

# Synthesis and Catalytic Activity of Mono(cyclopentadienyl)titanium(II) Complexes: X-ray Crystal Structures of $\text{CpTiX}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2$ ( $\text{X} = \text{Cl}$ , $\text{Me}$ , $\text{H}$ ) and $\text{Cp}^*\text{Ti}(\eta^2\text{-BH}_4)[\eta^2\text{-(Me}_2\text{PCH}_2)_3\text{Si}(t\text{-Bu})]$

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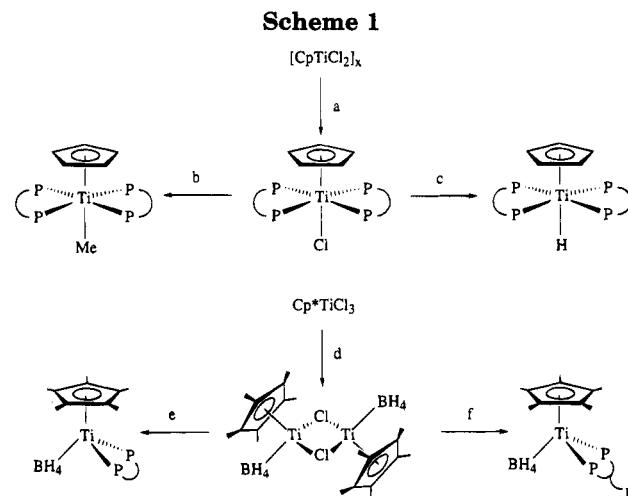
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**Summary:** New mono(cyclopentadienyl)- and mono(pentamethylcyclopentadienyl)titanium(II) complexes have been prepared that are active for the oligomerization of ethylene to the dimer 1-butene and the trimers 2-ethyl-1-butene and 3-methyl-1-pentene. The mechanism of the catalysis is proposed to involve titanacyclopentane intermediates.

Low-valent organotitanium complexes continue to be of interest as potential catalysts for the polymerization of alkenes<sup>1</sup> and as stoichiometric reagents in organic synthesis.<sup>2</sup> Low-valent titanium complexes with one cyclopentadienyl ring are especially rare;<sup>3</sup> we report here the synthesis and characterization of several new mono(cyclopentadienyl)titanium(II) complexes. The ability of these alkyl, hydride, and tetrahydroborate complexes to catalyze the oligomerization of ethylene will also be described.

Treatment of the titanium(III) compound  $(\text{CpTiCl}_2)_x$ <sup>4</sup> with 1 equiv of *n*-butyllithium and 2 equiv of 1,2-bis(dimethylphosphino)ethane (dmpe) in diethyl ether at  $-78^\circ\text{C}$ , followed by warming to room temperature, gives a dark brown-red solution from which black crystals of  $\text{CpTiCl}(\text{dmpe})_2$  (**1**) can be obtained in 50% yield after crystallization from pentane or diethyl ether (Scheme 1).<sup>5</sup> Interestingly, we have been unable to obtain this titanium(II) complex in good yield by using more



<sup>a</sup> (a)  $\text{Li}(n\text{-Bu})$ , dmpe; (b)  $\text{LiMe}$ ; (c)  $\text{Li}(n\text{-Bu})$ ; (d)  $\text{LiBH}_4$ ; (e)  $\text{Li}(n\text{-Bu})$ , dmpe; (f)  $\text{Li}(n\text{-Bu})$ , trimpsti.

conventional reducing agents such as sodium amalgam. Treatment of **1** with 1 equiv of methyl lithium in diethyl ether at  $-78^\circ\text{C}$ , followed by warming to  $-10^\circ\text{C}$  and crystallization from pentane, affords the titanium(II) alkyl  $\text{CpTiMe}(\text{dmpe})_2$  (**2**) as black crystals in 56% yield.<sup>6</sup> A similar reaction of **1** with 1 equiv of *n*-butyllithium affords the titanium(II) hydride  $\text{CpTiH}(\text{dmpe})_2$  (**3**) in 53% yield.<sup>7</sup>

These new mono(cyclopentadienyl)titanium(II) compounds are diamagnetic: all three show sharp <sup>1</sup>H and <sup>13</sup>C NMR signals for the Cp ring. For each complex, there are two  $\text{PMe}_2$  resonances for the dmpe ligand; these are due to the methyl groups that are proximal and distal with respect to the Cp ring. The <sup>1</sup>H NMR spectrum of **2** at  $-80^\circ\text{C}$  shows a quintet at  $\delta -1.18$  for the Ti-Me group ( $^3J_{\text{PH}} = 9.2$  Hz). This chemical shift is comparable to that of  $\delta -1.86$  seen for the Zr analogue  $\text{CpZrMe}(\text{dmpe})_2$ <sup>8</sup> but is deshielded relative to the  $\delta$

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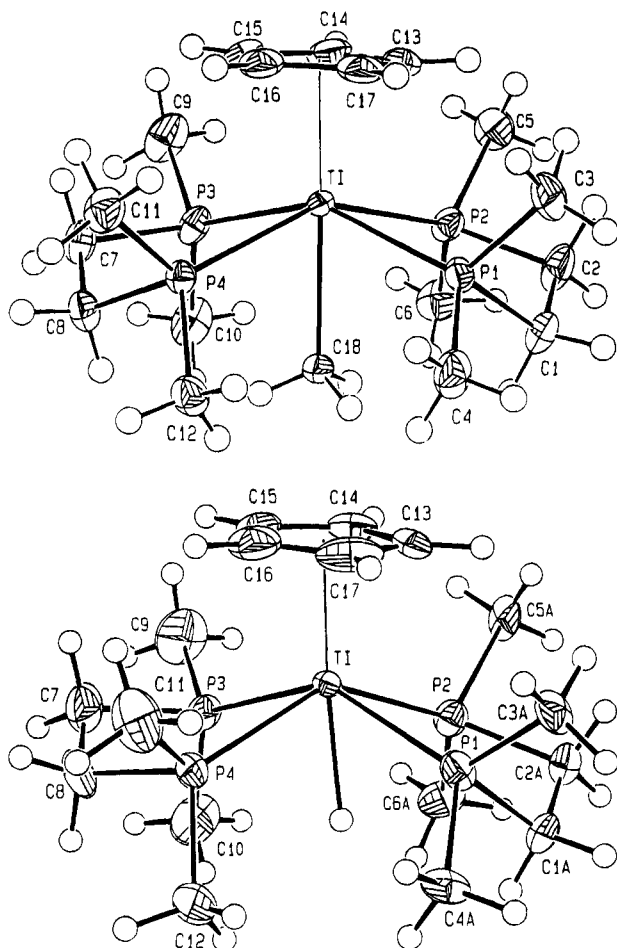
(4) Lucas, C. R.; Green, M. L. H. *Inorg. Synth.* **1976**, *16*, 237-240.

(5) Anal. Calcd for **1**: C, 45.5; H, 8.31; P, 27.6; Cl, 7.90; Ti, 10.7. Found: C, 45.1; H, 8.39; P, 27.2; Cl, 7.68; Ti, 10.8. <sup>1</sup>H NMR ( $\text{C}_7\text{D}_8$ ,  $-80^\circ\text{C}$ ):  $\delta$  4.25 (s, Ti-Cp), 1.67 (s,  $\text{PCH}_2$ ), 1.38 (s,  $\text{PMe}_2$ ), 0.65 (s,  $\text{PCH}_2$  +  $\text{PMe}_2$ ). <sup>13</sup>C{<sup>1</sup>H} NMR ( $\text{C}_7\text{D}_8$ ,  $-80^\circ\text{C}$ ):  $\delta$  87.8 (s, Ti-Cp), 30.5 (br s,  $\text{PCH}_2$ ), 18.6 (s,  $\text{PMe}_2$ ), 17.0 (s,  $\text{PMe}_2$ ). <sup>31</sup>P{<sup>1</sup>H} NMR ( $\text{C}_7\text{D}_8$ ,  $-80^\circ\text{C}$ ):  $\delta$  34.3 (s).

(6) Anal. Calcd for **2**: C, 50.5; H, 9.41; Ti, 11.2. Found: C, 49.7; H, 9.22; Ti, 11.4. <sup>1</sup>H NMR ( $\text{C}_7\text{D}_8$ ,  $-80^\circ\text{C}$ ):  $\delta$  4.37 (s, Ti-Cp), 1.44 (s,  $\text{PCH}_2$ ), 1.21 (s,  $\text{PMe}_2$ ), 0.87 (s,  $\text{PMe}_2$ ), 0.70 (s,  $\text{PCH}_2$ ), -1.18 (quintet,  $J_{\text{PH}} = 9.2$  Hz, Ti-Me). <sup>13</sup>C{<sup>1</sup>H} NMR ( $\text{C}_7\text{D}_8$ ,  $-80^\circ\text{C}$ ):  $\delta$  84.6 (s, Ti-Cp), 30.5 (s, br,  $\text{PCH}_2$ ), 18.9 (s,  $\text{PMe}_2$ ), 18.5 (s,  $\text{PMe}_2$ ), 11.3 (quintet,  $J_{\text{PC}} = 10.6$  Hz, Ti-Me). <sup>31</sup>P{<sup>1</sup>H} NMR ( $\text{C}_7\text{D}_8$ ,  $-80^\circ\text{C}$ ):  $\delta$  45.0 (s).

(7) Anal. Calcd for **3**: C, 49.3; H, 9.25; P, 29.9; Ti, 11.6. Found: C, 48.2; H, 9.07; P, 30.5; Ti, 11.0. <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ ,  $20^\circ\text{C}$ ):  $\delta$  4.32 (s, Ti-Cp), 1.37 (s,  $\text{PCH}_2$ ), 1.20 (s,  $\text{PMe}_2$ ), 1.02 (s,  $\text{PMe}_2$ ), 0.81 (s,  $\text{PCH}_2$ ), -0.06 (quintet,  $J_{\text{PH}} = 55.5$  Hz, Ti-H). <sup>13</sup>C{<sup>1</sup>H} NMR ( $\text{C}_6\text{D}_6$ ,  $20^\circ\text{C}$ ):  $\delta$  85.4 (s, Ti-Cp), 33.2 (pseudoquintet,  $J_{\text{PC}} = 7.9$  Hz,  $\text{PCH}_2$ ), 26.1 (s,  $\text{PMe}_2$ ), 20.0 (s,  $\text{PMe}_2$ ). <sup>31</sup>P NMR ( $\text{C}_6\text{D}_6$ ,  $20^\circ\text{C}$ ):  $\delta$  56.8 (br d,  $J_{\text{PH}} = 55.1$  Hz).

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**Figure 1.** (top) ORTEP plot of **2**. (bottom) ORTEP plot of **3**. The 35% probability density surfaces are shown. For **3**, only one of the disordered orientations of the dmpe ligand is shown.

−5.72 chemical shift seen for the 14-electron titanium(II) methyl complex  $\text{TiMe}_2(\text{dmpe})_2$ .<sup>9</sup> The <sup>1</sup>H NMR spectrum of **3** at 20 °C contains a binomial quintet for the titanium hydride ligand at  $\delta$  −0.06, with  $^2J_{\text{PH}} = 55.5$  Hz. For comparison, the chemical shifts of the titanium(II) carbonyl hydrides  $\text{CpTi}(\text{CO})_2(\text{dmpe})\text{H}$  and  $\text{Cp}^*\text{Ti}(\text{CO})_2(\text{dmpe})\text{H}$  are  $\delta$  −1.65 and −1.71, respectively.<sup>3g</sup>

Single-crystal X-ray studies of **1–3** reveal that the complexes are best described as pseudooctahedra with the two dmpe ligands occupying the equatorial positions.<sup>10</sup> The four phosphorus atoms are bent away from the  $\eta^5$ -Cp group (Figure 1). Compounds **1–3** are crowded molecules with unusually long metal–ligand

**Table 1.** Important Bond Distances (Å) and Angles (deg) for **1–3**

	$\text{CpTiCl}(\text{dmpe})_2$	$\text{CpTiMe}(\text{dmpe})_2$	$\text{CpTiH}(\text{dmpe})_2$
Ti–C(13)	2.316(3)	2.322(3)	2.294(5)
Ti–C(14)	2.271(3)	2.319(3)	2.338(5)
Ti–C(15)	2.365(3)	2.403(3)	2.415(5)
Ti–C(16)	2.470(3)	2.482(3)	2.411(5)
Ti–C(17)	2.445(3)	2.431(3)	2.336(5)
Ti–X	2.612(1)	2.385(2)	1.96(6)
Ti–P(av)	2.602(1)	2.571(1)	2.513(2)
Cn–Ti–X <sup>a</sup>	177.2	177.2	175.1
$\tau^b$	6.3	5.4	4.0

<sup>a</sup> Cn = centroid of Cp ring. <sup>b</sup> Tilt angle of Cp ring.

bond distances (Table 1), viz., the Ti–Cl bond distance of 2.612(1) Å in **1** is significantly longer than that of 2.446(4) Å in  $\text{TiCl}_2(\text{dmpe})_2$ <sup>11</sup> and is remarkably similar to the Zr–Cl bond distance of 2.629(2) Å in  $\text{CpZrCl}(\text{dmpe})_2$ .<sup>12</sup> The Ti–Me distance of 2.385(2) Å in **2** is also much longer than that of 2.219(2) Å in  $\text{TiMe}_2(\text{dmpe})_2$ .<sup>9</sup> The Ti–H bond distance of 1.96(6) Å in **3** can be compared to those of 1.75(7), 1.70(4), and 1.73 Å seen in  $\text{CpTi}(\text{CO})_2(\text{dmpe})\text{H}$ ,<sup>3h</sup>  $\text{Cp}^*\{\text{C}_5\text{Me}_4\text{CH}_2(\text{C}_5\text{H}_3\text{MeN})\}$ -TiH,<sup>13</sup> and  $\text{Cp}_2\text{Ti}_2(\mu\text{-H})_2(\text{C}_{10}\text{H}_8) \cdot 1.5\text{C}_6\text{H}_6$ ,<sup>14</sup> respectively. In **1–3**, the cyclopentadienyl ligands are tilted, so that the Ti–C bond distances vary by up to 0.20 Å: the tilt angles (defined by the angle between the metal–centroid vector and the vector normal to the ring plane) are 6.3, 5.4, and 4.0° for **1–3**, respectively.

Addition of ethylene (15 equiv) to toluene solutions of **1–3** results in the formation of 1-butene, 3-methyl-1-pentene, and 2-ethyl-1-butene in a molar ratio of about 70:15:15; the rate of catalysis is in the order **3** > **2** > **1**. For **3**, the ethylene is completely converted to these products in less than 1 h at 5 °C.<sup>15</sup> Similar catalytic activity has been seen for the 14-electron titanium(II) complexes  $\text{TiX}_2(\text{dmpe})_2$  (X = Cl, Me).<sup>16,17</sup> The absence of unbranched hexenes among the C<sub>6</sub> products rules out a mechanism involving sequential insertion of ethylene into a Ti–H or Ti–R bond. Instead, the products formed can be readily explained by a mechanism involving reductive coupling of two alkenes to give a metallacyclopentane intermediate;<sup>18,19</sup> this intermediate subsequently  $\beta$ -eliminates and then reductively eliminates to afford the product alkenes. The C<sub>6</sub> isomers formed indicate that reductive coupling of ethylene and 1-butene exclusively generates a metallacyclopentane with the ethyl substituent  $\beta$  to the metal. Low-temperature <sup>13</sup>C{<sup>1</sup>H} NMR spectra of solutions of **2** and excess ethylene contain peaks near  $\delta$  50.2 and 61.6 due to a bound ethylene ligand; we have formulated the product

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(10) Crystal data for **1** ( $T = 198$  K): monoclinic, space group  $P2_1/n$ ,  $a = 9.996(3)$  Å,  $b = 13.711(4)$  Å,  $c = 17.241(6)$  Å,  $\beta = 98.46(3)^\circ$ ,  $V = 2337.3(13)$  Å<sup>3</sup>,  $Z = 4$ ,  $R_F(I > 2\sigma(I)) = 0.0339$ , and  $R_{wF^2}(\text{all data}) = 0.0924$  for 216 variables and 3244 total data. Crystal data for **2** ( $T = 198$  K): orthorhombic, space group  $Pbca$ ,  $a = 13.780(4)$  Å,  $b = 17.776(6)$  Å,  $c = 18.726(6)$  Å,  $V = 4587(3)$  Å<sup>3</sup>,  $Z = 8$ ,  $R_F(I > 2\sigma(I)) = 0.0331$ , and  $R_{wF^2}(\text{all data}) = 0.0893$  for 328 variables and 4027 total data. Crystal data for **3** ( $T = 198$  K) monoclinic, space group  $C2/c$ ,  $a = 11.419(5)$  Å,  $b = 14.684(6)$  Å,  $c = 26.877(9)$  Å,  $\beta = 93.46(3)^\circ$ ,  $V = 4498(3)$  Å<sup>3</sup>,  $Z = 8$ ,  $R_F(I > 2\sigma(I)) = 0.0493$ , and  $R_{wF^2}(\text{all data}) = 0.1645$  for 270 variables, 163 restraints, and 3918 total data. For **1** and **2**, all non-H atoms were refined isotropically with  $U_{eq}$  set equal to 1.2 times that of the attached C atom. For **3**, all non-H atoms were refined anisotropically with rigid bond restraints ( $esd = 0.01$ ). Positional and isotropic thermal parameters were refined for the H atom bound to titanium; the remaining H atoms were included as fixed idealized contributors.

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(14) Troyanov, S. I.; Antropiusova, H.; Mach, K. *J. Organomet. Chem.* **1992**, *427*, 49–55.

(15) In comparison,  $\text{CpZr}(\text{C}_4\text{H}_8)(\text{dmpe})\text{Me}$  is inactive for the oligomerization of ethylene (Wielstra, Y.; Meetsma, A.; Gamborotta, S. *Organometallics* **1989**, *8*, 258–259) and  $\text{CpZr}(\text{C}_4\text{H}_8)(\text{dmpe})\text{Et}$  catalyzes the dimerization of ethylene at rates of only 0.1 turnover/h.<sup>8</sup>

(16) Spencer, M. D.; Morse, P. M.; Wilson, S. R.; Girolami, G. S. *J. Am. Chem. Soc.* **1993**, *115*, 2057–2059.

(17) Spencer, M. D. Ph.D. Thesis, University of Illinois at Urbana-Champaign, 1993.

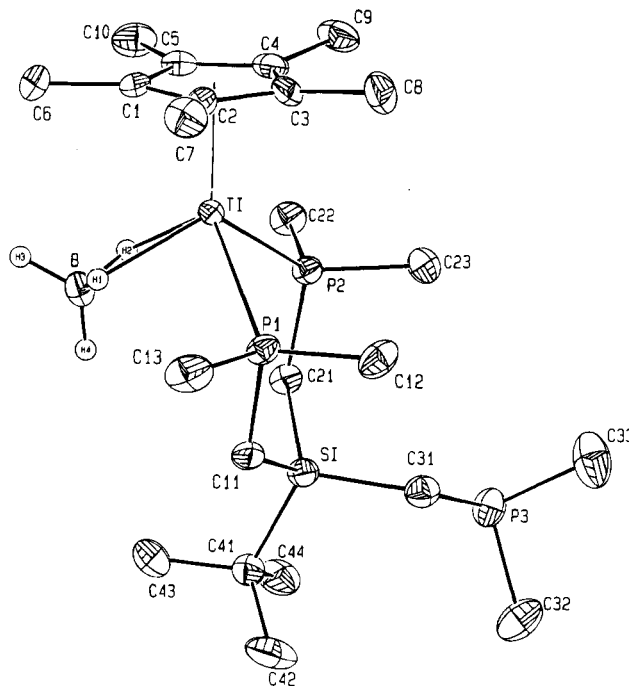
(18) Datta, S.; Fischer, M. B.; Wrsford, S. S. *J. Organomet. Chem.* **1980**, *188*, 353–366.

(19) McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 1315–1317.

of this reaction as the Ti<sup>II</sup> alkyl/alkene complex CpTiMe-(C<sub>2</sub>H<sub>4</sub>)(dmpe)( $\eta^1$ -dmpe).

We have also been able to prepare titanium(II) pentamethylcyclopentadienyl (Cp\*) complexes. Treatment of Cp\*TiCl<sub>3</sub><sup>20</sup> with excess LiBH<sub>4</sub> in diethyl ether at -78 °C, followed by warming to -10 °C and crystallization from toluene, affords in 48% yield the green titanium(III) complex [Cp\*TiCl(BH<sub>4</sub>)<sub>2</sub>] (4),<sup>21</sup> which is the Cp\* analogue of the previously reported complex [Cp-TiCl(BH<sub>4</sub>)<sub>2</sub>].<sup>22</sup> Treatment of 4 at -78 °C in Et<sub>2</sub>O with 1 equiv of *n*-butyllithium in the presence of dmpe or *tert*-butyltris[(dimethylphosphino)methyl]silane (trimpsil) yields dark brown crystals of the titanium(II) complexes Cp\*Ti(BH<sub>4</sub>)(dmpe) (5)<sup>23</sup> and Cp\*Ti(BH<sub>4</sub>)(trimpsil) (6)<sup>24</sup> in 65% and 55% yield, respectively, after crystallization from pentane.

Unlike 1-3, the Cp\* compounds 5 and 6 are paramagnetic. The infrared spectra of 4-6 in the 2000-2600 cm<sup>-1</sup> region indicate that the tetrahydroborate group is  $\eta^3$  in 4 but  $\eta^2$  in 5 and 6.<sup>25</sup> The X-ray crystal structure of the trimpsil complex 6 confirms the presence of the bidentate BH<sub>4</sub><sup>-</sup> group (Figure 2).<sup>26</sup> Somewhat surprisingly, the potentially tridentate trimpsil ligand is bound to the metal center in a bidentate fashion. These titanium(II) pentamethylcyclopentadienyl complexes also catalyze the oligomerization of ethylene to mixtures of 1-butene, 2-ethyl-1-butene, and 3-methyl-



**Figure 2.** ORTEP plot of 6. The 35% probability density surfaces are shown. Important bond distances (Å) and angles (deg): Ti-C = 2.340(5)-2.408(5), Ti-P = 2.570(2), Ti···B = 2.445(7), Ti-H<sub>b</sub> = 2.00(5), B-H<sub>b</sub> = 0.98(6), 1.05(5), B-H<sub>t</sub> = 1.11(6), 1.14(5); H<sub>b</sub>-B-H<sub>b</sub> = 106(3), H<sub>t</sub>-B-H<sub>t</sub> = 121(5), H<sub>b</sub>-Ti-H<sub>b</sub> = 54(2), P-Ti-P = 86.48(5).

1-pentene at a rate similar to that of 1. Other reactions of these new organotitanium(II) complexes are currently under investigation.

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**Supplementary Material Available:** Tables of crystal data, atomic coordinates, thermal parameters, and all bond distances and angles for 1-3 and 6 (47 pages). Ordering information is given on any current masthead page.

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(21) Anal. Calcd for 4: C, 51.5; H, 8.20; Cl, 15.2; B, 4.63; Ti, 20.5. Found: C, 52.1; H, 8.29; Cl, 14.9; B, 4.69; Ti, 21.0. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 20 °C):  $\delta$  2.58 (s, fwhm = 35 Hz, Ti-Cp\*).

(22) Semenenko, K. N.; Lobkovskii, E. B.; Shumakov, A. I. *J. Struct. Chem. (Engl. Transl.)* **1976**, *17*, 912-914.

(23) Anal. Calcd for 5: C, 55.2; H, 10.1; B, 3.11; Ti, 13.8. Found: C, 55.3; H, 10.2; B, 3.02; Ti, 12.7. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 20 °C):  $\delta$  65.7 (s, fwhm = 1700 Hz, Ti-Cp\*), 22.3 (s, fwhm = 500 Hz, PCH<sub>2</sub> + PMe<sub>2</sub>), -2.51 (s, fwhm = 240 Hz, PCH<sub>2</sub> + PMe<sub>2</sub>).

(24) Anal. Calcd for 6: C, 54.3; H, 10.3; B, 2.13; P, 18.3; Ti, 9.42. Found: C, 53.4; H, 10.3; B, 2.10; P, 17.5; Ti, 9.42. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 20 °C):  $\delta$  57.8 (s, fwhm = 5800 Hz, Ti-Cp\*), 34.6 (s, fwhm = 2700 Hz, Ti-PMe<sub>2</sub>-CH<sub>2</sub>), 15.7 (s, fwhm = 1100 Hz, Ti-PMe<sub>2</sub>), 1.0 (m, Ti-PMe<sub>2</sub> + *t*-Bu + Si-CH<sub>2</sub>-PMe<sub>2</sub>), -5.3 (s, fwhm = 1700 Hz, Ti-PMe<sub>2</sub>-CH<sub>2</sub>).

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(26) Crystal data for 6 (*T* = 198 K): monoclinic, space group *P*<sub>2</sub><sub>1</sub>/*n*, *a* = 16.279(4) Å, *b* = 9.103(2) Å, *c* = 20.746(5) Å,  $\beta$  = 100.13(2)°, *V* = 3026.4(12) Å<sup>3</sup>, *Z* = 4, *R*<sub>w</sub>(*I* > 2 $\sigma$ (*I*)) = 0.0576, and *R*<sub>int</sub>(all data) = 0.1483 for 470 variables and 5306 total data. All non-H atoms were refined anisotropically, and H atoms were refined isotropically with independent thermal coefficients.