

# Synthesis and Characterization of Group 4 Constrained Geometry Complexes Containing a Linked Cyclopentadienyl–*o*-Carboranyl Ligand

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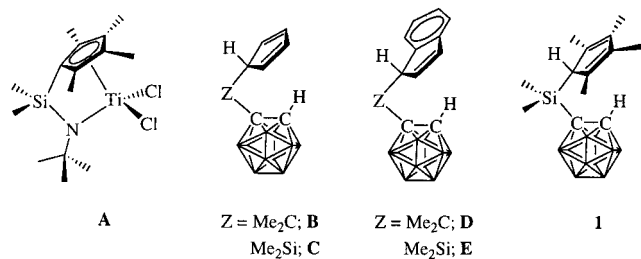
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**Summary:** Novel linked cyclopentadienyl–*o*-carboranyl group 4 metal complexes,  $[\eta^5\eta^1\text{-Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})\text{-TiCl}_2$  (**2**) and  $[\eta^5\eta^1\text{-Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})\text{-Zr}(\text{NMe}_2)_2$  (**3**), have been prepared via salt metathesis and amine elimination reactions utilizing the linked *o*-carboranyl ligand,  $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})(\text{C}_2\text{B}_{10}\text{H}_{11})$  (**1**). Their X-ray crystal structures are reported.

## Introduction

Group 4 single-site catalyst systems based on the linked cyclopentadienyl–amido ancillary ligand such as **A** have attracted considerable interest as efficient



catalysts for the copolymerization of ethylene with  $\alpha$ -olefins owing to their electron-deficient and sterically open so-called “constrained geometry” nature.<sup>1</sup> The synthesis of new constrained geometry catalyst (CGC) analogues has been achieved via variation of the ligand framework. Modifications of the ancillary ligand could be accomplished on three major parts of the  $6e\text{-}\pi$  donor, bridging group and  $\sigma$ -bonded heteroatom donor. Since

the bridging group modification is rather limited to short bridging groups such as monosilicon or two-carbon units that are essential in order to gain constrained geometry, recent studies have been directed mainly toward substitution of the cyclopentadienyl ligand (Cp) by cyclopentadienyl equivalents. For example, heterocycles containing phosphorus<sup>2</sup> or boron<sup>3</sup> atoms and open cyclohexadienyl groups<sup>4</sup> were found to be good Cp analogues. However, variation of the  $\sigma$ -bonded heteroatom donor was not investigated as much. Nitrogen<sup>1</sup> and oxygen<sup>5</sup> donors still constitute major the  $\sigma$ -donor atoms in CGC-type catalysts. From this point of view, the search for new Cp-linked  $\sigma$ -donor atom groups could be useful in designing new CGC-type catalysts.

Recently, Xie et al.<sup>6</sup> extensively investigated broad chemistry of *o*-carboranyl-substituted Cp lanthanide complexes utilizing various linked cyclopentadienyl–*o*-carboranyl ligands such as **C**, **D**, and **E**. Our group<sup>7</sup> also reported that the *o*-carboranyl carbon atom of the ligand, **B**, can be introduced to a group 4 metal ion as the anionic  $\sigma$ -donor. These studies have shown that the *o*-carboranyl carbon atom can effectively bind to the early-metal ions. Moreover, considering the dependence of catalytic performance on electronic and steric effects of the Cp group in CGC-type group 4 catalysts,<sup>1c,1m</sup> a permethylated Cp derivative such as **1** deserves to be more exploited. Here, we report the synthesis and structural characterization of novel CGC-type group 4

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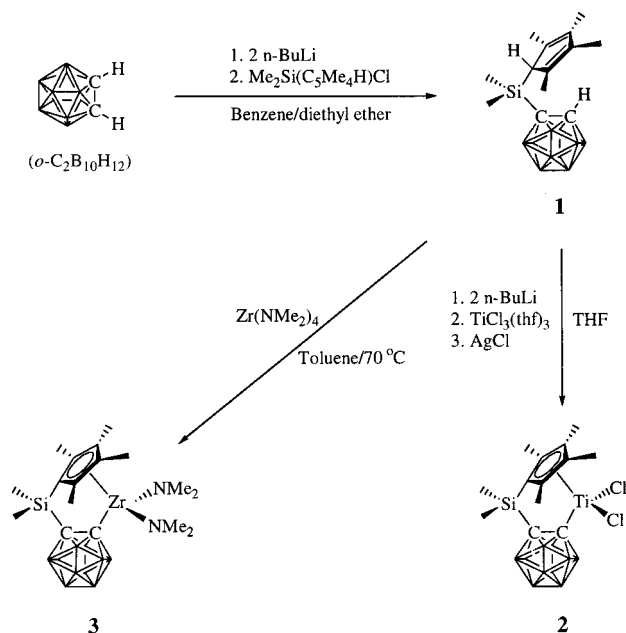
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## Scheme 1

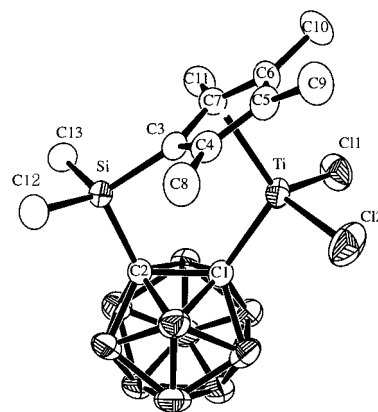


metal complexes  $[\eta^5:\eta^1\text{-Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{TiCl}_2$  (**2**) and  $[\eta^5:\eta^1\text{-Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Zr}(\text{NMe}_2)_2$  (**3**) derived from a new linked *o*-carboranyl ligand precursor  $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})(\text{C}_2\text{B}_{10}\text{H}_{11})$  (**1**). These complexes constitute the first examples of electron-deficient group 4 metal complexes containing linked  $\eta^5:\eta^1$ -metal-carbon bonds.

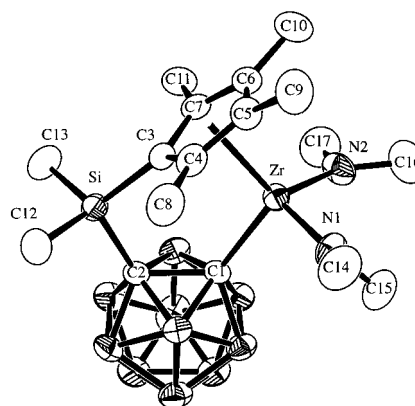
## Results and Discussion

The synthesis of **1**, **2**, and **3** is outlined in Scheme 1. The new *ansa*-ligand precursor  $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})(\text{C}_2\text{B}_{10}\text{H}_{11})$  (**1**) was prepared in 90% isolated yield by the reaction of  $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$ <sup>8</sup> with the dilithium derivative of *o*-carborane ( $\text{Li}_2\text{C}_2\text{B}_{10}\text{H}_{10}$ ) in refluxing benzene/diethyl ether solvent. The reaction of the dilithium salt of **1** with  $\text{TiCl}_3(\text{THF})_3$  followed by the oxidation with  $\text{AgCl}$  in THF and recrystallization from  $\text{CH}_2\text{Cl}_2/n$ -hexane at  $-20^\circ\text{C}$  afforded **2** in 42% yield. The red crystalline **2** is very soluble in THF, moderately in  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ , and slightly in toluene. The synthesis of **3** was effected by the amine elimination reaction<sup>9</sup> using a mixture of **1** and  $\text{Zr}(\text{NMe}_2)_4$  in toluene at  $70^\circ\text{C}$ . Recrystallization of the product from  $\text{CH}_2\text{Cl}_2$  solution layered with *n*-hexane at  $-20^\circ\text{C}$  gave light yellow cubic crystalline **3** in 57% yield. Complexes **2** and **3** were characterized by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{11}\text{B}$  NMR spectroscopy, elemental analysis, and X-ray diffraction.

The molecular structures of **2** and **3**, depicted in Figures 1 and 2, respectively, resemble the CGC-type complex **A** except for the presence of the *o*-carboranyl group instead of the amido group. The overall geometry of these complexes is pseudo-tetrahedral about the metal center and is of  $C_s$  symmetry with the *o*-plane including the metal, C(3), Si, and C(1) atoms. The three and four sets of methyl proton resonances in the  $^1\text{H}$  NMR spectra of **2** and **3**, respectively, are consistent



**Figure 1.** Molecular structure of  $[\eta^5:\eta^1\text{-Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{TiCl}_2$  (**2**). Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (deg)<sup>a</sup>: Ti-Cl(1), 2.240(1); Ti-Cl(2), 2.227(1); Ti-C(1), 2.178(4); Ti-Cn, 2.028. Cn-Ti-C(1), 115.4; Cl(1)-Ti-Cl(2), 106.0(1); Ti-C(1)-C(2), 122.4(2); C(1)-C(2)-Si, 113.7(2); C(2)-Si-C(3), 102.0(1). <sup>a</sup>Cn, centroid of C (3, 4, 5, 6, 7).



**Figure 2.** Molecular structure of  $[\eta^5:\eta^1\text{-Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Zr}(\text{NMe}_2)_2$  (**3**). Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (deg)<sup>a</sup>: Zr-N(1), 2.021(5); Zr-N(2), 2.035(4); Zr-C(1), 2.355(5); Zr-Cn, 2.240. Cn-Zr-C(1), 110.3; N(1)-Zr-N(2), 104.5(2); Zr-C(1)-C(2), 120.3(3); C(1)-C(2)-Si, 115.8(3); C(2)-Si-C(3), 105.8(2). <sup>a</sup>Cn, centroid of C (3, 4, 5, 6, 7).

with the retention of  $C_s$  symmetry in solution. The structure of **2** consists of  $\eta^5\text{-}\pi$  bonding of Ti with the  $\text{C}_5\text{Me}_4$  ring and  $\eta^1\text{-}\sigma$  bonding with the *o*-carboranyl carbon atom and the two terminal chlorine atoms. The lack of additional electron donation from the *o*-carboranyl carbon atom to the Ti center leads to the description of complex **2** as a formally 12-electron species instead of a 14-electron complex, as observed in usual amido CGC complexes. Although a Ti-Cn (Cn = Cp centroid) distance of 2.028 Å is comparable to that in  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N-}t\text{-Bu})\text{TiCl}_2]$  (**4**) (2.030 Å), a 14-electron system,<sup>10</sup> two Ti-Cl bond distances of 2.234(1) and 2.227(2) Å are slightly decreased compared with those of **4** (2.264(1) Å) owing to the consequence of the 12-electron nature of **2**. This fact would be further manifested by observing that both Ti-Cn distance (2.060 Å) and average Ti-Cl distance (2.304 Å) are substantially elongated in formally 16-electron species such as  $[\text{Me}_2\text{-}$

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$\text{Si}(\text{C}_5\text{Me}_4)(\eta^2\text{-NNMe}_2)\text{TiCl}_2$ ].<sup>1a,11</sup> Consistent with this observation is the trend in the distance between Ti and carboranyl C(1) carbon: the Ti–C(1) distance (2.178(4) Å) in **2** is shorter than those found in 16-electron species such as  $[(\text{C}_5\text{Me}_5)(\eta^5\text{-}\eta^1\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10}))\text{-TiCl}]$  (2.328(9) Å)<sup>12</sup> and *rac*- $[(\eta^5\text{-}\eta^1\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{-B}_{10}\text{H}_{10}))_2\text{Ti}]$  (2.308 Å).<sup>13</sup> The Cn–Ti–C(1) angle of 115.4° for the chelating ligand  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})]^{2-}$  is relatively larger than those observed in monosilyl-bridged CGC complexes.<sup>14</sup> An increase in bridge length by an additional *o*-carboranyl C(2) carbon atom appears to result in an increase of the angle.<sup>15</sup> No detectable deviation between the  $\text{C}_5\text{Me}_4$  ring plane and the C(3)–Si bond vector further supports the reduced strain in metallacycle in **2**.

The structural feature of **3** is essentially similar to that of **2** except for the replacement of the chlorine atoms with two amide groups. The short Zr–N(1) and Zr–N(2) bond distances (2.021(5) and 2.035(4) Å) and the planar geometry around the N(1) and N(2) nitrogen atoms indicate that both nitrogen atoms with  $\text{sp}^2$  hybridization are engaged in  $\text{N}(\text{p}_\pi) \rightarrow \text{Zr}(\text{d}_\pi)$  interactions. The lack of additional electron donation from the *o*-carboranyl carbon atom to the Zr center also strengthens this  $\text{p}_\pi \rightarrow \text{d}_\pi$  interaction noticeably, resulting in substantial decrease in Zr–N bond distances compared with the corresponding distances of 2.060(5) and 2.064(4) Å in  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N-}t\text{-Bu})\text{Zr}(\text{NMe}_2)_2]$ .<sup>10</sup> But, the Zr–C(1) bond distance of 2.355(5) Å is similar to those of the formally isoelectronic 16-electron complexes,  $[(\text{C}_5\text{-Me}_5)(\eta^5\text{-}\eta^1\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10}))\text{ZrCl}]$  (2.389(7) Å)<sup>12</sup> and *rac*- $[(\eta^5\text{-}\eta^1\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10}))_2\text{Zr}]$  (2.377(av) Å).<sup>7</sup> Comparison of the Cn–Zr–C(1) angle of 110.3° with those of other amido Zr CGC complexes<sup>16</sup> indicates the presence of reduced strain in **3**.

The derivative chemistry and the catalytic behavior toward  $\alpha$ -olefins of **2** and **3** are currently under investigation.

## Experimental Section

**General Considerations.** All operations were performed under an inert dinitrogen atmosphere using standard Schlenk and glovebox techniques. THF, toluene, benzene, and *n*-hexane were distilled from Na–K alloy,  $\text{Et}_2\text{O}$  from Na-benzophenone ketyl, and  $\text{CH}_2\text{Cl}_2$  from  $\text{CaH}_2$ . Chemicals were used without any further purification after purchasing from Aldrich ( $\text{Me}_2\text{-SiCl}_2$ , *n*-butyllithium and AgCl), Catchem (*o*-carborane), and Strem ( $\text{Zr}(\text{NMe}_2)_4$  and  $\text{Li}(\text{C}_5\text{Me}_4\text{H})$ ).  $\text{TiCl}_3(\text{thf})_3$  was prepared according to the literature procedure.<sup>17</sup>  $\text{CDCl}_3$  was dried over activated molecular sieves (4A) and used after vacuum transfer

to a Schlenk tube equipped with a J. Young valve.  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{11}\text{B}$  NMR spectra were recorded on Bruker AM 300 spectrometer at ambient temperature. All chemical shifts are reported in  $\delta$  units with reference to the residual peaks of  $\text{CDCl}_3$  for proton (7.24 ppm) and carbon (77.0 ppm) chemical shifts and to external  $\text{BF}_3\cdot\text{OEt}_2$  (0.00 ppm) for boron chemical shifts. HR EIMS experiments were performed by VG Auto Spec. at KAIST. Elemental analyses were carried out on an EA 1110-FISONS (CE Instruments) at KAIST.

**Synthesis of  $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})(\text{C}_2\text{B}_{10}\text{H}_{11})$  (**1**).** The literature methods<sup>6i,7</sup> were analogously employed in preparing **1**. A solution of 2.9 g (20 mmol) of *o*-carborane ( $\text{C}_2\text{B}_{10}\text{H}_{12}$ ) in 30 mL of benzene/diethyl ether (2:1) was treated with two equiv of *n*-butyllithium (16 mL of 2.5 M solution in *n*-hexane) at 0 °C. The reaction mixture was slowly allowed to warm to room temperature and stirred for 2 h. To the resulting dilithium solution was added 4.3 g (20 mmol) of  $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$  in 10 mL of benzene/diethyl ether (2:1) via cannula at 0 °C. The reaction mixture was allowed to warm to room temperature and heated at reflux overnight. The reaction was stopped by the addition of 30 mL of saturated aqueous solution of  $\text{NH}_4\text{-Cl}$ , and the organic portion was separated. The aqueous layer was further extracted with diethyl ether (30 mL), and the combined organic portions were dried over  $\text{MgSO}_4$ , filtered, and evaporated to dryness. The resulting sticky residue was purified by short column chromatography (silica gel, *n*-hexane eluent), giving light greenish, sticky solid of **1** after drying. Yield: 5.8 g (90%).  $^1\text{H}$  NMR (300.13 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.21 (s, 1H,  $\text{CB}_{10}\text{CH}$ ), 2.77 (s, 1H,  $\text{C}_5\text{Me}_4\text{H}$ ), 1.96 (s, 6H,  $\text{C}_5\text{Me}_4\text{H}$ ), 1.75 (s, 6H,  $\text{C}_5\text{Me}_4\text{H}$ ), 0.47 (s, 6H,  $\text{SiMe}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.47 MHz,  $\text{CDCl}_3$ ):  $\delta$  137.8, 133.5 ( $\text{C}_5\text{Me}_4$ ), 65.9, 59.0 ( $\text{C}_2\text{B}_{10}$ ), 53.7 ( $\text{C}_5\text{-Me}_4$ ), 14.8, 11.1 ( $\text{C}_5\text{Me}_4$ ), 0.5 ( $\text{SiMe}_2$ ).  $^{11}\text{B}\{^1\text{H}\}$  NMR (96.27 MHz,  $\text{CDCl}_3$ ):  $\delta$  –0.42 (1B), –2.89 (1B), –7.62 (2B), –11.43 (2B), –12.98 (2B), –13.73 (2B). HR EIMS: *m/z* calcd for  $\text{C}_{13}\text{H}_{30}\text{B}_{10}\text{-Si}$ , 324.3047; found, 324.3043.

**Synthesis of  $[\eta^5\text{-}\eta^1\text{-Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{TiCl}_2$  (**2**).** A solution of 1.6 g of **1** (5.0 mmol) in THF (20 mL) was treated with two equiv of *n*-butyllithium (4 mL of 2.5 M solution in *n*-hexane) at –78 °C. The reaction mixture was slowly allowed to warm to room temperature and stirred for 2 h. Into a precooled flask containing 1.9 g of  $\text{TiCl}_3(\text{THF})_3$  (5.0 mmol) slurry in THF (20 mL) was added via cannula the dilithium solution of **1** at –78 °C with vigorous stirring. The reaction mixture was slowly allowed to warm to room temperature over 2 h and stirred for 2 h at this temperature. To the resulting green solution was transferred 1.1 equiv of AgCl (0.79 g) as a solid. An immediate color change to orange-red with gradual precipitation of  $\text{Ag}^0$  was observed. After 30 min of stirring, the mixture was evaporated to dryness and extracted with 50 mL of  $\text{CH}_2\text{Cl}_2$ . The red solution was filtered through a Celite pad and concentrated to about 30 mL. Overnight cooling at –20 °C after the addition of 20 mL of *n*-hexane afforded 0.92 g (42%) of red crystals of **2**.  $^1\text{H}$  NMR (300.13 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.61 (s, 6H,  $\text{C}_5\text{Me}_4$ ), 2.32 (s, 6H,  $\text{C}_5\text{Me}_4$ ), 0.71 (s, 6H,  $\text{SiMe}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.47 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.1, 139.7 ( $\text{C}_5\text{Me}_4$ ), 132.2, 112.1 ( $\text{C}_2\text{B}_{10}$ ), 83.6 ( $\text{C}_5\text{Me}_4$ ), 18.2, 14.5 ( $\text{C}_5\text{Me}_4$ ), 1.4 ( $\text{SiMe}_2$ ).  $^{11}\text{B}\{^1\text{H}\}$  NMR (96.27 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.23 (1B), –0.30 (1B), –4.37 (4B), –9.66 (2B), –12.46 (2B). Anal. Calcd for  $\text{C}_{13}\text{H}_{28}\text{B}_{10}\text{SiCl}_2\text{Ti}$ : C, 35.54; H, 6.42. Found: C, 35.73; H, 6.64.

**Synthesis of  $[\eta^5\text{-}\eta^1\text{-Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Zr}(\text{NMe}_2)_2$  (**3**).** A solid mixture of **1** (2.0 mmol, 0.65 g) and  $\text{Zr}(\text{NMe}_2)_4$  (2.0 mmol, 0.54 g) was dissolved in toluene (30 mL) at room temperature and heated to 70 °C for 2 h with periodic  $\text{N}_2$  purges. The resulting solution was cooled to room temperature and dried in vacuo. Extraction of the residue with  $\text{CH}_2\text{Cl}_2$  (20 mL) and filtration through a Celite pad gave a light yellow-greenish solution. Concentration followed by layering by *n*-hexane (10 mL) and cooling overnight at –20 °C afforded light yellow cubic crystals of **3** in 57% (0.57 g) yield.  $^1\text{H}$  NMR (300.13 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.90 (s, 12H,  $\text{NMe}_2$ ), 2.25 (s, 6H,  $\text{C}_5\text{Me}_4$ ), 2.04 (s, 6H,  $\text{C}_5\text{Me}_4$ ), 0.56 (s, 6H,  $\text{SiMe}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR

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(14) Examples of Cn–Ti–N(append) angle: (a)  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N-}t\text{-Bu})]\text{TiCl}_2$ , 107.6°, see ref 10. (b)  $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{N-}t\text{-Bu})]\text{TiCl}_2$ , 107.0°, see ref 10. (c)  $[\text{Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{s-NCHMePh})]\text{TiCl}_2$ , 106.3°, see ref 1h. (d)  $[\text{Me}_2\text{Si}(\text{C}_4\text{PM}_3)(\text{N-}t\text{-Bu})]\text{TiCl}_2$ , 108.4°, see ref 2. (e)  $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_4\text{CMe}_2)(\text{N-}t\text{-Bu})]\text{TiCl}_2$ , 107.3°, see ref 4. (f)  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\eta^2\text{-NNMe}_2)]\text{TiCl}_2$ , 101.1°, see ref 11.

(15) Cn–Ti–N(append) angles for different bridging groups:  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N-}t\text{-Bu})]\text{TiCl}_2$ , 107.6°,  $[\text{C}_2\text{H}_4(\text{C}_5\text{Me}_4)(\text{N-}t\text{-Bu})]\text{TiCl}_2$ , 107.9°,  $[\text{Me}_4\text{Si}_2(\text{C}_5\text{Me}_4)(\text{N-}t\text{-Bu})]\text{TiCl}_2$ , 120.0°; see ref 1m.

(16) Examples of Cn–Zr–N(append) angle: (a)  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N-}t\text{-Bu})]\text{ZrCl}_2$ , 102.0°, see ref 10. (b)  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N-}t\text{-Bu})]\text{Zr}(\text{NMe}_2)_2$ , 100.2°, see ref 10. (c)  $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{N-}t\text{-Bu})]\text{ZrCl}_2(\text{NMe}_2\text{H})$ , 101.1°, see ref 10. (d)  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{NCH}_2\text{CH}_2\text{OMe})]\text{ZrMe}_2$ , 98.9°, see ref 1d.

(17) Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135.



**Table 1. Crystallographic Data and Parameters for **2** and **3****

	<b>2</b>	<b>3</b>
formula	C <sub>13</sub> H <sub>28</sub> B <sub>10</sub> SiCl <sub>2</sub> Ti	C <sub>17</sub> H <sub>40</sub> B <sub>10</sub> SiN <sub>2</sub> Zr
fw	439.34	499.92
crystal system	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	11.196(2)	10.694(3)
<i>b</i> (Å)	14.471(3)	17.842(1)
<i>c</i> (Å)	15.449(3)	14.085(3)
$\alpha$ (deg)	90	90
$\beta$ (deg)	111.32(2)	100.26(2)
$\gamma$ (deg)	90	90
<i>V</i> (Å <sup>3</sup> )	2331.6(8)	2644.5(9)
<i>Z</i>	4	4
<i>d<sub>c</sub></i> (g/cm <sup>3</sup> )	1.252	1.256
<i>F</i> (000)	904	1040
<i>T</i> (K)	293	293
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	0.64	0.47
scan mode	$\omega/2\theta$	$\omega/2\theta$
$\theta$ range (deg)	2.00; 24.97	2.21; 25.04
no. of unique rflns	3720	3930
no. of obsd rflns ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	3062	2780
no. of params refined	250	290
R1 <sup>a</sup>	0.0473	0.0543
wR2 <sup>b</sup>	0.1249	0.1089
GOF	1.145	1.066
min and max dens (e Å <sup>-3</sup> )	0.500, 0.429	0.536, 0.749

$$^a \text{R1} = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b \text{wR2} = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

(75.47 MHz, CDCl<sub>3</sub>):  $\delta$  129.7, 125.1 (*C*<sub>5</sub>Me<sub>4</sub>), 114.2, 96.9 (*C*<sub>2</sub>B<sub>10</sub>), 84.5 (*C*<sub>5</sub>Me<sub>4</sub>), 43.1 (*N*Me<sub>2</sub>), 14.7, 11.0 (*C*<sub>5</sub>Me<sub>4</sub>), 2.0 (*Si*Me<sub>2</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR (96.27 MHz, CDCl<sub>3</sub>):  $\delta$  0.03 (2B), -3.94 (2B), -9.26 (4B), -12.39 (2B). Anal. Calcd for C<sub>17</sub>H<sub>40</sub>B<sub>10</sub>SiN<sub>2</sub>Zr: C, 40.84; H, 8.06; N, 5.60. Found: C, 40.36; H, 7.91; N, 5.48.

**X-ray Structure Determination of **2** and **3**.** Single crystals suitable for X-ray structure determination were sealed in thin-walled glass capillary tubes under an inert dinitrogen

atmosphere. The measurements of diffraction intensity were carried out on an Enraf-Nonius CAD4TSB diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.710 73 Å) at 293 K. Accurate unit cell parameters and orientation matrices were determined from the least-squares fit of 25 accurately centered reflections in the range of 21.36° < 2 $\theta$  < 30.75° for **2** and 18.29° < 2 $\theta$  < 31.28° for **3**. Intensity data were collected by using  $\omega$ -2 $\theta$  scan mode with a range of 2.00° <  $\theta$  < 24.97° for **2** and 2.21° <  $\theta$  < 25.04° for **3**. All the intensity data were corrected for Lorentz and polarization effects. The structures were solved by semiinvariant direct method (SIR 92 in MoleN)<sup>18</sup> and refined by full matrix least-squares refinement (SHELXL 93)<sup>19</sup> with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon and boron atoms with isotropic thermal parameters. Final refinement based on the reflections (*I* > 2.0 $\sigma$ (*I*)) converged at R1 = 0.0473, wR2 = 0.1249, and GOF = 1.145 for **2** and at R1 = 0.0543, wR2 = 0.1089, and GOF = 1.066 for **3**. All calculations were performed on a Silicon Graphics Indigo2XZ workstation. The detailed data are listed in Table 1.

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**Supporting Information Available:** Tables of crystallographic data, atomic coordinates, thermal parameters, and bond distances and angles for complexes **2** and **3**, including ORTEP drawings with the full atom labeling scheme. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM000730F

(18) *MoleN*, An Interactive Structure Solution Program; Enraf-Nonius: Delft, Netherlands, 1994.

(19) Sheldrick, G. M. *SHELXL 93*, Program for Crystal Structure Determination; University of Göttingen: Germany, 1993.