Abstract

Project Title: “Understanding Nitrogen Fixation”

DOE Grant Number: DE-FG02-05ER15659

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Yearly Budget: $150,000 **Period of Execution:** 05/01/07 – 4/30/10

Year Started: 5/01/08 (Renewal); 5/01/05 (Original Proposal)

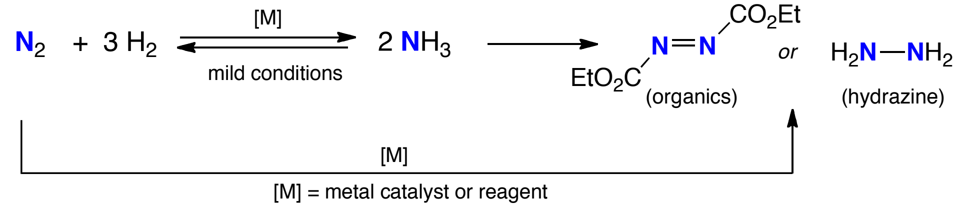
Overall Research Goals: The purpose of our program is to explore fundamental chemistry relevant to the discovery of energy efficient methods for the conversion of atmospheric nitrogen (N_2) into more value-added nitrogen-containing organic molecules. Such transformations are key for domestic energy security 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 pharamaceutical 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, $H_2NC(O)C(O)NH_2$, 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 $N{\equiv}N$ 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 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 20th 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.[1,2] 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.[3] Moreover, industrial H_2 synthesis via the water gas shift reaction and the steam reforming of methane is fossil fuel intensive and produces CO_2 as a byproduct. New synthetic methods that promote this thermodynamically favored transformation ($\Delta G° = -4.1$ 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 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]

General, Long-Term Goals:



Recent Chirik Group Contributions:

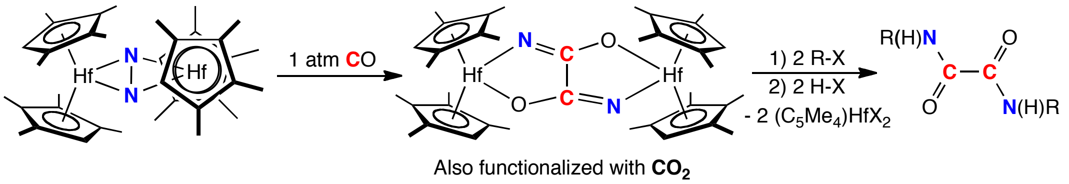


Figure 1. General goals for N_2 fixation and functionalization targeted by our program.

Specific highlights from our last funding cycle include:

- Discovery of CO-induced N_2 cleavage under mild conditions in solution to simultaneously form 1 C-C and 2 N-C bonds.
- Nitrogen-carbon bond formation by addition of electrophiles to a hafnium dinitrogen compound and rare observation of conversion to a hydrazonato ligand.
- Demonstration of N_2 hydrogenation by a strongly activated "end-on" rather than "side-on" dinitrogen complex broadening the scope and mechanistic understanding of the transformation.
- 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 N_2 Bond Cleavage. Synthetic transformations that couple the cleavage of the strong, non-polar bond of molecular nitrogen, 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 N_2 make dinitrogen an attractive feedstock for the preparation of these important compounds. However, the strong N≡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 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 *C*-source for nitrogen-carbon bond formation. Selective formation of carbon-carbon bonds from 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 N_2 and CO are isoelectronic, we sought to develop new N-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 N-N bond cleavage with N-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 N_2 dissociation and metallocene dicarbonyl formation.[15] The *ansa*-hafnocene complex, $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}^tBu)Hf]_2(\mu_2, \eta^2, \eta^2\text{-}N_2)$ (**4-N$_2$**),[16] was synthesized and contains an N-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 N_2 compounds prepared by Fryzuk[17,18] and Sita.[19]

Addition of 1-4 atmospheres of carbon monoxide to the *ansa*-hafnocene, **4-N$_2$** resulted in N-N bond cleavage with simultaneous assembly of one C-C and two N-C bonds (Figure 2).[16] The resulting bridging, tetraanionic ligand, $[N_2C_2O_2]^{4-}$, was to our knowledge unprecedented and was termed “oxamidide” because it is a conjugate base of oxamide, $H_2NC(O)C(O)NH_2$. At higher CO pressures, the C_2-symmetric isomer of the hafnocene oxamidide complex, **4-(N$_2$C$_2$O$_2$)-*C$_2$***, was observed. At lower pressures of approximately 1 atmosphere of carbon monoxide, the C_1-symmetric isomer, **4-(N$_2$C$_2$O$_2$)-*C$_1$***, predominated. Both hafnocene oxamidide products were identified by X-ray diffraction and by diagnostic $^1J_{N\text{-}C}$ coupling (and in the case of the C_1 isomer $^1J_{C\text{-}C}$ coupling) upon preparation of the ^{13}C and ^{15}N isotopologues from readily available ^{13}CO and $^{15}N_2$ gases, respectively. Treatment of either *ansa*-hafnocene oxamidide complex with a Brønsted acid furnished oxamide, $H_2NC(O)C(O)NH_2$, demonstrating that an important agrochemical can be synthesized, albeit stoichiometrically, from N_2 and CO: the diatomics with the two strongest bonds in chemistry. The details of this work have been published in *Nature Chemistry*.[16]

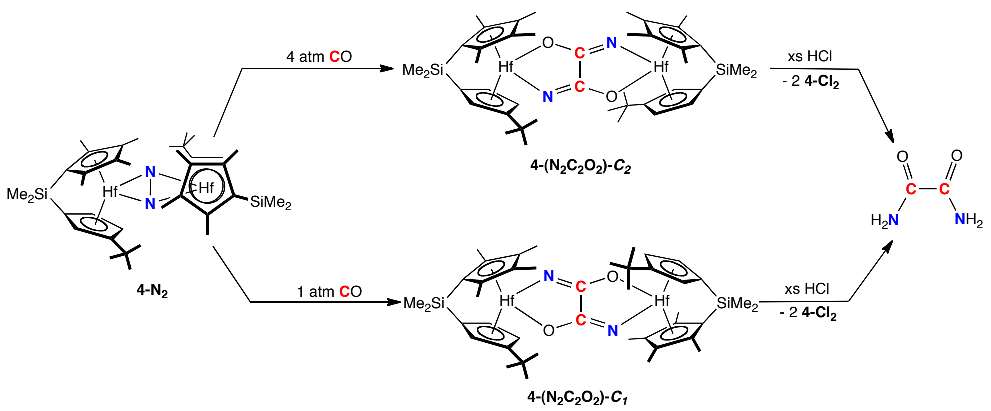
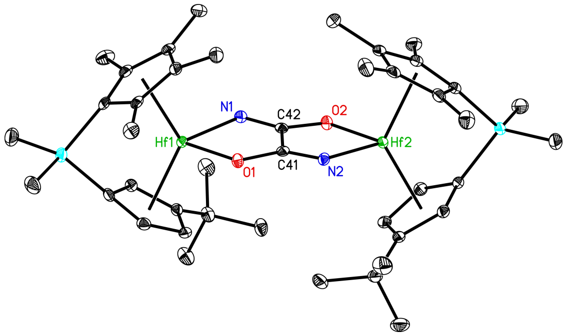
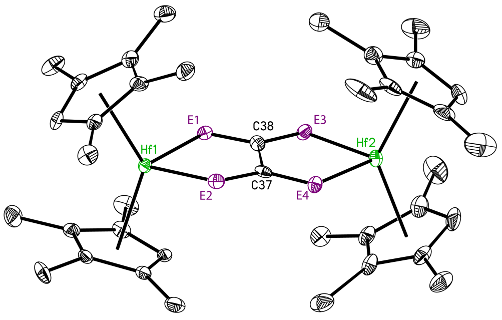


Figure 2. CO-induced N_2 cleavage to form oxamidide ligands, $[N_2C_2O_2]^{4-}$, promoted by an *ansa*-hafnocene complex. Protonation yields free oxamide.

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 N_2 at low temperature in solution.[20,21,22,23] An alternative strategy is ligand-induced N_2 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 N_2 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 CH_3I.[24] In tantalum dinitrogen chemistry, Fryzuk and coworkers have reported a rich N_2 cleavage and functionalization chemistry to form tantalum imides and nitrides from addition of simple hydride reagents such as boranes,[25,26] silanes,[27,28] alanes[29] and zirconium hydrides[30] to $([NPN]Ta)_2(\mu_2\text{-}H)_2(\mu_2, \eta^1, \eta^2\text{-}N_2)$ (NPN = $PhP(CH_2SiMe_2NPh)_2$).[31] Modification of the supporting ligand was often involved in the dinitrogen functionalization chemistry. The discovery of N_2 carbonylation with the *ansa*-hafnocene, **4-N$_2$**, 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.



Molecular structure of **4-(N$_2$C$_2$O$_2$)-*C*$_2$** at 30% probability ellipsoids. H-atoms omitted for clarity.



Molecular structure of **2-(N$_2$C$_2$O$_2$)** at 30% probability ellipsoids. H-atoms omitted for clarity.

The generality of CO-induced N_2 cleavage was explored with a family of zirconocene and hafnocene compounds with side-on bound dinitrogen ligands. The degree of N_2 activation in the ground state of the dinitrogen complex was systematically explored for the desired carbonylation chemistry. The zirconocene and hafnocene complexes, $[(\eta^5\text{-}C_5Me_4H)_2M]_2(\mu_2, \eta^2, \eta^2\text{-}N_2)$ (M = Zr, **1-N$_2$**;[32] = Hf,

2-N$_2$), 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 dicarbonyls 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]

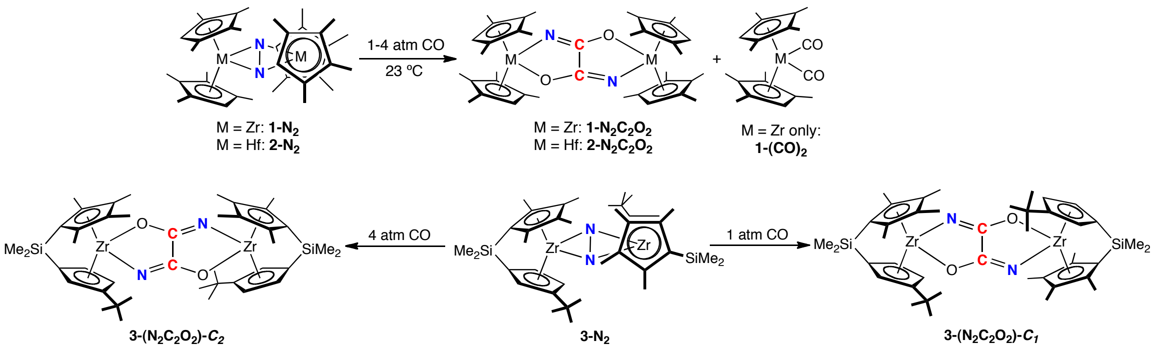


Figure 3. The scope of CO-induced N$_2$ cleavage in zirconocene and hafnocene complexes with side-on bound dinitrogen ligands.

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 $^1J_{N\text{-}C}$ coupling constants were observed by NMR spectroscopy for the [NCO] ligands.

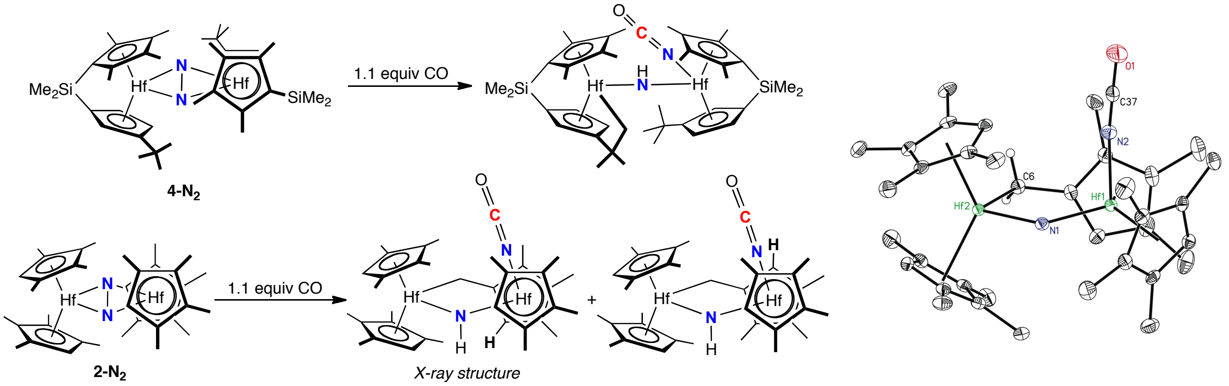


Figure 4. C-H activation and N-H bond formation coupled to CO-induced dinitrogen cleavage (left) and molecular structure of the product of the bottom transformation at 30% probability ellipsoids with hydrogen atoms (except those attached to C6) omitted for clarity (right).

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 β-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[34] 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.

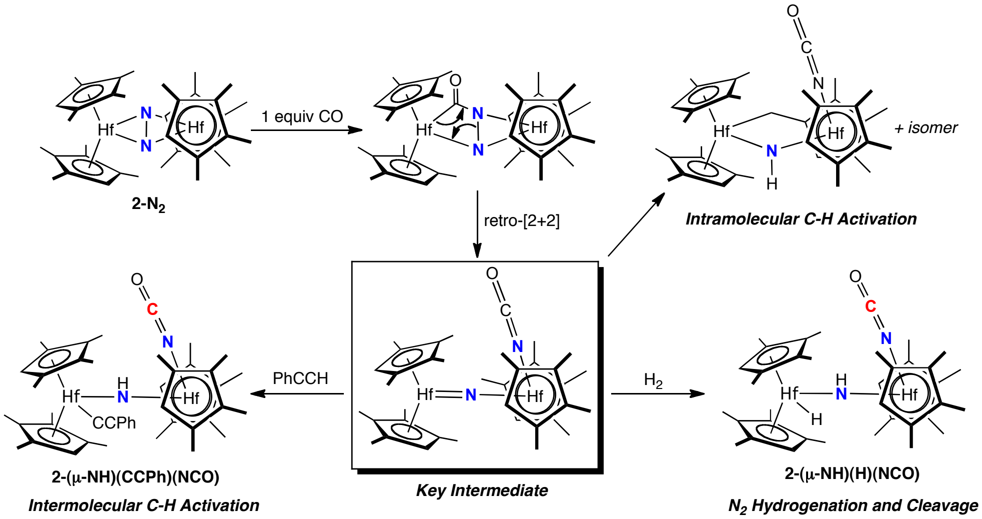


Figure 5. Proposed mechanism for N_2 carbonylation with one equivalent of carbon monoxide and coupling dinitrogen cleavage with hydrogenation and C-H activation.

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).[33] 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 μ-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.[31] Treatment of **4-N$_2$** with one equivalent of ^{n}HexylSiH$_3$ and 1 atm of CO (simultaneously) furnished a C_1 symmetric product identified as the μ-oxo hydrido hafnocene isocyanate (Figure 6).[33] 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 μ-oxo compound and differentiating it from another isomer of the μ-imidos. All of the experimental data: X-ray diffraction, NMR and IR spectroscopic studies and degradation experiments were consistent with the μ-oxo formulation and that the oxygen atom is derived from CO rather than adventious water. Notably, ^{n}HexylSi(CN)$_3$ was detected as a product of the reaction from addition of ^{n}HexylSiH$_3$, demonstrating that a free cyano silane, derived from

N_2 and CO cleavage and functionalization, could be removed from the coordination sphere of the hafnium (Figure 6).

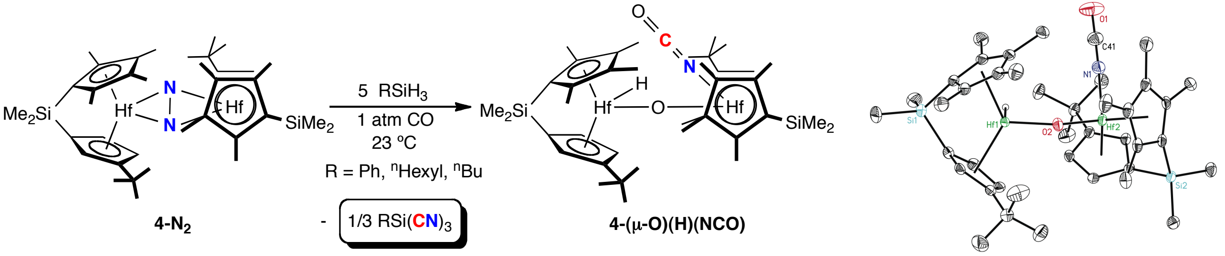


Figure 6. Cleavage of dinitrogen and carbon monoxide upon addition of silane and CO to **4-N$_2$** (left) and molecular structure of **4-(μ-O)(H)(NCO)** at 30% probability ellipsoids with hydrogen atoms (except the Hf-H) omitted for clarity (right).

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 $[N_2C_2O_2]^{4-}$ core into various organic molecules. DFT calculations at the B3LYP level on **2-N$_2$C$_2$O$_2$** (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 CH_3I to **2-N$_2$C$_2$O$_2$** resulted in rapid formal 1,2-addition of the carbon-iodide bond resulting in *N*-methylation and formation of **2-N$_2$C$_2$O$_2$-(CH$_3$I)**. 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-N$_2$C$_2$O$_2$**. In this manner both the dimethyl and diethyl derivatives were isolated and one example, **2-N$_2$C$_2$O$_2$-(CH$_3$I)$_2$**, 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'*-dialkyloxamides, which are known synthons for a variety of important small molecules and heterocycles (Figure 8, bottom).[35,36,37] Each example was readily labeled with ^{15}N and ^{13}C isotopes and provides a convenient method for accessing specifically labeled isotopologues 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.[38]

Computational studies on **2-N$_2$C$_2$O$_2$** and natural bond order analysis established modest π-donation from the nitrogen atoms of the oxamidide ligand to the electrophilic Hf(IV) centers[39] and demonstrate Hf-N multiple bond character and raise the possibility of cycloaddition reactivity.[40,41,42] Heterocumulenes such as ^tBuNCO and CO_2 undergo double cycloaddition to the Hf-N bonds of **4-N$_2$C$_2$O$_2$** to yield **4-N$_2$C$_2$O$_2$-(^{t}BuNCO)$_2$** and **4-N$_2$C$_2$O$_2$-(CO$_2$)$_2$**, 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-N$_2$C$_2$O$_2$-(CO$_2$)$_2$** demonstrates that an organic ligand can be synthesized from three typically inert and abundant small molecules – N_2, CO and CO_2.

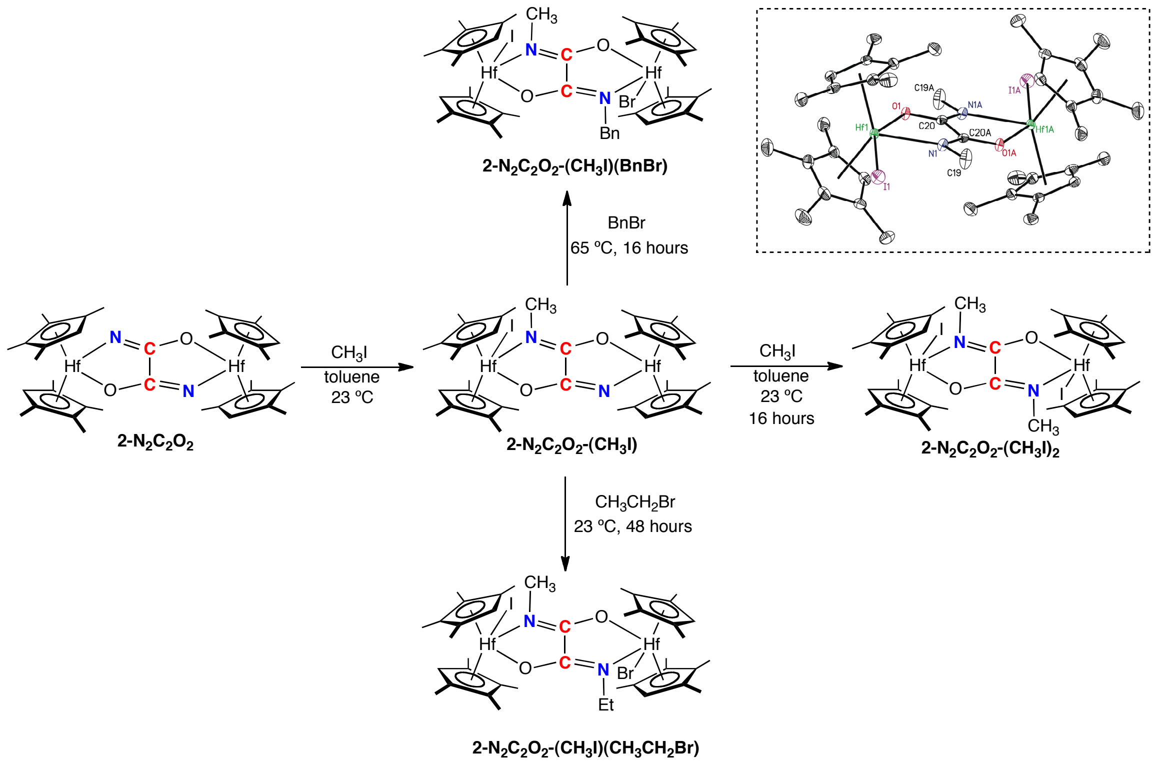


Figure 7. Methylation and subsequent alkylation of **2-N$_2$C$_2$O$_2$**.

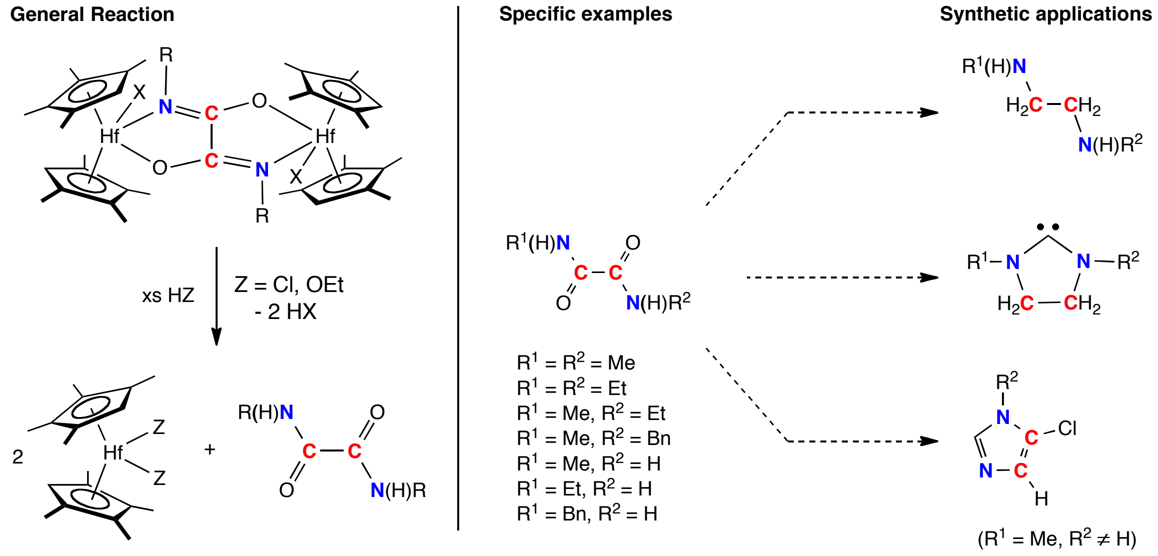


Figure 8. Synthesis of free *N*-monosubstituted and *N*,*N*'-disubstituted oxamides and potential applications to the preparation of heterocycles, *N*-heterocyclic carbenes and *N*,*N*'-diamines.

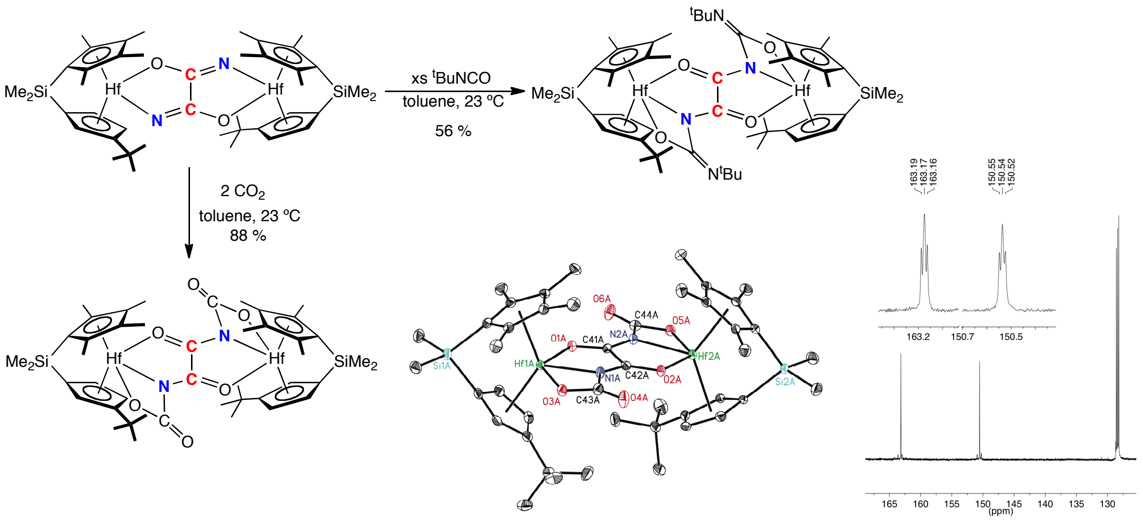
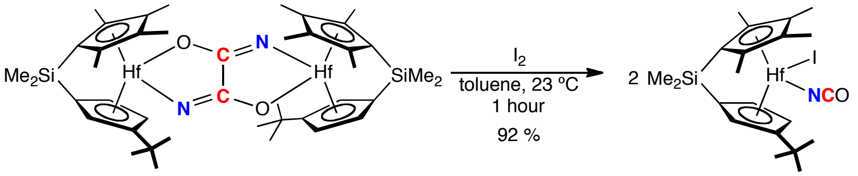


Figure 9. Functionalization of **4-$N_2C_2O_2$** by addition of heterocumulenes. The reaction with carbon dioxide demonstrates that an organic ligand can be prepared from three abundant and typically inert small molecules: N_2, CO and CO_2. Right: ^{13}C NMR spectrum of **4-$N_2{}^{13}C_2O_2$-($^{13}CO_2$)$_2$**.

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-$N_2C_2O_2$** (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-(I)(NCO)**, demonstrating that the C-C bond formation was chemically reversible. The resulting monomeric hafnocene was characterized by multinuclear (^{1}H, ^{13}C, ^{15}N) NMR spectroscopy as well as X-ray diffraction (Figure 10).



4-$N_2C_2O_2$-C_2+ isomer

4-(I)(NCO)

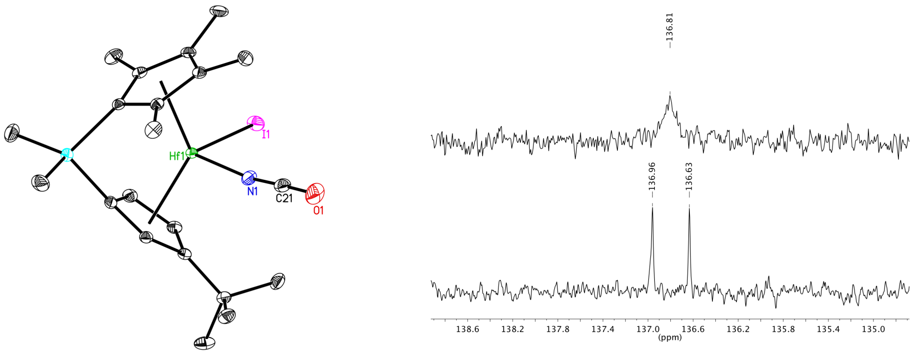


Figure 10. Top: Oxidative cleavage of the C-C bond in the oxamide ligand in **4-$N_2C_2O_2$** (both isomers) with iodine to yield **4-(I)(NCO)** as a single diastereomer. Bottom: Molecular structure of **4-(I)(NCO)** (left) and ^{13}C NMR spectra of **4-(I)(N^{13}CO)** (top spectrum) and **4-(I)(^{15}N^{13}CO)** (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 N_2 ligands was also explored. Historically, this synthetic route has been the most well studied method for N-C bond formation from coordinated N_2 and principally relies on group 6 dinitrogen complexes with phosphine ligands.[43,44,45] Extension of this approach to ill-defined titanium N_2 complexes was pioneered by van Tamelen[46] and later used by Mori[47] 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 CH_3CH_2Br[48] and a related observation by Fryzuk of benzylation of a tantalum dinitrogen compound with benzyl bromide.[49]

Treatment of the zirconocene congener, **1-N₂**, with alkyl halides or methyl triflate resulted in N_2 loss and observation of unusual 1,4-addition reactions. A full account of this chemistry has been published in *Organometallics*.[50] These outcomes are analogous to chemistry reported by Sita from bromination of a hafnium complex with a strongly activated N_2 ligand.[48] For the hafnocene, **2-N₂**, addition of 2.2 equiv of CH_3OTf 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*.[51]

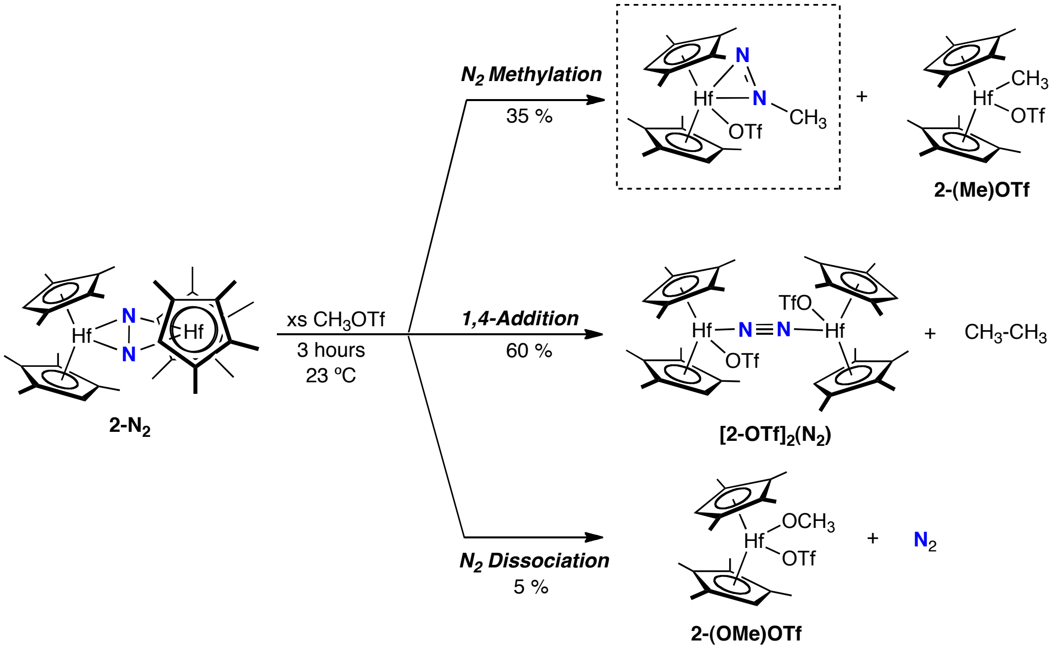


Figure 11. Products of methyl triflate addition to **2-N₂** including N_2 methylation.

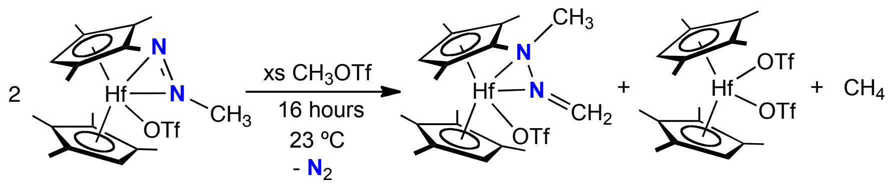


Figure 12. Synthesis of a hafnocene hydrazonato complex by addition of methyl triflate to the corresponding methyl diazenido compound.

Publications from this Funding Period (2008-2010)

Knobloch, D. J.; Lobkovsky, E.; Chirik, P. J. “Dinitrogen cleavage and functionalization by carbon monoxide promoted by a hafnium complex.” *Nature Chemistry* **2010**, *2*, 30-35.

Knobloch, D. J.; Benito-Garagorri, D.; Bernskoetter, W. H.; Keresztes, I.; Lobkovsky, E.; Toomey, H.; Chirik, P. J. “Addition of methyl triflate to a hafnocene dinitrogen complex: Stepwise N_2 methylation and conversion to a hafnocene hydrazonato compound.” *J. Am. Chem. Soc.* **2009**, *131*, 14903-14912.

Benito-Garagorri, D.; Bernskoetter, W. H.; Lobkovsky, E.; Chirik, P. J. “1,4-Addition of alkyl halides to a side-on bound hafnocene dinitrogen complex.” *Organometallics* **2009**, *28*, 4807-4813.

Hanna, T. E; Lobkovsky, E.; Chirik, P. J. “Dinitrogen complexes of bis(cyclopentadienyl) titanium derivatives: Structure diversity arising from substituent manipulation.” *Organometallics* **2009**, *28*, 4079-4088.

Pun, D.; Leopold, S. M.; Bradley, S. M.; Lobkovsky, E.; Chirik, P. J. “Bis(indenyl)hafnium chemistry: Ligand-induced haptotropic rearrangement and fundamental reactivity studies at a reduced hafnium center.” *Organometallics* **2009**, *28*, 2471-2484.

Pun, D.; Bradley, C. A.; Lobkovsky, E.; Keresztes, I.; Chirik, P. J. “N_2 hydrogenation from activated end-on bis(indenyl)zirconium dinitrogen complexes.” *J. Am. Chem. Soc.* **2008**, *130*, 14046-14047.

Pun, D.; Lobkovsky, E.; Chirik, P. J. “Indenyl dinitrogen chemistry: N_2 coordination to an isolated zirconium sandwich and synthesis of side-on, end-on dinitrogen compounds.” *J. Am. Chem. Soc.* **2008**, *130*, 6047-6054.

Knobloch, D. J.; Toomey, H. E.; Chirik, P. J. “Carboxylation of an *ansa*-zirconocene dinitrogen complex: Regiospecific hydrazine synthesis from N_2 and CO_2.” *J. Am. Chem. Soc.* **2008**, *130*, 4248-4249.

References

[1] Chagas, A. P. “The ammonia synthesis: Some historical aspects.” *Quimica Nova* **2007**, *30*, 240-247.

[2] Smil, V. “Nitrogen and food production: Proteins for human diets.” *Ambio* **2002**, *31*, 126-131.

[3] Schlogl, R. “Catalytic synthesis of ammonia – A never ending story?” *Angew. Chem. Int. Ed.* **2003**, *42*, 2004-2008.

[4] Asazawa, K.; Yamada, K.; Tanaka, H.; Oka, A.; Taniguchi, M.; Kobayashi, T. “A platinum-free zero-carbon-emission easy fuelling direct hydrazine fuel cell for vehicles.” *Angew. Chem. Int. Ed.* **2007**, *46*, 8024-8027.

[5] Smil, V. *Enriching the Earth: Fritz Haber, Carl Bosch, and the Transformation of World Food Production*; MIT Press: Cambridge, MA 2001.

[6] Dombeck, B. D. “Homogeneous catalytic hydrogenation of carbon monoxide: Ethylene glycol and ethanol from synthesis gas.” *Adv. Catal.* **1983**, *32*, 325-416.

[7] Maitlis, P. M.; Zanotti, V. “The role of electrophilic species in the Fischer-Tropsch reaction.” *Chem. Commun.* **2009**, 1619-1634.

[8] Miller, A. J M.; Labinger, J. A.; Bercaw, J. E. “Homogeneous CO hydrogenation: Dihydrogen activation involves a frustrated Lewis pair instead of a platinum complex.” *J. Am. Chem. Soc.* **2010**, *132*, 3301-3303.

[9] Evans, W. J.; Grate, J. W.; Hughes, L. A.; Zhang, H.; Atwood, J. L. “Reductive homologation of CO to a ketenecarboxylate by a low-valent organolanthanide complex: Synthesis and X-ray crystal-structure of $[(C_5Me_5)_4Sm_2(O_2CCCO)(THF)]_2$” *J. Am. Chem. Soc.* **1985**, *107*, 3728-3728.

[10] Summerscales, O. T.; Cloke, F. G. N.; Hitchcock, P. B.; Green, J. C.; Hazari, N. “Reductive cyclotrimerization of carbon monoxide to the deltate dianion by an organometallic uranium complex.” *Science* **2006**, *311*, 829-831.

[11] Summerscales, O. T.; Cloke, F. G. N.; Hitchcock, P. B.; Green, J. C.; Hazari, N. “Reductive cyclotetramerization of CO to square by a U(III) complex: The x-ray crystal structure of $[(\eta^8\text{-}C_8H_6(SiPr_3)\text{-}Pr\text{-}i\text{-}1,4\}_2[(\eta^5\text{-}C_5Me_4H)]_2(\mu, \eta^2, \eta^2\text{-}C_4O_4)$” *J. Am. Chem. Soc.* **2006**, *128*, 9602-9603.

[12] Frey, A. S.; Cloke, F. G. N.; Hitchcock, P. B.; Day, I. J.; Green, J. C.; Aitken, G. “Mechanistic studies on the reductive cyclooligomerisation of CO by U(III) mixed sandwich complexes; the molecular structure of $[U(\eta^8\text{-}C_8H_6(SiPr_3)\text{-}Pr\text{-}i\text{-}1,4\}_2[(\eta\text{-}Cp^*)]_2(\mu, \eta^1, \eta^1\text{-}C_2O_2)$” *J. Am. Chem. Soc.* **2008**, *130*, 13816-13817.

[13] Evans, W. J.; Drummond, D. K. “Samarium-mediated functionalization of N=N bonds: Double insertion of carbon monoxide into the N=N bond of azobenzene.” *J. Am. Chem. Soc.* **1986**, *108*, 7440-7441.

[14] Evans, W. J.; Drummond, D. K.; Chamberlain, L. R.; Doedens, R. J.; Bott, S. G.; Zhang, H.; Atwood, J. L. “Synthetic, structural, and reactivity studies of the reduction and carbon monoxide derivatization of azobenzene mediated by divalent lanthanide complexes.” *J. Am. Chem. Soc.* **1988**, *110*, 4983-4994.

[15] Manriquez, J. M.; Sanner, R. D.; Marsh, R. E.; Bercaw, J. E. “Reduction of molecular nitrogen to hydrazine – Structure of a dinitrogen complex of bis(pentamethylcyclopentadienyl) zirconium(II) and an N-15 labeling study of its reaction with hydrogen chloride.” *J. Am. Chem. Soc.* **1976**, *98*, 3042-3044.

[16] Knobloch, D. J.; Lobkovsky, E.; Chirik, P. J. "Dinitrogen cleavage and functionalization by carbon monoxide promoted by a hafnium complex." *Nature Chem.* **2010**, *2*, 30-35.

[17] Fryzuk, M. D.; Haddad, T. S.; Rettig, S. J. "Reduction of dinitrogen by a zirconium phosphine complex to form a side-on-bridging N_2 Ligand. Crystal Structure of $\{[(\mathrm{Pr}^i{}_2\mathrm{PCH_2SiMe_2})_2\mathrm{N}]\mathrm{ZrCl}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}\mathrm{N_2})$." *J. Am. Chem. Soc.* **1990**, *112*, 8185-8186.

[18] Cohen, J. D.; Fryzuk, M. D.; Loehr, T. M.; Mylvaganam, M.; Rettig, S. J. "Synthesis and structure of a zirconium dinitrogen complex with a side-on bridging N_2 unit" *Inorg. Chem.* **1998**, *37*, 112-119.

[19] Hirotsu, M.; Fontaine, P. P.; Zavalij, P. Y.; Sita, L. R. "Extreme $N\equiv N$ bond elongation and facile N-atom functionalization reactions within two structurally versatile new families of group 4 bimetallic "side-on-bridged" dinitrogen complexes for zirconium and hafnium." *J. Am. Chem. Soc.* **2007**, *129*, 12690-12692.

[20] Laplaza, C. E.; Cummins, C. C. "Dinitrogen cleavage by a three-coordinate molybdenum(III) complex." *Science* **1995**, *268*, 861-863.

[21] Laplaza, C. E., Johnson, M. J. A.; Peters, J. C.; Odom, A. L.; Kim, E.; Cummins, C. C.; George, G. N.; Pickering, I. J. "Dinitrogen cleavage by three-coordinate molybdenum(III) complexes: Mechanistic and structural data." *J. Am. Chem. Soc* **1996**, *118*, 8623-8638.

[22] Curley, J. J.; Cook, T. R.; Reece, S. Y.; Müller, P.; Cummins, C. C. "Shining light on dinitrogen cleavage: Structural features, redox chemistry, and photochemistry of the key intermediate bridging dinitrogen complex." *J. Am. Chem. Soc.* **2008**, *130*, 9394-9405.

[23] Akagi, F.; Matsuo, T.; Kawaguchi, H. "Dinitrogen cleavage by a diniobium tetrahydride complex: Formation of a nitride and its conversion into imide species." *Angew. Chem. Int. Ed.* **2007**, *46*, 8778-8781.

[24] Sobota, P.; Janas, Z. *J.* "Formation of a nitrogen-carbon bond from nitrogen molecule and carbon monoxide. Influence of magnesium chloride on the nitrogen reduction process in the system titanium tetrachloride/magnesium." *Organomet. Chem.* **1984**, *276*, 171-176.

[25] MacKay, B. A.; Johnson, S. A.; Patrick, B. O.; Fryzuk, M. D. "Functionalization and cleavage of coordinated dinitrogen via hydroboration using primary and secondary boranes." *Can. J. Chem.* **2005**, *83*, 315-323.

[26] Fryzuk, M. D.; MacKay, B. A.; Johnson, S. A.; Patrick, B. O. "Hydroboration of coordinated dinitrogen: A new reaction for the N_2 ligand that results in its functionalization and cleavage." *Angew. Chem. Int. Ed.* **2002**, *41*, 3709-3712.

[27] Fryzuk, M. D.; MacKay, B. A.; Patrick, B. O. "Hydrosilylation of a dinuclear tantalum dinitrogen complex: Cleavage of N_2 and functionalization of both nitrogen atoms." *J. Am. Chem. Soc.* **2003**, *125*, 3234-3235.

[28] MacKay, B. A.; Munha, R. F.; Fryzuk, M. D. "Substituent effects in the hydrosilylation of coordinated dinitrogen in a ditantalum complex: Cleavage and functionalization of N_2." *J. Am. Chem. Soc.* **2006**, *128*, 9472-9483.

[29] MacKay, B. A.; Patrick, B. O.; Fryzuk, M. D. "Hydroalumination of a dinuclear tantalum dinitrogen complex: N-N bond cleavage and ancillary ligand rearrangement." *Organometallics* **2005**, *24*, 3836-3841.

[30] Spencer, L. P.; MacKay, B. A.; Patrick, B. O.; Fryzuk, M. D. "Inner-sphere two-electron reduction leads to cleavage and functionalization of coordinated dinitrogen." *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 17094-17098.

[31] Fryzuk, M. D. "Side-on end-on bound dinitrogen: An activated bonding mode that facilitates functionalizing molecular nitrogen." *Acc. Chem. Res.* **2009**, *42*, 127-133.

[32] Pool, J. A.; Lobkovsky, E.; Chirik, P. J. "Hydrogenation and cleavage of dinitrogen to ammonia with a zirconium complex." *Nature* **2004**, *427*, 527-530.

[33] Knobloch, D. J.; Lobkovsky, E.; Chirik, P. J. "Carbon monoxide-induced dinitrogen cleavage with group 4 metallocenes: Reaction scope and coupling to N-H bond formation and CO deoxygenation." *J. Am. Chem. Soc.* **2010**, *132*, 10553-10564.

[34] Zhang, X.; Butschke, B.; Schwarz, H. "N_2 activation by a hafnium complex: A DFT study on CO-assisted dinitrogen cleavage and functionalization." *Chem. Eur. J.* **2010**, *16,* 12564.

[35] Blicke, F. F.; Godt, H. C. "Diuretics. I. 3-Substituted paraxanthines." *J. Am. Chem. Soc.* **1954**, *76*, 3653-3655.

[36] Denk, M. K., Hezarkhani, A.; Zheng, F. "Steric and electronic effects in the dimerization of Wanzlick carbenes: The alkyl effect." *Eur. J. Inorg. Chem.* **2007**, 3527-3534.

[37] Lambert, J. B.; Huseland, D. E.; Wang, G. "Synthesis of 1,3-disubstituted diazolidines." *Synthesis* **1986**, 657-658.

[38] Ruiz, R.; Faus, J.; Lloret, F.; Julve, M.; Journaux, Y. "Coordination chemistry of N,N'-bis(coordinating group substituted)oxamides: A rational design of nuclearity tailored polynuclear complexes." *Coord. Chem. Rev.* **1999**, *193-195*, 1069-1117.

[39] Knobloch, D. J.; Lobkovsky, E.; Chirik, P. J. "Functionalization of hafnium oxamidide complexes prepared from CO-induced N_2 cleavage." *J. Am. Chem. Soc.* **2010**, *132*, 15340.

[40] Hazari, N.; Mountford, P. "Reactions and applications of titanium imido complexes." *Acc. Chem. Res.* **2005**, *38*, 839-849.

[41] Fout, A. R.; Kilgore, U. J.; Mindiola, D. J. "The progression of synthetic strategies to assemble titanium complexes bearing the terminal imide group." *Chem. Eur. J.* **2007**, *13*, 9428-9440.

[42] Mindiola, D. J. "Oxidatively induced abstraction reactions. A synthetic approach to low-coordinate and reactive early transition metal complexes containing metal-ligand multiple bonds." *Acc. Chem. Res.* **2006**, *39*, 813-821.

[43] Hidai, M.; Mizobe, Y. "Chemical nitrogen fixation by using molybdenum and tungsten complexes." *Pure Appl. Chem.* **2001**, *73*, 261-263.

[44] Hidai, M. "Chemical nitrogen fixation by molybdenum and tungsten complexes." *Coord. Chem. Rev.* **1999**, *185-186*, 99-108.

[45] Hidai, M.; Mizobe, Y. "Recent Advances in the Chemistry of Dinitrogen Complexes." *Chem. Rev.* **1995**, *95*, 1115-1133.

[46] van Tamelen, E. E. “Design and development of an organic-inorganic system for the chemical modification of molecular nitrogen under mild conditions.” *Acc. Chem. Res.* **1970**, *3*, 361-367.

[47] Mori, M. “Activation of nitrogen for organic synthesis.” *J. Organomet. Chem.* **2004**, *689*, 4210-4227.

[48] Hirotsu, M.; Fontaine, P. P.; Zavalij, P. Y.; Sita, L. R. “Extreme $N\equiv N$ bond elongation and facile N-atom functionalization reactions within two structurally versatile new families of group 4 bimetallic “side-on-bridged” dinitrogen complexes for zirconium and hafnium.” *J. Am. Chem. Soc.* **2007**, *129*, 12690-12692.

[49] Fryzuk, M. D.; Johnson, S. A.; Patrick, B. O.; Albinati, A.; Mason, S. A.; Koetzle, T. F. “New mode of coordination for the dinitrogen ligand: Formation, bonding, and reactivity of a tantalum complex with a bridging N_2 unit that is both side-on and end-on.” *J. Am. Chem. Soc.* **2001**, *123*, 3960-3973.

[50] Benito-Garagorri, D.; Bernskoetter, W. H.; Lobkovsky, E.; Chirik, P. J. “1,4-addition of alkyl halides to a side-on bond hafnocene dinitrogen complex.” *Organometallics* **2009**, 4807-4813.

[51] Knobloch, D. J.; Benito-Garagorri, D.; Bernskoetter, W. H.; Keresztes, I.; Lobkovsky, E.; Toomey, H. E.; Chirik, P. J. “Addition of methyl triflate to a hafnocene dinitrogen complex: Stepwise N_2 methylation and conversion to a hafnocene hydrazonato compound.” *J. Am. Chem. Soc.* **2009**, *131*, 14903-14912.