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Titanium(II) and Titanium(III) Tetrahydroborates. Crystal Structures of $[Li(Et_2O)_2][Ti_2(BH_4)_5(PMe_2Ph)_4]$, $Ti(BH_4)_3(PMe_2Ph)_2$, and $Ti(BH_4)_3(PEt_3)_2$

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The molecular structures of the titanium(III) borohydride complexes $Ti(BH_4)_3(PEt_3)_2$ and $Ti(BH_4)_3(PMe_2Ph)_2$ have been determined. If the BH_4 groups are considered to occupy one coordination site, both complexes adopt distorted trigonal bipyramidal structures with the phosphines in the axial sites; the P–Ti–P angles deviate significantly from linearity and are near 156°. In both compounds, two of the three BH_4 groups are bidentate and one is tridentate. The deduced structures differ from the one previously described for the PMe_3 analogue $Ti(BH_4)_3(PMe_3)_2$, in which two of the tetrahydroborate groups were thought to be bound to the metal in an unusual "side-on" (η^2-B,H) fashion. Because the PMe_3, PEt_3, and PMe_2Ph complexes have nearly identical IR spectra, they most likely have similar structures. The current evidence strongly suggests that the earlier crystal structure of $Ti(BH_4)_3(PMe_3)_2$ was incorrectly interpreted and that these complexes all adopt structures in which two of the BH_4 groups are bidentate and one is tridentate. The synthesis of the titanium(III) complex $Ti(BH_4)_3(PMe_2Ph)_2$ affords small amounts of a second product: the titanium(II) complex $[Li(Et_2O)_2][Ti_2(BH_4)_5(PMe_2Ph)_4]$. The $[Ti_2(BH_4)_5(PMe_2Ph)_4]^-$ anion consists of two $Ti(\eta^2\text{-}BH_4)_2(PMe_2Ph)_2$ centers linked by a bridging η^2,η^2-BH_4 group that forms a Ti···(μ-B)···Ti angle of 169.9(3)°. Unlike the distorted trigonal bipyramidal geometries seen for the titanium(III) complexes, the metal centers in this titanium(II) species each adopt nearly ideal tbp geometries with P–Ti–P angles of 172–176°. All three BH_4 groups around each Ti atom are bidentate. One of the BH_4 groups on each Ti center bridges between Ti and an ether-coordinated Li cation, again in an η^2,η^2 fashion. The relationships between the electronic structures and the molecular structures of all these titanium complexes are briefly discussed.

Introduction

We have previously reported that the titanium(III) tetrahydroborate complex $Ti(BH_4)_3(Et_2O)_2$[1] reacts with tertiary phosphines to afford diadducts of the type $Ti(BH_4)_3(PR_3)_2$, where PR_3 is PMe_3 (**1**), PEt_3 (**2**), or PMe_2Ph (**3**).[2,3] At that time, we carried out a crystallographic study of $Ti(BH_4)_3(PMe_3)_2$, which suggested that two of the tetrahydroborate groups were bound to the metal in an unprecedented "side-on" fashion[4] involving three-center Ti···H−B interactions. The structure was similar to those in molecular dihydrogen complexes, in certain transition metal silane complexes, in compounds containing agostic M···H−C bonds, and to the transition state thought to be responsible for alkane activation processes.[5]

Three-center M···H−B interactions had been described previously in several transition metal carborane complexes.[6,7] Following our study of $Ti(BH_4)_3(PMe_3)_2$, other examples of "side-on" M···H−B interactions have been discovered, most notably those in catecholborane and pinacolborane complexes such as $Cp_2Ti(HBcat)_2$,[8] $Cp'Mn(HBcat)(CO)_2$,[9] $Cp_2Ti(HBcat)(PMe_3)$,[10] and $Ru(HBpin)(H_2Bpin)H(PCy_3)_2$.[11]

Although the locations of the hydrogen atoms in $Ti(BH_4)_3(PMe_3)_2$, as deduced from the X-ray diffraction experiment,

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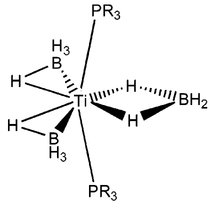
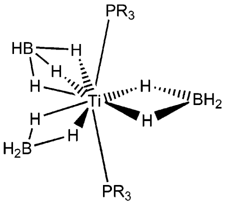
strongly suggested the side-on structure **A**, we considered



A



B

an alternative structural model in which the apparent presence of two side-on BH_4 groups was an artifact of disordering of a bidentate and a tridentate tetrahydroborate ligand across the crystallographic mirror plane, and that the actual molecular structure was structure **B**. For several reasons (to be discussed below), we concluded that structure **B** was less consistent with the data.

Some years after our work, Volatron and co-workers[12] carried out a theoretical study of the structure of $Ti(BH_4)_3(PMe_3)_2$. They found that the side-on structure **A** was not the ground state and that instead the lowest-energy geometry was structure **B**. The energy of structure **A** was calculated to be some 40 kcal/mol higher than that of structure **B**; furthermore, structure **A** was not even a local minimum on the potential energy surface. Their results extended theoretical calculations on $Ti(BH_4)_3L_2$ molecules previously reported by Rankin et al.[13]

Volatron's theoretical results, combined with residual doubts about the interpretation of our original X-ray work, prompted us to undertake a reinvestigation of the nature of the BH_4 binding modes in these complexes. We now report single-crystal X-ray diffraction studies of $Ti(BH_4)_3(PEt_3)_2$, $Ti(BH_4)_3(PMe_2Ph)_2$, and the novel Ti^{II} complex $[Li(Et_2O)_2][Ti_2(BH_4)_5(PMe_2Ph)_4]$. A summary of the relationship between the electronic structures and the molecular structures of these complexes is also presented.

Results

Synthesis and Characterization of $Ti(BH_4)_3(PR_3)_2$ Complexes. Treatment of $Ti(BH_4)_3(Et_2O)_2$[1] with 2 equiv of PEt_3 or PMe_2Ph, followed by crystallization from pentane/diethyl ether at −20 °C, gives blue crystals of the known[3] titanium(III) complexes $Ti(BH_4)_3(PEt_3)_2$ (**2**) and $Ti(BH_4)_3(PMe_2Ph)_2$ (**3**). As previously noted, strong infrared absorption bands at 2410, 2367, and 2115 cm^{-1} in the spectra of all three compounds indicate that both molecules contain at least one bidentate BH_4 group. A band at 2538 cm^{-1} signals the presence of another type of BH_4 binding mode.[14−16] This IR band could arise from a tridentate BH_4 group, but the X-ray crystal structure of the PMe_3 adduct $Ti(BH_4)_3(PMe_3)_2$ led us to conclude in 1988 that the IR band was due to the presence of the two side-on BH_4 groups.

Table 1. Crystallographic Data for $Ti(BH_4)_3(PEt_3)_2$ (**2**), $Ti(BH_4)_3(PMe_2Ph)_2$ (**3**), and $[Li(Et_2O)_2][Ti_2(BH_4)_5(PMe_2Ph)_4]$ (**4**)

	$TiB_3P_2C_{12}H_{42}$	$TiB_3P_2C_{16}H_{34}$	$Ti_2B_5P_4C_{40}H_{84}O_2Li$
T, °C	−75	−75	−75
space group	$P\bar{1}$	$C2/c$	$P2_1/c$
a, Å	8.0034(13)	14.4241(16)	12.4470(5)
b, Å	18.148(3)	12.7139(22)	18.1710(8)
c, Å	30.347(8)	13.3805(24)	24.0671(10)
α, deg	86.89(2)	90	90
β, deg	83.636(12)	116.380(12)	98.0380(10)
γ, deg	84.104(12)	90	90
V, Å^3	4353.5(15)	2198.3(6)	5389.9(4)
Z	8	4	4
M_r	328.73	368.70	977.74
ρ_{calcd}, g cm^{-3}	1.003	1.114	1.082
λ, Å	0.71073	0.71073	0.71073
μ_{calcd}, cm^{-1}	5.26	5.29	4.43
transmissn coeff	0.791−0.897	0.741−0.894	0.844−0.942
R_F[a]	0.0714	0.0272	0.0927
R_{wF}[b]	0.2113	0.0694	0.1993

[a] $R_F = \sum(||F_o| - |F_c||)/\sum|F_o|$ for reflections with $F_o^2 > 2\sigma(F_o^2)$. [b] $R_{wF} = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ for all reflections.

In our 1988 study, X-ray diffraction data for either **2** or **3** could not be obtained because we were unable to mount crystals of these highly reactive and low-melting compounds in capillaries. In the present reinvestigation, we have been able to collect data from crystals of $Ti(BH_4)_3(PEt_3)_2$ and $Ti(BH_4)_3(PMe_2Ph)_2$ by avoiding the use of capillaries and instead mounting the crystals at low temperatures on glass fibers with chilled Paratone oil. Crystal data for both compounds are given in Table 1. Tables 2 and 3 give selected bond lengths and angles for the two compounds.

Unlike molecules of the PMe_3 complex $Ti(BH_4)_3(PMe_3)_2$, which reside on crystallographic mirror planes,[3] molecules of the PEt_3 complex **2** reside on general positions within the unit cells. The asymmetric unit contains four independent molecules, all four of which have very similar structures.

We will begin our discussion by focusing on molecule 1 because it was the best behaved. If the BH_4 groups in $Ti(BH_4)_3(PEt_3)_2$ are each considered to occupy one coordination site, the five ligands about the Ti center in molecule 1 describe a distorted trigonal bipyramid with the phosphines in the axial sites (Figure 1). The structural feature of greatest interest is as follows: of the three BH_4 groups in **2**, *one is clearly tridentate and two are clearly bidentate*, as judged both from the Ti···B distances and from the locations of the hydrogen atoms. The hydrogen atoms were readily apparent in the difference maps, and their positions were refined subject to light restraints (see Experimental Section).

The average Ti···B(η^2) distance of 2.448(5) Å is longer than the tridentate Ti···B(η^3) distance of 2.194(5) Å by 0.254

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Table 2. Important Bond Lengths (Å) and Angles (deg) for $Ti(BH_4)_3(PEt_3)_2$ (**2**)

Bond Lengths			
Ti1−P1	2.6271(14)	P2−C21	1.830(4)
Ti1−P2	2.6244(14)	P2−C23	1.869(4)
Ti1···B1	2.191(5)	P2−C25	1.827(4)
Ti1···B2	2.446(5)	B1−H11	1.10(2)
Ti1···B3	2.449(5)	B1−H12	1.11(2)
Ti1−H11	2.03(3)	B1−H13	1.10(2)
Ti1−H12	2.15(3)	B1−H14	1.08(2)
Ti1−H13	2.01(3)	B2−H21	1.16(2)
Ti1−H21	1.98(3)	B2−H22	1.16(2)
Ti1−H22	1.97(3)	B2−H23	1.13(2)
Ti1−H31	2.03(3)	B2−H24	1.13(2)
Ti1−H32	1.97(3)	B3−H31	1.10(2)
P1−C11	1.816(5)	B3−H32	1.12(2)
P1−C13	1.846(5)	B3−H33	1.08(2)
P1−C15	1.838(5)	B3−H34	1.10(2)
Bond Angles			
P1−Ti1−P2	155.71(5)	Ti1−B2−H23	124.8(15)
B1−Ti1−B2	118.71(19)	Ti1−B2−H24	122.1(15)
B2−Ti1−B3	123.10(17)	Ti1−B3−H33	126.9(16)
B1−Ti1−B3	118.19(19)	Ti1−B3−H34	120.7(15)
P1−Ti1−B1	98.90(14)	H11−B1−H12	106.0(14)
P1−Ti1−B2	86.12(12)	H12−B1−H13	108.6(14)
P1−Ti1−B3	84.80(12)	H11−B1−H13	108.0(14)
P2−Ti1−B1	105.37(14)	H11−B1−H14	111.5(14)
P2−Ti1−B2	83.13(12)	H12−B1−H14	110.9(14)
P2−Ti1−B3	82.97(13)	H13−B1−H14	111.7(14)
H11−Ti1−H12	49.8(10)	H21−B2−H22	105.7(13)
H12−Ti1−H13	50.6(10)	H22−B2−H23	109.7(13)
H11−Ti1−H13	52.5(10)	H21−B2−H23	109.6(13)
H21−Ti1−H22	55.8(11)	H21−B2−H24	109.3(13)
H31−Ti1−H32	52.9(11)	H22−B2−H24	109.2(13)
Ti1−P1−C11	117.33(17)	H23−B2−H24	113.1(13)
Ti1−P1−C13	109.48(16)	H31−B3−H32	107.4(13)
Ti1−P1−C15	118.48(17)	H32−B3−H33	109.1(13)
Ti1−P2−C21	116.72(15)	H31−B3−H33	111.0(13)
Ti1−P2−C23	111.36(14)	H31−B3−H34	109.3(13)
Ti1−P2−C25	117.18(15)	H32−B3−H34	107.6(13)
Ti1−B1−H14	175.9(17)	H33−B3−H34	112.3(14)

Table 3. Important Bond Lengths (Å) and Angles (deg) for $Ti(BH_4)_3(PMe_2Ph)_2$ (**3**)

Bond Lengths			
Ti−P	2.5950(4)	B1−H11	1.18(1)
Ti···B1	2.450(2)	B1−H12	1.21(1)
Ti···B2	2.195(3)	B1−H13	1.12(2)
Ti−H11	1.91(2)	B1−H14	1.10(2)
Ti−H12	1.87(1)	B2−H21	1.12(1)
Ti−H21	1.95(3)	B2−H22	1.12(1)
Ti−H22	1.95(4)	B2−H23	1.12(1)
Ti−H23	1.83(3)	B2−H24	1.01(3)
Bond Angles			
P−Ti−P′	155.68(2)	Ti−B1−H14	128(5)
B1−Ti−B2	119.24(4)	Ti−B2−H24	180.000[a]
B1−Ti−B1′	121.52(8)	H11−B1−H12	97.1(9)
P−Ti−B1	83.22(4)	H12−B1−H13	110.6(10)
P−Ti−B1′	84.97(4)	H11−B1−H13	111.1(10)
P−Ti−B2	102.162(10)	H11−B1−H14	112.2(10)
H11−Ti−H12	56.6(6)	H12−B1−H14	109.8(10)
H21−Ti−H22	51.8(10)	H13−B1−H14	114.8(11)
H22−Ti−H23	56.1(9)	H21−B2−H22	99(2)
H21−Ti−H23	48.7(11)	H22−B2−H23	105(2)
Ti−P−C1	115.87(4)	H21−B2−H23	88(2)
Ti−P−C7	113.74(6)	H21−B2−H24	117.6(14)
Ti−P−C8	114.18(6)	H22−B2−H24	118(2)
Ti−B1−H13	116.7(8)	H23−B2−H24	124(2)

[a] Imposed by symmetry.

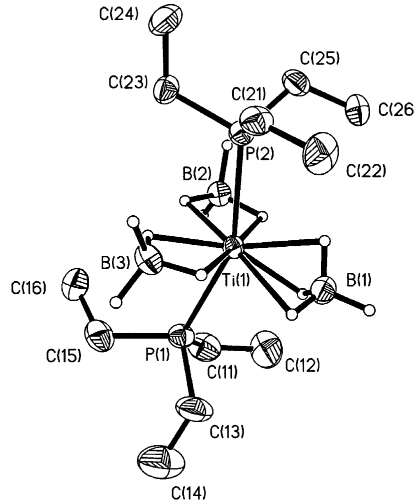

Figure 1. Molecular structure of $Ti(BH_4)_3(PEt_3)_2$ (**2**). Ellipsoids are drawn at the 30% probability level, except for hydrogen atoms, which are represented as arbitrarily sized spheres.

Å, which is near the ~0.3 Å difference in ionic radii for BH_4 in these bonding modes.[17] The $B(\eta^2)-Ti-B(\eta^3)$ angles average 118.5(2) ° whereas the $B(\eta^2)-Ti-B(\eta^2)$ angle is slightly larger at 123.1(2)°. The latter angle may be larger, owing to steric repulsion between the two η^2-BH_4 groups, which bond to the metal through Ti−H contacts that all lie in the trigonal plane. The $Ti-H_b$ distances for the η^2- and η^3-BH_4 groups are 1.99(3) and 2.07(3) Å, respectively. The B−H distances average 1.14(2) and 1.09(2) Å for the η^2- and η^3-BH_4 groups, respectively.

Although the two phosphine ligands occupy the axial sites of the trigonal bipyramid, the P−Ti−P angle of 155.73(4)° deviates significantly from linearity. That the P−Ti−P angle is bent is a consequence of electronic factors (see below); the direction of bending can be explained on the basis of steric effects. Specifically, the two phosphine ligands are bent away from the tridentate BH_4 group, which is more sterically demanding than the two bidentate BH_4 ligands.[16−18] The Ti−P distance of 2.625(2) Å for the PEt_3 complex falls within the narrow range of 2.58 ± 0.07 Å found for all Ti^0, Ti^{II}, and Ti^{IV} trialkylphosphine complexes in the literature.[3]

The other three molecules in the asymmetric unit also adopt the same structure with one tridentate BH_4 group and two bidentate BH_4 groups.[19]

The PMe_2Ph complex **3** possesses a crystallographically imposed 2-fold axis that passes through the Ti atom and a

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(19) In the asymmetric unit of $Ti(BH_4)_3(PEt_3)_2$ (**2**), molecules 2 and 4 clearly have the same structure as molecule 1. For molecule 3, the hydrogen atoms of the tridentate BH_4 group (centered on B7) were not readily evident in the difference map. The Ti···B7 distance is ca. 0.1 Å longer than expected for a tridentate tetrahydroborate ligand (but 0.15 Å shorter than expected for a bidentate binding mode), and we suspect that there is disorder in which B7 is a tridentate group in most of the unit cells but a bidentate group in others (either B8 or B9 would presumably be tridentate in the same unit cells, but this disorder did not interfere with locating the majority hydrogen atom positions). The P−Ti−P angle in molecule 3 refines to 170.58(7)°, a value that is considerably more obtuse than that in molecules 1, 2, or 4. We believe that this parameter is affected by the disorder in the location of the tridentate BH_4 group. Consistent with this hypothesis, the equivalent isotropic displacement parameters, U_{eq}, of the phosphorus atoms in molecule 3 are roughly twice as large as those for the phosphorus atoms in molecules 1 and 2.

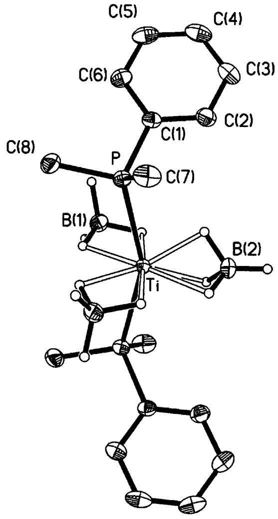

Figure 2. Molecular structure of $Ti(BH_4)_3(PMe_2Ph)_2$ (**3**). Ellipsoids are drawn at the 30% probability level, except for hydrogen atoms, which are represented as arbitrarily sized spheres.

tridentate BH_4 ligand. Consequently, the three bridging hydrogen atoms of the η^3-BH_4 ligand are disordered over two positions related by the 2-fold axis. Despite this disordering, it is clear that the structure of **3** (like **2**) contains one tridentate BH_4 group and two bidentate BH_4 groups (Figure 2). The P−Ti−P angle is 155.68(2)°, which is identical within experimental error to that seen in the PEt_3 analogue **2**. As before, the bidentate Ti···B(η^2) distances of 2.450(2) Å are longer than the tridentate Ti···B(η^3) distance of 2.195(3) Å by 0.255 Å. As seen in the structure of **2**, the B(η^2)−Ti−B(η^3) angle of 119.24(4)° is more acute than the B(η^2)−Ti−B(η^2) angle of 121.52(8)°.

The structures of **2** and **3** will be compared with that of the PMe_3 analogue **1** in the Discussion section.

Synthesis and Structure of [Li(Et₂O)₂][Ti₂(BH₄)₅(PMe₂Ph)₄]. As described above, treatment of $Ti(BH_4)_3(Et_2O)_2$ with PMe_2Ph affords blue crystals of the titanium(III) complex $Ti(BH_4)_3(PMe_2Ph)_2$. Among the blue crystals of this species, however, are occasionally found red crystals of a minor product. This minor product is a new compound, the titanium(II) complex $[Li(Et_2O)_2][Ti_2(BH_4)_5(PMe_2Ph)_4]$ (**4**). Although we have not been able to carry out mass balance studies to establish the reaction stoichiometry, this complex is presumably formed by reduction of **3** in the presence of $LiBH_4$:

$$2\,Ti(BH_4)_3(PMe_2Ph)_2 + LiBH_4 + 2\,Et_2O \rightarrow \underset{\mathbf{4}}{[Li(Et_2O)_2][Ti_2(BH_4)_5(PMe_2Ph)_4]} + H_2 + 2\,BH_3{\cdot}PMe_2Ph$$

To date, attempts to obtain pure samples of **4** have been unsuccessful.

Crystal data for **4** are given in Table 1, whereas selected bond distances and angles are given in Table 4. The structural analysis shows that $[Li(Et_2O)_2][Ti_2(BH_4)_5(PMe_2Ph)_4]$ forms chains in the solid state, the titanium centers being linked to one another and to lithium centers by bridging BH_4 groups (Figure 3). Other one-dimensional chains are known in which metal centers are linked by means of η^2,η^2-BH_4 groups;[39] two representative examples are $AlMe_2(BH_4)$[20] and $Be(BH_4)_2$.[21]

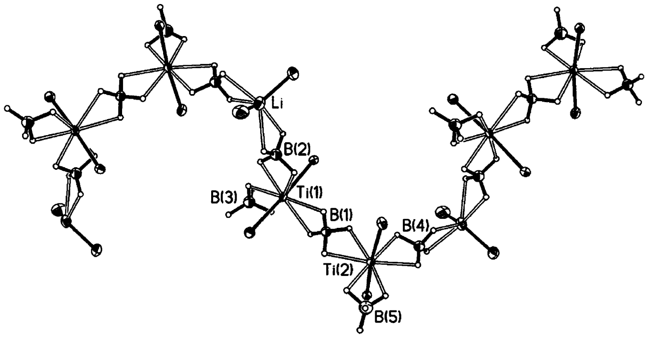

Figure 3. View of the chain structure of $[Li(Et_2O)_2][Ti_2(BH_4)_5(PMe_2Ph)_4]$ (**4**). Ellipsoids are drawn at the 30% probability level, except for hydrogen atoms, which are represented as arbitrarily sized spheres.

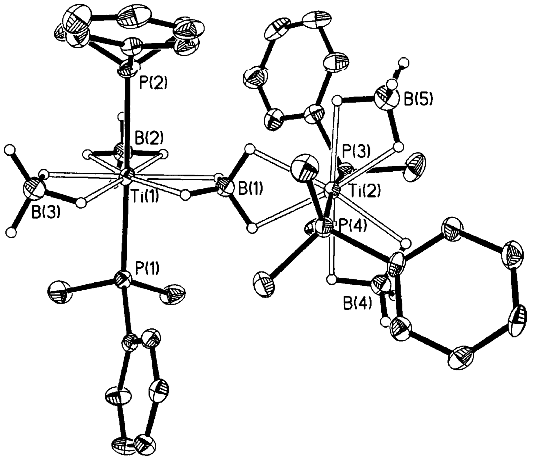

Figure 4. Molecular structure of the $[Ti_2(BH_4)_5(PMe_2Ph)_4]^-$ subunit of **4**. Ellipsoids are drawn at the 30% probability level, except for hydrogen atoms, which are represented as arbitrarily sized spheres.

The $[Ti_2(BH_4)_5(PMe_2Ph)_4]^-$ anion in **4** consists of two Ti(η^2-BH_4)$_2$(PMe_2Ph)$_2$ centers linked by a bridging η^2,η^2-BH_4 group (Figure 4). The Ti···(μ-B)···Ti angle is 169.9(3)°, and the two Ti···(μ-B) distances are essentially equal and average 2.506(7) Å. If the BH_4 groups are considered to occupy one coordination site, the titanium centers each adopt trigonal bipyramidal geometries with the phosphine ligands in the axial positions. The two independent P−Ti−P angles are 176.85(7)° and 171.75(6)° and describe a nearly ideal linear arrangement. The two ends of the molecule are staggered with respect to one another; the dihedral angle between the two Ti_2P_2 planes is 87.72(5)°. We note here that the staggered nature of the two ends of the molecule is enforced by the tetrahedral nature of the bridging BH_4 group and by the strong electronic preference for all three BH_4 groups about each metal center to orient with their bridging BH_2 units lying in the equatorial plane. Volatron has shown that a strong destabilization results if one or more of the BH_4 groups in a high-spin d^2 $M(BH_4)_3L_2$ complex are rotated so that the bound BH_2 units are orthogonal to the equatorial plane.[22]

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(21) Marynick, D. S.; Lipscomb, W. N. *Inorg. Chem.* **1972**, *11*, 820−823.

(22) Lledos, A.; Duran, M.; Jean, Y.; Volatron, F. *Inorg. Chem.* **1991**, *30*, 4440−4445.

Table 4. Important Bond Lengths (Å) and Angles (deg) for $[Li(Et_2O)_2][Ti_2(BH_4)_5(PMe_2Ph)_4]$ (**4**)

Bond Lengths

Ti1−P1	2.623(2)	P3−C38	1.816(6)	Ti1−H31	1.98(5)	B2−H22	1.162(14)
Ti1−P2	2.607(2)	P4−C41	1.832(5)	Ti1−H32	1.95(5)	B2−H23	1.07(2)
Ti2−P3	2.611(2)	P4−C47	1.816(6)	Ti2−H13	2.03(5)	B2−H24	1.07(2)
Ti2−P4	2.607(2)	P4−C48	1.802(5)	Ti2−H14	2.09(5)	B3−H31	1.162(14)
Ti1−B1	2.504(7)	Li−O1	1.960(11)	Ti2−H41	2.06(5)	B3−H32	1.162(14)
Ti1−B2	2.500(7)	Li−O2	1.989(11)	Ti2−H42	2.05(5)	B3−H33	1.09(3)
Ti1−B3	2.471(8)	O1−C51A	1.50(2)	Ti2−H51	1.78(5)	B3−H34	1.09(3)
Ti2−B1	2.508(7)	O1−C51B	1.454(11)	Ti2−H52	2.06(6)	B4−H41	1.162(14)
Ti2−B4	2.493(7)	O1−C53	1.437(7)	P1−C11	1.840(6)	B4−H42	1.162(14)
Ti2−B5	2.498(9)	O2−C55	1.420(8)	P1−C17	1.835(6)	B4−H43	1.07(2)
Li−B2	2.566(12)	O2−C57	1.540(10)	P1−C18	1.823(6)	B4−H44	1.07(2)
Li−B4	2.465(12)	B1−H11	1.162(14)	P2−C21	1.835(6)	B5−H51	1.162(14)
Ti1−H11	2.16(5)	B1−H12	1.162(14)	P2−C27	1.811(6)	B5−H52	1.162(14)
Ti1−H12	2.13(5)	B1−H13	1.162(14)	P2−C28	1.824(6)	B5−H53	1.09(3)
Ti1−H21	2.03(5)	B1−H14	1.162(14)	P3−C31	1.843(6)	B5−H54	1.09(3)
Ti1−H22	2.00(5)	B2−H21	1.162(14)	P3−C37	1.798(6)		

Bond Angles

P1−Ti1−P2	176.85(7)	Ti2−B1−H11	130(3)	H31−Ti1−H32	54.7(10)	H32−B3−H33	107(4)
P3−Ti2−P4	171.75(6)	Ti2−B1−H12	112(3)	H13−Ti2−H14	54.4(9)	H33−B3−H31	116(4)
B1−Ti1−B2	116.6(2)	Ti2−B4−H43	129(3)	H41−Ti2−H42	55.0(9)	H31−B3−H34	104(4)
B2−Ti1−B3	119.5(2)	Ti2−B4−H44	126(3)	H51−Ti2−H52	52.4(12)	H32−B3−H34	110(4)
B1−Ti1−B3	123.8(2)	Ti2−B5−H53	120(3)	H23−Li−H24	47(2)	H33−B3−H34	117(4)
B1−Ti2−B4	116.4(2)	Ti2−B5−H54	128(3)	Ti1−P1−C11	122.5(2)	H41−B4−H42	110(4)
B4−Ti2−B5	123.4(3)	Li−B2−H21	142(3)	Ti1−P1−C17	115.3(2)	H42−B4−H43	104(4)
B1−Ti2−B5	120.2(3)	Li−B2−H22	113(3)	Ti1−P1−C18	111.9(2)	H43−B4−H41	122(4)
B2−Li−B4	111.4(4)	Li−B4−H41	133(3)	Ti1−P2−C21	116.7(2)	H41−B4−H44	105(4)
P1−Ti1−B1	94.0(2)	Li−B4−H42	117(3)	Ti1−P2−C27	114.5(2)	H42−B4−H44	112(4)
P1−Ti1−B2	86.3(2)	H11−B1−H12	117(4)	Ti1−P2−C28	116.1(2)	H43−B4−H44	104(4)
P1−Ti1−B3	90.6(2)	H12−B1−H13	104(4)	Ti2−P3−C31	122.4(2)	H51−B5−H52	95(4)
P2−Ti1−B1	88.6(2)	H13−B1−H11	112(3)	Ti2−P3−C37	114.0(2)	H52−B5−H53	115(5)
P2−Ti1−B2	91.0(2)	H11−B1−H14	107(3)	Ti2−P3−C38	112.2(2)	H53−B5−H51	107(5)
P2−Ti1−B3	89.5(2)	H12−B1−H14	108(4)	Ti2−P4−C41	114.8(2)	H51−B5−H54	127(5)
P3−Ti2−B1	88.6(2)	H13−B1−H14	108(4)	Ti2−P4−C47	118.5(2)	H52−B5−H54	99(4)
P3−Ti2−B4	86.0(2)	H21−B2−H22	105(4)	Ti2−P4−C48	114.2(2)	H53−B5−H54	112(5)
P3−Ti2−B5	93.3(2)	H22−B2−H23	98(4)	Ti1−B1−H13	129(3)	O1−Li−O2	120.2(5)
P4−Ti2−B1	94.0(2)	H23−B2−H21	122(4)	Ti1−B1−H14	122(3)	O1−Li−B2	109.6(5)
P4−Ti2−B4	85.8(2)	H21−B2−H24	111(4)	Ti1−B2−H23	117(3)	O1−Li−B4	106.9(5)
P4−Ti2−B5	92.1(2)	H22−B2−H24	120(4)	Ti1−B2−H24	141(3)	O2−Li−B2	107.1(5)
H11−Ti1−H12	55.1(8)	H23−B2−H24	102(4)	Ti1−B3−H33	119(3)	O2−Li−B4	101.2(4)
H21−Ti1−H22	54.2(9)	H31−B3−H32	102(4)	Ti1−B3−H34	124(3)		

The average Ti−P distance of 2.612(2) Å in **4** is comparable to that of 2.626(1) Å in the only other known titanium(II) BH_4 complex, $Ti(\eta^2\text{-}BH_4)_2(dmpe)_2$, where dmpe is 1,2-bis(dimethylphosphino)ethane.[23] The three substituents on the phosphorus atom are oriented in a staggered fashion with respect to the three equatorial η^2-BH_4 groups, presumably so as to minimize steric repulsions.

The three Ti···B vectors about Ti(1) describe B−Ti−B angles of 123.8(2)°, 119.5(2)°, and 116.6(2)°; the corresponding angles about Ti(2) are 123.4(3)°, 120.2(3)°, and 116.4(2)°. The Ti···B distances confirm that the BH_4 groups are bidentate[17] and lie in a narrow range from 2.471(8) to 2.508(7) Å. For comparison, the Ti···B distances in $Ti(\eta^2\text{-}BH_4)_2(dmpe)_2$ are 2.534(3) Å.

One of the tetrahydroborate groups on each Ti center bridges between Ti and an ether-coordinated Li cation, again in a η^2,η^2 fashion. Specifically, individual $[Ti_2(BH_4)_5(PMe_2Ph)_4]^-$ units are linked together into a chain by interaction of hydrogen atoms on B2 and B4 with the lithium cations. The Ti···B···Li angles are 164.2(4)° and 171.3(4)°. The BH_4 groups that bridge between Ti and Li are nearly equidistant from these two centers: the Ti···B distances to these bridging BH_4 groups lie between 2.49(1) and 2.50(1) Å, and the Li···B distances lie between 2.46(1) and 2.57(1) Å. The Ti···B distances to the terminal BH_4 groups of 2.47(1) and 2.50(1) Å are comparable to those seen for the bridging BH_4 groups.

Hydrogen atoms bound to boron were readily apparent in the difference maps. For the BH_4 group that bridges between titanium centers, the Ti−H distance of 2.15(5) Å is slightly longer than for the 'terminal' BH_4 groups, which are equal within error at 2.02(5) and 1.97(5) Å, respectively. (All terminal B−H bond distances were constrained to be equal, all titanium-bridging B−H bond distances were constrained to be equal, and all lithium-bridging B−H bonds were constrained to be equal.) The titanium-bridging hydrogen atoms refined to positions 1.16(1) Å from the attached boron atoms. The B−H distances for the lithium-bridging hydrogen atoms on B2 and B4, and for the nonbridging hydrogen atoms on B3 and B5, were essentially equal at 1.07(2) and 1.09(3) Å, respectively.

The geometry about the titanium(II) centers in **4** is very similar to that seen in the vanadium(III) complex $V(BH_4)_3(PMe_3)_2$.[24] The similarities between the structures are not surprising in view of the fact that $[Ti(BH_4)_3(PR_3)_2]^-$ and $V(BH_4)_3(PR_3)_2$ both have d^2 valence shell electron configura-

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(23) Jensen, J. A.; Girolami, G. S. *Inorg. Chem.* **1989**, *28*, 2107−2113.

(24) Jensen, J. A.; Girolami, G. S. *Inorg. Chem.* **1989**, *28*, 2114−2119.

tions and, thus, are isoelectronic.[25] In both molecules, the five ligands describe a very regular trigonal bipyramidal structure, the P−M−P angle is essentially linear, and the three equatorial BH_4 groups are all bidentate and describe B−M−B angles that are very close to 120°. The V−P distance of 2.510(1) Å is shorter than the average Ti−P distance of 2.612(2) Å seen in **4**, and the V−B distance of 2.365(6) Å is also shorter than the average Ti−B distance of 2.496(8) Å in **4**. These differences reflect the smaller ionic radius of vanadium(III) relative to titanium(II).

Discussion

1. Reformulation of the Structure of $Ti(BH_4)_3(PR_3)_2$ Complexes. A previous study of the crystal structure of the titanium(III) tetrahydroborate $Ti(BH_4)_3(PMe_3)_2$ (**1**) suggested that two of the BH_4 groups in each molecule were coordinated in an unprecedented side-on fashion, whereas the third BH_4 group was bidentate. The Ti···B distances to the two side-on BH_4 ligands of 2.27(1) Å were intermediate between that of 2.40(1) Å for the bidentate BH_4 group and that of 2.20 Å expected for a tridentate BH_4 ligand bound to Ti. In later work, Volatron and co-workers carried out an ab initio study of the structure of $Ti(BH_4)_3(PMe_3)_2$.[12] Interestingly, they found that the side-on structure was not the ground state and that instead the lowest-energy geometry was one in which two of the BH_4 groups were bidentate and one was tridentate.

The findings of Volatron and co-workers (and our adoption of new methods that permit collecting diffraction data from thermally and air-sensitive solids) prompted us to carry out the present reinvestigation of these $Ti(BH_4)_3(PR_3)_2$ molecules. Our current crystallographic studies of $Ti(BH_4)_3(PEt_3)_2$ (**2**) and $Ti(BH_4)_3(PMe_2Ph)_2$ (**3**) clearly are consistent with the ab initio results and disagree with our previous suggestion that the structure of the PMe_3 analogue **1** contains side-on BH_4 ligands.

We can rule out the unlikely possibility that, for some reason, the PMe_3 complex is anomalous. The IR spectra of **1**, **2**, and **3** in the B−H region are essentially superimposable, and thus, we conclude (as we did in 1988) that all the complexes in this series have similar structures. We now believe that our earlier crystal structure of $Ti(BH_4)_3(PMe_3)_2$ was incorrectly interpreted and that all these species adopt structures in which one of the BH_4 groups is tridentate and two are bidentate. (From here on, we will follow the symbolism used by Volatron and co-workers and refer to this as the (2,2,3) structure, the three indices indicating the hapticities of the three BH_4 ligands.)

What, then, led to the incorrect interpretation of the crystal structure of the PMe_3 complex? At room temperature, molecules of **1** reside on crystallographic mirror planes that pass through the Ti and the two P atoms and that bisect a bidentate BH_4 ligand. The other two BH_4 groups lie off the mirror plane but are symmetry-related to one another by it. We now propose that that $Ti(BH_4)_3(PMe_3)$ adopts a (2,2,3) structure but that the apparent mirror symmetry seen in the crystal structure at room-temperature results from the mutual *disorder* of two chemically inequivalent BH_4 groups, one bidentate and the other tridentate.

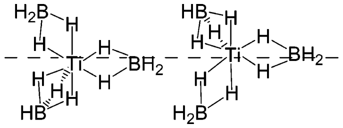

Figure 5. Disorder model for $Ti(BH_4)_3(PMe_3)_2$; the axial PMe_3 groups have been deleted for clarity. The crystallographic mirror plane is indicated by the dashed line. The disorder between the two left-most BH_4 groups across the mirror plane led to apparent hydrogen positions that deceptively resembled a “side-on” bonding mode.

In 1988, we[3] discussed this exact possibility: “The unusual bonding mode adopted by two of the tetrahydroborate ligands led us to consider whether the X-ray data could be interpreted in terms of a disordered model involving superposition of a bidentate and a tridentate BH_4 geometry across the crystallographic mirror plane. Such a model might account for the short Ti−B2 contacts [to the side-on BH_4 groups] as well as the somewhat elongated thermal ellipsoids (high U_{22} parameters) of the Ti and B1 atoms. However, the P1 and P2 atoms, and more importantly the B2 atoms..., possess nearly isotropic thermal parameters and do not suggest that any disorder of the side-on BH_4 groups is present. Furthermore, the positions of the hydrogen atoms on B2 are not consistent with the model, since at least two of the hydrogen atoms on B2 should be within bonding distance to the titanium center, rather than the one short contact...observed. Overall, we consider that a disordered model can be rejected as inconsistent with the evidence.”

We now believe that this disorder model, in fact, can account for all the crystallographic observations. As we pointed out in 1988, the elongations of the thermal ellipsoids for Ti and B1 are easily explained by such a disorder. What we did not realize in our original paper is that the nearly isotropic ellipsoids of P1, P2, and B2 also are consistent with this disorder and can be explained in the following manner: these atoms remain in relatively fixed positions, whereas Ti and B1 (which is always η^2) are disordered among two positions just off the crystallographic mirror plane (Figure 5). When the titanium center is below the mirror plane, the lower B2 atom is the site of a η^3-BH_4 group, whereas the upper B2 atom is the site of a η^2-BH_4 group. When the Ti center is above the mirror plane, the locations of the η^2- and η^3-BH_4 groups are reversed.

The result of the disorder is an apparent Ti···B2 distance that is intermediate between that of a bidentate and a tridentate BH_4 ligand, and average hydrogen atom locations that give the appearance of a side-on bonding mode. The disordering also causes the thermal ellipsoid for the titanium center (and for atom B2) to be elongated in a direction perpendicular to the mirror plane; such disordering of a metal center within a mostly ordered set of ligand atoms has been seen in a few other systems.[26]

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(25) We presume that the titanium(II) compound is high spin but have not been able to obtain it in sufficient amounts to verify this presumption.

(26) Howard, W. A.; Parkin, G.; Rheingold, A. L. *Polyhedron* **1995**, *14*, 25−44 and references therein.

This disorder makes the P−Ti−P angle appear to be some 15° larger than it is known to be in **2** and **3** (∼155°). This fact can be explained in the following way. As mentioned above, the locations of the phosphorus atoms are not significantly affected by the disorder; they reside on the crystallographic mirror plane. As a result, the P···P axis also lies in this mirror plane. In contrast, the positions of the titanium atoms, which actually lie off the plane, are averaged by the disorder. The effect of the disorder is to bring the apparent Ti position into the mirror plane and closer to the P···P axis, thus making the apparent P−Ti−P angle more obtuse than it actually is.

In our 1988 paper, we noted that **1** undergoes a phase transformation at ca. −25 °C, and that the crystals diffracted poorly below this temperature.[3] It is possible that, at temperatures below the −25 °C phase transition, the crystals lose their mirror symmetry; i.e., the two BH_4 ligands that at room temperature are related by the mirror plane become crystallographically inequivalent. Unfortunately, the phase transition is accompanied by loss of crystallinity, so this hypothesis cannot be verified experimentally.

2. Comparison of the Structures of $M(BH_4)_3L_2$ Complexes. As noted above, the reaction of $Ti(BH_4)_3(Et_2O)_2$ with PMe_2Ph affords two products, the titanium(III) complex $Ti(BH_4)_3(PMe_2Ph)_2$ (**3**) and the titanium(II) salt $[Li(Et_2O)_2][Ti_2(BH_4)_5(PMe_2Ph)_4]$ (**4**), whose anion can be considered as two $[Ti(BH_4)_3(PMe_2Ph)_2]^-$ units that share a BH_4 group. The titanium centers in **3** and **4** have identical ligand sets (three BH_4 groups and two PMe_2Ph ligands) but have d^1 and d^2 configurations, respectively. As a result, these complexes constitute an ideal system for determining the effects of electronic factors on geometry and BH_4 hapticity.

The structures of $Ti(BH_4)_3(PMe_2Ph)_2$, **3**, and the $[Ti(BH_4)_3(PMe_2Ph)_2]^-$ units in **4** differ in two significant ways: (1) the Ti^{III} complex has one tridentate and two bidentate BH_4 groups, whereas the Ti^{II} complex has three bidentate BH_4 ligands, and (2) the ligands about the Ti^{III} centers describe a distorted trigonal bipyramid, whereas the ligands about the Ti^{II} centers describe a nearly ideal trigonal bipyramid. The differences in the trigonal bipyramidal geometries are most clearly manifested in the P−Ti−P angles, which are 155.68(2)° for the Ti^{III} complex **3** and 174.30(7)° for the Ti^{II} complex **4**.

The crystal structures in the present paper firmly establish a trend in the structures of $M(BH_4)_3L_2$ complexes. Specifically, there is a periodic trend that relates the nature of the metal, M, to the numbers of bidentate vs tridentate BH_4 groups: $Sc(BH_4)_3(thf)_2$[27] has a (2,3,3) structure, $Ti(BH_4)_3(PR_3)_2$ complexes have a (2,2,3) structure, and $V(BH_4)_3(PR_3)_2$[23] and $[Ti(BH_4)_3(PR_3)_2]^-$ have (2,2,2) structures. The factors that lead to this trend will be discussed in the next section.

3. Factors that Affect the Hapticity of BH_4 Groups. As has long been known, when BH_4 groups bind to transition metals as terminal ligands, the number of hydrogen atoms that bridge to the metal can be one, two, or three.[16] An important issue is what factors influence the binding mode (hapticity) of coordinated BH_4 groups. Both steric and electronic factors could play a role.

3.1. Steric Factors. For BH_4 complexes of d^0 metal centers such as Be^{II}, Sc^{III}, Y^{III}, Zr^{IV}, Hf^{IV}, and Th^{IV}, steric factors often can explain the hapticities of the BH_4 ligands. Lobkovskii showed that the structures of such metal BH_4 complexes could often be predicted from a set of constants that represent the normalized solid angles subtended by the various coordinated ligands.[28] The structure adopted (i.e., the relative numbers of bidentate and tridentate BH_4 groups) is the one in which the solid angle for the entire coordination sphere is filled as completely as possible by the ligands. This approach successfully explains, for example, why $Be(BH_4)_2$[21] is polymeric in the solid state, each Be center being surrounded by three bidentate BH_4 groups, whereas $Hf(\eta^3\text{-}BH_4)_4$[29] is monomeric with four tridentate BH_4 groups. Lobkovskii's analysis is an example of the "solid angle sum" approach,[30−32] which has been applied to many different kinds of complexes besides those that contain BH_4 ligands.[33−35]

If steric effects dominate, then higher BH_4 hapticities should be observed for metals with larger radii. Comparisons of the Ti−L distances in the Ti^{II} anion $[Ti(BH_4)_3(PMe_2Ph)_2]^-$ **4** with those in the Ti^{III} compound $Ti(BH_4)_3(PMe_2Ph)_2$ **3** suggest that the sizes of Ti^{II} and Ti^{III} differ by roughly 0.05 Å or less, with Ti^{II} being slightly larger, as expected. The slightly larger radius for Ti^{II} should favor *higher* BH_4 hapticities based on steric grounds, yet the *opposite* trend is observed experimentally; the hapticities are higher for Ti^{III}. We conclude that the (2,2,2) structure adopted by $[Ti(BH_4)_3(PR_3)_2]^-$ vs the (2,2,3) structure adopted by $Ti(BH_4)_3(PR_3)_2$ cannot be rationalized on the basis of differences in the size of the metal center.

3.2. Electronic Factors. As we explained in 1988, d^1 molecules of the type $M(BH_4)_3L_2$ should be distorted away from idealized D_{3h} symmetry, owing to a Jahn−Teller effect, whereas high-spin d^2 complexes of this type should be perfect trigonal bipyramids.[3] This prediction is in accord with the facts. The d^1 titanium(III) complexes **1**−**3** *are* distorted: the P−M−P angle deviates by some 25° from linearity and the three BH_4 ligands adopt different ligation modes, two being bidentate and one tridentate. In contrast, the high-spin d^2 complexes **4** and $V(BH_4)_3(PMe_3)_2$ possess nearly ideal

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[27] Lobkovskii, E. B.; Kravchenko, S. E.; Semenenko, K. N. *J. Struct. Chem. (Engl. Trans.)* **1977**, *18*, 312−314.

[28] Lobkovskii, E. B. *J. Struct. Chem. (Engl. Transl.)* **1983**, *24*, 224−230.

[29] Broach, R. W.; Chuang, I.; Marks, T. J.; Williams, J. M. *Inorg. Chem.* **1983**, *22*, 1081−1084. Electronic factors may also play an important role in dictating the geometry of $Hf(BH_4)_4$: the observed tetra(trihapto) geometry can also be explained on the basis that only this structure affords an electron count of 18.

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trigonal bipyramidal geometries with linear P−M−P angles and three bidentate BH_4 groups.

Volatron and co-workers[12,22,36] showed that the exact hapticities of the BH_4 ligands in the series $Sc(BH_4)_3(thf)_2$, $Ti(BH_4)_3(PMe_3)_2$, and $V(BH_4)_3(PMe_3)_2$ could be understood in terms of the number of empty valence orbitals on the metal: nine for a d^0 species, eight for a d^1 species, and seven for a high-spin d^2 species. For complexes of the type $M(BH_4)_3L_2$, two of these valence orbitals on each metal center are involved in metal-phosphorus bonding, leaving seven, six, and five orbitals for metal−BH_4 bonding in d^0, d^1, and high-spin d^2 species, respectively. Under the D_{3h} point group, the equatorial BH_4 ligands can form one symmetry-adapted linear combination of a_2' symmetry that is purely ligand-based because none of the s, p, or d orbitals on the metal center has this symmetry. Therefore, maximal metal−ligand bonding for d^0, d^1, and d^2 species will be achieved if the ligands are arranged so as to create eight, seven, and six symmetry-adapted linear combinations of orbitals, respectively. This condition is realized by (2,3,3), (2,2,3), and (2,2,2) arrangements of the BH_4 ligands, as is observed for $Sc(BH_4)_3(thf)_2$, $Ti(BH_4)_3(PMe_3)_2$, and $V(BH_4)_3(PMe_3)_2$.

The preponderance of evidence strongly suggests that electronic factors are most important in determining the structures of $M(BH_4)_3L_2$ complexes.

Experimental Section

All operations were carried out in a vacuum or under argon with standard Schlenk techniques. Solvents were distilled under nitrogen from sodium benzophenone (pentane, diethyl ether, tetrahydrofuran) immediately before use. The phosphine PMe_2Ph[37] was prepared by a modification of a literature route; $LiBH_4$ (Strem) was used without purification, whereas $TiCl_4$ (Fisher) was distilled before use. $Ti(BH_4)_3(PEt_3)_2$ and $Ti(BH_4)_3(PMe_2Ph)_2$ were prepared as described previously.[3]

Bis(diethyl ether)lithium Pentakis(tetrahydroborato)tetrakis(dimethylphenylphosphine)dititanium(II). To $TiCl_4$ (1.5 mL, 14 mmol) in diethyl ether (200 mL) at 25 °C was added dropwise a solution of $LiBH_4$ (1.27 g, 58.3 mmol) in diethyl ether (50 mL). After the addition was complete, the solution was stirred for an additional 2 h. The dark blue-green solution was filtered and concentrated to 50 mL. After the solution was cooled to −78 °C, PMe_2Ph was added, causing the solution to turn bright blue. The solution was stirred for 1 h and then warmed to room temperature. The solution was filtered, and pentane (40 mL) was layered on top. Cooling the layered solution to −20 °C afforded a crop of blue crystals of $Ti(BH_4)_3(PMe_2Ph)_2$ that contained a few red crystals of the title compound. The crystals were washed with pentane and dried under vacuum. Attempts to obtain large amounts of the red titanium(II) compound free of the blue crystals of the titanium(III) compound were unsuccessful.

Crystallographic Studies.[38] Single crystals of $Ti(BH_4)_3(PEt_3)_2$ (**2**), grown by layering pentane on a diethyl ether solution, were mounted on glass fibers with Paratone-N oil (Exxon) and immediately cooled to −75 °C in a cold nitrogen gas stream on the diffractometer. Single crystals of $Ti(BH_4)_3(PMe_2Ph)_2$ (**3**) and $[Li(Et_2O)_2][Ti_2(BH_4)_5(PMe_2Ph)_4]$ (**4**), grown by layering pentane on diethyl ether solutions were treated similarly. Data for **2**−**4** were collected on an area detector, and the measured intensities were reduced to structure factor amplitudes and their esd's by correction for background and Lorentz and polarization effects. Although corrections for crystal decay were unnecessary, face-indexed absorption corrections were applied. Systematically absent reflections were deleted, and symmetry-equivalent reflections were averaged to yield the sets of unique data. All structures were solved using direct methods (SHELXTL). For **3** and **4**, the correct positions for all of the non-hydrogen atoms were deduced from an E-map. For **2**, subsequent least-squares refinement and difference Fourier calculations revealed the positions of the remaining non-hydrogen atoms. The analytical approximations to the scattering factors were used, and all structure factors were corrected for both real and imaginary components of anomalous dispersion. For **3**, hydrogen atoms were refined with independent isotropic displacement parameters; for **2** and **4**, the displacement parameters for all hydrogen atoms were set equal to a multiple of U_{eq} for the attached non-hydrogen atom (the multiplier was 1.5 for methyl and BH_4 hydrogens, and 1.2 for methylene and aromatic hydrogens). Successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle. Final refinement parameters for **2**−**4** are given in Table 1. Subsequent discussions for **2**−**4** will be divided into individual paragraphs.

2. The triclinic cell parameters narrowed the choice of space groups to $P1$ and $P\bar{1}$; the latter was more consistent with the average values of the normalized structure factors and was proven to be correct by successful refinement of the proposed model. One reflection (1 1 1) was a statistical outlier and was deleted, and the remaining 19 731 unique data were used in the least-squares refinement. Several ethyl carbon atoms were disordered over two sites; the site occupancy factors were constrained to add to unity, and the P−C and C−C bond distances involving disordered atoms were restrained to idealized values. The quantity minimized by the least-squares program was $\Sigma w(F_o^2 - F_c^2)^2$, where $w = \{[\sigma(F_o^2)]^2 + (0.110P)^2\}^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. In the final cycle of least-squares, anisotropic displacement factors were refined for the ordered non-hydrogen atoms; disordered carbon atoms were refined isotropically with a common displacement factor. Hydrogen atoms on the ethyl groups were fixed in idealized positions with C−H = 0.99 and 0.98 Å for methylene and methyl hydrogen, respectively. Hydrogen atoms in all of the BH_4 groups (except those attached to B7) were easily located in the difference maps. The B−H distances within each BH_4 unit were restrained to be equal to within a standard deviation of 0.03 Å; the H···H distances within each BH_4 unit were similarly restrained. The largest peak in the final Fourier difference map (0.66 Å e^{-3}) was located 0.95 Å from Ti4. A final analysis of variance between observed and calculated structure factors showed no apparent errors.

3. The systematic absences, hkl ($h + k \neq 2n$) and $h0l$ ($l \neq 2n$), were consistent with the monoclinic space groups Cc and $C2/c$; the latter was chosen from an analysis of the average values of the normalized structure factors and was proven correct by the success of the subsequent refinement. 2631 unique data were used in the least-squares refinement. The quantity refined by the least-squares refinement was $\Sigma w(F_o^2 - F_c^2)^2$, where $w = \{[\sigma(F_o^2)]^2 + (0.0418P)^2 + 0.151P\}^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were assigned independent isotropic displacement parameters. Hydrogen atoms were readily apparent in the difference maps, and

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(36) Lledos, A.; Duran, M.; Jean, Y.; Volatron, F. *Bull. Soc. Chim. Fr.* **1992**, *129*, 216−220.

(37) Frajerman, C.; Meunier, B. *Inorg. Synth.* **1983**, *22*, 133−135.

(38) For details of the crystallographic methods used, see Brumaghim, J. L.; Priepot, J. G.; Girolami, G. S. *Organometallics*, **1999**, *18*, 2139−2144.

(39) For other examples of bridging BH_4 groups, see Xu, Z.; Lin, Z. *Coord. Chem. Rev.* **1996**, *156*, 139−162.

their locations were refined freely, except that the B−H distances involving the three bridging H atoms attached to B2 (which are disordered over two positions related by the 2-fold axis that passes through Ti and B2) were constrained to be equal. The largest nine peaks in the final Fourier difference map (0.15−0.25 e Å^{-3}) were located near the midpoints of bonds and were clearly assignable to valence electron density. A final analysis of variance between observed and calculated structure factors showed no apparent errors.

4. The systematic absences, $h0l$ ($l \neq 2n$) and $0k0$ ($k \neq 2n$), were only consistent with the monoclinic space group $P2_1/c$. Five reflections, −1 2 1, 0 0 2, 1 0 0, 0 1 1, and 1 1 2, were statistical outliers and were deleted; the remaining 12728 unique data were used in the least-squares refinement. One of the ethyl groups of a diethyl ether molecule was disordered over two sites, the major site having an occupancy factor that refined to 0.684(10). The quantity minimized by the least-squares program was $\Sigma w(F_o^2 - F_c^2)^2$, where $w = \{[\sigma(F_o^2)]^2 + (0.0496P)^2\}^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. The C−O, C−C, and O···C distances within the two conformers of the disordered ethyl group were constrained to be similar. Hydrogen atoms on the diethyl ether and phosphine ligands were fixed in "idealized" positions (methyl hydrogens were optimized by rotation about the C−X axis) with C−H = 0.98 Å for the methyl hydrogens, 0.99 Å for the methylene hydrogens, and 0.95 Å for the aromatic hydrogens. Hydrogen atoms on the BH_4 groups were readily apparent in the difference maps, and their locations were refined subject to the following constraints: all terminal B−H bond distances were constrained to be similar, all titanium-bridging B−H bond distances were constrained to be equal, and all lithium-bridging B−H bonds were constrained to be equal. The largest peak in the final Fourier difference map (0.44 e Å^{-3}) was located 0.44 Å from C51A, a carbon atom in the disordered ethyl group. A final analysis of variance between observed and calculated structure factors showed no apparent errors.

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Supporting Information Available: X-ray structural data for **2**−**4** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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