

Nitrogen Fixation

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Catalytic Dinitrogen Reduction to Ammonia at a Triamidoamine–Titanium Complex

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Abstract: Catalytic reduction of N_2 to NH_3 by a Ti complex has been achieved, thus now adding an early *d*-block metal to the small group of mid- and late-*d*-block metals (Mo, Fe, Ru, Os, Co) that catalytically produce NH_3 by N_2 reduction and protonolysis under homogeneous, abiological conditions. Reduction of $[Ti^{IV}(Tren^{TMS})X]$ ($X = Cl$, **1A**; **1**, **1B**; $Tren^{TMS} = N(CH_2CH_2NSiMe_3)_3$) with KC_8 affords $[Ti^{III}(Tren^{TMS})]$ (**2**). Addition of N_2 affords $[(Tren^{TMS})Ti^{III}]_2(\mu-\eta^1:\eta^1-N_2)$ (**3**); further reduction with KC_8 gives $[(Tren^{TMS})Ti^{IV}]_2(\mu-\eta^1:\eta^1:\eta^2:\eta^2-N_2K_2)$ (**4**). Addition of benzo-15-crown-5 ether (B15C5) to **4** affords $[(Tren^{TMS})Ti^{IV}]_2(\mu-\eta^1:\eta^1-N_2)[K(B15C5)_2]$ (**5**). Complexes **3–5** treated under N_2 with KC_8 and $[R_3PH][I]$, (the weakest H^+ source yet used in N_2 reduction) produce up to 18 equiv of NH_3 with only trace N_2H_4 . When only acid is present, N_2H_4 is the dominant product, suggesting successive protonation produces $[(Tren^{TMS})Ti^{IV}]_2(\mu-\eta^1:\eta^1-N_2H_4)[I]_2$, and that extruded N_2H_4 reacts further with $[R_3PH][I]/KC_8$ to form NH_3 .

The conversion of dinitrogen, N_2 , into ammonia, NH_3 , is essential for supplying N_2 in a fixed form into the Earth's biosphere,^[1] and key to providing NH_3 to chemical industry on a vast scale.^[2] However, the $N\equiv N$ triple bond, with a bond strength of 944 kJ mol^{-1} , is one of the strongest chemical bonds known, and with a high ionisation potential, negative electron affinity, poor nucleophilicity and electrophilicity, large HOMO–LUMO gap, and no permanent dipole, there are major kinetic and thermodynamic barriers to activating N_2 , and thus to fixing it as NH_3 .^[3,4]

Nature uses homogeneous nitrogenases based on V, Mo, and Fe to execute multiple single-electron transfer and protonation steps to convert N_2 into NH_3 .^[5] In contrast, chemical industry uses N_2 and H_2 to produce NH_3 over heterogeneous catalysts in the Haber–Bosch process.^[6] However, each process is energy-intensive, reflecting the challenge of N_2 activation, and so there is interest in studying reactivity at molecular complexes to improve our understanding of these elementary transformations.^[7]

After the report that a molybdenum–triamidoamine complex catalytically reduces N_2 to NH_3 in the presence of H^+/e^- ,^[8] a few Mo, Fe, Ru, Os, and Co complexes have been shown to be catalytically competent in H^+/e^- mediated N_2 reduction cycles,^[9] and stoichiometric reduction and protonation/hydrogenation of N_2 and nitrides by a variety of metals have been reported.^[10] However, no abiological, early metal complex preceding Group 6 has ever been shown to catalytically convert N_2 into NH_3 , and even V-, Cr-, and W-triamidoamine complexes^[11] do not facilitate N_2 reduction/protonolysis to NH_3 like Mo analogues.^[8] Where Ti is concerned, cleavage of N_2 by molecular polyhydrides and low valent species and/or stoichiometric protonolysis has been reported.^[12] Recently, a heterogeneous Ti hydride was found to catalytically convert N_2 and H_2 into NH_3 , whilst TiO_2 is known to photolytically convert N_2 and H_2O into NH_3 and O_2 .^[13] These reports hint that Ti could hold significant promise in this arena. This is appealing because Ti is the ninth most abundant element in the Earth's crust, and second only to Fe for metals that can fix N_2 .

Herein, we report the first abiological, homogeneous Ti complex that is competent for catalytic reduction of N_2 to NH_3 . We find that N_2 binding and partial activation occurs at Ti^{III} supported by one of the simplest triamidoamine ligands, priming the N_2 for cooperative reduction by KC_8 . Protonation to give NH_3 in a catalytic cycle is facilitated by phosphonium salts that are the weakest proton source used in any catalytic system to date.

Under argon, reduction of yellow $[Ti^{IV}(Tren^{TMS})X]$ ($X = Cl$, **1A**;^[14] **1**, **1B**; $Tren^{TMS} = N(CH_2CH_2NSiMe_3)_3$) with KC_8 yields green $[Ti^{III}(Tren^{TMS})]$ (**2**).^[15] Three broad 1H NMR resonances are observed (C_6D_6 , 3.6, 1.0, and -22.3 ppm), whilst no ^{13}C or ^{29}Si NMR resonances could be detected, and an EPR spectrum of **2** in frozen toluene-pentane exhibits $g = 1.984$, 1.943, and 1.891. This is consistent with the presence of Ti^{III} , unfortunately **2** has resisted exhaustive attempts to isolate it. However, slow cooling of an N_2 -saturated pentane solution of **2** yields red crystals of $[(Tren^{TMS})Ti^{III}]_2(\mu-\eta^1:\eta^1-N_2)$ (**3**), Scheme 1.^[15] In the solid state **3** has an effective magnetic moment of $2.50 \mu_B$ at 298 K, which is close to the

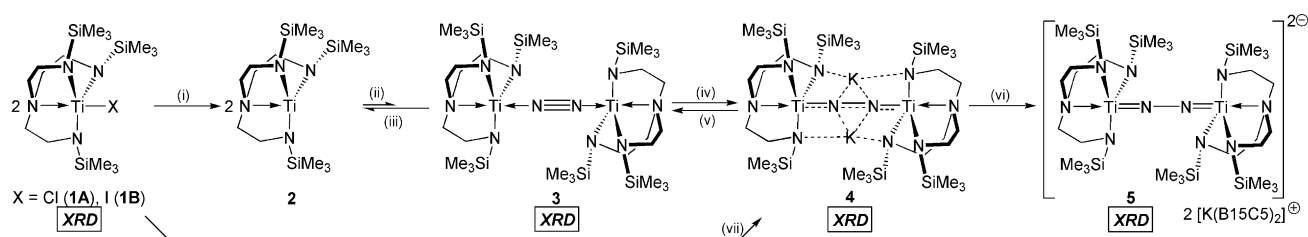
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Scheme 1. Synthesis of **2–5** from **1A/B**. Reagents and conditions: i) Ar, 2 KC_8 , -2KX , -2C_8 ; ii) N_2 , cool; iii) $-\text{N}_2$, warm; iv) 2 KC_8 ; v) I_2 , -2KI ; vi) 4 B15C5 ; vii) N_2 , 4 KC_8 , -2KX , -2C_8 .

spin-only value for two $s = 1/2$ species ($\mu_{\text{eff}} = 2.5 \beta_e$ for $g = 2.0$). The near temperature-independence of μ_{eff} indicates that any $\text{Ti}\cdots\text{Ti}$ interaction is very weak.^[15] EPR spectra of solid **3**, give apparently axial $g_{\perp} = 1.989$ and $g_{\parallel} = 1.940$ at room temperature; however on cooling these diverge to rhombic $g = 1.993$, 1.951, and 1.902 and are temperature-independent below 100 K, suggesting that molecular motion at higher temperatures gives higher effective symmetry. The magnetism and EPR spectra of **3** thus suggest the presence of Ti^{III} ions, and the structural and spectroscopic data (Table 1) are consistent with modest activation of the $\text{N}\equiv\text{N}$ triple bond.^[16]

Table 1: Key crystallographic bond lengths and Raman spectroscopic data for **3–5** and N_2H_x benchmarks ($x = 0, 2, 4$).^[15,24]

Cmpd	$\nu(\text{N}_2)$ [cm^{-1}] exp ($^{14}\text{N}/^{15}\text{N}$); calc	$d(\text{N}-\text{N})$ [Å]	$d(\text{Ti}-\text{NN})$ [Å]	$\angle(\text{Ti}-\text{N}-\text{N})$ [°]
N_2	2330	1.098(1)	–	–
N_2H_2	1583,1529	1.25	–	–
N_2H_4	1076	1.45	–	–
3	1701/1644;1724	1.121(6)	2.022(3)	180
4	1201/1164;1247	1.315(3)	1.814(2) 1.810(2)	166.6(2) 172.9(2)
5	1246/1203;1307	1.461(7)	1.712(4)	178.8(5)

The formulation of **3** is corroborated by DFT calculations;^[15] all attempts to model a $\text{Ti}^{\text{IV}}/\text{Ti}^{\text{IV}}/\text{N}_2^{2-}$ combination were intractable or produced the $\text{Ti}^{\text{III}}/\text{Ti}^{\text{III}}/\text{N}_2$ formulation. Computed $\text{Ti}-\text{NN}$ and $\text{N}-\text{N}$ Mayer bond orders of 0.56 and 2.38 are consistent with a weakly bound and activated N_2 . This is also supported by computed Ti spin densities/charges of $-0.55/0.99$ and a total net spin density/charge of $-0.9/-0.56$ on the N_2 -unit. The two SOMOs are orthogonal $\text{Ti}\rightarrow\text{N}_2 \pi^*$ back-bonding interactions.

The $^1\text{H NMR}$ spectrum of **3** (C_6D_6) reveals identical resonances to those of **2**, consistent with N_2 dissociation in solution. Complex **2** is similar to $[\text{Ti}(\text{Tren}^{\text{DMBS}})] [\text{Tren}^{\text{DMBS}} = \text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_2\text{Bu}^t)_3]$,^[17] and their optical spectra exhibit broad absorptions at about 620 and about 640 nm, respectively,^[15] which is responsible for their green colours. In line with this, $[\text{Ti}(\text{Tren}^{\text{TMS}})]$ exhibits computed HOMO to LUMO + 3/ + 4 (d–d) energy separations of 655/657 nm.

Addition of two or four equivalents of KC_8 to **3** or **1A**, respectively, under N_2 affords red–brown $\{[(\text{Tren}^{\text{TMS}})\text{Ti}^{\text{IV}}]_2(\mu-\eta^1:\eta^1:\eta^2-\text{N}_2\text{K}_2)\}$ (**4**; Scheme 1).^[15] The structure of **4** (Table 1) shows the N_2 ligand is bound in a near-linear manner. The $\text{N}-\text{N}$ bond distance is extended compared to **3**

and free N_2 and the $\text{Ti}-\text{NN}$ bond distances are short, inferring some Ti -imido character. These data along with Raman spectroscopy suggest strong activation of N_2 . Multinuclear NMR spectra of C_6D_6 solutions of **4** and $4\text{-}^{15}\text{N}_2$ are consistent with a C_3 -symmetric $\text{Ti}^{\text{IV}}/\text{Ti}^{\text{IV}}/\text{N}_2^{4-}$ formulation.

Only a closed-shell formulation for **4** gave a converged DFT calculation,^[15] where the Ti ions and N_2 unit carry computed charges of 0.52 (av.) and -1.1 (total), respectively; this implies a covalent bonding picture for the $\text{Ti}-(\mu-\text{N}_2)-\text{Ti}$ unit that is supported by $\text{Ti}-\text{NN}$ and $\text{N}-\text{N}$ Mayer bond orders of 1.25 and 1.44, respectively. For comparison, the $\text{Ti}-\text{N}_{\text{amide}}$ and $\text{Ti}-\text{N}_{\text{amine}}$ Mayer bond orders are about 0.7 and 0.25, respectively. The HOMO and HOMO–1 are two orthogonal, doubly occupied $\text{Ti}\rightarrow\text{N}_2 \pi^*$ back-bonding interactions. The K^{I} ions clearly play a stabilising role, but this is electrostatic, with $\text{K}-\text{N}$ Mayer bond orders of < 0.05 .

Addition of 4 equivalents of benzo-15-crown-5 (B15C5 ; Scheme 1) gives red $\{[(\text{Tren}^{\text{TMS}})\text{Ti}^{\text{IV}}]_2(\mu-\eta^1:\eta^1-\text{N}_2)\}[\text{K}(\text{B15C5})_2]_2$ (**5**).^[15] The solid-state molecular structure of **5** (Table 1) reveals that the $\text{Ti}-\text{N}-\text{Ti}$ axis is closer to linearity than in **4**. The $\text{N}-\text{N}$ and $\text{Ti}-\text{NN}$ bond distances in **5** are longer and shorter, respectively, suggesting strong N_2 activation and significant Ti -imido character. However, for **5** the $\nu(\text{N}_2)$ Raman stretch, a better indicator of N_2 activation than bond distances, suggests reduced N_2 activation compared to **4**, Table 1. UV/Vis spectra of **4** and **5** are essentially identical in THF, but different in benzene, suggesting that the K^{I} ions in **4** are labile in polar donor solvent, but remain coordinated in non-polar solvents.

Only a closed-shell formulation for the dianion part of **5** gave a converged calculation. The $\text{Ti}-\text{NN}$ and $\text{N}-\text{N}$ Mayer bond orders in **5** are 1.33 and 1.62, which are larger than the corresponding data for **4**; the latter is in-line with the Raman data, whilst the former suggests that more Ti -imido character results from removal of K^{I} ions. The fact that **5** contains a charge-rich dianion is reflected by $\text{Ti}-\text{N}_{\text{amide}}$ and $\text{Ti}-\text{N}_{\text{amine}}$ Mayer bond orders that are lower than in **4** at about 0.6 and 0.16, respectively. This is consistent with computed Ti charges of 0.99 in **5** that are higher than those in **4**, but the N_2 unit is less charged at -0.86 overall.

Having established N_2 reduction, attention turned to fixation (Table 2). Treatment of **4** (10 mM, pentane) with ethereal 1M HCl (10 equiv) yielded 0.88 N_2H_4 and 0.13 NH_3 equiv (entry 1). The near-stoichiometric yield of N_2H_4 confirms **4** as a hydrazido complex. In a control, when **1A** is identically quenched only 0.04 NH_3 equiv were detected. This suggests that the small amount of NH_3 produced is the result

Table 2: Catalytic acidification experiments for the reaction of **4** with acid and reductant under N₂ to produce NH₃ and N₂H₄.^[a]

Entry ^[b]	Solvent	Acid	Reductant	Acid [eq.]	Reductant [eq.]	NH ₃ [eq.]	N ₂ H ₄ [eq.]	Fixed-N ^[h] [eq.]	Efficiency ^[i] [%]
1	pentane	1 M HCl	–	10	–	0.13	0.88	1.89	–
2	Et ₂ O	[Cy ₃ PH][I]	–	10	–	0.05	0.52	1.09	–
3	Et ₂ O	[Cy ₃ PH][I]	KC ₈	120	120	6.41	0.15	6.71	17
4	Et ₂ O	[Cy ₃ PH][I]	KC ₈	300	300	11.91	0.06	12.03	12
5	Et ₂ O	[Cy ₃ PH][I]	KC ₈	400	300	10.81	0.10	11.01	11
6	Et ₂ O	[Cy ₃ PH][I]	KC ₈	600	600	17.77/17.4 ^[g]	0.03	17.83	9
7 ^[c,d]	Et ₂ O	[Cy ₃ PH][I]	KC ₈	600	600	17.70/17.6 ^[g]	0.08	17.86	9
8 ^[c,e]	Et ₂ O	[Cy ₃ PH][I]	KC ₈	300	300	1.53	0	1.53	–
9	pentane	[Cy ₃ PH][I]	KC ₈	300	300	5.82	0.29	6.40	6
10	toluene	[Cy ₃ PH][I]	KC ₈	300	300	3.89	0.21	4.31	4
11	THF	[Cy ₃ PH][I]	KC ₈	300	300	8.95	0	8.95	9
12	Et ₂ O	[Cy ₃ PH][I]	K(Nap)(THF)	300	300	0.36	0.07	0.50	0
13	Et ₂ O	[Cy ₃ PH][Cl]	KC ₈	300	300	2.45	0.05	2.55	3
14	Et ₂ O	[Cy ₃ PH][BAR ^F ₄]	KC ₈	300	300	4.77	0	4.77	5
15	Et ₂ O	[ⁿ Bu ₃ PH][I]	KC ₈	300	300	11.73	0.09	11.91	12
16	Et ₂ O	[^t Bu ₃ PH][I]	KC ₈	300	300	7.37	0.30	7.97	8
17 ^[f]	Et ₂ O	[Cy ₃ PH][I]	KC ₈	25	25	1.32	0.34	2.00	–

[a] Diazene (N₂H₂) was not analysed owing to its expected instability under these reaction conditions; however, complete disproportionation of N₂H₂ to N₂H₄ and N₂ can only be expected to produce a maximum N₂H₄ yield of 50%. [b] All experiments were performed under N₂ (unless otherwise noted) at –78 °C (2 h), followed by gradual warming to 25 °C and additional stirring for 15 h. [c] **4**-¹⁵N₂. [d] Under ¹⁵N₂. [e] Under Ar. [f] [N₂H₅][I]. [g] Yield calculated from ¹H NMR. [h] Fixed-N (eq.) = [NH₃ (eq.)] + 2[N₂H₄ (eq.)]. [i] Efficiency = 100%[Red. (eq.)]/{3[NH₃ (eq.)] + 4[N₂H₄ (eq.)]}.

of minor degradation of Tren^{TMS} under the action of very strong acid.

To achieve catalytic turnover of N₂, it was concluded that a milder acid than ethereal HCl (pK_a (Et₂O·H)⁺ = –3.59) would be required. Also, the synthesis of **4** requires strong K-based reductants, which react rapidly with strong, soluble acids. Confirming this, using HCl/KC₈ (30:30:4) resulted in a sub-stoichiometric yield of N₂H₄ and NH₃ (0.13 and 0.36 equiv, respectively). It was anticipated that a weaker acid could be effective for the protonation of activated N₂ whilst minimising deleterious side-reactions. However, commonly used *N*-based acids, such as lutidinium [2,6-(CH₃)₂C₅H₃NH]⁺ and arylammonium/alkylammonium salts were found to be susceptible to reduction by KC₈, and in some controls led to NH₃ formation; as such, we anticipated false-positive results. Thus, more stable, non-*N*-based acids were sought.

Trialkylphosphonium salts, [R₃PH][X], were examined because of their mild acidity (pK_a ≈ 8–12) and tuneable nature. Initial experiments were conducted with [Cy₃PH][I] (pK_a = 9.7). Addition to **4** (10:1 ratio) in Et₂O produced 0.5 N₂H₄ and 0.05 NH₃ equiv (entry 2). This is a lower yield of N₂H₄ compared to using HCl, but [Cy₃PH][I] is a weaker, less soluble acid so it was expected to be less reactive. However, with excess [Cy₃PH][I]/KC₈, **4** catalyses the production of up to 18 equiv of NH₃ per **4** (entries 3–11). Using **4**-¹⁵N₂ under ¹⁵N₂ confirmed the incorporation of ¹⁵N₂ into the ¹⁵NH₃/¹⁵NH₄Cl product.

A sub-stoichiometric yield was obtained using [K₂(C₁₀H₈)₂(THF)] as the reductant (entry 12), which is most likely due to its solubility in Et₂O and thus greater propensity to react with H⁺ in situ, consuming acid and reductant for H₂ production. Comparative runs in ethers (Et₂O and THF), in which intermediates may be solvated/stabilised, gave higher yields than those in toluene or pentane (entries 4 and 9–11).

The acid anion was also varied: [Cy₃PH][Cl] (Cl[–], higher coordinating ability) or [Cy₃PH][BAR^F₄][–] (BAR^F₄[–] = [[3,5-(CF₃)₂C₆H₃]₄B][–], non-coordinating; entries 4, 13, and 14). For both, this resulted in lower yields of NH₃, but supposed variation of a single parameter will simultaneously affect several properties that all influence catalytic turnover, preventing meaningful correlation. Similar catalytic turnovers were obtained using [Buⁿ₃PH][I] and [Bu^t₃PH][I] (pK_a = 8.4 and 11.4, respectively; entries 15 and 16), or using a 4:3 ratio of [Cy₃PH][I] to KC₈ (entry 5), which accounts for an additional equiv of acid being consumed through protonation of NH₃.

With KC₈, the major product is NH₃, with little N₂H₄ (< 0.15 per **4**) detected. That **4** does not react further with KC₈ in Et₂O implicates an initial protonation step rather than further reduction of **4** to form a Ti^{IV}-nitride species, which could be responsible for NH₃ production. A further control demonstrated that [N₂H₅][I] is converted into NH₃ in the absence of **4**/¹⁵N₂ (entry 17), and with entry 1, this suggests that the N₂H₄ to NH₃ reduction/protonation may occur after dissociation from the active species. We cannot rule out the presence of transient Ti^{IV}-nitrides,^[18] but these control experiments suggest that successive protonation may produce “[{(Tren^{TMS})Ti^{IV}]₂(μ-η¹:η¹-N₂H₄)[I]₂”, with subsequent extrusion of N₂H₄, that reacts with [Cy₃PH][I]/KC₈ to form NH₃; concomitant formation of **1B** closes the catalytic cycle.

Under conditions given in entry 4, **5** is catalytically competent producing 10 equiv of NH₃. Complex **3** produces 6 equiv of NH₃ under such conditions, showing catalytic competence, but on dissolution a significant proportion of **3** converts into **2** (Scheme 1), retarding reactivity. In isolation, **3** reacts with acid to produce 0.03 and 0.1 equiv of NH₃ and N₂H₄, respectively, underscoring the importance of KC₈ activation of the coordinated N₂ in **3**.

The reactivity of **5** is significant, because it is a clear-cut end-on: end-on bridging N₂ complex. To date, almost all N₂-fixing catalysts contain end-on terminal N₂,^[7] whereas those with end-on: end-on bridging N₂ have been proposed to dissociate to form end-on terminal complexes, or undergo N₂ cleavage to generate nitrides.^[7,9b,d,18–20] Side-on: side-on bridging, which usually results in strong N₂ activation, has been reported for stoichiometric N₂ activation only. Conversion of end-on: end-on bridging into side-on: side-on bridging in **5** seems unlikely on steric grounds, so the reactivity of **5** suggests that consideration might be given to recognising end-on: end-on bridging as a catalytically competent N₂ coordination mode. If this is the case, it would provide an unusual symmetrical functionalisation of N₂ to N₂H₄ (in the absence of reductant to cleave the N–N bond) compared to the traditional Chatt-type cycle,^[21] since only one molecular Fe complex is known to be selective for catalytic reduction of N₂ to N₂H₄ rather than NH₃.^[22]

To conclude, we have reported the first abiological early base metal complex that is competent for the homogeneous catalytic reduction of N₂ to NH₃ under ambient conditions, and this chemistry is supported by the simple Tren^{TMS} ligand. The proton sources in this catalysis, [R₃PH][I], are the weakest yet used in N₂ reduction to NH₃, underscoring the importance of balancing acid sources to strong reducing agents. We propose a plausible mechanism, where Ti^{IV} is reduced to Ti^{III}, which binds and weakly activates N₂, priming it for cooperative K-mediated reduction^[10e,23] to a strongly activated state, which can then be protonated. Transient nitrides cannot be ruled out at this point, but control experiments suggest that N₂H₄ is formed and then converted into NH₃ in the presence of acid and reductant. The catalytic activity of one of the Ti complexes suggests that the end-on: end-on bridging mode of N₂ should possibly no longer be discounted as a catalytically active coordination mode. These results add Ti to the small number of previously exclusively mid- and late-d-block metal ions (Mo, Fe, Ru, Os, Co) that can execute catalytic reduction of N₂ to NH₃.^[24]

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Conflict of interest

The authors declare no conflict of interest.

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