# **ORGANOMETALLICS**

# Side-on Dinitrogen Complexes of Titanocenes with Disubstituted Cyclopentadienyl Ligands: Synthesis, Structure, and Spectroscopic Characterization

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**Supporting Information** 

**ABSTRACT:** Reduction of the 1,3-disubstituted titanocene complexes,  $(\eta^{5}-C_{5}H_{3}-1,3^{-i}Pr_{2})_{2}$ TiI or *rac, meso*- $(\eta^{5}-C_{5}H_{3}-1^{-i}Pr_{3}-Me)_{2}$ TiI, with excess 0.5% sodium amalgam under an N<sub>2</sub> atmosphere furnished the corresponding titanocene dinitrogen compounds,  $[(\eta^{5}-C_{5}H_{3}-1,3^{-i}Pr_{2})_{2}Ti]_{2}(\mu_{2}\eta^{2},\eta^{2}-N_{2})$  and  $[(\eta^{5}-C_{5}H_{3}-1,3^{-i}Pr_{2})_{2}Ti]_{2}(\mu_{2}\eta^{2},\eta^{2}-N_{2})$  and  $[(\eta^{5}-C_{5}H_{3}-1^{-i}Pr-3-Me)Ti]_{2}(\mu_{2}\eta^{2},\eta^{2}-N_{2})$ . Crystallographic studies on both molecules revealed side-on bound,  $[N_{2}]^{2^{-}}$  ligands with N–N distances of 1.226(5) and 1.216(5) Å, respectively. Variable temperature magnetic susceptibility studies estab-



lished population of a triplet ground state at ambient temperature that is slightly higher in energy than the singlet. Reducing the size of the 1,3-cyclopentadienyl substituents to methyl groups,  $[(\eta^5-C_5H_3-1,3-Me_2)_2Ti]$ , resulted in crystallization of a trimetallic titanium dinitrogen complex with an activated  $\mu_3, \eta^2, \eta^1, \eta^1-N_2$  ligand with an N–N distance of 1.320(3) Å. Hydrogenation of the isomeric titanocene dimethyl complex,  $(\eta^5-C_5H_3-1,2-Me_2)_2TiMe_2$ , in the presence of dinitrogen did not result in N<sub>2</sub> coordination but rather furnished the bimetallic titanium compound,  $(\eta^5-C_5H_3-1,2-Me_2)_2Ti(\mu_2-H)Ti(\eta^5-C_5H_3-1,2-Me_2)(\eta^5,\eta^1-C_5H_2-1,2-Me_2)$ , resulting from C–H activation of a cyclopentadienyl ring position. Addition of PhC=CPh furnished  $(\eta^5-C_5H_3-1,2-Me_2)_2Ti(\eta^2-PhCCPh)$ , demonstrating that the C–H bond activation event was reversible. By contrast, a bridging formyl complex was obtained following addition of five equivalents of CO, highlighting the availability of hydride insertion chemistry.

# ■ INTRODUCTION

Zirconocene and hafnocene complexes with side-on bound dinitrogen ligands<sup>1-3</sup> exhibit strong activation of the N-N bond and offer a wealth of functionalization chemistry including  $N_2$  hydrogenation,<sup>4–7</sup> carboxylation,<sup>8</sup> silylation,<sup>9</sup> and CO-induced  $N_2$  cleavage.<sup>10</sup> Extending this chemistry to include titanium is of interest given that some of the attractive transformations for a potential catalytic cycle such as alkalimetal free routes to reduced dinitrogen complexes<sup>11</sup> and release of the functionalized product from the metal coordination sphere are likely more feasible with a first row transition metal. Titanium complexes also have a long-standing history in nitrogen fixation.<sup>12</sup> In 1966, Vol'pin and Shur reported that hydrolysis of mixtures of  $(\eta^5-C_5H_5)_2$ TiCl<sub>2</sub> and various Grignard reagents under an N2 atmosphere yielded free ammonia.<sup>13</sup> Subsequently, Sobota and workers reported isocyanate formation from carbonylation of N<sub>2</sub> in the presence of a  $(\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>TiCl<sub>2</sub>/Mg mixture,<sup>14</sup> while Mori and co-workers have evolved this and other related titanium-alkali metal combinations to elaborate molecular nitrogen into more complex organic molecules.<sup>15</sup> Gambarotta has also reported the partial hydrogenation, silvlation, and cleavage of N2 with titanium pyrollide complexes,<sup>16</sup> and in matrix isolation experiments, cleavage of  $N_2$  has been observed with bare titanium atoms and dimers to form titanium nitrides.<sup>17,18</sup>

Considerable effort has been devoted to preparing welldefined, molecular titanium compounds with activated, side-on

bound dinitrogen ligands. An early example is Pez and coworkers' crystallographic characterization of a tetrametallic titanocene cluster with a  $\mu_3, \eta^2, \eta^1, \eta^1-N_2$  ligand.<sup>19</sup> The N–N bond distance of 1.301(12) Å remains one of the most activated reported in titanocene dinitrogen chemistry. More typically, titanocene dinitrogen complexes or related examples with full valenes<sup>20</sup> are dimeric and exhibit weak activation of the  $\mu_2,\eta^1,\eta^1$ -dinitrogen ligand.<sup>12,21-25</sup> Noncyclopentadienyl titanium complexes have been prepared and contain modestly activated end-on dinitrogen ligands with N-N bond distances between  $1.255(7)^{26}$  and  $1.286(4)^{27}$  Å, consistent with two electron reduction and formation of  $[N_2]^{2-28,29}$  By comparison, complexes with side-on,  $\mu_2, \eta^2, \eta^2$ -N<sub>2</sub> ligands are less common. Fryzuk and co-workers have invoked this hapticity during formation of N-P bonds from phosphine ligands following dinitrogen cleavage, although no intermediates were observed or characterized.<sup>26</sup> Gambarotta and co-workers have reported the synthesis and crystallographic characterization of  $[[((Me_{3}Si)_{2}N)_{2}Ti]_{2}(\mu_{2}\eta^{2},\eta^{2}-N_{2})_{2}][(TMEDA)_{2}Li]$  (TMEDA) =  $N_1N_1N_1N_2$  + tetramethylethylenediamine), the first isolable titanium compound with a side-on bound dinitrogen ligand.<sup>30</sup>

Our laboratory has a long-standing interest in using cyclopentadienyl substituent effects to manipulate  $N_2$  hapticity and ultimately reactivity.<sup>31,32</sup> In both zirconocene<sup>5</sup> and

Received: February 26, 2012 Published: April 12, 2012 hafnocene<sup>6c</sup> chemistry, we have demonstrated that while  $[(\eta^5 - C_5Me_5)_2Zr(N_2)]_2(\mu_2,\eta^1,\eta^1-N_2)$  contains weakly activated endon dinitrogen ligands, removal of a methyl group from each ring furnishes  $[(\eta^5 - C_5Me_4H)_2Zr]_2(\mu_2,\eta^2,\eta^2-N_2)$ , a side-on bound dinitrogen complex that offers rich functionalization chemistry. For the smaller first row metal, titanium, Teuben and co-workers established that  $[(\eta^5 - C_5Me_4H)_2Ti]_2(\mu_2,\eta^1,\eta^1-N_2)$  is a weakly activated, end-on dinitrogen complex,<sup>23</sup> while our group later synthesized  $[(\eta^5 - C_5H_2 - 1,2,4-Me_3)_2Ti]_2(\mu_2,\eta^2,\eta^2-N_2)^{33}$  and demonstrated that side-on coordination was once again feasible by reducing the steric protection of the metal center by systematic removal of methyl groups (Figure 1).



Figure 1. End-on versus side-on dinitrogen coordination in bis-(cyclopentadienyl)titanium complexes.

Crystallographic characterization of  $[(\eta^5 - C_5H_2 - 1, 2, 4-Me_3)_2Ti]_2(\mu_2,\eta^2,\eta^2 - N_2)$  revealed an N–N bond distance of 1.216(3) Å, more consistent with an  $[N_2]^{2-}$  ligand rather than the four-electron reduction to  $[N_2]^{4-}$  observed with zirconium and hafnium complexes with side-on dinitrogen ligands.<sup>1,34,35</sup> Computational studies have posited that the preference for the less reducing titanium, the +3 oxidation state is preferred to +4. The resulting dinitrogen compound adopts a triplet rather than singlet ground state and results in decreased activation and accounts for the lack of reactivity with dihydrogen.<sup>36</sup>

Because of the prevalence of  $[N_2]^{2-}$  in lieu of  $[N_2]^4$ , we sought to explore even less sterically protected bis-(cyclopentadienyl)titanium dinitrogen complexes with the goal of increasing overlap between the metal and side-on N<sub>2</sub> molecular orbitals. Such a strategy has recently proved successful in hafnocene chemistry where  $[(\eta^5-C_5H_2-1,2,4-Me_3)_2Hf]_2(\mu_2,\eta^2,\eta^2-N_2)$  exhibits a more activated side-on dinitrogen ligand than  $[(\eta^5-C_5Me_4H)_2Hf]_2(\mu_2,\eta^2,\eta^2-N_2)$  and undergoes N<sub>2</sub> silylation, whereas the latter compound does not.<sup>9b</sup> Here we report the results of a related study with titanium supported by a family of disubstituted bis-(cyclopentadienyl) ligands.

## RESULTS AND DISCUSSION

Reduction of Titanocene Complexes with 1,3-Disubstituted Cyclopentadienyl Ligands:  $(\eta^5-C_5H_3-1,3-R_2)_2$ Til (R = Me, <sup>i</sup>Pr). Our studies commenced with the reduction of a family of 1,3-substituted bis(cyclopentadienyl)titanium(III) iodide compounds with the goal of synthesizing complexes with strongly activated, side-on bound dinitrogen ligands. The titanocene(III) iodide compounds,  $(\eta^5-C_5H_3-1,3-R_2)_2$ Til (R = Me, <sup>i</sup>Pr), were chosen due to the ease of their reduction and were readily synthesized by treatment of the corresponding chloride derivatives with Me<sub>3</sub>SiI as described previously.<sup>33</sup> Stirring  $(\eta^5-C_5H_3-1,3-Me_2)_2$ TiI with excess, typically four equivalents, of 0.5% sodium amalgam in toluene under a dinitrogen atmosphere did not yield the desired titanocene dinitrogen compound and produced an unidentified mixture of products. Repeating the reduction of  $(\eta^5-C_5H_3-1,3-Me_2)_2$ TiI in pentane with excess KC<sub>8</sub> for three days followed by filtration and recrystallization from pentane at -35 °C furnished a small quantity of blue-green crystals identified as the trimetallic sideon, end-on dinitrogen compound, **1** (eq 1). Unfortunately the



synthesis of 1 proved unreliable and time sensitive. Attempts to improve the yield and reproducibility of the reaction by stirring the reduction of  $(\eta^{5}-C_{5}H_{3}-1,3-Me_{2})_{2}$ TiI for longer time periods were unsuccessful and resulted in isolation of K[ $(\eta^{5}-C_{5}H_{3}-1,3-Me_{2})$ ].

The solid-state structure of 1 was determined by X-ray diffraction (Figure 2) and establishes a trimetallic titanium



Figure 2. Representation of the solid-state structure of 1 at 30% probability ellipsoids. Hydrogen atoms omitted for clarity.

dinitrogen complex with an activated  $\mu_3, \eta^2, \eta^1, \eta^1-N_2$  ligand and exhibits an N-N distance of 1.320(3) Å. The coordination environment of the N2 ligand is reminiscent of Pez and coworkers' structure of the tetranuclear titanium derivative where an N–N distance of 1.301(12) Å was reported.<sup>19</sup> In trimetallic 1, the titanocene unit bonded  $\eta^2$  to the  $N_2$  ligand is intact, while the two others exhibiting  $\eta^1$ -N<sub>2</sub> coordination are coupled through the 5-positions of the cyclopentadienyl ligands with a C-C distance of 1.458(3) Å, typical of fulvalene-type ligands in this structural motif.<sup>12</sup> To our knowledge, this is the longest observed N-N bond in a titanocene dinitrogen complex and is consistent with either an  $[N_2]^{3-}$  or  $[N_2]^{4-}$  ligand. While solidstate magnetic measurements on this compound were not obtained due to its irreproducible synthesis, a solution magnetic moment of 2.2(3)  $\mu_{\rm B}$  was determined at 20 °C by the method of Evans.<sup>37</sup> While conclusive assignment of titanium oxidation states in 1 is hampered by the lack of solid-state magnetic data, the extent of reduction of the dinitrogen fragment suggests that each titanocene is best described as Ti(III). The low solution magnetic moment may arise from antiferromagnetic coupling of the spin carriers through the  $N_2$  unit, though an in depth computational analysis and variable temperature magnetic analysis has not been undertaken.

To protect against cyclopentadienyl C–H activation and coupling, isopropyl substituents were introduced onto the rings. Reduction of either  $(\eta^{5}-C_{5}H_{3}-1-{}^{i}Pr-3-Me)_{2}TiI$  or  $(\eta^{5}-C_{5}H_{3}-1,3-{}^{i}Pr_{2})_{2}TiI$  with excess of 0.5% sodium amalgam in toluene under a dinitrogen atmosphere furnished  $[(\eta^{5}-C_{5}H_{3}-1-{}^{i}Pr-3-Me)_{2}Ti]_{2}(\mu_{2},\eta^{2},\eta^{2}-N_{2})$  and  $[(\eta^{5}-C_{5}H_{3}-1,3-{}^{i}Pr_{2})_{2}Ti]_{2}(\mu_{2},\eta^{2},\eta^{2}-N_{2})$  as dark blue crystals in 33 and 66% yields, respectively (eq 2). The diasteromeric purity of the starting monohalide,



 $(\eta^{5}-C_{5}H_{3}-1-iPr-3-Me)_{2}$ TiI, was determined by oxidation with I<sub>2</sub> and <sup>1</sup>H NMR analysis of the resulting titanocene diiodide. This procedure established formation of a 2.7:1 ratio of diastereomers of  $(\eta^{5}-C_{5}H_{3}-1-iPr-3-Me)_{2}$ TiI<sub>2</sub> with the major being the  $C_{1}$  symmetric *meso* isomer.

Upon reduction of the mixture of diastereomers of  $(\eta^5-C_5H_3-1-iPr-3-Me)_2$ TiI, only the *meso* diastereomer of the dinitrogen complex was isolated and crystallographically characterized (*vide infra*). The diasteromeric purity of bulk samples of paramagnetic  $[(\eta^5-C_5H_3-1-iPr-3-Me)_2\text{Ti}]_2(\mu_2\eta^2,\eta^2-N_2)$  was assayed by treatment with excess CO to form the diamagnetic titanocene dicarbonyl complex,  $(\eta^5-C_5H_3-1-iPr-3-Me)_2\text{Ti}(CO)_2$ . Analysis of the resulting yellow-brown solid by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy in benzene- $d_6$  established formation of only *meso*- $(\eta^5-C_5H_3-1-iPr-3-Me)_2\text{Ti}(CO)_2$ , consistent with the diastereomeric purity of the starting titanocene dinitrogen complex.

Both  $[(\eta^5 - C_5H_3 - 1^{-i}Pr - 3 - Me)_2Ti]_2(\mu_2, \eta^2, \eta^2 - N_2)$  and  $[(\eta^5 - C_5H_3 - 1, 3^{-i}Pr_2)_2Ti]_2(\mu_2, \eta^2, \eta^2 - N_2)$  were characterized by X-ray

diffraction, and representations of the molecular structures are presented in Figure 3. For  $[(\eta^5-C_5H_3-1-i^3Pr-3-Me)_2Ti]_2(\mu_2\eta^2,\eta^2-N_2)$ , only the *meso* isomer was present in the lattice. There is an inversion center at the midpoint of the dinitrogen fragment, which results in one-half of the dimer being generated by symmetry. The unit cell of  $[(\eta^5-C_5H_3-1,3-i^3Pr_2)_2Ti]_2(\mu_2,\eta^2,\eta^2-N_2)$  contains one full dimeric molecule and two half molecules which possess inversion centers similar to that of  $[(\eta^5-C_5H_3-1-i^3Pr_3-Me)_2Ti]_2(\mu_2,\eta^2,\eta^2-N_2)$ . All molecules in the asymmetric unit have their cyclopentadienyl rings geared to minimize steric repulsion between adjacent isopropyl groups.

The electronic ground state of  $[(\eta^5 - C_5H_3 - 1,3^{-i}Pr_2)_2Ti]_2(\eta^2,\eta^2 - N_2)$  was also investigated by SQUID magnetometry (Figure 4). The effective magnetic moment,



**Figure 4.** Variable temperature magnetic data for  $[(\eta^5-C_5H_3-1,3^{-1}Pr_2)_2Ti]_2(\eta^2,\eta^2-N_2)$ . Fit data:  $x_p = 1.0\%$  (monomeric S = 1/2 Ti(III) impurity), J = -55.0 cm<sup>-1</sup>, and  $x_{TIP} = 6.47 \times 10^{-5}$  cm<sup>3</sup>/mol.

 $\mu_{\rm eff}$  of 2.2  $\mu_{\rm B}$  per dimer at 300 K is in good agreement with the solution phase data obtained by the Evans method ( $\mu_{\rm eff}$  = 2.3(2)  $\mu_{\rm B}$ , 295 K) in benzene- $d_c$ . The temperature dependence of  $\mu_{\rm eff}$  is shown in Figure 4 and is indicative of moderate antiferromagnetic coupling between the two Ti(III) ions resulting in a diamagnetic ground state. At higher temperatures, population of the triplet state leads to an increase of  $\mu_{\rm eff}$ 



**Figure 3.** Representations of the solid state structures of *meso*, meso- $[(\eta^5 - C_5H_3 - 1 - i^Pr - 3 - Me)_2Ti]_2(\mu_2\eta^2, \eta^2 - N_2)$  (left) and  $[(\eta^5 - C_5H_3 - 1, 3 - i^Pr_2)_2Ti]_2(\mu_2, \eta^2, \eta^2 - N_2)$  at 30% probability ellipsoids. The former compound contained a minor monohalide impurity (3%). Disordered orientations of isopropyl groups and hydrogen atoms omitted for clarity.

approaching the spin-only value for two uncoupled S = 1/2 centers ( $\mu_{\text{eff}} = 2.45 \ \mu_{\text{B}}$ ) at 300 K. The data were corrected for temperature independent paramagnetism,  $x_{\text{TIP}} = 6.47 \times 10^{-5} \text{ cm}^3/\text{mol}$ , and readily fit using the usual exchange Hamiltonian  $H_{\text{ex}} = -2JS_1S_2$  with  $S_1 = S_2 = 1/2$  and a coupling constant  $J = -55 \text{ cm}^{-1}$ . The fit required a small contribution (1.0%) from a second paramagnetic species (S = 1/2) which is most likely due to a monomeric Ti(III) impurity. The value of the coupling parameter is smaller than that found for  $[(\eta^5 \cdot C_5H_3 - 1, 3 \cdot \text{tBu})_2\text{Ti}]_2(\text{N}_2)$  ( $J = 105 \text{ cm}^{-1}$ ) or  $[(\eta^5 \cdot C_5H_3 - 1, 3 \cdot (\text{SiMe}_3)_2) \cdot \text{Ti}]_2(\text{N}_2)$  ( $J = 100 \text{ cm}^{-1}$ ).<sup>24,38</sup> The difference in the size of the singlet—triplet gap (-2J) of the two sets of compounds may arise from the end-on versus side-on binding mode of the dinitrogen fragment and the resulting different coupling pathways.

Vibrational Data for Group 4 Metallocene Complexes with Side-On Dinitrogen Ligands. Solution Raman spectra were collected on  $[(\eta^5-C_5H_3-1-i^{\rm p}r-3-Me)_2Ti]_2(\eta^2,\eta^2-N_2)$  and  $[(\eta^5-C_5H_3-1,3-i^{\rm p}r_2)_2 Ti]_2(\eta^2,\eta^2-N_2)$ , to determine the N–N stretching frequencies of titanocene dinitrogen complexes with side-on bound N<sub>2</sub> ligands. Such data are often valuable for assigning the redox level and bond order of the N<sub>2</sub> ligand and hence understanding the overall electronic structure of metaldinitrogen compounds.<sup>39,40</sup> A representative spectrum is presented in Figure 5, and the N–N stretching frequencies



**Figure 5.** Raman spectra of  $[(\eta^{5}-C_{5}H_{3}-1,3-iPr_{2})_{2}Ti]_{2}(\eta^{2},\eta^{2}-N_{2})$  (blue) and  $[(\eta^{5}-C_{5}H_{3}-1,3-iPr_{2})_{2}Ti]_{2}(\eta^{2},\eta^{2-15}N_{2})$  (green) recorded in pentane solution.

for this and related end-on and side-on dinitrogen compounds are presented in Table 1. Data new to this study include the zirconocene and hafnocene side-on dinitrogen complexes,  $[(\eta^5 - C_5Me_4H)_2Zr]_2(\eta^2,\eta^2-N_2)$  and  $[(\eta^5 - C_5H_2 - 1,2,4-Me)_2Hf]_2(\eta^2,\eta^2-N_2)$ , representative spectra of which are reported in the Supporting Information.

As reported previously,<sup>40</sup> there is an essentially linear correlation of the N–N stretching frequency with the bond distance, in accordance with Badger's rule.<sup>41</sup> An updated correlation incorporating the data from this study is presented in Figure 6. The N–N stretching frequency of 1747 cm<sup>-1</sup> for  $[(\eta^5-C_5H_3-1,3-iPr_2)_2Ti]_2(\eta^2,\eta^2-N_2)$  is comparable to the values of 1749 and 1719 cm<sup>-1</sup> reported for the fulvalene and titanocene dinitrogen compounds,  $[(\eta^5-C_5Me_5)(\eta^6-C_5H_4CR_2)-Ti]_2(\eta^1,\eta^1-N_2)$  (R = tolyl)<sup>20b</sup> and  $[(\eta^5-C_5Me_4Et)_2Ti-(N_2)]_2(\eta^1,\eta^1-N_2),^{25}$  respectively. A change in hapticity of the N<sub>2</sub> ligand results in more dramatic changes of the N–N stretching frequency as evidenced by the much lower stretching frequency of 1284 cm<sup>-1</sup> for  $[(Me_2Si)_2N(TMEDA)-$ 

TiCl]<sub>2</sub>( $\eta^1, \eta^1$ -N<sub>2</sub>) (d<sub>NN</sub> = 1.289(9) Å). The N–N stretching frequency measured for  $[(\eta^5-C_5H_3-1,3^{-i}Pr_2)_2Ti]_2(\eta^2,\eta^2-N_2)$  is comparable to the value of 1736 cm<sup>-1</sup> reported by Evans and co-workers for the lutetium dinitrogen compound with an  $\eta^2, \eta^2$ dinitrogen ligand,  $[(\eta^5-C_5Me_5)(\eta^5-C_5Me_4H)Lu]_2(\eta^2,\eta^2-N_2)$ ,<sup>42</sup> again supporting like values within a given N<sub>2</sub> hapticity.

The electronic structure of  $[(\eta^5-C_5H_3-1-iPr-3-$ Me)<sub>2</sub>Ti]<sub>2</sub>( $\eta^2$ , $\eta^2$ -N<sub>2</sub>) was investigated by DFT calculations using the BP86 functional. The experimentally determined singlet ground state of the molecule was computed using the broken symmetry (BS) formalism. Importantly, this approach allows the spin-up and spin-down electrons to occupy different portions of the molecule, allowing magnetic coupling without forced pairing. The robustness of the BS solution was verified by a complementary calculation using a spin-restricted approach, which yielded a higher energy state. The structural parameters obtained from the BS(1,1) geometry optimization are in excellent agreement with the data from X-ray crystallography. A plot of the spin-density obtained from Mulliken population analysis is shown in Figure 7 and reveals that the spin density is almost exclusively centered on the Ti ions, corroborating the Ti(III) assignment with a singly occupied  $1a_1$  orbital on each titanocene fragment.<sup>46</sup> Small contributions are observed from the bridging N2 ligand and account for the antiferromagnetic coupling observed experimentally.

The triplet state of  $[(\eta^5-C_5H_3-1-i^{P}r-3-Me)_2Ti]_2(\eta^2,\eta^2-N_2)$  was obtained computationally via a simple spin-unrestricted calculation. The optimized geometry shows no significant differences from the structure obtained from the BS(1,1) calculation and is in good agreement with the experimental data. Consistent with the magnetic data, the triplet state is only 0.2 kcal/mol higher in energy than the diamagnetic BS(1,1) state. Using the formalism developed by Yamaguchi et al.<sup>47,48</sup> a coupling constant of J = -77.5 cm<sup>-1</sup> was calculated, which is in excellent agreement with the experimental value of -55 cm<sup>-1</sup> measured by SQUID magnetometry and further validates the computational output.

The oxidation of  $[(\eta^5-C_5H_3-1,3^{-i}Pr_2)_2Ti]_2(\eta^2,\eta^2-N_2)$  was also explored. Bouwkamp and co-workers have previously reported that oxidation of the weakly activated, end-on dinitrogen complex,  $[(\eta^5-C_5Me_5)(\eta^6-C_5H_4=C_{10}H_{14})Ti]_2(\eta^1,\eta^1-N_2)$  with  $[Cp_2Fe][BPh_4]$  in THF resulted in N<sub>2</sub> loss and formation of the corresponding Ti(III) compound,  $[(\eta^5-C_5Me_5)(\eta^6-C_5H_4=C_{10}H_{14})Ti(THF)][BPh_4]$ .<sup>20c</sup> To determine if N<sub>2</sub> coordination could be preserved upon oxidation with a more activated sideon dinitrogen compound, a THF solution of  $[(\eta^5-C_5H_3-1,3^{-i}Pr_2)_2Ti]_2(\eta^2,\eta^2-N_2)$  was treated with AgBPh<sub>4</sub>, which resulted in loss of dinitrogen and isolation of the cationic Ti(III) complex,  $[(\eta^5-C_5H_3-1,3^{-i}Pr_2)_2Ti(THF)][BPh_4]$  as dark green crystals in 74% yield (eq 3).



As expected for a titanium(III),  $d^1$  compound,  $[(\eta^5-C_5H_3-1,3^{-i}Pr_2)_2Ti(THF)][BPh_4]$  is paramagnetic with a solution magnetic moment (benzene- $d_6$ , 23 °C) of 1.7(1)  $\mu$ B. The solid-state structure was determined by X-ray diffraction and

entry	compound	$\nu$ (N–N) (cm <sup>-1</sup> )	d(N–N) (Å)	reference
1	$[(\eta^{5}-C_{5}Me_{5})(\eta^{6}-C_{5}H_{4}C(C_{6}H_{4}-4-Me)_{2})Ti]_{2}(\eta^{1},\eta^{1}-N_{2})$	1749	1.160(3)	20b
2	$[(\eta^{5}-C_{5}H_{3}-1,3-{}^{i}Pr_{2})_{2}Ti]_{2}(\eta^{2},\eta^{2}-N_{2})$	1747 ( <sup>14</sup> N) 1690 ( <sup>15</sup> N)	1.226(5)	this work
3	$[(\eta^{5}-C_{5}H_{3}-1-iPr-3-Me)_{2}Ti]_{2}(\eta^{2},\eta^{2}-N_{2})$	1742	1.216(5)	this work
4	$[(\eta^{5}-C_{5}Me_{5})(\eta^{5}-C_{5}Me_{4}H)Lu]_{2}(\eta^{2},\eta^{2}-N_{2})$	1736 ( <sup>14</sup> N) 1678 ( <sup>15</sup> N)	1.275(3)	42
5	$[(\eta^{5}-C_{5}Me_{4}Et)_{2}Ti(N_{2})](\eta^{1},\eta^{1}-N_{2})$	1719	1.150(2)	25
6	$[(\eta^{5}-C_{5}Me_{5})_{2}Zr(N_{2})]_{2}(\eta^{1},\eta^{1}-N_{2})$	1578	1.182(5)	43
7	$[(Me_2Si)_2N(TMEDA)TiCl]_2 (\eta^1,\eta^1-N_2)$	1284	1.289(9)	20b, 30
8	{[(Me <sub>3</sub> Si) <sub>2</sub> N] <sub>2</sub> (THF)Y} <sub>2</sub> ( $\mu_3$ - $\eta^2$ , $\eta^2$ , $\eta^2$ -N <sub>2</sub> )K	989 ( <sup>14</sup> N) 956 ( <sup>15</sup> N)	1.405(3)	44
9	$[(\eta^{5}-C_{5}Me_{4}H)_{2}Zr]_{2}(\eta^{2},\eta^{2}-N_{2})$	922 ( <sup>14</sup> N) 893 ( <sup>15</sup> N)	1.377(3)	this work, 5
10	$[(\eta^{5}-C_{5}H_{2}-1,2,4-Me)_{2}Hf]_{2}(\eta^{2},\eta^{2}-N_{2})$	818 ( <sup>14</sup> N) 782 ( <sup>15</sup> N)	1.457(5)	this work, 9b
11	$[(P_2N_2)Zr]_2(\eta^2,\eta^2-N_2)$	775 ( <sup>14</sup> N) 753 ( <sup>15</sup> N)	1.43(1)	45

Table 1. Dinitrogen Stretching Frequencies  $(cm^{-1})$  and Bond Distances (Å) of Compounds with End-on and Side-on Dinitrogen Ligands As Determined by Raman and Infrared Spectroscopy



**Figure 6.** N–N stretching frequencies of selected group 4 and lanthanide dinitrogen compounds of different bond orders and hapticities as a power function of their bond length.

establishes the identity of the molecule (Figure 8). The THF is coordinated in the central position of the metallocene wedge, and there are no close contacts between the titanocene cation and the  $[BPh_4]^-$  anion.



**Figure 7.** Spin density plot for  $[(\eta^5-C_5H_3-1-^iPr-3-Me)_2Ti]_2(\eta^2,\eta^2-N_2)$  obtained from a Mulliken population analysis. Positive spin density is shown in red and negative spin density in yellow.



**Figure 8.** Representation of the solid state structure of  $[(\eta^5-C_5H_3-1,3-^iPr_2)_2Ti(THF)][BPh_4]$  at 30% probability ellipsoids. Hydrogen atoms and disordered isopropyl groups omitted for clarity.

Chemistry of Reduced 1,2-Dimethyl-Substituted Tita**nocene Compounds.** Alkali metal reduction of  $(\eta^5 - C_5 H_3 - 1, 2 - 1)$ Me)<sub>2</sub>Til was explored with the goal of preparing a titanocene compound with an activated, side-on bound dinitrogen ligand. Stirring the titanocene iodide with excess 0.5% sodium amalgam resulted in an unidentified mixture of products with no evidence for formation of a dinitrogen compound. An alternative route to titanocene dinitrogen compounds is via reductive elimination of dihydrogen from a titanocene hydride complex in the presence of N2. For example, Teuben and coworkers have reported that exposure of  $(\eta^5-C_5Me_4H)_2$ TiH to an N2 atmosphere yields the weakly activated, end-on dinitrogen compound,  $[(\eta^5-C_5Me_4H)_2Ti]_2(\eta^1,\eta^1-N_2).^{23}$  Our laboratory extended this method to the preparation of the side-on bound titanocene dinitrogen complex,  $[(\eta^5-C_5H_2-1,2,4 Me_3)_2Ti]_2(\eta^1,\eta^1-N_2).^{33}$ 

Addition of two equivalents of methyl lithium to a diethyl ether solution of  $(\eta^5 \cdot C_5H_3 \cdot 1, 2 \cdot Me)_2 TiCl_2$  at -35 °C followed by stirring at ambient temperature for 3 h and subsequent purification furnished  $(\eta^5 \cdot C_5H_3 \cdot 1, 2 \cdot Me)_2 TiMe_2$  as diamagnetic, bright yellow crystals in 77% yield (Scheme 1). Exposure of a toluene solution of  $(\eta^5 \cdot C_5H_3 \cdot 1, 2 \cdot Me)_2 TiMe_2$  to 4 atm of a 90:10 mixture of  $H_2:N_2$  resulted in isolation of a diamagnetic

Scheme 1. Synthesis of  $(\eta^5$ -C<sub>5</sub>H<sub>3</sub>-1,2-Me)<sub>2</sub>TiMe<sub>2</sub> and 2



dark-blue green crystalline solid in 93% yield (Scheme 1). Repeating the reaction using only  $H_2$  gas produced the same product in similar yield. X-ray diffraction (Figure 9) established



**Figure 9.** Solid state structure of  $[(\eta^5-C_5H_3-1,2-Me_2)_2\text{Ti}(\mu_2-H)\text{Ti}(\eta^5-C_5H_3-1,2-Me_2)(\eta^5,\eta^1-C_5H_2-1,2-Me_2)(2)$  at 30% probability ellipsoids. Hydrogen atoms, except those attached to titanium, omitted for clarity.

the identity of the compound as the  $\mu$ -hydrido bis(titanium) derivative,  $(\eta^5-C_5H_3-1,2-Me_2)_2\text{Ti}(\mu_2-H)\text{Ti}(\eta^5-C_5H_3-1,2-Me_2)-(\eta^5,\eta^1-C_5H_2-1,2-Me_2)$  (2), arising from C–H activation of a cyclopentadienyl position, rather than the desired dinitrogen complex. The two titanium centers are inequivalent, one being coordinated by two intact  $[(\eta^5-C_5H_3-1,2-Me_2)]$  ligands and also  $\eta^1$ - bound to a bridging cyclopentadienyl ligand from the adjacent metallocene. A hydrogen atom bridging the two titanium centers was also located. The Ti(1)–Ti(2) distance of 2.9785(4) Å is consistent with a close contact between the two metals but is outside the range necessary for a metal–metal bond.

Pez has reported a similar structural motif following isolation of a crystalline solid from low temperature potassium naphthalenide reduction of  $(\eta^5-C_5H_5)_2TiCl_2$  in THF.<sup>49</sup> The original report established a bimetallic titanium complex with a bridging  $\eta^5, \eta^1$ -cyclopentadienyl ligand. One of the titanium centers also was coordinated by a molecule of THF. However, a bridging hydride was not identified in the original report. In 2002, Harrod and co-workers reported the structural revision of this compound and correctly identified it as  $[(\eta^5-C_5H_5)_2Ti(\mu_2-$ H)Ti( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)( $\eta^5$ , $\eta^1$ -C<sub>5</sub>H<sub>4</sub>)(THF) following treatment of ( $\eta^5$ - $C_5H_5)_2TiMe_2$  with PhMeSiH<sub>2</sub> in the presence of lactones.<sup>50</sup> The Ti–Ti distance of 3.329(5) Å is outside the range typically associated with a Ti-Ti bond and is longer than the value found in 2. The Pez and Harrod compound differs from the structure of "titanocene", initially elucidated by Brintzinger and Bercaw<sup>51</sup> and later crystallographically verified by Mach.<sup>52</sup>

The toluene- $d_8$  <sup>1</sup>H NMR spectrum of **2** contains a number of broad peaks at 20 °C. Cooling the sample to -60 °C resulted in a contraction of the resonances toward the diamagnetic region

(see the Supporting Information), but the peaks did not sharpen to show coupling or allow assignment. Solution magnetic measurements (Evans method) in benzene- $d_6$  at 20 °C were consistent with the solid-state data and a diamagnetic compound.

The unusual NMR behavior of 2 prompted us to examine the electronic structure of this compound by DFT calculations using the same approach as described for  $[(\eta^5-C_5H_3-1-iPr-3-$ Me)Ti]<sub>2</sub>( $\eta^2$ , $\eta^2$ -N<sub>2</sub>). A BS(1,1) solution successfully reproduced the structural parameters obtained by X-ray crystallography and was found to be significantly lower in energy than the corresponding spin-restricted alternative. The triplet state for 2 was only 1.5 kcal/mol higher in energy than the BS solution resulting in a calculated coupling constant of I = -537.5 cm<sup>-1</sup>. The magnitude of this exchange coupling suggests that the triplet state is not significantly populated at room temperature in agreement with the experimental magnetic data. However, the chemical shifts obtained from NMR spectroscopy are much more sensitive to small contributions from close-lying excited paramagnetic states,  $^{53,54}$  which explains the unusual shifts for 2 at room temperature. The experimental and computational evidence for a low lying excited triplet state led to a more careful analysis of the Ti-Ti interaction in 2. The Mayer population analysis for the BS(1,1) ground state yielded a bond order of only 0.52. The relatively low bond order for the Ti-Ti interaction can be further understood by an inspection of the magnetic orbitals<sup>55</sup> of the complex shown in Figure 10. Each



**Figure 10.** Magnetic orbitals of **2** obtained from an unrestricted corresponding orbital transformation.<sup>56</sup> The HOMO of the spin-up manifold is shown on the left, and the HOMO of the spin-down manifold is shown on the right.

Ti(III) ion carries one unpaired electron in an orbital of  $1a_1$  symmetry with respect to the titanocene fragment. These orbitals possess only small coefficients along the Ti–Ti vector resulting in a small spatial overlap of 0.40 and a weakly bonding interaction.

To probe whether C–H activation of the cyclopentadienyl ring was reversible and to determine whether **2** could serve as a source of  $[(\eta^5-C_5H_3-1,2-Me)_2Ti]$  or contained a reactive titanium-hydride, reactivity studies were conducted. Addition of PhC=CPh to a toluene solution of **2** resulted in rapid formation of a brown solution from which brown crystals identified as  $(\eta^5-C_5H_3-1,2-Me)_2Ti(\eta^2-PhCCPh)$  were isolated in 60% yield (Scheme 2). Diamagnetic  $(\eta^5-C_5H_3-1,2-Me)_2Ti$ 

Scheme 2. Reactivity of 2 with PhC≡CPh and Carbon Monoxide



 $(\eta^2$ -PhCCPh) was independently synthesized in 75% yield by reduction of  $(\eta^5$ -C<sub>5</sub>H<sub>3</sub>-1,2-Me)<sub>2</sub>TiCl<sub>2</sub> with excess magnesium in the presence of PhC=CPh. Thus, the addition of an internal alkyne established the reversibility of the C–H cyclometalation reaction.

Carbonylation of **2** was of interest because carbon monoxide and dinitrogen are isoelectronic. Exposure of a benzene solution of **2** to 5 equivalents of CO followed by removal of the volatiles and recrystallization from diethyl ether at -35 °C furnished **3** (Scheme 2). Concomitant with the formation of **3**, a small amount of  $(\eta^5 \cdot C_5H_3 \cdot 1, 2 \cdot Me)_2Ti(CO)_2$  was also observed by <sup>1</sup>H NMR spectroscopy. Continued carbonylation of the mixture produced  $(\eta^5 \cdot C_5H_3 \cdot 1, 2 \cdot Me)_2Ti(CO)_2$  as soon as the solutions were thawed; the fate of the formyl ligand in this transformation is unknown. The ratio of the two products was dependent on the pressure of added CO;  $(\eta^5 \cdot C_5H_3 \cdot 1, 2 \cdot Me)_2Ti(CO)_2$  was formed exclusively when benzene solutions of **2** were treated with 1 atm of CO.

The benzene- $d_6$ <sup>1</sup>H and <sup>13</sup>C NMR spectra of **3** established a  $C_1$  symmetric molecule suggesting the structural features of **2** were maintained. Repeating the carbonylation in benzene- $d_6$  with <sup>13</sup>CO produced a doublet ( ${}^{1}J_{C-H} = 141.5$  ppm) centered at 7.91 ppm in the <sup>1</sup>H NMR spectrum consistent with a bridging formyl compound. The formyl resonance was located at 221.3 ppm in the <sup>13</sup>C NMR spectrum. The observation of sharp <sup>1</sup>H and <sup>13</sup>C NMR resonances in the diamagnetic region of the spectrum establishes an electronic structure for **3** that is unique from **2**.

Schrock and co-workers have reported similar observations in tantalum hydride chemistry,<sup>56</sup> and the resulting formyl compound has been structurally characterized.<sup>57</sup> Addition of CO to  $[(\eta^5-C_5Me_4Et)Cl_2TaH]_2$  resulted in formation of a  $[\mu_2,\eta^2,\eta^2-CHO]$  ligand. The low temperature <sup>1</sup>H NMR spectrum exhibits a peak at 7.5 ppm assigned as the formyl proton, similar to the value observed for 3. The <sup>13</sup>C resonance for the tantalum compound is located at 168 ppm ( $^{1}J_{C-H} = 168$  Hz), upfield shifted from the titanium compound. Insertion of CO into a terminal thorocene hydride has also been reported by Marks and co-workers to yield enediolates,<sup>58</sup> chemistry also known with group 4 metallocenes.<sup>59</sup> Fryzuk and co-workers have also reported the synthesis of a zirconium formyl complex by insertion of CO into a terminal mathematical section of a zirconium formyl complex by insertion and accompanying P–C bond formation also stabilizes the formyl unit.

# CONCLUDING REMARKS

The dinitrogen chemistry of titanocene complexes bearing disubstituted cyclopentadienyl ligands has been explored. For the 1,3-dimethyl substituted titanocene, a trimetallic compound with a  $\mu_3, \eta^2, \eta^1, \eta^1$ -N<sub>2</sub> ligand and an N–N distance of 1.320(3) Å was, albeit irreproducibly, isolated and represents one of the most activated dinitrogen ligands observed in bis-(cyclopentadienyl) titanium chemistry. Increasing the size of the ring substituents to include an isopropyl group furnished the dimeric titanocene dinitrogen complexes,  $[(\eta^5-C_5H_3 [1,3^{-i}Pr_2)_2Ti]_2(\mu_2,\eta^2,\eta^2-N_2)$  and  $[(\eta^5-C_5H_3-1^{-i}Pr-3-1)^{-i}Pr-3^{$ Me)<sub>2</sub>Ti]<sub>2</sub>( $\mu_2, \eta^2, \eta^2$ -N<sub>2</sub>) with modestly activated, side-on bound,  $[N_2]^{2-}$  ligands with N–N distances of 1.226(5) and 1.216(5) Å, respectively. Magnetic studies establish the accessibility of both singlet and triplet states. Solution Raman data establish that the N-N stretching frequency is more sensitive to N<sub>2</sub> hapticity rather than formal oxidation state. For the 1,2-dimethyl substituted titanocene, hydrogenation of the dimethyl derivative,  $(\eta^5 - C_5 H_3 - 1, 2 - Me_2)$ TiMe<sub>2</sub>, furnished the bimetallic titanium compound,  $[(\eta^5-C_5H_3-1,2-Me_2)_2Ti(\mu_2-H) Ti(\eta^{5}-C_{5}H_{3}-1,2-Me_{2})(\eta^{5},\eta^{1}-C_{5}H_{2}-1,2-Me_{2})$ , which exhibited a bridging hydride that reduced CO to a  $\mu$ -formyl ligand.

Article

# 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.<sup>61</sup> Deuterated solvents for NMR spectroscopy were distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves. Nitrogen and hydrogen gas were purchased from Airgas Incorporated and passed through a column containing manganese oxide on vermiculite and 4 Å molecular sieves before admission to the high vacuum line. Carbon monoxide gas was passed through a column containing 4 Å molecular sieves before use. The titanium dinitrogen compound  $[(C_5H_3-1-iPr-3-Me)_2Ti]_2(\eta^2,\eta^2-N_2)$  was prepared by a slight modification of the literature procedure.<sup>62</sup> The titanocene halides,  $(C_5H_3-1,2-Me_2)_2TiCl_2^{63}$  and  $(C_5H_3-1,2-Me_2)_2TiCl^{64}$ were prepared as reported. All other reagents were used as received.

<sup>1</sup>H NMR spectra were recorded on a Varian Inova 400 spectrometer operating at 399.860 MHz. All chemical shifts are reported relative to SiMe<sub>4</sub> using <sup>1</sup>H (residual) chemical shifts of the solvent as a secondary standard. <sup>13</sup>C NMR spectra were recorded on a Bruker 500 spectrometer operating at 125.71 MHz. <sup>13</sup>C chemical shifts are reported relative to SiMe<sub>4</sub> using chemical shifts of the solvent as a

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secondary standard where applicable. For paramagnetic molecules, the <sup>1</sup>H NMR data are reported with the chemical shift followed by the peak width at half height in Hertz or multiplicity, followed by integration value and where possible, peak assignment. UV–visible spectra were recorded on a Shimadzu UV-2450 spectrophotometer equipped with a diode array detector from 200 to 1100 nm in pentane solution. Raman spectra were collected on a Thermo-Fisher DXR Raman with a 720 nm excitation wavelength. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Ledgewood, NJ.

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 molybdenum and copper X-ray tubes ( $\lambda$  = 0.71073 and 1.54184 Å respectively). Preliminary data revealed the crystal system. The collection routine was optimized using the Bruker COSMO software suite. 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.

Solution magnetic moments were determined by the method of Evans at 22 °C using a ferrocene standard unless otherwise noted.<sup>37</sup> Magnetic susceptibility balance measurements were performed with a Johnson Matthey instrument that was calibrated with  $HgCo(SCN)_4$ . SQUID magnetization data of crystalline powdered samples were recorded with a SQUID magnetometer (Quantum Design) at 10 kOe between 5 and 300 K for all samples. Values of the magnetic susceptibility were corrected for the underlying diamagnetic increment by using tabulated Pascal constants and the effect of the blank sample holders (gelatin capsule/straw). Samples used for magnetization measurement were recrystallized multiple times and checked for chemical composition by elemental analysis. The program julX written by E. Bill was used for (elements of) the simulation and analysis of magnetic susceptibility data.<sup>65</sup>

**Quantum-Chemical Calculations.** All DFT calculations were performed with the ORCA program package.<sup>66</sup> The geometry optimizations of the complexes and single-point calculations on the optimized geometries were carried out at the BP86 level<sup>67–69</sup> of DFT. The all-electron Gaussian basis sets were those developed by the Ahlrichs group.<sup>70–72</sup> Triple- $\zeta$  quality basis sets def2-TZVP with one set of polarization functions were used for all atoms. Auxiliary basis sets to expand the electron density in the resolution-of-the-identity (RI) approach were chosen to match the orbital basis.<sup>73–75</sup>

Throughout this paper we describe our computational results by using the broken-symmetry (BS) approach by Ginsberg<sup>76</sup> and Noodleman.<sup>77</sup> Because several broken symmetry solutions to the spin-unrestricted Kohn–Sham equations may be obtained, the general notation  $BS(m,n)^{78}$  has been adopted, where m(n) denotes the number of spin-up (spin-down) electrons at the two interacting fragments. Canonical and corresponding<sup>56</sup> orbitals as well as spin density plots were generated with the program Molekel.<sup>79</sup>

**Preparation of (η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>-1,3-Me<sub>2</sub>)<sub>2</sub>Til.** A 100 mL round-bottom flask was charged with 0.774 g (2.88 mmol) of (η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>-1,3-Me<sub>2</sub>)<sub>2</sub>TiCl, 1.74 g (8.66 mmol) of trimethylsilyl iodide, and approximately 30 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 resulting red residue was recrystallized from diethyl ether at -35 °C to yield 0.685 g (66%) of (η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>-1,3-Me<sub>2</sub>)<sub>2</sub>TiI as dark red crystals. Anal. Calcd for C<sub>14</sub>H<sub>18</sub>ITi: C, 46.57; H, 5.02. Found: C, 46.21; H, 4.85. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 23 °C): δ 28.3 ( $\Delta \nu_{1/2}$  = 1995 Hz, C<sub>5</sub>H<sub>3</sub>-1,3-*Me*<sub>2</sub>), 37.8 ( $\Delta \nu_{1/2}$  = 8190 Hz, C<sub>5</sub>H<sub>3</sub>-1,3-Me<sub>2</sub>). Magnetic Susceptibility (benzene-*d*<sub>6</sub>):  $\mu_{eff}$  = 2.5(2)  $\mu_{B}$ .

**Preparation of**  $(\eta^5-C_5H_3-1,3-Me_2)_2\text{Ti}(\mu_3,\mu_1,\eta^2,\eta^1,N_2)(\eta^5,\eta^5-C_{10}H_4-1,3-Me_4)[\eta^5-(C_5H_3-1,3-Me_2)\text{Ti}]_2$  (1). A 20 mL scintillation vial was charged with 0.200 g (0.55 mmol) of  $(\eta^5-C_5H_3-1,3-Me_2)_2\text{Ti}]$  and approximately 10 mL of pentane. The solution was stirred rapidly, and a suspension containing 0.313 g (2.2 mmol) of potassium graphite in approximately 5 mL of pentane was prepared. The suspension was added in small portions, and the resulting dark-red brown solution was stirred at room temperature for 3 days over which time a green-blue

reaction mixture was observed. The solution was filtered through a pad of Celite, the blue-green solution was collected, and the volatiles were removed in vacuo. Recrystallization of the residue from pentane afforded a small quantity of dark-blue crystals of  $(\eta^{5}-C_{5}H_{3}-1,3-Me_{2})_{2}Ti(\mu_{3,\mu}\mu_{,\eta}^{2},\eta^{1},N_{2})(\eta^{5},\eta^{5}-C_{10}H_{4}-1,3-Me_{4})[(C_{5}H_{3}-1,3-Me_{2})Ti]_{2}$  suitable for X-ray diffraction (27 mg, 20% yield based on Ti). Anal. Calcd for C<sub>42</sub>H<sub>52</sub>N<sub>2</sub>Ti<sub>3</sub>: C, 69.25; H, 7.19; N, 3.85. Found: C, 68.86; H, 7.19; N, 3.85. Magnetic Susceptibility (benzene- $d_{6}$ ):  $\mu_{eff} = 2.2(3)$   $\mu_{T}$ .

**Preparation of**  $(\eta^5 - C_5 H_3 - 1, 3 - i Pr_2)_2$ Til. This molecule was prepared in an identical manner to  $(\eta^5 - C_5 H_3 - 1, 3 - Me_2)_2$ Til, with 4.7 g (0.030 mol) of Li[C<sub>5</sub>H<sub>3</sub>-1,3<sup>-1</sup>Pr<sub>2</sub>] and 5.6 g (0.015 mol) of TiCl<sub>3</sub>(THF)<sub>3</sub> to generate  $(\eta^5 - C_5 H_3 - 1, 3 - i Pr_2)_2$ TiCl in situ. After filtration through Celite and treatment with 3.38 g (0.017 mol) of trimethylsilyl iodide, 3.35 g (47% based on Ti) of  $(\eta^5 - C_5 H_3 - 1, 3 - i Pr_2)_2$ TiI was obtained as a green solid following recrystallization from pentane. Anal. Calcd for  $C_{22}H_{34}$ ITi: C, 55.83; H, 7.24. Found: C, 56.02; H, 7.00. <sup>1</sup>H NMR (benzene- $d_{6i}23 \,^{\circ}$ C):  $\delta$  1.99 ( $\Delta \nu_{1/2} = 105$ Hz), 3.40 ( $\Delta \nu_{1/2} = 185$  Hz), 6.90 ( $\Delta \nu_{1/2} = 5$  Hz), unable to assign resonances based on integration. Magnetic Susceptibility: (benzene $d_6$ )  $\mu_{eff} = 1.9(2) \mu_{B}$ .

**Preparation of**  $(\eta^5-C_5H_3-1-iPr-3-Me)_2TiCl.$  A thick walled glass vessel was charged with a stirbar, 4.04 g (0.032 mol) of Li[C<sub>5</sub>H<sub>3</sub>-1-iPr-3-Me], 5.84 g (0.016 mol) of TiCl<sub>3</sub>(THF)<sub>3</sub> and 75 mL of tetrahydrofuran. The vessel was degassed and heated to reflux for 3 d. The solvent was removed from the brown solution in vacuo, and the resulting brown residue was dissolved in pentane and filtered through Celite to remove LiCl. The residue was recrystallized from diethyl ether at -35 °C to afford ( $\eta^5$ -C<sub>3</sub>H<sub>3</sub>-1-iPr-3-Me)<sub>2</sub>TiCl as a greenishbrown solid in 53% yield. Anal. Calcd for C<sub>18</sub>H<sub>26</sub>ClTi: C, 66.37; H, 8.05. Found: C, 66.82; H, 7.90. <sup>1</sup>H NMR (benzene-d<sub>6</sub>, 23 °C):  $\delta$  1.93 (br m, overlapping), 2.29 (br m, overlapping), unable to assign resonances based on integration. Magnetic Susceptibility: (benzened<sub>6</sub>)  $\mu_{eff} = 1.8(1) \mu_{B}$ .

**Preparation of (η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>-1-<sup>i</sup>Pr-3-Me)<sub>2</sub>Til.** A 100 mL roundbottom flask was charged with 2.00 g (6.15 mmol) of (η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>-1-<sup>i</sup>Pr-3-Me)<sub>2</sub>TiCl, 40 mL of toluene, and a stirbar. To this rapidly stirring solution was added 3.71 g (18.5 mmol) of trimethylsilyliodide. The resulting brown solution was stirred at room temperature for 3 d, after which time the volatiles were removed in vacuo. The resulting brown residue was recrystallized from diethyl ether in multiple crops to yield (η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>-1-<sup>i</sup>**Pr-3-Me**)<sub>2</sub>TiI as a brown solid (1.20 g, 47% yield). Anal. Calcd for C<sub>18</sub>H<sub>26</sub>ITi: C, 51.82; H, 6.28. Found: C, 52.13; H, 6.16. <sup>1</sup>H NMR (benzene-d<sub>6</sub>, 23 °C): δ 3.69 (br m, overlapping), 4.63 (br m, overlapping), unable to assign resonances based on integration. Magnetic Susceptibility: (benzene-d<sub>6</sub>) μ<sub>eff</sub> = 1.3(3) μ<sub>B</sub>.

Spectroscopic Characterization of  $(\eta^5-C_5H_3-1-iPr-3-Me)_2Til_2$ . In the glovebox, a 20 mL scintillation vial was charged with 40 mg (0.096 mmol) of  $(\eta^5$ -C<sub>5</sub>H<sub>3</sub>-1-<sup>i</sup>Pr-3-Me)<sub>2</sub>TiI and 5 mL of toluene. The solution was stirred rapidly, and a 1 mL toluene solution containing 12 mg (0.047 mmol) of iodine was added slowly. The solution was stirred for 18 h at room temperature, changing color from dark brown to dark red over the course of 30 min. The solvent was removed in vacuo, and the resulting oily red residue was analyzed by  $^1\mathrm{H}$  and  $^{13}\mathrm{C}$  NMR spectroscopy to reveal two isomers present in a 2.7:1 ratio of meso:rac diastereomers. *Meso*: <sup>1</sup>H NMR (benzene- $d_{6}$ , 23 °C):  $\delta$  0.88 (d, <sup>3</sup> $J_{HH}$  = 7.0, 3H,  $C_5H_3$ -1,3-Me-*i*Pr), 0.94 (d,  ${}^{3}J_{HH} = 7.0, 3H, C_5H_3$ -1,3-Me-*i*Pr), 1.13 (d,  ${}^{3}J_{HH} = 7.0$ , 3H, C<sub>5</sub>H<sub>3</sub>-1,3-Me-*i*Pr), 1.17 (d,  ${}^{3}J_{HH} = 7.0$ , 3H, C<sub>5</sub>H<sub>3</sub>-1,3-Me-*iPr*), 2.03 (s, 3H, C<sub>5</sub>H<sub>3</sub>-1,3-Me-*i*Pr), 2.06 (s, 3H, C<sub>5</sub>H<sub>3</sub>-1,3-Me-iPr), 3.08 (septet,  ${}^{3}J_{HH} = 7.0$ , 1H, C<sub>5</sub>H<sub>3</sub>-1,3-Me-*iPr*), 3.12 (septet,  ${}^{3}J_{HH} = 7.0, 1H, C_{5}H_{3}-1,3-Me-iPr$ ), 5.55 (m, 1H, C<sub>5</sub>H<sub>3</sub>-1,3-MeiPr), 5.63 (m, 1H, C<sub>5</sub>H<sub>3</sub>-1,3-Me-iPr), 5.67 (m, 1H, C<sub>5</sub>H<sub>3</sub>-1,3-Me-iPr), 5.72 (m, 1H, C<sub>5</sub>H<sub>3</sub>-1,3-Me-iPr), 7.06 (m, 1H, C<sub>5</sub>H<sub>3</sub>-1,3-Me-iPr), 7.09 (m, 1H, C<sub>5</sub>H<sub>3</sub>-1,3-Me-iPr). {<sup>1</sup>H}<sup>13</sup>C NMR (benzene- $d_{6}$ , 23 °C):  $\delta$ 18.7, 18.8 (C<sub>5</sub>H<sub>3</sub>-1,3-Me-iPr), 21.4, 22.2, 22.2, 24.1 (C<sub>5</sub>H<sub>3</sub>-1,3-Me-*iPr*), 31.3, 31.4 (C<sub>5</sub>H<sub>3</sub>-1,3-Me-*i*Pr), 113.4, 114.2, 114.7, 116.8, 117.2, 117.8, 125.9, 126.0, 129.4, 142.3 (C<sub>5</sub>H<sub>3</sub>-1,3-Me-iPr). Rac: <sup>1</sup>H NMR (benzene- $d_{6}$  23 °C):  $\delta$  1.04 (d,  ${}^{3}J_{HH}$  = 7.0, 6H, C<sub>5</sub>H<sub>3</sub>-1,3-Me-*iPr*), 1.05 (d,  ${}^{3}J_{HH} = 7.0$ , 6H, C<sub>5</sub>H<sub>3</sub>-1,3-Me-*iPr*), 1.77 (s, 6H, C<sub>5</sub>H<sub>3</sub>-1,3-MeiPr), 2.85 (septet,  ${}^{3}J_{HH} = 7.0$ , 2H, C<sub>5</sub>H<sub>3</sub>-1,3-Me-*iPr*), 6.32 (m, 2H, C<sub>5</sub>H<sub>3</sub>-1,3-Me-iPr), 6.41 (m, 2H, C<sub>5</sub>H<sub>3</sub>-1,3-Me-iPr), 6.55 (m, 2H, C<sub>5</sub>H<sub>3</sub>-1,3-Me-iPr). {<sup>1</sup>H}<sup>13</sup>C NMR (benzene- $d_{6i}$  23 °C): δ 20.6 (C<sub>5</sub>H<sub>3</sub>-1,3-Me-iPr), 24.3, 24.4 (C<sub>5</sub>H<sub>3</sub>-1,3-Me-iPr), 32.8 (C<sub>5</sub>H<sub>3</sub>-1,3-Me-iPr), 119.5, 120.1, 121.5, 141.8, 153.6 (C<sub>5</sub>H<sub>3</sub>-1,3-Me-iPr).

Preparation of  $[(\eta^5-C_5H_3-1,3-Pr)_2Ti]_2(\eta^2,\eta^2-N_2)$ . A 100 mL round-bottom flask was charged with 19.4 g of 0.5% sodium amalgam and approximately 10 mL of toluene. With vigorous stirring of the amalgam, a slurry containing 0.500 g (1.05 mmol) of ( $\eta^5$ -C<sub>5</sub>H<sub>3</sub>-1,3 $iPr_2)_2$ TiI in approximately 20 mL of toluene was added. The resulting dark blue-green reaction mixture was stirred at ambient temperature for 3 days under a dinitrogen atmosphere. After one day a color change to royal blue was observed. Following filtration through Celite, the solvent was removed in vacuo, and the resulting dark residue was recrystallized from pentane at -35 °C yielding 0.240 g (66%) of analytically pure dark blue crystals over the course of 1 day. Anal. Calcd for C44H68N2Ti2: C, 73.32; H, 9.51; N, 3.89. Found: C, 72.96; H, 9.52; N, 3.56. <sup>1</sup>H NMR (benzene- $d_{6i}$  23 °C):  $\delta$  1.41(br s overlapped), 1.75 (br s overlapped), 1.99 (br s overlapped), 21.1  $(\Delta \nu_{1/2} = 1180 \text{ Hz})$ , unable to assign resonances based on integration. Magnetic Susceptibility: (benzene- $d_6$ )  $\mu_{\text{eff}} = 2.3(2) \ \mu_{\text{B}}$ . UV-vis (pentane): 306 nm (11 954 M<sup>-1</sup> cm<sup>-1</sup>), 344 nm (9914 M<sup>-1</sup> cm<sup>-1</sup>), 570 nm (13 815 M<sup>-1</sup> cm<sup>-1</sup>). Raman (pentane):  $\nu_{\rm NN} = 1747$  cm<sup>-1</sup>  $({}^{14}N_2)$ , 1688 cm<sup>-1</sup>  $({}^{15}N_2)$ .

**Preparation of**  $[(\eta^5 - C_5 H_3 - 1 - i^{-} Pr - 3 - Me)_2 Ti]_2(\eta^2, \eta^2 - N_2)$ . This compound was prepared in a similar manner to  $(\eta^5 - C_5 H_3 - 1, 3 - i^{-} Pr)_2 Ti]_2(\eta^2, \eta^2 - N_2)$ , using 0.500 g (1.20 mmol) of  $(\eta^5 - C_5 H_3 - 1, 3 - Me - i^{-} Pr)_2 TiI$  and 22.1 g of 0.5% Na/Hg. Following filtration of the reaction mixture through Celite, the solvent was removed in vacuo, and the resulting dark residue was recrystallized from pentane at -35 °C to yield analytically pure dark blue crystals suitable for X-ray diffraction (125 mg, 33% yield). Anal. Calcd for  $C_{36}H_{52}N_2 Ti_2$ : C, 71.05; H, 8.61; N, 4.60. Found: C, 70.75; H, 8.19; N, 4.38. <sup>1</sup>H NMR (benzene- $d_6$ , 23 °C):  $\delta$  2.51, 2.77, 2.92, unable to assign resonances based on integration. Magnetic Susceptibility: (benzene- $d_6$ )  $\mu_{\text{eff}} = 2.4(2) \mu_{\text{B}}$ . UV-vis (pentane): 300 nm (11 801 M<sup>-1</sup> cm<sup>-1</sup>), 360 nm (13 215 M<sup>-1</sup> cm<sup>-1</sup>), 560 nm (3306 M<sup>-1</sup> cm<sup>-1</sup>). Raman (toluene):  $\nu_{\text{NN}} = 1742 \text{ cm}^{-1} ({}^{14}\text{N}_2)$ .

Spectroscopic Characterization of  $(\eta^5-C_5H_3-1-iPr-3-Me)_2Ti-$ (CO)<sub>2</sub>. In the glovebox was dissolved 10 mg (0.016 mmol) of  $[(\eta^5 C_5H_3-1-iPr-3-Me)_2Ti]_2(\eta^2,\eta^2-N_2)$  in benzene- $d_6$  (0.5 mL), and a dark blue solution formed. The tube was frozen in liquid nitrogen and degassed, and 1 atm of CO was admitted to the vessel. The contents of the tube were thawed and then shaken vigorously. A color change from blue to yellow-brown was observed. <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic analysis revealed the presence of only the meso diastereoisomer. <sup>1</sup>H NMR (benzene- $d_6$ , 23 °C):  $\delta$  1.00 (d, <sup>3</sup> $J_{HH}$  = 6.5, 3H,  $C_5H_3$ -1,3-Me-*iPr*), 1.02 (d overlapped,  ${}^3J_{HH} = 6.5$ , 6H,  $C_5H_3$ -1,3-Me-*iPr*), 1.05 (d,  ${}^{3}J_{HH} = 6.5$ , 3H, C<sub>5</sub>H<sub>3</sub>-1,3-Me-*iPr*), 1.76 (s, 3H, C5H3-1,3-Me-iPr), 1.78 (s, 3H, C5H3-1,3-Me-iPr), 2.29 (m overlapped, 1H, C<sub>5</sub>H<sub>3</sub>-1,3-Me-*iPr*), 2.32 m overlapped, 1H, C<sub>5</sub>H<sub>3</sub>-1,3-Me-*iPr*), 4.37 (m overlapped, 1H,  $C_5H_3$ -1,3-Me-iPr), 4.39 (m overlapped, 2H,  $C_5H_3$ -1,3-Me-iPr), 4.42 (m overlapped, 1H, C<sub>5</sub>H<sub>3</sub>-1,3-Me-iPr), 4.43 (m overlapped, 1H, C<sub>5</sub>H<sub>3</sub>-1,3-Me-iPr), 4.44 (m overlapped, 1H, C<sub>5</sub>H<sub>3</sub>-1,3-Me-iPr).  ${^{1}H}^{13}C$  NMR (benzene- $d_6$ , 23 °C):  $\delta$  15.8, 15.9 (C<sub>5</sub>H<sub>3</sub>-1,3-Me-iPr), 24.3, 24.3, 25.2, 25.3 (C<sub>5</sub>H<sub>3</sub>-1,3-Me-*iPr*), 29.2, 30.6, (C<sub>5</sub>H<sub>3</sub>-1,3-Me-iPr), 91.0, 93.4, 93.7, 94.1, 94.3, 106.8, 106.9, 121.1, 121.2, 129.7 ( $C_5$ H<sub>3</sub>-1,3-Me-iPr), 263.7, 263.8 (Ti-CO). IR(benzene- $d_6$ ):  $\nu_{CO}$ = 1960, 1882, 1850 cm<sup>-</sup>

**Preparation of**  $[(\eta^5-C_5H_3-1,3-Pr)_2Ti(THF)][BPh_4]$ . A 20 mL scintillation vial was charged with 0.200 g (0.278 mmol) of  $[(\eta^5-C_5H_3-1,3-Pr)_2Ti]_2(\eta^2,\eta^2-N_2)$ , a stirbar, and 5 mL of tetrahydrofuran. To this dark purple solution was added a suspension containing 0.260 g (0.620 mmol) of AgBPh\_4 in 5 mL of tetrahydrofuran. The resulting dark purple solution was stirred at ambient temperature for 18 h. The volatiles were removed in vacuo, and the brown residue was dissolved in approximately 10 mL of toluene and filtered through Celite. The filtrate was removed, and the resultant brown oil was recrystallized from fluorobenzene at -35 °C to afford 0.300 g (74%) of dark green needles identified as  $[(\eta^5-C_5H_3-1,3-iPr)_2Ti(THF)][BPh_4]$ . Anal. Calcd for  $C_{50}H_{61}$ OBTi: C, 81.41; H, 8.47; N, 0.00. Found: C, 81.38; H, 8.33;

N, <0.02. Magnetic Susceptibility: (Magnetic Susceptibility balance)  $\mu_{\rm eff}$  = 1.7(1)  $\mu_{\rm B}$ 

**Preparation of (η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>-1,2-Me<sub>2</sub>)<sub>2</sub>TiMe<sub>2</sub>.** A 20 mL scintillation vial was charged with 0.600 g (1.97 mmol) of (η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>-1,2-Me<sub>2</sub>)<sub>2</sub>TiCl<sub>2</sub> and approximately 10 mL of diethyl ether. The resulting solution was chilled to -35 °C, and 2.6 mL (5.60 mmol) of 1.6 M methyl lithium solution in diethyl ether was added. The resulting reaction mixture was stirred for 3 h at room temperature. The solvent was removed in vacuo, and the residue was extracted with pentane, filtered through Celite, and recrystallized from pentane to afford 0.400 g (77%) of (η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>-1,2-Me<sub>2</sub>)<sub>2</sub>TiMe<sub>2</sub> as bright yellow needles. Anal. Calcd for C<sub>16</sub>H<sub>24</sub>Ti: C, 72.73; H, 9.16. Found: C, 72.55; H, 8.88. <sup>1</sup>H NMR (benzene-d<sub>6</sub> 23 °C): δ -0.24 (s, 6H, TiMe<sub>2</sub>), 1.93 (s, 12H, C<sub>5</sub>H<sub>3</sub>-1,2-Me<sub>2</sub>), 5.02 (t, <sup>3</sup>J<sub>HH</sub> = 3.1, 2H, C<sub>5</sub>H<sub>3</sub>-1,2-Me<sub>2</sub>), 5.32 (d, <sup>3</sup>J<sub>HH</sub> = 3.1, 4H, C<sub>5</sub>H<sub>3</sub>-1,2-Me<sub>2</sub>), 1<sup>4</sup>H<sup>13</sup>C NMR (benzene-d<sub>6</sub>, 23 °C): δ 13.7 (C<sub>5</sub>H<sub>3</sub>-1,2-Me<sub>5</sub>), 44.3 (TiMe<sub>5</sub>), 106.3, 113.2, 123.4 (C<sub>5</sub>H<sub>3</sub>-1,2-Me<sub>5</sub>).

Preparation of  $[(\eta^5-C_5H_3-1,2-Me_2)_2Ti(\mu_2-H)Ti(\eta^5-C_5H_3-1,2 Me_2$ )( $\eta^5$ , $\eta^1$ -C<sub>5</sub>H<sub>2</sub>-1,2-Me<sub>2</sub>). A thick walled glass vessel was charged with 0.130 g (0.53 mmol) of  $(\eta^{5}-C_{5}H_{3}-1,2-Me_{2})_{2}TiMe_{2}$  and approximately 10 mL of toluene. The vessel was transferred to a high vacuum line, and the contents of the vessel cooled to 77 K and degassed. At this temperature, one atmosphere of hydrogen gas was admitted. The dark yellow solution was warmed to room temperature and shaken vigorously forming a dark green solution after 15 s. The solution was stirred for 1 h at room temperature before the solvent was removed in vacuo. Recrystallization of the dark green residue from pentane yielded 0.230 g (93%) of dark blue-green crystals. Similar results were obtained when a mixture of hydrogen and nitrogen gas was used. Anal. Calcd for C28H36Ti2: C, 71.81; H, 7.75. Found: C, 71.71; H, 7.42. <sup>1</sup>H NMR (benzene- $\tilde{d}_{6}$ , 23 °C):  $\delta$  –1.55 ( $\Delta \nu_{1/2}$  = 49 Hz), -0.79 ( $\Delta \nu_{1/2}$  = 56 Hz), 11.4 ( $\Delta \nu_{1/2}$  = 383 Hz), 13.2 ( $\Delta \nu_{1/2}$  = 317 Hz). <sup>1</sup>H NMR (toluene- $d_8$ , 19 °C):  $\delta$  –1.49 ( $\Delta \nu_{1/2}$  = 46 Hz),  $-0.71 \ (\Delta \nu_{1/2} = 46 \text{ Hz}), 7.03 \ (\Delta \nu_{1/2} = 214 \text{ Hz}), 11.4 \ (\Delta \nu_{1/2} = 225 \text{ Hz})$ Hz), 12.6  $(\Delta \nu_{1/2} = 208 \text{ Hz})$ , 13.9  $(\Delta \nu_{1/2} = 216 \text{ Hz})$ . <sup>1/2</sup> NMR (toluene- $d_8$ , -42 °C):  $\delta$  0.03  $(\Delta \nu_{1/2} = 45 \text{ Hz})$ , 0.97  $(\Delta \nu_{1/2} = 79 \text{ Hz})$ , 3.89 ( $\Delta \nu_{1/2}$  = 710 Hz), 7.66 ( $\Delta \nu_{1/2}$  = 418 Hz), 9.61 ( $\Delta \nu_{1/2}$  = 196 Hz). UV-vis (pentane): 404 nm (1157 M<sup>-1</sup> cm<sup>-1</sup>), 615 nm (228 M<sup>-1</sup>  $cm^{-1}$ ).

Preparation of  $(\eta^5-C_5H_3-1,2-Me_2)_2$ Ti $(\eta^2-PhCCPh)$ . Method 1: A 20 mL scintillation vial was charged with a stirbar, 0.036 g (0.08 mmol) of 2, and approximately 5 mL of toluene. The dark-green solution was stirred, and 0.050 g (0.28 mmol) of diphenylacetylene was added as a solution in approximately 2 mL of toluene. The solution was stirred at room temperature overnight before the solvent was removed in vacuo, and the yellow residue was recrystallized from diethyl ether:pentane to yield 60% of brown crystals identified as  $(C_5H_3-1,2-Me_2)_2$ Ti $(\eta^2$ -PhCCPh). Method 2: A 20 mL scintillation vial was charged with a stirbar, 0.050 g (0.19 mmol) of (C<sub>5</sub>H<sub>3</sub>-1,2-Me<sub>2</sub>)<sub>2</sub>TiCl, 0.036 g (0.20 mmol) of diphenylacetylene, and 0.044 g (1.90 mmol) of magnesium powder. The brown solution was stirred overnight before being filtered through Celite and recrystallized from diethyl ether to afford (C<sub>5</sub>H<sub>3</sub>-1,2-Me<sub>2</sub>)<sub>2</sub>Ti( $\eta^2$ -PhCCPh) in 75% yield. Anal. Calcd for C42H46Ti: C, 81.55; H, 6.84. Found: C, 81.58; H, 6.65. <sup>1</sup>H NMR (benzene- $d_{6}$ , 23 °C):  $\delta$  1.80 (s, 12H, C<sub>5</sub>H<sub>3</sub>-1,2- $Me_2$ ), 5.37 (t,  ${}^{3}J_{\rm HH}$  = 3.0, 2H, C<sub>5</sub>H<sub>3</sub>-1,2-Me<sub>2</sub>), 5.91 (d,  ${}^{3}J_{\rm HH}$  = 3.0, C<sub>5</sub>H<sub>3</sub>-1,2-Me<sub>2</sub>), 6.70 (m, 2H, Ar-CH), 6.95 (m, 4H, Ar-CH), 7.06 (m, 4H, Ar-CH). {<sup>1</sup>H}<sup>13</sup>C NMR (benzene- $d_6$ , 23 °C):  $\delta$  14.4 (C<sub>5</sub>H<sub>3</sub>-1,2-Me<sub>2</sub>), 109.9 (C<sub>5</sub>H<sub>3</sub>-1,2-Me<sub>2</sub>), 113.5 (C<sub>5</sub>H<sub>3</sub>-1,2-Me<sub>2</sub>), 125.9 (aryl CH), 127.5 (C<sub>5</sub>H<sub>3</sub>-1,2-Me<sub>2</sub>), 128.4 (aryl CH), 132.2 (aryl CH), 142.2 (aryl C), 198.2 (Ti-C).

Spectroscopic Characterization of  $[(C_5H_3-1,2-Me_2)_2Ti(\mu_2-C-(O)H)Ti(C_5H_3-1,2-Me_2)(\eta^5,\eta^1-C_5H_2-1,2-Me_2)$  (3). A thick walled glass vessel was charged with 0.045 g (0.10 mmol) of  $[(C_5H_3-1,2-Me_2)_2Ti(\mu_2-H)Ti(C_5H_3-1,2-Me_2)(\eta^5,\eta^1-C_5H_2-1,2-Me_2)$  and approximately 5 mL of benzene. The dark green solution was degassed at the vacuum line, and CO gas was added via calibrated gas bulb (71 Torr from a 100.1 mL gas bulb, 0.40 mmol). The dark green solution was shaken vigorously, and the color changed to dark brown upon mixing. <sup>1</sup>H and <sup>13</sup>C NMR analysis of the mixture revealed the presence of 3 and a small amount of  $(\eta^5-C_5H_3-1,2-Me_2)_2Ti(CO)_2$ . <sup>1</sup>H NMR

(benzene- $d_{6}$ , 23 °C):  $\delta$  1.64 (s, 3H, C<sub>5</sub>H<sub>3</sub>-1,2- $Me_2$ ), 1.70 (s, 3H, C<sub>5</sub>H<sub>3</sub>-1,2- $Me_2$ ), 1.81 (s, 6H, C<sub>5</sub>H<sub>3</sub>-1,2- $Me_2$ ), 1.86 (s, 6H, C<sub>5</sub>H<sub>3</sub>-1,2- $Me_2$ ), 1.90 (s, 3H, C<sub>5</sub>H<sub>3</sub>-1,2- $Me_2$ ), 2.22 (s, 3H, C<sub>5</sub>H<sub>3</sub>-1,2- $Me_2$ ), 4.87 (m, 1H, C<sub>5</sub>H<sub>3</sub>-1,2- $Me_2$ ), 5.10 (m, 1H, C<sub>5</sub>H<sub>3</sub>-1,2- $Me_2$ ), 5.29 (m, 1H, C<sub>5</sub>H<sub>3</sub>-1,2- $Me_2$ ), 5.32 (m, 1H, C<sub>5</sub>H<sub>3</sub>-1,2- $Me_2$ ), 5.39 (m, 1H, C<sub>5</sub>H<sub>3</sub>-1,2- $Me_2$ ), 5.32 (m, 1H, C<sub>5</sub>H<sub>3</sub>-1,2- $Me_2$ ), 5.39 (m, 1H, C<sub>5</sub>H<sub>3</sub>-1,2- $Me_2$ ), 5.41 (m, 1H, C<sub>5</sub>H<sub>3</sub>-1,2- $Me_2$ ), 6.00 (m, 1H, C<sub>5</sub>H<sub>3</sub>-1,2- $Me_2$ ), 7.43 (m, 1H, C<sub>5</sub>H<sub>3</sub>-1,2- $Me_2$ ), 7.91 (d, <sup>1</sup> $J_{CH}$  = 141.5, 1H, C(O)-H). {<sup>1</sup>H}<sup>13</sup>C NMR (benzene- $d_6$ , 23 °C):  $\delta$  12.6, 13.4, 13.6, 13.6, 14.0, 14.2, 14.6, 14.6, 14.6 (C<sub>5</sub>H<sub>3</sub>-1,2- $Me_2$ ), 89.4, 94.5, 98.9, 106.8, 107.1, 111.3, 112.9, 114.2, 115.0, 115.6, 115.7, 115.8, 119.2, 121.1, 122.6, 122.8, 126.8, 129.6, 134.0, 147.8 (C<sub>5</sub>H<sub>3</sub>-1,2- $Me_2$ ), 221.3 (C(O)-H).

**Preparation of**  $(\eta^5 - C_5 H_3 - 1, 2 - Me_2)_2 Ti(CO)_2$ . A thick walled glass vessel was charged with a stirbar, 0.040 g (0.15 mmol) of (C5H3-1,2-Me<sub>2</sub>)<sub>2</sub>TiCl, and 0.020 g (0.75 mmol) of magnesium powder. The vessel was removed from the glovebox, brought to the high vacuum line, and evacuated. Approximately 10 mL of diethyl ether was added by vacuum transfer, and 1 atm of CO gas was added at 77 K. The green-brown solution was stirred for 18 h at room temperature. The vessel was degassed and brought into the box, and the solution was filtered through Celite to remove excess magnesium. The residue was recrystallized from diethyl ether at -35 °C to afford (C<sub>5</sub>H<sub>3</sub>-1,2-Me<sub>2</sub>)<sub>2</sub>Ti (CO)<sub>2</sub> as an analytically pure brown powder in 80% yield. Anal. Calcd for C16H18O2Ti: C, 66.22; H, 6.25. Found: C, 65.88; H, 5.99. <sup>1</sup>H NMR (benzene- $d_{6}$ , 23 °C):  $\delta$  1.66 (s, 12H, C<sub>5</sub>H<sub>3</sub>-1,2-Me<sub>2</sub>), 4.41 (t,  ${}^{3}J_{HH}$  = 3.0, 2H, C<sub>5</sub>H<sub>3</sub>-1,2-Me<sub>2</sub>), 4.56 (d,  ${}^{3}J_{HH}$  = 3.0, 4H, C<sub>5</sub>H<sub>3</sub>-1,2-Me<sub>2</sub>). {<sup>1</sup>H}<sup>13</sup>C NMR (benzene- $d_{6}$ , 23 °C):  $\delta$  13.5 (C<sub>5</sub>H<sub>3</sub>-1,2-Me<sub>2</sub>), 89.3, 94.4, 108.1 ( $C_5H_3$ -1,2-Me<sub>2</sub>), 263.1 (Ti-CO). IR (benzene- $d_6$ ):  $\nu_{\rm CO} = 1954, 1876 \text{ cm}^{-1}$ 

#### ASSOCIATED CONTENT

#### **S** Supporting Information

Crystallographic details for 1,  $[(\eta^5-C_5H_3-1,3^{-i}Pr_2)_2Ti]_2(\eta^2,\eta^2-N_2)$ ,  $[(\eta^5-C_5H_3-1^{-i}Pr_3-Me)_2Ti]_2(\eta^2,\eta^2-N_2)$ ,  $[(\eta^5-C_5H_3-1,3^{-i}Pr)_2Ti(THF)][BPh_4]$ , and  $[(\eta^5-C_5H_3-1,2-Me_2)_2Ti(\mu_2-H)-Ti(\eta^5-C_5H_3-1,2-Me_2)(\eta^5,\eta^1-C_5H_2-1,2-Me_2)$  in cif format and additional spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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