Leveraging Molecular Metal-Support Interactions for H₂ and N₂ Activation

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Abstract

Many challenging chemical reactions require precious metal catalysts to proceed. Bio-inspired catalysts featuring multiple earth-abundant metals are an attractive alternative, as they offer boundless possibilities for facilitating processes that the constituent metals cannot mediate on their own. Our work utilizes a supporting metal as an electronic lever for tuning a base metal (Co, Ni) active site via a metal-metal bond. This approach has allowed for the development of metal-support catalysts for reductive N₂ silylation and olefin hydrogenation. The bimetallic catalysts display markedly enhanced activity compared to the analogous single metal centers. In this review, we investigate the role of the supporting metal in substrate binding, activation, and catalysis, to inform future efforts in the optimization and development of molecular metal-support catalysts.

1. Introduction

In addressing the problem of limited energy sources, a critical component is to catalyze challenging chemical reactions using sustainable, earth-abundant metals instead of precious metals. In particular, the multielectron conversion of small-molecule feedstocks into useful commodities is essential to the chemical industry, but inherently difficult to mediate efficiently. This difficulty stems from the kinetic challenge of directing the simultaneous transfer of multiple electron and/or proton equivalents, so as to bypass high energy intermediates during catalysis.

One strategy to replace precious metal catalysts while maintaining multielectron redox capability is to couple two or more first-row transition metals in a single catalyst or active site. Cooperativity among multiple earth-abundant metals underlies numerous essential biological processes, including the reduction of N_2 to ammonia, the oxidation of water to O_2 , and the reversible activation of H_2 . The cofactors that mediate these three challenging reactions inspire increasingly sophisticated designs of multimetallic catalysts, and they are briefly discussed below.

1.1 Biological Design Principles: Harnessing Multiple First-Row Metals for Multielectron Processes

The FeMo cofactor of nitrogenase, a cluster of 7 Fe centers and 1 Mo supported by 9 bridging sulfides and an unusual, central carbide, facilitates N_2 fixation to NH_3 [1-5]. It has been proposed that the key intermediate that is primed to bind and reduce N_2 is comprised of two $Fe(\mu-H)Fe$ fragments, which together store four reducing equivalents in the cofactor. Thus, the proximity of several Fe centers in the FeMo cofactor promotes multielectron reactivity by allowing the substantial buildup and storage of electron equivalents via the cooperative stabilization of bridging hydride moieties.

The oxygen-evolving complex (OEC) in Photosystem II also uses an active site featuring a cluster of first-row transition metals, Mn_4O_5Ca , which successively accumulate four electron holes at relatively mild potentials to mediate the oxidation of water to O_2 [6-11]. Though the Ca^{2+} ion is redox inactive, studies of the enzyme and model complexes have proposed that Ca^{2+} may play two important roles: (1) to inductively modulate the redox potential of the Mn_4O_5 cluster, and (2) to generate a reactive nucleophile, $Ca-OH$, that directly participates in O-O bond formation with a Mn-based oxo or oxyl moiety [6, 12, 13].

Lastly, a bimetallic active site rather than a metal cluster is responsible for the remarkable activity of [NiFe]-hydrogenase, which reversibly activates H_2 . To promote H_2 activation, the electronic properties of the Ni center are favorably altered via a flexible metal-metal interaction with Fe. The supporting Fe center, which remains divalent throughout the catalytic cycle, serves

to accommodate the changing electronic requirements of the active Ni center, which traverses Ni(I), Ni(II), and Ni(III) oxidation states [14-18]. In addition to tuning the redox properties of Ni through a flexible dative interaction, Fe also directly assists in substrate activation by stabilizing a bridging hydride moiety, Ni(μ -H)Fe [14].

1.2 Moving from Clusters to Bimetallic Catalysts

In developing multimetallic catalysts for functionalizing small molecules, chemists have long sought to understand and apply the design principles underlying the function of biological enzymes. As illustrated by enzyme active sites, synthetically coupling multiple metal centers in close proximity can allow for maximal storage of electrons (e.g., in FeMo-co) or electron holes (e.g., in OEC). However, large metal clusters, which are more difficult to synthetically assemble in the laboratory, are not prerequisites for rich redox profiles. Indeed, two first-row metals that are bonded together can promote multiple single-electron transfers [19]. Notably, the rich redox profile of a metal-metal bonded species may be synergistic in that it can be greater than the sum of its parts: electronic coupling of the metal centers may give rise to more accessible redox states than those of the individual constituent metals [19, 20]. Two metals in a metal-metal bonded unit are also in close enough proximity to engage in cooperative interactions with substrate, as was critical to stabilizing bridging hydride intermediates in both nitrogenase and [NiFe]-hydrogenase. In short, while enzymatic active sites no doubt rely upon all metal centers and the surrounding residues to function, the key design principles of redox versatility and cooperative substrate activation by multiple proximal metal centers may be captured by a bimetallic complex featuring two metals engaged in a metal-metal bond.

1.3 Bond Activation by Metal-Metal Bonded Complexes

An overarching goal of this review is to elucidate the role(s) of each metal in a bimetallic complex containing a metal-metal bond in substrate activation. The manner in which a metal-metal bonded (M_A-M_B) complex activates a substrate with an X-Y bond can be divided broadly into three categories (Figure 1): (1) cooperative activation across the M_A-M_B bond in which each metal directly interacts with substrate, (2) homolysis of the M_A-M_B bond to form two metalloradical fragments that cooperatively activate substrate, and (3) activation of substrate at an active metal (M_A) in which the supporting metal (M_B) primarily serves to electronically tune the active metal.

Figure 1. Three modes of X–Y bond activation at a metal-metal bonded unit (M_A-M_B)

Cooperative activation of the substrate X–Y bond across the M_A-M_B bond can occur in either a homolytic or heterolytic fashion, a distinction which typically depends on the polarity of both the M_A-M_B and X–Y bonds. Homolytic substrate activation is more common across homobimetallics and other relatively nonpolar M_A-M_B bonds. On the other hand, polar M_A-M_B bonds between disparate metals, such as the pairing of a late transition metal with an early or main-group metal, often leads to heterolytic substrate activation. Cooperative substrate activation by early-late heterobimetallics [21–27] has been more generally reviewed, as has the reactivity of metalloradicals formed *in situ* from metal-metal bonded precursors [28–30]. Rather, we focus on the case in which a single active metal binds and activates substrate, while the supporting metal tunes the electronic coordination environment of the active metal via a metal-metal bond.

1.4 Our Approach to Bimetallic Catalyst Design

A key concept of our design was to relegate the second metal, M_B , to a supporting role in which it primarily serves to modulate the electronic environment of the active metal, M_A . Coupling this paradigm with systematic variation of the supporting metal further streamlines understanding by isolating the effect of the supporting metal on substrate binding and catalysis at the active metal. The mixed amide-phosphine ligand (depicted in Figure 2, abbreviated as L) has proven to be particularly effective in stabilizing a wide variety of metal-metal complexes, with interactions ranging from weak dative to strong multiple bonds, as well as in accommodating metals of disparate sizes. Importantly, L has two distinct binding pockets: a triamido pocket best suited for ligating “hard”, early metals and a triphosphine pocket tailored for binding “soft”, late metals. The “double decker” nature of L with differentiated binding sites permits a step-wise metalation procedure that has allowed for facile variation of both the active and supporting metal sites within the bimetallic framework.

For the selection of active metals, we targeted Fe, Co, and Ni. Fe and Ni are found in the active sites of metalloenzymes that transform small molecules (H_2 , N_2 , CO_2), while Co was a reasonable addition since it lies between Fe and Ni on the periodic table. The high earth-abundance and low cost of these metals also make them attractive for catalyst development. However, in synthetic systems in which these metals are the lone metal center, they often are poor catalysts compared to their precious metal counterparts due to lower activity, selectivity, and/or robustness. Synthetically, we address these shortcomings by tuning the properties of Fe, Co, and Ni with a main group metal ion (Al, Ga, In) or another first-row metal (Ti, V, Cr, Co), which go beyond the scope of the metals used in nature.

This review focuses mainly on two series of isostructural complexes, NiML and CoML, each of which has a constant active metal with a varied supporting metal (Figure 2). Select NiML complexes bind H_2 in a side-on fashion and are catalytically competent in olefin hydrogenation. The CoML series are precursors to anionic CoML complexes with an apical end-on N_2 ,

$[(N_2)CoML]^-$, which are precatalysts for the reductive silylation of N_2 to $N(SiMe_3)_3$. For these Co–M and Ni–M systems, the choice of the supporting metal dictates both catalytic activity and selectivity.

Figure 2. Isostructural series of $(\eta^2-H_2)NiML$ and $[(N_2)CoML]^-$ complexes with varying supporting metals (M).

Furthermore, our design seeks to maximize the influence of the supporting metal on reactivity by positioning it directly *trans* to the substrate binding site at the active metal (Figure 2). This linear arrangement, $M_B-M_A-(\text{substrate})$, has important consequences on the interplay between the metal-metal interaction and the metal-substrate interaction, which is discussed in more detail below for the binding of N_2 and H_2 .

2. How does a Supporting Metal Promote Binding and Activation of H_2 and N_2 at Base Metals?

2.1 Orbital Interactions with Side-On H_2

We begin by examining how the orbital interactions of H_2 and N_2 with a single transition metal center (M) may be favorably perturbed by a supporting metal. Conventional metal– H_2 bonding occurs in a side-on fashion and is characterized by two bonding interactions: (1) σ -donation from the H_2 σ -bond to an empty metal d-orbital of appropriate symmetry, often $M d_z^2$, and (2) π -back-donation from the $M d_{xz}$ or d_{yz} orbital to the H_2 σ^* orbital (Figure 3) [31-33]. The interplay of these two bonding interactions dictate whether H_2 binds and the subsequent degree of H–H bond activation on the continuum between a nonclassical adduct, $M(\eta^2-H_2)$, and a metal dihydride, $M(H)_2$ [32].

Figure 3. Bonding interactions between a transition metal (M) and H₂ in the absence and presence of a Lewis acid support (LA).

The classic metal-H₂ bonding picture changes dramatically upon the incorporation of a supporting Lewis acidic center *trans* to the H₂ ligand. We specifically consider a main group metal ion in trigonal symmetry with a low-lying, empty p_z orbital. The engagement of such a Lewis acid support (LA) with a transition metal (M) results in an inverse dative σ -bond, M d_z² $\rightarrow$ LA p_z, which stabilizes the M d_z² orbital and destabilizes the LA p_z orbital [34-37]. Consequently, the M d_z² will likely be the lowest energy d-orbital and be filled (for d-count ≥ 2), making it unavailable to interact with the H₂ σ -bond. However, the empty M (n+1)p_z, by mixing with the M nd_z² and LA p_z orbitals, may become energetically available to accept electron donation from the H₂ σ -bond.¹

Through the M d_z² $\rightarrow$ LA p_z interaction, the Lewis acid imparts electrophilic character to the transition metal, thereby limiting π -back-bonding (M d_{xz} or d_{yz} $\rightarrow$ H₂ σ^*) and increasing σ -donation (H₂ σ $\rightarrow$ M). These dual effects should both further stabilize η^2 -H₂ binding in M-LA relative to the case of a single metal center, M [32]. As a practical consequence, employing Lewis acidic Group 13 metal ions as supports for a transition metal have led to the discovery and isolation of rare η^2 -H₂ adducts of d¹⁰ Ni(0) [38, 39]. To date we have not isolated any η^2 -H₂ adducts of M_AM_BL where M_B is a transition metal, and so orbital interactions with H₂ will not be considered here for the case of a supporting transition metal.

2.2 Orbital Interactions with End-On N₂

Compared to H₂, N₂ is a better π -acceptor but an inferior σ -donor. Hence, the dominant interaction in the M-N₂ end-on binding mode is π -back-bonding: (M d_{xz}, d_{yz})⁴ $\rightarrow$ (N₂ π^*)⁰ (Figure 4) [40, 41]. As in the case of H₂, a Lewis acid support (LA) will render a transition metal more electron-deficient and weaken M $\rightarrow$ N₂ π -back-bonding compared to a single metal center.

Nevertheless, a Lewis acid support can stabilize exceedingly low metal oxidation states, e.g. $M(-I)$, which may have greater electron-density to π -back-donate to N_2 . This paradigm has allowed for enhanced N_2 activation in $[(N_2)FeAlL]^-$ and $[(N_2)CoAlL]^-$ species via the stabilization of highly reduced $Fe(-I)$ and $Co(-I)$ by an $Al(III)$ supporting Lewis acid [42].

Figure 4. Bonding interactions between a transition metal (M) and N_2 in the absence and presence of a supporting metal engaged in metal-metal bonding. Red arrows indicate $M-M$ π -bonding interactions, while blue arrows indicate $M-N_2$ π -back bonding interactions. Note, the orbital depictions for the polarized $M_B-M_A-N_2$ case presumes that the electronegativity of M_A is greater than that of M_B .

Moving beyond Lewis acid supports, a supporting transition metal (M_B) is a more complex case because it can engage the active transition metal (M_A) to form a covalent bond of varying bond order and polarity. Such a metal-metal interaction arises from the mixing of the d-orbitals of M_A and M_B , from which a maximum bond order of five can be achieved (σ , 2 π , and 2 δ bonds). The bond order is dictated by the total d-electron count and by the energy overlap of d-orbitals at the two metals [19, 20]. Since π -back-donation to N_2 can only occur from the M_A-M_B π and π^* molecular orbitals, we consider only two limiting cases of metal-metal bonding (Figure 4): (1) delocalized $M-M$ π/π^* orbitals arising from M_A and M_B d-orbitals of similar energies, and (2) polarized $M-M$ π/π^* orbitals from M_A and M_B d-orbitals of disparate energies. In the former case, π -back-donation to N_2 should be more effective from the high-lying $M-M$ π^* orbital and less effective from the stabilized $M-M$ π orbital, compared to the corresponding π -back-donation interactions for a single metal center.

Our $Co-M_B$ bimetallics ($M_B = Ti, Cr, V$) mostly fall within the latter category, as the two metal centers are quite different and form a polarized metal-metal bond [43]. Since Co is more electronegative than M_B in these cases, the $Co-M_B$ π orbitals are localized on Co, while the $Co-M_B$ π^* orbitals are polarized towards M_B [19, 44]. Compared to a single Co center, the Co d_{xz}/d_{yz} electrons are slightly stabilized by the weak $Co-M_B$ π -bonding interaction, and thus are slightly worse at π -back-bonding to N_2 . However, additional π -back-bonding interactions unavailable to a single Co center can occur from the population of the high-lying $Co-M_B$ π^* orbitals, which have better energy overlap with the N_2 π^* orbitals and retain some Co character despite being primarily localized on M_B . Finally, the presence of M_B permits access to a highly

reduced anionic charged state, $[\text{CoM}_\text{BL}]^-$ ($\text{M}_\text{B} = \text{V}, \text{Cr}, \text{Co}$), that is sufficiently electron-rich to spontaneously bind N_2 and generate the corresponding $[(\text{N}_2)\text{CoM}_\text{BL}]^-$ species [43, 45].

2.3 H_2 Binding to Nickel–Group 13 Lewis Acid Bimetallics [38]

Varying the electronic environment of Ni by changing the supporting main group metal ion manifests in differential reactivity with H_2 . Exposure of the two most electron-deficient Ni complexes in the series, NiGaL and NiInL , to 1 atm H_2 generated rare, nonclassical $\text{Ni}(\eta^2\text{-H}_2)$ adducts. By contrast, the more electron-rich counterparts, NiAlL and NiLH_3 , showed no reactivity under 1 atm H_2 . The observed trend indicates that σ -donation from H_2 to Ni is the predominant interaction that induces H_2 binding in this series of complexes, as opposed to π -back-donation from Ni to H_2 .

In general, Ni tends to be both a poor π -back-donor and poor σ -acceptor toward H_2 ; thus, examples of H_2 reacting with Ni are uncommon [32, 39, 46-50]. Classical H_2 oxidative addition at a single Ni center has not been reported to our knowledge, attesting to the poor π -back-donor ability of Ni. H_2 σ -donation to Ni is also unfavorable. For zero-valent Ni, all of the d-orbitals are filled, and thus unable to accommodate donation from the H_2 σ -bond. Likewise, typical square-planar Ni(II) complexes have a filled d_{z^2} orbital. In light of these limitations, it is perhaps not surprising that thermally stable Ni- H_2 adducts were not discovered until the past decade, and are still rare [32]. Prior to our report of $(\eta^2\text{-H}_2)\text{NiGaL}$ and $(\eta^2\text{-H}_2)\text{NiInL}$ species (Figure 5), only one other Ni- H_2 adduct of Ni(0) had been reported, along with three such adducts of cationic Ni(II) [39, 47, 48]. Uniquely, the $(\eta^2\text{-H}_2)\text{NiML}$ species allow for instructive comparison since they only differ in the *trans* supporting metal. Intriguingly, varying degrees of H_2 activation and stability to H_2 loss were observed in $(\eta^2\text{-H}_2)\text{NiML}$ upon swapping the Lewis acid support from Ga to In.

The degree of H–H activation in $(\eta^2\text{-H}_2)\text{NiML}$ was investigated in two ways: (1) the H–D coupling in $(\eta^2\text{-HD})\text{NiML}$ isotopomers, and (2) spin-lattice (T_1) relaxation studies of bound H_2 protons. An intact H–D unit bound to a metal will typically exhibit a $^2J_{\text{HD}}$ coupling constant of 26 to 37 Hz (*cf.* 43 Hz for free HD gas) [32]. The $(\eta^2\text{-HD})\text{NiML}$ species exhibit $^2J_{\text{HD}}$ of 34 Hz and 32 Hz for the Ga and In supports, respectively (Figure 5) [38]. These coupling constants correspond to solution-state H–D distances of 0.87 Å and 0.91 Å for $(\eta^2\text{-HD})\text{NiGaL}$ and $(\eta^2\text{-HD})\text{NiInL}$, respectively (*cf.* 0.74 Å in free HD) [51]. The T_1 relaxation studies are also informative, as an intact H_2 unit should exhibit a short T_1 minimum value, typically <190 ms at 600 MHz, due to fast relaxation from strong dipolar-dipolar interactions between the two protons of H_2 [52]. This criterion is satisfied by $(\eta^2\text{-H}_2)\text{NiInL}$ and $(\eta^2\text{-H}_2)\text{NiGaL}$, which have $T_1(\text{min})$ of 23 and ≤ 16 ms, respectively (600 MHz). To estimate H–H distances from T_1 values, one can invoke either fast or slow rotation of the H_2 ligand relative to molecular tumbling in solution [52]. The assumption of fast rotation of H_2 about the Ni–M axis gives good agreement between estimated H–H distances from $T_1(\text{min})$ and $^2J_{\text{HD}}$. Facile rotation is also consistent with the lack of a preferential orientation of H_2 , as π -back-bonding interactions from Ni d_π to the H_2 σ^* orbital are degenerate and likely weak.

Figure 5. Solid-state structure of $(\eta^2\text{-H}_2)\text{NiInL}$, and the ^1H NMR signal of the HD ligand in $(\eta^2\text{-HD})\text{NiML}$ complexes. Thermal ellipsoids are shown at the 50% probability level, and H atoms were omitted except for clarity, with the exception of the apical H_2 ligand, which was refined with the constraint of side-on binding [38]. Phosphorus, nitrogen, and carbon atoms are displayed in orange, blue, and gray, respectively.

We propose that the elongated H–H bond in $(\eta^2\text{-H}_2)\text{NiInL}$ compared to $(\eta^2\text{-H}_2)\text{NiGaL}$ is the result of “pull-pull” σ -interactions, where the greater electrophilicity of Ni imparted by In induces increased σ -donation from H_2 to Ni, resulting in a slightly longer H–H distance for In. Both Lewis acid supports induce H_2 binding by making the Ni center more electrophilic compared to the single nickel analogue, NiLH_3 . The conducive *trans* effect of the LA for H_2 binding contrasts the more typical scenario of an unfavorable *trans* σ -donor, which could outcompete H_2 for binding to the metal. A favorable consequence of the linear bonding motif, $(\eta^2\text{-H}_2)\text{-Ni-LA}$, is that both $\text{H}_2 \rightarrow \text{Ni}$ and $\text{Ni} \rightarrow \text{LA}$ interactions utilize different Ni orbitals, Ni $4p_z$ and $3d_{z^2}$, respectively. The noncompetitive nature of the $\text{H}_2 \rightarrow \text{Ni}$ and $\text{Ni} \rightarrow \text{LA}$ interactions is illustrated structurally by a Ni–In series, where the σ -donors, H_2 and N_2 , bind to Ni without perturbing the Ni–In bond significantly. In comparing NiInL to $(\eta^2\text{-H}_2)\text{NiInL}$ and $(\text{N}_2)\text{NiInL}$, the Ni–In bond length elongates only slightly, from 2.46 to 2.49 and 2.53 Å.² These Ni–In distances all remain well within the sum of the covalent radii of Ni and In (2.66 Å) [53].

Consistent with a more intact H_2 ligand in $(\eta^2\text{-H}_2)\text{NiGaL}$, H_2 binding to NiGaL is a rapid equilibrium on the NMR timescale at room temperature, and is fully reversible upon the application of dynamic vacuum. However, H_2 binding is irreversible for $(\eta^2\text{-H}_2)\text{NiInL}$ even under vacuum; these differences in H_2 affinity and the fluxionality of $(\eta^2\text{-H}_2)\text{NiML}$ will have important consequences in the catalytic hydrogenation of olefins mediated by the activated $\text{Ni}(\text{H}_2)$ moiety.

2.4 N₂ Binding to Iron, Cobalt, and Nickel Bimetallics

2.4.1 Evaluating N₂ Binding through IR Spectroscopy, Solid-state Structure, and Cyclic Voltammetry

Neutral bimetallic complexes featuring zero-valent Fe, Co or Ni supported by a Lewis acidic main group ion were shown to bind N₂ in end-on fashion [38, 39, 42, 54-57]. The binding of N₂ in these bimetallics was investigated through IR spectroscopy and X-ray crystallography, with $\nu(\text{N}_2)$ providing a more precise measure of N₂ activation. Table 1 displays the degree of N₂ activation for various bimetallics. The range of N₂ activation in our bimetallic complexes (1925 to 2144 cm⁻¹) is consistent with marginal activation and an intact N₂ triple-bonded unit, and falls within the range reported for monometallic Fe-N₂ and Co-N₂ complexes [40, 58, 59].

Dinitrogen adducts of Ni are uncommon; (N₂)NiInL is one of only seven structurally characterized examples of an end-on Ni-N₂ adduct to our knowledge [39, 47, 48, 60, 61]. Though N₂ binding in (N₂)NiInL is irreversible under vacuum, the high $\nu(\text{N}_2)$ of 2144 cm⁻¹ and the short N-N bond length suggest that π -back-bonding from Ni to N₂ is minimal [40]. In moving from Ni to Co to Fe, the metal electronegativity decreases, resulting in higher lying 3d_{xz}/d_{yz} orbitals which should have better energy overlap with the N₂ π^* orbitals for π -back-bonding. Consistent with this rationale, the N₂ unit is much more activated in (N₂)FeAIL and (N₂)CoAIL, with Fe exhibiting lower $\nu(\text{N}_2)$ than Co by 71 cm⁻¹ (Table 1) [57].

Importantly, and in contrast to many complexes with a single Fe or Co center, the Lewis acidic Al(III) support enables the isolation of the highly reduced analogues, [(N₂)FeAIL]⁻ and [(N₂)CoAIL]⁻, where the metals are formally subvalent, M(-I), and N₂ is significantly more activated by ~85 cm⁻¹ compared to the neutral adducts. Of interest, the difference in $\nu(\text{N}_2)$ between the anionic Fe and Co adducts (70 cm⁻¹) is essentially identical to the aforementioned difference between their neutral counterparts [42].

Table 1. Summary of N₂ activation in various bimetallic complexes.

Complex	total d-electrons	ν_{N_2} (cm ⁻¹)	N-N (Å)	E° (V) ^a	ref
(N ₂)FeAIL	8	2010	1.146(7) ^b	-2.08	[57]
[(N ₂)FeAIL] ⁻	9	1925	1.135(4)		[42]
(N ₂)CoAIL	9	2081	1.107(4)	-2.11	[57]
[(N ₂)CoAIL] ⁻	10	1995	1.110(8)		[42]
(N ₂)NiInL	10	2144	1.098(8)	-2.34	[38]
[(N ₂)CoVL] ⁻	12	1971	1.133(4)	-2.48	[43]

$[(\text{N}_2)\text{CoCrL}]^-$	13	1990	1.128(7)	-2.32	[43]
$[(\text{N}_2)\text{Co}_2\text{L}]^-$	16	1994	1.114(4)	-2.11	[45]

^a Reduction potentials (vs. Fc/Fc^+) of $[(\text{N}_2)\text{FeAIL}]^{0/-}$, $[(\text{N}_2)\text{CoAIL}]^{0/-}$, $[\text{NiInL}]^{0/-}$, and $[\text{CoML}]^{0/-}$ for $\text{M} = \text{V}, \text{Cr}, \text{Co}$.

^b N–N bond length is from solid-state structure of a $\text{Fe-N}_2\text{-Fe}$ sandwich complex.

When the Lewis acidic main group ion support is replaced with a transition metal, it becomes more challenging to predict whether N_2 will bind and to understand the relative degrees of N_2 activation. For the transition metal supports, a striking observation is that neutral CoML ($\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Co}$) do not bind N_2 in the solid-state, unlike $(\text{N}_2)\text{CoAIL}$. Only upon reduction to the anionic analogues, $[(\text{N}_2)\text{CoML}]^-$ ($\text{M} = \text{V}, \text{Cr}, \text{Co}$), was N_2 found to bind strongly to the active Co center [43].³ Notably, relatively similar degrees of N_2 activation are observed in the $[(\text{N}_2)\text{CoML}]^-$ series, with N_2 activation decreasing for the supporting metals in the order: $\text{V} \gg \text{Cr} > \text{Co} \sim \text{Al}$ (Table 1). The minor differences in N_2 activation between the various supports was initially perplexing. However, N_2 binding at the active Co should disrupt Co-M π -interactions, such that the metal-core oxidation states in the $[(\text{N}_2)\text{CoML}]^-$ series are, or are close to, $\text{Co}(-\text{I})\text{M}(\text{III})$ for $\text{M} = \text{Al}, \text{V}, \text{Cr}$. Dicobalt $[(\text{N}_2)\text{Co}_2\text{L}]^-$ is a notable exception because the presence of a homometallic Co-Co single bond allows electron delocalization between the metals, giving a distinctly different $\text{Co}(0)\text{M}(\text{II})$ core. Interestingly, the $\text{Co}(0)$ active center engaged in a weak interaction with a $\text{Co}(\text{II})$ support appears to be electronically equivalent in terms of activating N_2 to a $\text{Co}(-\text{I})$ center that is strongly tied to an electron-withdrawing $\text{Al}(\text{III})$ ion ($\nu(\text{N}_2) = 1994$ and 1995 cm^{-1} , respectively). Collectively, $\nu(\text{N}_2)$ of $[(\text{N}_2)\text{CoML}]^-$ generally correlate with the CoML reduction potentials, such that milder potentials, and thus more electron-poor CoML , result in more weakly activated N_2 adducts. The CoML reduction potentials also follow a periodic trend, where the reduction potentials become increasing mild across the period, $\text{CoTiL} \ll \text{CoVL} < \text{CoCrL} < \text{Co}_2\text{L}$.

The cyclic voltammograms (CV) can also lend mechanistic insight into N_2 binding in Co complexes with a transition metal support (Table 1, Figure 6). The one-electron reduction processes for CoML are all irreversible under N_2 but become more reversible under argon. This behavior is consistent with an electron transfer / chemical reaction (EC) mechanism, where N_2 binding to $[\text{CoML}]^-$ is the chemical reaction (C_1) that follows initial electron transfer (E_1) (Figure 7) [62]. For Co_2L and CoCrL , a second reduction process (E_2) was observed. Notably, the second electron transfer is reversible, and was assigned to the redox couple for $[(\text{N}_2)\text{CoML}]^{2-}$. By switching the potential after the first electron-transfer and scanning anodically, the manifestation of yet another EC mechanism was observed, whereby oxidation of $[(\text{N}_2)\text{CoML}]^-$ to $(\text{N}_2)\text{CoML}$ (E_3) is followed by N_2 expulsion (C_2) to re-form neutral CoML .

Figure 6. Cyclic voltammograms of CoML complexes collected under an atmosphere of N₂ (colored lines) or argon (---) in 0.4 M [*n*Bu₄N]PF₆ in THF at a scan speed of 50 mV/s. Exceptions: 10 mV/s for CoCrL and Co₂L, and the latter was dissolved in 0.1 M [*n*Bu₄N]PF₆ in DME. Asterisk (*) marks the [CoML]^{0/-} redox couple. Adapted with permission from ref. [43] L.J. Clouston, V. Bernales, R.K. Carlson, L. Gagliardi, C.C. Lu, *Inorg. Chem.*, 54 (2015) 9263-9270. Copyright 2015 American Chemical Society.

Figure 7. Proposed mechanistic scheme (top) of the various EC steps in the cyclic voltammetry (CV) of CoML complexes, with a CV diagram of Co₂L illustrating the EC steps (bottom).

2.4.2 Identifying Factors that Govern N₂ Binding in Metal-Metal Complexes

While the study of N₂ binding in anionic [(N₂)CoML][−] complexes has been revealing, it is perhaps more intriguing to pose why N₂ binds to certain metal-metal pairings, but not to close analogues. Examples of bimetallics that do not bind N₂ include the neutral CoML complexes (for M = Ti, V, Cr, Co) and anionic [FeCrL][−] [63].³ To rationalize these reactivity differences, we employ molecular bonding arguments that pertain to the energy, composition, and electron population of the π -symmetry M_A–M_B orbitals, all of which are important factors that collectively govern the thermodynamics of N₂ binding in these bimetallic complexes. We present a couple instructive comparisons of similar bimetallic complexes to understand their different propensities to bind and activate N₂.

Case Study I: Neutral CoML versus anionic [(N₂)CoML][−]

When CoML has a total d-count ≥ 11 electrons, the high-lying Co–M π^* orbitals will be at least partially occupied, in accordance with the MO configuration $(\pi)^4(\sigma)^2(d_{Co})^4(\pi^*)^{1+n}$, where $n = 0$ to 3. Population of the Co–M π^* could benefit N₂ binding by providing additional π -back-bonding interactions from Co to N₂. However, the presence of Co–M π^* electrons alone is clearly not sufficient to induce N₂ binding, as neutral CoML with d-counts ≥ 11 do not bind N₂, including CoVL (d¹¹), CoCrL (d¹²), and CoCoL (d¹⁵). Hence, we propose that the Co center must surpass a certain threshold of electron-richness to engage in sufficient π -back-bonding interactions to bind N₂. An instructive comparison is that of neutral CoCrL with the hypothetical [CoVL][−] naked species, both of which are d¹² bimetallic species that would share a common configuration, $(\pi)^4(\sigma)^2(d_{Co})^4(\pi^*)^2$. We attribute the binding of N₂ to [CoVL][−] but not CoCrL to the lack of sufficient electron density at Co in CoCrL. Hence, the anionic charged state is necessary here to concentrate sufficient electron density at Co to bind N₂. Consistent with this idea, theoretical calculations reveal that the Co center has subvalent character, i.e. Co(−I), in anionic [(N₂)CoVL][−], but is closer to Co(0) in neutral CoCrL.

Case Study II: Anionic [FeCrL][−] versus anionic [(N₂)CoML][−]

The anionic iron species, [FeCrL][−], is a counterexample of an anionic d¹² bimetallic that does not bind N₂ [63]. Also, counterintuitively, swapping Fe in [FeCrL][−] for Co, which is generally worse at π -back-bonding to N₂, results in binding and in the formation of [(N₂)CoCrL][−]. To understand this dichotomy in N₂ binding, we must consider the orbital interactions between M_A–M_B π/π^* and N₂ π^* orbitals in more detail. The linear configuration of N₂–M_A–M_B requires that N₂ π -back-bonding competes with M_A–M_B π -bonding for M_A electron density. This competition is evidenced by an excessively large increase of ~ 0.5 Å in the Co–M distance from CoML to [(N₂)CoML][−], for M = V, Cr, and Co. The increase is primarily due to N₂ binding; the perturbation in the Co–M distance from gaining an additional anti-bonding electron into the Co–M π^* orbital is modest at ~ 0.1 Å.⁴

The necessity of cleaving the M_A–M_B bond while binding N₂ further underscores the difference between [FeCrL][−] and [(N₂)CoCrL][−]. Fe and Cr have more similar d-orbital energies

than do Co and Cr, which results in the formation of stronger and more delocalized π -bonds in $[\text{FeCrL}]^-$. The stronger Fe–Cr π -bonds also require more destabilized Fe–Cr π^* orbitals which are unfavorable to occupy, giving the electronic configuration $(\pi)^4 (\sigma)^2 (d_{\text{Fe}})^4 (d_{\text{Cr}})^2 (\pi^*)^0$. Thus, breaking the strong, delocalized Fe–Cr triple bond ($\sigma + 2\pi$) in order to bind N_2 is not as favorable as breaking the weaker, more polarized Co–Cr and Co–V π -bonds, explaining the dichotomy in N_2 binding.

To summarize this section, we have identified three important criteria which promote N_2 binding in first-row metal-metal bonded complexes:³

- (1) *Occupation of the metal-metal π^* orbitals favors N_2 binding by allowing additional π -back-bonding interactions.* As a corollary, the occupation of $\text{M}_\text{A}-\text{M}_\text{B}$ π^* orbitals further requires d-counts ≥ 11 . Indeed, all the isolated N_2 adducts of exclusively first-row bimetallics, thus far, have d-counts ≥ 12 . However, this single criterion is not sufficient to rationalize all N_2 binding behavior, since neutral complexes with partially filled $\text{M}_\text{A}-\text{M}_\text{B}$ π^* orbitals, e.g. CoCrL (d^{12}), do not bind N_2 .
- (2) *The active metal, M_A , must surpass a threshold of electron-richness to stabilize N_2 binding via π -back-bonding.* Neutral CoML complexes, where the Co oxidation states are between Co(0) and Co(I), are not electron-rich enough to induce N_2 binding. On the other hand, anionic $[(\text{N}_2)\text{CoML}]^-$ complexes with Co oxidation states between Co(0) and Co(–I) bind N_2 irreversibly. Notably, the anionic charge state of $[\text{M}_\text{A}\text{M}_\text{B}\text{L}]^-$ alone also does not guarantee N_2 binding, as $[\text{FeCrL}]^-$ does not bind N_2 .
- (3) *Binding N_2 in a linear $\text{M}_\text{B}-\text{M}_\text{A}-(\text{N}_2)$ arrangement will, by necessity, disrupt metal-metal multiple bonding. Hence, to promote N_2 binding, the metal-metal bond must be weakened, e.g. by population of the $\text{M}-\text{M}$ π^* orbital and/or by polarization.* If the $\text{M}_\text{A}-\text{M}_\text{B}$ bond is prohibitively strong, then breaking it to form an $\text{N}_2-\text{M}_\text{A}$ interaction will be unfavorable. This criterion does not preclude multiply bonded bimetallics from activating N_2 , as doubly bonded Co–V and Co–Cr cores both bind N_2 favorably with concomitant Co–M bond cleavage.

3. Metal-Support Interactions in Catalysis

3.1 Nickel-Group 13 Hydrogenation Catalysts

Nickel is typically a poor metal for effecting H_2 oxidative addition, and few homogeneous Ni hydrogenation catalysts have been reported [64-67]. To promote reactivity at Ni and other earth abundant metals, an emerging strategy is to design metal-Lewis acid (M–LA) bifunctional catalysts, where a main group Lewis acid support is coupled to the transition metal

[68]. In a seminal discovery, Peters and co-workers reported cooperative activation of H₂ across an inverse dative Ni→B σ-bond to generate a H–Ni(μ–H)B species that catalyzes olefin hydrogenation [39, 67]. The B(III) support was proposed to play a direct role in H–H cleavage in this and related systems [67, 69, 70]. We aimed to vary the Lewis acid support so as to systematically examine its role in promoting H₂ binding, cleavage, and hydrogenation catalysis in cooperation with an active transition metal. Specifically, we investigated the effect of heavier Group 13 supports (M = Al, Ga, In) on catalytic hydrogenation mediated by bimetallic NiML complexes. Changing the Lewis acid support could tune the favorability of H₂ binding to Ni, as well as affect its propensity to cleave H₂ by stabilizing H–Ni(μ–H)M intermediates, both of which are key steps in catalytic hydrogenation.

3.1.1 Catalysis Overview and Substrate Scope

The two supports that induced H₂ binding at Ni, M = In and Ga, were also found to be competent as supports in Ni-catalyzed olefin hydrogenation under mild conditions (1 atm H₂, room temperature, 5 mol% NiML, 0.087 M olefin in C₆D₆) [38]. The tuning effect of the supporting metal was critical for catalysis, as neither NiAlL nor the single Ni center in NiLH₃ was catalytically active. A substrate scope study using NiGaL, which is a more efficient catalyst than NiInL (*vide infra*), revealed a strong sensitivity to steric hindrance. High conversions were observed for unhindered hydrocarbon alkenes that are either mono-substituted, e.g. styrene, 1-octene, 1-hexene, and 4-phenyl-1-butene, or cyclic, e.g. *cis*-cyclooctene. Acyclic, di-substituted olefins such as *cis*-stilbene, *trans*-2-octene and 1,1-diphenylethylene gave little to no conversion to alkane product (0 to 10% yield). In the latter cases, the poor yields were attributed to steric clashes between the bulky olefin substituents and the ligand isopropyl groups, which likely preclude olefin binding.

Intriguingly, between the two competent catalysts, NiGaL and NiInL, two major differences in catalytic performance were observed. Catalysis proceeds much more rapidly for NiGaL than it does for NiInL, with about a 25-fold increase in TOF observed for styrene hydrogenation (2.4(1) h^{–1} for NiGaL). Secondly, for terminal olefins with allylic protons, NiGaL catalyzed hydrogenation exclusively, whereas NiInL was a nonselective catalyst for both hydrogenation to alkane and isomerization to internal olefins. For example, NiInL catalyzes the conversion of 1-octene to octane and 2-octene in approximately a 1:1 ratio, whereas catalysis with NiGaL results in only hydrogenation to octane. The divergent reactivity imparted by the various Lewis acid supports motivates in-depth mechanistic studies to understand the aforementioned differences in rate and product distribution.

3.1.2 Proposed Hydrogenation Mechanism

Based on preliminary kinetic experiments and literature precedent, a common mechanistic pathway is proposed for the Ni–Ga and Ni–In catalysts (Figure 8). The first step in the catalytic cycle is the binding of H₂ to generate the previously discussed (η²-H₂)NiML adducts

(A). Olefins were not observed to bind to NiML, even when present in large excess, which ruled out olefin-binding as the first step. The next two steps, olefin binding and H–H cleavage, could happen in either order. In either case, olefin binding would require the pre-dissociation of one of the three phosphine donors because the Ni center in **A** or **B** is saturated, either electronically (18 electrons) or coordinatively (6-coordinate), respectively. Olefin must compete with the dissociated phosphine for the Ni coordination sphere in the “open” intermediates **A*** and **B***. After H–H cleavage, olefin insertion into the Ni hydride **D** gives the Ni alkyl species **E**, which can then undergo reductive elimination to liberate alkane and regenerate NiML, completing the catalytic cycle.

Figure 8. Proposed mechanism for olefin hydrogenation catalyzed by NiML (M = Ga, In).

3.1.3 H–H Bond Cleavage and Olefin Binding

Considering the general difficulty of effecting H_2 oxidative addition at a single Ni center, H–H bond cleavage is likely to be the rate-determining step (RDS) in the catalysis. In support of this notion, a primary kinetic isotope effect (KIE) of approximately 1.7 was observed for the hydrogenation versus deuteration of styrene by NiGaL. H–H cleavage could occur directly from

(η^2 -H₂)NiML adducts (**A**) to give intermediate **B**, or alternatively it could be preceded by olefin binding with concomitant phosphine dissociation (via intermediate **C**). H–H cleavage could, in principle, occur from **A**, **A**^{*}, and/or **C**.

If H–H cleavage proceeded directly from **A** and/or **A**^{*}, then a logical implication is that the H₂ activation step could proceed in the absence of olefin. Furthermore, if **B** or **B**^{*} could be formed *in situ* from H₂ and NiML, then one might expect that using a H₂/D₂ gas mixture would lead to isotopic scrambling to generate HD in the absence of olefin.⁵ However, no H/D scrambling was observed for either NiGaL or NiInL in the absence of olefin, even with extended heating at 80°C.

Catalytic resting state studies are also useful to identify the dominant species that builds up prior to the RDS. For the Ni–In catalyst, **A** is the observed resting state. This is also the case for Ni–Ga below 233 K. However, at 298 K under catalytic conditions, the NMR spectra for Ni–Ga is characterized by a single, broad ³¹P NMR peak, whose chemical shift ranges from 40 to 47 ppm depending on the quantity and identity of the olefin present. Importantly, this peak does not correspond to (η^2 -H₂)NiML (48 ppm), NiGaL (38 ppm), or an olefin adduct (*vide supra*). Hence, we have proposed that olefin binding to (η^2 -H₂)NiGaL with the pre-dissociation of one phosphine arm is in rapid equilibrium on the NMR timescale (**A** → **A**^{*} → **C**), giving rise to the broad ³¹P signature of the catalytic resting state.⁶ Notably, no olefin-binding equilibrium with (η^2 -H₂)NiInL to give **C** was observed by NMR spectroscopy. Whether **C** is the intermediate that undergoes H–H cleavage or whether it is an off-pathway resting state is still unclear.

Regardless whether H–H cleavage occurs at **A**, **A**^{*}, and/or **C**, the slower catalytic rate for NiInL relative to NiGaL may be attributed to *the lower propensity for a more electron-poor Ni(0) center to oxidatively cleave H₂ to give H–Ni(II)(μ -H)M*. This would result in a higher barrier to rate-determining H–H cleavage for NiInL than NiGaL. Furthermore, intermediate **D**, the product of H–H cleavage, features a HNi(μ -H)M core, where the bridging hydride ought to have different stabilities for the different Lewis acid supports. Based on the known stabilities of Group 13 hydrides, Ga should provide greater stabilization of Ni(μ -H)M than In [71]. Furthermore, the greater thermodynamic stability of **D** for Ga relative to In may also translate into a lower rate-determining transition state barrier for H–H cleavage to form **D**. *Thus, another possible role of the Group 13 support is to stabilize the H₂ activated intermediate, H–Ni(μ -H)M, as typically Ni(II) dihydride species are unstable (as evidenced by the general incompetence of single Ni centers in H₂ oxidative addition).*

Another consideration is the effect of the supporting metal on the degree of phosphine lability and olefin affinity of intermediates **A** and **B**. We propose that the stronger interaction of Ni with both In and H₂ results in more labile Ni–P bonds. However, olefins are poorer ligands than the chelating ligand phosphine donors, and so a lower affinity for the third phosphine donor also means a lower affinity for olefin binding. *Hence, the Group 13 support induces different degrees of phosphine lability and/or olefin affinity through the Ni→M interaction.*

3.1.4 Olefin Insertion/ β -Hydride Elimination and Reductive Elimination

Olefin insertion in both 1,2- ($\mathbf{D} \rightarrow \mathbf{E}$) and 2,1-fashion ($\mathbf{D} \rightarrow \mathbf{E}'$) and de-insertion via β -hydride elimination ($\mathbf{E}/\mathbf{E}' \rightarrow \mathbf{D}$) are reversible and rapid relative to reductive elimination for NiGaL, as evidenced by the incorporation of deuterium from D_2 into all 3 vinylic positions of free styrene during catalysis. Reductive elimination from either intermediate $\mathbf{E}$ or $\mathbf{E}'$ would result in the loss of alkane and the regeneration of NiML. Alternatively, isomerization of terminal alkenes to give 2-alkenes, which only was observed to occur for In, is proposed to occur via initial 2,1-insertion ($\mathbf{D} \rightarrow \mathbf{E}'$) followed by internal β -H elimination to give a coordinated 2-alkene ($\mathbf{E}' \rightarrow \mathbf{D}'$) that is then liberated (Figure 9). 2-Alkenes, by virtue of their greater steric bulk, should be more labile, and once liberated would be less susceptible to re-enter the catalytic cycle because of the higher barriers associated with their binding and insertion at Ni [72]. Moreover, the olefin isomerization process can be mapped directly onto the proposed hydrogenation mechanism in Figure 8 by assuming that both 1,2- and 2,1-olefin insertions are occurring.⁷

Figure 9. Proposed pathway for terminal-to-internal olefin isomerization in the Ni-In system, where the barrier to reductive elimination is large enough for isomerization to compete with hydrogenation in the case of $\text{M}=\text{In}$.

To rationalize why NiGaL gives exclusively octane from 1-octene when NiInL generates both octane and 2-octene, we propose different relative rates of reductive elimination and β -hydride elimination from intermediates $\mathbf{E}$ and $\mathbf{E}'$ for the two supports. For Ni-In, we propose

that olefin isomerization is competitive with hydrogenation because of an increased barrier to reductive elimination as compared to that of Ni–Ga. The larger reductive elimination barrier essentially permits olefins to escape the hydrogenation cycle via β -hydride elimination and subsequent release of the isomerized olefins from the Ni center. The underlying reason as to why Ni–In has a greater barrier to reductive elimination than Ni–Ga is not yet well understood and is currently being investigated.

3.1.5 Catalytic Role of the Group 13 Support

In summary, we propose three critical roles that the supporting Group 13 Lewis acid plays in catalytic hydrogenation:

- (1) The electron-withdrawing Lewis acidic supports induce H₂ binding at Ni, which is the first step of the catalytic cycle. Larger, softer Group 13 supports render Ni more electron-deficient, which enables H₂ to bind (In > Ga >> Al). However, a delicate balance between H₂ binding and subsequent H–H cleavage must be struck; the more electron-poor Ni(0) centers will also be less susceptible to oxidative H–H cleavage. Supporting Ni with Ga appears to strike this balance: Ni is electron-poor enough to bind H₂, but not too electron-poor to hinder oxidative H–H cleavage.
- (2) Through the Ni→LA stabilizing interaction, the Lewis acid support can directly influence the electron density at the Ni center, which is also critical to the exchange of a phosphine ligand for an olefin at the Ni center. A stronger Ni→LA interaction (In > Ga) increases phosphine lability but may decrease olefin affinity.
- (3) The Lewis acid is also intimately involved in stabilizing bridging hydride moieties in intermediates **B**, **B***, **D**, and **E** (Ga > In), potentially affecting the rate of H–H cleavage as well as the competing rates of the reductive elimination and β -hydride elimination.

3.2 Reductive N₂ Silylation

The functionalization of N₂ is a challenge because of its thermodynamic stability and kinetic inertness. Biological nitrogen fixation (N₂ to NH₃) is performed by nitrogenases, where the active site is a fused dicubane cluster with a composition of Fe₇MoS₉C [2-4]. To date, no synthetic complex has come close to mimicking this cluster [73, 74]. Nonetheless, an increasing number of functional model complexes catalyze N₂ fixation using a single Mo or Fe center [75-81]. A complementary approach in N₂ functionalization is to form N–Si bonds by using electrophilic silyl reagents in place of protons [82-88]. The formation of N–Si bonds directly from N₂ has the potential to impact the production of silylamines, which are increasingly needed on large scale for use in the microelectronic industry [89, 90].

In N₂ functionalization, N–Si bonds were traditionally formed in a stoichiometric manner from a metal-N₂ precursor and a silyl electrophile. Chatt-type intermediates [91] featuring N–Si bonds tend to be more stable, and hence, easier to access than the N–H analogues. Of interest,

homogeneous catalysts that are active in N₂ silylation are typically ineffective in N₂ fixation. An important exception is an Fe-N₂ boratrane complex, which undergoes stepwise N-Si bond formations *and* catalyzes the formation of NH₃ from N₂ in 64 turnovers (13% yield) [76, 79]. The dichotomy is interesting considering that both types of catalysts are based primarily on Mo or Fe.⁸ However, in the last two years, Co has emerged as a new player in catalytic N₂ functionalization [45, 92, 93]. We have reported two Co bimetallic catalysts for N₂ silylation: Co-Al and Co-Co. Their activities are compared to better understand the role of the supporting metal in this catalysis.

3.2.1 Stoichiometric N-Si Bond Formation by an Iron Bimetallic

The tethered disilyl reagent, 1,2-bis(chlorodimethylsilyl)ethane, has been previously employed to generate disilylhydrazido metal species because of the favorable formation of a five-membered ring (Figure 10) [94]. Starting from [(N₂)FeAIL]⁻, this reagent enabled clean access to an Al-supported Fe disilylhydrazido complex [42]. Overall, two N-Si bonds are formed at the distal N atom, and the N-N bond elongates to 1.351(3) Å, which is consistent with a reduced N-N bond order of 1.5 [40].

The FeAIL parent complex was evaluated as a precatalyst in reductive N₂ silylation using excess Me₃SiCl and KC₈. Under standard catalytic conditions (*vide infra*), the silylamine product, N(SiMe₃)₃, was observed in limited turnover (turnover number (TON) = 9). The low catalytic activity of the Fe-Al system may correlate with the relative stability of the disilylhydrazido intermediate. In the case of Co-Al, stoichiometric reactions with 1,2-bis(chlorodimethylsilyl)ethane gave a complex mixture of unidentified products; however, the Co-Al system showed higher catalytic activity in N₂ silylation with a TON of 30 (*vide infra*).

Figure 10. Stoichiometric N₂ functionalization to form an Fe disilylhydrazido complex (solid-state structure in inset).

3.2.2 Catalytic N–Si Bond Formation by Cobalt Bimetallics

In reductive N_2 silylation, the standard catalytic conditions use low catalyst loadings, a large excess of Me_3SiCl , and a strong reductant (KC_8) under 1 atm N_2 at room temperature to generate $\text{N}(\text{SiMe}_3)_3$ as the only N_2 -derived product (Figure 11) [81]. A comparison of two Co bimetallic catalysts, $(\text{N}_2)\text{CoAIL}$ and Co_2L , demonstrated the impact of the supporting metal on the overall activity. The Co_2L catalyst was more effective by 6.5 times, with a TON of 195(25) compared to 30(9) for $(\text{N}_2)\text{CoAIL}$. We speculate that the better performance of the Co_2L catalyst results from the more flexible Co–M interactions during the catalytic cycle. Hemi-labile interactions have been previously proposed to facilitate N_2 fixation by Fe–B over Fe–Si and Fe–C catalysts.[76] Also, the robustness of Co_2L was tested by performing two consecutive catalytic cycles, giving an overall TON of 320(18), where the catalyst maintained ~65% of its initial activity in the second cycle.

Figure 11. Reductive N_2 silylation with Co bimetallic catalysts.

The supporting metal affects the cobalt active metal via the metal-metal interaction, as well as the formal charge balance between the two metal centers, i.e. formal oxidation states. In the dicobalt system, the core oxidation states of the neutral and anionic charged states, Co_2L and $[(\text{N}_2)\text{Co}_2\text{L}]^-$, are best described as $\text{Co}_A(\text{I})\text{Co}_B(\text{II})$ and $\text{Co}_A(0)\text{Co}_B(\text{II})$, respectively. Solid-state structures support a single covalent metal-metal bond in Co_2L , in contrast to a weak interaction in $[(\text{N}_2)\text{Co}_2\text{L}]^-$. In the Co–Al system, the neutral and anionic states, $(\text{N}_2)\text{CoAIL}$ and $[(\text{N}_2)\text{CoAIL}]^-$, have $\text{Co}(0)\text{Al}(\text{III})$ and $\text{Co}(-\text{I})\text{Al}(\text{III})$ cores, respectively. Both states retain a strong inverse dative interaction between the Co and Al centers. Of note, the oxidation states of the supporting metal do not change during the catalytic cycle (*vide infra*). The Co(II) and Al(III) supports represent opposite ends of an electronic continuum for tuning the electron density at the active cobalt center.

Since the bimetallics are proposed to operate via a single cobalt site, we also screened monocobalt complexes for catalysis (Table 2). Simple cobalt complexes showed low to modest turnovers, with the highest TON obtained for a monocobalt complex using the electron-donating phosphine ligand, $\text{PMe}(i\text{-Pr})_2$. The dicobalt system remains the most active catalyst we have

screened to date, and its TON is double that of its monocobalt counterpart. Hence, a supporting metal can dramatically tune the reactivity of an active cobalt center to make it better, Co₂L, or worse, N₂CoAIL, relative to that of a monocobalt catalyst.

Table 2. Yield and TON of N(SiMe₃)₃ by various catalysts under identical conditions (Figure 11).

Catalyst	% yield	TON
Co ₂ L	30	195 ± 25
N ₂ CoAIL	4	30 ± 9
N ₂ FeAIL	1	9 ± 2
CoCl ₂	1	6 ± 2
CoCl ₂ + 3 PMe(<i>i</i> -Pr) ₂	14	94 ± 19
Co nanopowder	0	0

3.2.3 Mechanistic Investigation of N₂ Silylation

Kinetic studies were performed on the highly active Co₂L to further probe the mechanism of N₂ silylation. Various control experiments establish that Co₂L is a homogeneous, bimetallic catalyst. Initial rates showed a pseudo-first-order dependence on catalyst concentration. In operando NMR studies were conducted to elucidate the catalytic resting state. The ¹H NMR spectrum revealed a few paramagnetic species as potential resting states. The only species that we could identify was [(N₂)Co₂L][−]. Although the other species remain unknown, quenching of the mixture with a drop of CD₂Cl₂ resulted in clean conversion to a single paramagnetic species, ClCo₂L. The observation of this product strongly suggests that the resting state species are bimetallic.

As the paramagnetic resting-state species proved challenging to identify and/or monitor, we turned to theory to gain mechanistic insights. With the assumptions that the mechanism primarily involves an anionic species and that N₂ silylation proceeds via a radical mechanism involving Me₃Si•, three different routes were examined (Figure 12). All three routes share a common intermediate, the disilylhydrazido species, [MN₂(SiMe₃)₂][−], which is formed by two consecutive Me₃Si• additions to the distal N of a metal-N₂ precursor. The first path (I) involves a third addition of Me₃Si• to the distal N, followed by the breaking of the N–N bond to form one equivalent of the trisilylamine and a cobalt nitride (Co≡N) intermediate. This path was ruled out due to a prohibitively high barrier (> 55 kcal/mol) for the addition of the third Me₃Si•. In the other two paths (II and III), the third Me₃Si• adds to the proximal N instead. Subsequent functionalization of the proximal N is precluded by steric congestion. In the second path (II), a fourth Me₃Si• adds to the distal N, which is followed by N–N bond cleavage to release one

$\text{N}(\text{SiMe}_3)_3$ and to form a cobalt imide intermediate ($\text{Co}=\text{N}$). This path is also ruled out by the high barrier for the distal $\text{Me}_3\text{Si}\cdot$ attack (39 kcal/mol).

Figure 12. Three general mechanistic pathways for reductive N_2 silylation, starting from the metal disilylhydrazido intermediate. Green circles represent SiMe_3 groups.

The most favorable path (III) involves the exothermic release of $[\text{N}_2(\text{SiMe}_3)_3]^-$ from the cobalt center. The $[\text{N}_2(\text{SiMe}_3)_3]^-$ ion converts spontaneously to two $\text{N}(\text{SiMe}_3)_3$ in the presence of excess Me_3SiCl and reductant (Figure 13). An important aspect, revealed by theory, is the necessity of one phosphine arm to de-coordinate from the active Co. The “open” disilylhydrazido intermediate ($\mathbf{D}^*$) is more stable than the closed form ($\mathbf{D}$), presumably because of a lessening of steric strain. Based on a shortening of the Co-Co distance from $\mathbf{D}$ to $\mathbf{D}^*$, we speculate that the Co-Co interaction is important to stabilize the active Co center in the open form. The re-coordination of the phosphine donor may induce the release of $[\text{N}_2\text{TMS}_3]^-$, completing the cycle to re-form Co_2L .

Figure 13. The predicted mechanism for reductive N_2 silylation by the dicobalt catalyst. Adapted with permission from ref. [45] R.B. Siedschlag, V. Bernales, K.D. Vogiatzis, N. Planas, L.J. Clouston, E. Bill, L. Gagliardi, C.C. Lu, J. Am. Chem. Soc., 137 (2015) 4638-4641. Copyright 2015 American Chemical Society.

A key change between N_2 fixation and N_2 silylation is the larger steric effects associated with the $SiMe_3$ groups. The isopropyl substituents on the ligand further contribute to the steric crowding at the active metal. Hence, the ability to de-coordinate a ligand donor to relieve steric strain is an important consideration in catalyst design. We postulate that a dynamic Co–M interaction may engender increased lability of the phosphine arm, allowing catalysis to proceed more efficiently. The increased Co–Co interaction in **D*** relative to **D** may compensate electronically for the loss of the phosphine donor, making it energetically favorable to open up the active site and to enable further N–Si bond formation.

4. Conclusions

Metal-support interactions are critical to an emerging class of privileged heterogeneous catalysts [95-99]. The ability to identify the optimal metal–support pair *a priori* for a specific catalytic application is a daunting task, but nonetheless an imperative one for both the homogeneous and heterogeneous communities. With so many possible combinations of metals, identifying targets that will have enhanced activity requires a thorough understanding of the interactions between diverse metals. Specifically, our systems have provided insight into which fundamental properties of a transition metal or Lewis acid support dictate enhanced bonding and electronic tuning of the active metal, priming it for reactivity.

Key to the identification of the optimal supporting metal for catalysis is our unique capability to target and dial in different metal pairings via a step-wise metalation procedure. We have been able to electronically tune the active metal (M_A) by varying the supporting metal (M_B) across the first-row period (for $M_A = \text{Co}$, $M_B = \text{Ti, V, Cr, Co}$) and by varying it down a periodic group (for $M_A = \text{Ni}$, $M_B = \text{Al, Ga, In}$). The versatility and success of our double-decker ligands stem from its ability to accommodate various metal sizes, and the tethering of two donor sets to buttress the metal-support interactions.

We described two metal-support systems that use earth-abundant base metals for catalytic reductive N_2 silylation and olefin hydrogenation. Both systems display a strong synergetic effect in which the presence of the optimal supporting metal significantly enhances catalytic activity relative to that of a single active metal center. Specifically, dicobalt (Co_2L) is a superior N_2 silylation catalyst compared to a single Co center ligated by $\text{PMe}(i\text{-Pr})_2$ (TON of $195 > 94$), and NiGaL catalyzes olefin hydrogenation (TOF of 2.4 h^{-1} for styrene, $>13.3 \text{ h}^{-1}$ for 1-octene) while a single Ni center, NiLH_3 , shows no activity. In the latter system, the larger, softer Lewis acid supports prime a late transition metal by imparting electrophilicity so to bind small-molecules (e.g. H_2) and engage directly in cooperative activation of a substrate (e.g. $\text{HNi}(\mu\text{-H})\text{M}_B$). A supporting transition metal is a more complex case in which the polarity and strength of the $M_A\text{--}M_B$ bond and the electron-richness of M_A are key factors in promoting reductive reactivity with N_2 .

Roles played by the supporting metal in both systems include optimizing the electronic state of the active metal for small molecule binding, inducing metal-ligand hemi-lability to allow further substrate activation, cooperatively stabilizing otherwise high energy intermediates, and dynamically weakening and strengthening its interaction with M_A as needed throughout catalysis. A delicate balance must be struck between stabilizing the metal-metal unit with strong metal-ligand and metal-metal bonds and allowing spatial access to incoming substrate via metal-ligand and metal-metal hemi-lability. Namely, both catalytic cycles invoke the dissociation of one of the three $M_A\text{--}P$ bonds; and, greater $M_A\text{--}P$ lability seems to result from stronger $M_A\text{--}M_B$ interactions. However, the metal-support interaction must not be prohibitively strong to preclude substrate binding, as is the case for triply bonded bimetallics in this framework. The flexible, or

dynamic nature of the metal-support interaction is critical to meet the fluctuating demands of the active metal center throughout catalysis to maximally stabilize the intermediates that must be traversed.

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Footnotes:

¹ For simplicity, the orbital analysis is restricted to interactions between pure p_z and d_{z^2} orbitals. Additional mixing interactions with the valence s-orbitals at the metal and LA are also occurring but are beyond the scope of this analysis.

² In isostructural Co–M systems, where binding of N_2 at Co is competitive with Co–M bonding, we typically observe Co–M bond changes of 0.5 Å upon N_2 binding, which is much greater than the observed bond elongation (0.07 Å) in the case of $(N_2)NiInL$.

³ It should be noted that the N_2 complexes considered here are examples where N_2 is strongly bound (i.e. stable to vacuum).

⁴ Preliminary structures of anionic $[CoCrL]^-$ and $[CoVL]^-$, which were obtained by excluding N_2 , show only a modest ~0.1 Å elongation of the Co–M bond relative to their neutral CoML counterparts.

⁵ Scrambling to HD would occur from the binding of D₂ (or H₂) to intermediate **B*** and subsequent sigma-bond metathesis with one of the Ni-H (or Ni-D) in **B***. It is worth noting that Peters and coworkers report rapid formation of HD upon exposing the similar [MesDPB^{Ph}]Ni, which has two phosphine donors and a Z-type Group 13 sigma-acceptor coordinated to Ni just like intermediate **B***, to an equimolar H₂/D₂ mixture. See: [64] W.H. Harman, J.C. Peters, J. Am. Chem. Soc., 134 (2012) 5080.

⁶ From this observation, it is likely that H–H cleavage takes place directly from (η²-H₂)NiInL. In any case, if there is an olefin binding equilibrium it lies so far toward (η²-H₂)NiInL that it is not observable by NMR spectroscopy even in vast olefin excess.

⁷ Olefin isomerization does not occur appreciably in the absence of H₂, further suggesting a common mechanistic link between the hydrogenation and isomerization catalytic cycles.

⁸ N₂ silylation catalysts based on a single W or Ti center are also known. See: [82] K. Komori, H. Oshita, Y. Mizobe, M. Hidai, J. Am. Chem. Soc., 111 (1989) 1939-1940. [84] M. Mori, J. Organomet. Chem., 689 (2004) 4210-4227.