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Dinitrogen Complexes of Bis(cyclopentadienyl) Titanium Derivatives: Structural Diversity Arising from Substituent Manipulation

Tamara E. Hanna,[†] Emil Lobkovsky, and Paul J. Chirik*

Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New York 14853. [†] Present address: Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409-1061

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Dinitrogen coordination to a family of bis(cyclopentadienyl)titanium sandwich complexes, $(\eta^5\text{-}C_5Me_4R)_2Ti$ (R = alkyl, aryl, silyl), has been systematically evaluated by in situ solution infrared spectroscopy. The maximum temperature of N_2 coordination (T_{max}) has been determined as a function of cyclopentadienyl substituent and has been correlated with the structural type (monomer or dimer) of the resulting dinitrogen complex. The electronic properties of each titanium sandwich complex were assessed by infrared spectroscopy of the dicarbonyl derivatives and by the oxidation potentials of the corresponding ferrocenes, $(\eta^5\text{-}C_5Me_4R)_2Fe$. From these data, the thermodynamic preferences for N_2 coordination have been established and they increase with smaller, electropositive substituents.

Introduction

The fixation of molecular nitrogen into more value-added nitrogen compounds is an area of continued interest given the utility of these molecules as fuels, fertilizers, pharmaceuticals, and other fine chemicals.[1] The advent of well-defined, soluble metal compounds[2] that coordinate, activate, and even functionalize[3] the otherwise inert N_2 molecule has provided insight into a number of pathways by which dinitrogen can be reduced. Significantly, homogeneous dinitrogen compounds present the unique opportunity to establish structure−reactivity relationships for nitrogen fixation and offer the possibility for new transformations by manipulation of the ancillary ligands.[4]

Titanium dinitrogen complexes[5,6] have received considerable attention given their historical role in solution ammonia synthesis[7] and the more recently discovered ability to use N_2 as the nitrogen source for complex molecular targets such as monomorine I, (±)-lycopodine, and pumiliotoxin C.[8,9] Despite this interest, one of the potentially simplest chemical transformations in the sequence−namely, the N_2 coordination event−is not well understood. This lack of insight is primarily a result of how early transition metal dinitrogen complexes are synthesized. Typically a metal halide precursor is reduced with an excess of a strong reducing agent such as sodium amalgam or potassium graphite, and often the resulting dinitrogen complex is merely a transient intermediate. Even when isolable N_2 complexes result, studying dinitrogen coordination is challenging given the ill-defined nature of the alkali metal reduction procedures.

The discovery of thermally stable, isolable monomeric bis(cyclopentadienyl)titanium sandwich complexes, $(\eta^5\text{-}C_5Me_4R)_2Ti$ (R = silyl), by Lawless[10] and Mach[11] has provided a unique opportunity to study dinitrogen coordination at a divalent titanium center. Of particular interest is the influence of cyclopentadienyl substitution on the azophilicity of the titanium as well as the molecularity (monomer versus dimer) of the resulting dinitrogen complex. Depending on the size of the ring substituents, a range of structural types has been observed and, in many cases, crystallographically characterized. For the purpose of this study, each of

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*Corresponding author. E-mail: pc92@cornell.edu.

(1) Smil, V. *Enriching the Earth: Fritz Haber, Carl Bosch, and the Transformation of World Food Production*; MIT Press, 2001.

(2) For reviews see: (a) Gambarotta, S.; Scott, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 5298. (b) Kozak, C. M.; Mountford, P. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 1186. (c) MacKay, B. A.; Fryzuk, M. D. *Chem. Rev.* **2004**, *104*, 385. (d) Shaver, M. P.; Fryzuk, M. D. *Adv. Synth. Catal.* **2003**, *345*, 1061.

(3) (a) Hidai, M.; Mizobe, Y. *Can. J. Chem.* **2005**, *83*, 358. (b) Schrock, R. R. *Chem. Commun.* **2003**, 2389. (c) Fryzuk, M. D. *Chem. Rec.* **2003**, *3*, 2. (d) Korobkov, I.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem., Int. Ed.* **2003**, *42*, 4958. (e) Spencer, L. P.; MacKay, B. A.; Patrick, B. O.; Fryzuk, M. D. *Proc. Natl. Acad. Sci.* **2006**, *103*, 17094. (f) Chirik, P. J. *Dalton Trans.* **2007**, 16. (g) Fryzuk, M. D. *Acc. Chem. Rev.* **2009**, *42*, 127.

(4) Pool, J. A.; Chirik, P. J. *Can. J. Chem.* **2005**, *83*, 286.

(5) For representative examples see: (a) Knobloch, D. J.; Toomey, H. E.; Chirik, P. J. *J. Am. Chem. Soc.* **2008**, *130*, 4248. (b) Scherer, A.; Kollak, K.; Luetzen, A.; Friedemann, M.; Haase, D.; Saak, W.; Beckhaus, R. *Eur. J. Inorg. Chem.* **2005**, *6*, 1003. (c) Hagadorn, J. R.; Arnold, J. *J. Am. Chem. Soc.* **1996**, *118*, 893. (d) Beydoun, N.; Duchateau, R.; Gambarotta, S. *Chem. Commun.* **1992**, 244. (e) Duchateau, R.; Gambarotta, S.; Beydoun, N.; Bensimon, C. *J. Am. Chem. Soc.* **1991**, *113*, 8986. (f) Baumann, R.; Stumpf, W. M.; Davis, W. M.; Liang, L. −C.; Schrock, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 7822.

(6) (a) Bercaw, J. E.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1971**, *93*, 2045. (b) Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 5087.

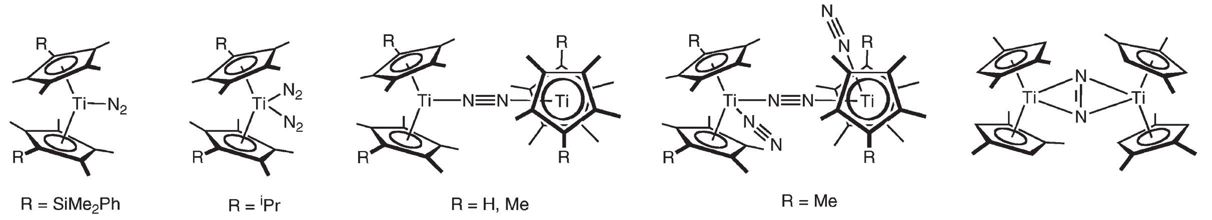
(7) Vol'pin, M. E.; Shur, V. B. *Nature* **1966**, *209*, 1236.

(8) Mori, M. *J. Organomet. Chem.* **2004**, *689*, 4210.

(9) Mori, M. *Heterocycles* **2009**, *78*, 281.

(10) Hitchcock, P. B.; Kerton, F.; Lawless, G. A. *J. Am. Chem. Soc.* **1998**, *120*, 10264.

(11) (a) Lukesová, L.; Horácek, M.; Stepnicka, P.; Fejfarová, K.; Gyepes, R.; Cisorová, I.; Kubista, J.; Mach, K. *J. Organomet. Chem.* **2002**, *663*, 134. (b) Horácek, M.; Kupfer, V.; Thewalt, U.; Stepnicka, P.; Polasek, M.; Mach, K. *Organometallics* **1999**, *18*, 3572.



I II III IV V

Figure 1. Structurally characterized examples of substituted bis(cyclopentadienyl)titanium dinitrogen complexes.

the major structural types is presented in Figure 1 and classified as type I, II, III, IV, or V. One unusual example not depicted in Figure 1 has been observed with the parent cyclopentadienyl complex where a μ_3-N_2 ligand is coordinated between three titanium centers.[12]

Our laboratory has recently added to the known structural types of titanocene dinitrogen complexes. Exposure of (η^5-$C_5Me_4^iPr$)$_2$Ti to 1 atm of N_2 at temperatures below −30 °C results in coordination of 2 equiv of dinitrogen, as judged by in situ infrared spectroscopy.[13] X-ray diffraction established a monomeric titanocene bis(dinitrogen) complex, (η^5-$C_5Me_4^iPr$)$_2$Ti(N_2)$_2$, isoelectronic and isostructural to more common dicarbonyl compounds. Elucidation of the solid state structure of (η^5-$C_5Me_4^iPr$)$_2$Ti(N_2)$_2$ verified formation of (η^5-C_5Me_5)$_2$Ti(N_2)$_2$, initially proposed by Bercaw on the basis of low temperature heptane solution spectroscopic studies.[6b] Introduction of larger, electron-withdrawing silyl substituents into the tetramethylated cyclopentadienyl rings has allowed spectroscopic observation[13] and ultimately crystallographic characterization of monomeric titanocene mono(dinitrogen) compounds, (η^5-$C_5Me_4SiMe_2Ph$)$_2$Ti(N_2) (Figure 1).[14] These compounds served as an inspiration for the synthesis of related titanocene monocarbonyl derivatives, (η^5-C_5Me_4R)$_2$Ti(CO) (R = ^{i}Pr, SiMe$_2$Ph, SiMe$_3$), and mixed carbonyl-dinitrogen species, (η^5-C_5Me_4R)$_2$Ti(CO)(N_2).[14] By reducing the size and number of the cyclopentadienyl substituents, μ_2, η^2, η^2-N_2 "side-on" coordination can be favored, as evidenced by the synthesis and crystallographic characterization of [(η^5-C_5H_2-1,2,4-Me_3)$_2$Ti]$_2$(μ_2,η^2,η^2-N_2).[15]

In this article, we report a more comprehensive synthetic and spectroscopic study aimed at elucidating the influence of cyclopentadienyl substitution on the thermodynamics of dinitrogen coordination by titanium sandwich compounds. This work also highlights how manipulation of ring substitution governs the structure of the resulting dinitrogen complex.

Results and Discussion

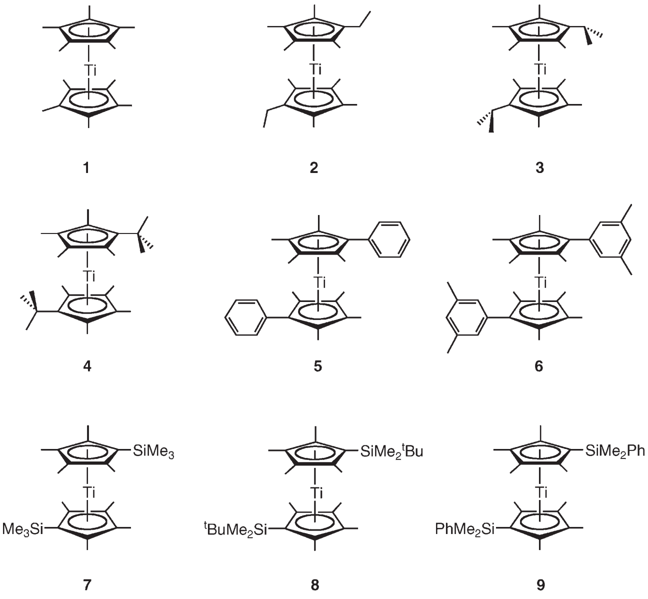
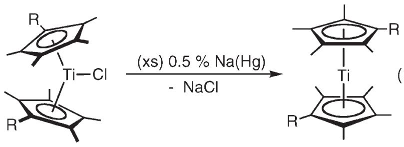


Figure 2. Bis(cyclopentadienyl)titanium sandwich complexes, (η^5-C_5Me_4R)$_2$Ti, used in this study.

Synthesis of Bis(cyclopentadienyl)titanium Sandwich Compounds and Dinitrogen Coordination Studies. As we have described previously,[14,13] in situ solution infrared spectroscopy is a convenient tool to assay N_2 coordination in titanium sandwich compounds, a consequence of the intense symmetric and asymmetric N≡N bands arising from the dinitrogen complex. Of the structural types presented in Figure 1, three contain infrared active N_2 ligands. One limitation of this technique is the detection of centrosymmetric, bridging end-on compounds (types III and V), where the μ_2-N_2 ligand is not infrared active.

The bis(cyclopentadienyl)titanium compounds used in this study and corresponding numbering scheme are presented in Figure 2. Many of these compounds have been previously reported by Brintzinger,[6a] Lawless,[10] Mach,[11] and our laboratory.[13,14] New additions include R = Et (**2**), Ph (**5**), and 3,5-Me_2-C_6H_3 (**6**). The majority of the titanium sandwiches used in this study were prepared by sodium amalgam reduction of the appropriate monochloride precursor, (η^5-C_5Me_4R)$_2$TiCl, in toluene solution (eq 1). Exceptions are **1** and **7**, where the titanocene dichloride, (η^5-C_5Me_4R)$_2$TiCl$_2$, was used.



(1)

The majority of the desired titanium sandwiches were isolated as burgundy solids following recrystallization from pentane at −35 °C. Sandwich compounds **2** and **5** were isolated as green solids. In certain instances (**1**−**3**, **5**, **6**), low temperature isolation furnished a dinitrogen complex.

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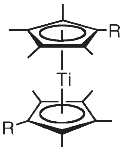
[12] Pez, G. P.; Apgar, P.; Crissey, R. K. *J. Am. Chem. Soc.* **1982**, *104*, 482.

[13] Hanna, T. E.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 14688.

[14] Hanna, T. E.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 6018.

[15] Hanna, T. E.; Bernskoetter, W. H.; Bouwkamp, M. W.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2007**, *26*, 2431.

Table 1. ^{1}H NMR Chemical Shifts of $(\eta^5\text{-}C_5Me_4R)_2Ti$ Compounds Recorded in Benzene-d_6 at 23 °C



compound	R	$\delta(CH_3)$ (ppm)	$\delta(CH_3)$ (ppm)	δ(R) (ppm)	reference
1	Me		62.0		13
2	Et	64.82	57.06	2.48 ($\mathrm{CH_2C}\mathit{H}_3$) 14.48 ($\mathrm{C}\mathit{H}_2\mathrm{CH_3}$)	this work
3	^{i}Pr	62.70	45.37	3.19 (C*H*Me$_2$) 4.87 (CH*Me*$_2$)	12
4	^{t}Bu	62.87	34.11	4.03	12
5	Ph	65.17	47.14	−8.59 (Ph) 3.72 (*m*-Ph) 9.47 (Ph)	this work
6	3,5-Me$_2$-C$_6$H$_3$	66.73	49.02	−8.94 (*o*-Ph) 1.40 (*m*-Me) 5.19 (*p*-Ph)	this work
7	SiMe$_3$	79.86	26.25	6.95	10
8	SiMe$_2^t$Bu	82.62	23.95	2.11 (Si*Me*$_2$) 6.71 (C*Me*$_3$)	9
9	SiMe$_2$Ph	78.67	25.12	7.52 (Ph) 8.78 (Ph) 9.98 (Ph)	10

Conversion to the bis(cyclopentadienyl) titanium sandwich was accomplished by stirring in pentane solution at ambient temperature. One exception was **1**, where competing cyclometalation pathways prevented isolation in the solid state, in agreement with the literature report.[6]

As expected for linear, d^2 metallocenes,[16] **1**−**9** are paramagnetic, with benzene-d_6 solution magnetic moments (Evans method[17]) consistent with $S = 1$ compounds (see Experimental Section). Compiled in Table 1 are the paramagnetically broadened and shifted ^{1}H NMR resonances for each compound. The purely hydrocarbyl-substituted derivatives, **1**−**6**, exhibit two inequivalent cyclopentadienyl methyl resonances in the vicinity of 60−70 and 34−57 ppm at 23 °C in benzene-d_6. This chemical shift dispersion is more pronounced in the silylated derivatives, **7**−**9**, where one methyl group appears around 80 ppm while the other is located between 20 and 26 ppm.

With a series of bis(cyclopentadienyl) titanium sandwich compounds in hand, the coordination of dinitrogen was monitored in pentane solution by in situ infrared spectroscopy. Because the dinitrogen complex derived from **1** has been isolated as a dimeric, end-on dinitrogen complex, $[(\eta^5\text{-}C_5Me_5)_2Ti]_2(\mu_2, \eta^1, \eta^1\text{-}N_2)$ (**[1]$_2$N$_2$**, type III), the ethylated titanocene, **2**, was initially studied. Cooling a 4.2 mM pentane solution of **2** under an atmosphere of dinitrogen to temperatures below 0 °C produced two intense bands centered at 2090 and 1984 cm^{-1}, assigned to the symmetric and asymmetric N≡N stretches of the monomeric titanocene bis(dinitrogen) complex $(\eta^5\text{-}C_5Me_4Et)_2Ti(N_2)_2$ (**2-(N$_2$)$_2$**, type II). Increasing the titanium concentration to 22 mM produced the infrared spectrum shown in Figure 3, where a new titanium dinitrogen complex in addition to **2-(N$_2$)$_2$** was detected. Three new bands were observed, two strong stretches centered at 2057 and 2024 cm^{-1} and one weaker band centered at 1719 cm^{-1}. Stretching frequencies in this region of the IR spectrum are similar to those reported for dimeric, end-on dinitrogen complexes with two terminal and one bridging N$_2$ ligand (type IV). For example, $[(\eta^5\text{-}C_5Me_5)_2Ti(N_2)]_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$ has ν_{N2}^{term} = 2058, 2020 and $\nu_{N2}^{bridging}$ = 1711 cm^{-1} (Nujol), similar to the values reported for crystallographically characterized $[(\eta^5\text{-}C_5Me_5)_2Zr(N_2)]_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$ (ν_{N2}^{term} = 2040, 2003, $\nu_{N2}^{bridging}$ = 1578 cm^{-1} (Nujol)).[18] Based on these data, the solution structure of the new compound formed at higher titanium concentrations is $[(\eta^5\text{-}C_5Me_4Et)_2Ti(N_2)]_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$ (**[2-(N$_2$)]$_2$N$_2$**) (eq 2). Recall that the type III complex $[(\eta^5\text{-}C_5Me_4Et)_2Ti]_2(\mu_2\ \eta^1,\eta^1\text{-}N_2)$ (**[2]$_2$N$_2$**) may also be present in these experiments (vide infra) but cannot be detected by infrared spectroscopy.

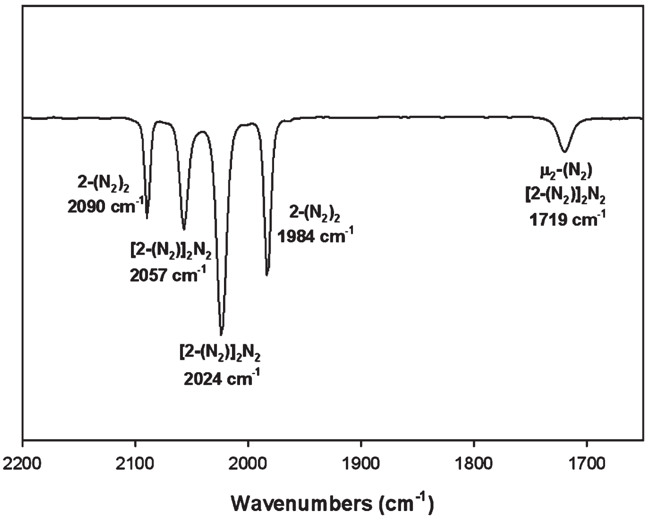
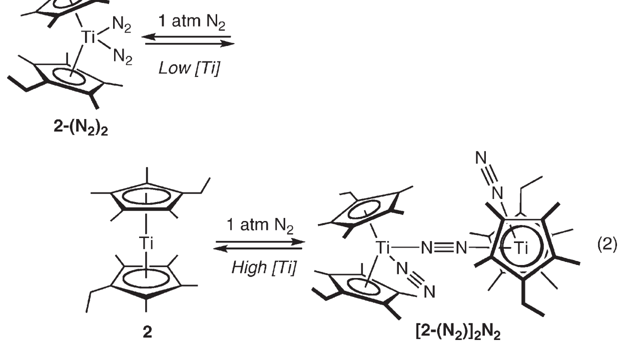


Figure 3. In situ infrared spectrum of a 22 mM solution of **2** under an atmosphere of dinitrogen at −78 °C.



(2)

On a preparative scale, cooling a ~50 mM pentane solution of **2** to −35 °C under an atmosphere of dinitrogen yielded deep blue crystals identified as **[2-(N$_2$)]$_2$N$_2$**. The solid state structure (Figure 4) established a molecular geometry that resembles $[(\eta^5\text{-}C_5Me_5)_2Zr(N_2)]_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$[19] with one bridging and two terminal dinitrogen ligands. To our knowledge, **[2-(N$_2$)]$_2$N$_2$** is the first example of a crystallographically characterized titanocene dinitrogen complex of this type (type IV). The more common structural motif in

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(16) Freitag, M. A.; Gordon, M. S. J. *Phys. Chem. A* **2002**, *106*, 7921.

(17) Sur, S. K. *J. Magn. Reson.* **1989**, *82*, 169.

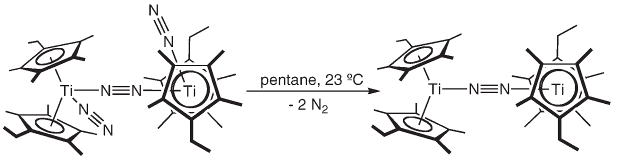
(18) Manriquez, J. M.; McAlister, D. R.; Rosenberg, E.; Shiller, A. M.; Williamson, K. L.; Chan, S. I.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 3078.

(19) Sanner, R. D.; Manriquez, J. M.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 8351.

titanocene chemistry is monobridging end-on (type III), as exemplified by $[(\eta^5\text{-}C_5Me_4R)_2Ti]_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$ (R = H,[20] Me[21]) and $[(\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_3)_2)_2Ti]_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$.[22] As mentioned above, the direct analogue of **$[2\text{-}(N_2)]_2N_2$**, $[(\eta^5\text{-}C_5Me_5)_2Ti(N_2)]_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$, has been observed only by infrared spectroscopy.[18]

The solid state structure of **$[2\text{-}(N_2)]_2N_2$** has idealized C_2 symmetry with the principal axis bisecting the N(1)−N(1A) bond (Figure 4). The dihedral angle between the planes defined by the metal and the titanium centroids is 78.6°. Overall the bond lengths in the core of the molecule are consistent with weakly activated dinitrogen ligands. The bridging dinitrogen ligand has an N(1)−N(1A) bond distance of 1.150(2) Å, slightly elongated from the corresponding distance of 1.1111(17) Å for the terminal N_2 ligands. The values are similar to those reported for $[(\eta^5\text{-}C_5Me_5)_2Zr(N_2)]_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$, where the N−N distances of 1.182(5) Å and 1.116(8), 1.114(7) Å are observed for the bridging and terminal dinitrogen ligands, respectively.[19]

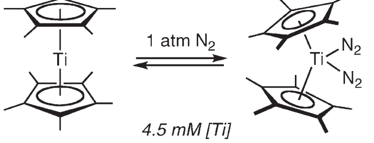
Dinitrogen coordination in **$[2\text{-}(N_2)]_2N_2$** is reversible. Stirring the compound in pentane solution at ambient temperature produced 2 equiv of noncombustible gas (Toepler pump), consistent with formation of **$[2]_2N_2$** (eq 3). Continued stirring under these conditions did not liberate additional N_2 gas. The third equivalent of dinitrogen was released only upon addition of diphenylacetylene to yield the corresponding titanocene diphenylacetylene compound, $(\eta^5\text{-}C_5Me_4Et)_2Ti(\eta^2\text{-}PhCCPh)$.



(3)

$[2\text{-}(N_2)]_2N_2$ **$[2]_2N_2$**

The observation of concentration-dependent dinitrogen complex formation prompted reinvestigation of the low temperature solution behavior of **1**. Bercaw previously reported the detection of transient **$1\text{-}(N_2)_2$** by infrared spectroscopy with the observation of two strong N≡N bands centered at 2086 and 1980 cm^{-1} in heptane solution.[6b] However, conditions were not reported where **$1\text{-}(N_2)_2$** was most likely the principal species in solution. In our hands, we found that cooling a 4.5 mM pentane solution of **1** to below 11 °C produced two intense N_2 bands centered at 2090 and 1982 cm^{-1} in the pentane solution in situ IR spectrum assigned to **$1\text{-}(N_2)_2$** (eq 4). Under these conditions no other titanocene dinitrogen complexes were detected, although it is possible that **$[1]_2N_2$** was present. Comparing these values to other known monomeric titanocene bis(dinitrogen) complexes provides conclusive evidence for Bercaw's spectral assignment for **$1\text{-}(N_2)_2$**.



(4)

1 **$1\text{-}(N_2)_2$**

Previously our laboratory reported that cooling concentrated pentane solutions of **3** to −35 °C under an atmosphere of dinitrogen produced X-ray quality crystals of the bis(dinitrogen) complex **$3\text{-}(N_2)_2$**. Because concentration-dependent solution behavior was observed with **1** and **2**, concentrated (50 mM) pentane solutions of **3** were prepared and cooled below −35 °C. Under these conditions, no evidence for dimeric titanium dinitrogen complexes was obtained by IR spectroscopy, suggesting that an isopropyl group on each ring is sufficiently large to prevent dimerization. Toepler pump experiments were also consistent with liberation of 2 equiv of N_2 per titanium, demonstrating that type III complexes are not formed in an appreciable amount.

The pentane solution dinitrogen coordination chemistry of the previously unpublished members of the series **5**, **6**, and **8** was also examined as a function of temperature by in situ IR spectroscopy. Cooling the phenyl-substituted titanocene, **5**, to −25 °C produced *six* new bands in the region of the infrared spectrum typically associated with terminal N≡N stretches (Figure 5). Four nearly equal intensity bands were observed at 2107, 2088, 2016, and 1984 cm^{-1}, while two weaker bands were observed at 2099 and 1995 cm^{-1}. One additional very weak stretch was located at 1603 cm^{-1} and was assigned to a μ_2-N_2 of a type IV complex, establishing formation of **$[5\text{-}(N_2)]_2N_2$**. Curiously this band appears at a significantly lower frequency than that observed for **$[2\text{-}(N_2)]_2N_2$**. N_2 coordination is reversible from all species, as warming the sample above −25 °C quantitatively regenerated **5**. The three sets of peaks appeared simultaneously and changes in concentration did not alter the relative intensities.

Similar infrared spectroscopic behavior was observed with **6**. Once again a total of *six* N≡N stretches (four major, two minor) were observed in the terminal N_2 stretching region. An additional weak N≡N band was observed at 1603 cm^{-1}, signaling formation of **$[6\text{-}(N_2)]_2N_2$**. As with **5**, the infrared spectrum of a 0.993 mM solution, the most dilute conditions experimentally possible, was indistinguishable from those recorded at more typical concentrations of 5.0 mM.

On the basis of the spectroscopic data for **5** and **6**, we tentatively conclude that one type IV and *two* type II dinitrogen complexes form upon cooling the aryl-substituted titanocenes. Detection of two different monomeric, type II titanocene dinitrogen complexes is most likely a result of population of different rotamers of the titanocene dinitrogen complex. Importantly, the different orientations of the cyclopentadienyl rings or substituents induce a measurable change in the frequency of the N_2 vibrations. Similar observations have been reported for bis(indenyl)zirconocene[25] and hafnocene[23] dicarbonyl complexes. Because this behavior is observed only in the aryl-substituted cases, the orientation of the aromatic ring relative to the cyclopentadienyl plane may be the origin of the spectroscopically distinct dinitrogen complexes. Attempts to favor one rotamer with the preparation of the titanocene derivative where R = 2,6-Me_2-C_6H_3 have been unsuccessful. Another possibility is that one type II dinitrogen complex forms along with two type IV compounds. However, the observation of a single, weak μ_2-N_2 stretch argues against this possibility. It is also curious that unlike the N_2 coordination chemistry of **2**, changes in titanium concentration do not change the ratio of dinitrogen complexes formed. The origin of this behavior

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(20) deWolf, J. M.; Blaauw, R.; Meetsma, A.; Teuben, J. H.; Gyepes, R.; Varga, V.; Mach, K.; Veldman, N.; Spek, A. L. *Organometallics* **1996**, *15*, 4977.

(21) Sanner, R. D.; Duggan, D. M.; McKenzie, T. C.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 8358.

(22) Hanna, T. E.; Keresztes, I.; Lobkovsky, E.; Bernskoetter, W. H.; Chirik, P. J. *Organometallics* **2004**, *23*, 3448.

(23) Pun, D.; Leopold, S. M.; Bradley, C. A.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2009**, *28*, 2471.

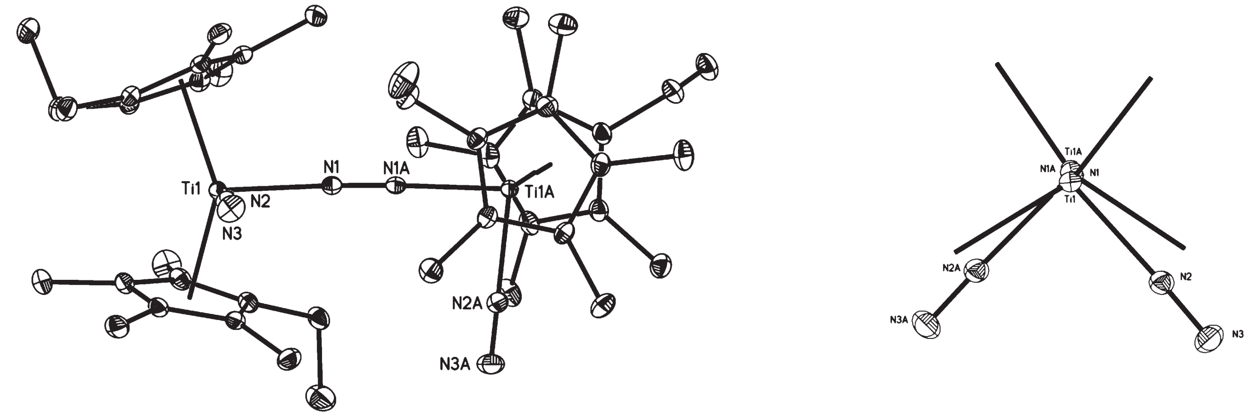


Figure 4. Molecular structure of **[2-(N$_2$)]$_2$N$_2$** at 30% probability ellipsoids (left) and a view of the core of the molecule (right). Hydrogen atoms are omitted for clarity.

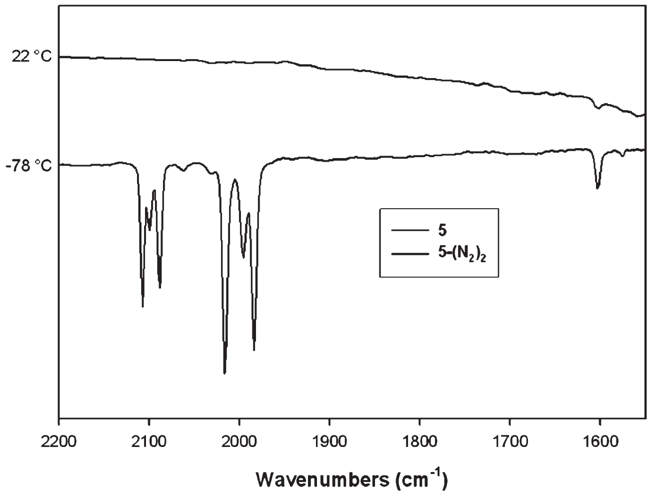


Figure 5. Pentane solution infrared spectrum of **5** under an atmosphere of dinitrogen as a function of temperature.

for the aryl-substituted titanocenes is not understood at this time.

On a preparative scale, cooling a pentane solution of **6** to −35 °C under a dinitrogen atmosphere produced dark purple crystals suitable for X-ray diffraction. The solid state structure (Figure 6) establishes a type III end-on bridging dinitrogen complex, **[6]$_2$N$_2$**. The overall geometry of the molecule is best described as idealized C_2 symmetric with the principal axis on the Ti−N$_2$−Ti vector. As is typically observed with this structural motif, a weakly activated dinitrogen ligand with a short N(1)−N(2) bond distance of 1.1574(11) Å is observed.

The crystallographic characterization of infrared-silent **[6]$_2$N$_2$** suggested that type III dinitrogen complexes must be considered in N$_2$ coordination studies. To determine if **[6]$_2$N$_2$**, not **6**, was actually the product isolated from the reduction of **6-Cl**, the titanium product was treated with PhC≡CPh and the progress of the reaction monitored with a Toepler pump. No detectable quantity of noncombustible gas was collected during the formation of **6-(PhC≡CPh)**. This experiment, in conjunction with a satisfactory combustion analysis, definitively established the identity of the reduction product as the bis(cyclopentadienyl)titanium sandwich, **6**. Therefore, **[6]$_2$N$_2$** forms only upon cooling to temperatures below −31 °C.

For the silylated bis(cyclopentadienyl) titanium sandwich, **8**, first reported by Lawless and co-workers,[10] no change was observed in the pentane solution infrared spectrum down to temperatures as low as −90 °C. This compound is the only titanium sandwich in the series that did not coordinate dinitrogen at temperatures conveniently accessed in the laboratory.

The infrared stretching frequencies and maximum temperatures (T_{max}) at which coordination was first observed for all of the monomeric bis(dinitrogen) titanocene complexes (type II) are compiled in Table 2. Because the band assignments for **5** and **6** are not definitive, the data for the type IV dinitrogen complex are also included. Within the series of purely alkylated bis(cyclopentadienyl) titanium sandwiches, **1**−**4**, T_{max} steadily decreases: R = Me (11 °C) > Et (0 °C) > ^{i}Pr (−30 °C) > ^{t}Bu (−75 °C). These compounds have very similar N$_2$ stretching frequencies with ν(N≡N)$_{sym}$ = 2090 cm^{-1} for each compound and ν(N≡N)$_{asym}$ varying by only 2 cm^{-1}. Only two silylated titanium sandwiches coordinate dinitrogen, **7** and **9**, with values of T_{max} generally lower than the alkylated compounds. Recall that both of these compounds form observable titanocene mono(dinitrogen) compounds (type I) that when cooled to lower temperatures or exposed to higher N$_2$ pressures convert to **7-(N$_2$)$_2$** and **9-(N$_2$)$_2$**.[13,14] In cases where dimeric structures are observed, appreciable amounts of the monomeric compounds remain in the infrared spectrum.

One potential complication in drawing conclusions from the maximum temperatures of dinitrogen coordination concerns the equilibrium constants for the formation of the monomeric titanocene bis(dinitrogen) complexes. Determining these values by in situ infrared spectroscopy is challenging, as the starting bis(cyclopentadienyl) titanium sandwich compounds do not have a distinct spectroscopic feature that allows reliable quantitation. To address this issue, a near equimolar mixture of **3** and the corresponding titanocene dicarbonyl complex, **3-(CO)$_2$**, was prepared in pentane solution and cooled to −78 °C under an atmosphere of dinitrogen. The resulting infrared spectrum of **3-(N$_2$)$_2$** and **3-(CO)$_2$** (Figure 7a) indicates a near equal concentration of titanocene bis(dinitrogen) and dicarbonyl complexes, suggesting that N$_2$ coordination to this particular titanocene is essentially quantitative. Previous work from our laboratory on mixed titanocene carbonyl dinitrogen complexes, (η^5-C$_5$Me$_4$R)$_2$Ti(CO)(N$_2$),[14] established that the extinction coefficients for N$_2$ and CO bands are similar.

Performing the same experiment with an equimolar mixture of **7** and **7-(CO)$_2$** at −78 °C revealed diminished quantities of **7-(N$_2$)$_2$** (Figure 7b), suggesting a lower equilibrium

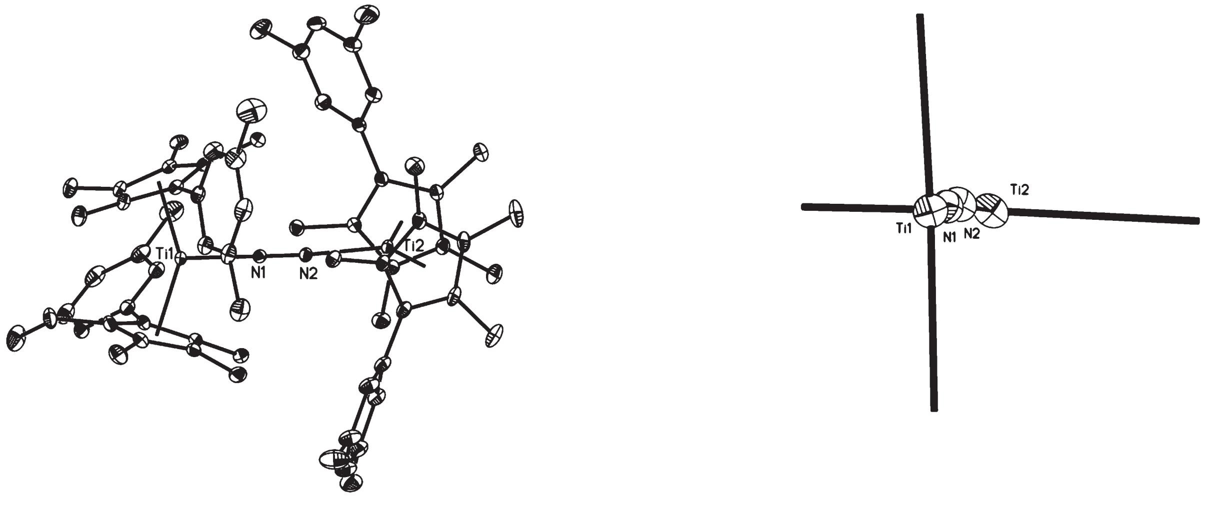


Figure 6. Molecular structure (left) of **[6]$_2$N$_2$** at 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. The core of the molecule is presented on the right.

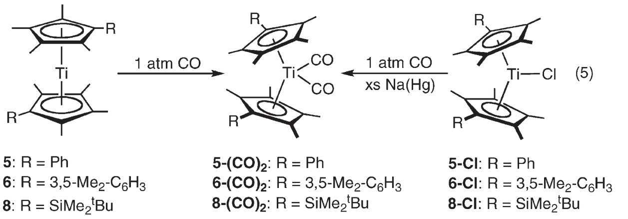
Table 2. Pentane Solution Infrared Stretching Frequencies and Temperature of Dinitrogen Coordination for a Series of Bis (cyclopentadienyl) Titanium Complexes, (η^5-C$_5$Me$_4$R)$_2$Ti

compound	R	T_{max} (°C)[a]	$\nu(N_2)_{sym}$	$\nu(N_2)_{asym}$
1	Me	11	2090	1982
2	Et	0	2090	1984
3	^iPr	−30	2090	1986
4	^tBu	−75	2090	1982
5	Ph	−24	2107[c]	2016[c]
			2099	1995
			2088[c]	1984[c]
6	3,5-Me$_2$-C$_6$H$_3$	−31	2105[c]	2013[c]
			2099	1993
			2086[c]	1982[c]
7	SiMe$_3$	−50 (−45)[b]	2098	2002
8	SiMe$_2^t$Bu	−90[d]		
9	SiMe$_2$Ph	−60 (−36)[b]	2096	2003

[a] Highest temperature (±2 °C) at which coordination of N$_2$ was detected by in situ IR spectroscopy. [b] T_{max} for mono(dinitrogen) complex formation. [c] Denotes major band. [d] No N$_2$ coordination detected at this temperature.

constant for N$_2$ coordination. Also evident in Figure 7b is a significant quantity of the titanocene mono(dinitrogen) complex, **7-N$_2$**. In the case of **9** and **9-(CO)$_2$** at −78 °C, the titanocene mono(dinitrogen) complex, **9-N$_2$**, is the dominant N$_2$ complex in solution, demonstrating a reduced concentration of the bis(dinitrogen) complex. Although in the silylated compounds dinitrogen coordination is not quantitative, qualitatively the equilibrium constants track with T_{max}. Thus, the titanium sandwich compounds that coordinate N$_2$ at higher temperatures also have larger equilibrium constants than those with lower values of T_{max}. As a result, T_{max} can be used as a qualitative assessment of the thermodynamic parameters of dinitrogen coordination as a function of cyclopentadienyl substituent.

Synthesis and Infrared Spectroscopy of Titanocene Dicarbonyl Compounds. To differentiate between steric and electronic contributions of each cyclopentadienyl substituent, a series of spectroscopic and electrochemical studies were carried out. As demonstrated by Parkin and co-workers[24] and subsequently our laboratory,[25,26] pentane solution infrared spectroscopy of group 4 metallocene dicarbonyl compounds has proven to be the most reliable method for assessing the electron density at the metal center as a function of cyclopentadienyl (indenyl)[25] substituent. To extend this approach to titanocene chemistry, dicarbonyl derivatives of each titanium sandwich presented in Figure 2 were prepared. Several examples, **1-(CO)$_2$**,[6a] **2-(CO)$_2$**,[27] **3-(CO)$_2$**,[13] **4-(CO)$_2$**,[13] **7-(CO)$_2$**,[13] and **9-(CO)$_2$**[14] have been reported previously; however the pentane solution infrared spectrum of each compound was recorded in our laboratory to ensure proper comparison. The new members of the series, **5-(CO)$_2$**, **6-(CO)$_2$**, and **8-(CO)$_2$**, were prepared either by addition of carbon monoxide to the titanium sandwich or by reduction of the titanocene monochloride with sodium amalgam in the presence of carbon monoxide (eq 5).



(5)

5: R = Ph
6: R = 3,5-Me$_2$-C$_6$H$_3$
8: R = SiMe$_2^t$Bu

5-(CO)$_2$: R = Ph
6-(CO)$_2$: R = 3,5-Me$_2$-C$_6$H$_3$
8-(CO)$_2$: R = SiMe$_2^t$Bu

5-Cl: R = Ph
6-Cl: R = 3,5-Me$_2$-C$_6$H$_3$
8-Cl: R = SiMe$_2^t$Bu

The pentane solution infrared stretching frequencies of each titanocene dicarbonyl compound are reported in Table 3. In agreement with trends established in related zirconocene chemistry,[24] alkyl-substituted cyclopentadienyl rings are more electron donating than their silylated counterparts, as evidenced by the shifting of the average ν_{CO} values to higher frequency for the latter class of compounds. Within the series of purely alkylated titanocenes, **1-(CO)$_2$-4-(CO)$_2$**, the *tert*-butyl-substituted ring is the most electron donating (ν_{CO}^{av} = 1894 cm^{-1}), while the electronic properties of R = Me, Et, ^{i}Pr derivatives are indistinguishable by IR spectroscopy. Comparison of the CO stretching frequencies of the

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(24) Zachmanoglou, C. E.; Docrat, A.; Bridgewater, B. M.; Parkin, G. E.; Brandow, C. G.; Bercaw, J. E.; Jardine, C. N.; Lyall, M.; Green, J. C.; Keister, J. B. *J. Am. Chem. Soc.* **2002**, *124*, 9525.

(25) Bradley, C. A.; Flores-Torres, S.; Lobkovsky, E.; Abruña, H. D.; Chirik, P. J. *Organometallics* **2004**, *23*, 5332.

(26) Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 2241.

(27) Bettinger, B.; Scherer, O. J.; Heckmann, G. *J. Organomet. Chem.* **1991**, *405*, C19.

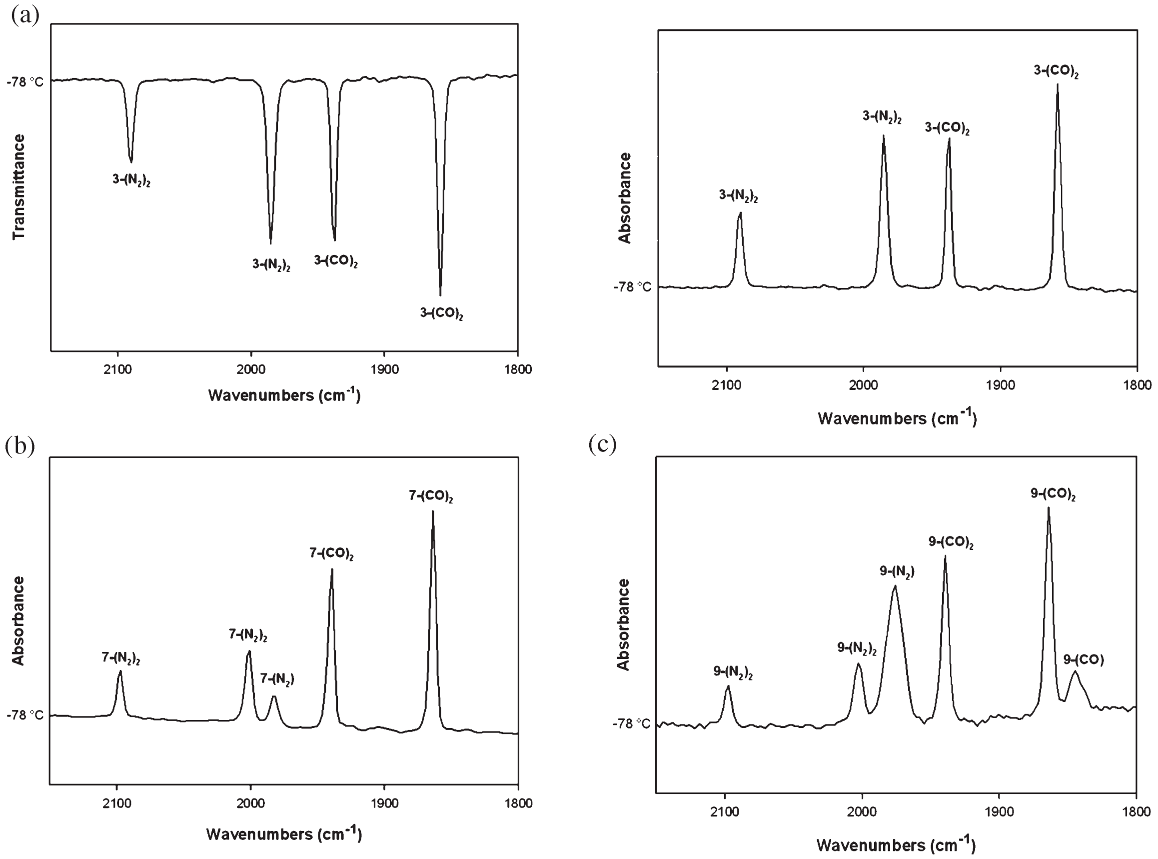

Figure 7. Pentane solution infrared spectrum of an equimolar mixture of (a) **3** and **3-(CO)$_2$**, (b) **7** and **7-(CO)$_2$**, and (c) **9** and **9-(CO)$_2$**. All spectra recorded at −78 °C under 1 atm of N_2.

aryl-substituted titanocene dicarbonyls, **5-(CO)$_2$** and **6-(CO)$_2$**, reveals a slight reduction of ν(CO) as methyl groups are added to the phenyl rings, further underscoring the electron-donating ability of alkyl-substituted cyclopentadienyls. Notably, both **5-(CO)$_2$** and **6-(CO)$_2$** exhibit only two carbonyl bands, suggesting that if different rotamers are responsible for the multiple bands observed with the corresponding type II dinitrogen complexes, they are not distinguishable by IR spectroscopy for the dicarbonyl derivatives.

The family of silyl-substituted titanocene dicarbonyls exhibit carbonyl bands at higher frequencies than the corresponding alkylated compounds, consistent with a less electron rich titanium center resulting from the inductively withdrawing nature of the silyl groups.[24−26] The data within this series display little variance and suggest that attempts to distinguish the electronic properties of these compounds based on infrared spectroscopy are not possible. Therefore from these studies, the relative electronic donation of the cyclopentadienyl substituents is R = ^{t}Bu > ^{i}Pr ~ Et ~ Me > 3,5-Me_2-C_6H_3 > Ph > SiR_3 (e.g., $SiMe_3$ ~ $SiMe_2^tBu$ ~ $SiMe_2Ph$).

Table 3. Pentane Solution Infrared Carbonyl Stretching Frequencies for a Series of Bis(cyclopentadienyl) Titanium Dicarbonyl Complexes, (η^5-$C_5Me_4R)_2Ti(CO)_2$

compound	R	$\nu(CO)_{sym}$	$\nu(CO)_{asym}$	$\nu(CO)_{av}$
1	Me	1939	1859	1899
2	Et	1939	1859	1899
3	^{i}Pr	1938	1859	1898.5
4	^{t}Bu	1933	1855	1894
5	Ph	1941	1862	1901.5
6	3,5-Me_2-C_6H_3	1940	1860	1900
7	$SiMe_3$	1941	1865	1903
8	$SiMe_2^tBu$	1942	1868	1905
9	$SiMe_2Ph$	1941	1865	1903

Electrochemical Studies on the Corresponding Ferrocene Derivatives. Because infrared spectroscopy was unable to distinguish the subtle differences between like substituents within a given series (e.g., alkyl, silyl), another independent measure of the electron density of the metal center as a function of the cyclopentadienyl substituent was sought. Ideally, electrochemical studies would confirm the general conclusions from the infrared spectroscopic studies on the titanocene dicarbonyls and provide better resolution within the series of alkyl and silyl groups. The corresponding ferrocenes, (η^5-$C_5Me_4R)_2Fe$, were initially targeted due to their ease of synthesis and well-defined voltammetric responses. It should be noted that these experiments were conducted to differentiate the electronic properties of cyclopentadienyl substituents, not to directly evaluate N_2 coordination by a 14-electron titanium sandwich compound. The numbering scheme for the bis(cyclopentadienyl) iron compounds is retained from the previous section but is slightly modified by the addition of "Fe" to each shorthand designator. Thus, (η^5-$C_5Me_4Et)_2Fe$ will be referred to as **2-Fe**. While **1-Fe** is commercially available, **2-Fe**,[28] **3-Fe**,[29] **5-Fe**,[30] and **8-Fe**[31] were reported previously but were prepared in our laboratory for the subsequent study. The remaining

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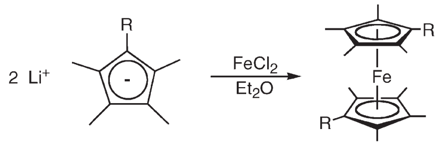
[28] Feitler, D.; Whitesides, G. M. *Inorg. Chem.* **1976**, *15*, 466.

[29] Bensley, D. M.; Mintz, E. A. *J. Organomet. Chem.* **1988**, *353*, 93.

[30] Threlkel, R. S.; Bercaw, J. E. *J. Organomet. Chem.* **1977**, *136*, 1.

[31] Constantine, S. P.; Hitchcock, P. B.; Lawless, G. A.; De Lima, G. M. *Chem. Commun.* **1996**, 1101.

compounds were prepared by straightforward salt metathesis of the lithium cyclopentadienide with ferrous dichloride and isolated as air-stable orange solids in excellent yield (eq 6).



(6)

4-Fe: R = ^{t}Bu
7-Fe: R = SiMe$_3$
9-Fe: R = SiMe$_2$Ph

The redox chemistry of each of the ferrocenes was studied in THF solution by cyclic voltammetry using a platinum counter electrode and a glassy carbon working electrode. A silver wire was used as a quasi reference electrode, and its potential was calibrated versus ferrocene, (η^5-C_5H_5)$_2$Fe. As expected, all of the compounds studied exhibited well-behaved cyclic voltammetric responses, and the voltammetric profiles are as anticipated for a freely diffusing redox couple that is chemically reversible. As reported previously,[25] the peak potential differences are larger than the expected 59 mV due to ohmic losses in solution rather than sluggish kinetics. Ferrocene itself exhibited a similar response due to the relatively high resistance of the THF solvent.

The formal potentials (Table 4) are negatively shifted relative to ferrocene, as expected from the introduction of electron-donating, methyl-substituted cyclopentadienyl rings. In agreement with the infrared spectroscopic data, the purely alkylated rings produce more electron rich iron centers, as evidenced by the more negatively shifted potentials. Similar trends have been established in other substituted ferrocenes[32] and dibenzoferrocenes.[25]

Within the series of alkyl-substituted ferrocenes, the formal oxidation potentials distinguish each of the hydrocarbyl groups, although some caution must be exercised when interpreting the data. As the size of the alkyl is steadily increased, R = Me < Et < ^{i}Pr, the oxidation potential becomes steadily more negative, thereby demonstrating that **3-Fe** has a more electron rich iron center than **1-Fe**. One exception is **4-Fe**, where a more positive potential than expected was obtained. The origin of this behavior is most likely steric. As established previously,[25,32] sterically hindered ferrocenes exhibit artificially positive oxidative potentials arising from alleviation of transannular interactions upon oxidation to the less congested ferrocenium ion.

The electrochemical studies also produced different oxidation potentials within the series of silylated ferrocenes. As expected from the trend established in the alkylated cases, introduction of more substituted silyl substituents produces more electron rich metal centers. Thus, the formal oxidation potential of [SiMe$_2^t$Bu]-substituted **8-Fe** is more negative than [SiMe$_3$]-substituted **7-Fe**. Introduction of an inductively withdrawing phenyl ring onto the silyl produces a relatively electron poor iron center. The oxidation potential of **9-Fe** is shifted 50 mV more positive than **7-Fe**. Notably, the phenyl-substituted ferrocene, **5-Fe**, has the most electron poor iron center in the series. From these data, the relative electron-donating ability of the substituents in (η^5-C_5Me_4R)$_2$Fe complexes is as follows:

$$R = \mathrm{Ph} < \mathrm{SiMe_2Ph} < \underset{\longrightarrow}{\mathrm{SiMe_3}} < \mathrm{SiMe_2{}^tBu} < \mathrm{Me} < \mathrm{Et} < {}^i\mathrm{Pr}$$

$$e^{-}\text{donating}$$

Table 4. Formal Potentials for a Series of (η^5-C_5Me_4R)$_2$Fe Compounds Recorded in THF Solution

compound	R	$E_{1/2}$(mV)[a]
1-Fe	Me	−404
2-Fe	Et	−438
3-Fe	^{i}Pr	−444
4-Fe	^{t}Bu	−409
5-Fe	Ph	−251
7-Fe	SiMe$_3$	−324
8-Fe	SiMe$_2^t$Bu	−358
9-Fe	SiMe$_2$Ph	−274

[a] Values reported relative to ferrocene/ferrocenium.

For a more relevant comparison, electrochemical measurements were also conducted on the bis(cyclopentadienyl) titanium sandwich complexes. However all of these compounds suffered from irreversible voltammetric responses in THF solution using [NBu$_4$][PF$_6$] as a supporting electrolyte and a scan rate of 100 mV/s.

Interpretation of Cyclopentadienyl Substituent Effects on Dinitrogen Coordination. From the combination of infrared spectroscopic data and electrochemical results, a general trend has emerged that is well established in the literature:[24−26,33] alkylated cyclopentadienyls are more electron donating than silylated cyclopentadienyls and as a result engender more electron rich titanium centers. These results allow interpretation of the thermodynamics of dinitrogen coordination as a function of cyclopentadienyl substituent. In the series of alkyl-substituted titanium sandwiches, **1**−**4**, the T_{max} and hence the equilibrium constants for dinitrogen coordination steadily *increase* as the size of the substituent *decreases* (e.g., $K_{eq}(^t\mathrm{Bu}) < K_{eq}(^i\mathrm{Pr}) < K_{eq}(\mathrm{Et}) < K_{eq}(\mathrm{Me})$). The origin of this effect is most likely dominated by steric effects, as smaller cyclopentadienyl substituents favor dinitrogen coordination over larger ones. However, the infrared carbonyl stretching frequencies in combination with the electrochemical studies also suggest that increasing the alkyl substitution yields a more electron rich metal center. Thus, **1** is the most electrophilic alkylated titanocene and coordinates dinitrogen with the largest equilibrium constant. From these data, it appears that the steric and electronic effects work in concert, where the most electrophilic titanium sandwiches bearing the smallest cyclopentadienyl substituents have the highest affinity for dinitrogen. This effect would be expected to be predominant if Ti−N$_2$ bonding was largely dictated by σ rather than π effects. The infrared stretching frequencies of the N$_2$ bands in the monomeric titanocene bis(dinitrogen) compounds appear at relatively high frequency, consistent with little back-bonding from the titanium center.

This trend is also obeyed with the silylated titanocenes (**7**−**9**). While more electrophilic than **1**−**4**, these compounds have the largest substituents and hence are least likely to coordinate N$_2$. For example, the largest member of the series, **8**, does not coordinate dinitrogen to any detectable

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(32) Okuda, J.; Albach, R. W.; Herdtweck, E. *Polyhedron* **1991**, *10*, 1741.

(33) (a) Gassman, P. G.; Campbell, W. H.; Macomber, D. W. *Organometallics* **1984**, *3*, 385. (b) Benn, R.; Rufinska, A. *J. Organomet. Chem.* **1984**, *273*, C51.

concentration, while reducing the size of the silyl substituent to [SiMe$_3$], as is the case with **7**, likewise increases the azophilicity. Again, steric and electronic effects work in concert, as the largest, most electron donating compound has the lowest affinity to coordinate N$_2$.

In cases where the steric protection around the titanocene is not sufficiently large, dimeric structures result. Specifically for the (η^5-C$_5$Me$_4$R)$_2$Ti family of compounds, the cases where R = Me, Et, Ph, and 3,5-Me$_2$-C$_6$H$_3$ form dimeric dinitrogen complexes, while the derivatives where R > ^{i}Pr form only monomeric N$_2$ compounds. No silyl-substituted (η^5-C$_5$Me$_4$R)$_2$Ti sandwich formed a dimeric dinitrogen compound.

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 M. Braun inert atmosphere drybox containing an atmosphere of purified nitrogen. The M. Braun 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. Deuterated solvents for NMR spectroscopy were purchased from Cambridge Isotope Laboratories and were distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves. 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 passed through a liquid nitrogen cooled trap immediately before use. **1**, **1-Cl$_2$**,[34] **1-(CO)$_2$**,[6a] **2-Cl**,[35] **2-(CO)$_2$**,[27] **2-Fe**,[28] **3-Cl**, **3-(N$_2$)$_2$**,[13] **3-(CO)$_2$**,[13] **3-Fe**,[29] **4-Cl**, **4**, **4-(CO)$_2$**, **4-(N$_2$)$_2$**,[13] **5-Cl**,[36] **5-Fe**,[30] **7**,[11b] **7-Cl$_2$**,[37] **7-(CO)$_2$**,[14] **7-(N$_2$)$_2$**,[13] **8-Cl**,[10] **8**,[10] **9-Cl**,[38] **9**,[11a] **9-N$_2$**,[14] and **9-(CO)$_2$**[14] were prepared according to literature procedures.

^{1}H NMR spectra were recorded on Varian Mercury 300 and Inova 400 and 500 spectrometers operating at 299.763, 399.780, and 500.62 MHz, respectively. All chemical shifts are reported relative to SiMe$_4$ using ^{1}H (residual) chemical shifts of the solvent as a secondary standard. For paramagnetic compounds, ^{1}H NMR data are reported with the chemical shift followed by the peak width at half-height in hertz, followed by integration value and, where possible, peak assignment. Unless stated otherwise, magnetic moments were measured at 22 °C by the method originally described by Evans[17] 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, transferred to a nylon loop, and then quickly transferred to the goniometer head of a Bruker X8 APEX2 diffractometer 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.

Cyclic voltammograms (CVs) were collected using 30 mL beakers as electrochemical cells with a 3 mm glassy carbon working electrode, Pt wire as a counter electrode, and Ag wire as a reference in a drybox equipped with electrochemical outlets. CVs were recorded using a Bioanalytical Systems CV-27 voltammograph. All CVs were run at a scan rate of 100 mV/s. Solutions of the individual compounds were prepared by charging 2 mg of compound (4.5 mmol) and 0.200 g of [n-Bu$_4$N][PF$_6$] in a vial and dissolving the solids in 5 mL of THF. This produced solutions of approximately 0.1 mM in compound and 0.1 M in electrolyte. After recording the baseline of a standard 0.1 M solution of electrolyte, CVs were collected for each compound, including (η^5-C$_5$H$_5$)$_2$Fe. Oxidation potentials were then referenced to the formal potential of (η^5-C$_5$H$_5$)$_2$Fe/(η^5-C$_5$H$_5$)$_2$Fe$^+$.

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 1 and a resolution of 4. 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$_5$Me$_4$Et)$_2$Ti]$_2$(μ_2,η^1,η^1-N$_2$) ([2]$_2$N$_2$). A 100 mL round-bottomed flask was charged with 15.48 g of 0.5% sodium amalgam and approximately 15 mL of toluene. With vigorous stirring, 0.255 g (0.668 mmol) of **2-Cl** was added as a purple-blue toluene solution, and the resulting reaction mixture was stirred for three days at ambient temperature. The green solution was filtered through a pad of Celite, and the toluene was removed *in vacuo*, leaving a green solid. Recrystallization from pentane yielded 0.121 g (50%) of a green crystalline solution identified as **[2]$_2$N$_2$**. ^{1}H NMR (benzene-d_6): δ 14.71 (br s, 6H, C$_5$Me$_4$*Et*), 55.88 (br s, 12H, C$_5$*Me$_4$*Et), 64.12 (br s, 12H, C$_5$*Me$_4$*Et).

Preparation of [(η^5-C$_5$Me$_4$Et)$_2$Ti(N$_2$)]$_2$(μ_2,η^1,η^1-N$_2$) ([2-(N$_2$)]$_2$N$_2$). A concentrated solution of [(η^5-C$_5$Me$_4$Et)$_2$Ti]$_2$-(μ^2,η^1,η^1-N$_2$) was recrystallized from pentane at −35 °C to yield crystallographically pure [(η^5-C$_5$Me$_4$Et)$_2$Ti(N$_2$)]$_2$(μ_2,η^1,η^1-N$_2$) as dark blue blocks. In addition, a React IR cell was charged with 0.105 g (0.146 mmol) of [(η^5-C$_5$Me$_4$Et)$_2$Ti]$_2$(μ_2,η^1,η^1-N$_2$) in 6.75 mL of pentane against a flow of dinitrogen. The cell was cooled to −78 °C, and a spectrum was recorded under a flow of dinitrogen. The temperature of binding was determined on the basis of recording spectra at different temperatures and looking for the N−N stretches. IR (pentane, −78 °C): ν, 1719 (bridging N$_2$), 2024, 2057 cm^{-1} (terminal N$_2$).

Preparation of (η^5-C$_5$Me$_4^t$Bu)$_2$Fe (4-Fe). A 20 mL scintillation vial was charged with 0.115 g (0.624 mmol) of Li[C$_5$Me$_4$CMe$_3$], 0.040 g (0.312 mmol) of FeCl$_2$, and approximately 5 mL Et$_2$O. The resulting reaction mixture was stirred overnight, changing to a bright orange color. The solution was filtered through a pad

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(34) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219.

(35) Mach, K.; Antropiusova, H.; Varga, V.; Hanus, V. *J. Organomet. Chem.* **1988**, *358*, 123.

(36) de Wolf, J. M.; Meetsma, A.; Teuben, J. H. *Organometallics* **1995**, *14*, 5466.

(37) Horacek, M.; Gyepes, R.; Cisarova, I.; Polesek, M.; Varga, V.; Mach, K. *Collect. Czech. Commun.* **1996**, *61*, 1307.

(38) Lukesova, L.; Horacek, M.; Stepnicka, P.; Fejfarova, K.; Gyepes, R.; Cisarova, I.; Kubista, J.; Mach, K. *J. Organomet. Chem.* **2002**, *663*, 134.

of Celite, the solvent removed in vacuo, and the residue recrystallized from cold pentane to yield 0.114 g (89%) of an orange solid identified as **4-Fe**. ^{1}H NMR (benzene-*d*$_6$): *δ* 1.40 (s, 18H, C$_5$Me$_4$C*Me$_3$*), 1.65 (s, 12H, C$_5$*Me$_4$*CMe$_3$), 1.87 (s, 12H, C$_5$*Me$_4$*CMe$_3$). ^{13}C NMR (benzene-*d*$_6$): *δ* 10.77, 14.28 (Me), 32.60 (C*Me$_3$*), 33.59 (*C*Me$_3$), 76.85, 80.01, 92.95 (Cp). Mass spectrum (direct detect, 70 eV), *m*/*z* (%): calc, 410.2636 (100); found, 410.2633 (100).

Preparation of (η^5-C$_5$Me$_4$Ph)$_2$Ti (5). A 100 mL round-bottomed flask was charged with 15.68 g of 0.5% sodium amalgam and approximately 15 mL of toluene. With vigorous stirring, 0.321 g (0.672 mmol) of **5-Cl** was added as a green toluene solution, and the resulting reaction mixture was stirred for three days at ambient temperature. The green-red solution was filtered through a pad of Celite, and the toluene was removed in vacuo, leaving a green-red solid. Recrystallization from pentane yielded 0.176 g (59%) of (η^5-C$_5$Me$_4$Ph)$_2$Ti. Anal. Calcd for C$_{30}$H$_{34}$Ti: C, 81.43; H, 7.74. Found: C, 81.08; H, 7.39. ^{1}H NMR (benzene-*d*$_6$): *δ* −8.59 (br s, 4H, C$_5$Me$_4$*Ph*), 3.72 (s, 2H, C$_5$Me$_4$*Ph*), 9.47 (s, 4H, C$_5$Me$_4$*Ph*), 47.14 (s, 12H, C$_5$*Me$_4$*Ph), 65.17 (s, 12H, C$_5$*Me$_4$*Ph). Magnetic susceptibility (benzene-*d*$_6$): $\mu_{\text{eff}} = 2.7\ \mu_B$.

Preparation of (η^5-C$_5$Me$_4$Ph)$_2$Ti(CO)$_2$ (5-(CO)$_2$). A thick-walled glass vessel was charged with 3.62 g of 0.5% sodium amalgam and approximately 10 mL of pentane. With vigorous stirring, 0.075 g (0.157 mmol) of **5-Cl** was added as a pentane solution and the vessel was brought out of the drybox and was immediately submerged in liquid nitrogen. On the high-vacuum line, the vessel was degassed and 1 atm of carbon monoxide was added at −196 °C. The contents of the vessel were thawed, and the reaction mixture was stirred for 18 h at ambient temperature. The solvent was removed in vacuo, and the vessel was brought into the drybox, filtered through a pad of Celite, and recrystallized from pentane to yield 0.056 g (72%) of a red solid identified as **5-(CO)$_2$**. ^{1}H NMR (benzene-*d*$_6$): *δ* 1.70 (s, 12H, C$_5$*Me$_4$*Ph), 1.71 (s, 12H, C$_5$*Me$_4$*Ph), 7.04 (s, 2H, C$_5$Me$_4$*Ph*), 7.17 (m, 8H, C$_5$Me$_4$*Ph*). ^{13}C NMR (benzene-*d*$_6$): *δ* 11.38, 12.29 (Me), 104.79, 106.05, 111.44 (Cp), 126.38, 131.39, 136.15 (Ph), 264.59 (CO). IR (pentane): *ν*, 1862, 1941 cm^{-1} (CO).

Preparation of (η^5-C$_5$Me$_4$-3,5-Me$_2$C$_6$H$_3$)$_2$TiCl (6-Cl). A 100 mL round-bottomed flask was charged with 1.005 g (4.33 mmol) of Li[C$_5$Me$_4$-3,5-Me$_2$C$_6$H$_3$] and 0.802 g (2.16 mmol) of TiCl$_3$(THF)$_3$. A reflux condenser and 180° needle valve were then attached. On the high-vacuum line, 50 mL of tetrahydrofuran was added by vacuum transfer at −78 °C, and the resulting mixture warmed to ambient temperature while stirring. The reaction mixture was then refluxed for 60 h, after which time the solvent was removed in vacuo, leaving a dark solid. The residue was brought into the drybox, dissolved in pentane, and filtered through a pad of Celite. The solvent was removed in vacuo, leaving a green solid. Recrystallization from pentane resulted in 0.736 g (64%) of **6-Cl**. Anal. Calcd for C$_{24}$H$_{38}$ClTi: C, 70.33; H, 9.34. Found: C, 69.88; H, 9.18. ^{1}H NMR (benzene-*d*$_6$): *δ* −4.85 ($\Delta\nu_{1/2}$ = 624 Hz), 2.12 ($\Delta\nu_{1/2}$=37.6 Hz), 6.01 ($\Delta\nu_{1/2}$=34.3 Hz). Magnetic susceptibility (benzene-*d*$_6$): $\mu_{\text{eff}} = 1.5\ \mu_B$.

Preparation of (η^5-C$_5$Me$_4$-3,5-Me$_2$C$_6$H$_3$)$_2$Ti (6). A 100 mL round-bottomed flask was charged with 8.24 g of 0.5% sodium amalgam and approximately 15 mL of toluene. With vigorous stirring, 0.190 g (0.356 mmol) of **6-Cl** was added as a green toluene solution, and the resulting reaction mixture was stirred for three days at ambient temperature. The red solution was filtered through a pad of Celite, and the toluene was removed *in vacuo*, leaving a red solid. Recrystallization of the residue from pentane yielded 0.160 g (90%) of **6**. Anal. Calcd for C$_{34}$H$_{42}$Ti: C, 81.91; H, 8.49. Found: C, 81.74; H, 8.29. ^{1}H NMR (benzene-*d*$_6$): *δ* −8.97 (br s, 4H, *o*-Ph), 1.40 (s, 12H, C$_5$Me$_4$-*3,5-Me$_2$*C$_6$H$_3$), 5.19 (s, 2H, *p*-Ph), 49.02 (br s, 12H, C$_5$*Me$_4$*-3,5-Me$_2$C$_6$H$_3$), 66.73 (br s, 12H, C$_5$Me$_4$-3,5-Me$_2$C$_6$H$_3$). Magnetic susceptibility (benzene-*d*$_6$): $\mu_{\text{eff}} = 2.5\ \mu_B$.

Preparation of (η^5-C$_5$Me$_4$-3,5-Me$_2$C$_6$H$_3$)$_2$Ti(CO)$_2$ (6-(CO)$_2$). A J. Young NMR tube was charged with 0.025 g (0.05 mmol) of **6** and dissolved in approximately 0.5 mL of benzene-*d*$_6$. On the high-vacuum line, the tube was submerged in liquid nitrogen and degassed, and 1 atm of carbon monoxide was added at −196 °C. The contents of the tube were thawed, producing a color change to bright red, signaling formation of **6-(CO)$_2$**. Anal. Calcd for C$_{36}$H$_{42}$O$_2$Ti: C, 77.96; H, 7.63. Found: C, 77.94; H, 7.83. ^{1}H NMR (benzene-*d*$_6$): *δ* 1.78 (s, 12H, C$_5$*Me$_4$*-3,5-Me$_2$C$_6$H$_3$), 1.82 (s, 12H, C$_5$*Me$_4$*-3,5-Me$_2$C$_6$H$_3$), 2.19 (s, 12H, C$_5$Me$_4$-*3,5-Me$_2$*C$_6$H$_3$), 6.72 (s, 2H, C$_5$Me$_4$-3,5-Me$_2$C$_6$*H$_3$*), 6.89 (s, 4H, C$_5$Me$_4$-3,5-Me$_2$C$_6$*H$_3$*). ^{13}C NMR (benzene-*d*$_6$): *δ* 11.47, 12.31 (Me), 21.36 (3,5-Me$_2$), 104.64, 106.03, 112.07, 129.61, 136.02, 137.04 (Cp/Ph), 264.86 (CO). *One Ph resonance not located.* IR (pentane): *ν*, 1860, 1940 cm^{-1} (CO).

Preparation of [(η^5-C$_5$Me$_4$-3,5-Me$_2$C$_6$H$_3$)$_2$Ti]$_2$(μ_2,η^1,η^1-N$_2$) ([6$_2$]N$_2$). A 20 mL scintillation vial was charged with 0.160 g (0.320 mmol) of **6** and approximately 5 mL of pentane. The solution was cooled to −35 °C, resulting in the precipitation of an analytically pure blue-green solid identified as **[6$_2$]N$_2$**. Anal. Calcd for C$_{68}$H$_{84}$N$_2$Ti: C, 79.67; H, 8.26; N, 2.73. Found: C, 80.08; H, 8.41; N, 2.51.

Preparation of (η^5-C$_5$Me$_4$SiMe$_3$)$_2$Fe (7-Fe). This molecule was prepared in an identical manner to **4-Fe** with 0.253 g (1.26 mmol) of Li[C$_5$Me$_4$SiMe$_3$] and 0.080 g (0.632 mmol) of FeCl$_2$ to yield 0.189 g (67.5%) of an orange solid identified as **7-Fe**. ^{1}H NMR (benzene-*d*$_6$): *δ* 0.35 (s, 18H, C$_5$Me$_4$Si*Me$_3$*), 1.70 (s, 12H, C$_5$*Me$_4$*SiMe$_3$), 1.83 (s, 12H, C$_5$*Me$_4$*SiMe$_3$). ^{13}C NMR (benzene-*d*$_6$): *δ* 2.32 (SiMe$_3$), 10.62, 13.18 (Me), 68.42, 83.53, 84.45 (Cp). Mass spectrum (direct detect, 70 eV), *m*/*z* (%): calc, 442.2175 (100); found, 442.2181 (100).

Preparation of (η^5-C$_5$Me$_4$SiMe$_2^t$Bu)$_2$Ti(CO)$_2$ (8-(CO)$_2$). A J. Young NMR tube was charged with 0.015 g (0.029 mmol) of **8** and approximately 0.5 mL of benzene-*d*$_6$. On the high-vacuum line, the tube was degassed and 1 atm of carbon monoxide was added at −196 °C. The tube was thawed and shaken, resulting in a color change from purple-gray to orange. The solvent and excess carbon monoxide were removed in vacuo, and the compound was recrystallized from pentane to yield 0.012 g (71%) of an orange solid identified as **8-(CO)$_2$**. ^{1}H NMR (benzene-*d*$_6$): *δ* 0.38 (s, 12H, C$_5$Me$_4$Si*Me$_2$*CMe$_3$), 0.91 (s, 18H, C$_5$Me$_4$SiMe$_2$C*Me$_3$*), 1.63 (s, 12H, C$_5$*Me$_4$*SiMe$_2$CMe$_3$), 1.80 (s, 12H, C$_5$*Me$_4$*SiMe$_2$CMe$_3$). ^{13}C NMR (benzene-*d*$_6$): *δ* −1.79 (SiMe$_2$), 11.47, 14.64 (Me), 20.93 (*C*Me$_3$), 27.88 (C*Me$_3$*), 93.33, 109.99, 111.67 (Cp), 263.18 (CO). IR (pentane): *ν*, 1868, 1942 cm^{-1} (CO).

Preparation of (η^5-C$_5$Me$_4$SiMe$_2$Ph)$_2$Fe (9-Fe). This molecule was prepared in an identical manner to **4-Fe** with 0.429 g (1.63 mmol) of Li[C$_5$Me$_4$SiMe$_2$Ph] and 0.104 g (0.817 mmol) of FeCl$_2$ to yield 0.379 g (81.8%) of an orange solid identified as **9-Fe**. ^{1}H NMR (benzene-*d*$_6$): *δ* 0.71 (s, 12H, C$_5$Me$_4$Si*Me$_2$*Ph), 1.73 (s, 12H, C$_5$*Me$_4$*SiMe$_2$Ph), 1.82 (s, 12H, C$_5$*Me$_4$*SiMe$_2$Ph), 7.18 (m, 6H, C$_5$Me$_4$SiMe$_2$*Ph*), 7.42 (d, *J* = 8 Hz, 4H, C$_5$Me$_4$SiMe$_2$*Ph*). ^{13}C NMR (benzene-*d*$_6$): *δ* 1.69 (SiMe$_2$), 10.66, 13.30 (Me), 66.48, 83.99, 85.31 (Cp), 128.75, 133.92, 141.50 (Ph). *One Ph resonance not located.* Mass spectrum (direct detect, 70 eV), *m*/*z* (%): calc, 566.2488 (100); found, 566.2474 (100).

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Supporting Information Available: Crystallographic data as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.