Abstract

Project Title: "Understanding Nitrogen Fixation"

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Overall Research Goals: The purpose of our program is to explore fundamental chemistry relevant to the discovery of energy efficient methods for the conversion of atmospheric nitrogen (N$_2$) into more value-added nitrogen-containing organic molecules. Such transformations are key for domestic energy security and the reduction of fossil fuel dependencies. With DOE support, we have synthesized families of zirconium and hafnium dinitrogen complexes with elongated and activated N-N bonds that exhibit rich N$_2$ functionalization chemistry. Having elucidated new methods for N-H bond formation from dihydrogen, C-H bonds and Brønsted acids, we have since turned our attention to N-C bond construction. These reactions are particularly important for the synthesis of amines, heterocycles and hydrazines with a range of applications in the fine and commodity chemicals industries and as fuels. One recent highlight was the discovery of a new N$_2$ cleavage reaction upon addition of carbon monoxide which resulted in the synthesis of an important fertilizer, oxamide, from the diatomics with the two strongest bonds in chemistry.

Significant Results and Achievements: Nitrogen-carbon bonds form the backbone of many important organic molecules, especially those used in the fertilizer and pharmaceutical industries. During the past year, we have continued our work in the synthesis of hydrazines of various substitution patterns, many of which are important precursors for heterocycles. In most instances, the direct functionalization of N$_2$ offers a more efficient synthetic route than traditional organic methods. In addition, we have also discovered a unique CO-induced N$_2$ bond cleavage reaction that simultaneously cleaves the N-N bond of the metal dinitrogen compound and assembles new C-C bond and two new N-C bonds. Treatment of the CO-functionalized core with weak Brønsted acids liberated oxamide, H$_2$NC(O)C(O)NH$_2$, an important slow release fertilizer that is of interest to replace urea in many applications.

Statement of Impact: The synthesis of ammonia, NH$_3$, from its elements, H$_2$ and N$_2$, via the venerable Haber-Bosch process is one of the most significant technological achievements of the past century. Our research program seeks to discover new transition metal reagents and catalysts to disrupt the strong N≡N bond in N$_2$ and create new, fundamental chemical linkages for the construction of molecules with application as fuels, fertilizers and fine chemicals. With DOE support, our group has discovered a mild method for ammonia synthesis in solution as well as new methods for the construction of nitrogen-carbon bonds directly from N$_2$. Ideally these achievements will evolve into more efficient nitrogen fixation schemes that circumvent the high energy demands of industrial ammonia synthesis.
Overview of Results from DE-FG02-05ER659. Industrially, atmospheric nitrogen enters the synthetic cycle by the well-established Haber-Bosch process whereby \( \text{N}_2 \) is hydrogenated to ammonia at high temperature and pressure. The commercialization of this reaction represents one of the greatest technological achievements of the 20\(^{th} \) century as Haber-Bosch ammonia is responsible for supporting approximately 50% of the world’s population and serves as the source of half of the nitrogen in the human body.\(^1\) The extreme reaction conditions required for an economical process have significant energy consequences, consuming 1% of the world’s energy supply mostly in the form of pollution-intensive coal.\(^2\) Moreover, industrial \( \text{H}_2 \) synthesis via the water gas shift reaction and the steam reforming of methane is fossil fuel intensive and produces \( \text{CO}_2 \) as a byproduct. New synthetic methods that promote this thermodynamically favored transformation (\( \Delta \text{G}^\circ = -4.1 \text{ kcal/mol} \)) under milder conditions or completely obviate it are therefore desirable. Most nitrogen-containing organic molecules are derived from ammonia (and hence rely on the Haber-Bosch and \( \text{H}_2 \) synthesis processes) and direct synthesis from atmospheric nitrogen could, in principle, be more energy-efficient. This is particularly attractive given the interest in direct hydrazine fuel cells.\(^4\)

\[
\text{N}_2 + 3 \text{H}_2 \overset{[\text{M}]}{\longrightarrow} \text{2NH}_3 \quad \text{mild conditions}
\]

\[
[\text{M}] = \text{metal catalyst or reagent}
\]

\[
\text{N} = \text{CO}_2 \text{Et} \quad \text{or} \quad \text{H}_2 \text{N-NNH}_2
\]

\[
(\text{organics})
\]

Recent Chirik Group Contributions:

1. Discovery of CO-induced \( \text{N}_2 \) cleavage under mild conditions in solution to simultaneously form 1 C-C and 2 N-C bonds.
2. Nitrogen-carbon bond formation by addition of electrophiles to a hafnium dinitrogen compound and rare observation of conversion to a hydrazonato ligand.
3. Demonstration of \( \text{N}_2 \) hydrogenation by a strongly activated “end-on” rather than “side-on” dinitrogen complex broadening the scope and mechanistic understanding of the transformation.
4. This work has produced a total of 15 publications: 2 in Nature Chemistry, 5 in the Journal of the American Chemical Society, and 8 in Organometallics.

A. CO-Induced \( \text{N}_2 \) Bond Cleavage. Synthetic transformations that couple the cleavage of the strong, non-polar bond of molecular nitrogen, \( \text{N}_2 \), with nitrogen-carbon bond formation are desirable, given the numerous applications of nitrogen-containing organic molecules as fertilizers, pharmaceuticals, dyes, semiconductors and fibers.\(^5\) The atmospheric abundance,
global availability and non-toxicity of \( \text{N}_2 \) make dinitrogen an attractive feedstock for the preparation of these important compounds. However, the strong \( \text{N}≡\text{N} \) triple bond of 225 kcal/mol and the lack of a dipole moment present significant kinetic and thermodynamic obstacles to reactivity. The direct conversion of \( \text{N}_2 \) to nitrogen-containing organic molecules offers the potential for substantial energy and fossil fuel savings as the high temperature and pressure (as well as hydrogen requirements) of the Haber-Bosch process are circumvented.

Carbon monoxide, due to its availability and established use as a carbon feedstock for organic molecules,\(^6\) is an excellent candidate as the \( \text{C} \)-source for nitrogen-carbon bond formation. Selective formation of carbon-carbon bonds from \( \text{CO} \) as a component of synthesis gas is a long-standing challenge in catalysis as an alternative to the non-selective Fischer-Tropsch process.\(^7\)\(^8\) Examples of selective CO homologation are known with organometallic complexes of samarium\(^9\) and most recently, uranium.\(^10\)\(^11\)\(^12\) Because \( \text{N}_2 \) and \( \text{CO} \) are isoelectronic, we sought to develop new \( \text{N} \)-\( \text{C} \) bond forming reactions that couple these two diatomics in an “aza-variant” of CO homologation. If such a reaction could also be coupled to hydrogenation, then an “aza-Fischer-Tropsch” process for the synthesis of amines would be possible. Evans and coworkers have provided precedent for such a process as \( \text{N} \)-\( \text{C} \) bond cleavage with \( \text{N} \)-\( \text{C} \) bond formation has been observed in an azobenzene (not dinitrogen) complex of decamethyl samarocene.\(^13\)\(^14\) We initially postulated that new, strongly activated zirconocene and hafnocene dinitrogen complexes would also be necessary to prevent competing pathways involving deleterious \( \text{N}_2 \) dissociation and metallocene dicarbonyl formation.\(^15\) The \( \text{ansa} \)-hafnocene complex, \([\text{Me}_2\text{Si}(\eta^5-\text{C}_5\text{Me}_4)(\eta^5-\text{C}_5\text{H}_3-3\text{-}^3\text{Bu})\text{Hf}]_2(\mu_2, \eta^2, \eta^2-\text{N}_2)\) \((4-\text{N}_2)\),\(^16\) was synthesized and contains an \( \text{N} \)-\( \text{N} \) bond length of 1.457(5) Å, the longest of any group 4 metallocene dinitrogen complex. However, this distance is shorter than the values reported for non-metallocene zirconium and hafnium \( \text{N}_2 \) compounds prepared by Fryzuk\(^17\)\(^18\) and Sita.\(^19\)

Addition of 1-4 atmospheres of carbon monoxide to the \( \text{ansa} \)-hafnocene, \( 4-\text{N}_2 \) resulted in \( \text{N} \)-\( \text{N} \) bond cleavage with simultaneous assembly of one \( \text{C} \)-\( \text{C} \) and two \( \text{N} \)-\( \text{C} \) bonds (Figure 2).\(^16\) The resulting bridging, tetraanionic ligand, \([\text{N}_2\text{C}_2\text{O}_2]^{4-}\), was to our knowledge unprecedented and was termed “oxamidide” because it is a conjugate base of oxamide, \( \text{H}_2\text{NC(O)C(O)NH}_2 \). At higher CO pressures, the \( C_2\)-symmetric isomer of the hafnocene oxamidide complex, \( 4-(\text{N}_2\text{C}_2\text{O}_2)\text{-C}_2 \), was observed. At lower pressures of approximately 1 atmosphere of carbon monoxide, the \( C_1\)-symmetric isomer, \( 4-(\text{N}_2\text{C}_2\text{O}_2)\text{-C}_1 \), predominated. Both hafnocene oxamidide products were identified by X-ray diffraction and by diagnostic \( J_{N-C} \) coupling (and in the case of the \( C_1 \) isomer \( J_{C-C} \) coupling) upon preparation of the \( ^{13}\text{C} \) and \( ^{15}\text{N} \) isotopologues from readily available \( ^{13}\text{CO} \) and \( ^{15}\text{N}_2 \) gases, respectively. Treatment of either \( \text{ansa} \)-hafnocene oxamidide complex with a Brønsted acid furnished oxamide, \( \text{H}_2\text{NC(O)C(O)NH}_2 \), demonstrating that an important agrochemical can be synthesized, albeit stoichiometrically, from \( \text{N}_2 \) and \( \text{CO} \): the diatomics with the two strongest bonds in chemistry. The details of this work have been published in *Nature Chemistry*.\(^16\)
Dinitrogen cleavage requires six-reducing equivalents. Traditionally, all six electrons are supplied solely by the transition metals as exemplified by Cummins’ 1995 report of soluble molybdenum compounds cleaving N₂ at low temperature in solution. An alternative strategy is ligand-induced N₂ bond cleavage where N≡N scission and N-C bond formation occur in a single transformation. This approach is potentially broader in scope as the transition metal complex does not need to supply all six electrons for N₂ cleavage and an array of reagents to promote the desired chemistry is plausible. In group 4 transition metal chemistry, Sobota and coworkers provided early experimental precedent with the discovery of N, N-dimethylformamide formation from treatment of an ill-defined titanium dinitrogen complex with carbon monoxide and subsequently CH₃SiH₂. In tantalum dinitrogen chemistry, Fryzuk and coworkers have reported a rich N₂ cleavage and functionalization chemistry to form tantalum imides and nitrides from addition of simple hydride reagents such as boranes, silanes, alanes and zirconium hydrides to ([NPN]Ta)₂(µ₂-H)₂(µ₂-η¹, η²-N₂) (NPN = PhP(CH₂SiMe₃NPh)₂). Modification of the supporting ligand was often involved in the dinitrogen functionalization chemistry. The discovery of N₂ carbylation with the ansa-hafnocene, 4-N₂, is a unique ligand-induced dinitrogen cleavage process because of the selective formation of two N-C and one C-C bond and can potentially serve as a template to construct N-containing organic molecules directly from atmospheric nitrogen.

The generality of CO-induced N₂ cleavage was explored with a family of zirconocene and hafnocene compounds with side-on bound dinitrogen ligands. The degree of N₂ activation in the ground state of the dinitrogen complex was systematically explored for the desired carbylation chemistry. The zirconocene and hafnocene complexes, [(η⁵-C₅Me₅H)₂M]₂(µ₂-η¹, η²-N₂) (M = Zr, 1-N₂, Hf,

Figure 2. CO-induced N₂ cleavage to form oxamidide ligands, [N₂C₂O₂]⁻, promoted by an ansa-hafnocene complex. Protonation yields free oxamide.

Molecular structure of 4-(N₂C₂O₂)-C₁ at 30% probability ellipsoids. H-atoms omitted for clarity.

Molecular structure of 2-(N₂C₂O₂) at 30% probability ellipsoids. H-atoms omitted for clarity.
were selected due to their relative ease of synthesis and ability to directly compare Zr and Hf congeners. For the zirconium examples, 1-N\(_2\) and 3-N\(_2\), dinitrogen loss becomes competitive with \(N_2\) carbonylation and significant quantities of the zirconocene dicarboxyls accompany oxamidide formation. By contrast, the hafnocene complex, 2-N\(_2\), undergoes clean carbonylative dinitrogen cleavage with no evidence for \(N_2\) loss (Figure 3). These results suggest that the identity of the metal influences reactivity more than dinitrogen activation in the ground state as the \(ansa\)-zirconocene, 3-N\(_2\), has a longer N-N bond than the hafnocene 2-N\(_2\).

Complete details of this chemistry have been published as an article in *J. Am. Chem. Soc.*.\(^{33}\)

![Figure 3](image)

**Figure 3.** The scope of CO-induced \(N_2\) cleavage in zirconocene and hafnocene complexes with side-on bound dinitrogen ligands.

Repeating the carbonylation of 4-N\(_2\) with only one equivalent of carbon monoxide resulted in \(N_2\) cleavage coupled to C-H bond activation to form the cyclometallated \(ansa\)-hafnocene complex with bridging imido and terminal isocyanate ligands (Figure 4).\(^{16}\) Analogous chemistry was observed with 2-N\(_2\), although cyclometalation across the dimer occurred and yielded two isomers, one of which was characterized by X-ray diffraction (Figure 4).\(^{33}\) Diagnostic IR bands and \(^1\)J\(_{N,C}\) coupling constants were observed by NMR spectroscopy for the [NCO] ligands.

![Figure 4](image)

**Figure 4.** C-H activation and N-H bond formation coupled to CO-induced dinitrogen cleavage (left) and molecular structure of the product of the bottom transformation at 30% probability ellipsoids with hydrogen atoms (except those attached to C6) omitted for clarity (right).

Although intermediates have yet to be observed with one equivalent of CO, a mechanism has been proposed for the formation of the cyclometalated hafnocene products (Figure 5) and recently explored computationally.\(^{34}\) The pathway for \(N_2\) cleavage likely begins with CO insertion into a Hf-N bond followed by a retro-[2+2] reaction, akin to a \(\beta\)-elimination, to generate the terminal isocyanate and a bridging nitrido. Subsequent 1,2-addition, where the carbon of the cyclopentadienyl methyl or tert-butyl group undergoes cyclometalation, yields the final product(s). The potential intermediacy of a bridging nitrido compound raised the possibility that
such a species could be intercepted with other reagents and thereby couple $N_2$ cleavage with other functionalization reactions. $1,2$-addition of non-polar molecules such as dihydrogen seemed particularly attractive and if successful, would couple $N_2$ cleavage and hydrogenation. One potential challenge with these experiments is the ratio of reagents used, as the reactivity of $H_2$ with the starting dinitrogen compound must be slower than the initial carbonylation and $1,2$-addition of $H_2$ must be faster than the subsequent CO addition step.

**Figure 5.** Proposed mechanism for $N_2$ carbonylation with one equivalent of carbon monoxide and coupling dinitrogen cleavage with hydrogenation and C-H activation.

Treatment of $2-N_2$, $3-N_2$ or $4-N_2$ with modified synthesis gas (3:1 CO:$H_2$) resulted in dinitrogen carbonylation and cleavage coupled with $N_2$ hydrogenation to form dihafnocene (or dizirconocene) complexes with a terminal isocyanate, a terminal hydride and a bridging imido ligand (Figure 5). Importantly, control experiments whereby the cyclometalated hafnocene compounds depicted in Figure 4 were exposed to 4 atm $H_2$, produced no reaction indicating that the proposed intermediate in Figure 5 was indeed intercepted by the $1,2$-addition of dihydrogen. Deuterium labeling studies also support this finding as none of the isotopic label was observed in any of the cyclopentadienyl substituents. This approach to $N_2$ functionalization and cleavage was also extended to include C-H activation of terminal alkynes. Performing the carbonylation of $2-N_2$ in the presence of phenylacetylene yielded the isocyanato, acetylide dihafnocene complex with a bridging imide, demonstrating that the proposed $\mu$-nitrido intermediate can also be captured by $1,2$-addition of the appropriate C-H bonds (Figure 5).

Attempts to couple CO-induced $N_2$ cleavage to dinitrogen hydrosilylation produced a different outcome. Inspiration for these studies derived, in part, from Fryzuk's observations of $N_2$ cleavage upon addition of silanes to tantalum dinitrogen compounds. Treatment of $4-N_2$ with one equivalent of $^3$HexylSiH$_3$ and 1 atm of CO (simultaneously) furnished a $C_7$ symmetric product identified as the $\mu$-oxo hydrido hafnocene isocyanate (Figure 6). This product was obtained from addition of other primary silanes, consistent with the silyl group not being incorporated into the final product. Considerable effort was devoted to establishing the identity of the $\mu$-oxo compound and differentiating it from another isomer of the $\mu$-imidos. All of the experimental data: X-ray diffraction, NMR and IR spectroscopic studies and degradation experiments were consistent with the $\mu$-oxo formulation and that the oxygen atom is derived from CO rather than adventitious water. Notably, $^3$HexylSi(CN)$_3$ was detected as a product of the reaction from addition of $^3$HexylSiH$_3$, demonstrating that a free cyano silane, derived from
N₂ and CO cleavage and functionalization, could be removed from the coordination sphere of the hafnium (Figure 6).

![Figure 6. Cleavage of dinitrogen and carbon monoxide upon addition of silane and CO to 4-N₂ (left) and molecular structure of 4-(µ-O)(H)(NCO) at 30% probability ellipsoids with hydrogen atoms (except the Hf-H) omitted for clarity (right).](image)

With a method for the simultaneous cleavage of the N≡N bond coupled to formation of N-C and C-C bonds in hand, methods were explored to elaborate the [N₂C₂O₂]⁺ core into various organic molecules. DFT calculations at the B3LYP level on 2-N₂C₂O₂ (selected to alleviate complications from isomers) demonstrated significant oxamidide nitrogen lone pair character in the HOMO, suggesting that the N-atom may be further functionalized by addition of the appropriate electrophiles. As illustrated in Figure 7, addition of one equivalent of CH₃I to 2-N₂C₂O₂ resulted in rapid formal 1,2-addition of the carbon-iodide bond resulting in N-methylation and formation of 2-N₂C₂O₂-(CH₃I). Because subsequent alkylations are relatively slow, a different alkylating agent can be used to functionalize the second nitrogen atom. In this manner, new complexes derived from addition of methyl iodide, benzyl bromide and ethyl bromide were prepared (Figure 7). Dialkylations with the same alkyl halide were also accomplished in higher yield by addition of two equivalents of the electrophile directly to 2-N₂C₂O₂. In this manner both the dimethyl and diethyl derivatives were isolated and one example, 2-N₂C₂O₂-(CH₃I)₂, was characterized by X-ray diffraction (Figure 7).

The functionalized oxamidate cores were then studied for release from the hafnium. Treatment with appropriate Brønsted acids released free N-monoalkyl- and N,N'-dialkylloxamides, which are known synthons for a variety of important small molecules and heterocycles (Figure 8, bottom). Each example was readily labeled with ¹⁵N and ¹³C isotopes and provides a convenient method for accessing specifically labeled isotoptopologues of various N-containing small molecules and heterocycles. There is also considerable interest in the synthesis of substituted oxamides for their coordination properties, in particular their interesting electronic behavior, when bound to late transition metals.

Computational studies on 2-N₂C₂O₂ and natural bond order analysis established modest π-donation from the nitrogen atoms of the oxamidide ligand to the electrophilic Hf(IV) centers and demonstrate Hf-N multiple bond character and raise the possibility of cycloaddition reactivity. Heterocumulenes such as BuNCO and CO₂ undergo double cycloaddition to the Hf-N bonds of 4-N₂C₂O₂ to yield 4-N₂C₂O₂-(BuNCO)₂ and 4-N₂C₂O₂-(CO₂)₂, respectively (Figure 9). Crystallographic studies on both products established cycloaddition of two molecules of the heterocumulene to each of the hafnium-nitrogen bonds with concomitant formation of new N-C and Hf-O bonds. The synthesis of 4-N₂C₂O₂-(CO₂)₂ demonstrates that an organic ligand can be synthesized from three typically inert and abundant small molecules – N₂, CO and CO₂.
Figure 7. Methylation and subsequent alkylation of 2-N₂C₂O₂.

Figure 8. Synthesis of free N-monosubstituted and N,N'-disubstituted oxamides and potential applications to the preparation of heterocycles, N-heterocyclic carbenes and N,N'-diamines.
Figure 9. Functionalization of $4\text{-}N_2\text{C}_2\text{O}_2$ by addition of heterocumulenes. The reaction with carbon dioxide demonstrates that an organic ligand can be prepared from three abundant and typically inert small molecules: $N_2$, $CO$ and $CO_2$. Right: $^{13}$C NMR spectrum of $4\text{-}N_2^{13}\text{C}_2\text{O}_2^{12}\text{CO}_2$.

In addition to heterocumulenes, the reactivity of the *ansa*-hafnocene oxamidide with oxidants such as elemental iodine was also explored. Addition of one equivalent of I$_2$ to a toluene solution of $4\text{-}N_2\text{C}_2\text{O}_2$ (mixture of $C_1$ and $C_2$ isomers) yielded a single new $C_1$-symmetric product identified as the monomeric iodo *ansa*-hafnocene isocyanate, $4\text{-}(I)(N\text{C}O)$, demonstrating that the C-C bond formation was chemically reversible. The resulting monomeric hafnocene was characterized by multinuclear ($^1\text{H}$, $^{13}$C, $^{15}$N) NMR spectroscopy as well as X-ray diffraction (Figure 10).

Figure 10. Top: Oxidative cleavage of the C-C bond in the oxamide ligand in $4\text{-}N_2\text{C}_2\text{O}_2$ (both isomers) with iodine to yield $4\text{-}(I)(N\text{C}O)$ as a single diastereomer. Bottom: Molecular structure of $4\text{-}(I)(N\text{C}O)$ (left) and $^{13}$C NMR spectra of $4\text{-}(I)(N^{13}\text{C}O)$ (top spectrum) and $4\text{-}(I)(^{15}\text{N}\text{C}O)$ (bottom spectrum).

**B. Methylation of a Hafnocene Dinitrogen Complex: Synthesis of a Hydrazonato Ligand.** During the past funding period, nitrogen-carbon bond formation by direct treatment of
the zirconocene and hafnocene compounds bearing side-on bound, strongly activated N₂ ligands was also explored. Historically, this synthetic route has been the most well studied method for N-C bond formation from coordinated N₂ and principally relies on group 6 dinitrogen complexes with phosphine ligands. Extension of this approach to ill-defined titanium N₂ complexes was pioneered by van Tamelen and later used by Mori to prepare a host of N-containing organic molecules including N-heterocycles and natural products. Despite these advances, little is known about the reactivity of well-defined zirconocene and hafnocene dinitrogen complexes such as 1-N₂ and 2-N₂ toward carbon-based electrophiles. Exceptions include a report from Sita describing N-C bond formation by ethylation of a dihafnium dinitrogen compound with CH₂CH₂Br and a related observation by Fryzuk of benzylation of a tantalum dinitrogen compound with benzyl bromide.

Treatment of the zirconocene congener, 1-N₂, with alkyl halides or methyl triflate resulted in N₂ loss and observation of unusual 1,4-addition reactions. A full account of this chemistry has been published in Organometallics. These outcomes are analogous to chemistry reported by Sita from bromination of a hafnium complex with a strongly activated N₂ ligand.

For the hafnocene, 2-N₂, addition of 2.2 equiv of CH₃OTf resulted in a mixture of products arising from three distinct pathways, one of which was the desired N-methylation event (Figure 11). Treatment of this compound with additional methyl triflate resulted in a second N-C bond forming reaction and yielded an unusual hafnocene hydrazonato complex (Figure 12). The mechanism of this unusual transformation was studied with isotopic labeling and the results are consistent with a pathway involving initial methylation of the unsubstituted nitrogen in the methyl diazenido ligand followed by deprotonation by triflate anion. A full account of this work has been published in the Journal of the American Chemical Society.

![Figure 11. Products of methyl triflate addition to 2-N₂ including N₂ methylation.](image-url)
Figure 12. Synthesis of a hafnocene hydrazonato complex by addition of methyl triflate to the corresponding methyl diazenido compound.

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