

# Low-Valent Pentafulvene Titanium Dinitrogen Complex as a Precursor for Cationic Titanium Complexes

Axel Scherer,<sup>†</sup> Detlev Haase,<sup>†</sup> Wolfgang Saak,<sup>†</sup> Rüdiger Beckhaus,<sup>\*,†</sup> Auke Meetsma,<sup>‡</sup> and Marco W. Bouwkamp<sup>\*,‡</sup>

<sup>†</sup>Institute of Pure and Applied Chemistry, University of Oldenburg, D-26111 Oldenburg, Germany <sup>‡</sup>Molecular Inorganic Chemistry Group, Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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Treatment of titanium dinitrogen complex  $[Cp^*(\eta^6-C_5H_4=C_{10}H_{14})Ti]_2(\mu-N_2)$  (1) with ferrocenium borate,  $[Cp_2Fe][BPh_4]$ , in THF results in oxidation of the titanium center, affording the titanium(IV) pentafulvene compound  $[Cp^*(\eta^6-C_5H_4=C_{10}H_{14})Ti(THF)][BPh_4]$  (2). Treatment of 1 with anilinium reagent [PhNMe\_2H][BPh\_4] results in the formation of cationic titanocene(III) complexes. In THF, the titanocene cation is stabilized by two THF solvent molecules, whereas the tetraphenylborate anion is bound to the metal center when the reaction is performed in toluene as a solvent. Treatment of 1 with B(C\_6F\_5)\_3 affords zwitterionic  $[Cp^*\{\eta^5-C_5H_3(C_{11}H_{14})(B\{C_6F_5\}_3)\}Ti(THF)]$  (7). Results show the versatility of pentafulvene complex 1 in the preparation of cationic titanium complexes.

## Introduction

Cationic complexes of early transition metals are of great importance as catalysts for a broad range of chemical transformations and in particular for olefin polymerization catalysis.<sup>1</sup> The performance of these catalysts is in part governed by the interaction of the cationic transition metal complex with its counterion. As these interactions are generally unfavorable, weakly coordinating anions have been developed to minimize interference of the counterion.<sup>2</sup> Over the years, many synthetic routes have been developed for the preparation of transition metal complexes with these weakly coordinating anions, among which the treatment of transition metal alkyl complexes with Lewis and Brønsted acidic borane and borate reagents.<sup>2,3</sup> Furthermore, the oxidation of low-valent metallocene complexes has been reported.<sup>4</sup>

Here we report the reactivity of the low-valent titanium dinitrogen complex  $[Cp^*Fv^{Ad}Ti]_2(\mu-\eta^2:\eta^2-N_2)$  (1,  $Cp^* =$ 

 $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>; Fv<sup>Ad</sup> =  $\eta^6$ -C<sub>5</sub>H<sub>4</sub>=C<sub>10</sub>H<sub>14</sub>)<sup>5</sup> with different borane and borate reagents, which allowed the isolation and characterization of a variety of new cationic titanium complexes. Results demonstrate the versatility of the pentafulvene ligand in titanium chemistry.

#### **Results and Discussion**

**Reaction with Ferrocenium Tetraphenylborate.** Treatment of the low-valent dinitrogen-bridged dimer  $[Cp*Fv^{Ad}Ti]_2$ - $(\mu-\eta^2:\eta^2-N_2)$  (1) with  $[Cp_2Fe][BPh_4]$  (1 equiv per titanium) in THF solution results in a color change from blue-green to orange. During the reaction gas evolution was observed, suggesting the release of dinitrogen. The <sup>1</sup>H NMR spectrum of the compound shows the correct number of peaks for the  $C_1$  symmetric titanium cation  $[Cp*Fv^{Ad}Ti(THF)][BPh_4]$  (2, Scheme 1), the result of oxidation of both titanium centers by the ferrocenium reagent. The resonances for the fulvene ring are found as four multiplets at 3.16, 4.96, 6.08, and 6.68 ppm, as expected for tucked-in complexes of this type.<sup>6</sup> The <sup>13</sup>C NMR shows a resonance at 126.0 ppm for the adamantyl carbon that is bound to the metal center.

Slow diffusion of cyclohexane into a THF solution of compound **2** resulted in orange crystals that were suitable for a single-crystal X-ray diffraction study. An ORTEP representation of the cation of **2** is depicted in Figure 1 (see Table 1 for selected bond distances and angles). The molecular structure of **2** is very similar to that of the corresponding titanium chloride compound,  $Cp*Fv^{Ad}TiCl$  (**3**), which was prepared by treatment of  $Cp*TiCl_3$  with adamantylfulvene in the presence of sodium amalgam (*vide infra*). The structure

<sup>\*</sup>Corresponding authors. E-mail: ruediger.beckhaus@uni-oldenburg. de; M.W.Bouwkamp@rug.nl.

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Figure 1. ORTEP representation at 30% probability level of compounds 2 and 3. Hydrogen atoms and [BPh<sub>4</sub>] counterions are omitted for clarity.



Table 1. Selected Bond Distances (Å) and Angles (deg) for Compounds 2 and  $3^a$ 

	2		3
Ti(1)-Cp*	2.0687	Ti(1)-Cp*	2.082
$Ti(1) - Fv^{Ad}$	1.9873	$Ti(1) - Fv^{Ad}$	1.988
Ti(1) - C(115)	2.306(3)	Ti(1) - C(2)	2.283(5)
Ti(1) - C(116)	2.448(2)	Ti(1) - C(3)	2.418(2)
Ti(1) - C(117)	2.414(3)	Ti(1) - C(4)	2.428(2)
Ti(1) - C(118)	2.264(3)	Ti(1) - C(5)	2.314(4)
Ti(1) - C(119)	2.181(3)	Ti(1) - C(1)	2.186(4)
Ti(1) - C(120)	2.564(3)	Ti(1) - C(6)	2.547(4)
Ti(1) - O(1)	2.138(2)	Ti(1)-Cl(1)	2.364(6)
C(119)-C120	1.422(4)	C(1) - C(6)	2.547(4)
Cp*-Til-Fv <sup>Ad</sup>	136.11	Cp*-Til-Fv <sup>Ad</sup>	137.14
$Fv^{Ad} - C(119) - C(120)$	152.4	$Fv^{Ad} - C(1) - C(6)$	151.06

<sup>*a*</sup>Cp\* is defined as the centroid of C(11)–C(15) (compound **2**) or C(16)–C(20) (compound **3**);  $Fv^{Ad}$  is defined as the centroid of C(115)–C(119) (compound **2**) or C(1)–C(5) (compound **3**).

of compound **3** is included in Figure 1 (see Table 1 for selected bond distances and angles) and shows a remarkable resemblance to that of compound **2**, with very similar bond distances and angles. The Ti(1)–C<sub>exofulvene</sub> bond distances in both complexes are relatively long for Ti–C(sp<sup>3</sup>) bonds (**2**, 2.564(3) Å; **3**, 2.547(4) Å), compared to fulvene complexes exhibiting a higher  $\sigma$ -bond content in the Ti–C<sub>exofulvene</sub> bond,<sup>7</sup> e.g., Cp\*( $\eta^{6}$ -C<sub>5</sub>Me<sub>4</sub>=CH<sub>2</sub>)Ti, 2.281(14) Å,<sup>8</sup> or Cp\*( $\eta^{6}$ -C<sub>5</sub>H<sub>4</sub>=C(H)('Bu)TiCl, 2.355(2) Å.<sup>6a</sup> On the other hand, Ti–C<sub>exofulvene</sub> distances comparable to **2** and **3** are found for Cp\*( $\eta^{6}$ -C<sub>5</sub>H<sub>4</sub>=C(Ph)<sub>2</sub>)TiCl (2.535(5) Å)<sup>6b</sup> or dinitrogen complex **1** (2.511(5) Å)<sup>5</sup> as well. The most noticeable difference between the structures of compounds **2** and **3** are the X–Ti(1)–C(6) angles (**2**, X = O, 100.03(5)°; **3**, X = Cl,

98.33(4)°) and Cp\*-Ti(1)-Fv<sup>Ad</sup> angles (**2**, 136.04°; **3**, 137.64°). As a result of the larger THF ligand, the X-Ti-(1)-C<sub>exofulvene</sub> angle is opened up, resulting in a concurrent decrease of the Cp\*-Ti(1)-Fv<sup>Ad</sup> angle.

Although compound 2 can be obtained in reasonable vields (54%), an alternative route via protonation of an appropriate methyl precursor was evaluated. As stated above, compound 3 can be prepared from Cp\*TiCl<sub>3</sub>, adamantylfulvene, and sodium amalgam in THF solution (Scheme 2). During the reaction a color change from red to greenish-brown was observed. Compound 3 could be isolated as brown crystals by recrystallization from hexane. Previously, the synthesis of the comparable titanium chloride compound,  $Cp^*(\eta^6 - C_5H_4 = C(p-Tol)_2)$ TiCl, was reported, exhibiting a fast rotation of the fulvene ligand around the Ti-fulvene axis at room temperature in toluene- $d_8$  solution.<sup>6b</sup> In the case of **3**, such a bond rotation was not observed at room temperature. Only at temperatures as high as 100 °C could coalescence of the fulvene protons be observed. At room temperature the four distinct fulvene protons are found at 3.08, 4.63, 5.56, and 6.68 ppm. The reduced fluxionality in the system can be ascribed to the increased steric bulk imparted by the adamantyl group relative to the two *p*-Tol groups. Treatment of compound **3** with methyl lithium in diethyl ether solution results in a green solution of the corresponding methyl complex, Cp\*Fv<sup>Ad</sup>TiMe (4, Scheme 2), which could be isolated as a green solid. Unfortunately, the reaction of methyl compound 4 with [PhNMe<sub>2</sub>H][BPh<sub>4</sub>] was not conclusive.

**Reaction with** *N*,*N*-Dimethylanilinium Tetraphenylborate. Compound 1 was treated with Brønsted acidic borate reagent, [PhNMe<sub>2</sub>H][BPh<sub>4</sub>] (1 equiv per titanium). In THF solution, immediate gas evolution was observed, similar to the reaction with ferrocenium tetraphenylborate, resulting in a green solution of a paramagnetic compound. Slow diffusion of cyclohexane into the THF solution resulted in

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Figure 2. ORTEP representation at 30% probability level of compounds 5 and 6. Hydrogen atoms except for H(215) and H(216) in compound 6 and the  $[BPh_4]$  counterion of 5 are omitted for clarity.





turquoise crystals, suitable for a single-crystal X-ray diffraction study. The structure of the compound, a bis-THF adduct of a cationic trivalent titanocene complex, [Cp\*CpAd-Ti(THF)<sub>2</sub>][BPh<sub>4</sub>] (5, Cp<sup>Ad</sup> =  $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>C<sub>10</sub>H<sub>15</sub>, Scheme 3), is depicted in Figure 2 (see Table 2 for selected bond distances and angles). Whereas a mono-THF adduct was obtained in the case of the decamethyltitanocene cation,<sup>9</sup> two molecules of THF are bound in compound 5, similar to the parent titanocene cation,  $[Cp_2Ti(THF)_2]^{+,10}$  This illustrates the reduced steric bulk of the adamantylcyclopentadienyl ligand, compared to the Cp\* ligand, which can be explained by the fact that the adamantyl group can be directed to one side of the molecule, reducing the effective steric bulk of the ligand. As expected for a four-coordinate bis-THF adduct, the  $Cp^*-Ti-Cp^{Ad}$  angle in 5 (133.77°) is smaller than the corresponding angle in the three-coordinate compound [Cp\*<sub>2</sub>Ti(THF)][BPh<sub>4</sub>] (142.11°).<sup>9</sup> This angle is larger compared

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds 5 and  $6^a$ 

	5	6
Ti(1)-Cp*	2.1049	2.0331
$Ti(1) - Cp^{Ad}$	2.0751	2.0083
Ti(1) - O(11)	2.2180(16)	
Ti(1) - O(12)	2.2409(17)	
Ti(1) - C(215)		2.6976(16)
Ti(1) - C(216)		2.6103(19)
Ti(1) - H(215)		2.6961
Ti(1) - H(216)		2.5122
$Cp^*-Ti(1)-Cp^{Ad}$	133.77	136.10
$\hat{O(11)} - \hat{Ti(1)} - \hat{O(12)}$	77.78	
(TiH <sub>2</sub> Ph)		77.26

<sup>*a*</sup>Cp<sup>\*</sup> is defined as the centroid of C(111)–C(115); Cp<sup>Ad</sup> is defined as the centroid of C(11)–C(15);  $\angle$ (TiH<sub>2</sub>, Ph) is defined as the angle between the Ti–H(215)–H(216) plane and the plane of C(213)–C(218).

to the one observed in  $[Cp_2Ti(THF)_2][BPh_4] (112.47^\circ)$ .<sup>10b</sup> Also, the Ti–O bond distances in **5** (2.180(16) and 2.2409(17) Å) are in the range for the  $[Cp_2Ti(THF)_2]$  cation (2.19–2.24 Å).<sup>10,11</sup>

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In toluene, the reaction of 1 with [PhNMe<sub>2</sub>H][BPh<sub>4</sub>] results in a base-free trivalent titanocene cation. During the reaction, gas evolution was observed. Conveniently, the reaction afforded blue crystals that were suitable for X-ray analysis. The molecular structure of the ion pair is depicted in Figure 2 (see Table 2 for selected bond distances and angles). The compound, a contact ion pair of the type Cp\*Cp<sup>Ad</sup>Ti- $(\eta^2$ -BPh<sub>4</sub>) (6), reveals, once again, that the adamantylcyclopentadienyl ligand is smaller compared to the Cp\* ligand. Whereas the coordination sphere of the decamethylmetallocene cation is too small to accommodate the counterion, the anion in compound 6 is bound to the metal center. In the case of the base-free [Cp\*2Ti] cation, the electron-deficient titanium center binds two C-H bonds of one of the penta-methylcyclopentadienyl ligands.<sup>9</sup> A similar binding of the anion as observed for compound 6 was also found in the decamethylscandocene cation,  $Cp*_2Sc(\eta^2-BPh_4)$ , in which the anion can bind to the metal center as a result of the larger ionic radius of the Sc<sup>3+</sup> ion versus the Ti<sup>3+</sup> ion.<sup>9,12</sup> The interaction with the anion is best described as two agostic interactions of the metal center with two C-H bonds of the anion (Ti-H = 2.696 and 2.512 Å; Ti-C = 2.6978(18) and2.6103(19) Å), similar to that in Cp\*<sub>2</sub>Sc( $\eta^2$ -BPh<sub>4</sub>). The angle between the planes defined by H-M-H and the coordinated phenyl group in  $6(77.26(4)^\circ)$  is larger compared to that in the scandium compound (58.0(9)°).

Reaction with Tris(pentafluorophenyl)borane. Addition of THF to a 2:1 mixture of  $B(C_6F_5)_3$  and compound 1 resulted in gas evolution and the formation of a dark blue solution of a paramagnetic compound. Slow diffusion of hexane into the THF solution resulted in dark blue crystals, which were analyzed using X-ray diffraction (see Figure 3 for an ORTEP representation and Table 3 for selected bond distances and angles). Surprisingly, a zwitterionic complex was obtained in which the borane moiety is bound to one of the carbon atoms of the cyclopentadienyl ring rather than the adamantyl carbon:  $[Cp^{*}{\eta^{5}-C_{5}H_{3}(C_{10}H_{15})(B{C_{6}F_{5}}_{3})}Ti-$ (THF)] (7, Scheme 4). The expected direct attack of the Lewis acid  $B(C_6F_5)_3$  on the nucleophilic exocyclic fulvene carbon, as found in the case of zirconium fulvene complexes,<sup>13</sup> is not observed. It is highly unlikely that the formation of compound 7 is the result of an initial addition of the borane reagent to the adamantyl carbon, as it is not expected that the resulting species would rearrange to form compound 7. Therefore, we would like to suggest that compound 7 is formed by initial addition of  $B(C_6F_5)_3$  to the 3-carbon of the cyclopentadienyl ring, affording a transient titanium hydride cation of the type  $[Cp\{\eta^6-C_5H_3(C_{10}H_{14})(B\{C_6F_5\}_3)\}TiH]^+$ . This species can rearrange into compound 7 after a reductive elimination involving the hydride ligand and the adamantyl carbon (Scheme 4). A similar electrophilic attack of  $B(C_6F_5)_3$ to a cyclopentadienyl ligand was previously observed by Rosenthal and co-workers.<sup>14</sup> The free coordination sites of the titanocene cation 7 are occupied by one molecule of THF



Figure 3. ORTEP representation at 30% probability level of compound 7. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for	r
Compound 7 <sup><i>a</i></sup>	

Fi1−Cp* Fi1−Cp <sup>Ad</sup>	2.055	Ti(1) - O(1) Ti(1) - F(15)	2.238(2)
Cp*-Ti-Cp <sup>Ad</sup>	135.99	O(1)-Ti(1)-F(15)	78.09(7)
<sup><i>a</i></sup> Cp* is defined as	s the centroid	of C34–C38; Cp <sup>Ad</sup> is de	fined as the

centroid of C1-C5.

and an *o*-CF bond, similar to the acetone adduct Cp( $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>B{C<sub>6</sub>F<sub>5</sub>}<sub>3</sub>)Ti(OCMe<sub>2</sub>).<sup>14b</sup> As a result, the C(33)–F(15) bond length (1.391(3) Å) is slightly elongated and the geometry of the borate anion is deviating from a perfect tetrahedron (C(4)–B(1)–C(28) angle is 116.2(2)°). The Ti–F bond distance in 7 (2.3063(16) Å) is longer compared to that in the zwitterion Cp( $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>B{C<sub>6</sub>F<sub>5</sub>})Ti(OCMe<sub>2</sub>) (2.252(2) Å) and fluorobenzene adduct [Cp\*<sub>2</sub>Ti(FPh)][BPh<sub>4</sub>].<sup>9</sup>

#### Conclusions

Low-valent titanium dinitrogen complex  $[Cp^*Fv^{Ad}Ti]_2$ -( $\mu$ -N<sub>2</sub>) (1) is an interesting synthon for a number of cationic titanium species. Oxidation of the titanium center results in cationic titanium(IV) complexes, whereas the treatment with Brønsted acidic borate reagents or Lewis acidic boranes results in trivalent titanium cations by selective protonation of the exocyclic fulvene carbon center. The initial step in each of these reactions is the release of molecular dinitrogen from the coordination sphere of the titanium center. X-ray analysis of the products shows that the Cp-adamantyl ligand obtained from a protonation reaction of the adamantylfulvene ligand is smaller compared to the Cp\* ligand, as a result of the fact that the adamantyl group can be directed to the side of the molecule, hence reducing the effective steric shielding of the ligand.

### **Experimental Section**

General Considerations. All manipulations of air- and moisture-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk line, vacuum line, and glovebox techniques. Reagents were purchased from commercial suppliers

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Scheme 4



unless stated otherwise. Compounds  $[Cp^*(\eta^6-Fv^{Ad})Ti]_2(\mu-N_2)$ ,<sup>5</sup>  $C_5H_4=C_{10}H_{14}$ ,<sup>15</sup>  $Cp^*TiCl_3$ ,<sup>16</sup>  $[Cp_2Fe][BPh_4]$ ,<sup>17</sup> [PhNMe<sub>2</sub>H]-[BPh\_4],<sup>18</sup> and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>19</sup> were prepared according to literature procedures. Solvents (THF, pentane) were dried by percolation under a nitrogen atmosphere over columns of alumina, molecular sieves, and supported copper oxygen scavenger (BASF R3-11) or by distillation from Na/K alloy (THF, hexane, cyclohexane, THF- $d_8$ , benzene- $d_6$ ). NMR spectra were recorded on Varian Inova 500, Varian Gemini VXR 400, Varian VXR 300, Varian Gemini 200, Bruker 500 AVANCE, and Bruker 300 AVANCE-NMR instruments. <sup>1</sup>H chemical shifts are referenced to residual protons in deuterated solvents and are reported relative to tetramethylsilane. Crystals suitable for a single-crystal X-ray analysis were grown as described in the text. For compounds 2, 5, and 6, a crystal was mounted on a glass fiber inside a drybox and transferred under an inert atmosphere to the cold nitrogen stream of a Bruker SMART APEX CCD diffractometer. Intensity data were corrected for Lorentz and polarization effects, scale variation, decay, and absorption: a multiscan absorption correction was applied, based on the intensities of symmetryrelated reflections measured at different angular settings (SADABS),<sup>20</sup> and reduced to  $F_0^2$ . The structures were solved by Patterson methods, and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF.<sup>21</sup> The positional and anisotropic displacement parameters for the non-hydrogen atoms were refined. Final refinement on  $F_2$  was carried out by full-matrix least-squares techniques. For compounds 3 and 7 crystals were measured using a STOE-IPDS diffractometer. The structures were solved using direct methods (SHELXS-97).<sup>22</sup> Final refinement on  $F^2$  was carried out by full-matrix least-squares techniques.

 $[Cp^*(\eta^6-C_5H_4C_{10}H_{14})Ti(THF)][BPh_4]$  (2). THF (0.5 mL) was added to a mixture of 1 (56.2 mg, 0.0711 mol) and [Cp<sub>2</sub>Fe][BPh<sub>4</sub>] (71.4 mg, 0.141 mmol). When no more gas evolution was observed, the color had changed from blue to orange, after which cyclohexane (3 mL) was layered carefully on top of the THF solution. After days, orange crystals had precipitated from the reaction mixture. The supernatant was decanted and the crystals were washed with pentane (2  $\times$  1 mL), affording the title compound (58 mg, 54%). <sup>1</sup>H NMR (THF-d<sub>8</sub>, 300 K): δ 1.86 (s, 15H, Cp\*), 0.7-3.5 (overlapping, 14 H, adametnyl), 3.16 (m, 1H, C<sub>5</sub>H<sub>4</sub>), 4.96 (m, 1H, C<sub>5</sub>H<sub>4</sub>), 6.08 (m, 1H, C<sub>5</sub>H<sub>4</sub>), 6.68 (t, 7.1 Hz, 4H, BPh<sub>4</sub>), 6.68 (m, 1H, C<sub>5</sub>H<sub>4</sub>), 6.82 (t, 7.4 Hz, 8H, BPh<sub>4</sub>), 7.24 (br,  $\Delta \nu_{1/2} = 15$  Hz, BPh<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (THF- $d_8$ , 300 K): δ 12.6 (Cp\*), 26.3, 28.3, 30.0, 33.7, 37.6, 37.8, 38.1, 46.7, 47.6 (adamantyl), 121.7 (p-BPh<sub>4</sub>), 121.8 (C<sub>5</sub>H<sub>4</sub>), 122.1 (C<sub>5</sub>H<sub>4</sub>), 123.9 (C<sub>5</sub>H<sub>4</sub>), 125.6 (overlapping C<sub>5</sub>H<sub>4</sub> and *m*-BPh<sub>4</sub>), 126.0 (C<sub>exo</sub> adamantyl), 129.0 (Cp\*), 137.1 (o-BPh4) 137.8 (Cipso C5H4), 165.1 C<sub>ipso</sub> BPh<sub>4</sub>) ppm. Anal. Calcd for C<sub>53</sub>H<sub>61</sub>BOTi C, 82.38; H, 7.96. Found: C, 82.66; H, 8.28. Melting point: 65 °C.

**Cp\***( $\eta^6$ -**C**<sub>5</sub>**H**<sub>4</sub>**C**<sub>10</sub>**H**<sub>14</sub>)**TiCl** (3). THF was added to Cp\*TiCl<sub>3</sub> (1.0 g, 3.45 mmol), adamantylfulvene (0.69 g, 3.45 mmol), and 20% Na/Hg (0.79 g, 6.91 mmol). The resulting suspension was stirred for 16 h at 200 mbar N<sub>2</sub> pressure, resulting in a color change from red to greenish-brown. The reaction mixture was filtered over Celite, and the volatiles were removed *in vacuo*. The resulting brown residue was recrystallized from hexane (20 mL), affording 1.2 g (83%) of the title compound. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 300 K): δ 1.70 (s, 15H, Cp\*), 0.9–3.1 (overlapping, 14H, adamantyl), 3.08 (m, 1H, C5H4), 4.63 (m, 1H, C5H4), 5.65 (m, 1H, C<sub>5</sub>H<sub>4</sub>), 6.68 (m, 1H, C<sub>5</sub>H<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>, 300 K): δ 12.7 (Cp\*), 28.4, 29.7, 33.4, 37.6, 38.2, 38.3, 45.0, 46.5 (adamantyl), 115.8 (C<sub>5</sub>H<sub>4</sub>), 118.5 (C<sub>5</sub>H<sub>4</sub>), 119.4 (C<sub>5</sub>H<sub>4</sub>), 122.9

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(Cp\*), 123.4 (C<sub>5</sub>H<sub>4</sub>), 131.3 (C<sub>ipso</sub> C<sub>5</sub>H<sub>4</sub>) ppm. Anal. Calcd for  $C_{25}H_{33}$ ClTi: C, 72.03; H, 7.98. Found: C, 71.82; H, 7.78. Melting point: 50 °C.

 $Cp^*(\eta^{6}-C_5H_4C_{10}H_{14})$ TiMe (4). Compound 1 (4.0 g, 9.6 mmol) was dissolved in ether (280 mL). The resulting solution was cooled to -80 °C, after which an 1.6 M ether solution of MeLi (6.0 mL, 9.6 mmol) was added by syringe. After stirring the reaction mixture for 1 h at -70 °C, the reaction mixture was slowly warmed to RT. During the reaction a color change from brown to green was observed. The ether was removed in vacuo, and the reaction mixture was extracted with pentane (200 mL). Distilling off the pentane and drying of the compound resulted in a green oily product (2.6 g, 65%). <sup>1</sup>H NMR (benzene- $d_6$ , 300 K): δ -1.03 (s, 3H, TiMe), 1.67 (s, 15H, Cp\*), 0.8-2.7 (overlapping, 14H, adamantyl), 3.35 (m, 1H,  $C_5H_4$ ), 4.63 (m, 1H,  $C_5H_4$ ), 5.57 (m, 1H,  $C_5H_4$ ), 6.47 (m, 1H,  $C_5H_4$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-d<sub>6</sub>, 300 K): δ 12.3 (Cp\*), 28.7, 29.9, 32.8, 36.7, 37.5, 38.4, 38.5, 44.3, 45.2 (adamantyl), 44.2 (TiMe), 114.1 (C5H4), 116.8 (C5H4), 117.1 (C5H4), 119.4 (Cexo adamantyl), 119.6 (Cp\*), 120.3 (C5H4), 133.1 (Cipso in C5H4). Anal. Calcd for C<sub>26</sub>H<sub>36</sub>Ti: C, 78.77; H, 9.15. Found: C, 78.01; H, 8.97.

 $[Cp^*(\eta^5-C_5H_4C_{10}H_{15})Ti(THF)_2][BPh_4]$  (5). THF (1 mL) was added to a mixture of 1 (100 mg, 126 mmol) and [PhNMe<sub>2</sub>H][BPh<sub>4</sub>] (112 mg, 253 mmol). When no more gas evolution was observed, cyclohexane (6 mL) was layered on top of the THF solution. Overnight, turquoise crystals had formed, which were isolated after decanting of the supernatant and washing with hexane. This afforded 203 mg (95%) of the title compound. The paramagnetic compound was characterized by X-ray diffraction. Anal. Calcd for C<sub>57</sub>H<sub>70</sub>BO<sub>2</sub>Ti: C, 80.94; H, 8.34. Found: C, 80.04; H, 8.11.

 $Cp^*(\eta^5-C_5H_4C_{10}H_{15})Ti(\eta^2-BPh_4)$  (6). Toluene (5 mL) was added to a mixture of 1 (100 mg, 126 mmol) and [PhNMe<sub>2</sub>H][BPh<sub>4</sub>] (112 mg, 253 mmol). Immediate gas evolution was observed. Over the course of days, blue crystals of the title compound had formed. The supernatant was decanted, and the crystals were washed with pentane, yielding 92 mg (52%) of compound 6. Anal. Calcd for C<sub>49</sub>H<sub>54</sub>BTi: C, 83.88; H, 7.76. Found: C<sub>2</sub> 83.41; H, 7.59.

[Cp\*{ $\eta^5$ -C<sub>5</sub>H<sub>3</sub>(C<sub>10</sub>H<sub>15</sub>)(B{C<sub>6</sub>F<sub>5</sub>}<sub>3</sub>)}Ti(THF)] (7). THF (1 mL) was added to a mixture of 100 mg (126 mmol) of compound 1 and 130 mg (254 mmol) of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. When no more gas evolution was observed, hexane (6 mL) was carefully layered on top of the THF solution. Over the course of days dark blue crystals had formed, which were isolated by decanting the supernatant and washing with hexane, affording 136 mg (56%) of the title compound. Anal. Calcd for C<sub>47</sub>H<sub>41</sub>BF<sub>15</sub>OTi: C, 58.47; H, 4.28. Found: C, 57.32; H, 3.54.

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**Supporting Information Available:** Crystallographic information files of compounds **2**, **3**, **5**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.