A Journal of the Gesellschaft Deutscher Chemiker
Angewandte Chemie
International Edition
www.angewandte.org

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To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201802576
Angew. Chem. 10.1002/ange.201802576

Link to VoR: http://dx.doi.org/10.1002/anie.201802576
http://dx.doi.org/10.1002/ange.201802576

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Catalytic Dinitrogen Reduction to Ammonia at a Triamidoamine-Titanium Complex

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Abstract: *We report unprecedented catalytic reduction of* N_2 *to* NH_3 *by a molecular Ti complex, 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 are capable of executing catalytic production of* NH_3 *by* N_2 *reduction and protonolysis under homogeneous, abiological conditions. Under Ar, reduction of* $[Ti^{IV}(Tren^{TMS})X]$ *(X = Cl,* **1A**; *I,* **1B**; $Tren^{TMS} = N(CH_2CH_2NSiMe_3)_3$*) with 1 equivalent of* KC_8 *affords* $[Ti^{III}(Tren^{TMS})]$ *(***2***). Addition of* N_2 *to* **2** *affords* $[\{(Tren^{TMS})Ti^{III}\}_2(\mu\text{-}\eta^1:\eta^1\text{-}N_2)]$ *(***3***); further reduction with* KC_8 *then gives* $[\{(Tren^{TMS})Ti^{IV}\}_2(\mu\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}N_2K_2)]$ *(***4***). Addition of 4 equivalents of benzo-15-crown-5 ether (B15C5) to* **4** *affords* $[\{(Tren^{TMS})Ti^{IV}\}_2(\mu\text{-}\eta^1:\eta^1\text{-}N_2)][K(B15C5)_2]_2$ *(***5***). Complexes* **3-5***, when treated under* N_2 *with excess* KC_8 *and* $[R_3PH][I]$*, the latter utilising the weakest* H^+*-sources yet used in* N_2 *reduction, produce up to 18 equivalents of* NH_3 *with only trace* N_2H_4*. When only acid is present* N_2H_4 *is the dominant product, suggesting successive protonation eventually produces* $[\{(Tren^{TMS})Ti^{IV}\}_2(\mu\text{-}\eta^1:\eta^1\text{-}N_2H_4)][I]_2$*, with subsequent extrusion of* N_2H_4*, that reacts further with* $[R_3PH][I]/KC_8$ *to form* NH_3*, and then concomitant reformation of* **1B** *closing the catalytic cycle.*

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≡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 to NH_3.[5] In contrast, chemical industry uses N_2 and H_2 to produce NH_3 over heterogeneous catalysts in Haber-Bosch processes.[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 Mo-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 to 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 to NH_3 whilst TiO_2 is known to photolytically convert N_2 and H_2O to 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 9th most abundant element in the Earths crust, 2nd only to Fe for metals that can fix N_2.

Here, 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] I, **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 $[\{(Tren^{TMS})Ti^{III}\}_2(\mu\text{-}\eta^1:\eta^1\text{-}N_2)]$ (**3**), Scheme 1.[15] In the solid state **3** has an effective magnetic moment of 2.50 μ_B at 298 K, which is close to the spin-only value for two $s = ½$ species ($\mu_{eff} = 2.5\ \beta_e$ for $g = 2.0$). The near temperature independence of μ_{eff} indicates that any Ti···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 pectroscopic data, Table 1, are consistent with modest activation of the N≡N triple bond.[16]

The formulation of **3** is corroborated by DFT calculations;[15] all attempts to model a $Ti^{IV}/Ti^{IV}/N_2^{2-}$ combination were intractable or produced the $Ti^{III}/Ti^{III}/N_2$ formulation. Computed Ti-NN and N-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 Ti→N_2-π* back-bonding interactions.

The ^1H 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 $[Ti(Tren^{DMBS})]$ [$Tren^{DMBS} = N(CH_2CH_2NSiMe_2Bu^t)_3$],[17] and their optical spectra exhibit broad absorptions at ~620 and ~640 nm, respectively,[15] which is responsible for their green colours. In line with this, $[Ti(Tren^{TMS})]$ exhibits computed HOMO to LUMO+3/+4 (d-d) energy separations of 655/657 nm.

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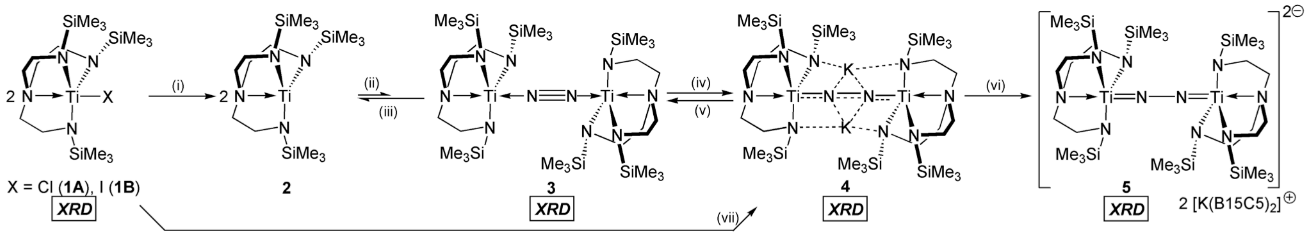

Scheme 1. Synthesis of **2**-**5** from **1A/B**. Reagents and conditions: (i) Ar, 2 KC_8, -2 KX, -2 C_8; (ii) N_2, cool; (iii) N_2, warm; (iv) 2 KC_8; (v) I_2, -2 KI; (vi) 4 B15C5; (vii) N_2, 4 KC_8, -2 KX, -2 C_8.

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

Compound	$\nu(N_2)$, cm^{-1} exp(^{14}N/^{15}N);calc	d(N–N) (Å)	d(Ti–NN) (Å)	∠(Ti-N-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)	166.6(2)
			1.810(2)	172.9(2)
5	1246/1203;1307	1.461(7)	1.712(4)	178.8(5)

Addition of two or four equivalents of KC_8 to **3** or **1A**, respectively, under N_2 affords red-brown $[\{(Tren^{TMS})Ti^{IV}\}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-}N_2K_2)]$ (**4**), Scheme 1.[15] The structure of **4**, Table 1, shows the N_2 ligand is bound in a near-linear manner. The N-N bond distance is extended compared to **3** and free-N_2 and the Ti-NN bond distances are short, inferring some Ti-imido character. These data along with Raman spectroscopy suggest strong activation of N_2. Multi-nuclear NMR spectra of C_6D_6 solutions of **4** and **4-^{15}N$_2$** are consistent with a C_3-symmetric $Ti^{IV}/Ti^{IV}/N_2^{4-}$ 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 Ti-(μ-N_2)-Ti unit that is supported by Ti-NN and N-N Mayer bond orders of 1.25 and 1.44, respectively. For comparison, the Ti-N_{amide} and Ti-N_{amine} Mayer bond orders are ~0.7 and 0.25, respectively. The HOMO and HOMO−1 are two orthogonal, doubly-occupied $Ti \rightarrow N_2\text{-}\pi^*$ back-bonding interactions. The K^I ions clearly play a stabilising role, but this is electrostatic, with K-N Mayer bond orders of <0.05.

Addition of 4 equivalents of benzo-15-crown-5 (B15C5), Scheme 1, gives red $[\{(Tren^{TMS})Ti^{IV}\}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2)][K(B15C5)_2]_2$ (**5**).[15] The solid state molecular structure of **5**, Table 1, reveals that the Ti-N-N-Ti axis is closer to linearity than in **4**. The N-N and Ti-NN bond distances in **5** are longer and shorter, respectively, suggesting strong N_2 activation and significant Ti-imido character. However, for **5** the $\nu(N_2)$ 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 Ti-NN and N-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 Ti-N_{amide} and Ti-N_{amine} Mayer bond orders that are lower than in **4** at ~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 equivalents) yielded 0.88 N_2H_4 and 0.13 NH_3 equivalents (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 equivalents were detected. This suggests that the small amount of NH_3 produced is the result of minor degradation of $Tren^{TMS}$ under the action of very strong acid.

To achieve catalytic turnover of N_2, it was concluded that a milder acid than ethereal HCl [pK_a $(Et_2O{\cdot}H)^+$ = −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/KC_8 (30:30:**4**) resulted in a sub-stoichiometric yield of N_2H_4 and NH_3 (0.13 and 0.36 equivalents, respectively). It was anticipated that a weaker acid could be effective for the protonation of activated N_2 whilst minimising deleterious side-reactions. However, commonly used *N*-based acids, such as lutidinium $[2,6\text{-}(CH_3)_2C_5H_3NH]^+$ and aryl/alkyl-ammonium salts were found to be susceptible to reduction by KC_8, and in some controls led to NH_3 formation; as such, we anticipated false-positive results. Thus, more stable, non-*N*-based acids were sought.

Trialkylphosphonium salts, $[R_3PH][X]$, were examined due to their mild acidity (pK_a ~8-12) and tunable nature. Initial experiments were conducted with $[Cy_3PH][I]$ (pK_a = 9.7). Addition to **4** (10:1 ratio) in Et_2O produced 0.5 N_2H_4 and 0.05 NH_3 equivalents (Entry 2). This is a lower yield of N_2H_4 compared to using HCl, but $[Cy_3PH][I]$ is a weaker, less soluble acid so it was expected to be less reactive. However, with excess $[Cy_3PH][I]/KC_8$, **4** catalyses the production of up to 18 equivalents of NH_3 per **4** (Entries 3-11). Using **4-^{15}N$_2$** under $^{15}N_2$ confirmed the incorporation of $^{15}N_2$ into the $^{15}NH_3$/$^{15}NH_4Cl$ product.

A sub-stoichiometric yield was obtained using $[K_2(C_{10}H_8)_2(THF)]$ as the reductant (Entry 12), likely due to its solubility in Et_2O and thus greater propensity to react with H^+ *in-situ*, consuming acid and reductant for H_2 production. Comparative runs in ethers (Et_2O 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: $[Cy_3PH][Cl]$ (Cl^-, higher coordinating ability) or $[Cy_3PH][BAr^F_4]$ ($BAr^F{}_4{}^-$ = $[\{3,5\text{-}(CF_3)_2C_6H_3\}_4B]^-$, non-coordinating) (Entries 4 and 13-14). For both this resulted in lower yields of NH_3, 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 $[Bu^n{}_3PH][I]$ and $[Bu^t{}_3PH][I]$ (pK_a = 8.4 and 11.4, respectively; Entries 15 and 16), or using a 4:3 ratio of $[Cy_3PH][I]$ to KC_8 (Entry 5), which accounts for an additional equivalent of acid being consumed through protonation of NH_3.

Table 2. Catalytic acidification experiments for the reaction of **4** with acid and reductant under N_2 to produce NH_3 and N_2H_4.†

Entry[a]	Solvent	Acid	Reductant	Acid (eq.)	Reductant (eq.)	NH_3 (eq.)	N_2H_4 (eq.)	Fixed-N[g] (eq.)	Efficiency[h] (%)
1	pentane	1M HCl	-	10	-	0.13	0.88	1.89	-
2	Et_2O	$[Cy_3PH][I]$	-	10	-	0.05	0.52	1.09	-
3	Et_2O	$[Cy_3PH][I]$	KC_8	120	120	6.41	0.15	6.71	17
4	Et_2O	$[Cy_3PH][I]$	KC_8	300	300	11.91	0.06	12.03	12
5	Et_2O	$[Cy_3PH][I]$	KC_8	400	300	10.81	0.10	11.01	11
6	Et_2O	$[Cy_3PH][I]$	KC_8	600	600	17.77/17.4[f]	0.03	17.83	9
7[b,c]	Et_2O	$[Cy_3PH][I]$	KC_8	600	600	17.70/17.6[f]	0.08	17.86	9
8[b,d]	Et_2O	$[Cy_3PH][I]$	KC_8	300	300	1.53	0	1.53	-
9	pentane	$[Cy_3PH][I]$	KC_8	300	300	5.82	0.29	6.40	6
10	toluene	$[Cy_3PH][I]$	KC_8	300	300	3.89	0.21	4.31	4
11	THF	$[Cy_3PH][I]$	KC_8	300	300	8.95	0	8.95	9
12	Et_2O	$[Cy_3PH][I]$	K(Nap)(THF)	300	300	0.36	0.07	0.50	0
13	Et_2O	$[Cy_3PH][Cl]$	KC_8	300	300	2.45	0.05	2.55	3
14	Et_2O	$[Cy_3PH][BAr^F{}_4]$	KC_8	300	300	4.77	0	4.77	5
15	Et_2O	$[^nBu_3PH][I]$	KC_8	300	300	11.73	0.09	11.91	12
16	Et_2O	$[^tBu_3PH][I]$	KC_8	300	300	7.37	0.30	7.97	8
17[e]	Et_2O	$[Cy_3PH][I]$	KC_8	25	25	1.32	0.34	2.00	-

† Diazene (N_2H_2) was not analysed for due to its expected instability under these reaction conditions, however, complete disproportionation of N_2H_2 to N_2H_4 and N_2 can only be expected to produce a maximum N_2H_4 yield of 50%. [a] All experiments were performed under N_2 (unless otherwise noted) at –78 °C (2 h), followed by gradual warming to 25°C and additional stirring for 15 h. [b] **4-^{15}N$_2$**, [c] under $^{15}N_2$; [d] under Ar; [e]$[N_2H_5][I]$; [f] yield calculated from ^1H NMR; [g] Fixed-N (eq.) = [NH_3 (eq.)] + 2[N_2H_4 (eq.)]; [h] Efficiency = 100%[Red. (eq.)]/{3[NH_3 (eq.)] + 4[N_2H_4 (eq.)]}.

With KC_8 the major product is NH_3, with little N_2H_4 (< 0.15 per **4**) detected. That **4** does not react further with KC_8 in Et_2O implicates an initial protonation step rather than further reduction of **4** to form a Ti^{IV}-nitride species, which could be responsible for NH_3 production. A further control demonstrated that $[N_2H_5][I]$ is converted to NH_3 in the absence of **4**/**4-^{15}N$_2$** (Entry 17), and with Entry 1, this suggests that the N_2H_4 to NH_3 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 "$[\{(Tren^{TMS})Ti^{IV}\}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2H_4)][I]_2$", with subsequent extrusion of N_2H_4, that reacts with $[Cy_3PH][I]/KC_8$ to form NH_3; concomitant formation of **1B** closes the catalytic cycle.

Under Entry 4 conditions, **5** is catalytically competent producing 10 equivalents of NH_3. Complex **3** produces 6 equivalents of NH_3 under such conditions, showing catalytic competence, but on dissolution a significant proportion of **3** converts to **2**, Scheme 1, retarding reactivity. In isolation, **3** reacts with acid to produce 0.03 and 0.1 equivalents of NH_3 and N_2H_4, respectively, underscoring the importance of KC_8 activation of the coordinated N_2 in **3**.

The reactivity of **5** is significant, because it is a clear-cut end-on:end-on bridging N_2 complex. To date, almost all N_2-fixing catalysts contain end-on terminal N_2,[7] whereas those with end-on:end-on bridging N_2 have been proposed to dissociate to form end-on terminal complexes, or undergo N_2 cleavage to generate nitrides.[7,9b,d,18-20] Side-on:side-on bridging, which usually results in strong N_2 activation, has been reported for stoichiometric N_2 activation only. Conversion of end-on:end-on bridging to 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 N_2 coordination mode. If this is the case, it would provide an unusual symmetrical functionalisation of N_2 to N_2H_4 (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 N_2 to N_2H_4 rather than NH_3.[22]

To conclude, we have reported the first abiological early base metal complex that is competent for the homogeneous catalytic reduction of N_2 to NH_3 under ambient conditions, and this chemistry is supported by the simple $Tren^{TMS}$ ligand. The proton sources in this catalysis, $[R_3PH][I]$, are the weakest yet used in N_2 reduction to NH_3, 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 N_2, 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 N_2H_4 is formed and then converted to NH_3 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 N_2 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 N_2 to NH_3.

Acknowledgements

We gratefully acknowledge the UK EPSRC (grants EP/M027015/1 and EP/P001386/1), ERC (grant CoG612724), Royal Society (grant UF110005), and The University of Manchester for generous funding and support, and the National EPSRC UK EPR Facility. Metrical parameters for the structures of compounds **1A**, **1B**, and **3-5** are available free of charge from the CCDC (1812642 to 1812646). All other data are available from the authors on request

Keywords: Dinitrogen reduction • Titanium • Ammonia • Nitrogen fixation • Phosphonium salt

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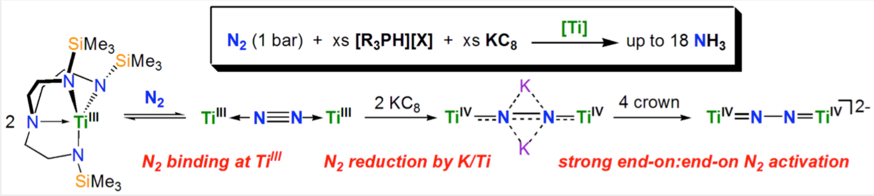

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