Nitrogen Fixation **Hot Paper**

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Conversion of Dinitrogen to Nitriles at a Multinuclear Titanium Framework

*Murali Mohan Guru, Takanori Shima, and Zhaomin Hou**

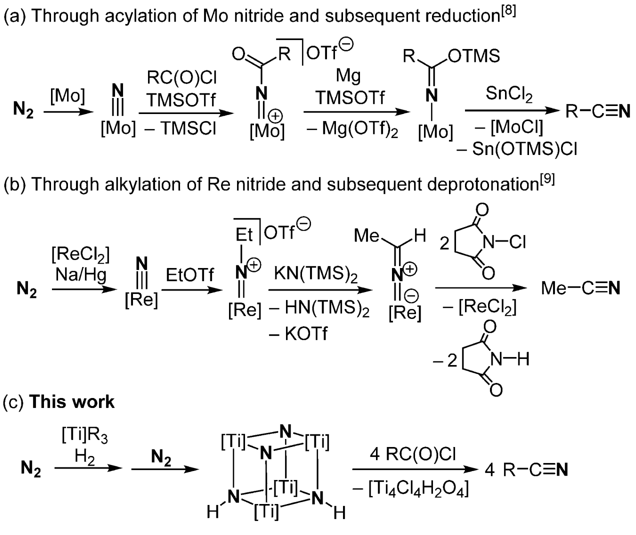
At present, ammonia (NH_3), produced by the energy-intensive Haber–Bosch process, is the only nitrogen source for the industrial preparation of nitrogen-containing organic products. Although the activation and functionalization of dinitrogen (N_2) under milder conditions have received much recent interest, studies on the direct use of N_2 as a feedstock for organic synthesis are still in their infancy. Herein we report the synthesis of nitriles using titanium-activated nitrogen species as a nitrogen source. We have found that a mixed diimide/dinitride tetranuclear titanium complex generated by N_2 activation serves as a unique platform for the synthesis of nitriles through reaction with acid chlorides. This protocol features simple reaction condition (60 °C in benzene), no requirement for extra reagents, and unprecedented functional group tolerance (compatible with aromatic C−X (X = Cl, Br, I) bonds, nitro group, and ammonia-sensitive aldehyde and chloromethyl moieties).

Activation and functionalization of dinitrogen (N_2) is a long-standing important research subject, as N_2 is an abundant and easily accessible resource but it is chemically inert under ordinary conditions. The only commercially successful process using N_2 gas as a reagent is the Haber–Bosch reaction, in which N_2 is completely reduced to ammonia (NH_3) with H_2 at high temperature (350–550 °C) and high pressure (150–350 atm) on solid catalysts.[1] To date, NH_3 (the fully hydrogenated form of N_2) is the only nitrogen source for the industrial preparation of nitrogen-containing organic products, while the direct use of N_2 as a feedstock for organic synthesis has remained a challenge.

Organic nitriles (RC≡N) are versatile intermediates for production of pharmaceuticals, agrochemicals, dyes, pigments, polyamides, and various fine chemicals.[2] Numerous ways are known for the preparation of nitriles, most of which are based on NH_3.[3] Cyanation reactions catalyzed or mediated by copper and palladium compounds were also reported for the synthesis of nitriles,[4] but this approach required the use of a toxic cyanide source whose synthesis again required NH_3.

In order to develop alternative routes without using NH_3 for the synthesis of nitrogen-containing chemicals, much effort has been devoted to the activation of N_2 using molecular organometallic complexes in the past decades. It has been reported that the reduction and cleavage of N_2 could be achieved under mild conditions by use of a combination of transition metal complexes with strongly reducing metal reagents such as KC_8, Na/Hg, and Mg[5] or with H_2.[6] The nitrogen species split in this way were evaluated in a number of E−N (E = H, C, Si, B) bond formation reactions.[7] Regarding nitrile synthesis via the direct use of metal-activated dinitrogen species, Cummins and co-workers reported the conversion of molybdenum and niobium nitride species to nitriles through reaction with acid chlorides (Scheme 1 a).[8] Very recently, Schneider and co-workers reported the synthesis of acetonitrile through the reaction of a rhenium nitride species with ethyl triflate (Scheme 1 b).[9] Despite these advances, the development of new molecular systems for the synthesis of nitriles using an N_2-based, functional group compatible route remained an important and attractive research subject.

We recently reported the formation of a tetranuclear titanium diimide/tetrahydride complex $[(\mathrm{Cp'Ti})_4(\mu_3\text{-NH})_2(\mu_2\text{-H})_4]$ (**1**, $\mathrm{Cp'} = \mathrm{C_5Me_4SiMe_3}$) by hydrogenolysis of a half-sandwich titanium trialkyl complex $[\mathrm{Cp'Ti(CH_2SiMe_3)_3}]$ with H_2 in the presence of N_2.[6a] This complex represents the first example of a tetranuclear metal complex derived from N_2 activation. In this paper, we report the conversion of



Scheme 1. Nitrile synthesis through conversion of metal-activated dinitrogen species.

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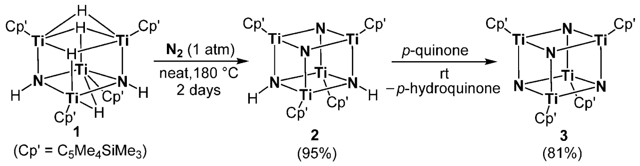
[*] Dr. M. M. Guru, Dr. T. Shima, Prof. Dr. Z. Hou
Advanced Catalysis Research Group, RIKEN
Center for Sustainable Resource Science
2-1 Hirosawa, Wako, Saitama 351-0198 (Japan)
E-mail: houz@riken.jp

Dr. T. Shima, Prof. Dr. Z. Hou
Organometallic Chemistry Laboratory, RIKEN
2-1 Hirosawa, Wako, Saitama 351-0198 (Japan)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201607426.

complex **1** to a novel diimide/dinitride complex [(Cp′Ti)$_4$(μ_3-NH)$_2$(μ_3-N)$_2$] (**2**) by reaction with N$_2$ and the use of the diimide/dinitride complex **2** as a nitrogen source for the synthesis of nitriles. We found that the reaction of the mixed diimide/dinitride complex **2** with various acid chlorides straightforwardly afforded the corresponding nitriles under simple conditions without requiring any extra reagents (Scheme 1 c). This transformation was compatible with a broad range of acid chloride substrates, including those with functional groups such as aromatic C−X (X = Cl, Br, I) bonds, nitro group, and ammonia-sensitive aldehyde and chloromethyl moieties. ^{15}N-isotope-labeled nitriles can also be efficiently prepared by using the ^{15}N-enriched analog **2-^{15}N** derived from ^{15}N$_2$ gas.



Scheme 2. Dinitrogen activation by a tetranuclear titanium hydride/imide complex.

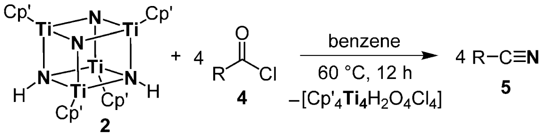
When the purple-brown titanium diimide tetrahydride complex **1** was heated in solid state under N$_2$ (1 atm) at 180 °C for two days, a dark-blue solid was obtained (Scheme 2). ^{1}H NMR analysis suggests that the product may contain a mixed valence Ti^{III}/Ti^{IV} diimide/dinitride complex [(Cp′Ti)$_4$(μ_3-NH)$_2$(μ_3-N)$_2$] (**2**) as a major component (ca. 95 %) together with a small amount of paramagnetic species (ca. 5 %). Attempts to separate **2** from the paramagnetic species by repeated recrystallization in various solvents did not give a pure product. Nevertheless, micro elemental analysis was in agreement with the formula of **2** (see the Supporting Information). The unique Ti$_4$N$_2$(NH)$_2$ cubane framework in **2** was confirmed by X-ray crystallographic studies (see the Supporting Information). These results suggest that both **2** and the unidentified species should have the similar crystallinity and similar composition.[10] In an analogous fashion, the reaction of [(Cp′Ti)$_4$(μ_3-^{15}NH)$_2$(μ-H)$_4$] (**1-^{15}N**), which was obtained by reaction of [Cp′Ti(CH$_2$SiMe$_3$)$_3$] with ^{15}N$_2$ and H$_2$,[6a] with ^{15}N$_2$ afforded the ^{15}N-enriched diimide/dinitride analog **2-^{15}N**.

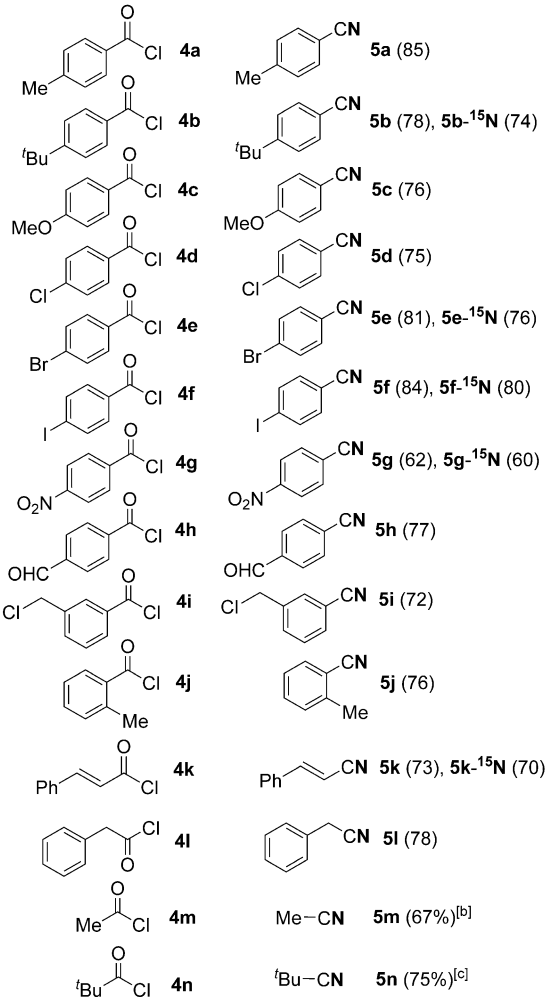
When **2** or **2-^{15}N** was allowed to react with 1.5 molar equiv of *p*-benzoquinone at room temperature, the corresponding dehydrogenated tetranitride complex **3** or **3-^{15}N** was obtained, respectively, as dark green solid in about 80 % yield (Scheme 2). The ^{15}N NMR spectrum of **3-^{15}N** showed a sharp singlet at δ_N 500.8 (using MeNO$_2$ as standard reference), in contrast to that of **2-^{15}N** which showed a broad singlet at δ_N 379.0 for the μ_3-^{15}N species and a broad singlet at δ_N −101.5 for the μ_3-^{15}NH unit. The solid structure of **3** was confirmed by X-ray crystallographic studies (see the Supporting Information).

In order to see if the imide and nitride species in a tetranuclear titanium framework could be incorporated into an organic substrate, the reaction of complexes **2** and **3** with *p*-toluoyl chloride **4a** was investigated. When the mixed diimide/dinitride complex **2** was heated with four equiv of **4a** in benzene at 60 °C for 12 h, *p*-tolunitrile **5a** was isolated in 85 % yield (Table 1).[11] In contrast, no reaction was observed between the tetranitride complexes **3** and **4a** under the same conditions.[12] These results suggest that the imide titanium species should be much more reactive than the nitrides.

The reaction of **2** with various acid chlorides was then examined in benzene at 60 °C. As shown in Table 1, aromatic acid chlorides bearing either electron-donating or electron-withdrawing groups were suitable substrates for this reaction.

Table 1: Synthesis of nitriles by reaction of a mixed imide/nitride titanium complex **2** with acid chlorides 4.[a]





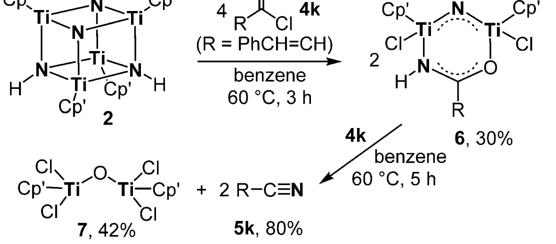
substrate	product / yield (%)
4a	**5a** (85)
4b	**5b** (78), **5b-^{15}N** (74)
4c	**5c** (76)
4d	**5d** (75)
4e	**5e** (81), **5e-^{15}N** (76)
4f	**5f** (84), **5f-^{15}N** (80)
4g	**5g** (62), **5g-^{15}N** (60)
4h	**5h** (77)
4i	**5i** (72)
4j	**5j** (76)
4k	**5k** (73), **5k-^{15}N** (70)
4l	**5l** (78)
4m	Me−CN **5m** (67%)[b]
4n	^{t}Bu−CN **5n** (75%)[c]

[a] Reaction conditions: **2** or **2-^{15}N** (0.02 mmol, 1 equiv), **4** (0.08 mmol, 4 equiv), benzene (2 mL), 12 h, isolated yield, unless otherwise noted. [b] **2** (0.01 mmol, 1 equiv), **4m** (0.05 mmol, 5 equiv), C$_6$D$_6$ (0.4 mL), 80 °C, 1 day, NMR yield. [c] **2** (0.01 mmol, 1 equiv), **4n** (0.06 mmol, 6 equiv), C$_6$D$_6$ (0.4 mL), 100 °C, 2 days, NMR yield.

The reaction of *para tert*-butyl (**4b**)- and methoxy (**4c**)-substituted benzoyl chlorides gave the desired nitrile products **5b** and **5c** in 78 % and 76 % isolated yields, respectively. Aromatic C−X (X = Cl (**4d**), Br (**4e**), I (**4f**)) bonds were compatible with the reaction conditions, leading to formation of the corresponding halogenated nitrile products **5d–f** in good yields. The reaction of **2** with *p*-nitrobenzoyl chloride **4g** selectively afforded the NO_2-substituted benzonitrile product **5g**. More remarkably, ammonia-sensitive functional groups such as aldehyde (**4h**) and chloromethyl (**4i**) also survived the present reaction conditions. 2-Methylbenzoyl chloride (**4j**) was easily transformed to *o*-tolunitrile **5j**, showing that a substituent at the *ortho* position of the acyl chloride group does not obstruct the reaction. α,β-Unsaturated acid chloride such as cinnamoyl chloride **4k** selectively afforded the corresponding α,β-unsaturated nitrile product **5k**. The reaction of phenylacetyl chloride **4l** gave the desired product phenylacetonitrile **5l** in high yield. Representative aliphatic nitriles such as acetonitrile (**5m**) and pivalonitrile (**5n**) were easily prepared by the corresponding reactions of acetyl chloride **4m** and pivaloyl chloride **4n** with **2**.

The ^{15}N-enriched nitriles **5-^{15}N** were efficiently obtained from the reaction of **2-^{15}N** with acid chlorides in an analogous fashion (Table 1). As a typical example, the $\mathrm{C{\equiv}^{15}N}$ unit in 4-bromobenzonitrile-^{15}N (**5e-^{15}N**) showed a singlet at δ_{N} −115.0 in the ^{15}N NMR spectrum and a doublet at δ_{C} 118.3 ($J_{15\mathrm{NC}} =$ 16.3 Hz) in the ^{13}C NMR spectrum. The $\mathrm{C{\equiv}^{15}N}$ bond in **5e-^{15}N** showed a strong signal at 2198 cm^{-1} in the IR spectrum, in contrast to that of **5e** (2222 cm^{-1}).

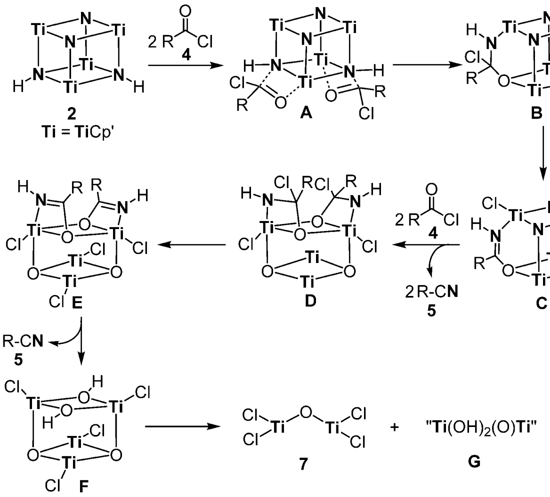
The present conversion of the diimide/dinitride titanium complex **2** to nitriles did not require any extra additives (either reducing agent or base) for the formation of a C≡N group, which stands in contrast with what was observed previously in the case of molybdenum[8] and rhenium[9] nitride species. To gain information on the reaction mechanism of the present transformation, we tried to isolate and characterize some reaction intermediates. In the reaction of **2** with cinnamoyl chloride **4k**, a binuclear titanium complex **6** with a bridging μ-amidate unit, a μ-nitride unit and a terminal chloride ligand bonding to each Ti atom was isolated in 30 % yield, after the reaction mixture was heated at 60 °C for 3 h (Scheme 3). The reaction of **2-^{15}N** with **4k** under the same conditions gave the ^{15}N-enriched analog **6-^{15}N** in 25 % isolated yield. The ^{1}H NMR spectrum of **6-^{15}N** showed a doublet at δ_{H} 6.41 ($J_{^{15}\mathrm{NH}} = 67.0$ Hz, 1 H) for the amidate NH unit. The ^{15}N NMR spectrum of **6-^{15}N** gave two sharp singlets at δ_{N} 433.6 and δ_{N} −176.3, which are assignable to the bridging nitride (μ-^{15}N) and amidate (^{15}NHC(O)R) units, respectively. The ^{13}C NMR spectrum of **6-^{15}N** showed a doublet at δ_{C} 181.6 with $J_{^{15}\mathrm{NC}} = 12.5$ Hz for the amidate carbon atom. An X-ray crystallographic diffraction analysis of **6** confirmed the molecular framework (see the Supporting Information), but further refinement was difficult because of disorder problems.



Scheme 3. Isolation and transformation of a binuclear titanium amidate/nitride complex **6**.

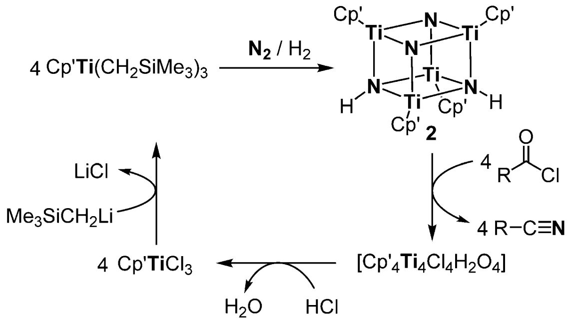
When **6** alone was heated in benzene at 60 °C for 12 h, only a trace amount of cinnamyl nitrile **5k** was observed. However, heating **6** with an equimolar amount of cinnamoyl chloride **4k** gave **5k** in 80 % yield, together with an oxo-bridged binuclear titanium chloride complex **7** (42 % yield) and some uncharacterized paramagnetic titanium species (Scheme 3). The solid structure of **7** was confirmed by X-ray diffraction study (see the Supporting Information).

On the basis of the above experimental observations, a proposed reaction mechanism is shown in Scheme 4. Nucleophilic addition of the imide units in **2** to the CO group of acid chloride **4** could give **B** via a possible transition state **A**. Chloride migration to titanium would lead to formation of **C**, which is analogous (albeit not identical) to the amidate/nitride intermediate **6** isolated in the reaction of **2** with **4k**.[13] The reaction of **C** with two molecules of acid chloride **4** would release the nitrile product **5** and give **D**, possibly through proton transfer from the amidate units to the nitride ligands and C−O bond cleavage in **C** followed by addition of the resulting imide species to the acid chloride **4**. Chloride migration to the metal center could give **E**, which upon dehydroxylation of the amidate units would release the nitrile product **5** and generate a mixed oxo/hydroxyl/chloride complex **F**. Ligand redistribution in **F** could yield the binuclear titanium oxo/chloride complex **7**, which was experimentally confirmed, together with uncharacterized paramagnetic Ti$^{\mathrm{III}}$ species such as **G**. The reaction of **6** with **4k** to give **5k** and **7** observed experimentally (Scheme 3) might take place through a process similar to the reaction of **C** with **4** to give **5**, **7**, and **G** via **D**, **E**, and **F**.[13]



Scheme 4. A plausible mechanism for nitrile formation.

To demonstrate the recyclability of the titanium complexes in the present N_2 activation and functionalization, a crude reaction mixture of **2** and an acid chloride was treated with 1.0 M HCl in Et_2O. The titanium trichloride complex was isolated in 83% yield. As reported previously,[6a] the titanium trichloride complex [$Cp'TiCl_3$] could be easily transformed to the trialkyl complex [$Cp'Ti(CH_2SiMe_3)_3$], which was able to activate N_2 with H_2. Thus, a synthetic cycle for the transformation of N_2 and acid chlorides to nitriles mediated by titanium could be realized as shown in Scheme 5.



Scheme 5. A synthetic cycle for the transformation of N_2 and acid chlorides to nitriles mediated by titanium complexes.

In summary, we have demonstrated that a mixed diimide/dinitride tetranuclear titanium complex **2** derived from the activation of N_2 can be easily converted to nitriles through reaction with acid chlorides. The reaction takes place efficiently under mild conditions without requirement for any extra reagents. Functional groups such as aromatic C-X (X = Cl, Br, I) bonds, nitro group, and ammonia-sensitive aldehyde and chloromethyl moieties are compatible. ^{15}N-isotope-labeled nitriles can be efficiently prepared by using the ^{15}N-enriched analog **2-^{15}N** derived from $^{15}N_2$ gas. The titanium complexes are recyclable in the present conversion of N_2 to nitriles. Moreover, the difference in behaviors for the nitrile formation observed among the diimide/dinitride complex **2**, its tetranitride analog **3**, and other metal nitride species reported in the literature demonstrates that an appropriate metal/ligand combination is highly important for the transformation of metal-activated nitrogen species. Studies on the activation and functionalization of dinitrogen by titanium complexes with different supporting ligands are currently in progress.

CCDC-1493845 (**2**), CCDC-1493846 (**3**), CCDC-1493848 (**6**), and CCDC-1493847 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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[10] The unidentified paramagnetic species might possibly be a further dehydrogenated trinitride monoimide species like $[(\mathrm{Cp'Ti})_4(\mu_3\text{-N})_3(\mu_3\text{-NH})]$. For more details, see the Supporting Information, and see also: J. Caballo, M. González-Moreiras, M. Greño, M. Mena, A. Pérez-Redondo, C. Yélamos, *Inorg. Chem.* **2014**, *53*, 8851.

[11] Other solvents such as toluene and THF were also suitable for this reaction, albeit giving a slightly lower yield of **5a** (ca. 70%).

[12] When the tetranitride complex **3** and **4a** was heated at 120°C overnight, **5a** was obtained in about 20% yield.

[13] The dimeric titanium amidate/nitride complex **6** could possibly be formed through isomerization (or rearrangement) of a reaction intermediate like **C** during the isolation process. For simplicity, the reaction mechanism is proposed on the basis of the original tetranuclear framework rather than the isolated dimeric species **6**.

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