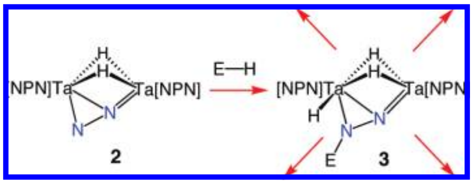
ACCOUNTS
of chemical research

Side-on End-on Bound Dinitrogen: An Activated Bonding Mode That Facilitates Functionalizing Molecular Nitrogen

MICHAEL D. FRYZUK*
Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, British Columbia V6T 1Z1, Canada

RECEIVED ON FEBRUARY 29, 2008

CONSPECTUS



Molecular nitrogen is the source of all of the nitrogen necessary to sustain life on this planet. How it is incorporated into the biosphere is complicated by its intrinsic inertness. For example, biological nitrogen fixation takes N_2 and converts it into ammonia using various nitrogenase enzymes, whereas industrial nitrogen fixation converts N_2 and H_2 to NH_3 using heterogeneous iron or ruthenium surfaces. In both cases, the processes are energy-intensive. Is it possible to discover a homogeneous catalyst that can convert molecular nitrogen into higher-value organonitrogen compounds using a less energy-intensive pathway? If this could be achieved, it would be considered a major breakthrough in this area.

In contrast to carbon monoxide, which is reactive and an important feedstock in many homogeneous catalytic reactions, the isoelectronic but inert N_2 molecule is a very poor ligand and not a common industrial feedstock, except for the above-mentioned industrial production of NH_3. Because N_2 is readily available from the atmosphere and because nitrogen is an essential element for the biosphere, attempts to discover new processes involving this simple small molecule have occupied chemists for over a century. Since the first discovery of a dinitrogen complex in 1965, inorganic chemists have been key players in this area and have contributed much fundamental knowledge on structures, binding modes, and reactivity patterns. For the most part, the synthesis of dinitrogen complexes relies on the use of reducing agents to generate an electron-rich intermediate that can interact with this rather inert molecule.

In this Account, a facile reaction of dinitrogen with a ditantalum tetrahydride species to generate the unusual side-on end-on bound N_2 moiety is described. This particular process is one of a growing number of new, milder ways to generate dinitrogen complexes. Furthermore, the resulting dinitrogen complex undergoes a number of reactions that expand the known patterns of reactivity for coordinated N_2. This Account reviews the reactions of $([NPN]Ta)_2(\mu\text{-}H)_2(\mu\text{-}\eta^1{:}\eta^2\text{-}N_2)$, **2** (where NPN $=$ $PhP(CH_2SiMe_2NPh)_2$), with a variety of simple hydride reagents, E-H (where E-H $=$ R_2BH, R_2AlH, $RSiH_3$, and $Cp_2ZrCl(H)$), each of which results in the cleavage of the N—N bond to form various functionalized imide and nitride moieties. This work is described in the context of a possible catalytic cycle that in principle could generate higher-value nitrogen-containing materials and regenerate the starting ditantalum tetrahydride. How this fails for each particular reagent is discussed and evaluated.

Introduction

A long-standing goal in chemistry is the activation and functionalization of molecular nitrogen. Despite its ready availability (78% of the air we breathe) and its importance to life in the biosphere of this planet,[1] this simple diatomic molecule is inert, which makes it challenging to use as a feedstock. Of course, exceptions to its lack of reactivity include the conversion of N_2 to ammonia (NH_3), industrially via the Haber—Bosch process[2,3] and biologically by nitrogenase enzymes contained in certain bacteria.[4,5]In fact, ammonia is one of primary biological inputs for protein synthesis and comprises one of the key elements of the nitrogen cycle. It is estimated that 40% of the nitrogen contained in the human body originates from ammonia produced by the Haber—Bosch process.[1]

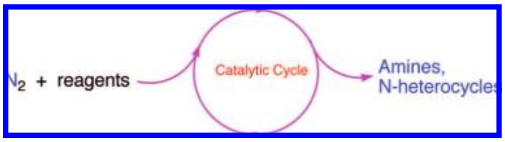
www.pubs.acs.org/acr
10.1021/ar800061g CCC: $71.50

The conversion of dinitrogen to ammonia has occupied the attention of inorganic chemists for some time.[6−8] Ammonia can be detected upon hydrolysis of reduced titanocene complexes,[9] hydrogenation of a dinuclear zirconium derivative,[10] and protonation of certain molybdenum− and iron−dinitrogen complexes.[11,12] The Chatt cycle refers specifically to the protonation of coordinated molybdenum− and tungsten−dinitrogen complexes and represents an enormous amount of work in attempts to model nitrogenase. A few years ago, a catalytic variant was reported that takes advantage of the different solubilities of a reducing agent and an acid to slow down a possible side reaction and allow the protonation of coordinated N_2 to produce ammonia catalytically with four turnovers using a soluble molybdenum catalyst.[13] This remarkable achievement is unfortunately not transferable to any other system.

Trisilylamines have also been produced catalytically via the reduction of dinitrogen at a molybdenum complex using sodium amalgam and reacting the system with Me_3SiCl.[14] This reaction is catalytic with 34 turnovers of $N(SiMe_3)_3$ produced. This reaction, while quite intriguing, is also flawed because the production of $Me_3SiSiMe_3$ indicates that the reducing agent and the electrophile (Me_3SiCl) undergo a competing short-circuiting reaction. However, it does represent a new kind of target to consider, that of a substituted amine.

All of the above reactions can be summarized as a lead up to what some call the "holy grail" of nitrogen fixation, that is, a homogeneously catalyzed process that converts readily available N_2 into some higher-value organonitrogen species, such as an amine, an N-heterocycle, or some related nitrogen-containing compound. This is represented in Scheme 1 using a simplified, generic cycle. In this Account, some hints about possible solutions to this lofty goal will be described in the context of some of our recent research involving a ditantalum−dinitrogen complex.

SCHEME 1



Catalysis Preamble

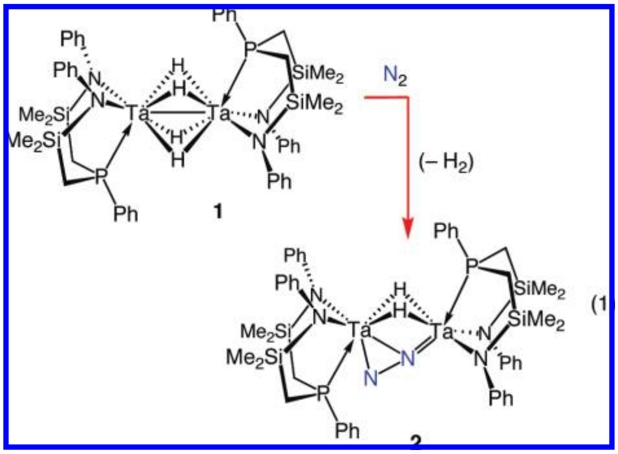
Catalytic cycles involving transition metal complexes have a number of elementary or fundamental steps that are common to many transformations. From the organometallic literature, terms such as migratory insertion, oxidative addition, and reductive elimination are part of the vocabulary of homogeneous catalysis.[15] For example, processes that involve CO as a reactant such as hydroformylation, acetic acid synthesis, and ethylene/CO polymerization all involve migratory insertion of the CO unit into a metal−carbon bond to generate acyl species. Yet with the isoelectronic N_2 molecule, there are no examples of dinitrogen undergoing any migratory insertion process.[16] In fact, formation of N−C or N−H bonds at a coordinated dinitrogen generally involves external attack by some reagent, typically an electrophile.[8,11] Thus, even with this very cursory analysis, it is clear that any catalytic process that involves molecular nitrogen will rely on alternative steps.

As already mentioned, the Haber−Bosch process generates NH_3 from N_2 and H_2. Can this heterogeneously catalyzed process provide hints as to what might work in a homogeneously catalyzed system? Dinitrogen is cleaved on the activated Fe or Ru surface to generate nitrides that react directly with surface hydrogen atoms to generate imido (=NH), amido ($-NH_2$), and ammine ($-NH_3$) species.[2] There are some interesting case studies on diiron−nitride complexes that can add H_2 to generate bridging imide−hydride structures.[17] However, in this particular case, the nitride was not generated from N_2 and so an important first step is missing.

One of biggest hurdles to the utilization of molecular nitrogen as a reagent in a homogeneous catalytic process is the fact that N_2 is a poor ligand. A central dogma to the activation of small molecules by transition metal complexes is that the small molecule must bind to the metal center at some point or at least be proximate to some reactive portion of the complex. Because N_2 has no dipole moment and is both a poor σ-electron donor and a poor π-acceptor, getting it to bind to metal complexes has been a long-standing challenge.

Background

In 1998, we serendipitously discovered a simple way to prepare a new dinitrogen complex.[18,19] The *eureka* transformation is shown in eq 1.



At the time we were heavily involved in group 5 chemistry using the macrocyclic P_2N_2 ligand (where P_2N_2 = PhP-

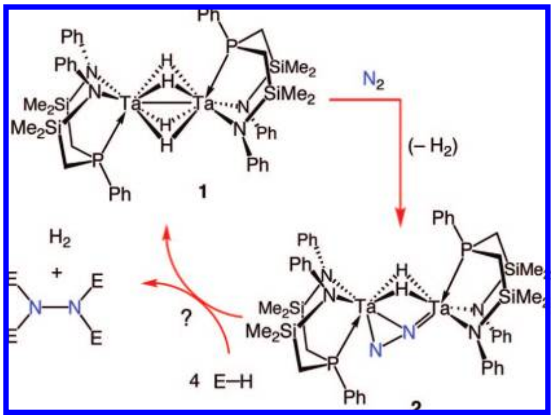
$(CH_2SiMe_2NSiMe_2CH_2)_2PPh)$, attempting to extend some intriguing group 4 dinitrogen chemistry.[20] Eventually we happened onto the Ta(V) starting material $TaMe_3Cl_2$ from which we could generate $TaMe_3[P_2N_2]$ in excellent yields.[21,22] Since the standard method of generating dinitrogen complexes is reduction of a high oxidation state halide complex, generally using an alkali metal reagent such as Na/Hg or KC_8, we examined ways to convert this precursor into some halide-containing material. To accomplish this, we first hydrogenated the trimethyl complex and obtained the dinuclear tetrahydride, $([P_2N_2]Ta)_2(\mu\text{-}H)_4$. While this complex does display some interesting reactivity, we were unable to convert the hydrides to halides by reaction with CH_3I because this resulted in oxidation to generate Ta(V)/Ta(IV) mixed-valent dinuclear species, $\{([P_2N_2]Ta)_2(\mu\text{-}H)_4\}^{+}I^{-}$.[21] We reasoned that the tetradentate P_2N_2 ligand system may be hindering attack at the metal by external reagents, so we examined a tridentate ligand system NPN that is derived from the P_2N_2 donor set. A similar sequence of generating the trimethyltantalum complex $TaMe_3[NPN]$ followed by reaction with H_2 generates the dinuclear tetrahydride $([NPN]Ta)_2(\mu\text{-}H)_4$. As shown in eq 1, we were surprised to discover that this dinuclear hydride reacts spontaneously with dinitrogen to generate a dinuclear dinitrogen complex that has a side-on end-on bound dinitrogen.[19]

This reaction was remarkable for a number of reasons. First, typical conditions for the preparation of dinitrogen complexes of the early transition elements (groups 4−6) require the addition of strong reducing agents such as the alkali metals (e.g., Na/Hg; KC_8) to reduce a precursor complex in the presence of N_2; by avoiding an external reducing agent, one can facilitate a possible catalytic cycle. Second, the coordinated dinitrogen formed during this process is activated on the basis of the lengthened N−N bond (from 1.1 Å in free N_2 to 1.342 Å in the complex). Third, the side-on, end-on coordination mode is itself unusual and represents a new motif in dinitrogen chemistry.

We reasoned that given the facility of this reaction, it might be possible to design a productive, potentially catalytic cycle that could generate functionalized hydrazines by multiple additions of simple element hydride reagents across the side-on end-on dinitrogen unit; in essence this would be a proof of principle of the generic cycle shown in Scheme 1. This proposed cycle is outlined in Scheme 2.

To us, this seemed like a straightforward matter of searching for the correct simple E-H reagent that would add multiple times across the coordinated N_2 unit. In retrospect, we were quite naive. But we ended up learning a lot about how things can go awry.

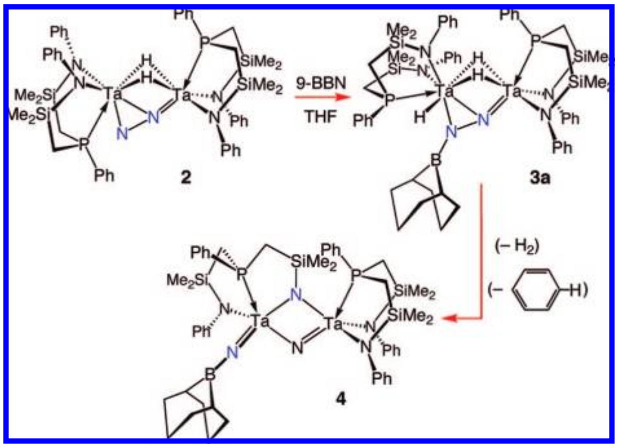
SCHEME 2



Addition of E-H = Boranes

Our first foray into finding that reagent was with 9-BBN (where 9-BBN = 9-borobicyclononane).[23] While this produced a very promising first result, it became clear that there were intrinsic problems to getting this reaction to succeed beyond a first B−H addition. The overall cascade of reactions is shown in Scheme 3.

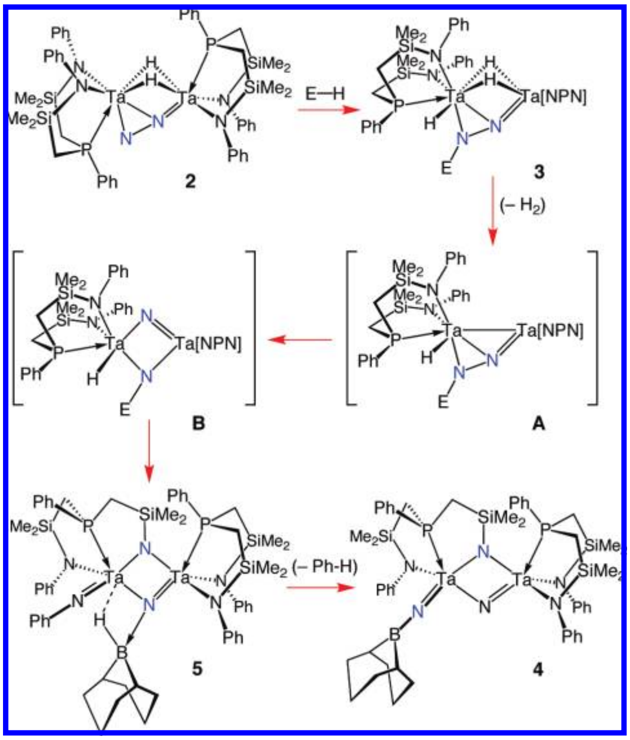
SCHEME 3



One equivalent of 9-BBN adds across **2** to generate adduct **3a**, which has been structurally characterized. Interestingly, attempts to grow crystals of **3a** over a long period of time resulted in the formation of a new product that was eventually characterized as borylimide **4**. This species is also accompanied by the formation of benzene, which originates from one N-Ph group of the ancillary ligand and the hydrogen originally installed from the hydroboration reagent; also produced is 1 equiv of H_2 that derives from the bridging hydrides. A mechanism was proposed on the basis of the isolation of a number of intermediates, and is shown in Scheme 4.

The formation of **3** (for E-H = 9-BBN, **3a** in Scheme 3) triggers loss of H_2 to produce the first general intermediate **A**, in which the pair of electrons that results from dihydrogen reductive elimination is stored as a Ta−Ta bond. How exactly the elec-

SCHEME 4



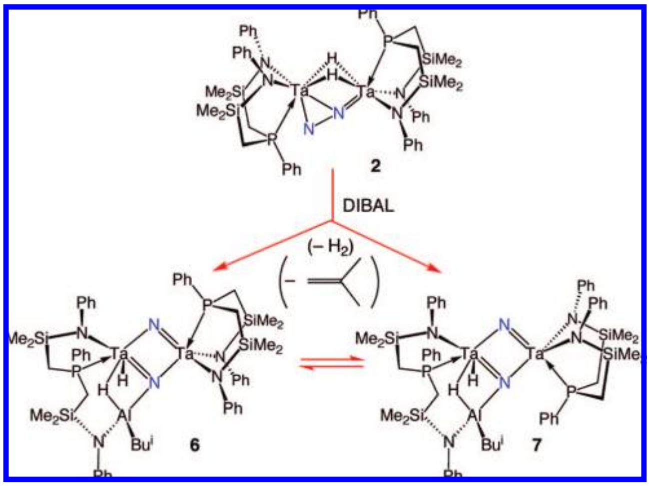
trons are stored is unimportant since they are shunted to the dinitrogen unit, which results in N—N bond cleavage to generate the imide—nitride intermediate **B**.[24] What occurs next is specific to boron hydride reagents; migration of a silyl group from one of the NPN arms of the ancillary ligand to the exposed nitride of **B** occurs to generate an isolable intermediate **5** that was structurally characterized. Without this particular structure, it would be difficult to propose a compelling mechanism for the conversion of **3a** to **4**. Further evidence for the migration of one of the silyl units to a bridging nitride was obtained by ^{29}Si NMR spectroscopy in which ^{15}N-labeled starting dinitrogen complex **2** resulted in evidence for the migrated silyl group attachment to a nitrogen atom that originated from coordinated N_2. Obviously this cascade of reactions in which the ancillary ligand undergoes an irreversible transformation is not a solution to the proposed catalytic cycle shown in Scheme 2.

We examined other readily available boron hydride reagents such as Cy_2BH and thexylborane, both of which gave similar outcomes.[25] Even when excess borane reagents are present similar silyl group migrations still occur, but the resulting excess borane reagents trap the final product.

Addition of E-H = Alanes

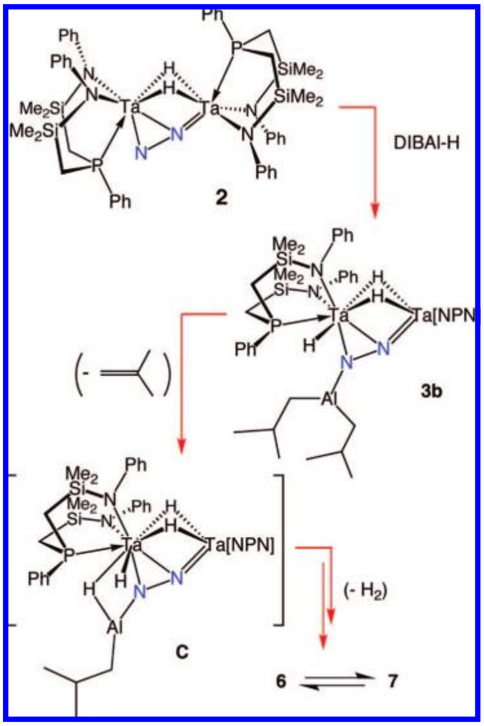
Another readily available simple element hydride reagent is DIBAL (diisobutylaluminum hydride, $(^{i}Bu_2AlH)_2$). Addition of 1 equiv of DIBAL to dinitrogen complex **2** resulted in a very fast reaction and the formation of two diastereoisomers **6** and **7**, the difference being in the relative stereochemistry of the intact NPN units.[26] This overall process is shown in Scheme 5.

SCHEME 5



As can be seen, a different kind of ligand rearrangement occurs with this E-H reagent; while both NPN ligands remain intact, one arm of one NPN undergoes a migration from Ta to Al. In addition to this ligand rearrangement, the bridging hydrides of **2** are eliminated along with 1 equiv of isobutene. By monitoring this reaction at low temperature, a series of intermediates could be observed, which provided the basis for the mechanism shown in Scheme 6.

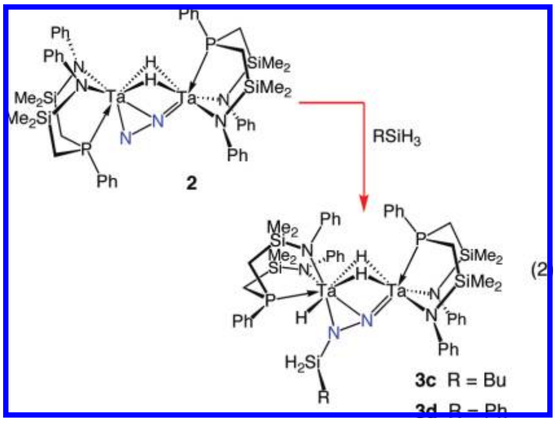
SCHEME 6



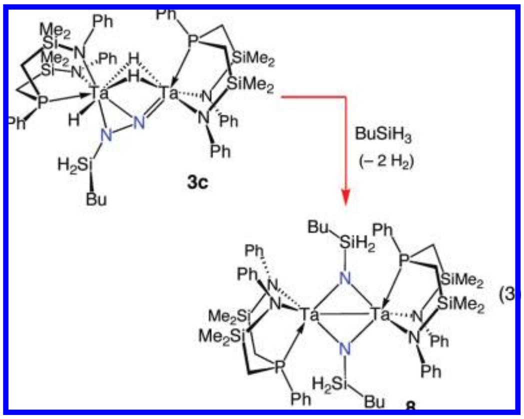
The first intermediate observed (at −60 °C) is the initial adduct **3b** that is identical to the hydroboration adduct **3a** formed in Scheme 2. However, the alane system diverges here as isobutene is eliminated to generate another intermediate **C** that loses H_2, undergoes N−N bond cleavage (presumably by the general process outlined in Scheme 4 via **A** and **B**), and ultimately undergoes migration of the one terminus of the NPN ligand from tantalum to aluminum.

Addition of E-H = Silanes

Primary silanes such as butylsilane or phenylsilane add to the dinitrogen complex **2** to generate analogous silyl−hydride adducts **3c** (R = Bu) and **3d** (R = Ph) shown below in eq 2.[27]



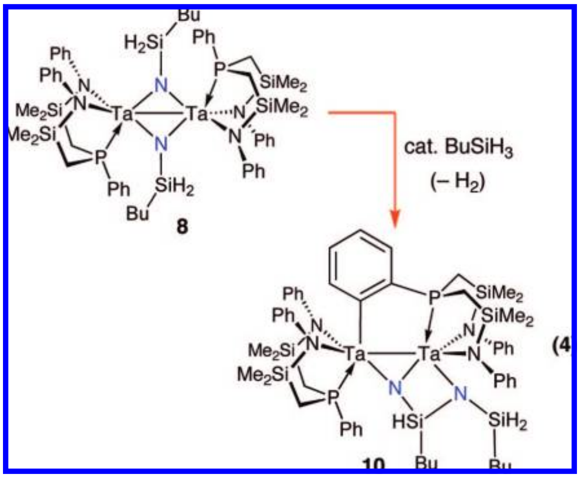
In the presence of excess butylsilane, **3c** cleanly converts into the disilylimide dimer **8** (eq 3).



The mechanism of this transformation has been elucidated by a similar sequence of studies already described for the hydroboration and hydroalumination reactions; this is shown in Scheme 7.

Similar to the hydroboration and hydroalumination, the first silane addition adduct **3c** triggers H_2 loss to generate the proposed Ta−Ta bonded intermediate, which subsequently generates the imide−nitride **9**; in the hydrosilyation sequence, we were able to structurally characterize **9** to provide further evidence for the viability of all of the mechanisms discussed for E-H addition and N−N bond cleavage. In the presence of an additional equivalent of H_3SiBu, addition of Si−H across the nitride double bond of **9** results in the formation of presumed intermediate **E**, which upon loss of H_2 generates the observed disilylimide product **8**.

The formation of **8** is tantalizingly close to achieving the goal outlined in Scheme 2. Indeed for a successful outcome, all that is needed is the addition of more silane, elimination of tris(butylsilyl)amine and regeneration of the ditantalum tetrahydride **1**. However, even in the presence of excess silane, no elimination of silylated amines could be detected; instead, a C−H activation process occurs along with a core rearrangement that thwarts the desired process; this is shown in eq 4.[28]

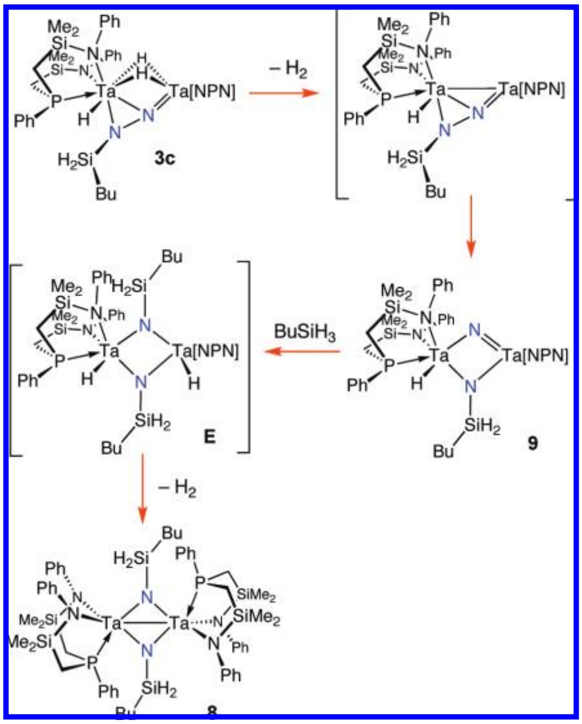


Interestingly, formation of **10** requires some silane to be present, even less than 1 equiv is sufficient to initiate loss H_2 via C−H and Si−H bond activations. In the absence of added silane, the disilylimide **8** is stable to heating at 100 °C for 8 h. The exact sequence of reactions in this process is not known.

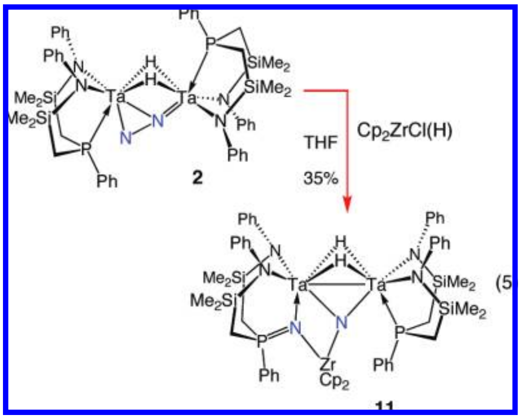
Addition of E-H = $Cp_2ZrCl(H)$

We decided to examine other hydridic reagents and chlorobis(cyclopentadienyl)−hydridozirconium(IV) (Schwartz's reagent) was investigated. The reaction of $Cp_2ZrCl(H)$ with **2** resulted in the formation of a deep purple material in rather modest yield (only 35%).[29] Unlike any of the other reactions thus far described, which always began with formation of the C_1-symmetric adducts of the general structure **3** (**3a**, E = BR_2; **3b**, E = $AlBu^i{}_2$; **3c**, E = SiH_2R), the material produced in this reaction was C_s-symmetric. Moreover, there was no evidence for a terminal hydride, which is also common for the initial

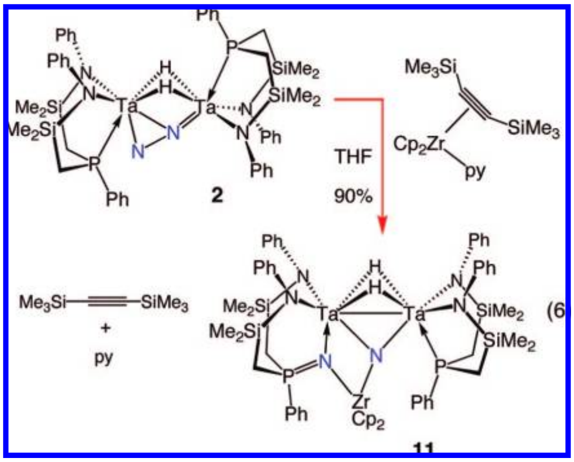
SCHEME 7



adducts **3**. The identity of this reaction product was shown to be **11** by X-ray crystallography (eq 5).



The outcome of the reaction of this zirconium hydride reagent is dramatically different from the previous main-group element hydrides described above. The new ditantalum–zirconium derivative **11** shows a zirconocene unit inserted into the N–N bond of the coordinated dinitrogen, and one of the phosphine donors has dissociated from tantalum and formed a phosphinimide unit. What was also unusual about this reaction was that the hydride of the starting zirconocene reagent was apparently not involved, *and the chloride was also missing*. We explored this process further by modifying the zirconocene reagent; for example, use of the chloride-free dihydride Cp_2ZrH_2 generated **11** in higher yield (76%) with release of H_2, implying that neither $Cp_2ZrCl(H)$ nor Cp_2ZrH_2 reacts as an E-H reagent as was originally anticipated. In fact, the highest yields of **11** were obtained by using a nonhydride source of zirconocene, $Cp_2Zr(Me_3SiCCSiMe_3)(py)$; this is shown in eq 6.



A mechanism for this transformation has been proposed that involves generation of zirconocene that binds to **2**, transfers two electrons to split the N–N bond, and then promotes phosphinimine formation by dissociation of the ancillary phosphine ligand and subsequent attack at the bridging nitride.[29]

Prognosis

With this particular combination of NPN ancillary ligand and group 5 metal, we have been able to achieve a number of remarkable transformations. The generation of the dinitrogen complex **2** from the tetrahydride precursor **1** is an important first step to any potential catalytic cycle. Bypassing the use of a strong reducing agent like an alkali metal is necessary to provide mild conditions for the incorporation of the N_2 ligand. And as already mentioned, if the dinitrogen could be functionalized by addition of simple hydride reagents such as E-H, this could in principle regenerate the precursor tetrahydride, as outlined in Scheme 2. Unfortunately, this could not be achieved despite a variety of simple hydride reagents examined. What did happen was that in every case, addition of hydride reagents resulted in nitrogen–nitrogen bond cleavage and functionalization at nitrogen. While these results were encouraging, other processes occurred that made these transformations problematic. Ancillary ligand rearrangements were observed in hydroboration, hydroalumination, and even in hydrosilylation in certain cases. Our attempts to extend this to hydrozirconation resulted in a different mechanism and outcome, but the ancillary ligand rearrangement was also observed.

Our present goals use the above successes as starting points and the obvious shortcomings as new leads to redesign the ancillary ligand. Some of the initial results are promising.[30] We also need to focus on how to release the functionalized nitrogen material away from the metal. Some synthetic cycles have been recently reported, which unfortunately are not catalytic. Part of the problem will ultimately rely on matching the right ancillary ligand set with the appropriate metal such that the combination will be azophilic enough to promote N_2 coordination and activation, but not so azophilic that a functionalized, higher value nitrogen material is not releasable. Searching chemical space for these particular combinations is the goal of many groups including our own.[30−32]

All of this work was generously funded by NSERC of Canada. Special thanks go to Samuel A. Johnson and Bruce A. MacKay for their insight and skill in advancing this project.

BIOGRAPHICAL INFORMATION

Michael D. Fryzuk was born in Sarnia, Ontario, and received his B.Sc. and Ph.D. degrees from the University of Toronto. He has been a faculty member at the University of British Columbia since 1979.

FOOTNOTES

*E-mail: fryzuk@chem.ubc.ca.

REFERENCES

1 Smil, V. *Enriching the Earth: Fritz Haber, Carl Bosch, and the Tranformation of World Food Production*; The MIT Press: Boston, MA, 2001.

2 Ertl, G. Heterogeneous Catalysis on the Atomic Scale. *Chem. Rec.* **2001**, *1*, 33–45.

3 Schlögl, R. Catalytic Synthesis of Ammonia - A “Never-ending” Story. *Angew. Chem., Int. Ed.* **2003**, *42*, 2004–2008.

4 Burgess, B. K.; Lowe, D. J. Mechanism of Molybdenum Nitrogenase. *Chem. Rev.* **1996**, *96*, 2983–3011.

5 Sellmann, D.; Sütter, J. In Quest of Competitive Catalysts for Nitrogenases and Other Metal Sulfur Systems. *Acc. Chem. Res.* **1997**, *30*, 460–469.

6 Gambarotta, S. Dinitrogen Fixation and Activation after 30 Years: A Puzzle Still Unsolved. *J. Organomet. Chem.* **1995**, *500*, 117–126.

7 Gambarotta, S.; Scott, J. Multimetallic Cooperative Activation of N_2. *Angew. Chem., Int. Ed.* **2004**, *43*, 5298–5308.

8 Hidai, M.; Mizobe, Y. Recent Advances in the Chemistry of Dinitrogen Complexes. *Chem. Rev.* **1995**, *95*, 1115–1133.

9 Pez, G. P.; Apgar, P.; Crissey, R. K. Reactivity of μ-(η^1:η^5-Cyclopentadienyl)-tris(η-cyclopentadienyl)dititanium ([μ-(η^1:η^5-C_5H_4)](η-C_5H_5)$_3$$Ti_2$) with Dinitrogen. Structure of a Titanium Complex with a Triply Coordinated Dinitrogen Ligand. *J. Am. Chem. Soc.* **1982**, *104*, 482–490.

10 Pool, J. A.; Lobkovsky, E.; Chirik, P. J. Hydrogenation and Cleavage of Dinitrogen to Ammonia with a Zirconium Complex. *Nature* **2004**, *427*, 527–530.

11 Chatt, J.; Dilworth, J. R.; Richards, R. L. Recent Advances in the Chemistry of Nitrogen Fixation. *Chem. Rev.* **1978**, *78*, 589–625.

12 Gilbertson, J. D.; Szymczak, N. K.; Tyler, D. R. Reduction of N_2 to Ammonia and Hydrazine Utilzing H_2 as the Reductant. *J. Am. Chem. Soc.* **2005**, *127*, 10184–10185.

13 Yandulov, D. V.; Schrock, R. R. Catalytic Reduction of Dinitrogen to Ammonia at a Single Molybdenum Center. *Science* **2003**, *301*, 76–78.

14 Komori, K.; Oshita, H.; Mizobe, Y.; Hidai, M. Catalytic Conversion of Molecular Nitrogen into Silylamines Using Molybdenum and Tungsten Dinitrogen Complexes. *J. Am. Chem. Soc.* **1989**, *111*, 1939–141.

15 Parshall, G. W. *Homogeneous Catalysis*; John Wiley and Sons: New York, 1980.

16 Fryzuk, M. D. Activation and Functionalization of Molecular Nitrogen by Metal Complexes. *Chem. Rec.* **2003**, *3*, 2–11.

17 Brown, S. D.; Mehn, M. P.; Peters, J. C. Heterolytic H_2 Activation Mediated by Low-Coordinate L_3Fe-(μ-N)-FeL_3 Complexes To Generate Fe(μ-NH)(μ-H) Species. *J. Am. Chem. Soc.* **2005**, *127*, 13146–13147.

18 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.

19 Fryzuk, M. D.; Johnson, S. A.; Rettig, S. J. A New Mode of Coordination for the Dinitrogen Ligand: A Dinuclear Tantalum Complex with a Bridging N_2 Unit That Is Both Side-On and End-On. *J. Am. Chem. Soc.* **1998**, *120*, 11024–11025.

20 Fryzuk, M. D.; Love, J. B.; Rettig, S. J.; Young, V. G. Transformations of Coordinated Dinitrogen by Reaction with Dihydrogen and Primary Silanes. *Science* **1997**, *275*, 1445–1447.

21 Fryzuk, M. D.; Johnson, S. A.; Rettig, S. J. Synthesis and Bonding in the Diamagnetic Dinuclear Ta(IV) Hydride Species $\{[P_2N_2]Ta\}_2(\mu\text{-}H)_4$ and the Paramagnetic Cationic Dinuclear Hydride Species $\{([P_2N_2]Ta)_2(\mu\text{-}H)_4\}^+I^-$ ($[P_2N_2]$ = $PhP(CH_2SiMe_2N\text{-}SiMe_2CH_2)_2PPh$): The Reducing Ability of a Metal—Metal Bond. *Organometallics* **2000**, *19*, 3931–3941.

22 Fryzuk, M. D.; Johnson, S. A.; Rettig, S. J. Synthesis and Structure of the Tantalum Trimethyl Complex $[P_2N_2]TaMe_3$ and Its Conversion to the Tantalum Methylidene Species $[P_2N_2]Ta{=}CH_2(Me)$ ($[P_2N_2]$ = $PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh$). *Organometallics* **1999**, *18*, 4059–4067.

23 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.

24 Studt, F.; MacKay, B. A.; Fryzuk, M. D.; Tuczek, F. N-N Splitting of a Functionalized μ-η^1:η^2 Coordinated N_2 Ligand Leading to a μ-Nitrido μ-Imido Core: Mechanistic Insight from DFT. *Dalton Trans.* **2006**, 1137–1140.

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 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.

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 Coordination Dinitrogen in a Ditantalum Complex: Cleavage and Functionalization of N_2. *J. Am. Chem. Soc.* **2006**, *128*, 9472–9483.

29 Spencer, L. P.; MacKay, B. A.; Patrick, B. O.; Fryzuk, M. D. Unanticipated Two-Electron Reduction Leads to Cleavage and Functionalization of Coordinated Dinitrogen. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 17094–17098.

30 MacLachlan, E. A.; Hess, F. M.; Patrick, B. O.; Fryzuk, M. D. New Side-On Bound Dinitrogen Complexes of Zirconium Supported by an Arene-Bridged Diamidophosphine Ligand and Their Reactivity with Dihydrogen. *J. Am. Chem. Soc.* **2007**, *129*, 10895–10905.

31 Hirotsu, M.; Fontaine, P. P.; Epshteyn, A.; Zavalij, P. Y.; Sita, L. R. Dinitrogen Activation at Ambient Temperatures: New Modes of H_2 and $PhSiH_3$ Additions for an “End-On-Bridged” $[Ta(IV)]_2(\mu\text{-}\eta^1\text{: }\eta^1\text{-}N_2)$ Complex and for the Bis(μ-nitrido) $[Ta(V)(\mu\text{-}N)]_2$ Product Derived from Facile N≡N Bond Cleavage. *J. Am. Chem. Soc.* **2007**, *129*, 9284–9285.

32 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.