.6. Group 9: Co, Rh, and Ir

Fewer examples of multimetallic dinitrogen complexes have been reported for these metals as compared to prior groups. This observation results partly from the increasing electronegativity and consequently poorer π -backdonation by the metal centers to a bound dinitrogen as one moves across the periodic table as our survey. As for Group 8, the dinitrogen coordination here is dominated by cobalt, with fewer examples for Rh, and only two for Ir.

3.6.1. Tridentate Ligands: Pseudo C_{3v} or fac Chelates. Despite the first report of a cobalt dinitrogen complex being contemporary with those for other transition metals,^{256–258} the coordination chemistry of dinitrogen at cobalt centers lay underexplored over the subsequent two decades. The first example of a polynuclear Co–N₂ complex was the report by Cecconi et al. of the zerovalent dicobalt complex 143, which was supported by 1,1,1-tris(diphenylphosphinomethyl)ethane or tppme (Figure 117).²⁵⁹ Almost 20 years after 143 was reported, Betley and Peters communicated the dicobalt(I)– dinitrogen complex 144, in which each metal center is ligated by a tris(diisopropylphosphinomethyl)borate (Figure 117).²⁴¹ Reduction of 144 by Na/Hg yielded the mixed-valent



Figure 117. Triphosphinoborate-coordinated dinuclear cobaltdinitrogen complexes 143, 144, and 144-red.

dicobalt(I/0) congener 144-red; both 144 and 144-red are isostructural with the iron analogs 130 and 130-red. The scorpionate tris(pyrazolyl)borate enforces a similar trigonal environment on the Co centers and affords isostructural dicobalt dinitrogen compounds (145-R/R'; Figure 118) as





143 and 144.²⁶⁰ In contrast to 143 and 144, which bear a stronger field arising from the P-donor set, the 145-R/R' exhibit a slightly bent Co–N–N–Co fragment, which arises from a pseudo-Jahn–Teller effect. For the series 143, 144-red, and 145-R/R' the N–N bond distances are all comparable and indicate a minimal metal–dinitrogen π -backbonding interaction with values of 1.18(2), 1.147(4), 1.14(3) (R/R' = Np/H), and 1.154(9) Å (R/R' = iPr/Me), respectively. These bond metrics are consistent with the vibrational data; for example, the ν_{N-N} stretching mode is at 2056 cm⁻¹ for 145-Np/H. Despite similar bond distances as observed for the Fe^I congeners, one notes that the vibrational data indicate greater π -backbonding from Fe^I as compared to Co^I (cf. 1779 cm⁻¹ for 125-1 and 2056 cm⁻¹ for 145-Np/H), in agreement with expectations based on changes in electronegativity.

The related tris(3,5-dimethylpyrazolyl)hydridoborate was reported as a ligand for a diiridium–dinitrogen complex, **146**

(Figure 119).²⁶¹ Similar to the differences between the Ru vs Fe tris(pyrazolyl)borate complexes, the Ir centers are not



Figure 119. Tp-ligated dinuclear iridium-dinitrogen complex 146.

constrained to being four coordinate as is the case for Co; the metal centers are six coordinate with the scorpionate occupying three sites, the μ -1,2-dinitrogen bound in one, and two phenylides ligands in the remaining two coordination sites. The N–N and Ir–N(N₂) bond distances are as expected for a weakly bound N₂, with d(N–N) = 1.13(3) Å and d(Ir–N(N₂)) = 1.93(2) Å.

Wu et al. reported a heteronuclear Ti–Co tris-(phosphinoamide) dinitrogen complex, which reacts with 1 equiv of azobenzene or 1,2-diphenylhydrazine resulting in the oxidation of one phosphinoamide arm and formation of the μ -1,2-dinitrogen complex 147 (Scheme 33).²⁶² The N–N bond distance of 1.065(4) Å, which is analogous to free N₂, agrees with the formal higher oxidation states for the metal centers as compared with 143 and 144.

Scheme 33. Synthesis of 147



A sulfur ligated dinuclear cobalt complex was prepared electrochemically by Fernandez et al. by using a phenyl-phosphanyldithiolate and bipyridine in the presence of a Co electrode. Complex $[(PhP(C_6H_4S)_2)(bipy)Co]_2(\mu-1,2-N_2),$ 148 (Figure 120), was structurally characterized and revealed two octahedral Co(II) centers with the S₂P chelate binding in a *fac* coordination mode and N–N and Co–N(N₂) bond distances of 1.156(7) Å and 1.910(4) Å.²⁶³

3.6.2. Tridentate Ligands: Meridional Chelates. Mindiola and co-workers reported a PNP-pincer ligated dicobalt-

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Figure 120. Tridentate phosphanyldithiolato-based dicobalt end-on/ end-on dinitrogen complex 148.

(I)-dinitrogen complex $[({}^{iPr}PNP)Co]_2(\mu$ -1,2-N₂) complex, **149-Co** (Figure 121), which is prepared by ^tBu-Li reduction of



M = Rh; d(N-N): 1.119(2) Å

Figure 121. Dinuclear Co and Rh dinitrogen adducts, 149-M, wherein each metal is ligated by a PNP-pincer chelate.

the monometallic Co(II) precursor under N_2 .²⁶⁴ The N–N bond distance and stretching frequency observed (1.144(3) Å and 2024 cm⁻¹, respectively) are indicative of minimal backbonding to the N_2 donor. Comparison to the rhodium analog **149-Rh** evidence the greater activation afforded by the lighter metal with the N–N and Rh–N(N₂) bond lengths of 1.119(2) and 1.904(1) Å for **149-Rh**.²⁶⁵

In 2015, Nesbit et al. synthesized a dicobalt(0) $-N_2$ complex with a bis(phosphino)borane chelate, **150** (Figure 122), which



Figure 122. Bis(phosphino)borane-ligated dicobalt(0)-dinitrogen complex, 150.

is isostructural with diiron complex 133.²⁶⁶ The dicobalt complex cocrystallized with the monometallic congener, with the dimetallic-monometallic equilibrium lying toward the monocobalt complex. The solid state structure of 150 revealed each cobalt center as five-coordinate with a $Co-C_{ipso}$ interaction making up the fifth coordination site, analogous to 133. The observed N–N bond distance of 1.129(3) Å is shorter than that for the Fe congener, reinforcing the effect of the changing electronegativity of the metal center on π backbonding.

A series of pincer-based dinitrogen complexes of Rh and Ir have been reported, the majority of which are from Milstein and co-workers (151-1 to 151-8; Figures 123 and 124).^{265,267-274} From the context of dinitrogen activation



Figure 123. PCP-pincer dinuclear rhodium- or iridium-dinitrogen complexes, 151-1 to -4.



Ar = 2,6-dimethylphenyl

Figure 124. Pincer-based dirhodium-dinitrogen compounds, 151-5 to -8.

and potential functionalization, these complexes are unremarkable with N–N bond lengths ranging from 1.108(3)-1.130(7) Å and Rh–N(N₂) distances from 1.912(2)-1.991(9) Å. These dimetallic species exist in equilibrium in solution with their

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mononuclear dinitrogen counterparts, with the exception of 151-7 and 151-8.

3.6.3. Bidentate Ligands. The only bidentate ligand reported to afford polynuclear cobalt dinitrogen species is the β -diketiminate, reported exclusively by Holland and coworkers. Reduction of the cobalt(II) chloride complexes of the same β -diketiminate ligands as in 134 afforded the isostructural dicobalt(I)-dinitrogen complexes, 152-R (R = ^tBu, Me) (Figure 125).²⁷⁵ As for the iron examples, further



Figure 125. $Bis(\beta$ -diketiminatocobalt)(μ -1,2-dinitrogen) complexes, 152.

1.220(4)

two-electron reduction of 152-^tBu can be effected to generate the di(potassium) or di(sodium) salts, in which the two alkali cations are tightly associated with the bridging N2 and the aromatic rings of the diisopropylphenyl substituents. As with the Fe examples, the N-N bond and metal- $N(N_2)$ bond distances evidence greater N2 activation with reduction and association of the alkali cations, as well as nominally weaker metal-dinitrogen π -backbonding for Co as compared to Fe. Specifically, the N–N bond distance in 152-^tBu is 1.1390(15) Å, which lengthens to 1.220(2) Å and 1.211(3) Å in 152-^tBu/ 2K, 152-^tBu/2Na, respectively. The $\nu_{\rm N-N}$ increases from 1589 cm⁻¹ (134-^tBu/2K) and 1583 cm⁻¹ (134-^tBu/2Na) to 1599 cm⁻¹ for 152–2K and 1598 cm⁻¹ for 152–2Na. Spitzer et al. reported the methyl congener, 152-Me/2K, for which the N-N bond lengths of 1.215(3) and 1.220(4) Å (depending on crystallization conditions) are comparable to those in 152-^tBu/ 2M.²⁷⁶ 152-^tBu/2K can also be prepared via a nonreductive approach. The dihydride congener $[(^{Dipp}NacNac^{tBu})Co]_2(\mu$ -H)₂ readily converts to the dinitrogen-bridged adduct upon exposure of the precursor solution to an atmosphere of N₂.²⁷⁷ Counter to the general trend that the N₂ activation appears to be less for Co vs Fe (albeit nominally in some cases), the N–N stretching frequency observed for 152-Me/2K at 1568 cm⁻¹ is notably lower in energy than the directly related Fe analog 134-Me/2K for which $\nu_{\rm NN} = 1625 \text{ cm}^{-1.245}$ **3.6.4. Monodentate Ligands.** Two final examples for Group 9 are presented here: the phosphine ligated dicobalt and -rhodium dinitrogen complexes. Both examples show minimal lengthening of the N–N bond, but the lack of reported vibrational data prevents a more complete evaluation of N₂ activation. First, Klein et al. reported the isolation and characterization of $[CoH(PMe_3)_3]_2(\mu$ -1,2-N₂), **153** (Figure 126), with a comparable N–N bond length to many other



Figure 126. Bis[hydrido-tris(trimethylphosphine)cobalt](μ -1,2-dinitrogen), 153, and bis[*trans*-hydrido-bis(triisopropylphosphine)-rhodium](μ -1,2-dinitrogen), 154.

penta-coordinate cobalt species discussed here.²⁷⁸ Second, Yoshida et al. reported the solid-state structure of $[(P^{i}Pr_{3})_{2}HRh]_{2}(\mu$ -1,2-N₂), **154** (Figure 126).²⁷⁹ The experimentally determined bond metrics are comparable to those for **142**, with N–N and Rh–N(N₂) bond lengths of 1.134(5) Å and 1.981(5)–1.973(5) Å, respectively.

3.7. Group 10: Ni, Pd, and Pt

The only examples of multimetallic dinitrogen complexes for Group 10 metals are of nickel. In 1971, Jolly et al. reported the structure of the first multinuclear nickel dinitrogen complex, **155-Cy**, which was synthesized by the reaction of AlMe₃, Ni(acac)₂, and PCy₃.²⁸⁰ The tris(isopropyl)phosphine congener **155**-ⁱPr was reported more recently;²⁸¹ for both complexes, the N–N distances are minimally elongated relative to free dinitrogen with d(N–N) of 1.1285(2) and 1.158(5) Å for **155-Cy** and -ⁱPr, respectively (Figure 127). Similarly, the



Figure 127. Dinickel-dinitrogen complexes, 155-R.

metal–N distances do not suggest metal–dinitrogen multiple bonding character, which is consistent with a mild N_2 activation, evidenced by the N–N stretching band at 1908 cm⁻¹ reported for 155-ⁱPr. The remainder of this survey is organized by decreasing ligand denticity as delineated for the preceding groups.

A repeated structural type in tridentate ligands is that of a *fac*-coordinating ligand comprised of two or three phosphorus donor atoms (Figure 128). The reported compounds herein employ a bis(phosphine)borane (156-B),²⁸² a triphosphine chelate (156-3P),²⁸³ a ferrocenyl triphosphine ligand (156-3P),²⁸³



Figure 128. Dinuclear nickel-dinitrogen adducts 156 bearing *fac*-coordinating tridentate ligands.

Fc3P),²⁸⁴ and the diphosphine-phosphinite ligated compounds (**156-2P,POR**; R = Me and ${}^{i}Pr$).²⁸⁵ The synthetic route of these complexes follows a typical reduction of the nickel halide precursor or metalation with Ni(COD)₂ with the exception of **156-2P,POR**, which is accessed by reaction of the phosphide-chlorido-nickel(II) complex with an alkoxide source under a N₂ atmosphere (Scheme 34). In these complexes, the metal

Scheme 34. Synthesis of 156-2P,POR



centers are in pseudotetrahedral environments, with N–N bond distances of 1.123(3), 1.124(3), 1.122(3), 1.112(5), and 1.133(4) Å for the **B**, **3P**, **Fc3P**, **2P**,**POMe**, and **2P**,**PO'Pr** compounds, respectively. The donors in **156-B** differ from the other examples insofar as the third chelate donor is the π -type orbital at B–C_{ipso}. The comparison of the energies of the N–N stretching vibrations is more informative, however; as one notes the minimal difference between the 2045 vs 2038 cm⁻¹ values for **156-3P** vs **156-2P**,**POMe**. The ligand field

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consequently appears to have minimal effect on the extent of N-N activation for Ni^0 species.

A related scorpionate or *fac*-coordinating ligand type as in **156-3P** wherein the P-Me is replaced by a silicide also accesses a dinitrogen-bridged complex (**157**), albeit by a slightly distinct route to the **156** complexes.²⁸⁶ Reaction of the nickel-hydride precursor with N₂ results in reductive elimination of the silicide and hydride to afford the silane. The newly formed Si–H participates in an agostic interaction with the Ni⁰ center and the dinitrogen binds in a μ -1,2 fashion. Compound **157** is in equilibrium in solution with the nickel hydride starting material and the mononuclear nickel–dinitrogen species (Scheme 35). The N–N bond distance is once again





comparable to the **156** complexes with a value of 1.127(3) Å as is the $\nu_{\rm N-N}$ of 2050 cm⁻¹. The dinickel-dinitrogen complex, **158**, can be considered as **157** without the agostic interaction to the Si-H bond (Figure 129).²⁸⁷ The longer N-N bond



Figure 129. Xantphos-ligated dinickel-µ-1,2-dinitrogen complex, 158.

distance of 1.144(3) Å in **158** compared to the prior examples suggests greater activation, but supporting vibrational data is not available. As noted in instances previously, N–N bond distances may not be sufficient for ascertaining the extent of π -backbonding.

As was the case for chromium, iron, and cobalt, the bis(β diketiminatonickel)dinitrogen complexes have also been reported (159, Figure 130).^{288–290} The complexes are isostructural with the iron (134) and Co (152) congeners, with the neutral (159) and one- (159-1K) and two-electron reduced complexes (159-2M, where M = Na or K, and 159-Na,K) reported. Solution magnetometry suggests an S = 1ground state for the dimetallic species ($\mu_{\text{eff}} = 2.40 \ \mu_{\text{B}}$), which agrees with the DFT calculation wherein the ground state is



Figure 130. [Bis(β -diketiminatonickel)](μ -1,2-N₂) complexes 159.

comprised of two uncoupled or weakly coupled nickel $S = \frac{1}{2}$ centers. The trend in N₂ bond activation with reduction of the complex is as noted before for the Fe and Co compounds, with the vibrational data evidencing less activation of N2 as compared to Co and Fe. Starting with 159 for which the N-N bond distance and stretching frequency are 1.120(4) Å and 2164 cm⁻¹, these values trend toward further N₂ reduction in 159-1K and 159-2K for which these values are 1.143(8) Å and 1825 cm⁻¹, and 1.185(8) Å and 1698 cm⁻¹, respectively. The alkali cation identity has minimal effect on the extent of N2 activation with 159-2Na and 159-Na,K having N-N bond distances and stretching frequencies of 1.192(3) Å and 1685 cm⁻¹ and 1.195(4) Å and 1689 cm⁻¹, respectively. As one might expect, the Ni $-N(N_2)$ bond distances contract with reduction. Calculations on the reduced complexes note accumulated spin density on the N2 bridge being stabilized by the proximal alkali cations.

The first example of dinitrogen coordination to a late transition metal in a side-on/side-on fashion was the phenylide cluster **160** (Figure 131). This cluster was accessed by reaction of Ni(CDT) (CDT: trans-1,5,9-cyclododecatriene) with phenyllithium ($[(C_6H_5Li)_6Ni_2N_2\{(C_2H_5)_2O\}_2]_2$, **160-1**) or a mixture of phenyllithium and phenylsodium ($\{C_6H_5[Na\cdot O(C_2H_5)_2]_2[(C_6H_5)_2Ni]_2N_2NaLi_6(OC_2H_5)_4\cdot O(C_2H_5)_2\}_2$, **160-2**) under a dinitrogen atmosphere.²⁹¹⁻²⁹³ The clusters are best described as dimers in which $[(Ph_2Ni)_2(N_2)]$ units are closely associated with the alkali countercations. The N–N bond axis is orthogonal to that of the Ni–Ni bond, reminiscent of the alkyne coordination to $Co_2(CO)_6^{.294}$ The formal metal oxidation states, association of many alkali cations with the



*Some Li atoms and solvent molecules are omitted for clarity **160-2** d(N–N): 1.359(18) Å

Figure 131. Side-on/side-on coordinated N_2 in phenylide Ni clusters (160).

reduced N₂ ligand, and side-on/side-on coordination of N₂ lead to substantial activation of the N–N bond, with the values of 1.36(2) Å for **160-1** and **-2** being among the longest reported for any late *d*-block metal.

3.8. Group 11: Cu, Ag, and Au

As has been stated for a number of instances thus far, the increasing electronegativity of the *d*-block metals on moving from Group 4 to Group 11 results in poorer π -backbonding from the metal to π -acid ligands. Therefore, one notes fewer examples for Ni vs Co or Fe. The changes to the reducing power of the 4d and 5d metals as one similarly traverses the table has a similar consequence on dinitrogen coordination chemistry with far fewer examples for Rh and Ir than Ta and Hf. Unsurprisingly then, molecular examples for Group 11 were absent from the literature until the past decade, and no examples of N₂ coordination to Au or Ag have been reported hitherto. We note that a gold hydrazide cluster was reported in which a N₂ ligand is present; however, the ligand likely arises from deprotonation of the hydrazine coreactant rather than N₂ coordination and activation based on spectroscopic data reported.295

The two molecular examples for Group 11 are copper(I) complexes and the observed extent of N–N bond activation extends the trend observed from iron to nickel. The first example is a tricopper(I) complex of a tris(β -diketiminate) cyclophane (161, Figure 132) and the second is a dicopper(I) species supported by tris(pyrazolyl)borates (162; Figure 133).^{296,297} In complex 161, the dinitrogen coordinating in a μ - η^1 : η^2 : η^1 mode is the major contributor in the structural solution, which is rare in dinitrogen coordination chemistry with only two other examples (1-Cp and 1-Cp^{Me13}) known.^{45,46} Monocopper(I) β -diketiminate complexes were previously demonstrated to prefer coordination to solvent ligands, such as arenes, ethers, or nitriles, rather than N₂; one

Figure 132. Tricopper(I)- μ - η^1 : η^2 : η^1 -N₂ unit housed in a tris(β -diketiminato)cyclophanate ligand scaffold.



Figure 133. Dicopper(I)-*µ*-1,2-dinitrogen complex supported by tris(pyrazolyl)borates.

concludes, therefore, that the steric constraints of the cyclophane, which prevent solvent approach within the cavity, effectively select N2 from the reaction milieu. The N-N bond distance of 1.0854(1) Å in 161 is comparable to that of free N₂, which is at odds with a substantial decrease in the N-N stretching frequency (1952 cm^{-1} for 161). The solution-phase thermally averaged symmetry of this complex is D_{3h} however, and may point to liberation or other effects as influencing the solid state bond metrics. Comparison to other β -diketiminate complexes is challenging given the differences in nuclearity; however, one notes the similarities to those effects of alkali cations on the N-N vibrational frequency for 134-Me/K and -Me/2K. Consistent with this interpretation, DFT calculations including QTAIM analysis of the Cu-N2 interactions suggest a primarily electrostatic interaction rather than substantial π backbonding from Cu^I to N₂.

The second example is from Warren and co-workers wherein the tris(pyrazolyl)borate ligand enforces pseudotetrahedral coordination environments at each copper center in the dicopper(I)-(µ-1,2-dinitrogen) complex 162.²⁹⁶ Similar to 161, N-N and Cu-N(N₂) bond distances of 1.112(5) Å and 1.829(3) Å, respectively, evidence minimal π -backbonding from Cu(I) to N_2 , consistent with the resonance Raman active N-N stretching mode at 2130 cm⁻¹. Considered against the vibrational and structural data for 125 and 145, the decreased activation of the bound N₂ is readily apparent; for example, the N-N stretching vibration is observed at 1779 and 2056 cm⁻¹ for 125-1 and 145-Np,H. As expected from inclusion of a sideon bound Lewis acid, the N-N stretching frequency for 161 is substantially lower than that of 162 and on par with the effects noted for the β -diketiminate complexes of other late 3d transition metals.

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3.9. Group 13: N₂ Activation by Boron

Beyond the lanthanides and actinides, the only other discrete complexes reported to activate dinitrogen are the boron complexes from Braunschweig and co-workers. In the reported examples, *in situ* formation of mononuclear borylene species by reduction of the dibromoborane under a N₂ atmosphere results in formation of the diboryl μ -1,2-dinitrogen adducts.^{298,299} The transient borylene in both reports is stabilized by the cyclic alkylaminocarbene (or CAAC) 1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene, and an aryl donor, which is either duryl (Dur) or triisopropylphenyl (TIPP). For Dur(CAAC)BBr₂, a mixture of two species is observed: one arises from C–H activation of the isopropyl group on the CAAC and the other from capture of 1 equiv of N₂ to generate [Dur(CAAC)B]₂(μ -1,2-N₂), **163-1** (Scheme 36). The bond

Scheme 36. Synthesis of 163-1



metrics for the B_2N_2 fragment are indicative of a B = N = NB formalism as the N–N and B–N distances are in the range of those in azo compounds (1.248(4) Å) and aminoboranes (1.423(4)-1.403(5)^Å). In addition, the C_{CAAC}-B bond distances of 1.528(5)-1.541(4) Å are shorter than for the starting dihaloborane precursors or the monohaloboryl, supporting substantial π -backbonding from the B into the CAAC ligand. Indeed, one can approximate the $C_2B_2N_2$ core of the product as consisting of delocalized double bond character extended from the N atom in one CAAC to that in the second carbene. The $C_2B_2N_2$ unit also adopts a zigzag arrangement with $\angle B-N-N = 146.1(2)^{\circ}$ and $\angle B-N-N =$ $131.9(2)^{\circ}$, which agrees with the partial double bond formalism and is distinct from the *d*-block compounds. DFT calculations are consistent with the bonding picture suggested by the X-ray structure. Related to 163-1 is the two-electron reduced congener 163-2, which can be accessed from the monobromoborane. One-electron reduction of Dur(CAAC)-BBr₂ yields the radical Dur(CAAC)BBr, which reacts with excess KC₈ under a dinitrogen atmosphere to afford K₂[Dur- $(CAAC)B](\mu-1,2-N_2)$, 163-2 (Scheme 37). The potassium cations interact with the N₂ fragment in an η^1 fashion, in contrast to the η^2 mode observed in Holland's and Limberg's reduced β -diketiminatometal compounds.^{244,245,275,276,28} The N-N and B-N bond lengths in 163-2 of 1.304(3) Å and 1.484(4) Å, respectively, are longer as compared to the metrics in 163-1 whereas the C_{CAAC}-B distance contracts to 1.470(4) Å. These changes imply weaker π -backbonding from B to N, consistent with reduction being primarily localized on the N₂ unit.

Scheme 37. Synthesis of 163-2



Varying the sterics on boron from duryl to triisopropylphenyl and executing similar reduction reactions starting from the chloroboryl results in an unexpected tetrazyl product 163-3 in which formal coupling of two N_2 fragments is observed (Scheme 38). Here the proposed mechanism involves

Scheme 38. Synthesis of 163-3



formation of a transient borylene-dinitrogen anion, which dimerizes to afford the B_2N_4 core in 163-3. As for 163-1 and -2, the bonding picture suggests delocalized double bond character across the ten-atom unit extending from one N_{CAAC} to the other. Arguably, the extent to which dimerization of the two purported borylene-dinitrogen anions is required to effectively trap the N_2 fixed species (i.e., equilibrium constant for formation of the transient anion) would distinguish the process from mono- vs diboron. Inclusion here is intended to reflect this ambiguity.

3.10. Rare Earth Elements and Actinides

Dinitrogen chemistry of the rare earth metals (REs) and actinides dates to the initial survey of catalysts for the Haber–Bosch process with cerium and uranium being reported as competent catalysts for ammonia production.³⁰⁰ The REs

exhibit bonding interactions reminiscent of the Group 4 and 5 metals; that is, the strongly reducing character leads to greater activation of N₂ through formal charge transfer. This survey for the rare earth metals begins with the cyclopentadienyl and related ligand systems and then proceeds through decreasing denticity of the supporting ligands. The only example of multimetallic N₂ activation by an actinide is for uranium; uranium complexes are considered at the end of this section.

Evans and co-workers reported the first example of a dinitrogen complex of an f-element with their report of the structure of $(Cp_2^*Sm)_2(\mu-\eta^2:\eta^2-N_2)$, 164-Sm, which was synthesized from the formally Sm(II) species, Cp*₂Sm.³⁰¹ Xray crystallography data evidenced the side-on/side-on coordination of dinitrogen between the two metal centers and a planar M₂N₂ fragment, making this compound the first such example of this structural motif. Despite the fact that the N–N bond length of 1.09(1) Å is comparable to that of free N₂, the Sm–N bond distances (2.347(6) and 2.368(6) Å) are comparable to those for Sm^{III}-NR₂ complexes (viz. 2.3-2.4 Å) and the later report of the N–N stretching frequency of 1416 cm⁻¹ implies significant backbonding or charge transfer from the Sm centers to the N₂ ligand.³⁰² This structure bears strong resemblance to the structure of the related Group 4 and 5 bis[bis(cyclopentadienyl)metal] dinitrogen compounds.

Building from this initial result, a few approaches were employed to generate additional members of this structure type, including reaction of divalent lanthanide salts with alkali cyclopentadienides or chemical reduction of the bis-(cyclopentadienyl)RE(III) halides with alkali metals under a dinitrogen atmosphere. These approaches have led to reports for various substituted cyclopentadienyl complexes of La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Tm, Lu, and Y with Cp* (164-M), 1,2,3,4-tetramethylcyclopentadienyl or Cp' (165-M), methylcyclopentadienyl (166-M), Cp (167-M), trimethylsilylcyclopentadienyl (168-Tm), 1,3-bis(trimethylsilyl)cyclopentadienyl (169-M), and 1,2,4-trit-butylcyclopentadienyl (170-Nd) (Figure 134).³⁰²⁻³¹¹ Steric constraints imposed by the cyclopentadienyl substituents dictate the coordination number of the RE, with less encumbered cyclopentadienyl ligands allowing for coordination of one solvent molecule to each metal center. Generally, these complexes exhibit similar N-N stretching vibrations from 1461 cm⁻¹ in 164-Sm to 1473 cm⁻¹ in 165-Nd. Greater variability is observed for the N-N bond distances although most are in the range of 1.24 Å; for example, the N-N bonds in 164-Sm and 164-Y are unexpectedly short at 1.09(1) and 1.172(6) Å, respectively. One also notes that the extent of activation is relatively insensitive to the coordination number; inclusion of one THF donor per metal center in 165-Gd affords similar bond metrics and N-N stretching frequency as 164-Gd (e.g., 1457 vs 1433 cm^{-1} , respectively). Arguably, the effects of sterics on precluding closer approach of the two metal fragments and incorporation of the additional ligand, which may have a similar steric effect, likely lead to the observed net similar outcome. The exception to this trend is the more encumbered tert-butyl substituted 170-Nd, which has the least activated N-N bond based on vibrational spectra ($\nu_{\rm NN}$ = 1622 cm⁻¹). Drawing parallels again to the Group 4 and 5 compounds discussed previously, one notes a similar trend wherein increasing ligand sterics disfavors close approach of the metal fragments and consequently lowers the extent of activation of N₂.

M = Y, L = none

M = Sm, L = none

M = Gd, L = none

M = Tb, L = none

M = Tm, L = none

M = Lu, L = none

M = Sc, L = none

M = Y, L = THF

M = La, L = THF

M = Ce, L = THF

M = Pr, L = THF



1.252(5)

1.235(6)

1461

1.243

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Demir et al. then expanded on these series with the reports of the one-electron reduced congeners of **165-M** for M = Gd, Tb, and Dy (Figure 135).³⁰⁸ The [((C₅Me₄H)₂(THF)Ln)₂(μ -



Figure 135. Reduced bis[bis(tetramethylcyclopentadienyl)RE](μ - $\eta^2:\eta^2\cdot N_2$) complexes 171 and 172 with formal N₂³⁻ ligands.

 $\eta^2:\eta^2\cdot N_2)$]⁻ (Ln = Gd, Tb, and Dy) -ate complexes retain the structure observed in **165-M** with the exception that the N–N bond is decidedly longer than the neutral **165-M** analogs with values ranging from 1.362(9) Å for **171-Gd**, which has a THF solvent molecule coordinated to the metal centers, to ~1.39(1) Å for the solvent-free complexes **172-Tb** and **172-Dy**. Formally these complexes are best described as containing N_2^{3-} ligands, which is consistent with the observed variable temperature magnetic susceptibility data. The bridging radical affords single molecule magnet behavior for these complexes. Loss of the solvent donor as in the **171-Tb** vs **172-Tb** facilitated by dissolution of the THF solvate in 2-methyltetrahydrofuran increases the magnetic anisotropy, which raises the blocking temperature and coercive fields.

Metalation of fully deprotonated meso-octaethylporphyrinogen (OEP) with trivalent Sm, Nd, or Pr followed by reduction with alkali metal sources (Li for Sm, Na for Nd, and Pr) resulted in complexes 173-M (Figure 136).^{312,313} The core $[(OEP)M]_2(\mu-\eta^2:\eta^2-N_2)$ for these complexes is comparable with the OEP coordinated in either an $\eta^3:\eta^1:\eta^3:\eta^1$ for 173-Sm or $\eta^5:\eta^1:\eta^5:\eta^1$ mode for 173-Nd and -Pr. The more notable difference however is the number and coordination number of the alkali cations. The η^3 and η^5 coordination of two pyrrolide rings is reminiscent of the bis(cyclopentadienyl) complexes discussed above, with the trans orientation noted in all cases. In the structure of 173-Sm from Gambarotta and co-workers, the N₂ ligand lies within the center of an octahedron defined by four equatorial lithium cations, of which two are η^2 and two are η^1 to the N₂ ligand, and two axial samarium centers with η^2 interactions. Given that the magnetic moment of 2.72 $\mu_{\rm B}$ is consistent with two Sm^{III} centers, the charge balance for the complex (assuming Li+ and SmIII), and the elongated N-N bond of 1.525(4) Å, 173-Sm approximates as two $[Li(OEt_2)]$ - $[(\eta^3:\eta^1:\eta^3:\eta^1:OEP)Sm^{III}]$ bridged by a planar Li₄N₂ unit. In the report by Floriani and co-workers for 173-Nd and -Pr, the structure bears similarity to 173-Sm when one considers the two fewer alkali cations. Two $[Na(solv)_2][(\eta^5:\eta^1:\eta^5:\eta^1:OEP)]$ -M^{III}] fragments (M/solv = Nd/1,4-dioxane, or Pr/DME) are

M = Nd, L = THF1.243 1473 M = Gd, L = THF1.247(3)1457 M = Tb, L = THF1.247 Å M = Dy, L = THF1.243(7)1454 M = Lu, L = THF1.243(12) [166-M] 1454 M = Y, L = THF1.250(2) M = Dy, L = THF1.250(4)1453 [168-Tm] M = Tm, L = THF1.236(8) Me₃Si [169-M] 1.259(4) M = Tm, L = noneSiMea M = Dy, L = noneMe₃Si 1.226(12) M = Nd, L = none1622 [170-Nd] ^tBu· -^tBu ^tBu M = La, L = THF1.243 [167-M] M = Ce, L = THF1.258(9) M = Pr, L = THF1.242(9) Figure 134. $[(Cp^{R})_{2}RE](\mu - \eta^{2} \cdot \eta^{2} \cdot N_{2})$ complexes 164–167.

[165-M]

F

(THF)₂L



Et Ft

Έt



Figure 136. Dinuclear Sm-, Nd-, or $Pr-(\mu-\eta^2:\eta^2-N_2)$ adducts (173-M) supported by *meso*-octaethylporphyrinogen (OEP) ligands.

bridged by $\{[Na(solv)]_2(\mu-1,2-N_2)\}$. Variable temperature magnetometry is consistent with the trivalent formalism provided above, and the observed N–N bond distances of 1.234(8) and 1.254(7) Å for 173-Nd and -Pr, respectively. As for the cyclopentadienyl series, one notes minimal difference in the extent of activation (based on crystallography exclusively here) as the metal ion is varied, but rather with the extent of reduction as the oxidation state of the RE is held approximately constant.

Encouraged by the extent of N₂ activation achieved by these OEP or tetrapyrrolide complexes, Gambarotta and co-workers varied the sterics of the *meso* substituents in the smaller dipyrrole ligands to evaluate the consequence on N₂ activation.³¹⁴ The substituents on the methylene bridges of the dipyrrolide are either two phenyl groups (174-Ph₂) or a cyclohexyl (174-Cy); reduction of the Sm^{III} complexes of these dipyrrolides affords structurally homologous tetrasamarium(III) complexes, [{[μ -RC($\eta^{1}:\eta^{5}$ -C₄H₃N)₂]Sm}₄(μ_{4} - $\eta^{2}:\eta^{2}:\eta^{1}:\eta^{1}$ -N₂)] (Figure 137; R = Ph or Cy). As for 173-Nd and -Pr, two



Figure 137. Tetranuclear samarium- $(\mu_4 \cdot \eta^2 : \eta^1 : \eta^1 \cdot N_2)$ complexes **174** supported by dipyrrolide ligands.

pyrrolide rings coordinate η^5 to each Sm center and two others in an η^1 fashion. In both compounds, the N–N bond distances are within error with values of 1.41(2) Å for 174-Ph₂ and 1.39(2) Å for 174-Cy. These results point to a cooperative activation of the bridging N_2 to afford a formally N_2^{4-} and four Sm^{III} centers. In an effort to effect complete N-N bond scission, 174-Cy was reduced with excess sodium, yielding the structurally similar dianionic complex [{[μ -CyC(η^1 : η^5 - $C_4H_3N_2$ [Sm}₄(μ_4 - η^2 : η^2 : η^1 : η^1 -N₂)]²⁻ or [174-Cy]²⁻. For this complex, the N-N bond is retained and the bond length of 1.37(2) Å is within error of the unreduced starting species. Consequently, one concludes that reduction here is likely metal centered, which is unexpected. The proposed rationale for metal rather than N2 reduction is that the rigidity of tetrametallic assembly limit sufficiently close approach of the metal centers to effect the complete cleavage of the N-N bond.

The only reported complexes with tetradentate ligands are the bis-O-alkylated calix[4]arene complexes, **175-M** where M = Sm or Pr from Floriani and co-workers (Figure 138).³¹⁵ Compound **175-Sm** was structurally characterized and is the only example of a μ_3 - η^2 : η^2 : η^2 -dinitrogen complex. The structure shows the three Sm centers bridged by two oxygen atoms from a calix[4]arene unit and by the N₂ ligand coordinated in a μ_3 - η^2 : η^2 : η^2 fashion. The N–N bond length is sufficiently long at 1.62(2) Å, that one questions the extent to which a N–N bond is present, although a hydrazide type ligand is presumed. An analogous structure for M = Pr was



Figure 138. Trinuclear Ln- $(\mu_3 - \eta^2 : \eta^2 : \eta^2 - N_2)$ complexes 175-M.

suggested on the basis of elemental analysis and gas-volumetric measurements.

Amide and alkoxide constitute the monodentate ligands employed thus far for RE-dinitrogen compounds. Complexes $[X_2(THF)_yRE]_2(\mu-\eta^2:\eta^2-N_2)$ (176-RE,X where X = $(Me_3Si)_2N$ as NR₂ and 2,6-di(*tert*-butyl)phenoxide as OAr) have been reported for which RE = Tm, Dy, Nd, Gd, Tb, Y, Ho, Er, and Lu, with X = $(Me_3Si)_2N$, 2,6-^tBu₂-OC₆H₃, and y = 1 or 2 (Figure 139). These complexes were prepared by



Figure 139. Amide and alkoxide dimetallic RE-dinitrogen adducts 176-RE,X.

treating the REX₃ precursor with alkali metal-based reductants or by reaction of the divalent diiodide with KX.^{302,316–318} As for the cyclopentadienyl compounds the N–N bond distances and vibrational frequencies fall within a fairly narrow range with values of 1.264(7)-1.305(6) Å for the former and 1413-1447 cm⁻¹ for the latter. The N–N stretching frequency decreases slightly as one moves to higher values of Z, which may arise from the increasing Lewis acidity of the metal ion. Again, recalling the cyclopentadienyl complexes, the RE centers here appear to be in the trivalent state, affording a formally diazenide bridging ligand.

In the initial report of the first members of the 176-RE,X family, Evans and co-workers reported concomitant formation of the related one-electron reduced congeners of 176-Y,NR₂ and 176-Dy,OAr. Two forms of these one-electron reduced species were characterized crystallographically: $[K(THF)_6]$ -[176-RE,X] and 177-RE,X in which the K⁺ cation is associated

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with the X-type ligand and the bridging N_2 ligand (Scheme 39).³¹⁸ These two one-electron reduced complexes both

Scheme 39. Interconversion between $[K(THF)_6][176-RE,X]$ and 177-RE,X



formally comprise RE^{III} centers and a N_2^{3-} bridge (*vide infra*) and are related by the loss or gain of THF, allowing for interconversion between the two species. As part of understanding the magnetic interactions mediated by the N_2^{3-} radical bridge, targeted syntheses were developed for the one-electron reduced [176-RE,X]⁻ and 177-RE,X (Figures 140 and 141).^{319–321} The observed N–N bond distances in

M+	$\begin{bmatrix} THF \\ X \\ RE \\ N \\ N \\ N \\ X \\ X = N(SiMe_3) \end{bmatrix}$	X EX THF 2		
RE	Μ	d(N–N) Å		
Y	K(18c6)(THF) ₂	1.396(3)		
Y	Na(THF) ₆	1.393(7)		
Y	K(THF) ₆	1.401(6)		
Gd	K(18c6)(THF) ₂	1.400(2)		
Tb	K(18c6)(THF) ₂	1.394(3)		
Dy	K(18c6)(THF) ₂	1.400(2)		
Но	K(18c6)(THF) ₂	1.405(3)		
Er	K(18c6)(THF) ₂	1.409(3)		
Er	Na(THF) ₆	1.403(4)		
Lu	K(THF) ₆	1.414(8)		
18c6 = 18-crown-6				

Figure 140. Anionic dimetallic rare-earth dinitrogen complexes [176-RE,X]⁻ featuring a side-on/side-on coordinated N_2^{3-} ligand.

the $[176\text{-RE},X]^-$ and 177-RE,X series vary within error with an approximate value of 1.4 Å, which lies between those for N₂Ph₂ (1.25 Å) and hydrazine (1.47 Å) and is consistent with a N₂³⁻ species.³²² This bond formalism was supported by DFT calculations in which the calculated structures and vibrational spectra—specifically, the N–N stretching vibrational frequency—were comparable. These calculations reveal a bonding picture wherein the π -donating orbitals on the RE



Figure 141. Complexes 177-RE,X.

fragment are nominally above the π^* orbitals of the N₂ ligand; the SOMO of the [176-RE,X]⁻ complexes is almost exclusively N₂ π^* in character. These results predate the proposed similar electronic structures for previously discussed Group 6 complexes.

In contrast with the side-on/side-on coordination of N_2 prevalent in rare-earth metals, Woen et al. reported the first example of an end-on/end-on dinitrogen coordination mode observed for a rare-earth metal (Figure 142).³²³ Complex 178



Figure 142. Bis[tris(hexamethyldisilazido)scandium](μ -1,2-dinitrogen), **178**.

or $[K(2.2.2.-cryptand)]_2(\{[(Me_3Si)_2N]_3Sc\}_2(\mu-1,2-N_2))$ was synthesized by the route described for 176-RE,X. The N–N and Sc–N(N₂) bond lengths are 1.221(3) Å and 2.032(3) Å, respectively, with the former metric being noticeably shorter than that of the μ - η^2 : η^2 -dinitrogen complexes discussed above. This conclusion is consistent with the vibrational data, which evidence a N–N stretching mode of 1644 cm⁻¹. As for the majority of the RE dinitrogen complexes, the Sm centers are best described as trivalent ions with a formal diazenide bridging ligand for this system.

Scott et al. reported the first example of a dinitrogen complex of uranium. The tren ligand bearing SiMe₂^tBu substituents on the secondary amide donors (i.e., tren^{SiMe2tBu}) allowed access to the dinitrogen bridged compound $[(\text{tren}^{SiMe2tBu})U]_2(\mu-\eta^2:\eta^2-N_2)$ or 179 (Figure 143). The combination of the N–N bond distance of 1.109(7) Å in



Figure 143. Tren^{3–}-chelated diuranium- μ - η^2 : η^2 -dinitrogen complex, 179.

this compound being comparable to that of free N₂, the solution magnetic moment of 3.22 $\mu_{\rm B}$ per uranium, and the solution phase UV/visible spectra—the latter two data sets are comparable to U^{III} complexes—imply that the complex is best described as two U^{III} centers with a bound N₂ ligand.³²⁴ Cloke and co-workers subsequently reported the synthesis of a dinculear uranium—dinitrogen complex, in which the N₂ ligand coordinates in a μ - η^2 : η^2 -N₂ fashion.³²⁵ Reaction of (η^5 -Cp*)[η^8 -C₈H₄(1,4-SiⁱPr₃)₂]U with dinitrogen affords {(η^5 -Cp*)[η^8 -C₈H₄(1,4-SiⁱPr₃)₂]U}₂(μ - η^2 : η^2 -N₂), **180** (Figure 144). The N–N and U–N(N₂) bond distances are 1.23(1)



Figure 144. Diuranium- μ - η^2 : η^2 -dinitrogen complex 180.

and 2.401(8)–2.423(8) Å, respectively; these crystallographic data are consistent with N–N double bond character and two formally U^{IV} centers, although additional spectroscopic data would be invaluable in corroborating the extent of π -backbonding.

Arnold and co-workers synthesized an unanticipated diuranium dinitrogen complex upon addition of 2,6-di-*tert*-butylphenol (HODtbp) or 2,4,6-tri-*tert*-butylphenol (HOTtbp) to $U(N(SiMe_3))_3$ under a dinitrogen atmosphere (Figure 145).³²⁶ Solid-state structures of the crystallized



Figure 145. Aryloxide-supported diuranium- μ - η^2 : η^2 -dinitrogen complexes, **181**.

products for the HODtbp reaction revealed two species: the first was the previously known but not structurally characterized monomeric U(ODtbp)₃ complex, and the second was the side-on/side-on diuranium-dinitrogen complex, [{U-(ODtbp)₃}₂(μ - η ²: η ²-N₂)], **181-Di** (Figure 145). Three molecules are present in the asymmetric unit with N–N bond lengths of 1.16(2), 1.20(2), and 1.20(2) Å. Use of HOTtbp afforded the isostructural complex, [{U(OTtbp)₃}₂(μ - η ²: η ²-N₂)] **181-Tri**, with a comparable N–N bond length of 1.19(2) Å as in **181-Di**. The N–N stretching frequency is observed in resonance Raman spectra of **181-Tri** at 1451 cm⁻¹, suggesting substantial backbonding from the U centers to the N₂ bridge. These two diuranium-N₂ complexes are stable in solution and show no N₂ loss after several freeze–pump–thaw cycles.

Shortly after the report of the two **181** complexes, the synthesis of another example of a diuranium–dinitrogen complex was communicated by the same group (Figure 146). Reaction of trimesitylsilanol with $U(N(SiMe_3)_2)_3$ affords

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Figure 146. Isomers of $[U{OSi(Mes)_3}_3]_2(\mu-\eta^2:\eta^2-N_2)$, 182.

the side-on/side-on dinitrogen complex $[U{OSi(Mes)_3}_3]_2(\mu - \eta^2:\eta^2-N_2)$, **182**.³²⁷ The Raman spectrum showed several signals in the unsaturated region making the assignment of ν_{N-N} inconclusive. The observed mode at 1437 cm⁻¹ in the ¹⁴N isotopolog is consistent with **181**, but the predicted frequency for the ¹⁵N complex is obscured. The solid-state structure of **182** demonstrates that the complex exists in a staggered or in an eclipsed conformer, although both have similar N–N bond lengths with values of 1.12(1) Å and 1.08(1) Å for the eclipsed and staggered, respectively. These values are notably shorter than the N–N bond in **181** complexes; however, one notes throughout this survey that N–N bond distances cannot be used exclusively to make definitive judgements on the extent of π -backbonding.

Recently, Mazzanti and co-workers reported a diuranium complex 183 in which the bridging N₂ approximates a N₂^{4–} donor (Figure 147). Exposure of $K_3\{[U(OR)_3]_2(\mu-N)\}$ to



Figure 147. Siloxide-supported diuranium- μ - η^2 : η^2 -N₂ complex 183 with a butterfly U₂N₂ core and a μ -N³⁻.

dinitrogen in the solid state or in solution affords the μ - η^2 : η^2 dinitrogen species in which the U₂N₂ core adopts a butterfly rather than planar configuration.³²⁸ The flexibility imparted by the siloxide donors plays a critical role by allowing the bridging nitride to be accommodated above the N2 unit with the U-N-U angle and U-U distance decreasing from 173.7(8)° to $106.0(5)^{\circ}$ and from 4.234(2) Å to 3.305(1) Å relative to the starting $K_3\{[U(OR)_3]_2(\mu - N)\}$. The N–N bond distance is surprisingly long at 1.52(2) Å and comparable with that for a N–N single bond. Formally then, the bond metric suggests oxidation of the U^{III} to U^V upon N_2 coordination, which is indeed consistent with EPR and variable temperature magnetic susceptibility data. This complex features the longest N-N bond length compared to any other uranium complex and one of the longest for any metal complex (vide supra). Addition of 1 equiv of 2,4,6-tri-tert-butylphenol to the dinitrogen complex resulted in the protonation of nitride to form a NH²⁻ species. The U_2N_3 core remains unchanged with no interaction between the potassium cations and the N24- or NH2- moiety being the only major difference.

4. OUTLOOK AND PERSPECTIVES

Substantial progress has been made with respect to multimetallic systems competent for dinitrogen activation; however, limitations remain in the ability to functionalize N₂ by catalytic and stoichiometric methods. The identity of the metal ion and the N_2 coordination mode dictate the cooperative N_2 activation in multimetallic systems; however, one challenge will be to develop systems that leverage this knowledge to favor activated N₂ species for nitrogen fixation to ammonia or equivalent molecules or as part of a N-atom transfer process from N₂ to organic substrates. Indeed, the latter could have a dramatic impact on current methodologies considering that Natom incorporation typically relies on N2 reduction and ammonia oxidation cycles to access desired reagents (e.g., azide). One challenge is to access systems capable of greater formal reduction (e.g., four- or six-electron reduction) of the bound N₂ without further addition of reducing agents will increase the possible options for N₂ functionalization; most reported examples result in formal one- or two-electron reduction of the bound N₂ and rely on further reduction to further activate the N₂ ligand. From this survey of multimetallic systems, we postulate the following foci as noteworthy and likely to advance N₂ activation, functionalization, and Natom transfer.

4.1. Evaluating the Effect of Composition of Polynuclear Metal Species on Reactivity toward Dinitrogen

A number of examples presented here, such as the heteronuclear Mo₃Ti cubanes $(34-K_2/K_3)$ or the various molybdenum-vanadium or -iron compounds (76-V, 79-V/ Mo_n n = 2 or 3, and 79-Fe/Mo₃, respectively) among many others, sought to evaluate the effect of metal compostion on N₂ activation. Generally, the effect of the heterometal on N₂ activation is consistent with the push-pull effect and these compounds are accessed by a spontaneous aggregation of monometallic species. However, the ability to design heterometallic complexes capable of binding dinitrogen upon reduction is an underexplored, but an important area of focus. Such systems can provide support for mechanisms for dinitrogen reduction in the Haber-Bosch process and by the nitrogenase cofactors; in the latter, the role of the heterometal as a possible N₂ coordination or functionalization site remains unresolved. In addition to metal ion composition, the effect of supporting donor atoms is topical and, in particular, systems that report on the possible function of the μ_6 -carbide in the nitrogenase cofactors. A number of groups have reported noncarbene anionic C donor ligands and many more are likely targeting molecular clusters bearing an interstitial carbide. Broad comparison of reactivity of polynuclear metal species across periodic series (i.e., nitride, carbide, and boride) will be an important contribution in this regard.

4.2. Evaluating Ligand-Field Effects on Dinitrogen Activation

Most examples hitherto have employed ligands imposing intermediate or strong ligand fields. These compounds contrast the weaker ligand fields of the known industrial and biological catalysts. Recent work on iron–sulfur clusters suggests that the energy gaps between the ground and low lying excited spin states are relatively small, suggesting that excited states may be critical for reactivity with dinitrogen, either by thermal population or by mixing of excited and ground states. Developing compounds that shed light on the properties that facilitate N_2 activation under ambient conditions with reasonably mild reductants—as compared to the ubiquitously employed alkali metal reductants—will have far reaching implications for N_2 utilization in future on-demand fixation technologies, chemical synthesis, and activation of other small molecule substrates.

4.3. Expanding Coordination Chemistry of Late Transition Metals and Utilizing Weaker Reducing Agents

The degree of activation of the N₂ fragment is strongly influenced by the coordination mode, as is apparent from work on the early transition metal ions in which all dimetallicdinitrogen coordination modes have been reported. Contrastingly, bridging modes other than μ -1,2 remain exceptionally rare for late transition metals.^{329,330} Late *d*-block complexes that access these rare bridging modes will mirror the diverse reactivities noted in the early metal compounds (e.g., hydrogenation, nucleophilic attack) but require weaker reducing agents given the relative electronegativities of metal centers. Rational approaches wherein metal-metal separation and relative orientation of the frontier orbitals can be tuned to favor one of these modes remain underexplored. More generally, polynuclear metal complexes for N_2 activation even for early transition metals-primarily arise from aggregation of monometallic species, resulting in serendipitous access to the various observed coordination modes. Rational and designed approaches to polynuclear early metal species would complement these seminal contributions and allow one to experimentally describe the parameters that dictate such coordination preferences.

4.4. Accessing Designed Polynuclear RE and Ac Complexes

Broadly, few systems have been reported for dinitrogen activation in which polynuclear metal complexes are templated by multinucleating ligands, with the most common examples being for the late first row transition metals. A plethora of multimetallic RE and actinide (specifically, uranium) compounds are known in which N_2 binding or activation results in sponateneous aggregation of monometallic precursors and, thus, a fruitful future direction in which multinucleating ligands afford predictable polynuclear RE or Ac complexes for the targeted activation of small molecule species, such as N_2 . Specifically, U with its reasonably accessible oxidation states would hold particular promise in a multimetallic context.

4.5. Coupling Multiple Metals with Secondary Coordination Sphere Effects

Incorporating secondary sphere effects in monometallic complexes has strong precedent, primarily in the arena of O_2 activation and H^+/CO_2 reduction, ^{331–335} with recent work expanding the concept to dinitrogen activation. ^{336–338} Unsurprisingly then, one envisions similar possibilities with respect to multimetallic systems, leading to systems that more closely mimic multimetallic active sites in metalloproteins. ^{339–342} Indeed, realizing such an approach will require creative solutions to afford reasonably facile access to conceptually complex ligand architectures.

To conclude, continued exploration of mutlimetallic N_2 activation and coupling this cooperativity to other reactive functionalities (e.g., push-pull effects with Lewis acids or hydrogen bonding interactions) will enhance our understanding of the biological and industrial processes as well as effecting as-yet-realized reactions utilizing dinitrogen (e.g., N-atom transfer). Such systems and particularly designed

complexes that can be readily tuned will also access unique and unexpected reactivity manifolds that extend beyond dinitrogen activation but to small molecule activation in general (e.g., O_2 reduction and O-atom transfer, H_2O oxidation, and CO_2 reduction).

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The manuscript was written through contributions of all authors.

Notes

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