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Preparation and Crystal Structures of a Series of Titanium(III) 9-BBN Hydroborate Complexes Containing Ti···H Agostic Interactions

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9-BBN hydroborate complexes $Ti\{(\mu\text{-}H)_2BC_8H_{14}\}_3(THF)_2$ (**1**), $Ti\{(\mu\text{-}H)_2BC_8H_{14}\}_3(OEt_2)$ (**2**), and $[K(OEt_2)_4][Ti\{(\mu\text{-}H)_2BC_8H_{14}\}_4]$ (**4**) were formed from the reaction of $TiCl_4$ with $K[H_2BC_8H_{14}]$ in diethyl ether or THF. $Ti\{(\mu\text{-}H)_2BC_8H_{14}\}_3(PhNH_2)$ (**3**) was isolated from the reaction of **2** with aniline in diethyl ether. In the formation of these complexes, Ti(IV) is reduced to Ti(III). The coordinated diethyl ether in **2** can be displaced by the stronger bases THF and aniline, to form **1** and **3**, respectively. All of the compounds were characterized by single-crystal X-ray diffraction analysis. In complex **1**, which contains two coordinated THF ligands, the titanium possesses a 17 electron configuration and there is no evidence for agostic interaction. Complexes **2** and **3** contain only one coordinated ether or aniline ligand, and the titanium possesses a 15 electron configuration. In these compounds, a C–H hydrogen on an α carbon on the BC_8H_{14} unit of a 9-BBN hydroborate ligand forms an agostic interaction with the titanium. Criteria for assessing the existence of agostic interactions are discussed. As the potassium salt, the anion of complex **4** is more stable than the complexes **1**–**3**. Organometallic anions of the type $[ML_4]^-$ for titanium(III) are rare.

Introduction

Interest in transition-metal tetrahydroborate derivatives is associated with their practical use in synthesis and catalysis and as models for studying the bonding modes of hydrogen bridges to metals.[1,2] However, hydroborate derivatives of Ti(III) are few in number, even though metal borohydrides are known for almost all of the metals throughout the periodic table.[1,3] The first example of a titanium(III) borohydride complex, $[Ti(BH_4)_3]$, was reported by Hoekstra and Katz[4] in 1949. Nöth reported syntheses of the similar complexes $[Ti(BH_4)_3L_n$ ($L = Et_2O$ or THF; $n = 0-2$)] in 1976.[5]

The molecular structure of $Ti(BH_4)_3$ has been determined by analysis of electron diffraction data[6] (Chart 1). This molecule contains three tridentate BH_4 groups generating a structure with C_{3v} symmetry overall, implying 9-fold coordination of the titanium atom and a planar TiB_3 skeleton. Some of the tetrahydroborate titanium compounds that have been synthesized and characterized structurally by X-ray

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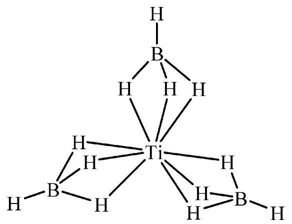
Chart 1

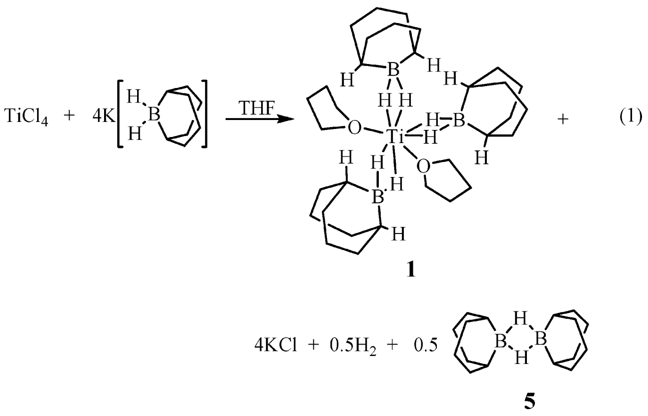


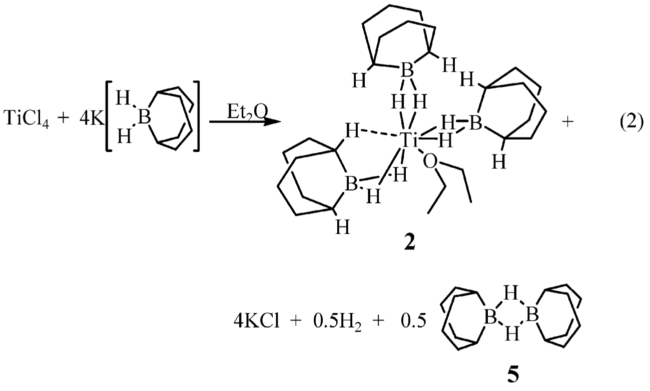
diffraction are the following: Ti(II), $Ti(\eta^2\text{-}BH_4)_2(dmpe)_2$,[3j] $Cp^*Ti(\eta^2\text{-}BH_4)((\eta^2\text{-}(Me_2PCH_2)_3Si(t\text{-}Bu)$[3g]; Ti(III), $Ti((\eta^2\text{-}BH_4)_3(PMe_3)_2$,[3i] $Cp_2Ti(\eta^2\text{-}BH_4)$[7] More recently, Ellis reported the first zerovalent titanium borohydride complex, $[Ti(CO)_4(\eta^2\text{-}BH_4)]^-$.[3b]

This laboratory has prepared three classes of organohydroborates (five-membered ring, $[(\mu\text{-}H)_2BC_4H_8]^-$, six-membered ring, $[(\mu\text{-}H)_2BC_5H_{10}]^-$, and 9-BBN, $[(\mu\text{-}H)_2BC_8H_{14}]^-$ ligands) bound to group 4 and group 5 metal mono(cyclopentadienyl)[9] and bis(cyclopentadienyl)[10] units such as $Cp^*Zr\{(\mu\text{-}H)_2BR\}_3$, $Cp^*Zr(Cl)\{(\mu\text{-}H)_2BC_8H_{14}\}_2$, and $Cp_2Ti\{(\mu\text{-}H)_2BR\}_2$ (where $Cp^* = C_5H_5$ and $C_5(CH_3)_5$; BR $= BC_5H_{10}$ and BC_8H_{14}). In our continuing studies of organohydroborate derivatives, we focus here on the preparation and molecular structures of titanium organohydroborate complexes that do not contain the cyclopentadienide ligand. In two of these complexes, α-C−H hydrogens on the BC_8H_{14} unit of the 9-BBN hydroborate ligand form an agostic interaction with the central titanium metal in the solid state. Even though organometallic compounds exhibiting agostic C−H···M interactions are known for most d-group elements including Ti(IV), few complexes of Ti(III) have been examined. Agostic interactions have attracted considerable interest since they often lead to C−H activation,[11,12] which can be important for organic, catalytic, and polymeric chemistry.[13]

Results and Discussion

I. Formation and Properties of $Ti\{(\mu\text{-}H)_2BC_8H_{14}\}_3(THF)_2$ (1), $Ti\{(\mu\text{-}H)_2BC_8H_{14}\}_3(OEt_2)$ (2), $Ti\{(\mu\text{-}H)_2BC_8H_{14}\}_3(PhNH_2)$ (3), and $[K(OEt_2)_4][Ti\{(\mu\text{-}H)_2BC_8H_{14}\}_4]$ (4). We attempted to prepare the 9-BBN hydroborate complex $Ti\{(\mu\text{-}H)_2BC_8H_{14}\}_3$ analagous to $Ti(BH_4)_3$. Since the 9-BBN hydroborate anion is only a bidentate ligand with respect to the formation of Ti−H−B bonds, it was of interest to determine to what extent the formation of C−H···Ti agostic interactions would compensate for the absence of additional B−H hydrogen to bind to Ti(III). Our attempts failed. Apparently, reaction of $TiCl_3$ with $K[H_2BC_8H_{14}]$ in toluene does not occur to any significant extent because the solubilities of both reactants are poor. When the coordinating solvents THF and diethyl ether were employed, the complexes $Ti\{(\mu\text{-}H)_2BC_8H_{14}\}_3(THF)_2$ (**1**) and $Ti\{(\mu\text{-}H)_2BC_8H_{14}\}_3(OEt_2)$ (**2**) were obtained in 40% and 42% yields from the reaction of $TiCl_4$ with 4 mol of $K[H_2BC_8H_{14}]$ in diethyl ether and THF, respectively (reactions 1 and 2). During the course of these reactions, the anion $[H_2BC_8H_{14}]^-$ functions as a bidentate ligand as well as a reducing agent to convert Ti(IV) to Ti(III). It in turn is oxidized to form a 9-BBN diborane, $[(C_8H_{14}B)(\mu\text{-}H)]_2$ (**5**), with evolution of H_2 gas.





Complexes **1** and **2** are green solids that are stable at room temperature in the absence of air. They are soluble in THF, diethyl ether, and benzene but slowly decompose to $[(C_8H_{14}B)(\mu\text{-}H)]_2$ (**5**) and unidentified products in solution. Reactions

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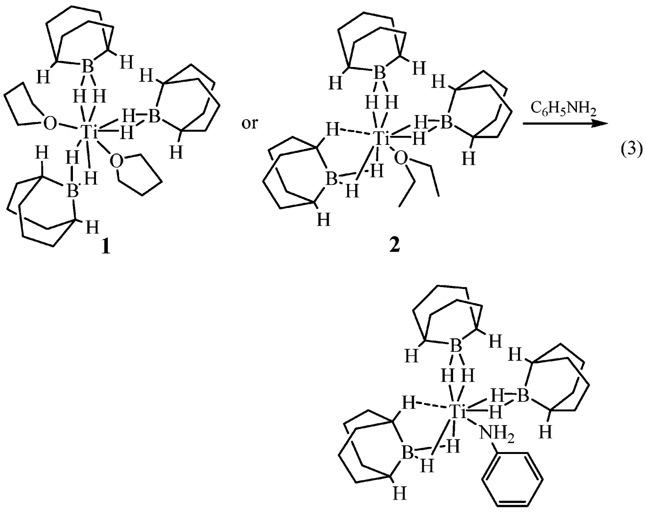
of $TiCl_4$ with $K[H_2BC_8H_{14}]$ in 1:2 and 1:3 mole ratios were performed, but only complex **1** or **2** formed, depending upon the solvent. The molecular structures, determined by single-crystal X-ray analyses, clearly showed the presence of an agostic interaction of one of the α-C−H hydrogens of a 9-BBN hydrobroate ligand with Ti(III) in complex **2**. Such an interaction appears to be absent in complex **1**. In complex **1**, Ti(III) is associated with 17 valence electrons. In complex **2** the Ti(III) is associated with 15 valence electrons from the 9-BBN hydroborate and diethyl ether ligands while the α-C−H hydrogen in the 9-BBN hydrobroate ligand contributes additional electron density. THF is a stronger Lewis base than diethyl ether. It apparently provides sufficient electron density to Ti(III) so that the interaction of Ti(III) with the α-C−H hydrogen is not required. On the other hand, the α-C−H interaction with Ti(III) in complex **2** suggests that its electron-donating ability is competitive with that of diethyl ether.

The reaction of complexes **1** and also **2** with aniline in reaction ratios varying from 1 mol of complex/mol of aniline up to 3 mol of aniline in diethyl ether, THF, and also toluene produced the unanticipated product $Ti\{(\mu\text{-}H)_2BC_8H_{14}\}_3(PhNH_2)$ (**3**) (reaction 3). Complex **3** is a dark green solid. It is air- and moisture-sensitive but less thermally sensitive than the diethyl ether and THF analogues.



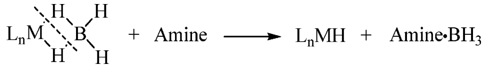
1 **2** (3)

3

The formation of **3** is of interest for several reasons. First of all, owing to the significant basicity of aniline, it is surprising that it is does not cleave the hydrogen bridge of the 9-BBN hydroborate ligand as expected.

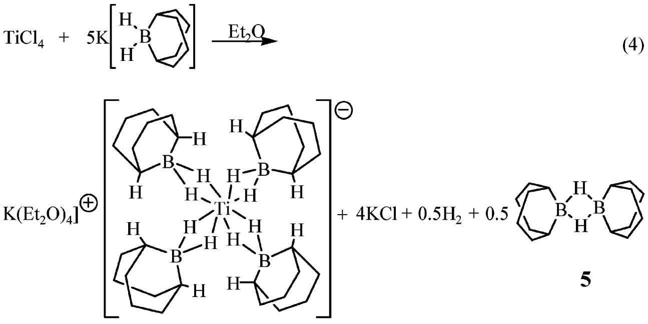
Second, while two THF's or Et_2O have been displaced by aniline from **1** and **2**, only one aniline coordinates to Ti(III) in compound **3**. To compensate for the electron deficiency created by replacement of two THF's of **1** by one aniline, an *agostic* interaction occurs between an α-C−H hydrogen of 9-BBN hydroborate ligand with Ti(III). As indicated above compounds with Ti(III) agostic interactions are rare.[14]

Scheme 1



The fact that tetrahydroborate derivatives of transition metals have been successfully employed for the preparation of hydrides by symmetrical cleavage of the hydrogen bridge (Scheme 1)[15] prompted us to attempt to obtain titanium hydrides for which a very high reactivity might be anticipated. However, from the reaction of complex **1** or **2** with pure aniline, we could not identify the product. After the reaction, a dark green solid was present. It does not dissolve in aniline.

The dark green complex $[K(OEt_2)_4][Ti\{(\mu\text{-}H)_2BC_8H_{14}\}_4]$ (**4**) was isolated from a diethyl ether reaction solution of $TiCl_4$ and $K[H_2BC_8H_{14}]$ in a 1:5 mole ratio (reaction 4). This compound is soluble in THF, diethyl ether, and benzene. Compared with complexes **1**−**3**, complex **4** is more stable as a solid at room temperature in the absence of air. The anion of complex **4** appears to be the first example of a Ti(III) bound to four (μ-H_2) bridging ligands.



(4)

4 **5**

^{11}B NMR spectra of all of the Ti(III) complexes could not be observed. The ^1H NMR spectra were very broad because of their proximity to the paramagnetic Ti(III) center. Infrared spectra of all the organohydroborate complexes reported here are similar. All of them show C−H stretches from 2995 to 2836 cm^{-1}. Extremely weak absorptions from 2654 to 2687 cm^{-1} are observed in the infrared spectra of **2** and **3**, respectively. Although these absorptions are consistent with the presence of agostic C−H···Ti interactions,[11] we believe that they are probably due to a very small amount of impurity because the bands are so weak, barely above the baseline, plus the fact that **4** does not contain an agostic interaction on the basis of X-ray single-crystal analysis.

II. Molecular Structures of Compounds 1−4. The solid-state structures of complexes **1**−**4** were determined by single-

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Table 1. Crystallographic Data for Ti{(μ-H)$_2$BC$_8$H$_{14}$}$_3$(THF)$_2$ (**1**), Ti{(μ-H)$_2$BC$_8$H$_{14}$}$_3$(OEt$_2$) (**2**), Ti{(μ-H)$_2$BC$_8$H$_{14}$}$_3$(PhNH$_2$) (**3**), and [K(OEt$_2$)$_4$][Ti{(μ-H)$_2$BC$_8$H$_{14}$}$_4$] (**4**)

	1	**2**	**3**	**4**
empirical formula	$C_{32}H_{64}B_3O_2Ti$	$C_{28}H_{58}B_3OTi$	$C_{60}H_{110}B_6N_2Ti_2$	$C_{48}H_{104}B_4KO_4Ti$
fw	561.16	475.085	1020.16	875.55
cryst syst	monoclinic	orthorhombic	triclinic	monoclinic
space group	$C2/c$	Pbca	$P\bar{1}$	$P2_1/n$
a, Å	17.4241(2)	20.3535(10)	11.0575(10)	10.88940(10)
b, Å	10.24600(10)	13.5503(10)	11.0868(10)	21.3740(2)
c, Å	18.5408(2)	21.6302(10)	26.5904(10)	24.0977(2)
α, deg	90	90	96.897(10)	90
β, deg	94.02	90	98.991(10)	92.82
γ, deg	90	90	107.892(10)	90
V, Å^3	3301.91(6)	5965.5(6)	3014.6(4)	5601.96(9)
Z	4	8	2	4
ρ(calcd), g cm^{-3}	1.129	1.094	1.124	1.038
T, K	200(2)	200(2)	150(2)	200(2)
μ, mm^{-1}	0.285	0.304	0.302	0.263
R$_1$^{a} [$I > 2.0\sigma(I)$]	0.0365	0.0405	0.0419	0.0756
wR$_2$^{b} (all data)	0.0466	0.0798	0.0645	0.0997

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$.

Table 2. Bond Lengths (Å) and Angles (deg) for Ti{(μ-H)$_2$BC$_8$H$_{14}$}$_3$(THF)$_2$ (**1**)

Ti−O(1)	2.1580(9)	Ti−O(1A)	2.1580(9)
Ti−B(10)	2.4337(15)	Ti−B(10A)	2.4337(15)
Ti−B(20)	2.421(2)	Ti−H(1)	1.843(17)
Ti−H(2)	1.857(15)	Ti−H(3)	1.819(16)
B(10)−H(1)	1.197(17)	B(10)−H(2)	1.237(16)
B(20)−H(3)	1.240(16)	C(11)−H(11A)	0.982(1)
O(1)−Ti−O(1A)	151.55(5)	O(1)−Ti−B(10)	83.29(5)
O(1)−Ti−B(10A)	88.74(5)	O(1)−Ti−B(20)	104.22(3)
O(1A)−Ti−B(10A)	88.74(5)	O(1A)−Ti−B(20)	104.22(3)
O(1A)−Ti−B(10)	83.29(5)	B(20)−Ti−B(10A)	106.41(4)
B(20)−Ti−B(10)	106.41(4)	B(10)−Ti−B(10A)	147.18(8)
Ti−B(10)−C(11)	132.58(10)	Ti−B(10)−C(15)	119.40(9)
Ti−B(20)−C(21)	125.61(9)	Ti−B(20)−C(25)	125.61(9)
H(1)−Ti−H(3)	88.1(7)	H(2)−Ti−H(3)	139.7(7)
H(2)−Ti−H(1)	57.8(7)	H(2)−B(10)−H(1)	94.5(11)
Ti−B(10)−H(2)	48.3(7)	Ti−B(10)−H(1)	47.2(8)
Ti−B(20)−H(3)	48.3(8)		

Table 3. Bond Lengths (Å) and Angles (deg) for Ti{(μ-H)$_2$BC$_8$H$_{14}$}$_3$(OEt$_2$) (**2**)

Ti(1)−O(1)	2.0912(13)	Ti(1)−B(1)	2.217(2)
Ti(1)−B(2)	2.417(2)	Ti(1)−B(3)	2.417(2)
Ti(1)−H(3B)	1.879(15)	Ti(1)−H(3A)	1.833(16)
Ti(1)−H(1B)	1.856(16)	Ti(1)−H(1A)	1.895(18)
Ti(1)−H(2B)	1.857(16)	Ti(1)−H(2A)	1.909(19)
B(1)−H(1A)	1.176(17)	B(1)−H(1B)	1.180(18)
B(2)−H(2A)	1.179(19)	B(2)−H(2B)	1.229(16)
B(3)−H(3A)	1.222(17)	B(3)−H(3B)	1.212(16)
Ti(1)···C(15)	2.561(2)	Ti(1)···H(15)	2.192(17)
C(15)−H(15)	0.941(9)		
O−Ti(1)−B(1)	100.87(8)	O−Ti(1)−B(2)	108.25(7)
O−Ti(1)−B(3)	99.28(7)	B(1)−Ti(1)−B(2)	114.75(9)
Ti−B(1)−C(11)	169.29(17)	Ti−B(1)−C(15)	82.13(13)
Ti−B(2)−C(21)	108.45(17)	Ti−B(2)−C(25)	128.54(14)
Ti−B(3)−C(31)	111.44(13)	Ti−B(3)−C(35)	140.74(15)
B(1)−Ti(1)−B(3)	126.60(9)	B(2)−Ti(1)−B(3)	104.66(8)
H(3B)−Ti(1)−H(3A)	57.2(7)	H(1B)−Ti(1)−H(1A)	55.9(7)
H(2B)−Ti(1)−H(2A)	58.5(7)	H(1B)−B(1)−H(1A)	96.5(12)
H(2B)−B(2)−H(2A)	99.7(12)	H(3B)−B(3)−H(3A)	93.7(11)

crystal X-ray diffraction analyses. Crystal data are given in Table 1, and structures are shown in Figures 1−4, while selected bond distances and angles are reported in Tables 2−5. Table 6 is a summary of Ti···H$_{\mathrm{agostic}}$ distances and Ti−C$_\alpha$−C$_\beta$ and Ti−B−C angles and where appropriate dihedral angles.

Table 4. Bond Lengths (Å) and Angles (deg) for Ti{(μ-H)$_2$BC$_8$H$_{14}$}$_3$(PhNH$_2$) (**3**)

Ti(1)−N(11)	2.2148(17)	Ti(1)−B(11)	2.204(2)
Ti(1)−B(12)	2.414(2)	Ti(1)−B(13)	2.386(2)
Ti(1)···C(115)	2.515(2)	Ti(1)···H(115)	2.15(2)
Ti(1)−H(1C)	1.831(19)	Ti(1)−H(1E)	1.791(19)
Ti(1)−H(1A)	1.87(2)	Ti(1)−H(1B)	1.91(2)
Ti(1)−H(1F)	1.830(19)	Ti(1)−H(1D)	1.87(2)
B(11)−H(1A)	1.18(2)	B(11)−H(1B)	1.202(19)
B(12)−H(1C)	1.243(18)	B(12)−H(1D)	1.17(2)
B(13)−H(1E)	1.214(19)	B(13)−H(1F)	1.217(19)
C(115)−H(115)	1.00(2)		
N−Ti−B(11)	102.33(8)	N−Ti−B(12)	85.83(7)
N−Ti−B(13)	111.28(7)	B(11)−Ti(1)−B(13)	117.72(9)
Ti(1)−B(11)−C(111)	170.74(16)	Ti(1)−B(11)−C(115)	80.26(12)
Ti(1)−B(12)−C(121)	131.48(14)	Ti(1)−B(12)−C(125)	120.14(14)
Ti(1)−B(13)−C(131)	127.53(15)	Ti(1)−B(13)−C(135)	123.42(15)
B(11)−Ti(1)−B(12)	130.29(8)	B(13)−Ti(1)−B(12)	103.83(8)
H(1A)−Ti(1)−H(1B)	56.5(8)	H(1E)−Ti(1)−H(1F)	59.7(8)
H(1C)−Ti(1)−H(1D)	58.1(9)	H(1A)−B(11)−H(1B)	97.8(13)
H(1C)−B(12)−H(1D)	96.6(13)	H(1E)−B(13)−H(1F)	95.7(13)

Table 5. Bond Lengths (Å) and Angles (deg) for [K(OEt$_2$)$_4$][Ti{(μ-H)$_2$BC$_8$H$_{14}$}$_4$] (**4**)

Ti−B(10)	2.386(4)	Ti−B(20)	2.391(4)
Ti−B(30)	2.398(4)	Ti−B(40)	2.389(4)
Ti−H(1)	1.87(3)	Ti−H(2)	1.89(3)
Ti−H(3)	1.83(4)	Ti−H(4)	1.85(3)
Ti−H(5)	1.84(3)	Ti−H(6)	1.83(4)
Ti−H(7)	1.89(3)	Ti−H(8)	1.83(4)
B(10)−H(1)	1.20(3)	B(10)−H(2)	1.18(3)
B(20)−H(3)	1.21(4)	B(20)−H(4)	1.25(3)
B(30)−H(5)	1.20(3)	B(30)−H(6)	1.12(4)
B(40)−H(7)	1.26(4)	B(40)−H(8)	1.19(4)
K−O(60)	2.639(4)	K−O(50)	2.671(3)
K−O(65)	2.686(4)	K−O(55)	2.765(4)
B(10)−Ti−B(40)	113.75(14)	B(10)−Ti−B(20)	116.91(14)
B(40)−Ti−B(20)	98.83(14)	B(10)−Ti−B(30)	99.37(13)
Ti(1)−B(10)−C(11)	120.5(2)	Ti(1)−B(10)−C(15)	131.7(2)
Ti(1)−B(20)−C(21)	130.0(3)	Ti(1)−B(20)−C(25)	122.8(3)
Ti(1)−B(30)−C(31)	129.5(3)	Ti(1)−B(30)−C(35)	125.0(3)
Ti(1)−B(40)−C(41)	133.7(3)	Ti(1)−B(40)−C(45)	118.1(3)
B(40)−Ti−B(30)	114.87(14)	B(20)−Ti−B(30)	114.04(15)
H(1)−Ti−H(2)	58.3(14)	H(3)−Ti−H(4)	60.8(17)
H(5)−Ti−H(6)	56.0(17)	H(7)−Ti−H(8)	59.9(16)
H(1)−B(10)−H(2)	101(2)	H(3)−B(20)−H(4)	98(2)
H(5)−B(30)−H(6)	96(3)	H(7)−B(40)−H(8)	99(2)

The molecular structure of **1** is shown in Figure 1. The geometry around the titanium metal center is that of a distorted trigonal bipyramid with three 9-BBN hydroborate

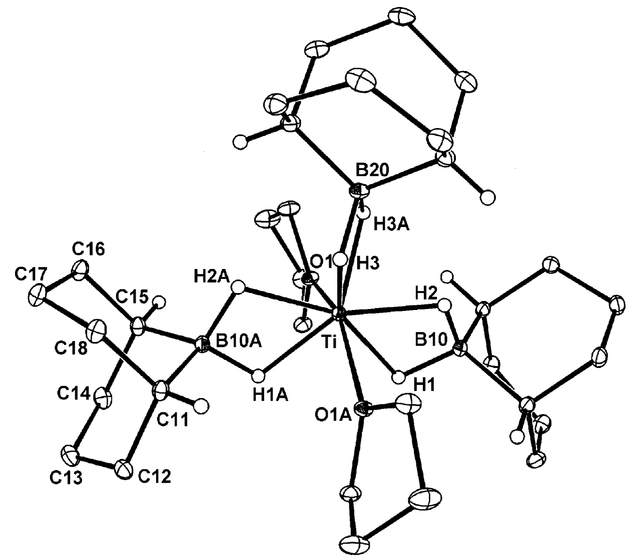

Figure 1. Molecular structure of Ti{(μ-H)$_2$BC$_8$H$_{14}$}$_3$(THF)$_2$ (**1**).

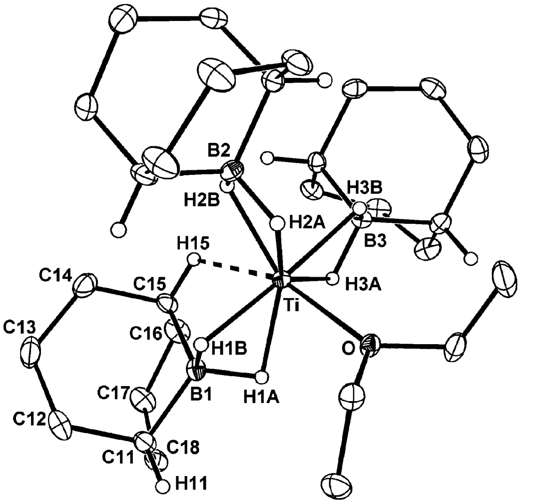

Figure 2. Molecular structure of Ti{(μ-H)$_2$BC$_8$H$_{14}$}$_3$(OEt$_2$) (**2**).

ligands defining the equatorial plane (B(20)−Ti−B(10A) = 106.41(4)°, B(20)−Ti−B(10) = 106.41(4)°, B(10)−Ti−B(10A) = 147.18(8)°). Two molecules of THF are in the axial positions trans with respect to each other (O(1)−Ti−O(1A) = 151.55(5)°). The coordination geometry resembles that previously reported for Ti(BH$_4$)$_3$(PMe$_3$)$_2$[3i]. Complex **1** possesses crystallographically imposed 2-fold symmetry with the axis passing through Ti and B(20). The Ti···B distances of this complex are very close to each other, 2.421(2) and 2.4337(15) Å. They are slightly longer than those in a known Ti(III) tetrahydroborate complex: Cp$_2$Ti(η^2-BH$_4$)[7,16] (Ti···B = 2.37(1) Å). Because of the larger size of Ti(III) versus Ti(IV), the Ti−B distance of complex **1** is larger than those observed in Ti(IV) tetrahydroborate complexes, [Me$_3$CNCH$_2$CH$_2$NCMe$_3$]Ti(Cl)(BH$_4$)[8] (Ti···B = 2.175(4) Å) and [Me$_3$CNCH$_2$CH$_2$NCMe$_3$]Ti(BH$_4$)$_2$[8] (Ti···B = 2.304(3) Å and Ti···B = 2.175(3) Å) and they are shorter in Ti(II) tetrahydroborate complexes, Cp*Ti(η^2-BH$_4$)[η^2-(Me$_2$PCH$_2$)$_3$Si(t-Bu)][3j] (Ti···B = 2.445(7) Å) and Ti(BBH$_4$)$_2$(dmpe)$_2$[3j] (Ti···B = 2.534(3) Å). The average titanium bridge hydrogen distance in **1** is 1.840 Å. This is similar to the corresponding titanium bridge hydrogen distance in the titanium(III) derivative Cp$_2$Ti(μ-H)$_2$BC$_8$H$_{14}$}.[17]

Figure 2 presents the molecular structure of complex **2**. There is an interaction between the C−H hydrogen on one of the 9-BBN hydroborate ligands and the titanium(III) metal center. The distance of Ti···H(15) is 2.192(17) Å, comparable to the agostic hydrogen···metal distances in known Ti(IV) complexes.[18,19] Compared with d^0 transition metal complexes, agostic hydrogen interactions with d^1 transition metals are rare. This interaction results in a Ti···B(1) distance of 2.217(2) Å that it is significantly shorter than those of 2.417(2) Å of Ti···B(2) and 2.417(2) Å of Ti···B(3), where an agostic interaction is not involved. Furthermore, the Ti−B(1)−C(15) angle of 82.13(13)° is much smaller than those angles Ti−B(1)−C(11) (169.29(17)°), Ti−B(2)−C(21) (108.45(17)°), Ti−B(2)−C(25) (128.54(14)°), Ti−B(3)−C(31) (111.44(13)°), and Ti−B(3)−C(35) (140.74(15)°), thereby providing additional strong evidence for the interaction between the titanium and H(15). The distorted tetrahedral geometry about the titanium atom (B(1)−Ti−B(2) = 114.75(9)°, B(1)−Ti−B(3) = 126.60(9)°, B(2)−Ti−B(3) = 104.66(8)°, O−Ti−B(1) = 100.87(8)°, O−Ti−B(2) = 108.25(7)°, O−Ti−B(3) = 99.28(7)°) is defined by three 9-BBN hydroborate ligands and one molecule of diethyl ether (Ti−O = 2.0912(13) Å). The average titanium bridge hydrogen bond lengths in **2** is 1.871 Å.

The molecular structure of **3** is shown in Figure 3. Complex **3** is isostructural and isoelectronic with complex **2**; the titanium center adopts a distorted tetrahedral stereochemistry which is similar to that in complex **2** (N−Ti(1)−B(11) = 102.33(8)°, N−Ti(1)−B(12) = 85.83(7)°, N−Ti(1)−B(13) = 111.28(7)°, B(11)−Ti(1)−B(13) = 117.72(9)°, B(11)−Ti(1)−B(12) = 130.29(8)°, B(13)−Ti(1)−B(12) = 103.83(8)). Ti is bound by three 9-BBN hydroborate ligands and one molecule of coordinated aniline (Ti(1)−N(1) = 2.214(8) Å); the Ti−N distance is normal and compares well with that of the other titanium borohydride complex

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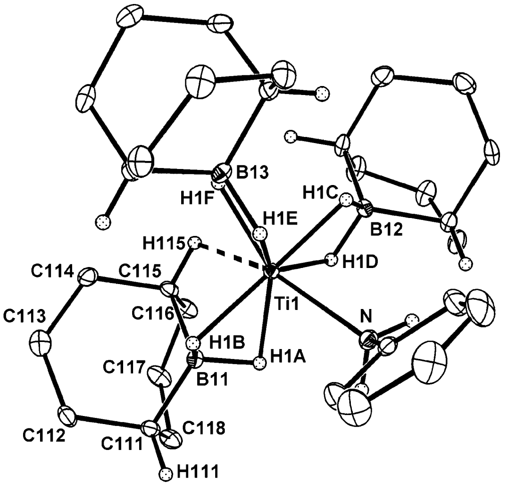

Figure 3. Molecular structure of Ti{(μ-H)$_2$BC$_8$H$_{14}$}$_3$(PhNH$_2$) (**3**).

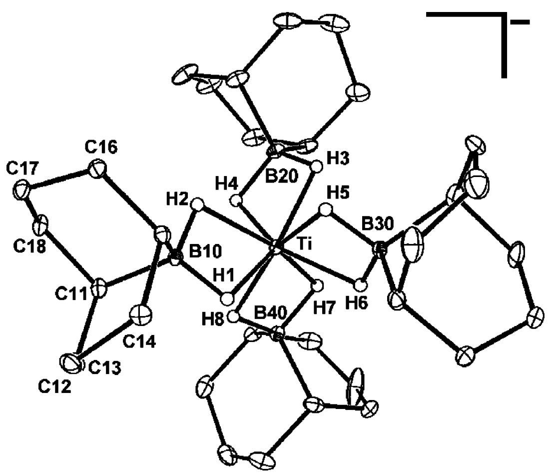

Figure 4. Molecular structure of the anion of [K(OEt$_2$)$_4$][Ti{(μ-H)$_2$BC$_8$H$_{14}$}$_4$] (**4**).

[(Me$_2$Si$_2$N]Ti(py)$_2$(BH$_4$)$_2$[20] (Ti(1)−N(1) = 2.214(3) Å, Ti(1)−N(2)= 2.221(3) Å). Like complex **2**, there is a strong interaction between Ti and the α-hydrogen in one 9-BBN hydroborate ligand. The Ti(1)−H(115) distance of 2.15(2) Å is also shorter than that in complex **2** (2.192(17) Å) as well. The Ti(1)−B(11) distance of 2.204(2) Å in the 9-BBN hydroborate ligand with α-agostic hydrogen is shorter than the Ti(1)−B(12) distance of 2.414(2) Å and Ti(1)−B(13) distance of 2.386(2)Å in the other two 9-BBN hydroborate ligands with no agostic hydrogen. Like complex **2**, the Ti−B(11)−C(115) angle of 80.26(12)° is much smaller than the angles of Ti(1)−B(11)−C(111) (170.74(16)°), Ti(1)−B(12)−C(125) (120.14(14)°), Ti(1)−B(12)−C(121) (131.48(14)°), Ti(1)−B(13)−C(131) (127.53(15)°), and Ti−B(13)−C(135) (123.42(15)°) due to the agostic hydrogen interaction in complex **3**. The average titanium bridge hydrogen bond length in **3** is 1.850 Å.

The molecular structure consists of [K(OEt$_2$)$_4$][Ti{(μ-H)$_2$BC$_8$H$_{14}$}$_4$] (**4**) as a discrete cation and anion pair. The organometallic anion [ML$_4$]$^-$ for titanium(III) is rare; however, the Ti(IV) organometallic anions [Ti(CH$_3$)$_5$]$^-$ and [Ti$_2$(CH$_3$)$_9$]$^-$ are known.[21] The anion [Ti{(μ-H)$_2$BC$_8$H$_{14}$}$_4$]$^-$, shown in Figure 4, is composed of four 9-BBN hydroborate ligands arranged in a slightly distorted tetrahedral fashion around the titanium atom [B(10)−Ti−B(40) = 113.17(14)°, B(10)−Ti−B(20) = 116.91(14)°, B(40)−Ti−B(20) = 98.83(14)°, B(10)−Ti−B(30) = 99.37(13)°, B(40)−Ti−B(30) = 114.87(14)°, B(20)−Ti−B(30) = 114.04(15)°], with each of the 9-BBN hydroborates functioning as a bidentate ligand, bound to the titanium ion through two hydrogen bridges as those in **1**−**3**. The Ti−B distances in this anion are similar to each other, Ti−B(10) = 2.386(4) Å, Ti−B(20) = 2.391(4) Å, Ti−B(30) = 2.398(4) Å, and Ti−B(40) = 2.389(4) Å. They are in agreement with those in titanocene organohydroborates, Cp$_2$Ti{(μ-H)$_2$BR$_2$} (R$_2$ = C$_4$H$_8$, 2.409(4) Å, C$_5$H$_{10}$, 2.446(3) Å, and C$_8$H$_{14}$, 2.428(2) Å).[10g]

III. Agostic Interactions in Complexes 2 and 3. It is now well-known that "when a transition metal center has a vacant orbital of suitable energy and direction, C−H groups, even of an aliphatic system, can act essentially as a "lone pair" which can donate to suitable empty metal orbitals; suitable metal centers are likely to be found for ≤16-electron transition metal complexes".[18f] Many examples of agostic interactions are known,[11] identified through X-ray and neutron diffraction, infrared and NMR spectroscopy, and also, where appropriate, ESR spectroscopy. Such interactions have also been the subject of theoretical studies.[18a−c]

Agostic hydrogen−metal interactions can occur over a continuum of distances. A question of practical value is when can the approach of a C−H hydrogen to a transition metal be called an agostic interaction on the basis of structural evidence? To make an informed decision, we believe that several criteria must be considered for the existence of an agostic interaction. These could include a "short" metal-hydrogen distance, a "short" metal---carbon distance, a reduced bond angle M−C−C (M−B−C for complexes **2** and **3**), and a reduced dihedral angle between the TiH$_2$ and H$_2$B planes (for complexes **2** and **3**) that arise from the C−H hydrogen interacting with the unsaturated metal. (At a dihedral angle of 180°, the α-C−H hydrogens of the 9-BBN hydroborate ligand are farthest from the metal.) Furthermore, since there is no absolute value for distance or angle, one must compare these values with related structural features in the molecule where an agostic interaction is unlikely. These comparisons are made in the discussions concerned with structural data given in Tables 2−6.

From analyses of structural reports, Green and Brookhart[11b,d] suggest that a metal−hydrogen distance no larger than 1.2 times the distance of a normal M−H distance would be consistent with an agostic interaction. This approxamation suffers from the fact that terminal M−H bond distances are dependent upon their environment. Later we suggested that a distance less than the sum of the metal covalent radius and the hydrogen van der Waals radius implys an agostic interaction.[9] With a covalent radius of 1.45 Å for Ti and a van der Waals radius of 1.2 Å[22] for H, the limiting distance

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Table 6. Distance of Ti···H (Å), Angles of Ti−C−C or Ti−B−C (deg), and Dihedral Angles (deg)

compound	Ti···$H_{agostic}$	Ti−C−C or Ti−B−C	dihedral angles of TiH_2 and H_2B
$Ti^{III}(BBN)_3OEt_2$ (**2**)	2.19(2)[a]	82.13(13)[a]	127.3[a]
this work	3.60[b,c]	128.53 (14)[b]	158.0[b]
		140.73(15)[b]	172.3[b]
$Ti^{III}(BBN)_3PhNH_2$ (**3**)	2.15(2)[a]	80.26(12)[a]	124.1[a]
this work	3.60[b,c]	120.14(14)[b]	170.8[b]
		123.42(15)[b]	179.8[b]
$[EtTi^{IV}(PH_3)H$[18a]	2.23[a,d]	88.8[a,d]	
$[EtTi^{IV}Cl_2]^+$ [18b]	2.06[a,d]	85.0[a,d]	
$Ti^{IV}(Cl)_3(dmpe)Et$[18c−f]	2.12[a,d]	85.1[a,d]	
	2.10[a]	84.5(1)[a]	
	2.11(8)[a]	84.0(4)[a]	
	2.06(2)[a]	84.57(9)[a]	
	2.29[a]	85.89(58)[a]	
$CpTi^{IV}(Cl)_2[N(^iC_3H_7)_2]$[18h]	2.25[a]	101.4(2) (Ti−N−C)	

[a] Agostic interaction. [b] No agostic interaction. [c] Average distances of Ti···H. [d] Calculated.

for an agostic interaction according to our criterion is about 2.6 Å. This “loose” criterion should be supported by angular criteria discussed above.

Table 6 lists Ti···H distances for agostic interactions, bond angles, and where appropriate dihedral angles for complexes **2** and **3** and several other titanium(III) complexes. It is noted that for complexes **2** and **3** there is clearly one agostic interaction for each compound with distances and angles in good accord with values reported for other complexes in Table 6. Complexes **2** and **3** also have a Ti···H distance that is well beyond the limit of our critereon for an agostic interaction which is also reflected in the relatively large angles.

Experimental Section

General Procedures. All manipulations were carried out on a standard high-vacuum line or in a drybox under a nitrogen or argon atmosphere. Diethyl ether, tetrahydrofuran, and toluene were dried over sodium/benzophenone and freshly distilled prior to use. Hexane was stirred over concentrated sulfuric acid for 2 days and then decanted and washed with water. Next, the hexane was stirred over calcium hydride for 6 days, decanted and stirred over sodium/benzophenone for 5 days, and finally distilled into a storage bulb containing sodium/benzophenone. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were vacuum transferred from a Na/K alloy before use. $TiCl_4$ and $[(C_8H_{14}B)(\mu\text{-}H)]_2$ (9-BBN dimer) were purchased from Aldrich and used as received. Potassium hydride (35 wt % dispersion in mineral oil) was purchased from Aldrich and was washed with hexane prior to use. $K[H_2BC_8H_{14}]$[10f,23] was prepared by literature procedures. NMR spectra were recorded on a Bruker AM-250 NMR spectrometer operating at 250.11 at 303 K, and boron-11 spectra were externally referenced to BF_3OEt_2 ($\delta = 0.00$ ppm). Infrared spectra were recorded on a Mattson Polaris Fourier transform spectrometer with 2 cm^{-1} resolution. Elemental C and H analyses were done by Galbraith Laboratories, Inc.

X-ray Structure Determination. Suitable crystals of $Ti\{(\mu\text{-}H)_2BC_8H_{14}\}_3(THF)_2$ (**1**) were grown from THF solution, and $Ti\{(\mu\text{-}H)_2BC_8H_{14}\}_3(OEt_2)$ (**2**), $Ti\{(\mu\text{-}H)_2BC_8H_{14}\}_3(PhNH_2)$ (**3**), and $[K(OEt_2)_4][Ti\{(\mu\text{-}H)_2BC_8H_{14}\}_4]$ (**4**) were grown from diethyl ether solution. Single-crystal X-ray diffraction data were collected using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å) on a Nonius KappaCCD diffraction system. Single crystals of **1**−**4** were mounted on the tip of a glass fiber coated with Fomblin oil (a perfluoro polyether, Aldrich). Crystallographic data was collected at 200 K for **1**, **2,** and **4** and 150 K for **3**. Unit cell parameters were obtained by indexing the peaks in the first 10 frames and refined by employing the whole data set. All frames were integrated and corrected for Lorentz and polarization effects using the Denzo-SMN package (Nonius BV, 1999).[24] All of the structures were solved by direct methods and refined using the SHELXTL-97 (difference electron density calculation, full-matrix least-squares refinements) structure solution package.[22] For each structure, all the non-hydrogen atoms were located and refined anisotropically. There are two independent molecules in the asymmetric unit cell of **3**.

Preparation of $Ti\{(\mu\text{-}H)_2BC_8H_{14}\}_3(THF)_2$ (1). A solution of $K[H_2BC_8H_{14}]$ (324.2 mg, 2.0 mmol) in 50 mL of THF was added dropwise to a solution of $TiCl_4$ (94.8 mg, 0.5 mmol) in 100 mL of THF. H_2 gas was observed at beginning of the reaction. After the solution was stirred at room temperature for 12 h, the white solid (KCl) was removed by filtration and a green product was obtained after removing the solvent under vacuum, This green solid was redissolved in ether and kept at −30 °C for crystallization. Green crystalline $Ti\{(\mu\text{-}H)_2BC_8H_{14}\}_3(THF)_2$ was obtained in 40% yield. IR (KBr): 2983 (w), 2922 (m), 2870 (s), 2836 (m), 1704 (s), 1655 (m), 1297 (m), 1109 (m), 1052 (m, br), 896 (m), 803 (w). Anal. Calcd for $C_{32}H_{64}B_3O_2Ti$: C, 68.49; H, 11.50. Found: C, 68.28; H, 11.82.

Preparation of $Ti\{(\mu\text{-}H)_2BC_8H_{14}\}_3(OEt_2)$ (2). A solution of $K[H_2BC_8H_{14}]$ (324.2 mg, 2.0 mmol) in 50 mL of diethyl ether was added dropwise to a solution of $TiCl_4$ (94.8 mg, 0.5 mmol) in 100 mL of diethyl ether. H_2 gas was observed at beginning of the reaction. After the solution was stirred at room temperature for 12 h, the white solid (KCl) was removed by filtration and a green product was obtained after removing the solvent under vacuum. This green solid was redissolved in ether and kept at −30 °C for crystallization. Green crystalline $Ti\{(\mu\text{-}H)_2BC_8H_{14}\}_3(OEt_2)$ was obtained in 42% yield. IR (KBr): 2982 (m), 2953 (m), 2862 (s), 2838 (s), 2661 (w), 2654 (w), 1960 (m), 1956 (m), 1562 (m), 1461 (m), 1356 (s), 1328 (m), 1226 (w), 1107 (m), 1084 (w), 1036 (w), 892 (m), 823 (w). Anal. Calcd for $C_{28}H_{58}B_3OTi$: C, 68.48; H, 11.90. Found: C, 68.68; H, 12.02.

Preparation of $Ti\{(\mu\text{-}H)_2BC_8H_{14}\}_3(PhNH_2)$ (3). A solution of $PhNH_2$ (46.6 mg, 0.5 mmol) in 10 mL of diethyl ether was added dropwise to a solution of $Ti\{(\mu\text{-}H)_2BC_8H_{14}\}_4(OEt_2)$ (245.5 mg, 0.5 mmol) in 10 mL of diethyl ether. After the solution was stirred at room temperature for 12 h, the white solid (KCl) was removed by filtration and a green product was obtained after removing the solvent under vacuum. This green solid was redissolved in ether and kept at −30 °C for crystallization. Green crystalline $Ti\{(\mu\text{-}H)_2BC_8H_{14}\}_3(PhNH_2)$ was obtained in 90% yield. IR (KBr): 2983 (w), 2918 (s), 2876 (s), 2838 (s), 2687 (w), 2654 (w), 1996 (w), 1397 (s), 1286 (m), 1208 (m), 1052 (m), 931 (w), 892 (w), 802 (w). Anal. Calcd for $C_{30}H_{55}B_3NTi$: C, 70.64; H, 10.87. Found: C, 70.06; H, 11.21.

Preparation of $[K(OEt_2)_4][Ti\{(\mu\text{-}H)_2BC_8H_{14}\}_4]$ (4). A solution of $K[H_2BC_8H_{14}]$ (324.2 mg, 2.0 mmol) in 50 mL of diethyl ether was added dropwise to a solution of $TiCl_4$ (75.9 mg, 0.4 mmol) in

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[23] (a) Singaram, B.; Cole, T. E.; Brown, H. C. *Organometallics* **1984**, *3*, 1520. (b) Köster, R.; Seidel, G. *Inorg. Synth.* **1983**, *22*, 198.

[24] Otwinowski, Z.; Minor, W. In *Methods in Enzymology*; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1997; Vol. 276A, p 307.

100 mL of diethyl ether. H_2 gas was observed at beginning of the reaction. After the solution was stirred at room temperature for 12 h, the white solid (KCl) was removed by filtration and a dark green product was obtained after removing the solvent under vacuum. This dark green solid was redissolved in ether and kept at −30 °C for crystallization. Dark green crystalline $[Ti\{(\mu\text{-}H)_2BC_8H_{14}\}_4]$-$[K(OEt_2)_4]$ was obtained in 80% yield. IR (KBr): 2995 (m), 2954 (m), 2931 (m, br), 2886 (s), 2836 (m), 2688 (w), 2657 (w), 1573 (m), 1562 (m), 1401 (w), 1308 (w), 1194 (w), 1108 (w), 1077 (w), 890 (m), 825 (w). Anal. Calcd for $C_{48}H_{104}B_4O_4Ti$: C, 65.85; H, 11.97. Found: C, 65.68; H, 12.02.

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Supporting Information Available: Detailed X-ray structural data including a summary of crystallographic parameters, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and H atom coordinates for **1**−**4** (CIF) and IR spectra for **1**−**4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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