# Dinitrogen Activation by Titanium Sandwich Complexes

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Low-valent titanium complexes have played a prominent role in the activation and functionalization of atmospheric nitrogen. Interest in these molecules originates with the report of N_2 fixation to ammonia by protonolysis of a $(\eta^5\text{-}C_5H_5)_2TiCl_2$/alkyllithium mixture.[1] Recently, these systems have received renewed attention due to their ability to promote the catalytic synthesis of heterocycles using atmospheric N_2 as the nitrogen source.[2] In addition, Mori and co-workers have elegantly applied this N_2-based methodology to the synthesis of several complex molecular targets, including monomorine I, ($\pm$)-lycopodine, and pumiliotoxin C.[3]

Despite this utility, the activation of dinitrogen by low-valent titanium complexes is poorly understood. Particularly intriguing is the reactivity dichotomy surrounding titanium sandwich compounds. Some titanocenes such as $(\eta^5\text{-}C_5Me_5)_2Ti$ (**1**),[4] $(\eta^5\text{-}C_5Me_4H)_2Ti$ (**2**),[5] and $(\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_3)_2)_2Ti$ (**3**)[6] react rapidly with even trace amounts of N_2 to form dimeric, end-on bound dinitrogen complexes. In contrast, the seemingly related silyl-substituted sandwiches, $(\eta^5\text{-}C_5Me_4SiR_3)_2Ti$ ($SiR_3 = Si^tBuMe_2$,[7] $SiMe_3$ (**4**),[8] etc.) are isolable, crystallographically characterized molecules that are reported to be resistant to N_2 coordination.[8b]

1: R = Me
2: R = H
3
4
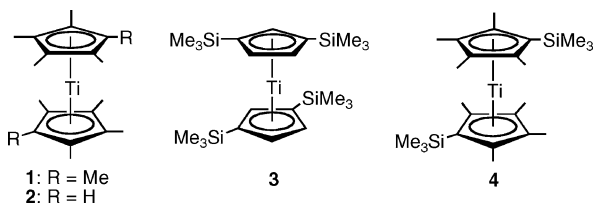
Previous work with related zirconocenes has demonstrated that small perturbations in cyclopentadienyl substitution can have profound influence on dinitrogen chemistry. For example, manipulation of Cp methyl substituents produced a zirconocene dinitrogen complex that hydrogenates N_2 to NH_3.[9] Here we explore similar substituent effects on the activation of N_2 by isolated titanocene complexes and demonstrate that *all* titanocenes investigated do indeed react with dinitrogen. Crystallographic characterization of an unprecedented monomeric titanium bis-dinitrogen complex[10] that is both isoelectronic and isostructural with more familiar dicarbonyl derivatives is also presented.

Because each of the titanocenes **1**−**4** have differing stereoelectronic properties, two new sandwiches, $(\eta^5\text{-}C_5Me_4R)_2Ti$ (R = CMe_3, **5**; $CHMe_2$, **6**), were studied.[11] We reasoned that **5** would be sterically similar to **4** but mimic the electronic environment of **1**. Reduction of $(\eta^5\text{-}C_5Me_4CMe_3)_2TiCl$ (**5-Cl**) with Na(Hg) in the presence of N_2 afforded a red solid identified as the titanocene, **5**, on the basis of NMR spectroscopy, elemental analysis, and reactivity studies.

Because **5** did not yield an isolable N_2 complex, steric rather than electronic effects seemed to dictate dinitrogen activation. To test this assertion, the [CMe_3] groups were replaced with [$CHMe_2$] substituents. As with **5**, reduction of **6-Cl** produced a red solid identified as the titanium sandwich, **6**.[11]
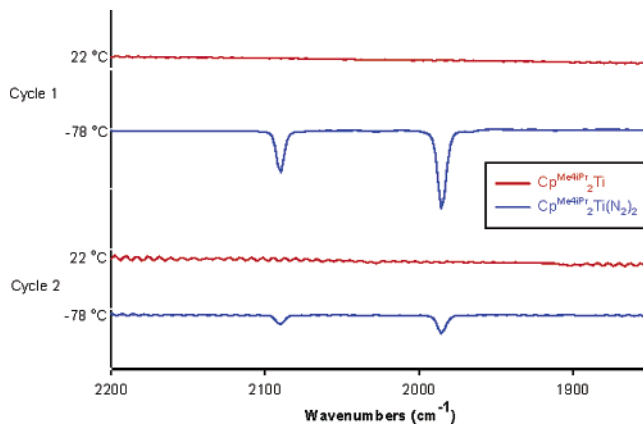

Figure 1. N_2 region of the React IR spectra of **6** (22 °C) and **6-(N₂)₂** (−78 °C) in pentane solution.

Cooling pentane or toluene solutions of isolated **6** to temperatures below −35 °C in the presence of N_2 induced a dramatic, reversible color change from red to intense blue, suggestive of dinitrogen activation. Examination of electronic spectra of chilled solutions of **6** revealed a new charge-transfer transition centered at 655 nm. This band disappears at the expense of those corresponding to **6** upon warming.[11] Additional evidence for N_2 coordination was obtained from variable-temperature in situ solution IR studies. At 22 °C, only C−H peaks assigned to **6** are observed. However, cooling to −78 °C under 1 atm of N_2 produced *two* new bands centered at 1986 and 2090 cm^{-1}. Dinitrogen coordination is completely reversible; cycling the temperature between 22 and −78 °C up to five times resulted in disappearance and reappearance of the N_2 stretches, respectively (Figure 1).

Observation of two bands in this region of the IR spectrum is reminiscent of the symmetric and asymmetric stretches of the corresponding titanocene dicarbonyl complexes and consistent with formation of $(\eta^5\text{-}C_5Me_4R)_2Ti(N_2)_2$ (**6-(N₂)₂**) (eq 1). While N_2 and CO are isoelectronic, synthesis of a monomeric, dicarbonyl-like structure with N_2 has not been previously realized.

(1)
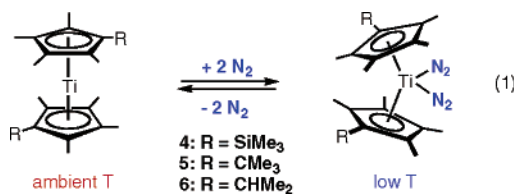
The structure of **6-(N₂)₂** has been established by X-ray diffraction (Figure 2). The C_2-symmetric molecule contains two weakly activated N_2 ligands with Ti−N(1) and N(1)−N(2) bond lengths of 2.043(1) and 1.110(2) Å, respectively. The N−N bond distance is indistinguishable from the value of 1.0976 Å found in free N_2. The presence of two N_2 ligands was confirmed by warming pentane
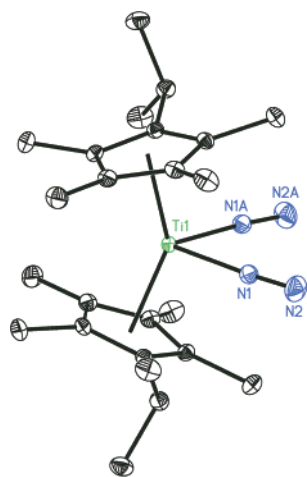
Figure 2. Molecular structure of **6-(N₂)₂** at 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

solutions prepared from crystals of **6-(N₂)₂** to ambient temperature and collecting 2 equiv per titanium of N_2 gas by a Toepler pump.

Solid-state magnetometry (Guoy balance) indicated a diamagnetic molecule, consistent with a closed-shell, 18-electron formulation. However, attempts to observe low-temperature ^{1}H NMR spectra of **6-(N₂)₂** have been unsuccessful. We believe that in solution, loss of some fraction of N_2 affords the paramagnetic sandwich **6**, which is in rapid exchange with the **6-(N₂)₂**, precluding observation of NMR signals. Support for this hypothesis is provided by the disappearance of the paramagnetically shifted peaks of **6** upon exposure to trace quantities of N_2.

Low-temperature N_2-activation by **6** prompted reinvestigation of the solution behavior of **4** and **5** by in situ IR spectroscopy. Cooling solutions of **4** to −45 °C under 1 atm of N_2 produces a single new IR stretch centered at 1984 cm^{-1}, which is complemented by two additional bands at 2002 and 2098 cm^{-1} upon further cooling to −50 °C. Bubbling N_2 through the solution at −78 °C results in a reduction of the single band with concomitant growth of the other two.[11] These results suggests that the band centered at 1984 cm^{-1} is the 16-electron, mono-dinitrogen complex, whereas the bands at 2002 and 2098 cm^{-1} correspond to **4-(N₂)₂** (eq 1). Similar temperature-dependent IR spectra were recorded for **5**, with (only) two N_2 bands being observed at 1982 and 2090 cm^{-1} at −78 °C.

The maximum temperature of N_2 binding for each titanocene was determined to establish the relative azophilicity of each sandwich (Figure 3).[11] The N_2 and CO stretching frequencies of the related bis-dinitrogen and dicarbonyl complexes are also presented for comparison. Interestingly, the bands for the N_2 complexes are more red-shifted relative to free N_2 than the corresponding dicarbonyl compounds are to free CO. These observations suggest greater N_2 activation than indicated by the metric parameters of **6-(N₂)₂**. For the alkyl-substituted titanocenes, the experimental data establishes that the N_2 binding affinity increases in the order **5 < 6 < 1**. While **5** is slightly more electron rich than **6** and **1**, the reduced azophilicity of the [CMe₃]-substituted sandwich is most likely steric in origin. It is important to note that the least crowded member of the series, **1**, forms an isolable dimeric N_2 compound.[4] Silyl-substituted **4** binds N_2 more strongly than **5** and is a consequence of the increased electrophilicity of silylated

	5	**4**	**6**	**1**
T_{max} (°C)	-75	-45,^{a} -50^b	-30	> 22
ν(N₂) (cm^{-1}) 2331 (free)	1982 2090	2002 2098	1986 2090	
ν(CO) (cm^{-1}) 2143 (free)	1855 1933	1865 1941	1859 1938	1859 1939

Figure 3. Relative N_2 binding affinities of the titanium sandwich complexes along with N_2 and CO solution IR stretching frequencies. (a) Coordination of 1 equiv of N_2. (b) Coordination of 2 equiv of N_2. Errors in temperatures are ±2 °C.

metallocenes[12−14] and the longer Cp−Si bond reducing steric bulk around the titanium center.

In summary, we have elucidated cyclopentadienyl substituent effects on the activation of dinitrogen by titanium sandwich complexes. Ligands containing sterically demanding ^{i}Pr, ^{t}Bu, and SiMe₃ substituents are blocked from dimerization and yield observable, monomeric titanium bis-dinitrogen complexes that are both isoelectronic and isostructural with more common dicarbonyl complexes. This fundamental understanding of dinitrogen activation, coupled with observation of new structural types, may aid in the understanding of stoichiometric and catalytic N_2 functionalization processes promoted by low-valent titanium.

Supporting Information Available: Experimental procedures, IR spectra, and crystallographic data for **6-(N₂)₂** (CIF, PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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