Organometallics **2007,** *26,* 2431−2438

Bis(cyclopentadienyl) Titanium Dinitrogen Chemistry: Synthesis and Characterization of a Side-on Bound Haptomer

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Received December 30, 2006

The titanocene dinitrogen complex $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Ti]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$ (**1-N$_2$**) has been prepared both by dihydrogen reductive elimination from the in situ generated monohydride derivative and by alkali metal reduction of the corresponding monoiodide. In the solid state, **1-N$_2$** contains a side-on bound N_2 ligand with an N−N bond length of 1.216(3) Å, consistent with a significant contribution from a two-electron-reduced diazenido ($[N_2]^{2-}$) fragment. Attempts to maintain side-on coordination of the N_2 ligand but increase the wedge dihedral by introducing isopropyl or *tert*-butyl substituents induced a change in hapticity to end-on and a less activated bridging dinitrogen ligand. The *ansa*-titanocene dinitrogen complexes *rac*-$[Me_2Si(\eta^5\text{-}C_5H_2\text{-}2\text{-}SiMe_3\text{-}4\text{-}{}^tBu)_2Ti]_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$ (**4-N$_2$**) and $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}{}^tBu)Ti]_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$ (**5-N$_2$**) have also been prepared and crystallographically characterized and shown to have weakly activated, end-on dinitrogen ligands. The latter example coordinates two additional equivalents of N_2 upon cooling under a dinitrogen atmosphere in pentane solution.

Introduction

Group 4 transition metal dinitrogen compounds containing side-on bound (η^2,η^2) bridging N_2 ligands continue to be attractive synthetic targets, owing to the enhanced reactivity often attributed to the increased activation imparted by this once rare hapticity.[1] Functionalization reactions such as N_2 hydrogenation,[2−4] carboxylation,[5] protonation with weak Brønsted acids,[6] and alkyne[7] and isocyanate[8] addition appear to be unique to side-on coordination, as dinitrogen loss is often observed for the analogous reactions with end-on ligated derivatives. Computational studies from our laboratory[9] and others[10] support additional back-bonding interactions present in the side-on compounds, resulting in elongated and hence more reactive N−N bonds.

While now a commonly encountered hapticity in zirconium dinitrogen chemistry[1,11] with related hafnium examples having been reported,[12,13] side-on coordination in titanium N_2 complexes remains rare. Understanding the fundamental coordination preferences of dinitrogen in titanium chemistry may ultimately prove important in elucidating the mechanism of how atmospheric nitrogen is incorporated into organic molecules using in situ generated titanium N_2 species as well as open new vistas for N_2 functionalization.[14]

The possibility of a titanocene complex with a side-on bound dinitrogen ligand was first considered by Brintzinger and co-workers with the synthesis of $[(\eta^5\text{-}C_5Me_5)_2Ti]_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$.[15] Eventually definitive structural characterization by X-ray crystallography established an η^1,η^1-dinitrogen ligand.[16] Pez and co-workers later obtained structural evidence for both end-on and side-on N_2 in a tetranuclear titanium compound.[17] Since these seminal studies, η^2,η^2-N_2 ligands have been spectroscopically characterized in bare titanium atoms in low-temperature matrixes[18,19] and by X-ray diffraction with the synthesis of $[[((Me_3Si)_2N)_2Ti]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)_2][(TMEDA)_2Li]$ (TMEDA = *N*,*N*,*N′*,*N′*-tetramethylethylenediamine).[20] In more recent chemistry, Fryzuk and co-workers have implicated the intermediacy of a side-on bound titanium dinitrogen complex during the formation of nitrogen−phosphorus bonds from coordinated N_2.[21]

Efforts in our laboratory have been focused on how cyclopentadienyl substituents can be manipulated to favor side-on hapticity in zirconocene and hafnocene dinitrogen complexes

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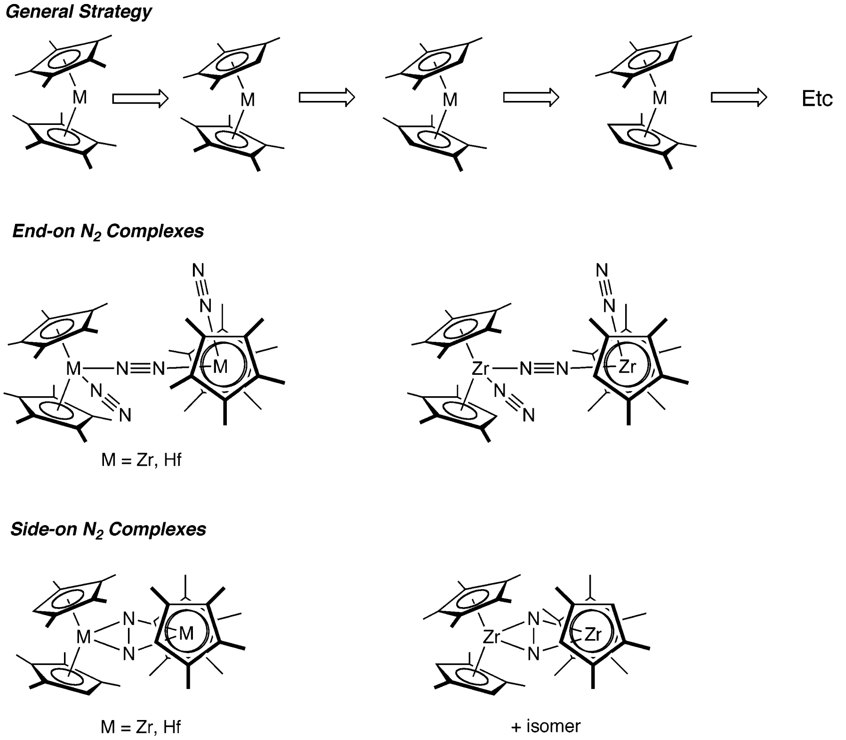

Figure 1. End-on versus side-on N_2 coordination in bis(cyclopentadienyl)zirconium and hafnium dinitrogen complexes.

(Figure 1).[11] As both $[(\eta^5\text{-}C_5Me_5)_2M(\eta^1\text{-}N_2)]_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$ (M = Zr,[22] Hf[23]) contain weakly activated, terminal and bridging end-on dinitrogen ligands, we reasoned that systematic removal of methyl groups from the $[(\eta^5\text{-}C_5Me_5)_2M]$ core would provide a more sterically accessible and electron-poor metal center and potentially favor $\eta^2,\eta^2\text{-}N_2$ coordination. In titanocene chemistry, the maximum number of cyclopentadienyl methyl groups to support side-on coordination has yet to be elucidated. As expected for the smallest metal in the triad, less than eight methyl groups will be required, as $[(\eta^5\text{-}C_5Me_4H)_2Ti]_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$[24] has been structurally characterized and shown to have an η^1,η^1-dinitrogen ligand. One possible complication with continued removal of methyl substituents is the potential for competing C−H activation of the sp^2-hybridized cyclopentadienyl ring hydrogens.[25]

In this contribution, we describe our efforts to prepare a side-on bound titanocene dinitrogen complex. A cyclopentadienyl substitution pattern that favors $\eta^2,\eta^2\text{-}N_2$ hapticity and protects the metal center from potentially deleterious C−H activation reactions has been discovered. Exploration of related *ansa*-titanocene dinitrogen chemistry along with structural characterization of several N_2 complexes is also described.

Results and Discussion

Synthesis of a Side-on Bound Bis(cyclopentadienyl)titanium Dinitrogen Complex. On the basis of the results of Teuben and co-workers, who established end-on (η^1,η^1) coordination in $[(\eta^5\text{-}C_5Me_4H)_2Ti]_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$,[24] titanocene complexes bearing fewer methyl groups were targeted with the goal of encouraging $\eta^2,\eta^2\text{-}N_2$ hapticity. For this reason, the chemistry of titanocene compounds bearing two 1,2,4-trimethyl cyclopentadienide rings was initially explored. We also reasoned that this disposition of substituents would protect the titanium from competing C−H activation reactions.

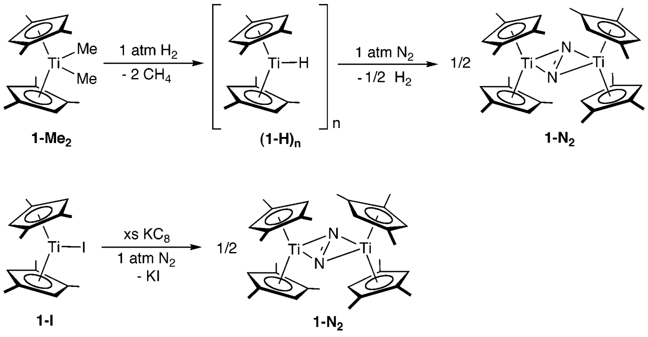

Figure 2. Synthesis of **1-N$_2$** by reductive elimination of dihydrogen and alkali metal reduction.

One method of preparing titanocene dinitrogen complexes is by reductive elimination of dihydrogen from the corresponding monohydride compounds.[26] The titanocene(III) hydride complexes are routinely accessed by hydrogenation of the dimethyl derivative. The desired titanocene dimethyl complex, $(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2TiMe_2$ (**1-Me$_2$**), was prepared by straightforward methylation of the corresponding dichloride precursor, **1-Cl$_2$**.[27] Exposure of a pentane solution of **1-Me$_2$** to 1 atm of dihydrogen followed by addition of N_2 yielded the desired titanocene dinitrogen complex, $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Ti]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$ (**1-N$_2$**), as a blue-purple solid (Figure 2). Presumably hydrogenation of **1-Me$_2$** furnishes the titanocene monohydride, $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2TiH]_n$ (**1-H**)$_n$, which undergoes bimolecular reductive elimination in the presence of N_2 to form **1-N$_2$**.[24] Attempts to observe the titanocene monohydride by ^1H NMR spectroscopy have proven challenging, as the spectra are complex, indicating

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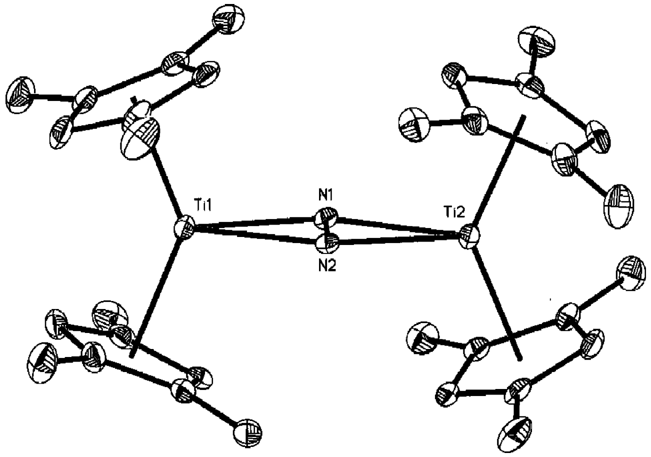


Figure 3. Molecular structure of **$1\text{-}N_2$** at 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

a mixture of paramagnetic monomeric and dimeric titanium hydride compounds. In addition, (**1-H**)$_n$ converts rapidly to **$1\text{-}N_2$** upon exposure to even trace amounts of dinitrogen,[24] further complicating handling and storing the compound.

The dark blue-purple titanocene dinitrogen complex, **$1\text{-}N_2$**, was also synthesized by alkali metal reduction (Figure 2). Both alkali metal reduction of titanocene monohalides and binuclear H_2 reductive elimination from the monohydride derivative are long standing and equivalent methods for the synthesis of titanocene dinitrogen complexes. In most cases, the reduction procedure is preferred, as fewer synthetic steps are required. Stirring **1-I** with excess KC_8 under 1 atm of dinitrogen followed by filtration and recrystallization from pentane furnished **$1\text{-}N_2$** as analytically pure crystals. **$1\text{-}N_2$** could also be prepared from reduction of **1-Cl**[28] with excess 0.5% sodium amalgam, although trace quantities of the titanocene monochloride persisted in the final product and could not be removed by repeated crystallizations. Use of the titanocene monoiodide complex, **1-I**, and KC_8 (rather than Na(Hg)) obviated this complication and produced **$1\text{-}N_2$** free of monohalide contaminants.

The electronic spectrum of **$1\text{-}N_2$** in pentane solution exhibits a moderately intense ($\epsilon = 4700$ M^{-1} cm^{-1}) band at $\lambda_{max} = 571$ nm. Notably, no other absorptions were observed in the near-IR region of the spectrum, unlike side-on bound zirconocene dinitrogen complexes with strongly activated hydrazido ($[N_2]^{4-}$) type ligands.[4] A solid-state magnetic moment of 2.7(2) μB was determined for **$1\text{-}N_2$** at 23 °C. This value is slightly attenuated to 2.2(2) μB in benzene-d_6 solution.[29] Both values are close to the spin-only value expected for a symmetric bimetallic complex bearing two Ti(III), d^1 centers.[30] Accordingly, the benzene-d_6 ^{1}H NMR spectrum of **$1\text{-}N_2$** exhibits three paramagnetically broadened and shifted resonances that have proven useful for identifying the compound. Confirmation of the presence of coordinated dinitrogen has also been provided by Toepler pump analysis, where treatment of **$1\text{-}N_2$** with excess PhC≡CPh yielded 74% of the expected noncombustible gas (N_2) and (η^5-C_5H_2-1,2,4-Me_3)$_2$Ti(PhC≡CPh) (**1-(PhCCPh)**).

Single crystals of **$1\text{-}N_2$** suitable for X-ray diffraction were obtained from a concentrated pentane solution at −35 °C, and a representation of the molecular structure is presented in Figure 3. The N−N and Ti−N bond lengths for this and all crystallographically characterized compounds in this work are reported in Table 1. Notably, the crystal structure establishes a rare example of side-on N_2 coordination in a titanocene dinitrogen complex. The N−N bond length of 1.216(3) Å is longer than the values of ∼1.1 Å typically observed in the weakly activated end-on haptomers.[16,24,31] This distance is shorter than the N−N distance of 1.379(21) Å reported by Gambarotta for [[((Me$_3$Si)$_2$N)$_2$Ti]$_2$(μ_2,η^2,η^2-N_2)$_2$][(TMEDA)$_2$Li].[20] The N−N bond distance along with the observed magnetism support a two-electron-reduced $[N_2]^{2-}$ ligand.

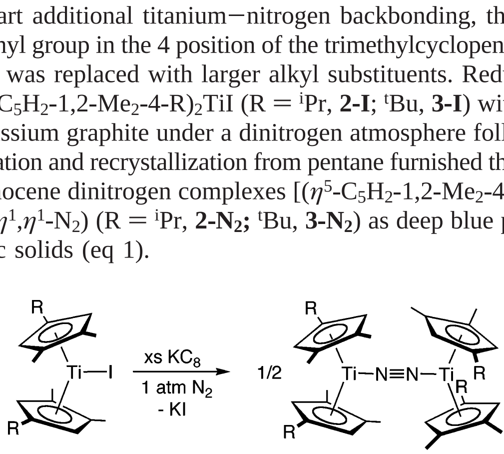
Table 1. N−N and Ti−N Bond Distances in Titanocene Dinitrogen Complexes

compound	*d*(N−N) Å	*d*(Ti−N) Å
$1\text{-}N_2$	1.216(3)	2.142(2)
		2.157(2)
$2\text{-}N_2$	1.168(3)	1.9713(13)
$4\text{-}N_2$	1.174(3)	2.0096(14)
$5\text{-}N_2$	1.165(3)	1.991(2)
		1.990(2)
$5_2\text{-}(N_2)_3$	1.153(3) (br)	1.997(2)
	1.101(3) (term)	2.068(3)
	1.109(3) (term)	1.995(2)
		2.068(2)

The cyclopentadienyl ligands in the solid-state structure of **$1\text{-}N_2$** are oriented in an idealized *C_2* disposition about each titanium. A small torsional angle[32] of 12.2° is observed in the solid state and does not offer the appropriate geometry for effective overlap for significant backbonding between the N_2 π^* and the $1a_1$ titanocene orbitals.[9] The lack of backbonding is evident in the reduction of the dinitrogen ligand, where an $[N_2]^{2-}$ rather than $[N_2]^{4-}$ fragment is observed. This may not only be due to the lack of a torsional angle but also be related to the lower reduction potential and spin state of the first-row metal as compared to its second- and third-row counterparts.[44]

As expected for a complex with a small wedge dihedral angle and a weakly activated dinitrogen ligand, addition of 1 atm of dihydrogen to **$1\text{-}N_2$** did not result in N−H bond formation. Instead, no change was observed even upon heating to 65 °C. Attempts to induce N_2 hydrogenation at higher temperatures resulted in decomposition of the titanocene complex. Importantly, these studies establish that in titanocene dinitrogen chemistry six cyclopentadienyl methyl groups favor side-on coordination, while those with larger zirconium and hafnium ions tolerate eight methyl ring substituents.

In an attempt to enforce a larger wedge dihedral angle and impart additional titanium−nitrogen backbonding, the unique methyl group in the 4 position of the trimethylcyclopentadienide ring was replaced with larger alkyl substituents. Reduction of (η^5-C_5H_2-1,2-Me_2-4-R)$_2$TiI (R = ^{i}Pr, **2-I**; ^{t}Bu, **3-I**) with excess potassium graphite under a dinitrogen atmosphere followed by filtration and recrystallization from pentane furnished the desired titanocene dinitrogen complexes [(η^5-C_5H_2-1,2-Me_2-4-R)$_2$Ti]$_2$(μ_2,η^1,η^1-N_2) (R = ^{i}Pr, **$2\text{-}N_2$;** ^{t}Bu, **$3\text{-}N_2$**) as deep blue paramagnetic solids (eq 1).



(1)

2-I: R = ^{i}Pr
3-I: R = ^{t}Bu
$2\text{-}N_2$: R = ^{i}Pr
$3\text{-}N_2$: R = ^{t}Bu

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[32] The wedge dihedral angle is defined as the angle between planes formed by the metal center and the cyclopentadienyl centroids.

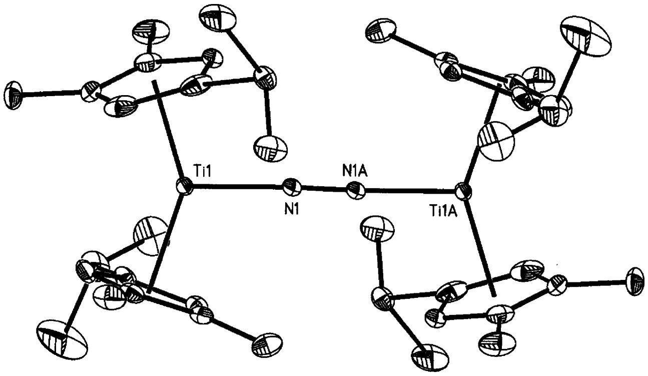
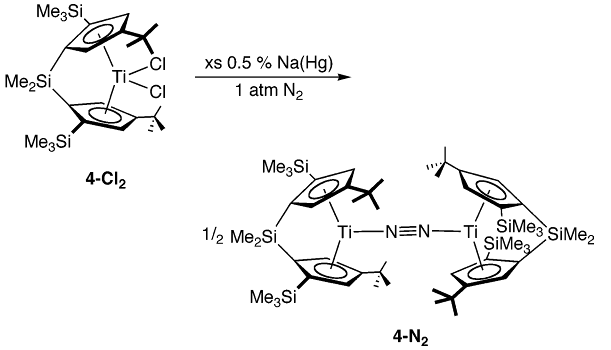


Figure 4. Molecular structure of **2-N$_2$** at 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

The end-on hapticity of the dinitrogen ligand in **2-N$_2$** was confirmed by X-ray diffraction (Figure 4). As is typical in dinitrogen complexes of this type,[33] a relatively short N≡N bond length of 1.168(3) Å is observed, consistent with weak activation. The bent titanocene fragments that compose the dimer are related by an inversion center between N(1) and N(1A). Accordingly, the wedge dihedral angle is 0°. The small torsional angles observed in **1-N$_2$** and **2-N$_2$** are similar to that reported for $[(\eta^5\text{-}C_5Me_4H)_2Ti]_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$[24] but contrast the near orthogonal values reported for $[(\eta^5\text{-}C_5Me_5)_2Ti]_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$,[16] which is likely due to the alleviation of crowding between the sterically demanding [C_5Me_5] rings. X-ray data collected on poor-quality crystals of **3-N$_2$** also support end-on hapticity of the N_2 ligand in this compound. As a result, it appears that introduction of larger cyclopentadienyl substituents does not impart a "twist"' in the wedge dihedral but rather induces a change in hapticity from side-on to end-on.

***ansa*-Titanocene Dinitrogen Complexes.** An alternative strategy for the preparation of side-on bound titanocene dinitrogen complexes is to use *ansa*-bis(cyclopentadienyl) ligands, whereby the two rings are tethered by an [Me_2Si] bridge. The conformational stability, increased electrophilicity, and more exposed metal center imparted by this class of ligand[34] suggested that η^2,η^2-N_2 hapticity may result. In addition, two side-on bound zirconocene dinitrogen complexes bearing [Me_2Si]-bridged ligands, $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}^tBu)Zr]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$[35] and *rac*-$[Me_2Si(\eta^5\text{-}C_5H_2\text{-}2\text{-}SiMe_3\text{-}4\text{-}^tBu)_2Zr]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$,[36] have been reported.

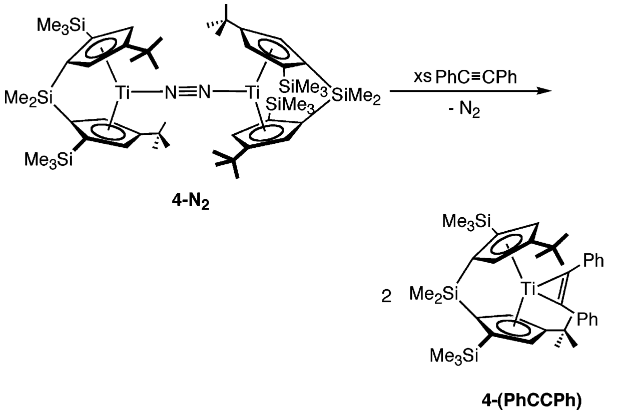
Reduction of a toluene slurry of *rac*-$Me_2Si(\eta^5\text{-}C_5H_2\text{-}2\text{-}SiMe_3\text{-}4\text{-}^tBu)_2TiCl_2$[37] (**4-Cl$_2$**) with excess 0.5% sodium amalgam in the presence of an atmosphere of dinitrogen furnished a deep blue solution from which the dinitrogen complex *rac*-$[Me_2Si(\eta^5\text{-}C_5H_2\text{-}2\text{-}SiMe_3\text{-}4\text{-}^tBu)_2Ti]_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$ (**4-N$_2$**) was isolated (eq 2). A benzene-d_6 solution magnetic moment of 2.1(2) μB was measured at 23 °C and is consistent with the values determined for other μ_2-N_2 titanocene complexes with two Ti(III), d^1 centers.



(2)

The solid-state structure of **4-N$_2$** was determined by X-ray diffraction, and a representation of the molecular structure is presented in Figure 5. The metrical parameters for the Ti−N and N−N bonds are reported in Table 1, while those associated with the *ansa* ligand are shown in Table 2. A C_2 homochiral dimer is observed in the solid state with the principal axis bisecting the N(1)−N(1A) bond. The structure also establishes end-on coordination of the dinitrogen ligand with a short N−N bond distance of 1.174(3) Å, consistent with weak activation. This hapticity contrasts the zirconium congener where side-on coordination is observed[36] and demonstrates the amplified steric environment imparted by the same ligand with the smaller first-row ion. Notably, a wedge dihedral angle of 43° is observed in **4-N$_2$** and is close to the value reported for the zirconium complex.[36]

Confirmation that **4-N$_2$** retains its dinitrogen ligand in solution was provided by a Toepler pump analysis. Treatment of the N_2 complex with excess diphenylacetylene liberated 83% of the expected noncombustable gas, consistent with coordination of 1 equiv of dinitrogen. From this procedure, the titanocene alkyne complex *rac*-$Me_2Si(\eta^5\text{-}C_5H_2\text{-}2\text{-}SiMe_3\text{-}4\text{-}^tBu)_2Ti(PhC{\equiv}CPh)$ (**4-PhCCPh**) was isolated as a diamagnetic, red crystalline solid (eq 3).



(3)

The observation of end-on hapticity in **4-N$_2$** prompted investigation of other *ansa*-cyclopentadienyl ligands with either smaller or fewer ring substituents. $[Me_2Si(C_5Me_4)(C_5H_3\text{-}3\text{-}^tBu)]^{2-}$ was explored, as this ligand has been shown to support a side-on coordinated zirconocene dinitrogen complex that undergoes facile N_2 hydrogenation upon exposure to H_2.[35] Boiling a THF solution containing equimolar amounts of $Li_2[Me_2Si(C_5Me_4)(C_5H_3\text{-}3\text{-}^tBu)]$ and $TiCl_3(THF)_3$ for 24 h followed by filtration and recrystallization from pentane yielded the *ansa*-titanocene monochloride complex, $Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}^tBu)TiCl$ (**5-Cl**), a paramagnetic ($\mu_{\text{eff}} = 1.5\ \mu_B$, benzene-$d_6$, 23 °C), red-brown solid. Reduction of **5-Cl** in toluene with an excess of 0.5% sodium amalgam under a

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[37] Chacon, S. T.; Coughlin, E. B.; Henling, L. M.; Bercaw, J. E. *J. Organomet. Chem.* **1995**, *497*, 171.

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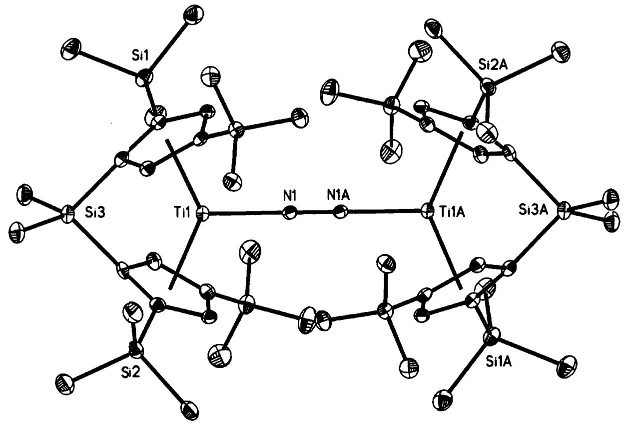


Figure 5. Molecular structure of **(S,S)-4-N$_2$** at 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

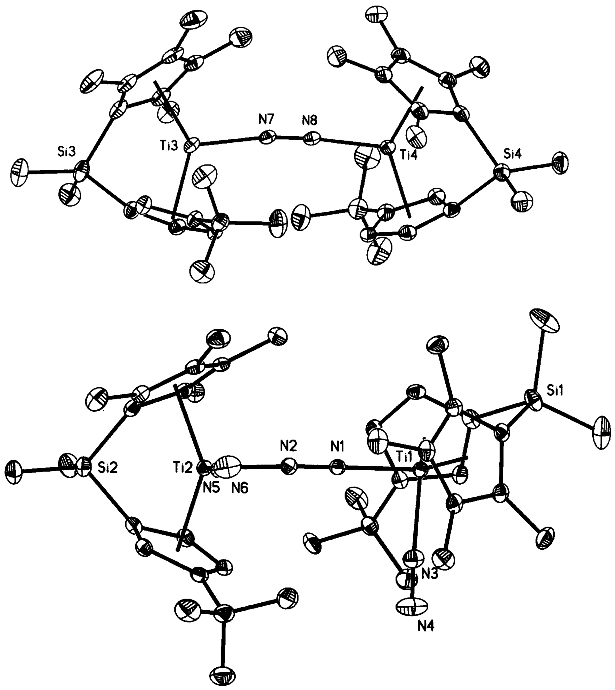
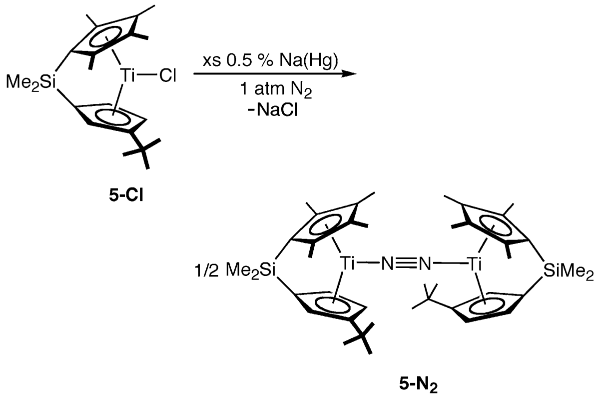


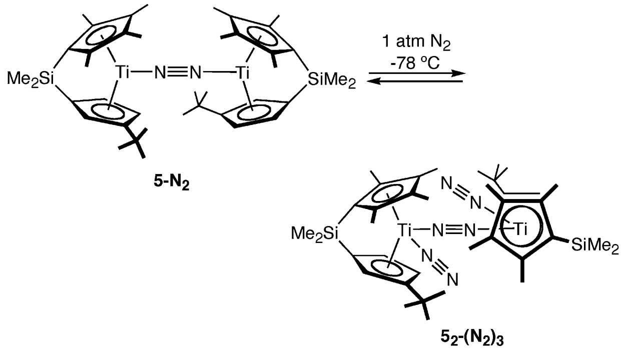
Figure 6. Molecular structures of cocrystallized **(SS)-5-N$_2$** (top) and **(SS)-5$_2$-(N$_2$)$_3$** (bottom) at 30% probability ellipsoids. Hydrogen atoms and cocrystallized pentane molecules are omitted for clarity.

dinitrogen atmosphere furnished a blue solution, from which [Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$-3-^{t}Bu)Ti]$_2$(μ_2,η^1,η^1-N$_2$) (**5-N$_2$**) was isolated at ambient temperature (eq 4).



(4)

Previous work from our laboratory has demonstrated that unconstrained titanocene complexes of the general formula (η^5-C$_5$Me$_4$R)$_2$Ti (R = alkyl, silyl) coordinate 1 or 2 equiv of dinitrogen upon cooling in hydrocarbon solution.[38,39] Cooling an approximately 0.005 M pentane solution of **5-N$_2$** to −78 °C produced two new bands centered at 2059 and 2086 cm^{-1}, signaling formation of [Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$-3-^{t}Bu)Ti(η^1-N$_2$)]$_2$(μ_2,η^1,η^1-N$_2$) (**5$_2$-(N$_2$)$_3$**) (eq 5). The stretch for the μ_2-N$_2$ ligand was not located.



(5)

The additional dinitrogen coordination is reversible, as cycling the temperature between 23 and −78 °C resulted in the disappearance and reappearance of these peaks, respectively. The maximum temperature of N$_2$ coordination was found to be −19 °C and is comparable to the range previously reported for unconstrained compounds.[38] Variable-temperature ^{1}H NMR spectroscopy also allowed detection of additional dinitrogen coordination. Cooling a toluene-*d*$_8$ solution of **5-N$_2$** to −70 °C under 4 atm of N$_2$ produced the number of resonances expected for two homochiral diamagnetic titanocene dinitrogen complexes of **5$_2$-(N$_2$)$_3$**. The presence of two isomers was confirmed by ^{15}N NMR spectroscopy, where the major isomer exhibited three peaks, while the minor exhibited six. Observation of three peaks for the major isomer is consistent with a C_2-symmetric, homochiral dimer with *transoid* terminal N$_2$ ligands. The presence of six peaks for the minor indicates a homochiral dimer with *cisoid* terminal N$_2$ ligands. Warming the sample to 23 °C regenerated the paramagnetically broadened and shifted peaks attributed to **5-N$_2$**.

Recrystallization of **5-N$_2$** from a concentrated pentane solution at −35 °C produced single crystals suitable for X-ray diffraction. The X-ray data established a cocrystal comprised of an equimolar mixture of **5-N$_2$** and **5$_2$-(N$_2$)$_3$** (Figure 6) along with two molecules of pentane. Comparing the two solid-state structures revealed interesting conformational differences between the two dinitrogen compounds. As was observed with the corresponding zirconium dinitrogen complex,[35] reduction of **5-Cl** yielded only the homochiral diastereomer of the N$_2$ compound.[40] **5-N$_2$** has a wedge dihedral angle of 36.7°, whereas **5$_2$-(N$_2$)$_3$** has a much larger twist with a torsional angle of 61.4°. The larger value observed with coordination of additional dinitrogen is likely due to the ability to increase backbonding interactions upon twisting the dimer.

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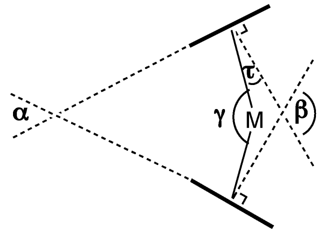
(39) Hanna, T. E.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 6018.

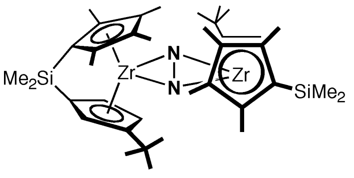
(40) In the static limit, each homochiral dimer has the possibility of distinct conformers. Sighting down the Ti−Ti vector, clockwise rotation away from a dihedral angle of 0° gives the positive synclinal conformation, while counterclockwise rotation yields the negative synclinal conformation. Because only one set of peaks for the homochiral diastereomer is observed by NMR spectroscopy, a fluxional process occurs in solution to rapidly interconvert the conformers. For a discussion of synclinal and anticlinal conformers see: Carroll, F. A. *Perspectives on Structure and Mechanism in Organic Chemistry*; Brooks-Cole: Pacific Grove, CA, 1998; pp 121−122.

(41) Pangborn, A.; Giardello, M.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

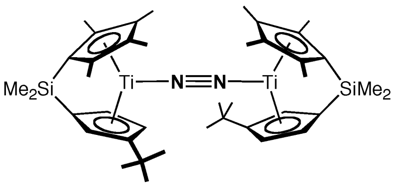
Table 2. Selected Metrical Parameters for the *ansa*-Ligands in 4-N_2, 5-N_2, and 5_2-$(N_2)_3$ and Comparison to Zr Congeners



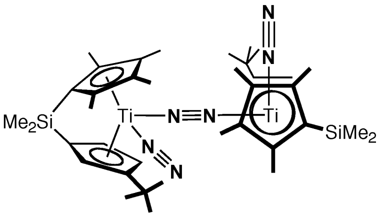
$\alpha = 180 - \beta$; $\alpha = 2\tau - \gamma$; $\tau = 0.5(\gamma - \beta)$



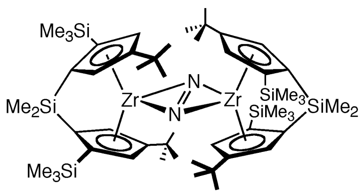
$\alpha = 60.2^{\circ}$
$\beta = 119.8^{\circ}$
$\gamma = 125.5^{\circ}$
$\tau = 2.85^{\circ}$
Dihedral Angle = 54.1°



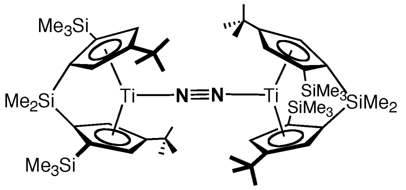
5-N_2
$\alpha = 48.8^{\circ}$
$\beta = 131.2^{\circ}$
$\gamma = 135.9^{\circ}$
$\tau = 2.35^{\circ}$
Dihedral Angle = 36.7°



5_2-$(N_2)_3$
$\alpha = 55.9^{\circ}$
$\beta = 124.1^{\circ}$
$\gamma = 135.9^{\circ}$
$\tau = 5.9^{\circ}$
Dihedral Angle = 61.4°



***rac*-$[BpZr]_2(\mu_2, \eta^2, \eta^2\text{-}N_2)$**
$\alpha = 61.7^{\circ}$
$\beta = 118.3^{\circ}$
$\gamma = 125.1^{\circ}$
$\tau = 3.4^{\circ}$
Dihedral Angle = 46.4°



4-N_2
$\alpha = 52.6^{\circ}$
$\beta = 127.4^{\circ}$
$\gamma = 134.7^{\circ}$
$\tau = 3.65^{\circ}$
Dihedral Angle = 43.2°

Both compounds exhibit weakly activated dinitrogen ligands, as is typical of end-on coordination.[33] In **5-N_2**, an N(7)−N(8) bond distance of 1.165(3) Å was observed, whereas in **5_2-$(N_2)_3$** the bridging dinitrogen ligand has an N(1)−N(2) distance of 1.153(3) Å and the terminal N_2 ligands have slightly shorter bond lengths of 1.101(3) and 1.109(3) Å.

Concluding Remarks

Synthesis of a rare example of a side-on bound titanocene dinitrogen complex has been accomplished by reducing the number of cyclopentadienyl methyl substituents about the metallocene core. As has been observed in analogous zirconium and hafnium chemistry, η^2,η^2 hapticity of the bridging N_2 ligand results in greater activation of the dinitrogen fragment as compared to related end-on compounds. However, in $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Ti]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$, both the metrical parameters and the observed magnetism are consistent with a two-electron-reduced diazenido ligand rather than a four-electron-reduced $[N_2]^{4-}$ core. Accordingly, no addition of dihydrogen across the titanium−nitrogen bonds was observed. Attempts to prepare side-on dinitrogen complexes using $[Me_2Si]$-bridged bis(cyclopentadienide) ligands have been unsuccessful, as only end-on haptomers have been structurally characterized. In one example, additional N_2 coordination was observed both in the solid state and in solution upon cooling. These results highlight the importance of ligand design in controlling dinitrogen hapticity and activation.

Experimental Section

General Considerations. All air- and moisture-sensitive manipulations were carried out using standard high-vacuum line, Schlenk, or cannula techniques or in an MBraun inert atmosphere drybox containing an atmosphere of purified nitrogen. The MBraun drybox was equipped with a cold well designed for freezing samples in liquid nitrogen. Solvents for air- and moisture-sensitive manipulations were dried and deoxygenated using literature procedures.[41] Benzene-d_6 and toluene-d_8 were purchased from Cambridge Isotope Laboratories and were distilled from sodium metal under an atmosphere of argon. The toluene-d_8 was further dried over "titanocene".[42] Hydrogen and argon gas were purchased from Airgas Incorporated and passed through a column containing manganese oxide supported on vermiculite and 4 Å molecular sieves before admission to the high-vacuum line. Carbon monoxide was purchased from Aldrich and passed through a liquid-nitrogen-cooled trap immediately before use. Me_2SiCl_2 was dried over CaH_2 prior to use. Preparations of **1-Cl_2**,[27] **1-Cl**,[28] $Li_2[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}{}^tBu)]$,[43] and **4-$Cl_2$**[37] were accomplished according to literature procedures.

^1H NMR spectra were recorded on Varian Mercury 300 and Inova 400 and 500 spectrometers operating at 299.763, 399.780,

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(42) Marvich, R. H.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1971**, *93*, 2046.

(43) Antiñolo, A.; López-Solera, I.; Otero, A.; Prashar, S.; Rodríguez, A. M.; Villaseñor, E. *Organometallics* **2002**, *21*, 2460.

(44) Musaev, D. G.; Bobadov-Parvanova, P.; Morokuma, K. *Inorg. Chem.*, published online Mar 7, 2007 http://dx.doi.org/10.1021/ic062405b.

and 499.92 MHz, respectively. ^{13}C NMR spectra were recorded on the spectrometers operating at 75.383, 100.54, and 125.716 MHz, respectively. All chemical shifts are reported relative to $SiMe_4$ using the ^{1}H (residual) chemical shift of the solvent as a secondary standard. Gradient-selected DQCOSY was acquired with a sweep width of 1.8 kHz in phase-sensitive mode. A total of 64 complex points were collected in the indirectly detected dimension with 2 scans and 1K points per increment. The resulting matrix was zero filled to 2K × 2K complex data points, and 90 shifted squared sinusoidal window functions were applied in both dimensions prior to Fourier transform. EXSY spectra were acquired with a sweep width of 1.8 kHz and a mixing time of 0.2 s in phase-sensitive mode. A total of 64 complex points were collected in the indirectly detected dimension with 16 scans and 1K points per increment. The resulting matrix was zero filled to 2K × 2K complex data points, and 90 shifted squared sinusoidal window functions were applied in both dimensions prior to Fourier transform.

Unless noted otherwise, magnetic moments were measured at 23 °C by the method originally described by Evans[15] with stock and experimental solutions containing a known amount of a ferrocene standard. Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox and were quickly transferred to the goniometer head of a Siemens SMART CCD area detector system equipped with a molybdenum X-ray tube (λ = 0.71073 Å). Preliminary data revealed the crystal system. A hemisphere routine was used for data collection and determination of lattice constants. The space group was identified, and the data were processed using the Bruker SAINT program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Madison, NJ. Infrared spectroscopy was conducted on a Mattson RS-10500 Research Series FT-IR spectrometer calibrated with a polystyrene standard.

Solution infrared spectra were recorded with an in situ IR spectrometer fitted with a 30-bounce, silicon-tipped probe optimized for sensitivity. The spectra were acquired in 16 scans (30 s intervals) at a gain of one and a resolution of four. A representative reaction was carried out as follows: The IR probe was inserted through a nylon adapter and O-ring seal into a flame-dried, cylindrical flask fitted with a magnetic stir bar and T-joint. The T-joint was capped by a septum for injections and a nitrogen line. Following evacuations under full vacuum and flushing with nitrogen, the flask was charged with pentane and a background was recorded at ambient temperature and at −78 °C. The flask was then charged with a pentane solution of titanocene to make the final reaction volume 10.0 mL with approximately 5.0 mM concentration. The samples were cooled using ethanol/dry ice or acetone/dry ice baths, and the temperatures were monitored using an external, low-temperature thermometer. The reactions were recorded between 20 and 40 intervals.

The maximum temperature for N_2 coordination was determined by monitoring the IR spectrum as a function of temperature. The temperature of the sample was raised in five degree increments until the N_2 stretches were no longer observed. Once the approximate binding temperature was recorded, the temperature of the sample was then changed in approximately one degree increments until a more precise value was measured. The error associated with the measurements is ±2 °C.

Preparation of (η^5-C_5H_2-1,2,4-Me_3)$_2$TiMe$_2$ (1-Me$_2$). A 20 mL scintillation vial was charged with 0.790 g (2.37 mmol) of **1-Cl$_2$** and approximately 10 mL of diethyl ether. The solution was chilled to −35 °C, and 3.5 mL (5.60 mmol) of 1.6 M methyl lithium solution in diethyl ether was added. The resulting reaction mixture was stirred overnight. The solvent was removed and the residue extracted with pentane, filtered through Celite, and recrystallized at −35 °C to yield 0.616 g (89%) of **1-Me$_2$** as a yellow solid. Anal. Calcd for $C_{18}H_{28}Ti$: C, 73.96; H, 9.66. Found: C, 73.86; H, 9.90. ^{1}H NMR (benzene-d_6, 23 °C): δ −0.17 (s, 6H, Ti-*Me*) 1.60 (s, 6H, C_5H_2*Me*$_3$), 1.86 (s, 12H, C_5H_2*Me*$_3$), 5.30 (s, 4H, C_5*H*$_2$Me$_3$). {^{1}H}^{13}C NMR (benzene-d_6, 23 °C): δ 13.63, 15.58 (Cp*Me*), 45.39 (Ti*Me*), 115.79, 119.01, 122.23 (Cp).

Preparation of (η^5-C_5H_2-1,2,4-Me_3)$_2$TiI (1-I). A 25 mL round-bottom flask was charged with 0.180 g (0.605 mmol) of **1-Cl**, 0.400 g (2.00 mmol) of trimethylsilyl iodide, and approximately 15 mL of toluene. The resulting dark reaction mixture was stirred for 3 days, after which time the solvent and volatiles were removed in vacuo. The brown residue was recrystallized from diethyl ether at −35 °C to yield 0.202 g (79%) of **1-I** as a green solid. Anal. Calcd for $C_{16}H_{22}TiI$: C, 49.39; H, 5.70. Found: C, 48.99; H, 5.77. Magnetic susceptibility (benzene-d_6, 23 °C): μ_{eff} = 1.3 μB. ^{1}H NMR (benzene-d_6, 23 °C): δ −20.1 (4H, C_5*H*$_2$Me$_3$), 17.1 (12H, C_5H_2*Me*$_3$), 29.5 (6H C_5H_2*Me*$_3$)

Preparation of [(η^5-C_5H_2-1,2,4-Me_3)$_2$Ti]$_2$(μ_2,η^2,η^2-N_2) (1-N$_2$). Method A: A thick walled glass reaction vessel was charged with 0.101 g (0.346 mmol) of **1-Me$_2$** and approximately 10 mL of pentane. On the high-vacuum line, the contents of the vessel were frozen at 77 K and partially degassed, and 1 atm of hydrogen was admitted to produce a mixed atmosphere of nitrogen and hydrogen. Upon thawing, the solution immediately changed from yellow to dark purple-blue. The reaction mixture was stirred for 1 h and the solvent removed in vacuo. The resulting dark residue was recrystallized from pentane at −35 °C to yield 0.077 g (80%) of **1-N$_2$** as dark purple-blue crystals. Method B: A 20 mL scintillation vial was charged with 0.200 g (0.514 mmol) of **1-I**, approximately 10 mL of pentane, and 0.277 g (2.05 mmol) of potassium graphite. The reaction mixture was stirred for 3 days, the resulting suspension was filtered through Celite, and the solvent was removed. The dark residue was recrystallized from pentane at −35 °C to yield 0.057 g (41%) of **1-N$_2$** as dark purple-blue crystals. Anal. Calcd for $C_{32}H_{44}N_2Ti_2$: C, 69.57; H, 8.03; N, 5.07. Found: C, 69.48; H, 7.72; N, 4.81. Magnetic susceptibility: (magnetic susceptibility balance, 23 °C) μ_{eff} = 2.7(1) μ_B; (Evans method, benzene-d_6, 23 °C) μ_{eff} = 2.2(2) μ_B. ^{1}H NMR (benzene-d_6, 23 °C): δ 16.9 (24H, C_5H_2*Me*$_3$), 22.2 (12H, C_5H_2*Me*$_3$), 54.3 (8H, C_5*H*$_2$Me$_3$). UV−vis (pentane): 310 nm (10 400 M^{-1} cm^{-1}), 353 nm (11 500 M^{-1} cm^{-1}), 571 nm (4700 M^{-1} cm^{-1}).

Preparation of [(η^5-C_5H_2-1,2-Me_2-4-^{i}Pr)$_2$TiI (2-I). This molecule was prepared in an identical manner to **1-I**, with 0.290 g (2.04 mmol) of Li[C_5H_2-1,2-Me_2-4-^{i}Pr] and 0.370 g (0.99 mmol) of $TiCl_3(THF)_3$ to generate **2-Cl** in situ. After filtration through Celite and treatment with 0.652 g (3.26 mmol) of trimethylsilyl iodide, 0.351 g (68% based on Ti) of **2-I** was obtained as a green solid. Magnetic susceptibility (benzene-d_6, 23 °C): μ_{eff} = 1.3 μB. ^{1}H NMR (benzene-d_6, 23 °C): δ 1.54, 5.83, 13.8, unable to assign resonances based solely on integration, one resonance not located.

Preparation of [(η^5-C_5H_2-1,2-Me_2-4-^{i}Pr)$_2$Ti]$_2$(μ_2,η^1,η^1-N_2) (2-N$_2$). This molecule was prepared in an identical manner to **1-N$_2$** using method A, with 0.222 g (0.499 mmol) of **2-I** and 0.337 g (2.49 mmol) of potassium graphite, yielding 0.092 g (55%) of **2-N$_2$** as purple-blue crystals. Anal. Calcd for $C_{40}H_{60}N_2Ti_2$: C, 72.28; H, 9.10; N, 4.21. Found: C, 71.90; H, 9.25; N, 3.90. Magnetic susceptibility: (Evans method, benzene-d_6, 23 °C) μ_{eff} = 2.1(2) μ_B. ^{1}H NMR (benzene-d_6, 23 °C): δ 3.1, 23.4, 28.2. one resonance not located. UV−vis (pentane): 304 nm (29 800 M^{-1} cm^{-1}), 578 nm (40 700 M^{-1} cm^{-1}).

Preparation of [(η^5-C_5H_2-1,2-Me_2-4-^{t}Bu$_2$)TiI (3-I). This molecule was prepared in an identical manner to **1-I**, using 1.00 g (6.41 mmol) of Li[C_5H_2-1,2-Me_2-4-^{t}Bu] and 1.18 g (3.19 mmol) of $TiCl_3(THF)_3$ to generate **3-Cl** in situ. After filtration through Celite and treatment with 1.40 g (7.00 mmol) of trimethylsilyl iodide, 0.663 g (44% based on Ti) of **3-I** was obtained as a green solid. Anal. Calcd for $C_{22}H_{34}TiI$: C, 55.83; H, 7.24. Found: C, 55.72; H, 7.55.

Magnetic susceptibility (benzene-d_6, 23 °C): $\mu_{\mathrm{eff}} = 1.1\ \mu\mathrm{B}$. ^{1}H NMR (benzene-$d_6$, 23 °C): δ 7.9.

Preparation of $[(\eta^5\text{-C}_5\text{H}_2\text{-1,2-Me}_2\text{-4-}^t\text{Bu})_2\text{Ti}]_2(\mu_2,\eta^1,\eta^1\text{-N}_2)$ (3-N_2). This molecule was prepared in an identical manner to **1-N_2** using method A, with 0.150 g (0.317 mmol) of **3-I** and 0.214 g (1.59 mmol) of potassium graphite, yielding 0.070 g (61%) of **3-N_2** as purple-blue crystals. Anal. Calcd for $C_{44}H_{68}N_2Ti_2$: C, 73.32; H, 9.51; N, 3.89. Found: C, 73.05; H, 9.20; N, 3.46. Magnetic susceptibility: (Evans method, benzene-d_6, 23 °C) $\mu_{\mathrm{eff}} = 2.1(2)\ \mu_{\mathrm{B}}$. ^{1}H NMR (benzene-$d_6$, 23 °C): δ −2.6 (24H, $\mathrm{C_5H_2}Me_2{}^t\mathrm{Bu}$), 5.1 (36H, $\mathrm{C_5H_2Me_2}{}^tBu$), 16.0 (8H, $\mathrm{C_5}H_2\mathrm{Me_2}{}^t\mathrm{Bu}$). UV−vis (pentane): 311 nm (22 000 M^{-1} cm^{-1}), 594 nm (46 600 M^{-1} cm^{-1}).

Preparation of $[\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{H}_2\text{-2-SiMe}_3\text{-4-}^t\text{Bu})_2\text{Ti}]_2(\mu_2,\eta^1,\eta^1\text{-N}_2)$ (4-N_2). A 100 mL round bottomed flask was charged with 9.85 g of 0.5% sodium amalgam and 50 mL of toluene. With stirring, 0.222 g (0.395 mmol) of **4-Cl_2** was added as a toluene slurry and the resulting reaction mixture stirred for 3 days at ambient temperature. The blue solution was decanted from the amalgam and filtered through Celite, and the toluene was removed in vacuo. The resulting residue was recrystallized from pentane to yield 0.196 g (98.0%) of **4-N_2** as a blue powder. Anal. Calcd for $C_{52}H_{92}N_2Si_6Ti_2$: C, 61.86; H, 9.19; N, 2.77. Found: C, 61.59; H, 8.98; N, 2.37. ^{1}H NMR (benzene-d_6): δ 0.87 ($\Delta\nu_{1/2} = 44$ Hz), 1.25 ($\Delta\nu_{1/2} = 205$ Hz), 2.21 ($\Delta\nu_{1/2} = 211$ Hz). Magnetic susceptibility (benzene-d_6): $\mu_{\mathrm{eff}} = 2.1(2)\ \mu_{\mathrm{B}}$.

Preparation of $[\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{H}_2\text{-2-SiMe}_3\text{-4-}^t\text{Bu})_2]\text{Ti}(\eta^2\text{-PhC-CPh})$ (4-(PhCCPh)). A 20 mL scintillation vial was charged with 0.016 g (0.017 mmol) of **4-N_2** and approximately 3 mL of diethyl ether. Diphenylacetylene (0.003 g, 0.017 mmol) was added, resulting in a color change to bright green. After stirring overnight, the solvent was removed to yield a red solid that was recrystallized from pentane to yield 0.014 g (77.8%) of **4-(PhCCPh)**. ^{1}H NMR (benzene-d_6): δ 0.24 (s, 18H, SiMe_3), 0.53 (s, 6H, SiMe_2), 1.28 (s, 18H, CMe_3), 5.78 (s, 2H, Cp), 6.92 (t, $J = 7$ Hz, 2H, Ph), 7.06 (d, $J = 7$ Hz, 4H, Ph), 7.12 (t, $J = 7$ Hz, 4H, Ph), 9.37 (s, 2H, Cp). ^{13}C NMR (benzene-d_6): δ −0.68 (SiMe_2), 2.22 (SiMe_3), 14.24, 22.68 ($C{=}C$), 31.77 (CMe_3), 34.02 (CMe$_3$), 124.66, 125.09, 126.17, 128.85, 131.80, 136.24, 143.82, 150.10, 203.96 (Cp/Ph).

Preparation of $[\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{Me}_4)(\eta^5\text{-C}_5\text{H}_3\text{-3-}^t\text{Bu})]\text{TiCl}$ (5-Cl). A 100 mL round bottomed flask was charged with 1.08 g (3.44 mmol) of $\mathrm{Li_2[Me_2Si(C_5Me_4)(C_5H_3\text{-}3\text{-}{}^tBu)]}$ and 1.27 g (3.44 mmol) of $\mathrm{TiCl_3(THF)_3}$, and a reflux condenser and 180° needle valve were attached. On the high-vacuum line, approximately 40 mL of tetrahydrofuran was added by vacuum transfer at −78 °C, and the resulting mixture was warmed to ambient temperature with stirring. The reaction mixture was then heated to reflux for 24 h, after which time the solvent was removed in vacuo, leaving a red-brown solid. The assembly was transferred into the drybox, and the desired product was extracted into pentane and filtered through Celite. The pentane was removed in vacuo, leaving a brown solid. Recrystallization from pentane yielded 0.356 g (27%) of **5-Cl**. Anal. Calcd for $C_{20}H_{30}ClSiTi$: C, 62.91; H, 7.92. Found: C, 62.86; H, 7.64. ^{1}H NMR (benzene-d_6): δ −0.60 ($\Delta\nu_{1/2} = 62$ Hz), 4.25 ($\Delta\nu_{1/2} = 280$ Hz). Magnetic susceptibility (23 °C, benzene-d_6): $\mu_{\mathrm{eff}} = 1.5(1)\ \mu_{\mathrm{B}}$.

Preparation of $[\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{Me}_4)(\eta^5\text{-C}_5\text{H}_3\text{-3-}^t\text{Bu})\text{Ti}]_2(\mu_2,\eta^1,\eta^1\text{-N}_2)$ (5-N_2). A 100 mL round-bottomed flask was charged with 11.34 g of 0.5% sodium amalgam and approximately 15 mL of toluene. With vigorous stirring, 0.180 g (0.471 mmol) of **5-Cl** was added as a brown toluene solution, and the resulting reaction mixture was stirred for 3 days at ambient temperature. The blue solution was filtered through a pad of Celite, and the toluene was removed in vacuo, leaving a blue solid. ^{1}H NMR (benzene-d_6): δ −0.26 ($\Delta\nu_{1/2} = 99$ Hz), 0.36 ($\Delta\nu_{1/2} = 74$ Hz), 2.99 ($\Delta\nu_{1/2} = 97$ Hz). Magnetic susceptibility (Evans method, benzene-d_6, 23 °C): $\mu_{\mathrm{eff}} = 1.8\ \mu_{\mathrm{B}}$.

Characterization of $[\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{Me}_4)(\eta^5\text{-C}_5\text{H}_3\text{-3-}^t\text{Bu}_3)\text{Ti}(\eta^1\text{-N}_2)]_2(\mu_2,\eta^1,\eta^1\text{-N}_2)$ (5_2-$(N_2)_3$). A concentrated solution of **5-N_2** was recrystallized from pentane at −35 °C to yield 0.078 g (42.6%) of a blue crystalline solution identified as **5_2-$(N_2)_3$**. Anal. Calcd for $C_{40}H_{60}N_6Si_2Ti_2$: C, 61.85; H, 7.77; N, 10.82. Found: C, 62.01; H, 8.15; N, 10.92. ^{1}H NMR (toluene-d_8, −78 °C): δ 0.25 (s, 12H, SiMe$_2$), 0.39 (s, 12H, SiMe$_2$), 1.16 (s, 3H, Me), 1.38 (s, 3H, Me), 1.56 (s, 6H, Me), 1.81 (s, 18H, ^{t}Bu), 1.87 (s, 6H, Me), 1.97 (s, 3H, Me), 4.43 (s, 2H, Cp), 4.74 (s, 2H, Cp), 4.77 (s, 2H, Cp), 4.78 (s, 2H, Cp), 5.94 (s, 2H, Cp), 6.02 (s, 2H, Cp). Multiple Me/^{t}Bu peaks not located due to peak broadening. ^{15}N NMR (toluene-d_8, −78 °C, major isomer): δ 386.6, 445.7, 514.5. ^{15}N NMR (toluene-d_8, −78 °C, minor isomer): δ 306.0, 388.3, 439.1, 524.3, 528.9, 530.2. IR (pentane, −78 °C): ν, 2059, 2086 cm^{-1} (terminal N$_2$). Bridging N$_2$ not located.

Toepler Pump Analysis of 1-N_2. Approximately 5 mL of toluene was condensed onto a mixture of 0.023 g (0.042 mmol) of **1-N_2** and 0.020 g (0.112 mmol) of PhC≡CPh in a sealed glass vessel. The resulting reaction mixture was stirred for 24 h, and the volatiles were opened to the Toepler pump. Using this procedure, 31 Torr of an expected 42 Torr of noncombustible gas was collected. Characterization data of $(\eta^5\text{-C}_5\text{H}_2\text{-1,2,4-Me}_3)_2\text{Ti(PhCCPh)}$: ^{1}H NMR (benzene-$d_6$, 23 °C): δ 1.41 (s, 6H, $\mathrm{C_5H_2}Me_3$), 1.60 (s, 12H, $\mathrm{C_5H_2}Me_3$), 5.94 (s, 4H, $\mathrm{C_5}H_2\mathrm{Me_3}$), 7.01, (d, 4H, $Ph_2\mathrm{C_2}$), 7.10 (t, 2H, $Ph_2\mathrm{C_2}$), 7.55 (d, 4H, $Ph_2\mathrm{C_2}$). {^{1}H}^{13}C NMR (benzene-d_6, 23 °C): δ 14.05, 15.04 (CpMe), 90.02 ($\mathrm{Ph_2}C_2$), 114.07, 122.31, 124.02, 125.75, 126.22, 132.06, 142.10 (Cp/$Ph_2\mathrm{C_2}$).

Acknowledgment. We thank Professor John Bercaw and his research group for a sample of $\mathrm{Me_2Si(C_5H_3\text{-}SiMe_3\text{-}{}^tBu)_2}$. We also thank the Department of Energy, Office of Basic Energy Sciences (DE-FG02-05-ER659), for financial support. P.J.C. is a Cottrell Scholar sponsored by the Research Corporation, a David and Lucille Packard Fellow in Science and Engineering, and a Camille Dreyfus Teacher-Scholar. T.E.H. was also partially supported by an NSF CSIP fellowship. M.W.B. was partially supported by a TALENT fellowship by the Netherlands Organization for Scientific Research.

Supporting Information Available: Crystallographic data for **1-N_2**, **2-N_2**, **4-N_2**, and **5-N_2** as cif files. These data are available free of charge via the Internet at http://pubs.acs.org.

OM0611913