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Controlling Dinitrogen Functionalization at Rhenium through Alkali Metal Ion Pairing

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The rhenium(I) salt $Na[Re(\eta^5\text{-}Cp)(BDI)]$ can be cooled in solution under a dinitrogen atmosphere to selectively access complexes containing rhenium(III) centers bound to direduced, doubly-bonded N_2 (*i.e.* diazenide) fragments. We demonstrate this reactivity is critically dependent on ion pairing involving the Na^+ ion in the starting material, as N_2 binding by $Na[Re(\eta^5\text{-}Cp)(BDI)]$ proved to be much less favorable when the Na^+ was sequestered by benzo-12-crown-4. The analogous chemistry of $Na[Re(\eta^5\text{-}Cp)(BDI)]$ with carbon monoxide (CO) and 2,6-xylylisocyanide (XylNC) was also investigated, which provided structural and spectroscopic bases for determining the impact of ion pairing on π-acid activation in this system.

Introduction

Reduction of dinitrogen, whether by natural or synthetic means, is a prerequisite for biological life. While humans are capable of producing ammonia from dinitrogen via the high pressure, high temperature conditions of the industrially-important Haber-Bosch process, naturally-occurring nitrogenase enzymes can achieve the same transformation under ambient conditions. From both industrial and endogenous perspectives, chemists maintain a deep curiosity about the elementary steps and intermediates that are generated throughout the process of dinitrogen reduction and functionalization.[1-4] Accordingly, synthetic chemists have uncovered a number of molecular systems capable of the reduction of dinitrogen to ammonia or other reduced nitrogen species.[5-26]

One active area in the development of new dinitrogen reducing systems focuses on understanding the effects of secondary interactions of transition metal dinitrogen complexes with Lewis acids. These efforts are in part motivated by the long-known fact that alkali metal ions, typically potassium, enhance the activity of Haber-Bosch catalysts: it is presumed that this enhancement is due to K^+ assisting iron sites with N_2 binding and the first reductive step, which are kinetically limiting in the production of ammonia by these systems.[27-30] Lewis acidic and hydrogen bonding interactions also play a crucial role in the function of metalloenzymes like nitrogenase, which carry out N_2 reduction at remarkably low overpotentials.[31-33] The prevailing model for the interaction of metal dinitrogen complexes with secondary Lewis acids is summarized by the "push-pull" hypothesis: in a metal N_2 complex, a low valent transition metal "pushes" electron density onto the π-acidic N_2 through metal-ligand back bonding, which enhances the ability of a secondary Lewis acid to "pull" additional electron density onto the N_2 ligand via one of its π^* orbitals (which is populated by back bonding from the metal center).[34] The combination of these "pushing" and "pulling" interactions mutually leads to weakening of the N-N bond and potentiates N_2 functionalization.

In line with this model, it has been shown by IR spectroscopy that interactions of alkali metals with transition metal-bound N_2 ligands can lead to modest increases in N_2 activation; however, it has also been shown in other circumstances that these interactions can lead to a decrease in N_2 activation.[30,35-39] These studies have involved both neutral and anionic transition metal dinitrogen complexes, and largely the enhancement of N_2 activation brought about by alkali metal interactions has not been found to systematically vary in line with the overall charge of the transition metal fragment. The binding of a variety of boron Lewis acids to a transition metal dinitrogen complex has also been found to enhance N_2 activation to a degree significantly beyond that achieved by alkali cations.[38]

Here, we report the functionalization of dinitrogen promoted by a rhenium(I) compound, $Na[Re(\eta^5\text{-}Cp)(BDI)]$ (BDI = N,N'-bis(2,6-diisopropylphenyl)-3,5-dimethyl-β-diketiminate),[40] and our subsequent studies that demonstrate this reactivity depends on ion pairing interactions with Na^+ to enhance the reversible binding of N_2 by Re. Crucially, we found that N_2 functionalization employing $Na[Re(\eta^5\text{-}Cp)(BDI)]$ is significantly diminished by sequestering the Na^+ ion with crown ethers. Additionally, the carbon monoxide (CO) and 2,6-xylylisocyanide (XylNC) adducts of $Na[Re(\eta^5\text{-}Cp)(BDI)]$ have also been synthesized, and yielded explicit structural and spectroscopic bases for understanding the binding of N_2 by $Na[Re(\eta^5\text{-}Cp)(BDI)]$. The fact that N_2 is reversibly bound in solution by $Na[Re(\eta^5\text{-}Cp)(BDI)]$ prior to its functionalization allows for the facile experimental control of metal N_2 binding in this system.

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Results and Discussion

Discovery and Control of Dinitrogen Functionalization at an Anionic Rhenium(I) Complex

Having determined in previous studies that Na[Re(η^5-Cp)(BDI)] can behave as a reductant, base, or nucleophile depending on its reaction partner, we were interested to see the behavior of this compound upon silylation.[40,41] The reaction of Na[Re(η^5-Cp)(BDI)] with excess Me$_3$SiCl at room temperature yielded, upon workup, a crystalline mixture of pentane-soluble products. The major product of this reaction **1** (Scheme 1), was identified on the basis of its ^{1}H NMR spectrum, which clearly indicated substitution of the Cp ligand by one trimethylsilyl group, as well as the presence of a metal hydride based on a sharp, one proton singlet at -28.52 ppm. For reference, the closely related rhenium(III) hydride complex Re(H)(η^5-Cp)(BDI) has a characteristic signal in its ^{1}H NMR spectrum at -27.95 ppm that corresponds to the hydride ligand.[40] A weak peak in the IR absorbance spectrum of **1** at 2029 cm^{-1}, as well as a high quality X-ray crystal structure of this compound, both confirm its structural assignment (Supporting Information, Figure S25). We verified that the metal hydride in **1** is likely derived from deprotonation of the Cp ligand following electrophilic substitution by performing the reaction of Na[Re(η^5-Cp)(BDI)] with excess Me$_3$SiCl in THF-d$_8$ in a silylated NMR tube and observing no incorporation of deuterium into the metal hydride site or the formation of any unidentifiable side products (Supporting Information, Figure S24).[42]

The minor product formed in the reaction of Na[Re(η^5-Cp)(BDI)] with excess Me$_3$SiCl at room temperature was isolated in low yield (23 %) as red crystals. The ^{1}H NMR spectrum of this compound indicated the incorporation of one trimethylsilyl moiety; however, in this case the Cp and BDI ligands both appeared intact. We believed the formation of a metal silyl complex to be unlikely, and this hypothesis was confirmed by the X-ray crystal structure, which showed that the silyl group was not bound to the Cp ligand, BDI ligand, or the metal center, but rather to a metal-bound dinitrogen molecule taken up from the atmosphere used in performing the reaction (Figure 1). Until the isolation of this product, **2** (Scheme 1), we had seen no indication that Na[Re(η^5-Cp)(BDI)] binds N$_2$; however, this product showed that trapping reversibly-bound N$_2$ can occur upon the addition of a large, redox-inactive, cationic electrophile to Na[Re(η^5-Cp)(BDI)]. The bond metrics of the N$_2$ unit in **2** led us to assign this compound as a rhenium(III) silyldiazenide complex: the N-N distance of 1.251(12) Å is in the range of a N=N double bond, and the Si-N-N angle of 127.5(7)$^\circ$ is indicative of an sp^2 geometry (and thus a lone pair) at the N atom bound to the trimethylsilyl group. Additionally, an IR absorption band for **2** at 1617 cm^{-1} further supports the assignment of the N$_2$ unit as being reduced to a diazenide fragment.[35,43-47] Following our initial characterization of **2**, we pursued reaction conditions that led to selective generation of this silylazenide complex rather than the metal hydride product **1**. Accordingly, we found that the yield of **2** could be substantially increased by carrying out the reaction at -78 °C rather than at room temperature (Scheme 1). While it has been

shown that transient, coordinatively unsaturated rhenium(II) species can cleave N$_2$ in a bimetallic fashion to form rhenium(V) nitrides (which can then be used to form organic nitriles), the formation of **2** from Na[Re(η^5-Cp)(BDI)] represents the first example of end-on N$_2$ silylation promoted by rhenium.[48-52]
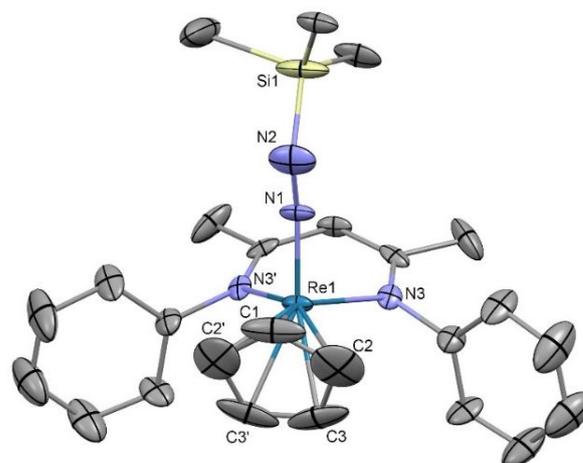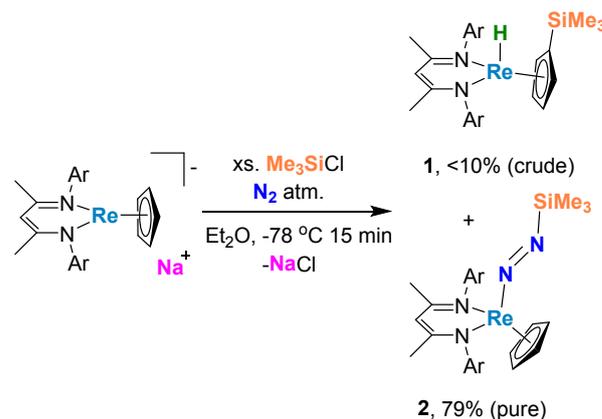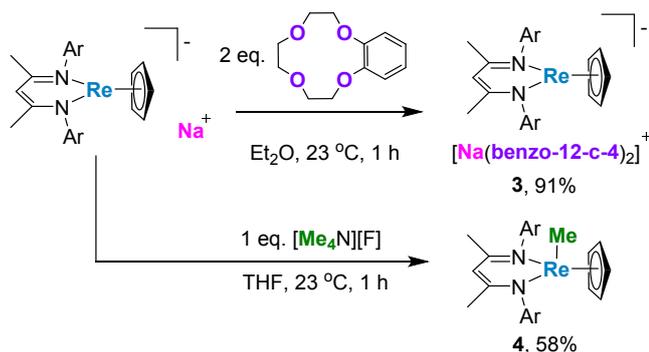

Fig 1. X-ray crystal structure of **2** with 50% probability ellipsoids. BDI isopropyl groups, hydrogen atoms, and disordered fragments (BDI aryl and Me$_3$Si) have been omitted for clarity. Selected bond distances (Å) and angles (°): Re1-N1 = 1.782(7), Re1-N3 = 2.118(5), Re1-Cp(centroid) = 1.916(4), N1-N2 = 1.251(12), N2-Si1 = 1.744(9), Re1-N1-N2 = 159.6(7), N1-N2-Si1 = 127.5(7).

Scheme 1. Syntheses of complexes **1** and **2** under optimal N$_2$ functionalization conditions.

Beyond simply establishing a route to form **2** selectively, we were also interested in testing the impact of sequestering the Na$^+$ in the reaction mixture, and aimed to make salts containing the [Re(η^5-Cp)(BDI)]$^-$ anion with non-coordinating cations. We found that addition of two equivalents of benzo-12-crown-4 (b-12-c-4) to a diethyl ether solution of Na[Re(η^5-Cp)(BDI)] led to the precipitation of dark crystals of the desired product **3** (Scheme 2). X-ray crystallography confirmed that the Na$^+$ ion is entirely sequestered by both equivalents of crown ether (Figure 2). There is a very slight contraction of the binding parameters to the Re center in **3** as compared to the analogous parameters in the solid state structure of Na[Re(η^5-Cp)(BDI)], which formed 1-D chains with Na$^+$ making contact with both the Cp and BDI ligands. Compared to those of the reported neutral rhenium(II)

complex, Re(η5-Cp)(BDI), the bonds to the Re center in **3** are also slightly shorter.[40,53]

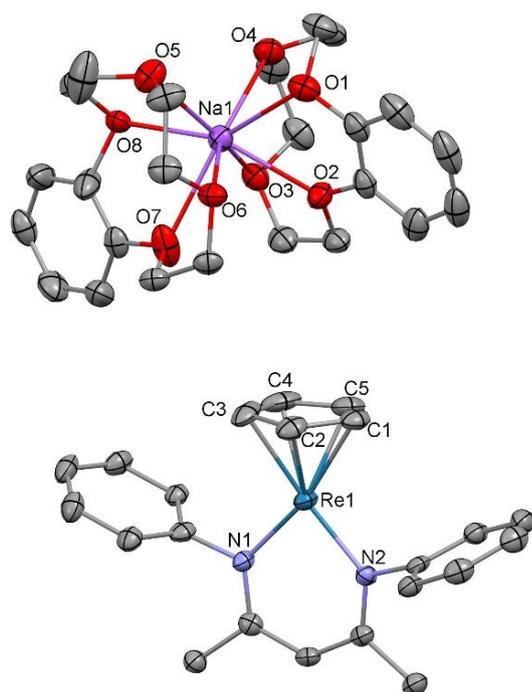**Scheme 2.** Syntheses of compounds **3** and **4**.

Fig 2. X-ray crystal structure of **3** with 50% probability ellipsoids. BDI isopropyl groups, hydrogen atoms, solvent, and disordered fragments (crown ether) have been omitted for clarity. Selected bond distances (Å) and angles (°): Re1-N1 = 2.032(2), Re1-N2 = 2.022(2), Re1-Cp(centroid) = 1.838(2), Na1-O(average) = 2.447.

We also attempted to make salts similar to **3** that contained quaternary ammonium or phosphonium ions in place of Na⁺. However, we found that reactions between Na[Re(η5-Cp)(BDI)] and a variety of such cations led to neutral products rather than salts. Specifically, combination of Na[Re(η5-Cp)(BDI)] with tetraphenylphosphonium iodide led to a mixture of Re(η5-Cp)(BDI) and Re(H)(η5-Cp)(BDI). Workup of the mixture formed on reaction of Na[Re(η5-Cp)(BDI)] with tetraethylammonium chloride led to the isolation of a mixture of Re(H)(η5-Cp)(BDI) and a species that, based on its ¹H NMR spectrum, we believe to be the rhenium(III) ethyl complex Re(Et)(η5-Cp)(BDI). This mixture of compounds indicates that Na[Re(η5-Cp)(BDI)] can react with tetraalkylammonium cations by either β-deprotonation (*i.e.* Hoffman elimination) of an alkyl group, or

by nucleophilic attack at the α-position to yield metal alkyl species. In order to resolve this selectivity issue and obtain a single product, we combined Na[Re(η5-Cp)(BDI)] with tetramethylammonium fluoride, [NMe₄][F], to give solely the rhenium(III) methyl complex **4** (Scheme 2). This result demonstrates that Re(H)(η5-Cp)(BDI) can only form from reactions with tetraalkylammonium cations that have β-positions, and that this reactivity is very likely the result of the basic and nucleophilic behavior of Na[Re(η5-Cp)(BDI)] rather than some radical or redox mechanism. The X-ray crystal structure of **4** shows a geometry at the metal center that is very similar to that seen in Re(H)(η5-Cp)(BDI), with the methyl ligand projecting out at an angle approximately orthogonal to the Cp_centroid-Re-BDI plane (Supporting Information, Figure S26). A similar geometry at Re was also observed in the dative metal-metal bonding of the [Re(η5-Cp)(BDI)]⁻ anion to zinc(I).[40]

Addition of two equivalents of benzo-12-crown-4 to a THF solution of Na[Re(η5-Cp)(BDI)] (to generate the crowned salt **3**) at -78 °C, followed by the addition of excess Me₃SiCl led to the isolation of **1** and **2** as a crystalline mixture, representing 47% and 23% crude yields, respectively. Upon carrying out the silylation of Na[Re(η5-Cp)(BDI)] in the presence of benzo-12-crown-4 at 23 °C, a further decrease in the crude yield of **2** (12%) was observed, while the crude yield of **1** was unaffected (47%; Scheme 3). These results indicate that the effects of lowering the reaction temperature on dinitrogen binding by [Re(η5-Cp)(BDI)]⁻ are essentially negated when the Na⁺ ion is sequestered, indicating that ion pairing plays a crucial role in facilitating the selective formation of **2**. In an attempt to observe these effects spectroscopically, we collected an IR absorbance spectrum for an Et₂O solution of Na[Re(η5-Cp)(BDI)] with the hope of observing a feature attributable to N₂ binding; however, a large, broad peak at ca. 1965 cm⁻¹, attributable to a C-O stretching overtone of the Et₂O solvent, overlapped the region where an N₂ ligand stretch would likely be observed. Similar results were obtained when the IR absorbance spectrum of **3** was collected in THF solvent, precluding our attempts to observe any changes attributable to diminished N₂ binding by this compound. Considering that Na[Re(η5-Cp)(BDI)] and **3** are only soluble in coordinating solvents (*e.g.* Et₂O, THF), combined with the accumulated indications that Na[Re(η5-Cp)(BDI)] only substantially binds N₂ under conditions that allow for greater ion pairing, we concluded that an IR spectroscopic observation of N₂ bound to Na[Re(η5-Cp)(BDI)] was not likely to be possible using routine methods.
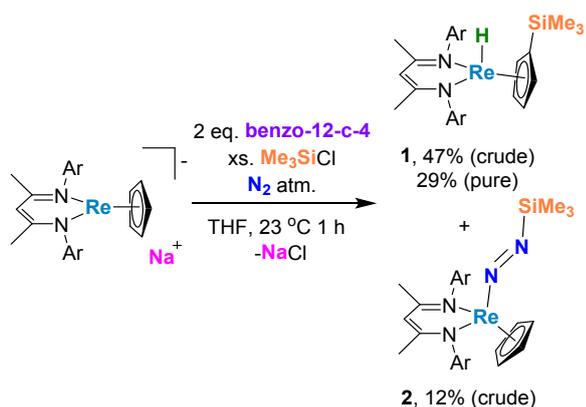
Scheme 3. Syntheses of complexes **1** and **2** in the presence of benzo-12-crown-4.

Scheme 4. Synthesis of the heterotrimetallic complex **5**.

The importance of ion pairing to the formation of **2** from Na[Re(η⁵-Cp)(BDI)] and Me₃SiCl is an intriguing feature of this system, as almost all other systems able to functionalize N₂ first form stable N₂ complexes *in the absence* of a second metal cation or a directly interacting Lewis acid prior to the addition of the functionalizing reagent (i.e. a proton or silyl source). As mentioned, it has been established that the coordination of alkali metals to stable metal dinitrogen complexes can lead to direct interactions between the bound N₂ and the alkali metal, but these interactions have not been shown to promote N₂ binding by metal complexes that otherwise could not display this behavior. However, in the case of Na[Re(η⁵-Cp)(BDI)], it appears N₂ binding critically depends on a pre-equilibrium in which ion pairing to an alkali metal has a substantial impact.

We next sought another cationic fragment able to assist Na[Re(η⁵-Cp)(BDI)] with the trapping and reduction of N₂, to complement the silylation route to form **2** and provide some generality to this behavior. We found that combining 0.5 equivalent of zirconocene dichloride (Cp₂ZrCl₂) with Na[Re(η⁵-Cp)(BDI)] at -78 °C led to the formation of a dark purple product, which ¹H NMR spectroscopy indicated to contain one zirconocene fragment for every two BDI ligands. Further characterization by X-ray diffraction studies confirmed the product to be the heterotrimetallic complex **5** (Scheme 4, Figure 3), in which a single zirconocene fragment bridges two rhenium centers through N₂ moieties. The N-N distance for the bound N₂ units in **5** (1.208(5) Å) is somewhat shorter than the corresponding value in **2** (1.251(12) Å), suggesting a diminished degree of dinitrogen reduction. The IR absorbance band for the N₂ in **5** was measured at 1667 cm⁻¹, which is ca. 50 wavenumbers higher than the N-N stretching frequency measured for **2**. Early transition metals and metal-based Lewis acids have previously been used as capping or bridging ligands with metal dinitrogen complexes, as observed in complex **5**.⁵⁴⁻⁵⁸
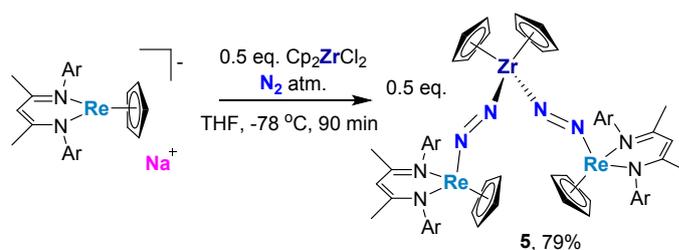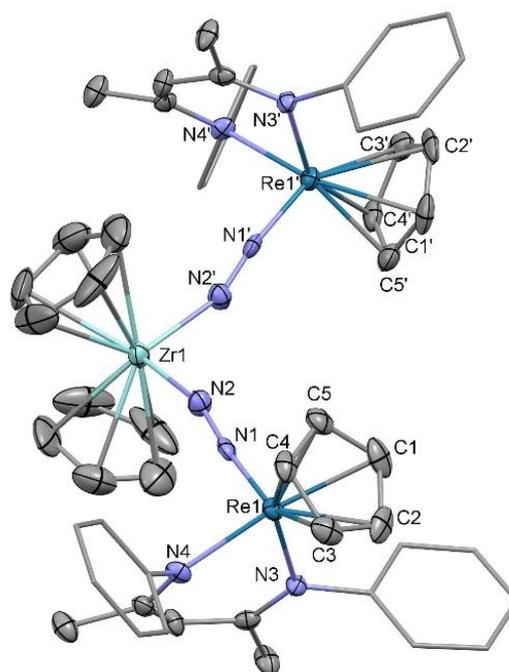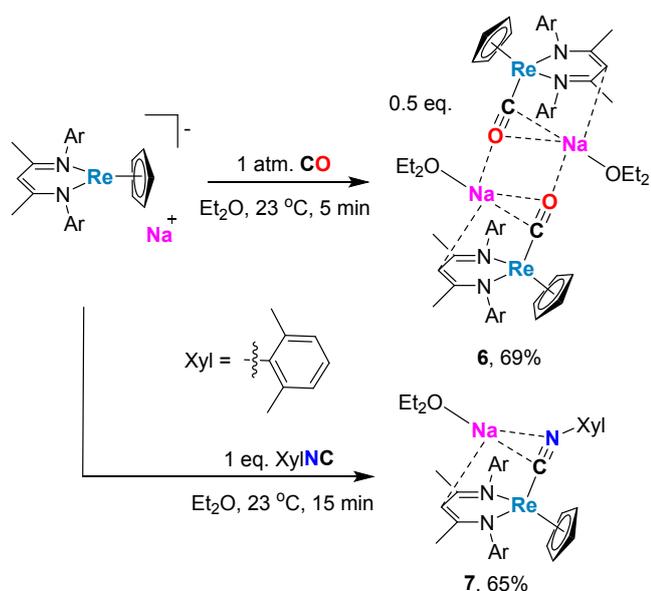

Fig 3. X-ray crystal structure of **5** with 50% probability ellipsoids. BDI isopropyl groups, hydrogen atoms, and solvent have been omitted for clarity. Selected bond distances (Å) and angles (°): Re1-N1 = 1.805(4), Re1-N3 = 2.154(4), Re1-N4 = 2.140(4), Re1-Cp(centroid) = 1.911(3), N1-N2 = 1.208(5), N2-Zr1 = 2.082(4), Re1-N1-N2 = 172.7(4), N1-N2-Zr1 = 160.0(4).

Determining the Effects of Ion Pairing in Carbon Monoxide and 2,6-Xylylisocyanide Adducts of Na[Re(η⁵-Cp)(BDI)]

After establishing that the binding and functionalization of N₂ promoted by Na[Re(η⁵-Cp)(BDI)] is dependent on temperature and, even more so, ion pairing, we sought structural analogs for the putative N₂ complexes that form reversibly in solution. As such, we began to study the behavior of Na[Re(η⁵-Cp)(BDI)] with isoelectronic and/or isolobal analogs of N₂ that are stronger π-acceptors, namely carbon monoxide (CO) and 2,6-xylylisocyanide (XylNC). We found that the addition of ca. one atmosphere of CO to a solution of Na[Re(η⁵-Cp)(BDI)] in Et₂O led to the precipitation of dark green crystals (Scheme 5). Meanwhile the addition of one equivalent of XylNC to Na[Re(η⁵-Cp)(BDI)] in Et₂O gave a dark orange solution, which upon concentration and storage at -40 °C yielded similarly dark crystals. Structural characterization of these products by X-ray diffraction studies confirmed the formation of the intended adducts, the monocarbonyl **6** and the XylNC complex **7** (Figure 4).

Scheme 5. Syntheses of the CO and XylNC complexes **6** and **7**.

2.149(6) and 2.139(6), Re1-Cp(centroid) = 1.928(3) and 1.925(4), C1-N1 = 1.294(9) and 1.275(9) , N1-Na1 = 2.336(7) and 2.291(7), C1-Na1 = 2.612(8) and 2.634(8), C17-Na1 = 2.541(8) and 2.558(9), O1-Na1 = 2.270(6) and 2.141(15), Re1-C1-N1 = 176.8(6) and 174.5(7), C1-N1-C7 = 131.5(6) and 129.1(7), N1-Na1-C17 =117.5(3) and 113.7(3).

The Na$^+$ ions in the solid-state structures of **6** and **7** lie in analogous coordination environments, with the qualification that **6** forms a dimer through contact of the Na$^+$ ion to the O atom of an adjoining unit of **6**. Intriguingly, each Na$^+$ ion makes close contact to both atoms of the CO molecule or isocyanide CN unit, as well as to the backbone C-H position of the BDI ligand, which is indicative of charge buildup on that site as a consequence of π-acid binding to the metal center. Considering that **6** and **7** provide close analogs for the putative N$_2$ complex formed reversibly when Na[Re(η^5-Cp)(BDI)] is cooled in solution, the observation of this direct, side-on contact between the Na$^+$ ion and the π-acidic ligands in these complexes provides an explicit structural basis for understanding how the alkali cation may play a key role in promoting N$_2$ binding by this system.

Beyond structural determinations of **6** and **7**, we also attempted to sequester the Na$^+$ ions in these compounds using benzo-12-crown-4; however, we found that addition of crown ether to the CO adduct **6** did not lead to complete sequestration of the Na$^+$ ions. Instead, addition of benzo-12-crown-4 to **6** in THF gave the salt **8** (Scheme 6), which contains a complex monoanion composed of two equivalents of rhenium(I) carbonyl adduct coordinated to a single Na$^+$, which displays contacts to the CO and BDI ligands akin to those observed in **6** (Figure 5). This result implies that the localized charge density on the CO ligands (a direct consequence of back bonding from Re) and the BDI backbone is high enough to lead to substantial electrostatic interactions with the Na$^+$ ion. In contrast, addition of benzo-12-crown-4 to the XylNC adduct **7** led to complete sequestration of the Na$^+$ ions, forming **9** (Scheme 6): presumably, the steric bulk of the 2,6-xylyl group prevented the formation of a complex monoanion akin to that found in **8**.
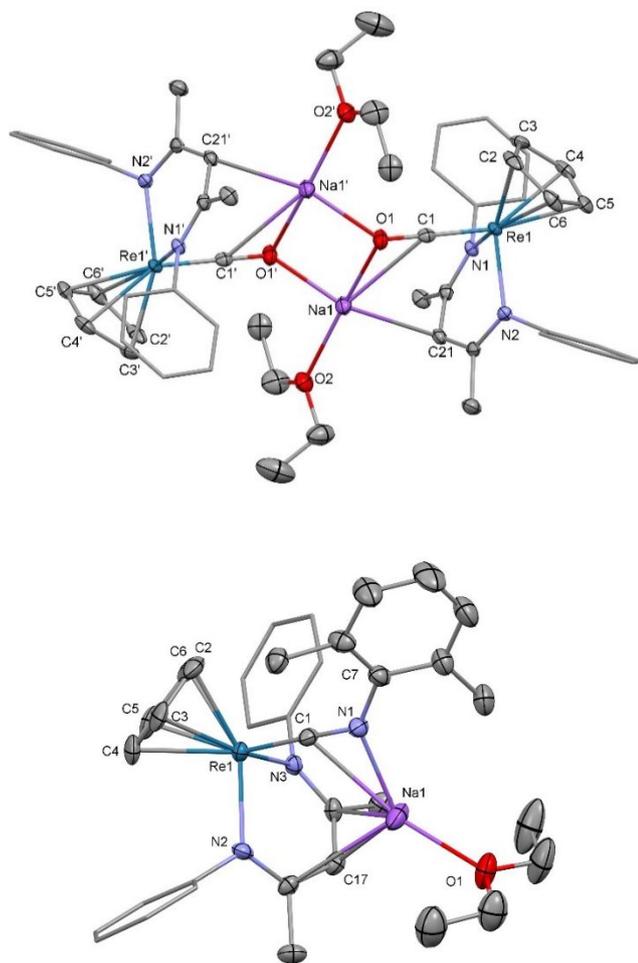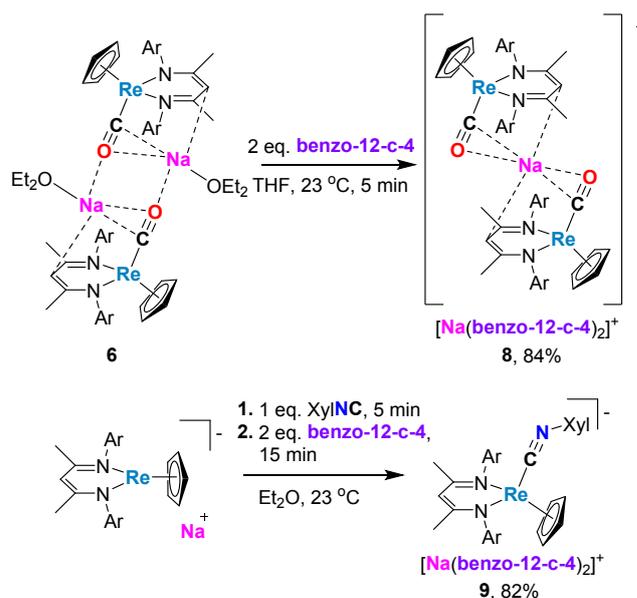

Fig 4. X-ray crystal structures of **6** (top) and **7** (bottom) with 50% probability ellipsoids. BDI isopropyl groups and hydrogen atoms have been omitted for clarity. Compound **7** also crystallizes with an additional formula unit in the ASU. Selected bond distances (Å) and angles (°) for **6**: Re1-C1 = 1.815(2), Re1-N1 = 2.166(2), Re1-N2 = 2.149(2), Re1-Cp(centroid) = 1.925(1), C1-O1 = 1.224(3), O1-Na1 = 2.254(2), C1-Na1 = 2.857(2), C21-Na1 = 2.755(2), O2-Na1 = 2.325(2), Re1-C1-O1 = 178.83(18), O1-Na1-C21 = 95.89(7). Selected bond distances (Å) and angles (°) for **7**: Re1-C1 = 1.821(7) and 1.832(7), Re1-N2 = 2.169(6) and 2.157(6), Re1-N3 =

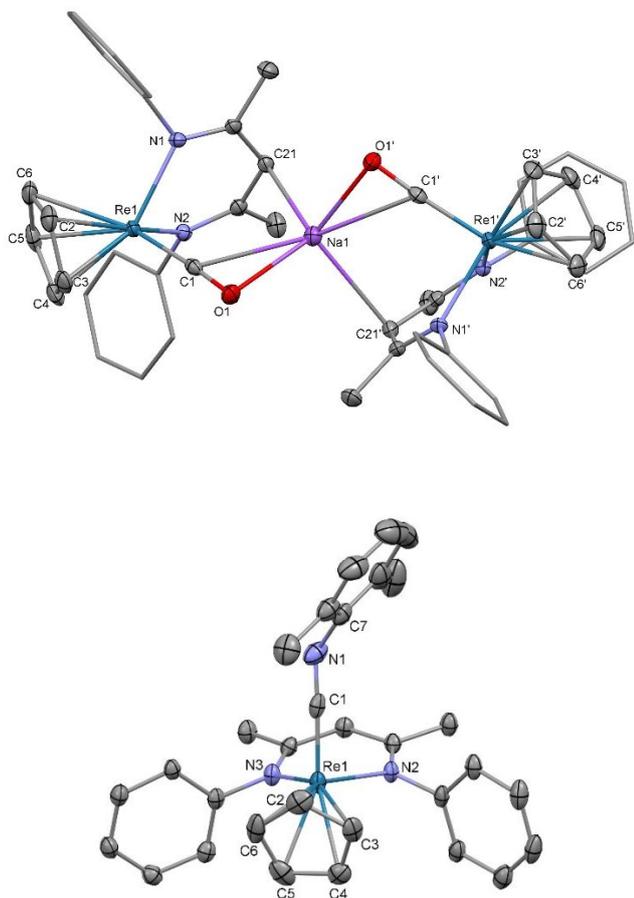**Scheme 6.** Syntheses of the crowned salts **8** and **9**.

Fig 5. X-ray crystal structures of the anionic portions of **8** (top) and **9** (bottom) with 50% probability ellipsoids. BDI isopropyl groups, [Na(benzo-12-crown-4)₂]⁺ cations, hydrogen atoms, and solvent have been omitted, and the aryl rings of compound **8** are displayed as capped sticks for clarity. Selected bond distances (Å) and angles (°) for **8**: Re1-C1 = 1.827(2), Re1-N1 = 2.160(2), Re1-N2 = 2.162(2), Re1-Cp(centroid) = 1.910(1), C1-O1 = 1.217(3), O1-Na1 = 2.349(2), C1-Na1 = 2.655(2), C21-Na1 = 2.717(2), Re1-C1-O1 = 174.77(17), O1-Na1-C21 = 107.73(6). Selected bond distances (Å) and angles (°) for **9**: Re1-C1 = 1.839(2), Re1-N2 = 2.148(2), Re1-N3 = 2.153(2), Re1-Cp(centroid) = 1.926(1), C1-N1 = 1.255(3), Re1-C1-N1 = 176.54(18), C1-N1-C7 =135.0(2).

Cumulatively, the structural and spectroscopic parameters of **6**, **7**, **8**, and **9** all indicate a large degree of activation of the CO and XylNC ligands. The CO bond lengths in the X-ray crystal structures of **6** and **8** are 1.224(3) Å and 1.217(3) Å, respectively (elongated from 1.128 Å in free CO), while the XylNC C-N distances in the X-ray crystal structures of **7** and **9** are 1.294(9) Å and 1.255(3) Å, respectively (elongated from 1.160(3) Å in crystalline XylNC).[59] The carbonyl complexes **6** and **8**, which both feature direct contacts between the CO unit and a Na⁺ ion, have similar CO stretching frequencies of 1639 cm⁻¹ and 1667 cm⁻¹ (vs. 2143 cm⁻¹ in free CO), which quite low given the range of IR stretches observed in anionic metal carbonylate species.[60] The difference in XylNC stretching frequencies between **7** and **9** however is much starker: a broad IR absorbance peak at 1560 cm⁻¹ was measured for **7**, while a similarly shaped feature was measured at 1695 cm⁻¹ for **9** (compared to 2116 cm⁻¹ in solid XylNC).[61] This difference of ca. 135 wavenumbers can be wholly attributed to the sequestration of the Na⁺ ion. As seen in the IR absorbance data, there is a substantial enhancement of π-acid activation associated with ion pairing to these adducts, which verifies our observation that sequestering the Na⁺ ion of

Na[Re(η⁵-Cp)(BDI)] in solution drastically hinders its ability to bind N₂. In all, the analogy provided by the IR absorbance measurements of **7** versus those of **9** shows a direct relationship between the tethered, side-on ion pairing interactions observed by X-ray crystallography and a substantial degree of π-acid activation.

Similar alkali sequestration experiments have been reported with alkali metal salts of anionic transition metal-N₂ complexes though a high degree of variability has been observed: while a 56 cm⁻¹ increase in N₂ stretching frequency was measured following the sequestration of K⁺ from the tungsten complex ([3,5-(2,4,6-ⁱPr₃C₆H₂)₂C₆H₃N(CH₂)₂]₃N)W(η¹:η¹-N₂)K, it has also been found that the removal of alkali-N₂ interactions in the molybdenum complex (3,5-Me₂C₆H₃[ⁱPr]N)₃Mo(η¹:η¹-N₂)Na(THF)₃ led to a 55 cm⁻¹ *lowering* of the N₂ frequency.[30,35,39] Notably, these sequestration experiments all involved the removal of end-on alkali-N₂ interactions, rather than side-on interactions. Similar sequestration experiments to measure the impact of side-on alkali-N₂ interactions have not been reported, likely due to the fact that the N₂ ligands in question tend to be bridged between two transition metals in a symmetric environment, rendering the N₂ stretching mode IR-inactive. Thus, while the present work is limited to sequestration studies with CO and XylNC derivatives, the magnitude of impact on the IR spectroscopy data suggests that the tethered, side-on coordination of Na⁺ to the π-acidic ligands in **6** and **7** may have a greater effect on enhancing π-acid activation than other previously studied coordination modes. Consequently, the design of complexes that make use of this specific mode of ion pairing may lead to greater efficiency in homogeneous N₂ reduction catalysts.

Addition of alkali cations to solutions containing neutral metal dinitrogen complexes has also led to measurable decreases in N₂ stretching frequencies. For example, a tris(phosphine) pincer ligand containing a crown ether moiety was employed to bring alkali cations into the secondary coordination sphere of a bound molybdenum dinitrogen fragment: it was found that small decreases in N₂ stretching frequency, ranging from ca. 20-40 cm⁻¹, could be observed in solution IR measurements of these alkali-bound species.[37] In another case, the solution-state N₂ stretching frequency of a neutral iron(0) N₂ complex was monitored upon the addition of alkali cations or boron Lewis acids. In this study it was found that the enhancement of N₂ activation could be directly correlated with the strength of the Lewis acid. While the addition of Li⁺ led to a 69 cm⁻¹ decrease in N₂ stretching frequency, the addition of the boron Lewis acid B(OC₆F₅)₃ led to a 172 cm⁻¹ decrease.[38] Despite the strength of these interactions between neutral metal N₂ complexes and added Lewis acids in solution, many of these species could not be isolated. In summary, based on the accumulation of data the overall charge state of the transition metal fragment, whether neutral or anionic, does not appear to have an overall impact on the changes in N₂ stretching frequency in these alkali sequestration/addition experiments.

We concluded our reactivity studies by attempting to make analogs of **2** and **5** containing CO or XylNC in place of the trapped N₂ unit. Combining **6** with excess Me₃SiCl or 0.5

equivalent Cp_2ZrCl_2 at room temperature afforded **10** or **11**, respectively (Scheme 7). Conversely, compound **7** only yielded intractable mixtures of products when combined with Me_3SiCl or Cp_2ZrCl_2. It is likely that the additional steric bulk of the 2,6-xylyl group hinders the binding of the relatively bulky trimethylsilyl or zirconocene fragments to the N atoms of the bound isocyanide. Regardless, the syntheses of **10** and **11** demonstrate that **6** behaves analogously to the N_2 adduct of $Na[Re(\eta^5-Cp)(BDI)]$ that we posit to form reversibly in solution.
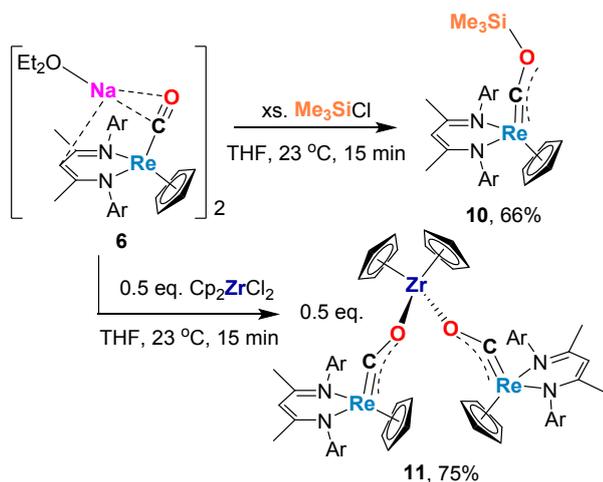
Scheme 7. Synthesis of the functionalized CO complexes **10** and **11**.

Complexes **10** and **11**, while structurally similar to their N_2-containing analogs, must necessarily have a different electronic structure owing to the inability of the CO unit to maintain a formal double bond upon functionalization of the oxygen atom. The solid state C–O IR stretching frequencies for the CO units in **10** and **11**, measured at 1408 cm^{-1} and 1410 cm^{-1}, respectively, each indicate an intermediate bond order between 1 and 2. Meanwhile, the Re-CO distances in **10** and **11** (1.776(4) Å and 1.785(3) Å, respectively) are sufficiently short as to imply the presence of metal-ligand multiple bonding beyond the degree expected in a metal carbonyl complex, and are on the order observed in rhenium alkylidyne complexes (Supporting Information, Figure S27 and Figure S28).[62,63] A resonance form that has been used to depict similarly functionalized metal CO complexes is that of a siloxycarbyne, with a well-defined C–O single bond and a metal-carbon triple bond, however based on the combined spectroscopic and structural data, we suggest that **10** and **11** are better depicted as resonance-stabilized carbyne complexes.[64-69]

Conclusions

We have discovered the ability of $Na[Re(\eta^5-Cp)(BDI)]$ to act as a platform for N_2 functionalization, and have shown that this reactivity relies on a reversible N_2 binding process in which ion pairing interactions are crucial to enhancing the activation of metal-bound N_2. Key to this result is the demonstrated ability to effectively switch off N_2 binding by $Na[Re(\eta^5-Cp)(BDI)]$ through the sequestration of the Na^+ cation with crown ethers.

Structural characterization of CO and 2,6-xylylisocyanide (XylNC) adducts of $Na[Re(\eta^5-Cp)(BDI)]$ show the presence of a tethered, side-on interaction of Na^+ with the π-acidic ligands. Sequestration of the Na^+ from these CO and XylNC complexes allowed for the impacts of ion pairing on π-acceptor activation to be directly measured by IR spectroscopy.

Conflicts of interest

There are no conflicts to declare.

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