The Boratacyclooctatetraene Ligand: An Isoelectronic Trianionic Analogue of the Cyclooctatetraene Dianion**

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*Dedicated to Professor Gerhard E. Herberich
and Professor Arthur J. Ashe III*

The cyclooctatetraene dianion (COT^{2-}) and its derivatives are versatile ligands for transition metal atoms.[1] When bound to metal centers, they are formally considered as dianionic 10π electron donors. Their use in actinide and lanthanide chemistry, in particular, has been well documented.[1c] Representative examples from the literature include uranocene, $[(C_8H_8)_2U]$, and $[(C_8H_8)_2Ce]$.[2] Catalytic species can also be designed, for instance $[Ni_2(COT)_2]$ serves as an effective catalyst for acetylene tetramerization.[3]

Interest in the chemistry of boracycloalkenes, boraarenes and borataarenes stems from the concepts of π-electron aromaticity and conjugation across sp^2-hybridized boron.[1] Boratabenzene, the most representative example of this class of compound, is an anionic 6π electron main-group heterocycle, which was initially identified coordinated to transition-metal centers.[4] Recent applications of boratabenzene in transition-metal catalysis are of interest, because the electron density of the metal center can be modulated by the choice of the exocyclic boron substituent.[5] Changes in electron density

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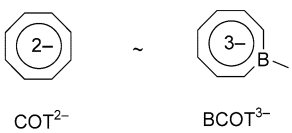
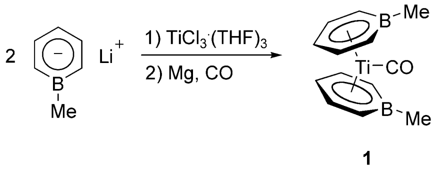
result in modified catalytic activities and selectivities.[5e] Similar control of reactivity by exocyclic substituents in the cyclopentadienyl ligand is more difficult to achieve.[6]

Initial interest in applying the reactivity control by boracyclic ligands to other transition-metal-catalyzed processes prompted us to examine the synthesis and reactivities of low-valent titanium carbonyl complexes. Much of the motivation was provided by the alkyne hydroboration reactions catalyzed by $[Cp_2Ti(CO)_2]$ ($Cp = \eta^5\text{-}C_5H_5$).[7] Herein, we report on the synthesis of $[(C_5H_5B{-}Me)_2Ti(CO)]$ (**1**) and the conversion of boratabenzene into the formally trianionic boratacyclooctatetraene (BCOT) ligand upon insertion of acetylene into the intraring B−C bond. The BCOT ligand should facilitate the synthesis of novel transition-metal, lanthanide, and actinide complexes with reactivity that can be controlled by the electronic properties of the boron substituent.[5e]



The synthesis of $[(C_5H_5B{-}Me)_2Ti(CO)]$ (**1**) is shown in Scheme 1.[8] Reaction in THF of lithium 1-methyl boratabenzene[9] with $TiCl_3{\cdot}(THF)_3$,[10] followed by treatment with

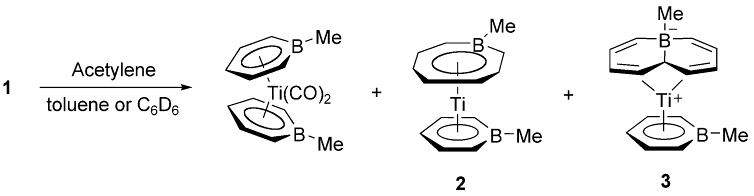


Scheme 1. Synthesis of $(C_5H_5B{-}Me)_2Ti(CO)$.

magnesium powder under one atmosphere of CO and extraction with hot toluene affords **1** in 47% yield as cubic dark-red crystals. The IR spectrum of **1** shows a single band in the carbonyl-stretching region, at $\tilde{\nu} = 1954\ \text{cm}^{-1}$. Single crystals suitable for X-ray diffraction experiments were obtained by crystallizing the product in hexane at room temperature and the result of these diffraction studies (see Supporting Information) is consistent with the structural assignment given in Scheme 1.[12b]

A study by ^{1}H NMR spectroscopy indicates that an addition of excess CO to a solution of **1** in C_6D_6 results in the formation of $[(C_5H_5B{-}Me)_2Ti(CO)_2]$, the spectrum of which shows broad signals at $\delta = 5.43$ (4H), 4.41 (4H) and 4.34 ppm (2H). As the resonance signals arising from $[(C_5H_5B\text{-}Me)_2Ti(CO)_2]$ increase, there is a concomitant decrease in the signals from **1**. Furthermore, two IR bands in the carbonyl region are observed at $\tilde{\nu} = 1996$ and $1949\ \text{cm}^{-1}$, which are consistent with the symmetric and antisymmetric CO-stretching combinations of a metal center with two carbonyl ligands. The removal of solvent regenerates **1**, thus indicating that the second carbonyl ligand is not strongly bound to titanium.

In the process of examining the reactivity of **1** with a variety of acetylinic substrates, we monitored the reaction of **1** with acetylene in C_6D_6 by using ^{1}H NMR spectroscopy (Scheme 2). Addition of one equivalent of acetylene yields three organometallic products. One was readily identified as $[(C_5H_5B{-}Me)_2Ti(CO)_2]$. A second product shows a resonance peak pattern reminiscent of the previously reported borate complex, [4a-phenyl-8a*H*-4a-boratanaphthalene][1-phenylboratabenzene]-zirconium(II).[11] Attempts to obtain single crystals of this species for X-ray structural determination were unsuccessful. We tentatively assign this product as compound **3** in Scheme 2. The third product shows resonance peaks at $\delta = 6.55$ (dd), 6.06 (t), 5.95 (d), and 5.68 ppm (dd). Such a pattern would be consistent with a 1-methyl-boratacyclooctatetraene (BCOT) ring structure. This structural assignment was also supported by high-resolution mass spectrometry.



Scheme 2. Reaction of **1** with acetylene

We anticipated increased yields of **2**, relative to **3**, at low acetylene pressures by noting that the formation of **3** requires two equivalents of acetylene, whereas **2** is obtained by a single insertion. Indeed, when one monitors the reaction of **1** with acetylene at lower concentrations of C_2H_2, the ratio of **2** to **3** increases. As a preparatory method, we intentionally used an argon buffer layer on the top of a solution of **1** in toluene and then carefully layered 1.2 equivalents of acetylene on the top of the argon. The purpose of the argon layer is to decrease the diffusion rate of acetylene gas and reduce the effective acetylene concentration in toluene. The removal of solvent and recrystallization in hexane afford the desired BCOT complex **2** in 50% yield.

Dark-red single crystals of **2** were obtained by slow diffusion of pentane into a toluene solution at −35 °C. The results of X-ray diffraction studies show that there are four independent molecules of composition $[(C_7H_7B{-}Me)(C_5H_5B{-}Me)Ti]$ in the crystal lattice. Figure 1 shows a representative structure.[12] The overall molecular geometry is that of a parallel sandwich metallocene with an η^8-boratacyclooctatetraene ligand and an η^6-boratabenzene ligand. Average Ti−C and Ti−B distances are statistically shorter to the BCOT ligand (av. Ti−C = 2.269(6) Å, av. Ti−B = 2.416(6) Å) than to the boratabenzene ligand (av. Ti−C = 2.363(6) Å, av. Ti−B = 2.517(6) Å). These metrical data, together with the shorter Ti−(C_7B) centroid distance (1.313(6) Å), reflect the higher charge on the C_7B ring, relative to the C_5B ring (Ti−(C_5B) centroid distance:

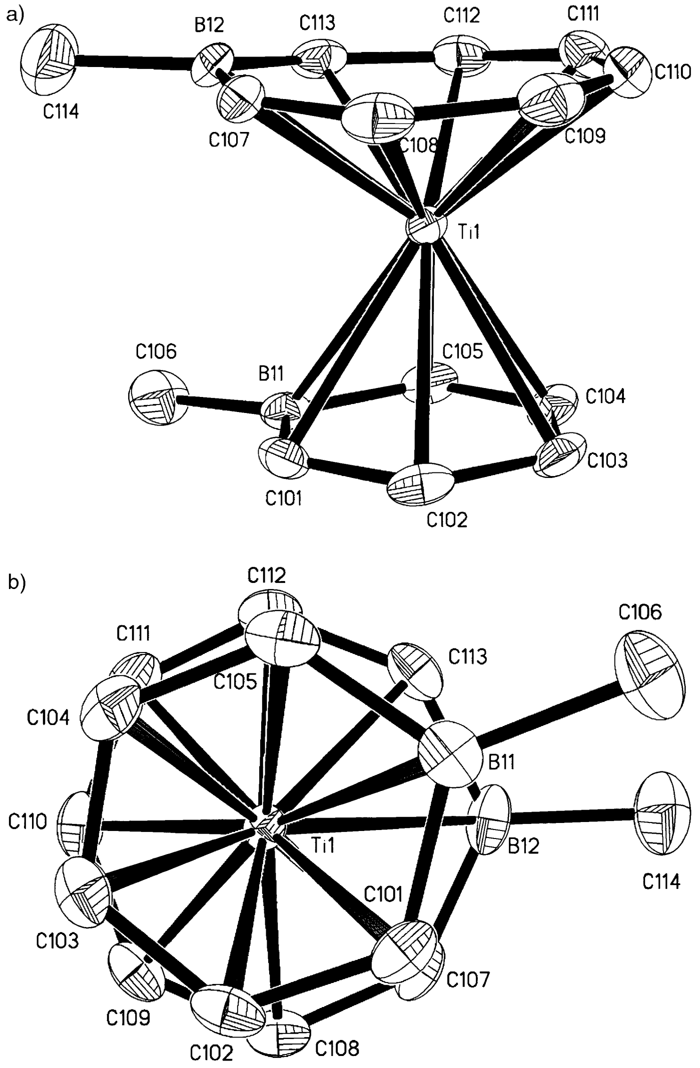
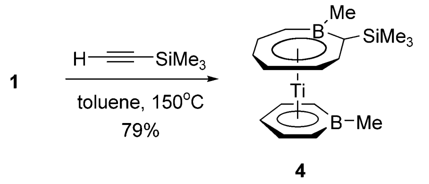


Figure 1. ORTEP diagrams of the molecular structure of compound **2**: a) side view; b) top view. Thermal ellipsoids set at the 30% probability level.

1.909(6) Å). The intraring C−C bond distances in the BCOT ring in **2** (**2**: 1.394(9)–1.426(9) Å) are within the range of coordinated aromatic boracycles.[4a] The intraring B−C bond lengths (**2**: 1.506(10)–1.508(10) Å) are considerably shorter than the exocyclic B−C bond lengths (**2**: 1.586(10) Å), which indicate an extensively delocalized structure within the BCOT ring. It is also significant that in **2** the resonance signals of the protons on the BCOT ring ($\delta = 5.68$–6.55 ppm in C_6D_6) are shifted to lower fields, relative to those of the boratabenzene ring ($\delta = 4.52$–5.57 ppm in C_6D_6), thus indicating strong ring current within the BCOT ligand.

Having determined that acetylene can insert into the boratabenzene fragment, we examined whether any regioselectivity was possible by using a monosubstituted substrate (Scheme 3). Thus, a solution of **1** in toluene was treated with 1.0 equivalent of trimethylsilylacetylene at 150 °C to afford [(2-SiMe$_3$−C$_7$H$_6$B−Me)(C$_5$H$_5$B−Me)Ti] (**4**) in 79% yield. A crystal of **4** suitable for X-ray diffraction studies was grown from hexane at 20 °C and the trimethylsilyl group was unambiguously found at the C_α site of the BCOT ring (Figure 2).[12] The corresponding ^{1}H NMR spectrum shows a coupling pattern of the boratacyclooctatetraene ligand protons in the bulk product that is consistent with the solid-state structure.



Scheme 3. Study of the reaction selectivity by using a substituted alkyne.

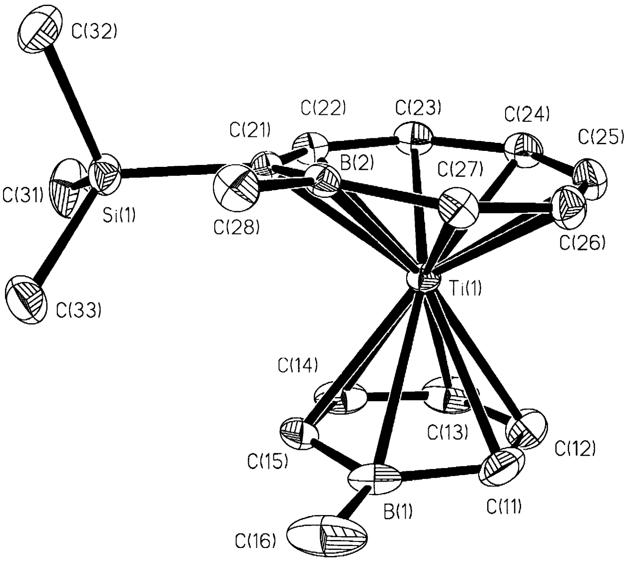
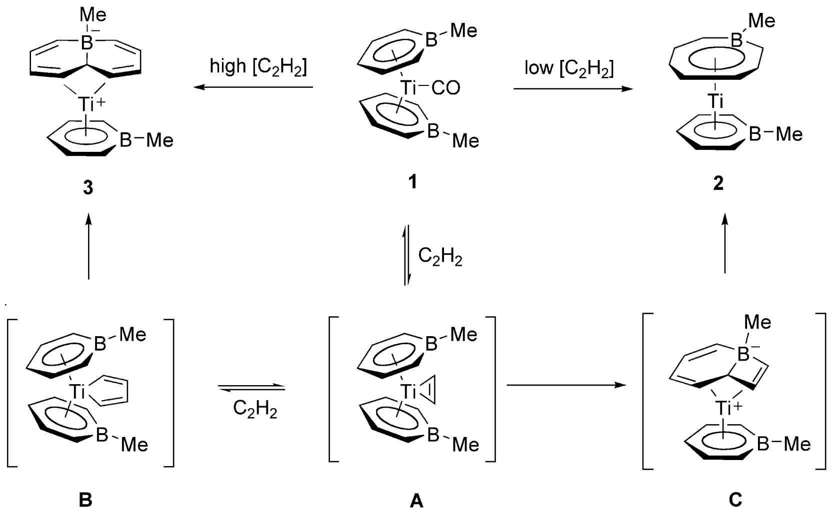


Figure 2. ORTEP diagram of the molecular structure of **4**. Thermal ellipsoids set at the 30% probability level.

A mechanism for the formation of **2** is proposed in Scheme 4. It is well-accepted that {Cp$_2$Ti^{II}}species can oxidatively coordinate one or two acetylene molecules to form titannacyclopropene or titannacyclopentadiene intermediates, respectively.[13] By analogy, a similar oxidative coupling process may be adopted by the {(C$_5$H$_5$B−Me)$_2$Ti^{II}} fragment.[11] In Scheme 4, the first intermediate is the titannacyclopropene species **A**, which forms upon coordination of acetylene to **1**. One equivalent of carbon monoxide is generated by this reaction, which is trapped by **1** to form [(C$_5$H$_5$B−Me)$_2$Ti(CO)$_2$] (not shown in Scheme 4, but observed in solution). Associative displacement reactions with [(C$_5$H$_5$B−Me)$_2$Ti(CO)$_2$] are not significant because of its inert 18 electron configuration. Compound **A** can undergo two types of reactions, depending on the acetylene concentration. At low concentrations of C_2H_2, direct transmetallation and subsequent reductive elimination affords the annulated bicyclic intermediate **C**. Next, the four-membered ring expands to yield the BCOT ligand. When the acetylene concentration is high, the intermediate **A** is trapped by a second equivalent of acetylene to give **B**, before the intra-



Scheme 4. Proposed mechanism for the formation of **2**.

molecular ring expansion can take place. Compound **B** ultimately converts to **3**.[11]

The Lewis acidity of the boron atom plays an important role in facilitating the transmetallation step. We note that $[(C_5H_5B{-}NMe_2)_2Ti(CO)]$, in which B–N π bonding increases the electron density at boron, does not react with acetylenes under conditions similar to those in Scheme 2.[14] As electrophilic attack on vinylsilanes occurs selectively at the Si-C_α site,[15] we propose that the transmetallation step should be viewed as an electrophilic attack of boron on the coordinated acetylene ligand. The transition state of the regioselective insertion of trimethylsilylacetylene is depicted in Figure 3. The alignment between the electrophilic *p* orbital on boron and the nucleophilic *p* orbital on the C_α atom of the vinyl group prompts the concerted four-center four-electron transition state. These electronic requirements lead to placing the bulky trimethylsilyl group adjacent to the sterically more demanding methyl-substituted boron atom, instead of C_β substitution.

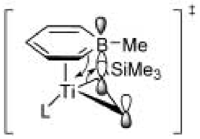


Figure 3. Transition state of the regioselective insertion of trimethylsilylacetylene.

In summary, we have demonstrated that the boratacyclooctatetraene (BCOT) ring system can be obtained from boratabenzene by a simple ring insertion step. A low concentration of acetylene in toluene favors the single insertion. The BCOT formation is most likely a result of an electrophilic attack of the boron atom on the coordinated acetylene fragment. The electronic requirements of this transmetallation step control the insertion regiochemistry. The existence of BCOT should facilitate the synthesis of transition-metal, lanthanide, and actinide complexes that are isoelectronic and isostructural to COT-containing compounds, but have an additional negative charge. We also foresee that the reactivity of BCOT complexes will be controlled by the choice of exocyclic boron substituents.

Experimental Section

Chemicals were obtained from Aldrich, Strem, Acros, and Fisher and, unless otherwise specified, were used without further purification. Alkynes were degassed, flushed with argon, dried over activated molecular sieves (4 Å) and distilled. Carbon monoxide and acetylene were purchased from PRAXAIR. All manipulations were carried out under an inert atmosphere by using standard glovebox and Schlenk techniques. Toluene and THF were distilled from sodium benzophenone ketyl. Hexane was distilled from sodium/potassium alloy. Methylene chloride was distilled from CaH_2. NMR spectra were recorded with a Varian Unity 400 or 500 spectrometer. ^1H and ^{13}C NMR spectra were calibrated by using signals from solvent and were reported downfield from $SiMe_4$. ^{11}B NMR spectra were calibrated and reported from external $BF_3{\cdot}EtO_2$. Mass spectrometric analyses were obtained by using a VG-70E double-focusing magnetic sector instrument operated with an OPUS-SIOS data system. Elemental analyses were performed at Desert Analytics, Inc., Tucson, AZ and Analytical Lab, Marine Science Institute, the University of California, Santa Barbara.

Lithium 1-methylboratabenzene[9] and $TiCl_3{\cdot}(THF)_3$[10] were synthesized according to the literature procedures.

1: THF (20 mL) was vacuum transferred to a 500 mL Schlenk tube containing a mixture of 1-methylboratabenzene lithium salt (1.00 g, 10.2 mmol) and $TiCl_3{\cdot}(THF)_3$ (1.90 g, 5.1 mmol) and a magnetic stirrer. The mixture was stirred at 20 °C for 10 h, after which time the volatile fractions were removed in vacuo. An excess of magnesium powder (147 mg, 6.1 mmol) was loaded, and THF (50 mL) were vacuum transferred to the Schlenk tube, which had been cooled to −196 °C. The resulting mixture was then stirred at 20 °C under one atmosphere of CO for 10 h. The volatile fractions were removed in vacuo and the black residue was extracted with toluene (2 × 25 mL). These extractions were filtered, and the solvent was removed in vacuo to give a dark residue, which was further extracted with hot toluene (30 mL). The solvent was again removed in vacuo, and the remaining solid was dissolved in hexane. Crystallization of the product at 25 °C afforded dark-red cubic crystals (630 mg, 47 % yield): m.p. 164–165 °C; IR (hexane): $\tilde{\nu} = 1955\ cm^{-1}$ (C≡O); ^1H NMR (400 MHz, C_6D_6, 25 °C, TMS): $\delta = 4.93$ (dd, $J = 9.6, 2.0$ Hz, 2H; H_α), 4.86 (tt, $J = 7.2, 2.0$ Hz, 1H; H_γ), 4.47 (dd, $J = 9.6, 7.2$ Hz, 2H; H_β), 1.17 ppm (s, 3H; B-Me); ^{13}C NMR (100 MHz, C_6D_6, 25 °C, TMS): $\delta = 121.4$ (C_β), 108.6 (b, C_α), 100.0 (C_γ), 5.72 ppm (b, B–Me); ^{11}B NMR (160 MHz, C_6D_6, 25 °C, $BF_3{\cdot}Et_2O$): $\delta = 31.7$ ppm; Elemental analysis calcd (%) for $C_{13}H_{16}B_2OTi$: C 60.57, H 6.26; found: C 59.99, H 6.33.

2: A bomb flask containing a solution of **1** (88 mg, 0.34 mmol) in toluene (20 mL) was attached through an adapter flask on the vacuum line. The bomb flask was evacuated and refilled with argon. The adapter flask (93.8 mL) was evacuated and recharged with acetylene gas ($\Delta p = 8$ mmHg, 1.2 equiv). Acetylene was allowed to slowly diffuse into the solution of **1** through the argon layer at 25 °C. The solution was stirred well at 25 °C for four days. The solvent was removed in vacuo, the product was extracted with hexane, and the crude product was obtained by crystallization at −35 °C. Recrystallization of the product by slow diffusion of pentane into the toluene solution at −35 °C afforded dark-red crystals of **2** (43 mg, yield 50 %): m.p. 88 °C; ^1H NMR (400 MHz, C_6D_6, 25 °C, TMS): $\delta = 6.55$ (dd, $J = 14.6, 12.4$ Hz, 2H; BCOT), 6.06 (t, $^3J = 13.5$ Hz, 1H; BCOT), 5.95 (d, $^3J = 14.6$ Hz, 2H; BCOT), 5.68 (dd, $J = 13.5, 12.4$ Hz, 2H; BCOT), 5.57 (dd, $J = 10.2, 7.2$ Hz, 2H; Bb), 5.03 (dd, $J = 10.2, 1.6$ Hz, 2H; Bb), 4.52 (tt, $J = 7.2, 1.6$ Hz, 1H; Bb), 1.61 (s, 3H; B-CH_3(BCOT)), 0.72 ppm (s, 3H; B-CH_3(Bb)); ^{13}C NMR (100 MHz, C_6D_6, 25 °C, TMS): $\delta = 116.8, 114.1$ (b), 105.1, 101.3 (b), 100.8, 97.7, 96.4 ppm, Me not observed; ^{11}B (160 MHz, C_6D_6, 25 °C, $BF_3{\cdot}Et_2O$): $\delta = 31.1$, 26.6 ppm; HRMS: m/z calcd for $C_{14}H_{18}{}^{11}B_2{}^{48}Ti$, 256.1082; found, 256.1079; Elemental analysis calcd (%) for $C_{14}H_{18}B_2Ti$: C 65.74, H 7.09; found: C 65.41, H 6.81.

4: A solution of **1** (100 mg, 0.39 mmol) in 5 mL of toluene was treated with a solution of trimethylsilylacetylene (1.0 equiv) in 5 mL of toluene in a bomb reactor. The mixture was heated to 150 °C for 12 h. After removal of volatile fractions under reduced pressure, the residue was extracted with hot hexane (20 mL). The hexane extract was filtered and concentrated. The crystallization took place at 25 °C to afford dark-red parallelopiped crystals as the product (100 mg, yield 79 %): m.p. 114 °C; ^{1}H NMR(400 MHz, C_6D_6, 25 °C, TMS): $\delta =$ 6.97 (d, $^3J = 11.0$ Hz, 1H; BCOT), 6.54 (dd, $J = 14.3$, 11.0 Hz, 1H; BCOT), 6.09 (t, $^3J = 13.2$ Hz, 1H; BCOT), 5.92 (d, $^3J = 14.3$ Hz, 1H; BCOT), 5.79–5.71 (m, 3H; 2H(BCOT) and 1H(Bb)), 5.62 (ddd, $J =$ 10.0, 7.0, and 2.0 Hz, 1H; Bb), 5.12 (ddd, $J = 10.0$, 3.0, and 2.0 Hz, 1H; Bb), 4.90 (ddd, $J = 10.7$, 3.0, and 2.0 Hz, 1H; Bb), 4.72 (tt, $J = 7.0$, 2.0 Hz, 1H; Bb), 1.60 (s, 3H; B-Me(BCOT)), 0.67 (s, 3H; B-Me(Bb)), 0.55 ppm (s, 9H; $SiMe_3$); ^{13}C NMR (100 MHz, C_6D_6, 25 °C, TMS): $\delta =$ 121.4, 116.8, 116.2, 108.4, 104.5, 100.8, 98.5, 96.5, 3.6 ppm ($SiMe_3$), B-Me not observed; ^{11}B NMR (160 MHz, C_6D_6, 25 °C, $BF_3{\cdot}Et_2O$): $\delta =$ 31.8, 29.9 ppm; HRMS: m/z calcd for $C_{17}H_{26}{}^{11}B_2{}^{28}Si^{48}Ti$, 328.1479, found 328.1478; Elemental analysis calcd (%) for $C_{17}H_{26}B_2SiTi$: C 62.25, H 7.99; found: C 61.54, H 7.97.

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[12] a) Crystal data for **2**: $C_{14}H_{18}B_2Ti$, $M_r = 255.80$, space group $C2/c$, $a = 25.024(7)$ Å, $b = 11.862(3)$ Å, $c = 39.738(10)$ Å, $\beta = 92.632(5)°$, $V = 11\,783(5)$ Å^3, $Z = 36$, dark red, crystal size $0.34 \times 0.26 \times 0.1^6$ mm^3, $Mo_{K\alpha}$, $\lambda = 0.71073$ Å, $T = 150$ K, $R = 7.59$ %, $wR = 19.8$ % for 723 parameters and 6076 unique reflections with $I > 2\sigma(I)$. Crystal data for **4**: $C_{17}H_{26}B_2SiTi$, $M_r = 327.99$, space group $P2_12_12_1$, $a = 10.3510(18)$ Å, $b = 10.8200(19)$ Å, $c = 15.739(3)$ Å, $V = 1762.7(5)$ Å^3, $Z = 4$, $T = 150$ K, dark red, crystal size $0.24 \times 0.24 \times 0.2^4$ mm^3, $Mo_{K\alpha}$, $\lambda = 0.71073$ Å, $R = 4.61$ %, $wR = 11.9$ % for 196 parameters and 3797 unique reflections with $I > 2\sigma(I)$. b) CCDC-210722 (**1**), 210544 (**2**), and 210545 (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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