Published in final edited form as:

Catal Today. 2017 May 15; 286: 21–40. doi:10.1016/j.cattod.2016.08.014.

Coordination chemistry insights into the role of alkali metal promoters in dinitrogen reduction

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Abstract

The Haber-Bosch process is a major contributor to fixed nitrogen that supports the world's nutritional needs and is one of the largest-scale industrial processes known. It has also served as a testing ground for chemists' understanding of surface chemistry. Thus, it is significant that the most thoroughly developed catalysts for N_2 reduction use potassium as an electronic promoter. In this review, we discuss the literature on alkali metal cations as promoters for N_2 reduction, in the context of the growing knowledge about cooperative interactions between N_2 , transition metals, and alkali metals in coordination compounds. Because the structures and properties are easier to characterize in these compounds, they give useful information on alkali metal interactions with N_2 . Here, we review a variety of interactions, with emphasis on recent work on iron complexes by the authors. Finally, we draw conclusions about the nature of these interactions and areas for future research.

Graphical abstract

Keywords

Haber-Bosch; nitrogen; ammonia; alkali metals; iron

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1. Introduction

1.1. Perspectives, Goals

Many heterogeneous catalysts are promoted by addition of alkali cations, and the study of promoters is important for development of more efficient catalysts [1-4]. The Haber-Bosch (H-B) process for N_2 conversion to NH_3 is one example of a very well-studied heterogeneous process that benefits from alkali cation promoters [5-7]. There has been a resurgence of interest in N_2 reduction because of its potential as a carbon-free fuel and because of the energy savings that would accrue from even small improvements in this very large-scale process [7-9]. Despite the fact that N_2 reduction is one of the best-studied surface processes, the atomic-level detail of the interactions between the alkali-metal cation and the substrate are still not clear.

Atomic-level detail is much easier to acquire for soluble molecular compounds, which are amenable to X-ray crystallography to $< 1 \text{ \AA}$ resolution as well as a variety of solution methods that elucidate dynamics that would be difficult or impossible to resolve on a surface. Moreover, the ability to isolate pure, structurally-characterized samples of homogeneous species enables mechanistic studies that are simpler to interpret. Though many interactions are not identical between solution and surface species, advances in the understanding of solution compounds can provide models and analogies that are useful for further development of the potential surface chemistry on heterogeneous catalysts.

With this idea in mind, this article presents a review focusing on the roles of alkali metal cations during the binding and cleavage of N_2 in solution complexes. As will be seen below, interactions between these cations and N_2 can greatly facilitate cleavage of the N-N bond, and current research is making significant strides in elucidating the interactions that are important in solution alkali-metal promoters. It is our hope that these emerging results will lead to new ideas for surface promoters as well.

1.2. Mechanism of the Fe-catalyzed Haber-Bosch process

During the H-B process, a feedstock of H_2 and N_2 gas in a 3:1 ratio is reacted over a promoted Fe catalyst at $\sim 700 \text{ K}$ and $\sim 100 \text{ bar}$. The technical catalyst, developed by Mittasch close to a century ago, is a fused-Fe catalyst promoted with alumina and potash (a mixture of water-soluble potassium salts such as KOH and K_2CO_3) [10, 11]. The average oxidation state of Fe in the Mittasch catalyst is between 0 and +1 [12]. The direct observation of the technical H-B catalyst under catalytic conditions is difficult, so many studies probing the mechanism and kinetics of the H-B process are done using single-crystal Fe surfaces [13]. Samples where the Fe(111) plane is exposed are the most active single-crystal Fe catalysts for the H-B process [14]. Somorjai attributed this to the fact that the Fe(111) plane has the highest concentration of exposed C_7 sites (where an Fe atom has seven nearest neighboring Fe atoms), at which the high-coordination number facilitates charge-transfer reactions (such as N_2 reduction) via local electronic fluctuations [15, 16]. However, the Fe(111) surface reconstructs and incorporates subsurface nitrides under reaction conditions [17, 18]. In addition to the Fe(111) plane, the Fe(211) and Fe(310) planes are quite active towards small

molecule activation [19-21]. Figure 1 illustrates the Fe(111) and Fe(211) planes, each of which exposes C₇ sites [15].

On surfaces, extensive kinetic studies have shown that the mechanism of N₂ reduction to NH₃ involves dissociative H₂ and N₂ adsorption to the Fe surface, followed by hydrogenation of adsorbed N-atoms, and ultimately desorption of NH₃ [5, 6]. On single-crystal Fe catalysts, the dissociation of adsorbed N₂ to form two nitrides is the rate-limiting step of catalysis [22-26]. An analogous mechanism occurs using the Mittasch catalyst, with the dissociative adsorption of N₂ generally considered to be the rate-limiting step [27, 28].

1.3. Promoters in the Fe-catalyzed Haber-Bosch process

During the development of the technical ammonia synthesis catalyst in the early 20th century, Mittasch discovered that the addition of foreign substances to the magnetite (Fe₃O₄) catalyst had a more pronounced effect on activity than the nature of the magnetite itself [10]. This prompted Mittasch and coworkers to systematically test the effect of thousands of additives on Fe catalysts for ammonia synthesis. Building from these studies, industrial Mittasch catalysts for the H-B process are synthesized through the fusion of Fe₃O₄ with various amounts of Al₂O₃, CaO, MgO, SiO₂, and K₂O. The first four are considered structural promoters that increase catalyst surface area, stabilize catalytically active Fe sites on the surface, and prevent sintering of the magnetite [29-32]. The potassium is generally considered to be an “electronic promoter;” its large ionic radius prevents incorporation into the magnetite during synthesis, and therefore it is localized at the surface [32]. Catalytic activity reaches a maximum at a certain amount of added potassium, both on polycrystalline Fe foil [33] and in the technical H-B catalyst [31]. The dropoff at higher surface coverage is explicable since the K⁺ resides on the surface and large amounts could block Fe active sites.

The seminal research by Mittasch, as well as many other subsequent studies, notes that other alkali metals also promote the technical catalyst [10, 28, 34-36]. Ruthenium-based H-B catalysts are also promoted with alkali metals [32]. In general, Ru catalysts exhibit higher activity with larger alkali metals, but recently Li was found to be a competent promoter [6, 37-39]. Analogous studies on alkali metal promoters for Fe catalysts do not always agree on the relative changes in activity when changing the alkali metal [28, 32, 34-36]. Understanding the precise role that these alkali metals play in improving the activity of structurally-promoted catalysts is vital for developing new ammonia synthesis catalysts with higher activity and robustness.

1.3.1. Determining the role of potassium in the Mittasch catalyst—The specific role of potassium in promoting the technical H-B catalyst is a topic of great interest, considering the enhancement of catalytic activity upon addition of potash to the iron oxide precursor [32, 34]. Hypothetical explanations include potassium involvement in N₂ chemisorption to the Fe surface, hydrogenation of adsorbed N-atoms, and desorption of NH₃ [40] [33] [30] [31] [41] [28] [42] [11]. Auger electron spectroscopy data indicate that the concentration of N₂ adsorbed to an Fe(111) single-crystal surface increases in the presence of co-adsorbed potassium, suggesting that potassium increases the N₂ adsorption energy to the Fe(111) surface [43]. Further investigating this effect, Whitman et al. reported that co-

adsorption of potassium to Fe(111) specifically stabilizes N₂ adsorption parallel to the surface, which is the precursor for N₂ dissociation. They hypothesized that the potassium lowers the energy barrier for conversion of terminally bound N₂ to the parallel-bound N₂ dissociation precursor. Interestingly, no shift in the N-N stretching frequency (ν_{NN}) occurs for perpendicular or parallel adsorbed N₂ in the presence of potassium, suggesting the absence of direct potassium-N₂ interactions that weaken the N-N bond [41]. This contrasts with the shift of vibrational frequency of adsorbed CO between bare and cation-promoted surfaces in some cases [44, 45].

Potassium may also have electronic effects on the Fe surface that play a role. In studies done on the technical H-B catalyst, Altenburg et al. found that the amount of potassium added to the Fe/Al₂O₃ catalyst affects the reaction order of H₂ in the reduction of NH₃ [40]. Nielsen et al., expanding on Temkin's original kinetic model for the H-B process, established that the overall rate of NH₃ formation depends on the order of H₂ in the rate law [46, 47]. The order of H₂ is in turn dependent on the ratio of N*, NH*, and NH₂* (where the asterisk indicates surface-adsorbed fragments) formed after rate-determining N₂ chemisorption to the Fe catalyst; N*, NH*, and NH₂* react with 1.5, 1, and 0.5 equiv of H₂ to form NH₃*, respectively. This relationship implies that potassium promotes formation of N* species over partially hydrogenated species, leading to an increase in order of H₂ and faster NH₃ generation under catalytic conditions.

Altenburg et al. proposed a model in which stabilization of NH* and NH₂* by hydrogen bonding with acidic OH groups inhibits the rate [40]. In this model, the presence of K⁺ on the surface decreases the coverage of surface Al³⁺-OH groups that would form stronger hydrogen bonds, and thus K⁺ gives a greater dependence of the rate on [H₂] and faster rates at high pressure. This model predicts that the rate should be faster for cations with a smaller charge-to-radius ratio. Direct evidence supporting this theory is limited to kinetic data; however, observations by Au et al. that hydroxyl groups present on Zn(0001) hydrogenate chemisorbed N* to form NH* and NH₂* support the tenets of this theory [48].

In the technical catalyst, K⁺ is certainly not reduced to a zerovalent state, and since it is introduced as potassium carbonate, is likely O-bound because alkali metal to transition metal interactions are weak [42, 49]. Chemical analysis and thermodynamic considerations argue that it is similar to KOH on the surface [50]. Arabczyk et al. proposed a double-layer model of the Mittasch catalyst surface under catalytic conditions (Figure 2) [51]. In this model, oxygen atoms on the surface of a bulk Fe lattice interact with cation promoters in a bridged Fe-O-M motif (where M is the cation). A double layer of oxygen and potassium covering the technical catalyst during H-B is consistent with spectroscopic evidence reported by Muhler et al. and Weinberg et al [52, 53]. Other models for the structure of the active technical catalyst also exist [18, 54]. Huo et al. recently reported that addition of a potassium promoter during the preparation of the technical ammonia synthesis catalyst results in a larger proportion of highly active Fe(211) and Fe(310) sites, further suggesting that alkali cations can be structural promoters [21].

The presence of K⁺ affects the local electrostatic potential of the Fe surface [55]. Because of the greater radial extent of its orbitals, the calculated influence on electrostatic potential

from K^+ is much more pronounced than the influence from the O, which would result in higher electron density on Fe atoms surrounding the O-K unit [42, 56]. The localization of electron density in Fe atoms surrounding the potassium atom is expected to destabilize NH_3 adsorption, allowing the more facile release of NH_3 . It has been shown experimentally that NH_3 adsorption to a single-crystal Fe(111) surface is lower in the presence of potassium promoters [49, 57]. Therefore, potassium-promoted enhancement of catalytic activity in this system (and by analogy, the H-B process) can occur because the product NH_3 is released more easily.

1.3.2. Promoting iron catalysts with other alkali cations—Many of the theories above can be explained through electrostatic influences of potassium on the catalyst surface. If the role of potassium as a promoter is purely electrostatic, replacing potassium in the technical catalyst with a different alkali cation should result in predictable relative enhancements to catalytic activity based on periodic trends. The depth at which the electrostatic potential of a surface is felt increases with the ionic radius of the cation, and as a result Cs^+ is expected to have the largest and Li^+ the smallest spatial extent of electronic effects [55]. This is often quantified through the charge-to-radius ratio (z/r) of the alkali promoter, and Mittasch catalyst activity increases with decreasing z/r (Figure 3) [34]. Bosch et al. also roughly observed this trend when testing Altenburg et al.'s theory of potassium-promoted formation of N^* species in favor of NH^* or NH_2^* species (Figure 4), demonstrating that replacement of potassium with cesium increases activity by ~20%. However, in this report the promoter effect of rubidium was found to be less than that of potassium [35].

In opposition to the periodic trend discussed above, some sources refer to potassium as the best alkali metal promoter for the technical H-B catalyst [28, 58]. Using the double-layer model presented above (Figure 2), the valence of the promoter cation and its ionic radius are expected to affect the density of open Fe active sites for N_2 chemisorption; thus, changing the alkali cation has both electronic and structural consequences. Based on these criteria, potassium could provide the highest density of Fe(111) and Fe(100) active sites during catalysis conditions (Table 1) [51].

Lithium is predicted to be a poor promoter for the Mittasch catalyst [35, 51]. With the highest z/r ratio, lithium cations have the smallest electrostatic effect on surrounding Fe atoms, and they also lead to better hydrogen bonding of OH groups that could stabilize $*N$, $*NH$, and $*NH_2$ [40]. In the double layer model, the lithium promoted catalyst is predicted to have no free active sites for N_2 chemisorption due to geometric packing effects [51]. Previous studies experimentally support the predicted low activity of lithium-promoted catalysts (see Figures 3-4) [34, 35]. In contrast, a recent study by Arabczyk et al. reports that doping the technical catalyst with lithium hydroxide results in enhanced catalytic activity, even exceeding the activity of the industrially used catalyst per surface area unit [36]. These contradicting reports, as well as inconsistencies between Cs and Rb promoted activity, indicate that alkali metal promotion of the Mittasch catalyst is still not fully understood.

2. Using homogeneous systems to better understand alkali cation interactions

Many of the difficulties in elucidating the nature of alkali cation promotion in the technical catalyst are rooted in limitations on the ability to observe atomic-scale interactions on the surface. Additionally, surface studies on the technical catalyst are complicated by the fact that the predominant species on the surface is unlikely to be the actual active catalyst. This makes direct observation of a catalytically active Fe site interacting with the substrate and promoters exceptionally difficult.

2.1. Advantages and disadvantages of studying homogeneous systems

Studying homogeneous systems that mimic the interaction of reduced Fe (or other transition metals) with alkali metals and N₂ can provide insight into these interactions with atomic-level resolution. With coordination complexes, it is much easier to isolate and characterize catalysts, products, and intermediates. X-ray crystallography can show structural details of synthetic compounds on an atomic scale, which allows the study of precise atomic interactions. Atomic-level structural resolution also provides a firm link between the structure of a synthetic compound and its spectroscopic characteristics. This correlation enables one to predict structures based on spectroscopic data, which can be vital when studying complicated interactions between multiple species *in situ*. Comparing the spectroscopy of homogeneous analogs to heterogeneous catalysts allows one to make predictions about interactions on the surface based on conclusions from solution studies. Additionally, it is possible to follow the changes in structures through an entire reaction pathway in solution studies. This allows homogeneous studies to target systems with the most relevant interactions and study how these interactions influence the reaction. In the context of the H-B process, effects of alkali cations on N₂ activation by transition metal complexes can be quantitatively measured through various parameters: the stretching frequency of the N-N bond (ν_{NN}), which is directly correlated to the N-N bond order; bond distances between N atoms, alkali cations, and metal complexes; changes in catalyst structure due to alkali interactions; and, the reduction potentials of the metal center [59]. These parameters provide insight into structural and electronic effects of the alkali cation, even distinguishing these in favorable cases. Electronic effects of the alkali cation on the metal center, which may affect N₂ activation, can be explored in homogeneous systems via cyclic voltammetry and spectroscopy.

It is important to note that, despite these advantages, homogeneous compounds can never provide a completely accurate representation of a surface. The use of solvents introduces numerous interactions (discussed in the next section) that are not present during the gas-phase conditions of ammonia synthesis. Additionally, the supporting ligands used to solubilize transition metal complexes have strong influences on the reactivity of the complexes with N₂. Finally, the localized molecular orbitals in molecular complexes do not necessarily translate well to the delocalized band structure of orbitals in extended materials.

2.2. Fundamental reactivity of alkali cations in solution

When evaluating alkali cation interactions in homogeneous systems, it is important to consider the behavior of alkali cations in solution. Cations in solution engage in numerous non-covalent interactions that are not relevant in gas-solid reactions as in the H-B process. This represents a significant limitation when comparing the homogeneous systems discussed in this review to the industrial ammonia synthesis process. Cation noncovalent interactions are primarily electrostatic, so the strength of these interactions typically increases with increasing z/r of the cation [60]. In contrast, electrostatic effects from cations on a surface are more pronounced for larger cations of the same valence [55].

Solvent interactions—Alkali cations form weak bonding interactions with electronegative O- and N-donor solvents. Solvents such as THF and Et₂O promote solubility of alkali cations as well as charge-transfer during multi-electron N₂ reduction and are thus often employed in homogeneous N₂ reduction chemistry. Solvent-cation interactions can promote rearrangement of cations in solution, leading to flexible cation-complex and cation-N₂ interactions. Relevant thermodynamic measurements of alkali cations with O-donor solvents are summarized in Table 2 [61]. These thermodynamic data suggest that Li⁺ forms stronger interactions with O-donor solvents. This is similar to one DFT study that calculated the free energy of alkali cation adsorption to an MgO surface, predicting that Li⁺ binds more strongly ($E_{\text{adsorption}} = -69.5$ kJ/mol) than Na⁺, K⁺, Rb⁺, and Cs⁺ ($E_{\text{adsorption}} = -24.1$ to -27.0 kJ/mol, no trend) to the metal oxide [62]. Since Li⁺ is not a potent promoter of the H-B process and all other alkali cations have comparable adsorption free energies to MgO, it is unlikely that the binding energy of an alkali cation to the catalyst surface is a dominating factor towards the efficacy of that cation as a promoter.

Cation- π interactions—Cations engage in electrostatic interactions with electron density from π -orbitals of aromatic systems [63, 64]. These interactions are relatively strong, and numerous examples are known in synthetic complexes as well as isolated proteins [65]. Owing to the electrostatic nature of this interaction, the strength of cation- π interactions increases with increasing z/r (Table 3). Electron-donating substituents on the arene result in stronger cation- π interactions, although this effect is more pronounced for smaller cations [61].

Interactions with crown ethers—Alkali cations form strong interactions with chelating macrocycles such as crown ethers and cryptands. These macrocycles are commonly employed in synthetic studies to sequester alkali cations due to the thermodynamic stability of chelated macrocycle-cation interactions over other noncovalent interactions [66-75]. The effect of alkali cation sequestration by crown ethers on alkali cation interactions to N₂ will be discussed below. Relevant sequential bond dissociation energies for alkali-crown-ether complexes are listed in Table 4 [61].

3. Effects of alkali cations on N₂ activation by transition metal complexes

Hundreds of transition metal-N₂ complexes have been described that encompass a wide variety of metals, supporting ligands, and binding motifs. Comprehensive reviews have been

published detailing N₂ complexes and their reactivities [59, 76-81]. In this review, we focus on N₂ complexes that incorporate alkali cation interactions with the N₂ ligand itself, thus demonstrating a direct influence of the alkali metal on activation of N₂. Most commonly, N₂ complexes that incorporate alkali cations have either an end-on interaction, where alkali cations interact with electron density from the N₂ σ -orbital and promote polarization of the N₂ ligand, or a side-on interaction, where alkali cations interact with electron density from N₂ π -orbitals (Figure 5).

These systems are advantageous for exploring the effects of the alkali metals because they can be systematically varied and contain spectroscopic handles that quantitatively describe the degree of N₂ activation. Specifically, the stretching frequency of the N-N bond (ν_{NN} , 2359 cm⁻¹ for unbound N₂) allows for the direct assessment of the strength of the N-N bond (Figure 6), with lower frequencies indicating a higher degree of reduction (due to more electron density in the π -antibonding orbitals of N₂) [82]. Similarly, in a solid-state crystal structure the distance between N atoms can be measured to give another estimation of N₂ reduction (1.098 Å for atmospheric N₂), as longer distances imply lower bond order. When considering these quantitative measures, ν_{NN} is usually considered the more accurate indicator of N₂ activation, since it can be measured *in situ* and is not affected by crystal-packing effects, crystal disorder, or uncertainties of the atom positions due to thermal motion.

3.1. End-on interactions between alkali cations and N₂

Complexes exhibiting an end-on interaction usually contain a linear M-N $\equiv$ N-A motif (M = transition metal; A = alkali metal). In all cases described, the end-on interaction is resultant from reduction of a transition-metal complex under N₂ with an alkali metal-based reductant. The alkali cation is stabilized by coordinating solvents (THF, Et₂O), cation- π interactions with the ancillary ligand, or chelating crown ethers. Figure 7 summarizes some examples of structurally characterized transition metal-N₂ complexes with an end-on interaction to an alkali cation.

3.1.1. Molybdenum and tungsten complexes—Mo and W dinitrogen complexes have been a focus of study for N₂ reduction chemistry since the discovery of Mo in nitrogenase enzymes that reduce N₂ [83, 84]. Based on the early work of Chatt on stoichiometric N₂ reduction to ammonia at a single Mo or W center, the chemistry of a rich variety of Mo and W dinitrogen complexes has been explored, including the electrochemical generation of NH₃ from N₂ by a homogeneous complex [85-87]. A few of these Mo- and W-N₂ complexes exhibit end-on interactions to alkali cations. For example, Peters et al. reported that the slow cleavage of N₂ by (N[R]Ar)₃Mo (R = C(CD₃)₂CH₃, Ar = 3,5-Me₂C₆H₃) to give (N[R]Ar)₃Mo $\equiv$ N is facilitated by the addition of Na/Hg [88]. This reaction is proposed to proceed through an activated terminal (N[R]Ar)₃Mo(N₂) complex with a weak end-on interaction from Na⁺, which quickly reacts with another equiv of (N[R]Ar)₃Mo to form [Mo(N[R]Ar)₃]₂(μ -N₂). The μ -N₂ complex cleaves N₂ to form 2 equiv of (N[R]Ar)₃Mo $\equiv$ N over a few hours. However, reduction of the more sterically hindered (N[Ad]Ar)₃Mo analog with Na/Hg prevents the formation of a bimetallic μ -N₂ complex, instead halting the reaction at (N[Ad]Ar)₃Mo(μ -N₂)Na(THF)₃ (**1**). **1** contains a strong end-on interaction with Na⁺ in

the solid state. While $(\text{Ar}[\text{Ad}]\text{N})_3\text{Mo}(\mu\text{-N}_2)\text{Na}(\text{THF})_3$ does not cleave N_2 , the Na-bound N atom was found to form bonds with various electrophiles. A similar complex $(\text{Ar}^i\text{Pr})_3\text{Mo}(\mu\text{-N}_2)\text{Na}(\text{THF})_3$ (**2**) complex also behaves as a nucleophile at the Na-coordinated N-atom, reacting with methyl tosylate to form a new N-C bond [89].

In another system, Yandulov et al. explored N_2 reduction using various Mo complexes utilizing a tetradentate triamidoamine supporting ligand and discovered the first homogeneous catalyst for ammonia production from N_2 [90]. Reduction of $([\text{ArN}(\text{CH}_2)_2]_3\text{N})\text{MoCl}$ ($\text{Ar} = \text{C}_6\text{H}_5$, 4- FC_6H_4 , 4- tBuC_6H_4 , 3,5- $\text{Me}_2\text{C}_6\text{H}_3$) with 2 equiv of sodium naphthalenide results in the formation of the N_2 species $([\text{ArN}(\text{CH}_2)_2]_3\text{N})\text{Mo}(\mu\text{-N}_2)\text{Na}(\text{THF})_x$, which dimerize upon crystallization but are monomeric in solution [67]. These N_2 complexes contain an end-on interaction with Na^+ , and stabilization of the cation with 15-crown-5 allowed isolation of $([4\text{-tBuC}_6\text{H}_4\text{N}(\text{CH}_2)_2]_3\text{N})\text{Mo}(\mu\text{-N}_2)\text{Na}(15\text{-crown-5})$ (**3**) and $([3,5\text{-Me}_2\text{C}_6\text{H}_4\text{N}(\text{CH}_2)_2]_3\text{N})\text{Mo}(\mu\text{-N}_2)\text{Na}(15\text{-crown-5})$. Addition of Me_3SiCl to the dinitrogen complexes results in silylation to form a diazenido ligand. A similar, more sterically encumbered ligand was employed for $([3,5\text{-}\{2,4,6\text{-}^i\text{Pr}_3\text{C}_6\text{H}_2\}_2\text{C}_6\text{H}_3\text{N}(\text{CH}_2)_2]_3\text{N})\text{WCl}$, which forms $([3,5\text{-}\{2,4,6\text{-}^i\text{Pr}_3\text{C}_6\text{H}_2\}_2\text{C}_6\text{H}_3\text{N}(\text{CH}_2)_2]_3\text{N})\text{W}(\mu\text{-N}_2)\text{K}$ (**4**) upon reduction with 2.5 equiv of KC_8 [96]. Interestingly, the solid-state structure of **4** shows that the K^+ does not lie along the W-N=N axis, but it interacts strongly with an arene in the supporting ligand to form a bent N=N-K interaction. In this case, the cation is stabilized via cation- π interactions rather than by coordinating solvents or crown ethers. Cation exchange using $^n\text{Bu}_4\text{NCl}$ quantitatively removes the K^+ . **4** can be protonated at the nucleophilic N-atom using strong acids to form $([3,5\text{-}\{2,4,6\text{-}^i\text{Pr}_3\text{C}_6\text{H}_2\}_2\text{C}_6\text{H}_3\text{N}(\text{CH}_2)_2]_3\text{N})\text{WN=NH}$ and $([3,5\text{-}\{2,4,6\text{-}^i\text{Pr}_3\text{C}_6\text{H}_2\}_2\text{C}_6\text{H}_3\text{N}(\text{CH}_2)_2]_3\text{N})\text{W=NNH}_2[\text{BAr}_4']$.

A more recent system described by Miyazaki et al. employs a Mo complex with strongly donating ferrocenyldiphosphine and pentamethylcyclopentadienyl supporting ligands [68]. Reduction of the dimer $[\text{Cp}^*\text{MoCl}_4]_2(\mu\text{-1,1'-}[\text{PEt}_2]_2\text{Fc})$ with excess Na/Hg under N_2 gives $[\{1,1'\text{-}(\text{PEt}_2)_2\text{Fc}\}(\text{Cp}^*)\text{Mo}](\mu\text{-N}_2)\text{Na}(\text{THF})_x$ as the major product, with Na^+ interacting end-on to the N_2 ligand. Addition of 1 equiv of 15-crown-5 gives the isolated product $[\{1,1'\text{-}(\text{PEt}_2)_2\text{Fc}\}(\text{Cp}^*)\text{Mo}](\mu\text{-N}_2)\text{Na}(15\text{-crown-5})$ (**5**). In contrast to triamidoamine scaffolds, **5** does not react with strong acids to form a diazenido or hydrazido complex; however, the nucleophilic N-atom reacts with Me_3SiCl to form the expected silyldiazenido complex.

3.1.2. Iron complexes—Dinitrogen reduction using homogeneous Fe complexes is of particular interest due to the discovery that N_2 is reduced at a tetrairon face by the FeMo-cofactor in nitrogenase [91-93] and the use of a promoted Fe catalyst in the Haber-Bosch process. As with Mo and W dinitrogen complexes, many examples of reduction of N_2 with Fe complexes via alkali metal-based reductants result in products with end-on interactions between N_2 and alkali cations. For example, studies by Fernandez et al. on (PDI)Fe systems (PDI = 2,6- $[2,6\text{-}^i\text{Pr}_2\text{PhN}=\text{C}(\text{CH}_3)]_2(\text{C}_5\text{H}_3\text{N})$; pyridinediimine) showed that (PDI)FeBr₂ is reductively arylated with 2 equiv phenyllithium to form (PDI)Fe(Ph), which is reduced by an additional equivalent of phenyllithium to form $[(\text{PDI})\text{Fe}(\text{Ph})](\mu\text{-N}_2)\text{Li}(\text{OEt}_2)_3$ [94]. While this complex could not be crystallized, the tolyl analog $[(\text{PDI})\text{Fe}(p\text{-tol})](\mu\text{-N}_2)\text{Li}(\text{OEt}_2)_3$ (**6**) was prepared and crystallographically characterized to confirm the end-on $\text{Li}^+\text{-N}_2$

interaction. Despite this interaction, the N₂ ligand of **6** is barely activated due to preferential reduction of the supporting ligand, exhibiting a ν_{NN} of 2068 cm⁻¹ and N-N distance of 1.138(3) Å. A similar complex is synthesized by addition of neopentylolithium to (PDI)Fe(N₂)₂ to form [(PDI)Fe(CH₂^tBu)](μ-N₂)Li(OEt₂)₃ (**7**). This complex has a slightly more activated N₂ ligand, with ν_{NN} = 1948 cm⁻¹ [69]. An interesting study of the reduction of (PDI)FeCl₂ with NaH by Scott et al. showed a diverse array of products depending on the amount of reductant used [95]. Using 3 equiv of NaH, the reduced complex (2-[2,6-ⁱPr₂C₆H₃N=CMe]-6-[2,6-ⁱPr₂C₆H₃N-C=CH₂]C₅H₃N)Fe(N₂)[η²-Na(THF)] (**8**) was isolated, containing a side-on interaction between the N₂ ligand and Na⁺. Using 6 equiv of NaH, two complexes containing end-on interactions between Na⁺ and N₂ were isolated: (2-[2,6-ⁱPr₂C₆H₃N=CMe]-6-[2,6-ⁱPr₂C₆H₃N-C=CH₂]C₅H₃N)Fe(μ-N₂)Na(Et₂O)₃ (**9**) in which the Na⁺ is solvated with diethyl ether and (2,6-[2,6-ⁱPr₂C₆H₃N=CMe]₂C₅H₃N)Fe(μ-N₂)Na[Na(THF)₂] (**10**) in which the end-on Na⁺ is coordinated to one of the ligand arenes (and which contains an additional Na⁺ coordinated to the ancillary PDI ligand). An additional reduced complex (2-[2,6-ⁱPr₂C₆H₃N=CMe]-6-[2,6-ⁱPr₂C₆H₃N-C=CH₂]C₅H₃N)Fe(N₂) (**11**), which is devoid of cation interactions, was isolated as one of the products from reduction of (PDI)FeCl₂ with 12 equiv NaH. Scheme 1 summarizes the synthesis of **8-11**. All three complexes containing cation-dinitrogen interactions display slight N₂ activation. For the side-on coordination product **8**, ν_{NN} is 1912 cm⁻¹. **9** has a ν_{NN} of 1965 cm⁻¹, which is significantly higher than that of **10** (ν_{NN} = 1899 cm⁻¹). When comparing **8-10** to **11**, which has a ν_{NN} of 2156 cm⁻¹, it seems that the presence of cations significantly promotes N₂ activation. However, **11** has a surprisingly high ν_{NN} , especially when compared to another neutral complex with the same supporting ligand (2,6-[2,6-ⁱPr₂C₆H₃N=CMe]₂C₅H₃N)Fe(N₂) (**12**), reported by Bart et al., which has a ν_{NN} of 2036 cm⁻¹ [96]. Instead, **11** seems more closely related to the neutral bis-N₂ complex (2,6-[2,6-ⁱPr₂C₆H₃N=CMe]₂C₅H₃N)Fe(N₂)₂ (**13**), which has two N₂ stretches at 2058 and 2122 cm⁻¹ (although both stretching frequencies are still lower than that of **11**). There is no clear correlation between the type of interaction of Na⁺ with N₂ and ν_{NN} in this system.

The Peters group has studied N₂ reduction using Fe complexes supported by tris(phosphino)silane, borane, and alkyl ligands. Reduced Fe-N₂ complexes using these ligands were prepared through reduction of parent halide complexes with strong alkali-based reductants. Reduction of (Si(*o*-C₆H₄P(ⁱPr)₂)₃)Fe(N₂) with sodium naphthalenide gives (Si(*o*-C₆H₄P(ⁱPr)₂)₃)Fe(μ-N₂)Na(THF)₃ (**14**), which exhibits an end-on interaction between Na⁺ and N₂. **14** reacts with Me₃SiCl to give the silylated diazenido product, demonstrating the nucleophilic reactivity of the distal N-atom [71]. Analogous to **14**, reduction of (B(*o*-C₆H₄P(ⁱPr)₂)₃)FeBr with 2.5 equiv of sodium naphthalenide gives (B(*o*-C₆H₄P(ⁱPr)₂)₃)Fe(μ-N₂)Na(THF)_x (**15**) [72]. Remarkably, this complex catalytically reduces N₂ to NH₃ with excess KC₈ and HBAr^F₄, achieving up to 64 equiv of NH₃ per Fe center [97, 98]. The alkyl analog (C(*o*-C₆H₄P(ⁱPr)₂)₃)Fe(μ-N₂)K(Et₂O)₃ (**16**) is synthesized by the reduction of (C(*o*-C₆H₄P(ⁱPr)₂)₃)FeCl with excess KC₈. **16** is also catalytically active towards NH₃ production from N₂ with excess KC₈ and HBAr^F₄, producing 47 equiv of NH₃ per Fe center [73, 98].

Ung et al. reported a low-coordinate Fe-CAAC system (CAAC = cyclic(alkyl)(amino)carbene) that, when reduced with KC₈ in the presence of 18-crown-6, forms

(CAAC)₂Fe(μ-N₂)K(18-crown-6) (**17**) [74]. In contrast to other examples where addition of a crown ether results in sequestration of the coordinated cation, end-on K⁺ still forms a contact ion pair with the anionic Fe-N₂ complex even when chelated by 18-crown-6, similar to the Mo complex **3**. **17** catalyzes N₂ reduction to NH₃, achieving 3.4 equiv of NH₃ per Fe complex with excess KC₈ and HBAr^F₄.

3.1.3. Cobalt complexes—A few examples of reduced Co-N₂ complexes displaying end-on cation coordination to N₂ also exist. Reduction of the Co-hydride complex (P(C₆H₅)₃)₃CoH(N₂) with ⁿBuLi gives (P(C₆H₅)₃)₃Co(μ-N₂)Li(Et₂O)₃ (**18**) or (P(C₆H₅)₃)₃Co(μ-N₂)Li(THF)₃ (**19**), depending on the solvent used. Alternatively, use of Na metal instead of BuLi as the reductant gives (P(C₆H₅)₃)₃Co(μ-N₂)Na(THF)₃ (**20**). In all cases, the cation interacts with the reduced N₂ ligand in an end-on fashion, and addition of concentrated acid to the complexes releases substoichiometric amounts of hydrazine and ammonia (in addition to H₂ and N₂). This system enables two interesting comparisons: a) the effect of Li⁺ vs. Na⁺ on N₂ activation and b) the effect of solvation of Li⁺ on N₂ activation. The N-N bond in **19** (ν_{NN} = 1890 cm⁻¹) is slightly weaker than the one in **20** (ν_{NN} = 1910 cm⁻¹), suggesting that Li⁺ is a slightly better promoter for N₂ activation than Na⁺ in this system. Et₂O forms a slightly stronger bond with Li⁺ than THF (see Table 2), which results in greater N₂ activation in **19** (ν_{NN} = 1890 cm⁻¹) than in **18** (ν_{NN} = 1900 cm⁻¹). Addition of 12-crown-4 to **18** magnifies this effect, increasing ν_{NN} from 1900 to 1920 cm⁻¹. Stronger interactions between the cation and solvent molecules or chelators thus results in less N₂ activation, presumably by competing with the end-on interaction between the cation and N₂ [75].

In another system, Evers et al. synthesized bimetallic Co-Nb and Co-Ta complexes with weak dative interactions between the metals [99]. Reduction of the complexes under N₂ with excess Na/Hg results in the formation of bimetallic N₂ complexes ^tBuN=Nb[μ-(ⁱPr)N-P(C₆H₅)₂]₃Co(μ-N₂)Na(THF)₅ (**21**) and ^tBuN=Ta[μ-(ⁱPr)N-P(C₆H₅)₂]₃Co(μ-N₂)Na(THF)₅ (**22**), both of which exhibit end-on interactions of N₂ to Na⁺. The identity of the ancillary metal does not affect the N-N bond order in this system (ν_{NN} = 1940 cm⁻¹ for both complexes).

3.1.4. Summary and analysis of trends in complexes with end-on alkali binding

—The aforementioned complexes with end-on alkali cation to dinitrogen interactions exhibit weakened N-N bonds in most cases, with ν_{NN} from 1757-1965 cm⁻¹ and N-N distances from 1.220(8) to 1.035(4) Å (Table 5). The distance between the alkali metal cation and N₂ shows no evident correlation with ν_{NN}. The ν_{NN} values suggest mildly reduced N₂ ligands, which is also evident from the nucleophilic nature of the distal N-atom in many cases. However, since the systems described utilize widely varying metals, supporting ligands, and oxidation states, it is difficult to identify specific trends of reactivity between different alkali cations. In the case of **19** and **20**, where only the alkali cation is varied, the change in ν_{NN} is marginal. Additionally, none of the complexes displaying end-on interactions to alkali cations contain Rb⁺ or Cs⁺ as the cation, further limiting the ability to identify more general periodic trends.

Despite insufficient data to confidently define a periodic trend between the alkali cation identity and extent of electronic promotion on N₂ activation through an end-on interaction, it is worth noting that the presence of an end-on bound alkali cation often promotes reactivity of the N₂ ligand. For example, the distal N-atom in complexes **1-5** and **14** reacts with electrophiles to form new N-C, N-Si, or N-H bonds, depending on the complex. Additionally, **16** and **17** are catalysts for reduction of N₂ to NH₃. The potential role of the alkali cation in these catalytic systems will be discussed later in this review. It is reasonable to conclude that end-on coordination of an alkali cation promotes nucleophilicity of the N-atom due to Coulomb attraction of electron density into the terminal N atom of the N₂ ligand (see below).

Despite the variation in the complexes showcasing end-on interactions, a common strategy is the sequestration of the alkali cation with a crown ether to decrease other interactions, such as cation-ligand, cation-N₂, or cation-solvent interactions, in favor of coordination to the chelating macrocycle. Following this reaction spectroscopically gives insight into the direct effect that the end-on interaction has on dinitrogen activation. Most commonly, addition of a crown ether results in an increase in ν_{NN} , indicating a decrease in backbonding from loss of the direct interaction (Table 6). In one of the clearest examples, a study by Tondreau et al. showed that the 1e⁻ reduction of (2,6-[2,6-ⁱPr₂C₆H₃N=CMe]₂C₅H₃N)Fe(N₂) (**12**) using sodium naphthalenide generates [(2,6-[2,6-ⁱPr₂C₆H₃N=CMe]₂C₅H₃N)Fe(N₂)] [Na(THF)_x] (**23**) and shifts the ν_{NN} from 2036 to 1917 cm⁻¹ (the authors also report a second stretch at 1966 cm⁻¹, attributed to different cation-coordination modes) [70]. To avoid the complicated range of products formed when reducing (PDI)Fe(N₂) complexes with Na-based reductants (described above, see **8-11**), Tondreau et al. added 15-crown-5 or 18-crown-6 to **23** to reduce cation interactions. They found that addition of 15-crown-5 shifts ν_{NN} higher by 39 cm⁻¹ to 1956 cm⁻¹ and use of 18-crown-6 shifts ν higher by 32 cm⁻¹ to 1949 cm⁻¹, demonstrating an increase in N-N bond order when sequestering the cation. In another case, K⁺ in **4** is replaced with non-coordinating ⁿBu₄N⁺, resulting in an increase of ν_{NN} by 56 cm⁻¹ [100]. This suggests that the end-on coordination of an alkali cation has a direct electronic effect on the N₂ ligand, facilitating backbonding from the metal into the π^* -orbitals of the N₂ ligand. From a molecular orbital standpoint, this can be explained through a) the polarization of orbital density and b) the shift in orbital energy induced by the proximity of a positive charge to the distal N-atom. In response to the nearby positive charge, the distal N-atom becomes more electronegative, polarizing the N₂(π) HOMO towards the cation-coordinated N-atom and N₂(π^*) LUMO towards the metal-bound N-atom. This allows better orbital overlap between N₂ π^* - and metal d-orbitals, facilitating d→ π^* backbonding. The cation-promoted polarization also shifts the N₂ π^* -orbital lower in energy, making backbonding more energetically favorable. Typically, these cation-promoted electronic effects lead to greater N₂ activation, resulting in a lower ν_{NN} by 26-56 cm⁻¹ when end-on cation interactions are present. There are, however, a few exceptions to this trend. In the case of **3**, there is no change of ν_{NN} when the cation is sequestered by 15-crown-5 [67]. Alternatively, the addition of 2 equiv of 12-crown-4 to **2** reportedly results in a shift of ν_{NN} from 1783 to 1728 cm⁻¹, indicating a *decrease* in N-N bond order upon removal of the cation [89].

3.2. Side-on interactions between alkali cations and N₂

In complexes with side-on interactions between alkali cations and N₂, the cation interacts with the electron density in the N₂ π -bonding orbitals. These complexes are once again synthesized by the reduction of precursors with alkali metal-based reductants under N₂. In many cases, the N₂ ligand is bridging between two metal centers, preventing any end-on interactions between N₂ and an alkali cation. When this is the case, since orthogonal side-on cation interactions do not polarize the N-N bond, the N₂ stretching vibration is IR-silent. Spectroscopic parameters of transition metal N₂ complexes exhibiting side-on interactions with alkali cations are summarized in Table 7.

3.2.1. Group 3-6 complexes—Early transition metals activate and often completely cleave N₂ since they contain high-energy d-orbitals that favorably donate into the π^* -orbitals of N₂. In some systems, reduction of early transition metal-N₂ complexes with alkali metal-based reductants leads to activated N₂ complexes with side-on cation interactions (Figure 8). In one case, Evans et al. studied the reduction of N₂ by Y-based trisamide complexes with KC₈ [101]. They found that changing the rate and method of KC₈ addition allowed the isolation of reduced μ - η^2 : η^2 -N₂ dimers with varying K⁺ coordination. Interestingly, they were able to crystallize [(SiMe₃N)₂Y(THF)]₂(μ - η^2 : η^2 -N₂)[K(THF)₆] (**24**), which contains a solvated K⁺ counter-ion, and [(SiMe₃N)₂Y(THF)]₂(μ - η^2 : η^2 -N₂)(η^2 -K)(THF) (**25**) which contains a K⁺ with a strong side-on interaction to N₂. Raman data for **25** indicate that ν_{NN} is only 989 cm⁻¹, which suggests an exceptionally low N-N bond order and an N₂³⁻ ligand. No Raman data were collected for **24**, but DFT frequency calculations predict a ν_{NN} of 1002 cm⁻¹ for **24**, which is 13 cm⁻¹ higher than the predicted (and experimental) ν_{NN} for **25**. The N-N bond distances were identical at 1.401(6) Å for **24** and 1.405(3) Å for **25**. Thus the effect of direct side-on coordination of K⁺ to N₂ in **25** compared to loosely associated K⁺ in **24** is small.

A few Zr systems containing isolated complexes with side-on N₂ interactions to alkali metal cations have been recently reported. Bis(indenyl)-Zr halide complexes can be reduced with Na/Hg under N₂ to give [(η^5 -C₉H₅-1-ⁱPr-3-Me)₂ZrCl]₂(μ -N₂)(η^2 -Na)₂ (**26**), [(η^5 -C₉H₅-1-ⁱPr-3-Me)₂ZrBr]₂(μ -N₂)(η^2 -Na)₂ (**27**), and [(η^5 -C₉H₅-1-ⁱPr-3-Me)₂ZrI]₂(μ -N₂)(η^2 -Na)₂ (**28**), each of which contains two Na⁺ cations anchored by cation- π interactions with indenyl and cation-halide interactions. Comparing the solid state structures of **26** and **28** indicates that the N₂ ligand is more reduced in **26** than in **28**, with a difference in N-N bond distance of 0.036(7) Å. This was attributed to effects of the halide on the reduction potential of the metal center, but structural effects due to differences in ionic radii of the halides may also play a role. No crystal structure or spectroscopic data detailing the N-N bond of **27** was reported. Addition of H₂ to **26-28** results in the formation of hydrazido complexes. Notably, attempted sequestration of the Na⁺ cations using 18-crown-6 or 15-crown-5 resulted in multiple products, significant structural changes, and loss of reactivity towards H₂ [102]. In another system, zirconocene complex [Me₂Si(η^5 -C₅Me₄)(η^5 -C₅H₃-3-²Ad)]ZrCl₂ binds N₂ upon reduction with KC₈ but not with Na/Hg. This is more likely due to differences in reduction potential rather than alkali cation identity. The resulting complex [{Me₂Si(η^5 -C₅Me₄)(η^5 -C₅H₃-3-²Ad)}ZrCl]₂(μ -N₂)(η^2 -K) (**29**) contains a side-on interaction with a single K⁺, which is coordinated to two chlorides as well [103].

An early example of a Group 5 metal-N₂ complex containing side-on alkali cation interactions was reported by Ferguson et al., who reduced (2,4,6-Me₃C₆H₃)₃V(THF) with sodium metal under N₂ to form [(2,4,6-Me₃C₆H₃)₃V]₂(μ-N₂)(η²-Na) (**30**). The reaction also proceeds with potassium metal, but no analogous structure was reported [104]. In another system, N₂ can be cleaved into two bridging nitrides by a Nb-calix[4]arene cluster via stepwise reduction with sodium metal. Partial reduction intermediates exhibit significant side-on interactions of N₂ with Na⁺, such as in [{*p*-^tBu-calix[4]-(O)₄}Nb]₂(μ-η²:η²-N₂)(μ-Na)₃Na (**31**) [105].

In their study of Mo complexes supported with various “hybrid” tetradentate triamidoamine ligands, Weare and coworkers isolated [{3,5-(2,4,6-ⁱPr₃C₆H₂)N(CH₂)₂}]₂(3,5-Me₂C₆H₃)N(CH₂)N]Mo(N₂)[η²-Na(THF)₂] (**32**) from the reduction of [{3,5-(2,4,6-ⁱPr₃C₆H₂)N(CH₂)₂}]₂(3,5-Me₂C₆H₃)N(CH₂)N]MoCl with Na/Hg under N₂. In **32**, the N-N-Na angle is 110°, suggesting an intermediate side-on end-on interaction [106].

3.2.2. Group 8-10 complexes—Group 8-10 transition metal complexes with side-on alkali cation to N₂ interactions are exclusively bimetallic systems with bridging N₂ ligands (with the exception of **8**), and only a few systems have been described (Figure 9). The first concerns a Co-pincer complex (PNP)CoCl (PNP = N(2-P(CHMe)₂-4-MeC₆H₃)₂), which coordinates N₂ upon reduction with excess sodium naphthalenide to form a dimer containing a [Co(μ-N₂)Na]₂ core (**33**). Each N₂ ligand has a side-on interaction with one Na⁺ and pseudo-end-on interaction with another, resulting in a ν_{NN} of 1784 cm⁻¹. Adding two extra equivalents of the parent halide (PNP)CoCl forms the bridging N₂ complex [(PNP)Co]₂(μ-N₂) [107]. The second example comes from the reduction of a porphyrin-supported Ru-vinylidene complex with sodium metal under N₂. This reduction gives [(*meso*-Me₈(porph)Ru(C≡CH))₂(μ-N₂)(η²-Na)₄] (**34**), which has significant side-on interactions of the bridging N₂ with four Na⁺ cations [108].

The use of bidentate β-diketiminato ligands (^RL, where ^RL = [(2,6-ⁱPr₂C₆H₃NCR)₂CH]) to support Fe-, Co-, and Ni-N₂ complexes has been extensively studied due to highly activated N₂ ligands found in these complexes. Traditionally, late-group transition metals are poorly activating towards N₂ ligands due to their relatively low-energy d-orbitals, which limits backbonding into the N₂ π*-orbital. However, sterically bulky β-diketiminato ligands such as ^{Me}L and ^{tBu}L force the metal center to adopt a three-coordinate, pseudo-trigonal planar geometry that raises the energy of d-orbitals containing the correct symmetry for interaction with N₂ π-orbitals. This facilitates N₂ activation via backbonding within these complexes [109].

Stepwise N₂ reduction by complexes utilizing these ligands typically proceeds by reduction of the parent complex ^RLMX (where R = Me, ^tBu; M = Fe, Co, Ni; X = Cl, Br) with 1 equiv of a strong reductant to form a bimetallic [LM]₂(μ-N₂) species. Subsequent reduction of this species with 1 additional equiv of a strong reductant per M gives A₂[LM]₂(μ-N₂), where A is an alkali cation. The alkali cations show a strong side-on interaction to the N₂ ligand and are stabilized by cation-π interactions with the proximal arenes. The first example was described by Smith et al., who isolated the complexes Na₂[^{tBu}LFe]₂(μ-N₂) (**35**) and K₂[^{tBu}LFe]₂(μ-N₂) (**36**) from reduction of [^{tBu}LFe]₂(μ-N₂) with sodium or potassium metal,

respectively. The $2e^-$ reduction of $[\text{tBuLFe}]_2(\mu\text{-N}_2)$ to form **35** and **36** results in a significant decrease in the N-N bond order, evident from significant N-N bond lengthening in the solid-state structure (0.05-0.06 Å) and decrease in ν_{NN} (189-195 cm^{-1}) [110]. The difference in alkali cation between **35** and **36** seems to have very little effect on N_2 activation in this case, as N-N distances are within 0.01 Å and ν_{NN} differs only by 6 cm^{-1} between the complexes. Ding et al. later explored the analogous Co complexes, isolating $\text{Na}_2[\text{tBuLCo}]_2(\mu\text{-N}_2)$ (**37**) and $\text{K}_2[\text{tBuLCo}]_2(\mu\text{-N}_2)$ (**38**) via reduction of tBuLCoCl with excess sodium metal or 2 equiv of KC_8 , respectively. **37** and **38** have slightly shorter N-N bond distances and higher ν_{NN} than their Fe analogs, which is due to lower energy d-orbitals on Co compared to Fe. As with the Fe analogs, the identity of the alkali cation has little effect on the extent N_2 activation [111, 112].

The first Ni analog of **36** was reported by Pffirman et al. from the reduction of tBuLNiBr with 2 equiv of KC_8 to form $\text{K}_2[\text{tBuLNi}]_2(\mu\text{-N}_2)$ (**39**). Following the periodic trend of d-orbital energies, **39** exhibits a shorter N-N bond and higher ν_{NN} than its Co analog, indicating less N_2 weakening. Interestingly, the authors found that reduction of tBuLNiBr with 1.5 equiv of KC_8 results in the formation of $\text{K}[\text{tBuLCo}]_2(\mu\text{-N}_2)$, which contains a side-on interaction between the bridging N_2 and a single K^+ on one side [113]. Horn et al. found that reacting this partially-reduced complex with sodium metal gives the mixed-alkali product $\text{NaK}[\text{tBuLNi}]_2(\mu\text{-N}_2)$ (**40**) [114]. Furthermore, reduction of the previously reported $[\text{tBuLNi}]_2(\mu\text{-N}_2)$ with excess sodium metal afforded the $\text{Na}_2[\text{tBuLNi}]_2(\mu\text{-N}_2)$ species (**41**), completing a series of reduced Ni- N_2 species that differ only by the intercalated alkali cations. Comparison of these complexes gives insight into the effect of the alkali cation on N_2 activation, since no other variables are changed. A tentative relationship between the degree of N_2 activation and charge-to-radius ratio of the alkali cation is evident through Raman spectroscopy: **41** shows the lowest ν_{NN} (1685 cm^{-1}), followed by **40** (1689 cm^{-1}), then **39** (1696 cm^{-1}), suggesting that Na gives more weakening than K. (However, this trend is not seen in related iron complexes; see below). This trend does not extend to N-N bond distances in the solid-state structures of **39-41**, which are all identical within uncertainty limits.

Reduced N_2 complexes featuring the less bulky ligand MeL have also been reported. The reduction of $[\text{MeLFeCl}]_2$ with 2 equiv of KC_8 gives $\text{K}_2[\text{MeLFe}]_2(\mu\text{-N}_2)$ (**42-K**), which contains side-on interactions between N_2 and two K^+ cations. This complex has a slightly shorter N-N bond distance in the solid state structure (1.215(6) Å) when compared to **36** and a slightly stronger ν_{NN} (1625 cm^{-1}) [115]. Recently, this system was chosen by McWilliams et al. for a systematic study of effects that changing the alkali cation may have on N_2 activation or bimetallic structure. $\text{Na}_2[\text{MeLFe}]_2(\mu\text{-N}_2)$ (**42-Na**) was synthesized via reduction of $[\text{MeLFeBr}]_2$ with excess sodium metal, while $\text{Rb}_2[\text{MeLFe}]_2(\mu\text{-N}_2)$ (**42-Rb**) and $\text{Cs}_2[\text{MeLFe}]_2(\mu\text{-N}_2)$ (**42-Cs**) were synthesized via reduction of $[\text{MeLFeBr}]_2$ with 2 equiv RbC_8 or CsC_8 , respectively. Spectroscopic and crystallographic parameters from this series of complexes are summarized in Table 8. Changing the alkali cation results in only minor changes in N-N bond distance, ν_{NN} , and Mössbauer isomer shift (an indicator of electron-richness of the Fe center). This implies that changing the charge-to-radius ratio of the side-on cation has very little effect on the ability for the Fe metal to reduce N_2 . However, the

radius of the alkali cation was shown to influence the relative solid-state geometries of the backbone ligands: the diketiminate backbone rotates and aryl-substituents twist to accommodate the larger cations in **42-K**, **42-Rb**, and **42-Cs**. The ligand distortion results in higher torsion angles between the two Fe-N-C-C-N planes as the radius of the cation increases (Figure 10). Cation to N-atom distances also increase with the radius of the cation. In the case of **42-Na**, Na⁺ is not large enough to fill the entire arene cavity, which is evident by elucidation of two crystallographically independent structures with slight shifts in Na⁺ positions within the cavity. The inability for Na⁺ to fill the cavity and maximize cation- π stabilizing interactions results in the decomposition of **42-Na** in THF. In contrast, **42-K**, **42-Rb**, and **42-Cs** are all stable in THF, and cation-exchange experiments with triflate salts suggest that they have relatively similar stabilities. Attempts to synthesize Li₂[^{Me}LFe]₂(μ -N₂) were unsuccessful, presumably because the small radius of Li⁺ makes it even more inept at filling the arene cavity, resulting in decomposition [116].

When studying the reduction of [LM]₂(μ -N₂) to A₂[LM]₂(μ -N₂), it is unclear what effect the side-on interaction of the alkali cations has in the mechanism of this reduction, since an intermediate in which *only* cation intercalation or *only* 2e⁻ reduction occurs has never been elucidated. Additionally, attempts to remove the alkali cations from the arene cavities (similar to the sequestration of end-on alkali cations previously discussed) resulted in decomposition of the complex. To address this dilemma, Smith et al. used computational methods in an attempt to identify the separate contributions that the 2e⁻ reduction and cation intercalation have towards reducing N₂ in **42-K**. To the truncated model compound LFe-N, 1e⁻ and two side-on cations were added sequentially. Reduction of LFe-N₂ by 1e⁻ to [LFe-N₂]⁻ resulted in lengthening of the N-N bond by 0.036 Å, and subsequent addition of 2 Na⁺ resulted in further lengthening of the N-N bond by 0.032 Å (0.017 Å for 2 K⁺). The fact that electron addition and alkali cation coordination activate N₂ by similar amounts suggests that these steps act cooperatively [115]. In a separate study, Ding et al. sought to determine whether N₂ activation in **38** was primarily due to reduction of the Co or coordination of the alkali cations. Once again, computations indicated that both steps significantly reduce the N-N bond order, suggesting a cooperative interaction between the reduced Co center and side-on coordinated cations to activated N₂ [112]. In both cases, it is likely that the presence of the positive charge proximal to the N₂ encourages backbonding that increases electron density near the cation. In this sense, the influence is similar to that postulated in the Fe-based H-B catalyst.

3.2.3. Analysis of trends in complexes with side-on alkali binding—The studies on N₂ reduction by late-group β -diketiminato complexes allows some understanding of the role of alkali cations in the stepwise reduction of N₂ by these complexes. Side-on coordinated cations clearly stabilize the structure of the A₂[LM]₂(μ -N₂) motif through cation- π interactions with ligand-based arenes, because sequestration of the cations in coordinating solvents (**42-Na**) or with crown ethers (**42-K**) eliminates the formation of these bimetallic complexes. Additionally, the conformational shifts of the supporting diketiminato ligand to accommodate larger cations in **42-Rb** and **42-Cs** suggests that the cation itself plays a large role in determining the overall structure of the complex. However, it is unclear whether the structural contribution of the cations is to facilitate greater N₂ reduction by

influencing the geometry of reaction intermediates or whether the cations merely stabilize the reduced product. In the case of **26-28**, removal of coordinated cations results in significant structural changes *and* loss of reactivity of the complex towards H₂, which suggests that cation interactions may indeed play a role in organizing reactive intermediates in multi-step N₂ reduction.

The electronic effects of side-on coordinated alkali cations are even more difficult to elucidate. Comparison of the various alkali cation analogs of **42** indicates that, when the cation interaction is present, changing z/r of the cation does not impact the extent of N₂ activation. This observation is consistent in other systems where only the alkali cation identity is varied: comparisons between **39-41**, between **37** and **38**, and between **35** and **36** show no appreciable change in N₂ activation. Additionally, tight ion-pairing with side-on coordination of K⁺ to N₂ in **25** rather than solvent-separated ion-pairing of K⁺ in **24** does not affect activation of the N₂ ligand, which implies that proximity of the K⁺ cation does not have an electronic effect in that system. Computations suggest that side-on interactions of alkali cations to N₂ cooperate with reduction of the metal center to enhance overall N₂ ligand activation. This hypothesis has not been tested experimentally due to the inability to isolate the cation-deficient anionic analogs of any of the complexes discussed in this section. The origin of this cooperative effect from a molecular orbital standpoint has so far only been described vaguely in the literature [115]. A system that allows the independent addition/removal of electrons and alkali cations would be particularly insightful towards determining the specific electronic effects of side-on alkali cation coordination to N₂.

4. Effects of alkali cations on N₂ cleavage by transition metal complexes

The rate-limiting step of catalytic NH₃ production in the Haber-Bosch process is thought to be the initial homolytic cleavage of N₂ to form absorbed nitride species. To better understand how alkali cations could facilitate the complete cleavage of N₂, it is useful to study homogeneous systems in which N₂ cleavage is closely associated with alkali cation interactions. Only a few such examples have been described so far, but each of them utilize multiple metal sites to split N₂ into bridging nitrides, which are stabilized by nitride-cation interactions (Figure 11).

4.1. Vanadium and niobium complexes

Early group transition metal complexes that achieve cation-facilitated N₂ cleavage include a V diamidoamine complex that binds and cleaves N₂ upon reduction with 2 equiv of KC₈ to form the bridging V₂(N)₂ complex K[{(Me₃SiNCH₂CH₂)₂(Me₃Si)N}V]₂(μ-N)₂ (**43**). The K⁺ is coordinated to the diamidoamine ligand and one of the bridging nitrides [117]. In another system, reduction of a dimeric Nb complex supported with a tridentate tris-phenoxide ligand with 6 equiv LiBHET₃ enables N₂ cleavage to form a Nb₂(μ-N)₂ complex (**44**) that is similar to **43**. Once again, cations are coordinated to the bridging nitrides and supporting ligand [118]. Another Nb system supported with a tetradentate calix[4]arene ligand can achieve stepwise N₂ cleavage upon reduction with sodium metal. Some products with partially reduced N₂ show side-on Na⁺ to N₂ interactions (as discussed earlier, see **31**),

and the product in which N₂ is completely cleaved to two bridging nitrides shows coordination of a Na⁺ cation to each of the nitrides (**45**) [105].

4.2. Iron complexes

Fe-based homogeneous systems that cleave N₂ serve as the best analogies to N₂ reduction by the Mittasch catalyst, which utilizes a potassium-promoted Fe surface. The first Fe system that can reversibly cleave and regenerate N₂ was described by Rodriguez et al., in which reduction of the β -diketiminato Fe complex $[(\{2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NCMe}\}_2\text{CMe})\text{Fe}(\mu\text{-Cl})_2$ (**46**) with 2 equiv KC₈ results in the cleavage of N₂ to form a tetrairon bis-nitride complex (**47-K**) [119]. In the product, the two nitrides bridge a triiron cluster, with one of the nitrides stabilized by two coordinating K⁺ cations. These cations are anchored by cation- π interactions with arenes from the triiron core as well as coordination to a fourth Fe dichloride moiety. This tetrairon bis-nitride species quantitatively releases N₂ when 12 equiv of a strongly coordinating ligand (CO, benzonitrile) are added [120]. The specific role that K⁺ plays in this reaction was explored in a computational study by Figg et al., who used DFT studies to examine the sequential addition of Fe¹⁺- β -diketiminate fragments to free N₂ [121]. The authors found that N₂ cleavage to the bis-nitride is only achieved when three Fe¹⁺ fragments work cooperatively. The presence of a K⁺ ion coordinated to the bis-nitride cluster was found to significantly stabilize the nitride product relative to the Fe₃(N₂) isomer. Thus the N₂ cleavage becomes thermodynamically favorable when the K⁺ cation can interact with the nitrides. Interestingly, the stabilizing effect of K⁺ towards the bis-nitride product is lessened in polar solvents relative to nonpolar solvents or the gas phase, suggesting that a tight cation-nitride interaction in a nonpolar environment is ideal.

Another study by Grubel et al. on this system investigated the effects of changing the coordinating alkali cations (Scheme 2) [122]. In analogy with the synthesis of **47-K**, **46** can be reduced with sodium metal, RbC₈, or CsC₈. Reduction of the parent halide with 2 equiv of RbC₈ gives a tetrairon bis-nitride complex analogous to **47-K** containing Rb⁺ cations in the place of K⁺ cations (**47-Rb**). **47-Rb** features the same Fe₃N₂ core as its K⁺-containing analog, but the Rb⁺ cations are slightly closer to the “terminal” nitride and slightly distanced from the coordinated arenes. The thermal stability of **47-Rb** in benzene is higher than that of **47-K**, which suggests that the larger Rb⁺ ions more effectively fill the nitride-arene cavity than K⁺ (similar to the relative stability of **42-K** vs. **42-Na**). The relative stability of **47-Rb** over **47-K** is confirmed by treatment of **46** with 2 equiv of RbOTf, which results in complete cation exchange to form **47-Rb**.

Interestingly, reduction of the parent halide with sodium metal or CsC₈ does not give an analogous tetrairon bis-nitride product. Reduction of **46** with excess sodium metal results in the formation of a triiron bis-nitride complex (**48-Na**) in which the “terminal” nitride is capped with a single Na⁺ cation. The Na⁺ is also coordinated to a ligand-based arene and two THF molecules. Interestingly, **48-Na** is more thermodynamically stable than **47-K** and **47-Rb**, both of which convert to **48-Na** upon treatment with excess NaOTf. Reduction of **46** with 2 equiv of CsC₈, on the other hand, gives a triiron bis-N₂ complex with a Fe₃($\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2$)₂Cl core with two Cs⁺ cations intercalated between ligand-based arenes (**49-Cs**). This complex is only partially reduced, which is evident by retention of the chloride ligand. The

lack of a cleaved N₂ unit is surprising considering that the reducing equivalents and reducing power used to synthesize **49-Cs** should be at least as great as in the Na, K, and Rb analogs [122].

4.3. Analysis of trends in N₂ cleavage involving alkali-metal cations

Studies on the N₂-cleaving Fe system provide insight into the role that alkali cations may play in cooperative reduction of N₂ by multiple iron sites. Plausible roles that the K⁺ could play in this system include structurally organizing participating Fe complexes into the necessary geometry for N₂ reduction, thermodynamically promoting N₂ reduction by stabilizing the reduced products, or facilitating N₂ reduction electronically by promoting back-bonding from Fe complexes into the N₂ π^* -orbital. The DFT calculations by Figg et al. suggest that stabilization of the bis-nitride product by K⁺ cations is vital for thermodynamically favoring the 6e⁻ reduction of N₂ by the electron-rich Fe sites [121]. These calculations also suggest that the alkali metal-N₂ interaction may be more pronounced in non-polar solvents, which is a closer approximation of the gas phase Haber-Bosch conditions.

Changing the alkali cation used during reduction of **46** results in the formation of reduced multiiron clusters containing Na⁺, K⁺, Rb⁺, and Cs⁺ cations. However, while the reduction of **46** with these reductions is related, cation identity has pronounced effects on the product generated, as evident by the stark differences in structure between **48-Na**, **47-K** and **47-Rb**, and **49-Cs**. The variability in the structures of these products prevents quantitative comparison of electronic effects that the alkali cations may have, which are normally established by comparison of N-N bond distances, stretching frequencies, and reduction potentials. However, the relative stability of **47-Rb** over **47-K** suggests that the ability for the cation to efficiently fill the arene-nitride cavity is more important than the strength of cation- π interactions when determining overall stability of the complex. Since K⁺ has a higher charge-to-radius ratio than Rb⁺, it has a stronger electrostatic interaction with the π -orbitals of arenes (see Table 3). If this were the dominating stabilizing factor, **47-K** would be more stable relative to **47-Rb**. Furthermore, it is evident from this study that the use of Cs⁺ prohibits complete cleavage of N₂ in this system. The possible origin of this observation will be discussed in the next section.

5. Structural influences from cations leading to changes in reactivity with N₂

While some studies of alkali cations affecting the structure of N₂ complexes were discussed in the previous sections, the extent to which alkali cations can influence reactivity of complexes towards N₂ in these systems is unclear. In the examples above, reduction and cation coordination is done in tandem with N₂ activation. A recent study by Chiang et al. shows that the cation influences on the structure of a reduced metal complex can influence its ability to bind N₂ [123]. In this study, reduction of a β -diketiminato-supported Fe-phenolate complex ([2,6-ⁱPr₂C₆H₃NC^tBu]₂CH)Fe(OC₆H₅) (**50**) with 1 equiv KC₈ in the absence of N₂ results in an Fe¹⁺ complex with K⁺ intercalation, forming an Fe-O-K subunit. However, the structure of the reduced complex is dependent on solvent interactions,

resulting in a monomeric $[(\{2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NC}^t\text{Bu}\}_2\text{CH})\text{Fe}(\text{OC}_6\text{H}_5)][\text{K}(\text{OEt}_2)_2]$ complex (**51**) in diethyl ether but a dimeric $\text{K}_2[(\{2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NC}^t\text{Bu}\}_2\text{CH})\text{Fe}(\text{OC}_6\text{H}_5)]_2$ complex (**52**) in toluene. In **51**, K^+ is coordinated to the phenolate O-atom, one of the diketiminate arenes, and two Et_2O molecules. Alternatively, **52** contains K^+ cations that are coordinated to a phenolate O-atom and locked between two arenes (one diketiminate and one phenolate) to form two strong cation- π interactions for each K^+ . The change in structure in coordinating solvent (Et_2O) is attributed to the ability of Et_2O ligands to stabilize the K^+ in the complex's monomeric form. Interestingly, the dimeric structure of **52** seems to be necessary for reactivity of the reduced Fe complex with N_2 . Under N_2 atmosphere, **52** binds N_2 to form the reduced bridging N_2 complex **36**, but the monomeric complex **51** does not (Scheme 3). The structure-reactivity dependence was further demonstrated by addition of crown ethers (18-crown-6 and cryptand-222) to **52**, which results in separation of the K^+ ion from the iron-phenoxide. **52** no longer reacts with N_2 when these crown ethers are present, suggesting that removing the K^+ breaks up the dimeric structure that is necessary for N_2 binding. This supports the hypothesis that alkali cations can facilitate the organization of key intermediate structures that are necessary for N_2 binding and activation.

This study is particularly relevant to the Haber-Bosch process because it involves N_2 activation by an Fe-O-K subunit, which mimics the Fe-O-K sites on the surface of the Mittasch catalyst (see Figure 2). In **52**, oxygen bridges provide important interactions for holding the K^+ and Fe atoms in a geometry that allows N_2 binding, which suggests that it is reasonable for the oxygen bridges in the Mittasch catalyst to play a similar role during catalytic N_2 reduction. Additionally, the inability of **51** (and other structures that separate K-O interactions) to bind N_2 suggests that cooperation between multiple iron sites may play a key role in N_2 reduction in both this system and the Haber-Bosch process.

The structural influence of alkali cations on reactivity of reduced Fe complexes with N_2 was further explored in the study by Grubel et al. [122]. While reduction of the parent halide complex **46** with 2 equiv of KC_8 or RbC_8 results in complete reduction of N_2 to form bis-nitride complexes (**47-K** and **47-Rb**), reduction of **46** with 4 equiv of KC_8 or RbC_8 results in *incomplete* reduction of N_2 . Instead, the reduction yields trinuclear complexes with $\text{A}_2[\text{Fe}(\mu\text{-N}_2)]_3$ cores (A = K, **53-K**; A = Rb, **53-Rb**). An analogous complex is formed by the reduction of **46** with 4 equiv of CsC_8 (**53-Cs**), which is once again different from the reduction product when 2 equiv of CsC_8 are used (**49-Cs**). The alkali cations in these trinuclear complexes are intercalated between three ligand-based arenes, out of the $[\text{Fe}(\mu\text{-N}_2)]_3$ plane (Figure 12). In all three of these cases, the reducing power and number of equivalents of the reductant should be similar, which suggests that the limiting parameter in N_2 cleavage in these systems is actually the available geometries of $\text{Fe}_x\text{N}_2\text{A}_x$ species formed during the reduction [122]. As mentioned above, DFT studies suggest that N_2 cleavage is achieved cooperatively by three Fe^{1+} fragments and promoted by the stabilizing effects of the alkali cation [121]. Consequently, studies of Fe-diketiminate complexes in which the ligand is too sterically bulky to allow access of a third Fe^{1+} fragment show that these systems are unable to completely cleave N_2 [115]. Similarly, the cation-arene interactions in **53-K**, **53-Rb**, and **53-Cs** when extra alkali cation equivalents are present organize the formation of bulky trinuclear cores in which only two Fe^{1+} fragments can interact with any

one N₂ ligand, preventing N₂ cleavage. This supports the hypothesis that the way cations organize the geometry of reduced Fe fragments directly affects the ability for the Fe to reduce N₂. However, in this system the geometry of Fe¹⁺ subunits is dominated by cation- π interactions. Since the technical Mittasch catalyst does not contain arenes, this is not directly relevant to the Haber-Bosch process. A future challenge is thus to design and study homogeneous systems in which cation- π interactions are less dominant or eliminated altogether.

6. Comparing alkali cation promotion of homogeneous N₂ reduction to alkali cation promotion of the Haber-Bosch process

The effect of alkali cation interactions with N₂ ligands of transition metal complexes depends heavily on the geometry. When coordinated to N₂ in an end-on fashion, alkali cations are often electronic promoters, which is evident from experiments that sequester end-on alkali cations with crown ethers. This effect can be explained from a molecular orbital standpoint, suggesting that the alkali cation promotes backbonding from metal d-orbitals into the N₂ π^* -orbitals. This provides strong evidence that N₂ molecules bound to a metal can be further activated by a proximal electropositive alkali metal. Unfortunately, to our knowledge there has been no systematic study of the effect of alkali cation identity on N₂ activation in end-on systems.

However, end-on interactions may not be particularly relevant to the H-B process for a few reasons. Firstly, promotion of a single-crystal Fe catalyst with potassium does not result in a change in ν_{NN} of adsorbed N₂, suggesting that a N $\equiv$ N-K unit is not present [41]. Secondly, end-on cation to N₂ interactions in homogeneous species frequently involve a monometallic complex. In contrast, N₂ cleavage on the technical ammonia synthesis catalyst may use transition states involving multiple Fe sites. Finally, alkali cations coordinated end-on to N₂ ligands are relatively far away from the transition metal center, which is likely not the case in the Mittasch catalyst where potassium exists as an Fe-O-K unit. Although these differences weaken the analogy between homogeneous systems containing end-on interactions and the technical H-B catalyst, the observation that alkali cations enhance N₂ activation in cooperation with reduced metal systems is still notable, especially since a number of systems incorporating various metals, ligands, and cations showcase this phenomenon.

Examples of side-on alkali cation interactions to N₂ bridged between two metal centers are perhaps more relevant to the H-B process since multiple metals on a surface could achieve this geometry. The precise electronic effects of side-on alkali cations have not yet been completely elucidated. Computational studies suggest that N₂, when bridged between two reduced Fe centers, becomes more reduced with the interaction of two K⁺ cations in a side-on fashion. However, altering the identity of the cation in otherwise identical complexes has little, if any, effect on the activation of the N₂ ligand. This may be due to the strong cation- π interactions that lock the side-on coordinated cations in place. It is evident that changing the z/r of the cation significantly changes the size of the cation-arene cavity [116], but not the extent of N₂ activation. Since reduction of N₂ and intercalation of the cations occurs in the

same synthetic step, elucidation of the role of the cation is difficult. A system in which electrons and cations can be added separately would give more insight into whether or not the alkali cation can serve as an electronic promoter for N₂ reduction.

Despite the inability to establish electronic promotion of N₂ *activation* in multimetallic systems, a key piece of evidence from solution studies that points to K⁺ as an electronic promoter in the complete *cleavage* of N₂ comes from the computational studies on the bis-nitride system (**47-K**) [121]. These studies suggest that N₂ cleavage by multiple Fe¹⁺ fragments to form the bis-nitride complex is only thermodynamically favored when a K⁺ cation can stabilize the nitride product. This is particularly applicable to the H-B process, since a) the rate-limiting step of ammonia synthesis is proposed to be chemisorption of N₂ on the surface to form an Fe-nitride species and b) the process of chemisorption is likely a cooperative effort by multiple Fe atoms. Calculations also suggested that the stabilizing effect of the cation is larger in the gas phase than in solution, which more closely resembles the H-B reaction conditions.

Alkali cations clearly play a structural role in homogeneous multiiron systems that reduce N₂. This is most evident in β -diketiminato complexes, in which reducing the same Fe complex in the presence of different alkali cations has a pronounced effect on the reaction and the stability of the products [122]. The structural effects of the alkali cations are dominated by cation- π interactions. In fact, when excess equivalents of alkali cations are present during N₂ reduction, cation- π interactions actually *prevent* N₂ cleavage into bis-nitride products, presumably by favoring geometries in which only two Fe¹⁺ fragments can cooperatively reduce N₂. The dominating role that cation- π interactions display in this study is a significant limitation when considering its relevance to the H-B process, which does not contain any π -systems.

The study by Chiang et al. further supports the observation that structural influences from alkali cations affect the reactivity of reduced Fe complexes [123]. In this system, the K⁺ cations help to assemble two Fe¹⁺ fragments into a geometry that can react with N₂. Again, this structural influence is dependent on cation- π interactions; however, this study clearly shows that two juxtaposed Fe¹⁺-O-K units can more effectively reduce N₂ than one Fe¹⁺-O-K unit. The enhancement of N₂ reduction via cooperation of two reduced Fe atoms supports the idea that multiple Fe atoms could be involved in the rate-limiting dissociation of N₂ during industrial ammonia synthesis.

While studying homogeneous systems that incorporate alkali cation interactions with N₂ has been helpful towards understanding the role of the alkali promoters in the H-B process, more work is needed. Systems that can separate cation addition from reduction of the metal complex would give much more insight into the electronic effects that alkali cations may have. This can be difficult because molecular systems that reduce N₂ often require extremely strong (alkali metal-based) reductants. One solution to this dilemma could be to use an electrode as the electron source and an alkali salt as the separate cation source. Another focus of future homogeneous studies on alkali cation-promoted N₂ reduction should be to minimize cation- π effects that significantly alter the geometry of multimetallic systems.

Systems in which the structure of the complex can remain unchanged as alkali cations are varied would help resolve electronic effects of the alkali cations from structural effects.

7. Do alkali cations play a role in the catalytic reduction of N₂ to NH₃ by homogeneous systems?

Studying homogeneous systems that can catalytically synthesize ammonia from N₂ is an important area of research since these systems, in contrast to most of the systems discussed above, mirror the total conversion of N₂ to NH₃ achieved by the H-B process. However, it is important to note that all molecular catalysts use protons and electrons to hydrogenate N₂; none are yet known that can use H₂ as in industrial ammonia synthesis. Despite this shortcoming, it is still important to determine the effects, if any, that alkali cations may play in facilitating the catalytic reduction of N₂ to NH₃ in homogeneous systems in hopes of learning lessons for future systems.

Relatively few well-defined molecular systems can catalyze the difficult conversion of N₂ into ammonia (Figure 13). Pickett and Talarmin reported the first cyclic conversion of N₂ to NH₃ using *trans*-[W(N₂)₂(Ph₂PCH₂CH₂PPh₂)₂], which can be protonated to form the diazenido complex *trans*-[W(NNH₂)(OTs)(Ph₂PCH₂CH₂PPh₂)₂] (**54**) and subsequently electrolyzed at -2.6 V vs. Fc^{+/0} to regenerate the parent N₂ complex in up to 95% yield and 0.2 equiv NH₃ per equiv W complex [87]. The cycle to produce NH₃ can be repeated at least three times via stepwise protonation and electrolysis events within the same cell, although electrolysis in excess acid to achieve catalytic turnover was not possible. Yandulov and Schrock reported the first homogeneous system that catalytically reduces N₂ to NH₃ in >60% total yield over six turnovers using a Mo complex supported with a tetradentate triamidoamine ligand (**55**) [90, 124, 125]. The Nishibayashi group reported the second catalytic system, which utilizes a [Mo(N₂)₂(PNP)]₂(μ-N₂) complex (**56**), where PNP is a pincer ligand [126]. Related complexes with other, similar pincer-type ligands also demonstrate catalytic activity for N₂ reduction to NH₃, generating up to 63 equiv NH₃ depending on the catalyst [127-129]. The third system capable of catalytic reduction of N₂ to NH₃ has been explored by the Peters group, utilizing Fe tris(phosphino)borane and -alkyl complexes (**15**, **16**), which can produce up to 64 equiv NH₃ per Fe depending on the catalyst [73, 97, 98]. The Peters group also recently reported an Fe-CAAC system (**17**) that can catalytically reduce N₂ to generate up to 3.4 equiv NH₃ [74].

Each of these molecular catalytic systems utilizes moderate-to-strong reductants and strong acids to drive the reduction of N₂ to NH₃; however, only the Fe systems use alkali metal-based reductants. Instead, **54** uses an electrode as the source of electrons, and catalysts related to **55** and **56** employ organometallic reductants such as cobaltocene (CoCp₂), decamethylchromocene (CrCp₂^{*}), and decamethylcobaltocene (CoCp₂^{*}). Although **56** and related bridging N₂-complexes can be synthesized via reduction of the parent (PNP)MoCl₃ complex with 6 equiv Na/Hg or KC₈, the resulting species are neutral, and no further use of alkali metal-based reductants or additives is required [126-129]. This is likely due to relatively mild reduction potentials of the catalytic intermediates in these systems, which do not merit the need of strongly-reducing alkali metal-based reductants.

In contrast, studies of **15** indicate that KC_8 is the most effective reductant when compared to CoCp_2^* , CrCp_2^* , K metal, and Na/Hg (KC_8 is also the preferred reductant for catalysis using **16**) [73, 97, 98]. While the ineffectiveness of CoCp_2^* and CrCp_2^* as reductants can be explained by thermodynamic arguments, considering that catalytic intermediates using **15** and **16** require reduction potentials more cathodic than $-2.2\text{ V vs. Fc}^{+/0}$, the difference in activity between KC_8 , K metal, and Na/Hg is interesting. Since each of these reductants is strong enough to generate the reduced, anionic Fe- N_2 intermediate $[(\text{B}^{\text{iPr}}_3)\text{Fe}(\text{N}_2)]^-$ for the case of **15** and $[(\text{C}^{\text{iPr}}_3)\text{Fe}(\text{N}_2)]^-$ for the case of **16**, the use of KC_8 likely kinetically favors the reductive generation of NH_3 over other reductive side-reactions. Isolated structures from independent syntheses of $[(\text{B}^{\text{iPr}}_3)\text{Fe}(\text{N}_2)]^-$ by reduction of **15** with sodium naphthalenide or $[(\text{C}^{\text{iPr}}_3)\text{Fe}(\text{N}_2)]^-$ by reduction of **16** with KC_8 indicate that each anionic complex demonstrates tight ion-pairing with Na^+ or K^+ in solution, respectively, unless sequestered with crown ethers [72, 73]. Del Castillo et al. report freeze-quench Mössbauer spectroscopy data that identify the $S = \frac{1}{2}$ $[(\text{B}^{\text{iPr}}_3)\text{Fe}(\text{N}_2)]^-$ complex, which is likely tightly ion-paired to K^+ , as present during catalytic conditions [98]. It is possible that the alkali cation may thus play a role in promoting selective reduction of the N_2 ligand over generation of H_2 , perhaps by disfavoring a proposed off-cycle hydride resting state and instead favoring the $[(\text{B}^{\text{iPr}}_3)\text{Fe}(\text{N}_2)]^-$ intermediate. Alternatively, differences in catalytic reactivity may be due to the difference in the nature of KC_8 vs Na/Hg as a reductant, as KC_8 is a solid, high-surface area powder while Na/Hg is a liquid. **15** can also generate 2.2 equiv of NH_3 per Fe via electrolysis at $-2.3\text{ V vs Fc}^{+/0}$ with excess HBAr^{F}_4 and using $\text{NaBAr}^{\text{F}}_4$ was employed as the electrolyte, and the participation of alkali cations during NH_3 generation is possible here as well.

At this early level of development, it is difficult to draw meaningful conclusions about the role of alkali cations during homogeneous catalytic reduction of N_2 to NH_3 . Systematically altering the identity of the alkali metal reductant (varying the alkali metal) in existing homogeneous catalytic systems could give insight into the possible role of alkali cations during this reaction. Similarly, the efficacy of soluble alkali metal-based salts as an additive for promotion of NH_3 production in homogeneous catalytic or electrocatalytic systems should be explored.

8. Conclusion and Future Studies

Elucidating the role of potassium and other alkali promoters in the H-B process is vital for understanding the control factors for ammonia synthesis. Homogeneous studies on transition metal N_2 complexes that exhibit strong interactions with alkali cations demonstrate that alkali cations have the ability to serve as both electronic activators and structural promoters for N_2 reduction. In systems that include cooperative N_2 reduction by multiple metal centers, which are most relevant to the H-B process, cation-dependent structural organization of reduced metal complexes seems to be far more important than electronic effects. However, since cation addition and reduction happens in the same step, electronic effects of the cation have not been fully resolved. It is thus recommended to develop new homogeneous systems in which alkali cations can be added separately from electrons, and in which strong cation- π interactions are minimized.

Acknowledgments

We thank the National Institutes of Health (GM065313) and the Center for Enabling New Technologies through Catalysis (CHE-1205189) for support. We thank Sean McWilliams for feedback on the manuscript.

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Highlights

- Alkali metals promote the Haber-Bosch catalyst, but are incompletely understood.
- Coordination compounds with alkali metals and N₂ can show roles of alkali metals.
- We review complexes in which transition metals, N₂, and alkali metals interact.
- Parallels between homogeneous and heterogeneous compounds motivate new research.

Figure 1.

Examples of Fe planes that expose highly active C_7 sites for ammonia synthesis. Reprinted with permission from [15]. Copyright Elsevier, 1987.

Figure 2.
Double-layer model of promoted Fe catalyst surface. Reprinted with permission from [51].
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Figure 3. Activity of fused Fe catalyst with different alkali metal-oxides as promoters. Reprinted with permission from [34, 36]. Copyright Elsevier, 2009.

Figure 4. Activity vs. z/r of alkali cation-promoted Fe catalyst at 10 MPa and 673 K (empty circles denote use of alkali carbonate solution, filled circles denote use of alkali hydroxide solution) Reprinted with permission from [35]. Copyright Elsevier, 1985.

Figure 5.
Side-on (A) and end-on (B) interactions of alkali cations with metal-N₂ complexes.

Figure 6.
N-N bond distances and stretching frequencies of N₂ in reduced forms [82].

Figure 7. Transition metal N₂ complexes with end-on interaction to an alkali cation.

Figure 8.
Group 3-6 N₂ complexes with side-on interactions to alkali cations.

Figure 9.
Group 8-10 N₂ complexes with side-on interactions to alkali cations.

Figure 10.
Effect of alkali cation on twisting of FeNNFe core, with torsion angle listed [116].

Figure 11.
Cation-assisted N_2 cleavage by transition metal complexes.

53-K: A = K
53-Rb: A = Rb
53-Cs: A = Cs

Figure 12.
Products from reduction of **44** with 4 equiv of different alkali-based reductants [122].

Scheme 1.

Selected products from reduction of $(\text{PDI})\text{FeCl}_2$ with various equivalents of NaH (Ar = 2,6- $\text{iPr}_2\text{C}_6\text{H}_3$). **12** and **13** are shown for comparison.

Scheme 2.

Products from reduction of **46** with 2 equiv of different alkali-based reductants [122].

Scheme 3. Structure-dependent N_2 cleavage by Fe-O-K complex [123].

Table 1

Relationship between atomic radius of electronic promoters in Fe catalysts and number of available active sites for N₂ chemisorption [51].

Promoter	atom radius (pm)	no. of promoter atoms in monolayer		no. of active sites available for N ₂ chemisorption		surface area (m ² g ⁻¹)		no. of active sites available for N ₂ chemisorption (m ² g ⁻¹)	
		Fe(111)	Fe(100)	Fe(111)	Fe(100)	Fe(111)	Fe(100)	Fe(111)	Fe(100)
Li	152	14	12	0	0	20	20	0	0
Na	186	9	9	5	3	12	15	60	45
K	227	6	6	8	6	8.5	10	68	60
Rb	248	5	5	9	7	7	8	63	56
Cs	267	4.3	4.3	9.7	7.7	6	7	59	55

Table 2

Bond Dissociation Free Energies (kJ/mol) of M^+L with organic ligands for selected O-donors. Uncertainties in parentheses [61].

M^+	$L = \text{MeOH}$	$L = \text{Et}_2\text{O}$	$L = \text{THF}$
Li^+	152 (10)	175 (11)	173 (11)
Na^+	92 (6)	117 (3)	-
K^+	92 (2)	93 (6)	-

Table 3

Sequential Bond Dissociation Free Energies (kJ/mol) of $M^+(L)_x$ complexes for π -ligands. Uncertainties in parentheses [61].

M^+	$L = (C_6H_6)$		$L = (MeC_6H_5)$		$L = (N,N-Me_2-C_6H_5)$	
	$x = 1$	$x = 2$	$x = 1$	$x = 2$	$x = 1$	$x = 2$
Li+	161 (14)	104 (7)	183 (16)	117 (3)	210 (8)	128 (4)
Na+	93 (6)	80 (6)	112 (4)	87 (2)	129 (4)	99 (2)
K+	74 (4)	68 (7)	80 (5)	75 (5)	99 (3)	76 (3)
Rb+	69 (4)	63 (8)	71 (4)	68 (4)	92 (2)	72 (3)
Cs+	65 (5)	59 (8)	64 (4)	62 (4)	83 (2)	66 (3)

Table 4

Sequential Bond Dissociation Free Energies (kJ/mol) of $M^+(L)_x$ complexes for crown ethers. Uncertainties in parentheses [61].

M^+	L = 12-crown-4		L = 15-crown-5		L = 18-crown-6	
	x = 1	x = 2	x = 1	x = 2	x = 1	x = 2
Li+	372 (51)	135 (10)	-	-	-	-
Na+	252 (13)	144 (10)	294 (18)	118 (10)	296 (19)	-
K+	189 (12)	135 (10)	205 (15)	138 (10)	234 (13)	-
Rb+	93 (13)	128 (10)	114 (7)	133 (10)	191 (13)	-
Cs+	85 (9)	110 (10)	100 (6)	125 (10)	168 (9)	120 (10)

Table 5Transition metal N₂ complexes with end-on interactions to an alkali cation.

Complex	alkali cation	N-N bond length (Å)	ν_{NN} (cm ⁻¹)	cation-N distance (Å)
(3,5-Me ₂ C ₆ H ₃ [Ad]N) ₃ Mo(μ-N ₂)Na(THF) ₃ (1)	Na	1.152(8)	1783, 1757	2.227(9)
(3,5-Me ₂ C ₆ H ₃ [ⁱ Pr]N) ₃ Mo(μ-N ₂)Na(THF) ₃ (2)	Na	1.186(8)	1783	2.196(7)
[(4- ⁱ BuC ₆ H ₄ N) ₃ N]Mo(μ-N ₂)Na(15-crown-5) (3)	Na	1.161(5)	1815	2.362(5)
([3,5-(2,4,6- ⁱ Pr ₃ C ₆ H ₂) ₂ C ₆ H ₃ N(CH ₂) ₂] ₃ N)W(μ-N ₂)K (4)	K	1.220(8)	1745	2.536(7)
[{1,1'-(ⁱ PEt ₂) ₂ Fe}](Cp*)Mo(μ-N ₂)Na(15-crown-5) (5)	Na	1.168(7)	1791	2.302(5)
(2,6-[2,6- ⁱ Pr ₂ C ₆ H ₃ N=CMe] ₂ C ₅ H ₃ N)Fe(<i>p</i> -tol)(μ-N ₂)Li(Et ₂ O) ₃ (6)	Li	1.138(3)	2068	2.092(5)
(2,6-[2,6- ⁱ Pr ₂ C ₆ H ₃ N=CMe] ₂ C ₅ H ₃ N)Fe(CH ₂ ⁱ Bu)(μ-N ₂)Li(Et ₂ O) ₃ (7)	Li	1.138(3)	1948	2.083(6)
(2-[2,6- ⁱ Pr ₂ C ₆ H ₃ N=CMe]-6-[2,6- ⁱ Pr ₂ C ₆ H ₃ N-C=CH ₂] ₂ C ₅ H ₃ N)Fe(μ-N ₂)Na(Et ₂ O) ₃ (9)	Na	1.154(6)	1965	2.389(6)
(2,6-[2,6- ⁱ Pr ₂ C ₆ H ₃ N=CMe] ₂ C ₅ H ₃ N)Fe(μ-N ₂)Na[Na(THF) ₂] (10)	Na	1.149(6)	1899	2.333(5)
(Si(o-C ₆ H ₄ P(ⁱ Pr) ₂) ₃)Fe(μ-N ₂)Na(THF) ₃ (14)	Na	1.147(4)	1891	2.282(3)
(B(o-C ₆ H ₄ P(ⁱ Pr) ₂) ₃)Fe(μ-N ₂)Na(THF) _x (15)	Na	1.149(2)	1879	-
(C(o-C ₆ H ₄ PCPr) ₂) ₃ Fe(μ-N ₂)K(Et ₂ O) ₃ (16)	K	1.153(2)	1870	2.656(2)
(CAAC) ₂ Fe(μ-N ₂)K(18-crown-6) (17)	K	1.035(4)	1850	2.726(4)
(P(C ₆ H ₅) ₃) ₃ Co(μ-N ₂)Li(Et ₂ O) ₃ (18)	Li	1.17(2)	1900	1.96(4)
(P(C ₆ H ₅) ₃) ₃ Co(μ-N ₂)Li(THF) ₃ (19)	Li	1.19(4)	1890	2.06(9)
(P(C ₆ H ₅) ₃) ₃ Co(μ-N ₂)Na(THF) ₃ (20)	Na	-	1910	-
ⁱ BuN=Nb[μ-(ⁱ Pr)N-P(C ₆ H ₅) ₂] ₃ Co(μ-N ₂)Na(THF) ₅ (21)	Na	1.115(4)	1940	2.489(3)
ⁱ BuN=Ta[μ-(ⁱ Pr)N-P(C ₆ H ₅) ₂] ₃ Co(μ-N ₂)Na(THF) ₅ (22)	Na	1.124(4)	1940	2.484(4)

Table 6

Effect of adding a sequestering agent to a transition metal N₂ complex containing end-on interactions with an alkali cation.

Complex	alkali cation	sequestering agent	ν_{NN} before (cm ⁻¹)	ν_{NN} after (cm ⁻¹)	ν_{NN} (cm ⁻¹)
2	Na ⁺	12-crown-4 (2 equiv)	1783	1728	– 55
3	Na ⁺	15-crown-5	1815	1815	0
4	K ⁺	ⁿ Bu ₄ N ⁺	1745	1801	+ 56
7	Li ⁺	12-crown-4	1948	1996	+ 48
14	Na ⁺	12-crown-4 (2 equiv)	1891	1920	+ 29
15	Na ⁺	12-crown-4 (2 equiv)	1879	1905	+ 26
16	K ⁺	12-crown-4 (2 equiv)	1870	1905	+ 35
18	Li ⁺	12-crown-4	1900	1920	+ 20
23	Na ⁺	15-crown-5	1917 [*]	1956	+ 39
23	Na ⁺	18-crown-6	1917 [*]	1949	+ 32

^{*} The authors also report a second stretch at 1966 cm⁻¹ attributed to different cation-coordination modes

Table 7

Transition metal N₂ complexes with side-on interactions to alkali cations.

Complex	alkali cation	N-N bond length (Å)	ν_{NN} (cm ⁻¹)	cation-N distances (Å)
(2-[2,6- ⁱ Pr ₂ C ₆ H ₃ N=CMe]-6-[2,6- ⁱ Pr ₂ C ₆ H ₃ N-C=CH ₂]C ₅ H ₃ N)Fe(N ₂)[η^2 -Na(THF)] (8)	Na	1.090(5)	1912	2.954(4), 2.287(5)
[(SiMe ₃ N) ₂ Y(THF)] ₂ (μ - η^2 : η^2 -N ₂)(η^2 -K)(THF) (25)	K	1.405(3)	989	2.864(2), 2.885(2)
[(n ⁵ -C ₉ H ₅ -1- ⁱ Pr-3-Me) ₂ ZrCl] ₂ (μ -N ₂)(η^2 -Na) ₂ (26)	Na	1.352(5)	-	2.543(3), 2.619(3)
[(n ⁵ -C ₉ H ₅ -1- ⁱ Pr-3-Me) ₂ Zr] ₂ (μ -N ₂)(η^2 -Na) ₂ (28)	Na	1.316(5)	-	2.461(3), 2.556(3)
[(Me ₂ Si(η^5 -C ₅ Me ₄)(η^5 -C ₅ H ₃ -3- ² Ad))ZrCl] ₂ (μ -N ₂)(η^2 -K) (29)	K	1.223(9)	-	-
[(2,4,6-Me ₃ C ₆ H ₃) ₃ V] ₂ (μ -N ₂)(η^2 -Na) (30)	Na	1.28(2)	-	2.55(3), 2.63(3)
[{ <i>p</i> - ^t Bu-calix[4]-(O) ₄]Nb] ₂ (μ - η^2 : η^2 -N ₂)(μ -Na) ₃ Na (31)	Na	1.403(8)	-	η^1 : 2.33(4) [*] , η^2 : 2.5(1) [*]
[{3,5-(2,4,6- ⁱ Pr ₃ C ₆ H ₂)N(CH ₂) ₂] ₂ (3,5-Me ₂ C ₆ H ₃)N(CH ₂)N]Mo(N ₂)[η^2 -Na(THF) ₂] (32)	Na	1.171(6)	-	2.976(5), 2.353(6)
[{N(2-P(CHMe ₂) ₂ -4-MeC ₆ H ₃) ₂]Co(μ -N ₂ -Na)] ₂ [η^2 -Na(THF) ₂] ₂ (33)	Na	-	1784	-
[(<i>meso</i> -Me ₈ (porph)Ru(C $\equiv$ CH)] ₂ (μ -N ₂)(η^2 -Na) ₄ (34)	Na	1.28(2)	-	2.59(7) [*]
[{(2,6- ⁱ Pr ₂ C ₆ H ₃ NC ^t Bu) ₂ CH}Fe] ₂ (μ -N ₂)(η^2 -Na) ₂ (35)	Na	1.213(4)	1583	2.488(7) [*]
[{(2,6- ⁱ Pr ₂ C ₆ H ₃ NC ^t Bu) ₂ CH}Fe] ₂ (μ -N ₂)(η^2 -K) ₂ (36)	K	1.241(7)	1589	2.70(1) [*]
[{(2,6- ⁱ Pr ₂ C ₆ H ₃ NC ^t Bu) ₂ CH}Co] ₂ (μ -N ₂)(η^2 -Na) ₂ (37)	Na	1.211(3)	1598	2.49(1) [*]
[{(2,6- ⁱ Pr ₂ C ₆ H ₃ NC ^t Bu) ₂ CH}Co] ₂ (μ -N ₂)(η^2 -K) ₂ (38)	K	1.220(2)	1599	2.706(3) [*]
[{(2,6- ⁱ Pr ₂ C ₆ H ₃ NC ^t Bu) ₂ CH}Ni] ₂ (μ -N ₂)(η^2 -K)	K	1.143(8)	1825	2.77(1) [*]
[{(2,6- ⁱ Pr ₂ C ₆ H ₃ NC ^t Bu) ₂ CH}Ni] ₂ (μ -N ₂)(η^2 -K) ₂ (39)	K	1.185(8)	1696	2.716(9) [*]
[{(2,6- ⁱ Pr ₂ C ₆ H ₃ NC ^t Bu) ₂ CH}Ni] ₂ (μ -N ₂)(η^2 -Na)(η^2 -K) (40)	Na/K	1.195(4)	1689	Na: 2.608(4) [*] K: 2.730(4) [*]
[{(2,6- ⁱ Pr ₂ C ₆ H ₃ NC ^t Bu) ₂ CH}Ni] ₂ (μ -N ₂)(η^2 -Na) ₂ (41)	Na	1.192(3)	1685	2.524(4) [*]
[{(2,6- ⁱ Pr ₂ C ₆ H ₃ NCMe) ₂ CH}Fe] ₂ (μ -N ₂)(η^2 -K) ₂ (42-K)	K	1.215(6)	1625	2.78(4) [*]

* Denotes average of distances

Table 8Effect of different alkali cations on N₂ activation by β -diketiminato iron complexes [116].

Complex	N-N bond distance (Å)	ν_{NN} (cm ⁻¹)	cation-N distances (Å)	δ (mm/s)	$ E_Q $ (mm/s)
42-Na	1.254(6)	1612	2.51(7) [*]	0.44	2.52
42-K	1.215(6)	1625	2.78(4) [*]	0.47	2.48
42-Rb	1.257(6)	1621	2.91(5) [*]	0.46	2.34
42-Cs	1.33(2)	1613	3.09(2) [*]	0.48	2.20

^{*} Denotes average of distances