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Bimetallic Cooperative Cleavage of Dinitrogen to Nitride and Tandem Frustrated Lewis Pair Hydrogenation to Ammonia

Laurence R. Doyle, Ashley J. Wooles, and Stephen T. Liddle*

Abstract: Although reductive cleavage of dinitrogen (N_2) to nitride (N_3^-) and hydrogenation with dihydrogen (H_2) to yield ammonia (NH_3) is accomplished in heterogeneous Haber Bosch industrial processes on a vast scale, sequentially coupling these elementary reactions together with a single metal complex remains a major challenge for homogeneous molecular complexes. Here, we report that reaction of a chloro titanium triamidoamine complex with magnesium effects complete reductive cleavage of N_2 to give a dinitride dititanium dimagnesium ditriamidoamine complex. Tandem H_2 splitting by a phosphine-borane Frustrated Lewis Pair (FLP) shuttles H-atoms to the N_3^- , evolving NH_3 . Isotopic labelling experiments confirm N_2 - and H_2 -fixation. Though not yet catalytic, these results give unprecedented insight into coupling N_2 - and H_2 -cleavage and N-H bond formation steps together, highlight the importance of heterobimetallic cooperativity in N_2 -activation, and establish FLPs in NH_3 synthesis.

Ammonia, NH_3 , is a key chemical feedstock for the production of a vast array of organo-nitrogen compounds.^[1] Nitrogenase enzymes produce NH_3 from dinitrogen, N_2 , at ambient temperature and pressure, but this requires eight protons, H^+ , eight electrons, e^- , and hydrolysis of sixteen ATP molecules per N_2 .^[2] In contrast, chemical industry produces NH_3 using the Haber Bosch, HB, process where N_2 and H_2 combine to give NH_3 over heterogeneous metal catalysts.^[2] However, high temperatures and pressures are required in HB NH_3 synthesis, reflecting the challenge of cleaving the N_2 triple bond.

Following the inception of HB NH_3 synthesis, considerable efforts have been made to gain insight into the chemical and physical processes involved.^[3] The rate-limiting step is N_2 chemisorption on the metal catalyst and N-N bond cleavage to give surface-bound nitrides, N_3^- , which then combine with adsorbed H-atoms, produced by essentially barrier-less H_2 dissociation on the metal surface, to give NH_3 . Because the reaction is heterogeneous it is difficult to study in atomic detail; however, there is evidence that multi-metallic sites are integral to N_2 activation, and that the presence of various Group 1 and 2 metal oxides enhances catalyst reactivity by direct interaction with N_2 or as “electronic” promoters.^[3] Thus, there is great interest in studying homogeneous complexes as surrogates for heterogeneous HB NH_3 synthesis as they can provide detailed information on reaction intermediates and mechanisms.^[1-3]

Ti, V, Mo, Fe, Ru, Os, and Co complexes have been shown to catalytically reduce N_2 to NH_3 with H^+/e^- .^[4,5] These catalytic cycles are based on sequential biomimetic-type protonation/reduction of M- N_2 linkages, contrasting to direct cleavage of N_2/H_2 in HB chemistry. Indeed, molecular species

that spontaneously cleave N_2 to N_3^- are rare,^[6] and none of the resulting metal-nitrides react with H_2 ; other metal-nitrides can react with H_2 , to make a metal-amide, M- NH_2 , or NH_3 , but they derive from azides rather than N_2 -splitting.^[7] Very few complexes bind N_2 and react further with H_2 , giving mono-protonation of coordinated N_2 ,^[8] NH_3 in low yield,^[9] or NH_3 after exposure to H^+ .^[10] Weakly acidic M- H_2 complexes can effect protonation of M- N_2 complexes to give M- NNH_2 ,^[11] and in one case NH_3 was formed.^[11b] Thus, in contrast to HB NH_3 synthesis, activating and cleaving H_2 appears to be the impediment to progress. In an alternative approach that side-steps the H_2 -activation issue, transition metal hydrides can activate N_2 and cleave it to N_3^- ,^[12] but no subsequent hydrogenation occurs,^[12a,b] or reactions stop at $\mu-N(H)$ or $\mu-NH_2$ stages.^[9,12c,d,13] It has been proposed that Frustrated Lewis Pairs (FLPs), that are capable of activating and splitting H_2 , could be combined with metal-based reductive cleavage of N_2 .^[14] However, despite the burgeoning nature of FLP-mediated hydrogenations of organic substrates,^[15] combining this concept with N_2 activation to make NH_3 has remained an unmet goal,^[16] but mono-/di-protonation of metal- N_2 units, borylation/silylation of M- N_2 -B FLPs, and a model for FLP- N_2 activation have now been realised.^[17]

Here, we report homogeneous reductive cleavage of N_2 to N_3^- by a Ti-Mg complex supported by a simple triamidoamine ligand, and conversion of N_3^- to NH_3 using hydrogen from H_2 split by a FLP. Heterobimetallic cooperativity facilitates reductive cleavage of N_2 , and by using a FLP the barrier to activating and cleaving H_2 is overcome. The bridging nature of the nitride renders it amenable to full protonation to give NH_3 that can be removed by vacuum distillation without the need for acidification, thereby introducing FLPs to NH_3 -synthesis.

Previously,^[5] we reported that $[Ti(Tren^{TMS})Cl]$ (**1**, $Tren^{TMS} = \{N(CH_2CH_2NSiMe_3)_3\}^3$) can be reduced by K (K mirror, KC_8 , or $KC_{10}H_8$) to give $[Ti(Tren^{TMS})]$; this can bind to N_2 to give the end-on: end-on N_2 -complex $\{[Ti(Tren^{TMS})]_2(N_2)\}$ and further reduction with K gives $\{[Ti(Tren^{TMS})]_2(N_2K_2)\}$ (**2**) that formally contains N_2^{4-} where the N-N bond is retained, Scheme 1. Nevertheless, **2** produces up to 18 equivalents of NH_3 when treated with excess H^+/e^- .^[5] Since it is clear that K ($E^\circ = -2.92$) plays a cooperative, directing role in that reduction chemistry we investigated what effect replacing it with the milder reducing agent Mg ($E^\circ = -2.37$) would have.^[18] Thus, **1** was treated with excess Mg in N_2 -saturated 1,2-dimethoxyethane (DME) solvent, in the presence of ten equivalents of 1,4-dioxane, Scheme 1. Brief sonication is required to initiate the reaction - we assume due to a kinetic delay from surface passivation of the Mg - as demonstrated by a colour change from orange to green. After a 3 day stir, a white precipitate forms with a purple-brown supernatant, which was concentrated and removed by filtration. The remaining solids were extracted with THF and filtered from the excess Mg and insoluble $[MgCl_2(1,4-dioxane)]_\infty$ by-product. Removal of the THF and recrystallisation of the resulting solid from toluene gives colourless crystals of diamagnetic $\{[Mg(Tren^{TMS})]_2\{(\mu_3-N)_2(Ti)_2\}\}$ (**3**), Scheme 1, in a ~20% crystalline yield.^[19]

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Scheme 1. The Ti complex **1** gives different N₂-reduction products depending on the nature of the reducing agent, producing the hydrazido complex **2** when reduced with KC₈ (reference 5j), or the dinitride complex **3** when reduced with elemental Mg (this work).

The solid-state structure of **3**, Figure 1, consists of two Ti centres, each coordinated by two [Mg(Tren^{TMS})][−] fragments (both κ¹-N:κ¹-N') and two μ₃-N^{3−} ligands, which bridge both Ti centres and a Mg centre each. The resulting Ti(μ-N)₂Ti core is planar, with each pyramidalised nitride (sum of angles = 280.91(14)°) residing 1.04 Å from the center of each Ti₂Mg plane. Multi-nuclear ¹H, ¹³C, and ²⁹Si NMR spectra of C₆D₆ solutions of **3** exhibit sharp resonances within normal diamagnetic ppm ranges consistent with a closed-shell, diamagnetic Ti^{IV}/Ti^{IV} complex, and are congruent with the solid-state structure in which the usual 3-fold symmetry of (Tren^{TMS})^{3−} is lost and the two distinct SiMe₃ environments are retained (2:1 ratio).

Figure 1. Molecular structure of [{Mg(Tren^{TMS})}]₂{(μ₃-N)₂(Ti)₂} (**3**) at 100 K with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°) are: Ti1-N2, 2.0147(19); Ti1-N3A, 2.0400(19); Ti1-N5, 1.8524(19); Ti1-N5A, 1.8532(19); Mg1-N1, 1.996(2); Mg1-N2, 2.518(2); Mg1-N3, 2.432(2); Mg1-N4, 2.1544(19); Mg1-N5, 2.1330(19); Ti1-N5-Ti1A, 92.62(9); Ti1-N5-Mg1, 94.88(8); Ti1A-N5-Mg1, 93.41(8).

The nitride assignment and origin from incorporation of gaseous N₂ into **3** was confirmed by repeating the synthesis under an atmosphere of ¹⁵N₂; this reproducibly gives the ¹⁵N₂-isotopologue [{Mg(Tren^{TMS})}]₂{(μ₃-¹⁵N)₂(Ti)₂} (**3**-¹⁵N) that exhibits a singlet resonance at 405.4 ppm in its ¹⁵N NMR spectrum in C₆D₆. The FTIR and Raman spectra of **3** and **3**-¹⁵N do not exhibit any ¹⁴N/¹⁵N isotopically shifted absorptions in the range of N-N single, double, or triple bond stretches, whilst a much weaker Raman band at 754 cm^{−1} (**3**) and 730 cm^{−1} (**3**-¹⁵N) is likely to be a breathing mode; the N5⋯N5A distance of 2.560(2) Å in the crystal structure further rules out the presence of any N-N bond in **3** and **3**-¹⁵N. Thus, the reduction of **1** to **3** involves the binding, activation, and complete six-electron reductive cleavage of a

single molecule of N₂, with concomitant rearrangement of the (Tren^{TMS})^{3−} ligand to support both Ti^{IV} and Mg^{II} centres that in turn stabilise the two nitride ligands formed.

In order to verify the formulations of **3** and **3**-¹⁵N and probe their reactivity, we performed acidification experiments assaying NH₃ as its conjugate acid NH₄⁺ by ¹H quantified-NMR (qNMR) spectroscopy and the indophenol spectrophotometric method, Scheme 2. NH₃ was isolated from the reaction mixture as NH₄Cl via a standard base-distillation procedure employing a HCl trap. Acidification of **3** or **3**-¹⁵N in DME with ten equivalents of HCl (1 M in Et₂O, pK_a^{aq} (Et₂O·H)⁺ = −3.59) yielded NH₄Cl (av. 1.94 eq., 97%) or ¹⁵NH₄Cl (av. 1.84 eq., 92%), respectively, in near quantitative yields. ¹H NMR spectra of the HCl-trapped volatile fractions in DMSO revealed diagnostic triplet (7.29 ppm, J_{NH} = 51 Hz) and doublet (7.20 ppm, J_{NH} = 71 Hz) resonances for ¹⁴NH₄⁺ and ¹⁵NH₄⁺, respectively, and the ¹⁵N NMR spectrum for the latter reveals a quintet resonance at −357.0 ppm (J_{NH} = 71 Hz). Notably, treating **3** with the weaker acid [Cy₃PH][I] (10 eq.; pK_a^{aq} = 9.7, H₂O; pK_a^{THF} = 9.7)^[20] also gave a good yield of NH₄Cl (av. 1.44 eq., 72%).

Encouraged by the reactivity of **3** and **3**-¹⁵N towards H⁺ we turned our attention towards effecting reactivity with H₂. Complex **3** is unreactive towards H₂ (1–4 bar) in various hydrocarbon, aromatic, or ethereal solvents. However, since the strongly basic nitride ligands in **3** were readily protonated by the relatively weak phosphonium acid [Cy₃PH][I]^[5j] we surmised that **3** might be reacted with H₂ in tandem via the H₂-activated complex [tBu₃PH][HBCF] (BCF = B(C₆F₅)₃),^[21] generated from the known P^tBu₃/BCF FLP system using H₂ in toluene.^[19] Gratifyingly, treatment of **3** with [tBu₃PH][HBCF] (6 eq.) in THF yielded NH₃ (0.97 eq., 49%), isolated from the reaction by distillation onto frozen DCl (200 eq.; 2 M in Et₂O) to form NH_xD_yCl (NH₃DCl expected), Scheme 2. The D⁺ trapping acid was employed in order to unequivocally differentiate chemically this step from the preceding NH₃-forming reaction with [tBu₃PH][HBCF]. Analogously, reactions between **3**/**3**-¹⁵N and [tBu₃PD][DBCF] (synthesized from D₂) generated ND₃ (N = ¹⁴N/¹⁵N, 0.76–1.25 eq., 38–63%), trapped with HCl to form NH_xD_yCl (NHD₃Cl expected). The ammonium salts were redissolved in dry DMSO-d₆ and analysed by ¹H qNMR, then subsequently reanalysed after conversion to NH₄Cl by hydrolysis with HCl_{aq} to effect complete H/D exchange. This enabled a comparison of the relative ¹H integrals for the NH_xD_yCl resonances before (x + y = 4) and after (x = 4) hydrolysis, from which the values of both x and y could be determined (see SI). Thus, incorporation of either H⁺ from [tBu₃PH][HBCF] or D⁺ from [tBu₃PD][DBCF] into the ammonium product is unequivocally demonstrated, although the quantified values are lower than expected due to some H/D exchange. This H/D exchange occurs prior to the hydrolysis reaction, which cannot be avoided by variation of the experimental procedure,

Scheme 2. The reaction of $3\text{-}^{15}\text{N}$ with HCl produces up to 1.94 equivalents of NH_3 , pre-prepared $[\text{tBu}_3\text{PD}][\text{DB}(\text{C}_6\text{F}_5)_3]$ in THF produces 1.25 equivalents of $^{15}\text{ND}_3$, whereas *in situ* treatment of $3\text{-}^{15}\text{N}$ with P^tBu_3 , $\text{B}(\text{C}_6\text{F}_5)_3$, and D_2 produces 0.29 equivalents of $^{15}\text{ND}_3$.

but the extent of H-D and D-H exchange essentially mirror each other internally validating this hypothesis. Further, one possible cause is thought to be the co-distillation of NH_3 with the P^tBu_3 by-product, which was chemically trapped with the HCl or DCl acid as $[\text{tBu}_3\text{PH}][\text{Cl}]$ and $[\text{tBu}_3\text{PD}][\text{Cl}]$, respectively ($^{31}\text{P}\{^1\text{H}\}$ NMR (DMSO-d_6): 51.68 ppm, s; and 50.88 ppm, t, $J_{\text{PD}} = 70$ Hz, respectively). Thus, partial H^+/D^+ exchange may occur within an equilibrium mixture of $\text{NH}_3/\text{NH}_4^+$ ($\text{p}K_{\text{a}} = 9.3$, H_2O) and $^t\text{Bu}_3\text{P}/^t\text{Bu}_3\text{PH}^+$ ($[\text{tBu}_3\text{PH}]^+$, $\text{p}K_{\text{a}} = 11.4$, H_2O ; $\text{p}K_{\text{a}}^{\text{THF}} = 10.7$).^[20]

Having established tandem N_2 and H_2 activation prior to conversion to NH_3 , a preliminary *in situ* reaction suggests that FLP-chemistry has potential to emerge as an effective vehicle in this area. Hydrogenation of $3\text{-}^{15}\text{N}$ performed *in situ* using $\text{P}^t\text{Bu}_3/\text{BCF}$ in 1,2-difluorobenzene (DFB) under a D_2 atmosphere (~ 2 bar) and volatile-trapping with frozen HCl yielded NH_4Cl [$0.29(\pm 0.05)$ eq., 15%], Scheme 2. At that level D-incorporation could not be unequivocally confirmed due to relatively increased H/D exchange occurring under these conditions. The lower yield for an *in situ* tandem reaction rather than stepwise suggests that yet to be determined competitive side-reactions are operating. However, it is encouraging that NH_3 could be isolated by vacuum distillation from this preliminary, unoptimised experiment.

The observed colour change of orange to green then purple-brown when **1** is reduced with Mg suggests that, as is the case for K-mediated reduction that gives **2**,^[5] **1** is reduced to $[\text{Ti}(\text{Tren}^{\text{TMS}})]$, which is green, and reversibly binds N_2 to form $[\{\text{Ti}(\text{Tren}^{\text{TMS}})\}_2(\text{N}_2)]$ transiently. Further reduction with magnesium then gives **3**, in which complete reductive cleavage of N_2 to N^{3-} has occurred, in contrast to partial reduction by K to afford **2**; this may be accounted for by the more polarizing nature of Mg^{2+} compared to K^+ , since the former has a high charge to radius ratio, possibly resulting in additional polarization of the N_2 molecule promoting its complete rupture. The fact that K-reduction of **1** gives N_2^{4-} with retention of a N-N bond but milder magnesium gives complete cleavage to N^{3-} underscores how cooperative effects are key to N_2 -activation.^[10a] Although high valent transition metal nitrides are often unreactive towards H_2 , on account of their strong $\text{M}\equiv\text{N}$ triple bonds,^[7b] the polymetallic bridging nitrides in **3** are readily fully protonated with strong acid to give quantitative liberation of NH_3 demonstrating complete N-N dissociation and two highly basic nitrides in **3**. Thus, when **3** is treated with $[\text{tBu}_3\text{PH}][\text{HBCF}]$ (or $[\text{tBu}_3\text{PD}][\text{DBCF}]$), all three successive protonation steps occur from N^{3-} to NH_3 (or ND_3), which can be isolated from the reaction by vacuum distillation, circumventing the need for additional acid to be employed.^[22] These points can be related to HB chemistry, where the ability to reductively cleave N_2 to N^{3-} and any subsequent reactivity is

dominated by polymetallic activation and heterobimetallic cooperative effects.^[2a,3,10a,10b] By combining FLP-splitting of H_2 with Ti-Mg-mediated cleavage of N_2 to produce NH_3 , the heterogeneous hydrogenation of N_2 in HB chemistry has been partially replicated, adding NH_3 -synthesis, prominent by its absence, to the family of FLP hydrogenation reactions.^[14,16]

In conclusion, by harnessing a cooperative combination of Ti and Mg we have cleaved N_2 to two nitrides in a six-electron reduction. The resulting nitrides are basic and liberate NH_3 when treated with acids. By employing a FLP to cleave H_2 we have sidestepped an apparent barrier to H_2 -activation, enabling the resulting phosphonium-borohydride to fully protonate the nitrides to give NH_3 , thus establishing FLPs in NH_3 synthesis from N_2 -activation and hydrogenation chemistry. The polymetallic nature and reactivity of this N_2 -fixation chemistry, which uniquely combines key heterogeneous HB steps together at a single homogeneous metal complex, when most complexes can only execute an individual reaction step, provides a simple molecular system amenable to further atomic-level study.^[23]

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Keywords: Dinitrogen reduction • Frustrated Lewis pairs • Titanium • Ammonia • Nitrogen fixation

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- [22] The identity of the Ti-Mg by-product after NH₃ is removed is currently unknown since it is an intractable yellow oil, but ¹¹B and ¹⁹F NMR spectroscopies unequivocally confirm the presence of the [HBCF][−] anion, so the product is likely to empirically be [Ti(Tren^{TMS})Mg]_n[HBCF]_{3n}. Supporting this, on one occasion standing the yellow oil in THF for 6 weeks resulted in the isolation of highly disordered crystals of [Mg(THF)₆][HBCF]₂ (**4**) in low yield (see the Supporting Information), which implies Tren^{TMS}-transfer to give [Ti(Tren^{TMS})(HBCF)].
- [23] CCDC 1859461 (**3**) and 1859462 (**4**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre. All other data are available from the corresponding author on request.

Entry for the Table of Contents

COMMUNICATION

Text for Table of Contents

Laurence R. Doyle, Ashley J. Wooles,
and Stephen T. Liddle*

Page No. – Page No.

**Bimetallic Cooperative Cleavage of
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