Fixation of Dinitrogen at an Asymmetric Binuclear Titanium N_2 Complex

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Dedication ((optional))

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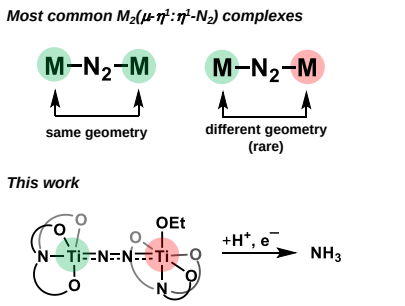
Abstract: A new type of dinitrogen dititanium complex supported by a triphenolamine (TPA) ligand is reported. Analysis by single-crystal X-ray diffraction, Raman, and NMR spectroscopy reveals different coordination geometries for the two titanium centers. Hence, coordination of TPA and a nitrogen ligand results in trigonal bipyramidal geometry while an octahedral titanium center is obtained upon additional coordination of an ethoxide generated upon C–O bond cleavage in a diethyl ether solvent molecule. The titanium complex successfully generates ammonia in presence of an excess amount of PCy_3HI and KC_8 in 154% yield (per Ti atom). A titanium complex with a bulkier TPA does not form a N_2 complex and mononuclear titanium N_2 complexes were not accessible, presumably due to high tendency of early transition metals to form N_2 binuclear complexes.

Molecular dinitrogen (N_2) has been utilized as an important starting feedstock for value-added nitrogen-containing compounds such as ammonia because it is abundant, readily accessible, and inexpensive.[1] However, the N_2 molecule has one of the highest bond-dissociation energy known (226 kcal/mol), poor σ-donating and π-accepting abilities, large HOMO (–15.6 eV)-LUMO (+7.3 eV) energy difference, and non-polarized character.[2] In nature, production of ammonia from N_2 under ambient conditions is achieved by metalloenzymes. Haber-Bosch process, which produces ammonia from N_2 on an industrial-scale - more than 160 million tons annually, is a highly energy-intensive process mainly due to the inertness of molecular nitrogen. About 1–2% of the world's annual energy supply is needed to produce ammonia through the process. Furthermore, carbon dioxide is produced as a by-product in significantly higher yield than ammonia.[3] Thus, this process has limitations from an energetic and environmental point of view and new methods that requires lower energy consumption and avoid CO_2 production are intensively sought after. Since transition metal complexes were found to fix molecular dinitrogen effectively, transition metal catalysis for N_2 reduction has been intensively studied for the past several decades.[4] Over this time, numerous research groups have developed various systems that fix and functionalize molecular dinitrogen.[5]

Schrock and Yandulov reported the first example of the catalytic system for dinitrogen reduction to ammonia and isolated eight key intermediates of the distal pathway.[6] The Peters group has been working on catalytic nitrogen reduction to ammonia ever since they reported the first nitrogen-fixing iron catalyst.[7] Nishibayashi and co-workers showed a molybdenum catalyst with the highest catalytic turnover for this reaction.[8] In addition, the same group also reported the first examples of vanadium complexes that transform nitrogen gas into tris(trimethylsilyl)amine catalytically.[9] Low-valent mononuclear dinitrogen titanocene complexes were reported by the Chirik group.[10] As first examples of early transition metal catalysts for ammonia generation from N_2, the Liddle group reported a titanium–triamidoamine system.[11] Catalytic conversion of dinitrogen to tris(trimethylsilyl)amine was also explored by the Okuda group with a titanium complex.[12] Kawaguchi developed activation/cleavage of N_2 by a titanium complex, followed by the formation of nitrogen–carbon bond with various electrophiles.[13] Hou and co-workers reported a multinuclear titanium framework that cleaves N_2 and converts it to nitriles, as well as titanium PNP pincer complexes that promote cleavage, alumination, silylation, and hydrogenation of the N_2 unit.[14] The Ohki group developed a Mo–Ti–S cluster that activates N_2 at the titanium center.[15]

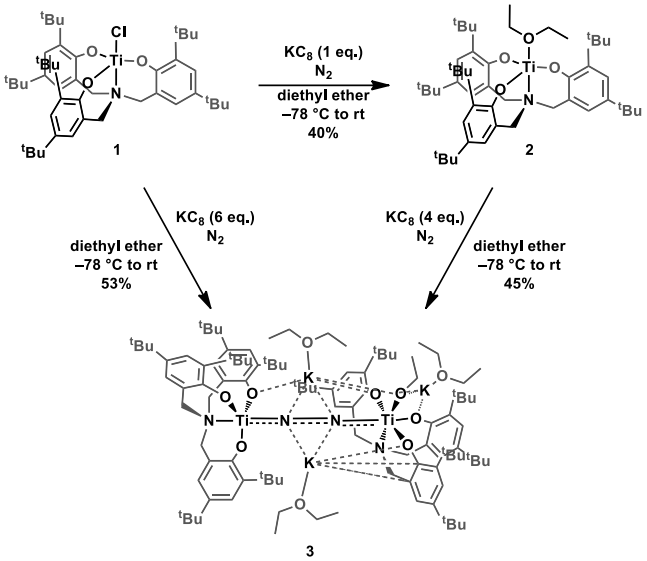
Scheme 1. Reported end-on/end-on dinitrogen transition metal complexes and an asymmetric binuclear titanium N_2 complex



- **First example of binuclear transition metal N_2 complex with trigonal bipyramidal and octahedral geometries**
- **First triphenolamine (TPA) based N_2 complex**

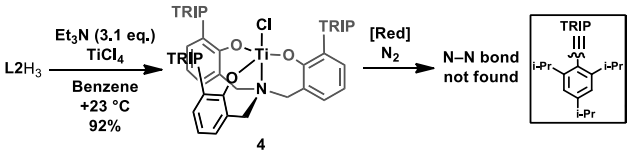
Notwithstanding the significant development in the synthesis of transition metal N_2 complexes, the number of known binuclear transition metal N_2 complexes with a different geometry on each metal center is still limited. Especially, to the best of our knowledge, a binuclear transition metal N_2 complex with octahedral and trigonal bipyramidal coordination geometries of the metal centers has never been reported. Inspired by the excellent examples of binuclear titanium N_2 complexes reported by the Liddle and Kawaguchi groups,[11,13a,13c] we explored triphenolamine (TPA) as a ligand for titanium in a catalytic N_2 activation reaction. TPA has been utilized as a ligand in many transition metal catalyzed reactions such as ring-opening and

olefin polymerization, and sulfoxidation.[16] However, TPA complexes have never been utilized for N_2 activation. Herein, we report the first example of a new end-on/end-on dinitrogen dititanium TPA complex with octahedral and trigonal bipyramidal geometries capable of catalytic nitrogen reduction to ammonia.



Scheme 2. Synthesis of titanium diethyl ether complex **2** and dititanium dinitrogen complex **3**

Reduction of the titanium chloride complex **1**[17] supported by tris(4,6-di-*tert*-butyl-2-hydroxybenzyl)amine (**L1**H_3) with one equivalent of potassium graphite (KC_8) yielded light violet-colored paramagnetic (1.79 μ_B) titanium(III) diethyl ether complex **2** (Scheme 2). The complex was purified by recrystallization from diethyl ether and single crystals of **2** were grown from the concentrated solution at room temperature. Single-crystal X-ray analysis shows that **2** adopts a trigonal bipyramidal geometry (τ = 0.97); typical for the early transition metal triphenolateamine (TPA) complexes (Figure 1 (a)).[16] The lengths of Ti–O(ether) and Ti–O_{avg}(phenolate) bonds are 2.159(3) Å and 1.911 Å, respectively while the bond distance of Ti–N is 2.181(4) Å. These lengths are similar to those observed in other known titanium TPA complexes.[16] As **1** is reduced to **2**, the distance between the titanium center and the mean plane defined by the three oxygen atoms of phenolates is shortened to 0.067 Å from 0.224 Å.[18] Notably, the formation of other titanium complexes was not observed by IR or ^{1}H NMR spectroscopy (Figure S21 and S22) when 3 equivalents of KC_8 were used for the reduction of **1** (*vide infra*).



Scheme 3. Synthesis of titanium chloride complex **4** with **L2**

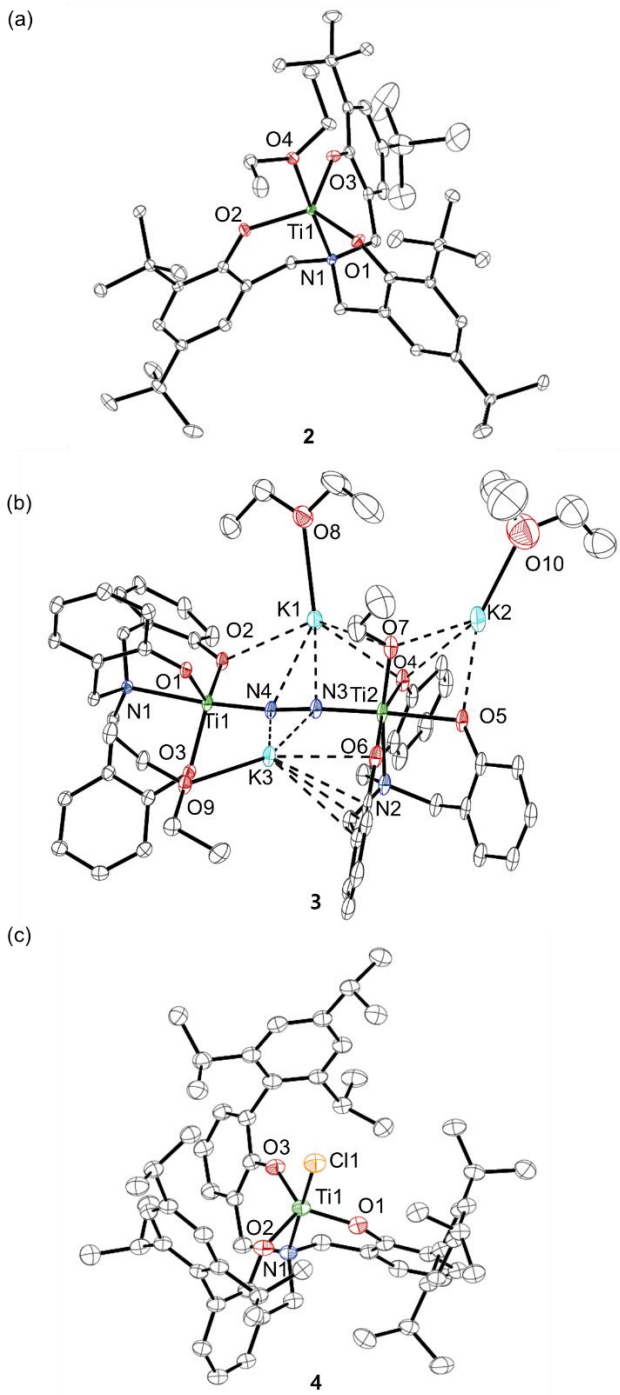


Figure 1. Crystal structures of (a) **2**, (b) **3**, and (c) **4** showing thermal ellipsoids at the 30% probability level. Hydrogen atoms and some ^{t}Bu groups were omitted for clarity. Selected bond lengths (Å) and angles (°) for complexes: **2**, Ti1–O1 1.868(2), Ti1–O4 2.159(3), Ti1–N1 2.181(4), N1–Ti1–O4 178.0(1), O1–Ti1–O2 126.1(1), N1–Ti1–O1 86.5(1); **3**, Ti1–O1 1.984(2), Ti1–N1 2.258(2), Ti1–N4 1.791(3), N3–N4 1.288(4), Ti2–N3 1.803(3), Ti2–N2 2.258(5), Ti2–O5 2.156(3), O1–Ti1–O2 118.6(1), N1–Ti1–N4 174.0(1), Ti1–N4–N3 172.6(3), N4–N3–Ti2 169.5(3), N3–Ti2–N2 89.1(1) N2–Ti2–O7 171.0(1), O4–Ti2–O5 81.6(1); **4**, Ti1–O1 1.810(2), Ti1–N1 2.302(2), Ti1–Cl1 2.283(1), N1–Ti1–Cl1 179.04(6), O1–Ti1–O2 118.46(9).

Treatment of **1** or **2** with respectively six or four equivalents of KC_8 under N_2 atmosphere yielded dark brownish-purple crystals. XRD analysis revealed the structure of the dititanium complex **3** (Scheme 2), with N_2 bound in a nearly linear manner (Figure 1 (b)). Interestingly, an odd (three) number of potassium ions stabilizes **3**, which results in a complex of low symmetry. One of the titanium centers adopts a trigonal bipyramidal (TBP) geometry (τ = 0.92) while the other is octahedral. This combination of geometries has not been reported previously to the best of our knowledge (Table S3). Dinitrogen is bound as an end-on/end-on bridging ligand between the two titanium centers, in the axial position with respect to the TBP titanium center (∡N1–Ti1–N4 = 174.0(1)°) and also positioned *cis* to the nitrogen atom of the TPA ligand of the octahedral titanium center (∡N2–Ti2–N3 = 89.1(1)°).

The Schrock group demonstrated that molybdenum N_2 complexes could be obtained either as mononuclear or binuclear complexes, depending on the steric congestion of their ligand scaffolds.[6a,6e,6f,19] Inspired by these results, we sought to investigate the steric effect of the TPA scaffold on N_2 binding. Hence, the *ortho tert*-butyl substituents were changed to 2,4,6-triisopropylphenyl (TRIP) groups in ligand **L2**H_3 (Scheme 3), studied previously by our group.[20] In a subsequent step, we expected to observe a mononuclear **L2**Ti–N_2 complex due to the sterically congested environment on the titanium center. To validate this hypothesis, a titanium complex **4** carrying the **L2** ligand was prepared and its reactivity towards dinitrogen investigated (Scheme 3). XRD analysis of **4** (Figure 1 (c)) provided the depth of the cavity, which is defined as the distance from the titanium center to the mean plane of the furthest ^{i}Pr hydrogen atoms blocking the cavity, is ~5.743 Å which is enough to hinder the formation of binuclear titanium N_2 complexes. However, despite extensive efforts, we could not obtain any dinitrogen complexes starting from **4**. This result indicates the strong tendency of early transition metals such as titanium to activate dinitrogen preferentially as binuclear complexes. Consequently, a mononuclear titanium dinitrogen complex bearing **L2** was not obtained even in the presence of the bulky TRIP groups.[21]

The N–N bond of **3** is elongated to 1.288(4) Å, which is closer to the standard length of the N–N double bonds (1.240 Å), from 1.098 Å in molecular dinitrogen and falls within the range reported for other binuclear titanium N_2 complexes.[11-13,15,22] However, it is among the shortest N–N bond distances observed in bridged N_2K_2 binuclear titanium complexes so far.[11-13,15] The Ti–N_2 bonds (Ti1–N4 1.791(3), Ti2–N3 1.803(3) Å) are shortened revealing partial titanium–imido character. The titanium ion of TBP geometry in **3** is located 0.239 Å above the mean plane defined by the three phenolates as it is re-oxidized to Ti^{IV}.

Simultaneously with dinitrogen ligand coordination, an ethoxide ligand binds to one of the titanium centers *trans* to the amine nitrogen of the TPA ligand, resulting in an octahedral geometry. Ethoxide generation from diethyl ether (solvent) and potassium graphite via C–O bond cleavage is well-documented in the literature.[13b,23] To further verify the presence of the ethoxide ligand, **3** was reacted with TMSOTf providing TMSOEt, as observed by ^{1}H NMR spectroscopy (Figure S23). Due to the C–O bond cleavage, more equivalents of KC_8 are needed to afford **3** than expected for the molecular dinitrogen capture process alone. All attempts to obtain intermediates anticipated during the formation of complex **3** from **2** failed. Furthermore, replacing potassium graphite with sodium (up to 6 equiv.) in the reduction of **1** yielded titanium diethyl complex **2** exclusively.

We believe that the change in titanium coordination geometry from TBP to octahedral in **3** is crucial for nitrogen binding due to the high steric hindrance of the active site caused by the ^{t}Bu groups of **L1**. In case of **2**, the depth of the cavity, defined as the distance from the titanium center to the mean plane of the furthest ^{t}Bu hydrogen atoms blocking the cavity,[24] is approx. ~2.496 Å. Therefore, **2** is too congested to accumulate a bridging N_2K_2 ligand between the titanium centers while maintaining TBP geometry on each metal center. In comparison, when the titanium center of **3** changes its geometry to octahedral the depth of the cavity decreases to ~1.123 Å toward the *trans* amine nitrogen, and the depth of the cavity of the opposite TBP center is also decreased to ~2.144 Å. In comparison, in Kawaguchi's [TiO_3] analogous complex,[13a] the starting complex shows lower cavity depth (~1.125 Å), which decreases to ~0.891 and ~0.900 Å, respectively, as it transforms to the binuclear titanium N_2 complex of high symmetry. Even though our system is structurally similar to Kawaguchi's system, the depth of the cavity is different because of the chelating ligand ring size. While six-membered rings are present in the case of complex **3**, the Kawaguchi system features five-membered rings resulting in a less hindered metal center.

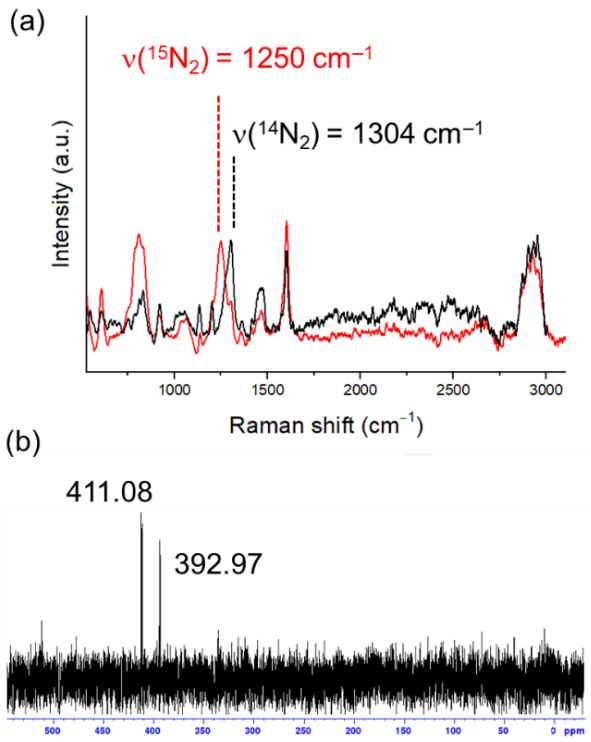
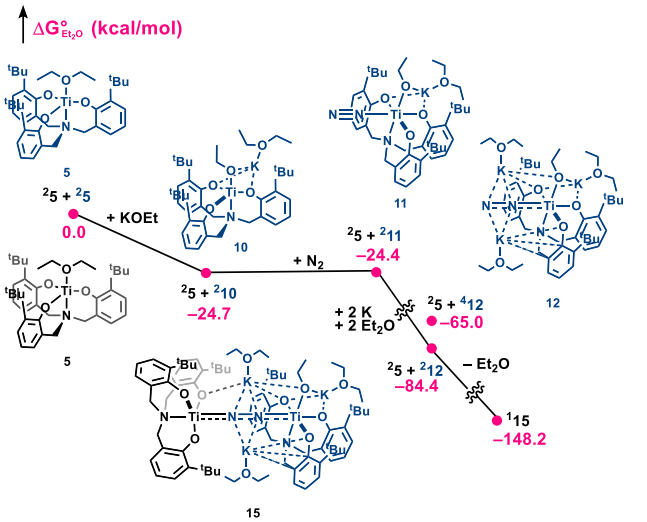


Figure 2. Selected spectral data of **3**. (a) Raman spectra of **3** (black) and **3-$^{15}N_2$** (red). (b) ^{15}N NMR spectrum (86.2 MHz) of **3-$^{15}N_2$**.

In a Raman spectrum of **3** the (N–N) band is observed at 1304 cm^{-1} which indicates a high degree of activation of the N_2 ligand (Figure 2 (a)). The corresponding ν(^{15}N–^{15}N) band of **3-$^{15}N_2$** is observed at 1250 cm^{-1}, as expected due to isotope effects.[25] The N–N band could not be observed by IR spectroscopy due to low IR activity and the presence of various

peaks in the fingerprint region.[19a] The ^{15}N NMR spectrum of the enriched $^{15}N_2$ isotopologue **3-$^{15}N_2$** features two doublets at δ = 411.08 and 392.97 (Figure 2 (b)) unlike one singlet observed in symmetric dinuclear N_2 complexes. The diamagnetic character is consistent with the $Ti^{IV}/Ti^{IV}/N_2^{4-}$ formulation, which is also supported by DFT calculations.



Scheme 4. Thermodynamic profile of a feasible mechanism for the formation of the titanium dinitrogen complex with schematic structures and relative free energies (kcal/mol) computed at the M06L/BSI//BSII, SMD level in the solution (Et_2O) phase. Ground state energies are relative to the sum of 2 equivalents of **5**. Superscripts indicate spin multiplicities.

DFT calculations were used to better understand the electronic properties and formation mechanism of **3** with a simplified ligand system (*para tert*-butyl groups of **L1** were replaced by hydrogen atoms for computational efficiency). Compound **15** (Scheme 4), which is equivalent to **3**, exhibits near-degenerated HOMO and HOMO–1 orbitals (ΔE = –2.80 kcal/mol) that are orthogonal and can be interpreted in terms of Ti→N_2 π* back bonding interactions (Figure S25). The titanium atoms transferred their electrons through the dπ electron density to the π* orbitals on the N_2 ligand. It should be noted that the z-axis of Ti2 in **15** is along the N3–Ti2–O5 bond in contrast to the starting compounds **1** and **2** (N1–Ti1–Cl1/N1–Ti1–O4), so that π back bonding from Ti2 to N_2 ligand is possible. Consequently, the calculated N–N stretching frequency is significantly lower (1430 cm^{-1}) compared to unbound nitrogen. The antibonding contribution to the Ti2–O5 interaction results in a relatively long bond (Ti2–O5 = 2.177 Å), as observed in the crystal structure of **3** (Ti2–O5 = 2.156(3) Å). In addition, the calculated Mayer bond orders of Ti1–N4, N4–N3, and Ti2–N3 of **15** are 1.41, 1.31, and 1.30, respectively, in good agreement with the bond lengths of Ti1–N4, N4–N3, and Ti2–N3 (1.791(3), 1.288(4), 1.803(3) Å) in **3** that shows strongly activated N_2. The Ti1–N1 and Ti2–O5 Mayer bond orders are 0.22 and 0.46 respectively (Figure S26).

Next, we turned our attention to the formation mechanism of **3** with an aid of DFT calculations (Scheme 4). Unlike Liddle's,[11] Chirik's,[10a] and Kajita's cases,[5ba] except the complexes **2** and **3**, other mononuclear or binuclear titanium N_2 complexes (See Scheme S1, S2, and S3), were neither observed nor isolated when **1** was reduced under various reaction conditions under N_2 atmosphere or when **2** was stored at low temperature (< –40 °C) (Figure S24). It is reasoned that the high energy barrier for the formation of **6** (Scheme S3) and the sterically congested *tert*-butyl groups block the formation of **13** even though it is thermodynamically favorable. Therefore, the formation of **3** through the reduction of **8** or **13** is unlikely. Instead, we propose that KOEt, formed in the C–O bond cleavage of Et_2O by KC_8, binds to complex **5** forming **10**. The compound is further reduced to **12** through the octahedral intermediate **11**. Complex **12** reacts with **5** to form binuclear **15**, in analogy to previous reports.[21a,26]

Table 1. NH_3 and N_2H_4 generation from the N_2 complex **3**

Entry[a,b]	Solvent	Proton source	Reductant	NH_3 (%)[c]	N_2H_4 (%)[c]
1	Et_2O	PCy_3HCl	KC_8	66	0.8
2	Et_2O	PCy_3HI	KC_8	154	1.2
3	pentane	PCy_3HI	KC_8	105	1.1
4	toluene	PCy_3HI	KC_8	82	0.2
5	Et_2O	$HBAr^F{}_4{\cdot}2Et_2O$	KC_8	88	0.7
6	Et_2O	HCl	KC_8	12	0.4
7	Et_2O	$PCy_3HBAr^F{}_4$	KC_8	83	0.1

[a] All reactions were performed under N_2 atmosphere, starting at –78 °C and gradually warming to +25 °C over 34 hours. [b] The yield was averaged over at least 3 runs. [c] Yields based on titanium ion.

With **3** in hand, we investigated its catalytic activity in N_2 reduction to ammonia (Table 1). A trace amount (<1%) of ammonia was detected when quenching **1** with strong acids such as ethereal HCl or $HBAr^F{}_4{\cdot}Et_2O$, demonstrating that strong acids can be used as proton donors for **3**. N-based acids may decompose to yield ammonium (NH_4^+) in presence of KC_8 as found by Liddle and our group,[11,27] therefore, such acids were not considered suitable proton sources. In addition, the stabilizing effect of the potassium ions in **3** has to be taken into account for the proper choice of the reducing agent. With these considerations in mind, the catalytic conversion of N_2 in **3** was examined under various conditions.

In the presence of weak acids such as PCy_3HCl and $PCy_3HBAr^F{}_4$ ($BAr^F{}_4^-$ = $B\{3,5\text{-}(CF_3)_2C_6H_3\}_4^-$) and reductant KC_8, a near-stoichiometric amount (66 and 83% respectively) of ammonia was synthesized (entries 1 and 7). While switching to strong acids, HCl/KC_8 combination resulted in lowered yield (12%) of ammonia (entry 6) while a sub-stoichiometric amount (88%) of ammonia was obtained when $HBAr^F{}_4{\cdot}2Et_2O$ was used (entry 5). When the fixation proceeded in the presence of PCy_3HI and KC_8 (entry 2), 154% per Ti was obtained. When the reduction of **3-$^{15}N_2$** with excess PCy_3HI/KC_8 was performed under $^{15}N_2$ atmosphere, $^{15}NH_4^+$ was obtained (Figure S5 and S6), confirming the N_2 gas as the nitrogen source. Notably, reductions performed in diethyl ether proceeded in better yields than those in pentane or toluene (entries 2–4), presumably due to intermediate stabilization by this solvent. In addition to ammonia, a trace amount of hydrazine was observed in all entries. It is speculated that as the reaction proceeds, the number of titanium complexes with the ethoxide ligand increases, inhibiting the regeneration of **3**. Therefore, the catalytic activity would improve if the generation of titanium ethoxide complexes was suppressed. Even though the yields of ammonia formation are lower compared to other catalysts, our results clearly demonstrate that **3** can be used as a catalyst for N_2 reduction.

In summary, we synthesized and characterized unprecedented asymmetric titanium dinitrogen complex **3** which adopts TBP-Oh geometries on the Ti centers. The preference of early transition metal complexes to activate dinitrogen as binuclear species and the decrease of the depth of the cavity of the titanium center by switching to octahedral geometry are considered the driving force for the formation of **3**. In addition, **3** is the first example of a transition metal N_2 complex supported by a TPA ligand. Complex **3** produced ammonia in more than stoichiometric amount; 154% per titanium ion in the presence of an excess amount of PCy_3HI and KC_8, a promising result in the context of N_2 reduction catalyst development. Further reactivity studies and optimization of catalytic performance in N_2 fixation are currently underway in our laboratory.

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Keywords: nitrogen fixation • dinitrogen activation • ammonia • amino triphenolate • titanium

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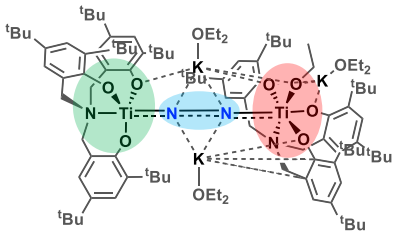

- ***First example of M(TBP)–N_2–M(Oh) geometries***
- ***First triphenolamine (TPA) based N_2 complex***
- ***N_2 reduction by K/Ti***
- ***NH_3 synthesis in the presence of H^+/e^- (up to 154%)***

We report the first example of a binuclear Ti–N_2 complex with triphenolamine that adopts trigonal bipyramidal and octahedral geometries on the Ti centers. The activated N_2 was reduced to ammonia with 154% yield (per Ti atom) in the presence of proton and electron sources.