

reaction temperature (determined before and after the run with ethylene glycol). After allowing 10 min for equilibration of the sample, and after all the initial **13** had been consumed, the disappearance of the olefinic protons of norbornene was monitored relative to the internal standard. A plot of [NBE] versus time gave k_{obsd} , where $k_{\text{obsd}} = k_1[\mathbf{13}]$. All runs were monitored for at least 3 half-lives, and in all cases acceptable R values were obtained from the subsequent kinetic plots. An analogous procedure was employed for the reactions of **12** and **6** with norbornene, except that the signal from $\text{C}_6\text{D}_6\text{H}$ was utilized as the internal standard. For **6**, a plot of $\ln[\text{NBE}]$ versus time gave $k_{\text{obsd}}[\mathbf{6}]$. For the reaction of **15** with NBE-2,3- d_2 , samples were prepared as described above employing stock solutions of NBE-2,3- d_2 in toluene- d_8 and **15** in benzene- d_6 . The rate of ring opening of **15** was determined by monitoring the disappearance of the α proton at 5.23 ppm.

Capping Living Polymers; Spin Simulation Experiments. A sample of **14** ($x_{\text{av}} = 7$) was treated with 3 equiv of benzaldehyde in C_6D_6 at 65 °C. A ^1H NMR spectrum of the resulting $\text{PhH}_A\text{C}=\text{CH}_B[\text{C}_5\text{H}_8\text{CH}=\text{CH}]_x\text{-}t\text{-Bu}$ displayed olefinic resonances in the region 6.0–6.5 ppm for H_A and H_B (Figure 5b). On the basis of related studies²⁸ in which only the trans isomer (of the phenyl-substituted capping olefin group) is observed, the resonances at 6.38 and 6.33 ppm were assigned to H_A , and those at 6.18–6.10 ppm were assigned to H_B of the trans isomer. Using the values $\delta \text{H}_A = 1905$ Hz and $\delta \text{H}_B = 1841$ Hz at 300 MHz, $J_{AB} = 16$ Hz and $J_{BX} = 8$ Hz (H_X is the first cyclopentyl tertiary proton), a theoretical spectrum for the trans isomer was calculated (Figure 6a), utilizing a software program based on the iterative spin simulation program LAME. The results of the calculated spectrum suggest that resonances for $\text{H}_{A,\text{cis}}$ isomer overlap with those for $\text{H}_{A,\text{trans}}$ isomer between 6.30 and 6.45 ppm in the observed spectrum (Figure 6b). The resonances for $\text{H}_{B,\text{cis}}$ isomer are assumed to occur upfield of those for $\text{H}_{B,\text{trans}}$ resonances at 6.18–6.10 ppm and are obstructed by polynorbornene resonances at ~ 5.2 –5.6 ppm. This type of shift is generally observed for an olefinic proton trans to a phenyl group ($\text{H}_{B,\text{cis}}$) relative to one cis to a phenyl group ($\text{H}_{B,\text{trans}}$). For example, using a general formula,²⁹ $\text{H}_{B,\text{cis}}$ is calculated to resonate at 5.62 ppm, while $\text{H}_{B,\text{trans}}$ is calculated to res-

onate at 6.09 ppm, consistent with what we propose. Utilizing the above data the trans/cis capped polymer ratio can be easily determined by comparing the integrations of the resonances at 6.30–6.45 ppm ($\text{H}_{A,\text{trans}}$ plus $\text{H}_{A,\text{cis}}$) with those for the resonances at 6.18–6.10 ppm ($\text{H}_{B,\text{trans}}$). In this way the double bond formed by reaction of **14** with benzaldehyde was determined to be 68% trans and 32% cis. In an analogous manner the terminal double bond formed by reaction of $\text{Ta}[(\text{CHC}_5\text{H}_8\text{CH})_x\text{CH-}t\text{-Bu}](\text{TIPT})_3(\text{THF})$ ($x_{\text{av}} = 10$) with 3 equiv of benzaldehyde in C_6D_6 at 25 °C was determined to be 64% cis and 36% trans.

Acknowledgment. R.R.S. thanks the National Science Foundation (Grant CHE 84-02892) and the Office of Naval Research (N00014-87-K-0099) for support, and K.C.W. thanks the Central Research Department of the DOW Chemical Company for a predoctoral fellowship. We also thank the U.S. Department of Energy, Division of University and Industry Programs, for funds to purchase the X-ray diffractometer (Grant DE-FG05-86ER 75292).

Registry No. **1**, 114530-92-6; **2**, 114492-13-6; **3**, 105969-47-9; **4**, 114492-14-7; **5**, 114530-93-7; **6**, 114492-15-8; **7**, 114530-94-8; **8**, 114492-16-9; **9**, 114492-17-0; **10** (α,β -isomer), 114492-18-1; **10** (α,α -isomer), 114530-95-9; **11a**, 104532-85-6; **11b**, 104532-84-5; **12**, 105945-15-1; **13**, 114530-96-0; **15**, 114492-20-5; **16**, 114492-21-6; **17**, 104548-87-0; **18**, 104532-85-6; **19**, 114492-22-7; LiDIPP, 72727-49-2; LiDMP, 24560-29-0; LiTIPT, 107847-82-5; NBE, 498-66-8; NBE-2,3- d_2 , 13317-75-4; (NBE) $_x$, 25038-76-0; $\text{Ta}(\text{CH}_2\text{-}t\text{-Bu})_2\text{Cl}_3$, 61645-40-7; $\text{Ta}(\text{CH-}t\text{-Bu})(\text{THF})_2\text{Cl}_3$, 75331-92-9; $[\text{Ta}(\text{CH-}t\text{-Bu})(\text{TIPT})_3]_2$, 114492-23-8; $[\text{C}_5\text{H}_8\text{CH}=\text{CH}_2]_x$, 30229-22-2; styrene, 100-42-5; trimethylsilylethylene, 754-05-2; ethylene, 74-85-1; benzaldehyde, 100-52-7; acetone, 67-64-1; pivaldehyde, 630-19-3; cis-2-pentene, 627-20-3.

Supplementary Material Available: Tables of final atomic coordinates and temperature factors and a fully labeled figure for $\text{Ta}[\text{CH}(\text{C}_5\text{H}_8)\text{CHCH}(t\text{-Bu})](\text{DIPP})_3$ (5 pages); listing of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page. Supplementary material for $\text{Ta}[\text{CH}(\text{Ph})\text{CH}(t\text{-Bu})\text{CH}_2](\text{DIPP})_3$ was provided in a preliminary communication.^{14a}

(28) Krouse, S. A., unpublished results.

(29) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; John Wiley and Sons: New York, 1981; p 227.

Titanium(III) Tetrahydroborates. Preparation and Crystal Structure of $\text{Ti}(\text{BH}_4)_3(\text{PMe}_3)_2$ Containing an Unusual $\text{Ti}\cdots\text{H}\cdots\text{B}$ Agostic Interaction

James A. Jensen, Scott R. Wilson, and Gregory S. Girolami*

Contribution from the School of Chemical Sciences, The University of Illinois at Urbana—Champaign, 505 South Mathews, Urbana, Illinois 61801. Received November 2, 1987

Abstract: The reaction of trialkylphosphines with $\text{Ti}(\text{BH}_4)_3(\text{Et}_2\text{O})$, prepared in situ from TiCl_4 and LiBH_4 in diethyl ether, gives dark blue adducts of stoichiometry $\text{Ti}(\text{BH}_4)_3(\text{PR}_3)_2$, where PR_3 is PMe_3 , PEt_3 , PMe_2Ph , or $\text{P}(\text{OMe})_3$. Magnetic susceptibility and ESR measurements indicate that these are monomeric titanium(III) species. An X-ray crystal structure of $\text{Ti}(\text{BH}_4)_3(\text{PMe}_3)_2$ (orthorhombic; $Pnma$; $a = 10.757$ (1), $b = 11.145$ (2), $c = 14.270$ (3) Å; $V = 1710.8$ (8) Å³; $Z = 4$; $R_F = 6.4\%$; $R_{wF} = 4.8\%$) reveals an approximate trigonal-bipyramidal geometry, with the phosphines occupying the axial positions: $\text{Ti-P} = 2.571$ (3), 2.539 (3) Å; $\text{P-Ti-P} = 170.27$ (9)°. One of the three equatorial BH_4^- groups is bidentate, $\text{Ti-H}_b = 1.90$ (6) Å, $\text{Ti}\cdots\text{B} = 2.40$ (1) Å, $\text{B-H}_b = 1.03$ (7) Å, $\text{B-H} = 1.00$ (8) Å, whereas the other two BH_4^- groups possess unusual geometries involving interaction of the titanium center with one B-H bond in a "side-on" manner, $\text{Ti-H}_c = 1.73$ (7) Å, $\text{Ti-B} = 2.27$ (1) Å, $\text{B-H}_c = 0.95$ (6) Å, $\text{B-H}_c = 0.96$ (6) Å. This unusual interaction may be a type of Jahn-Teller distortion and closely resembles one proposed transition state for the activation of the isoelectronic molecule methane.

Titanium trichloride and triethylaluminum are the key components of industrial catalysts for the polymerization of olefins.¹⁻³ The actual active species in these systems are thought to be

(1) Boor, J. *Ziegler-Natta Catalysts and Polymerizations*; Academic: New York, 1979.

(2) Gavens, P. D.; Bottrill, M.; Kelland, J. W.; McMeeking, J. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Chapter 22-5.

(3) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99-149.

titanium alkyls that are able to insert olefins sequentially into the Ti-C bond. Although it is not known with certainty which oxidation state of titanium is primarily responsible for the polymerization catalysis, several studies indicate that there is a correlation between the concentration of trivalent titanium and the rate of polymerization.⁴⁻⁷ Despite the uncertainty in oxidation state,

(4) Adema, E. H. *J. Polym. Sci., Part C* **1968**, *16*, 3643-3645.

it is important to understand the chemistry of titanium(III) compounds as completely as possible, since they serve as catalyst precursors, if not the actual catalysts, in olefin polymerization systems.

The interaction of TiCl_4 and excess LiBH_4 has long been known to yield the unstable titanium(III) tetrahydroborate complex $\text{Ti}(\text{BH}_4)_3$,^{8,9} and this species has been reported in the patent literature to be an active olefin polymerization catalyst (or catalyst precursor).¹⁰ Unfortunately, the structure of $\text{Ti}(\text{BH}_4)_3$ is not known, and the mechanism by which it polymerizes olefins has not been studied. In order to elucidate the nature of this interesting species and more generally to investigate the chemistry of trivalent titanium complexes, we have prepared and characterized several tertiary phosphine adducts of $\text{Ti}(\text{BH}_4)_3$. Of primary interest is the presence of a highly unusual tetrahydroborate bonding mode, in which one B-H bond of a BH_4^- unit is coordinated in a "side-on" fashion to the titanium center. This bonding mode closely resembles one proposed transition state for the activation of alkanes.¹¹

Results

Synthesis and Characterization of $\text{Ti}(\text{BH}_4)_3(\text{PR}_3)_2$ Complexes.

The reaction of TiCl_4 with excess LiBH_4 affords a convenient in situ preparation of the thermally unstable titanium(III) tetrahydroborate complex $\text{Ti}(\text{BH}_4)_3(\text{Et}_2\text{O})$.⁹ Addition of 2 equiv of a tertiary phosphine to solutions of $\text{Ti}(\text{BH}_4)_3(\text{Et}_2\text{O})$, followed by crystallization from pentane or diethyl ether, gives the blue crystalline complexes $\text{Ti}(\text{BH}_4)_3(\text{PR}_3)_2$, where PR_3 is PMe_3 , PEt_3 , PMe_2Ph , or $\text{P}(\text{OMe})_3$. All of these molecules are air-sensitive, and the thermal stabilities of these complexes decrease as the phosphine becomes larger or less basic. Thus, $\text{Ti}(\text{BH}_4)_3(\text{PMe}_3)_2$ is stable under argon at room temperature for up to 1 week, while the PMe_2Ph and $\text{P}(\text{OMe})_3$ analogues noticeably decompose in a matter of a few hours; all are indefinitely stable at -20°C . Attempts to isolate the $\text{P}(t\text{-Bu})_3$ analogue were unsuccessful due to the low thermal stability of the adduct, as expected on steric grounds. In contrast, the bidentate phosphine 1,2-bis(dimethylphosphino)ethane, dmpe, gives a thermally stable adduct of stoichiometry $\text{Ti}(\text{BH}_4)_3(\text{dmpe})$. However, this complex is completely insoluble in solvents with which it does not react and evidently adopts a polymeric structure linked by bridging dmpe ligands. The inability of dmpe to form a monomeric chelate complex suggests that the phosphine ligands in the $\text{Ti}(\text{BH}_4)_3(\text{PR}_3)_2$ compounds occupy mutually trans positions in the coordination sphere.

Magnetic susceptibility measurements in toluene at room temperature by Evans' method indicate that the $\text{Ti}(\text{BH}_4)_3(\text{PR}_3)_2$ compounds possess magnetic moments characteristic of monomeric d^1 species. Thus, the magnetic moments of $1.7 \mu_B$ for $\text{Ti}(\text{BH}_4)_3(\text{PMe}_3)_2$ and $1.5 \mu_B$ for $\text{Ti}(\text{BH}_4)_3(\text{PEt}_3)_2$ are near the spin-only value for one unpaired electron. The solution ESR spectra in toluene at room temperature show a binomial triplet centered at $g_{\text{iso}} = 1.97$, indicative of hyperfine coupling to two equivalent $I = 1/2$ phosphorus nuclei. The isotropic ^{31}P hyperfine coupling constant of 0.0025 cm^{-1} falls within the narrow $0.0025\text{--}0.0026\text{-cm}^{-1}$ range reported for other Ti^{III} phosphine complexes.^{12,13} Small wing peaks are evident in the spectrum

Table I. Crystal Data for $\text{Ti}(\text{BH}_4)_3(\text{PMe}_3)_2$ (25°C)

space gp: <i>Pnma</i>	$Z = 4$
$a = 10.757 (1) \text{ \AA}$	mol wt = 244.58
$b = 11.145 (2) \text{ \AA}$	$d_{\text{calcd}} = 0.950 \text{ g cm}^{-3}$
$c = 14.270 (3) \text{ \AA}$	$\mu_{\text{calcd}} = 6.45 \text{ cm}^{-1}$
$V = 1710.8 (8) \text{ \AA}^3$	size = $0.3 \times 0.4 \times 0.4 \text{ mm}$
diffractometer: Enraf-Nonius CAD-4	
radiatn: Mo $\text{K}\alpha$, $\lambda = 0.71073 \text{ \AA}$	
monochromator: graphite crystal, $2\theta = 12^\circ$	
scan range, type: $2.0 \leq 2\theta \leq 53.0^\circ$, ω/θ	
scan speed, width: $2\text{--}16^\circ \text{ min}^{-1}$	
$\Delta\omega = 1.50(1.00 + 0.35 \tan \theta)^\circ$	
reflcs: 2105, 1866 unique, 777 with $I > 1.96\sigma(I)$	
$R_F = 6.4\%$	variables 113
$R_{wF} = 4.8\%$	p factor 0.010

Table II. Atomic Coordinates for $\text{Ti}(\text{BH}_4)_3(\text{PMe}_3)_2$

	x/a	y/b	z/c
Ti	0.7881 (1)	0.25	0.02869 (9)
P1	0.6206 (2)	0.25	-0.0999 (1)
P2	0.9795 (2)	0.25	0.1328 (2)
C1	0.464 (1)	0.25	-0.0580 (10)
C2	0.625 (1)	0.1199 (8)	-0.1766 (5)
C3	0.940 (1)	0.25	0.2582 (9)
C4	1.082 (1)	0.125 (1)	0.121 (1)
B1	0.934 (1)	0.25	-0.0982 (8)
B2	0.7156 (9)	0.0767 (10)	0.0921 (7)
H1	0.442 (6)	0.188 (7)	-0.025 (5)
H2	0.394 (9)	0.25	-0.109 (6)
H3	0.700 (6)	0.144 (6)	-0.213 (5)
H4	0.609 (7)	0.052 (6)	-0.142 (5)
H5	0.557 (6)	0.136 (6)	-0.216 (4)
H6	0.884 (7)	0.188 (7)	0.264 (5)
H7	1.024 (8)	0.25	0.277 (6)
H8	1.118 (7)	0.124 (7)	0.055 (4)
H9	1.026 (8)	0.066 (8)	0.125 (7)
H10	1.131 (7)	0.125 (8)	0.160 (6)
H11	0.906 (9)	0.25	-0.163 (6)
H12	1.029 (8)	0.25	-0.089 (6)
H13	0.892 (6)	0.179 (6)	-0.064 (4)
H14	0.717 (6)	-0.000 (6)	0.136 (4)
H15	0.646 (6)	0.067 (7)	0.070 (5)
H16	0.777 (5)	0.049 (6)	0.046 (4)
H17	0.722 (6)	0.157 (5)	0.113 (5)

that are ascribable to hyperfine coupling with the ^{47}Ti and ^{49}Ti isotopes. The isotropic hyperfine coupling of 0.0012 cm^{-1} is at the upper end of the $0.0002\text{--}0.0013\text{-cm}^{-1}$ values reported for other Ti^{III} species.¹²⁻¹⁵ The absence of hydrogen or boron hyperfine coupling in the ESR spectra suggests that the unpaired electron lies in an orbital possessing a nodal plane that passes through the boron nuclei. Given an approximate trigonal-bipyramidal geometry (see below), we can assign the unpaired electron to a molecular orbital having d_{xz} or d_{yz} character.

The ^1H NMR spectrum of $\text{Ti}(\text{BH}_4)_3(\text{PMe}_3)_2$ shows a broad PMe_3 resonance at $\delta = -1.65$ (full-width at half-maximum 325 Hz) that changes only slightly from -40 to $+25^\circ\text{C}$. The BH_4^- protons could not be observed at any temperature, evidently due to their proximity to the paramagnetic center. No ^{11}B or ^{31}P NMR resonances from the compounds could be located, for an undoubtedly similar reason.

The IR spectra of all the $\text{Ti}(\text{BH}_4)_3(\text{PR}_3)_2$ compounds are closely similar, and the strong bands at 2410, 2367, and 2115 cm^{-1} are diagnostic of the presence of at least one bidentate BH_4^- group.¹⁶ The presence of a second tetrahydroborate bonding mode in the $\text{Ti}(\text{BH}_4)_3(\text{PR}_3)_2$ molecules is indicated by an absorption at 2538 cm^{-1} . Although this band might at first glance be ascribable to a tridentate tetrahydroborate ligand, the other marker bands in the $2200\text{--}2500\text{-cm}^{-1}$ region that would support this assignment

(5) Bartelink, H. J. M.; Bos, H.; Smidt, J.; Vrinssen, C. H.; Adema, E. H. *Recl. Trav. Chim. Pays-Bas* **1962**, *81*, 225-237.

(6) Kollar, L.; Simon, A.; Osvath, J. *J. Polym. Sci., Polym. Chem. Ed.* **1968**, *6*, 919-926.

(7) However, for studies that suggest Ti^{IV} to be the active oxidation state in a noncommercial system, see: Henrici-Olive, G.; Olive, S. *J. Polym. Sci., Part C* **1967**, *22*, 965-970; and recent work cited in: Jordan, R. F. *J. Chem. Educ.* **1988**, *65*, 285-289.

(8) Hoekstra, H. R.; Katz, J. J. *J. Am. Chem. Soc.* **1949**, *71*, 2488-2492.

(9) Franz, H.; Fusstetter, H.; Nöth, H. *Z. Anorg. Allg. Chem.* **1976**, *427*, 97-113.

(10) Raum, A. L. J.; Fraser, D. A. Br. Patent 801 401, 1958.

(11) Jensen, J. A.; Girolami, G. S. *J. Chem. Soc., Chem. Commun.* **1986**, 1160-1162.

(12) Kenworthy, J. G.; Myatt, J.; Symons, M. C. R. *J. Chem. Soc. A* **1971**, 3428-3430.

(13) Schmulbach, C. D.; Kolich, C. H.; Hinckley, C. C. *Inorg. Chem.* **1972**, *11*, 2841-2843.

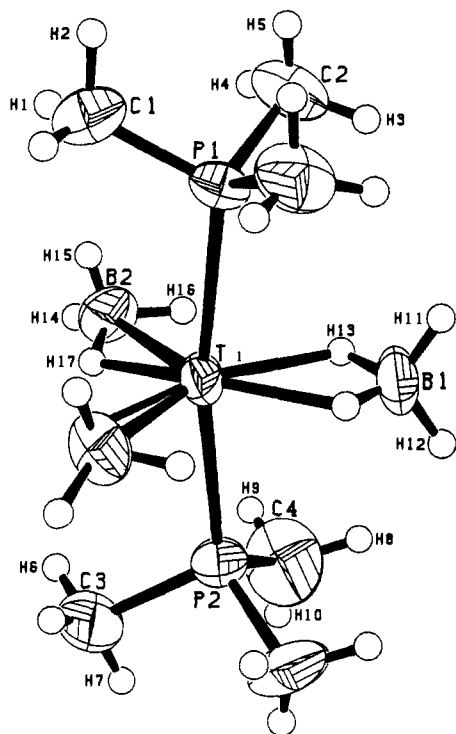
(14) Dessey, R. E.; King, R. B.; Waldrop, M. *J. Am. Chem. Soc.* **1966**, *88*, 5112-5117.

(15) Symons, M. C. R.; Mishra, S. P. *J. Chem. Soc., Dalton Trans.* **1981**, 2258-2262.

(16) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263-293.

Table III. Anisotropic Thermal Parameters for $\text{Ti}(\text{BH}_4)_3(\text{PMe}_3)_2$

	U_{11}, U_{180}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ti	0.0707 (10)	0.201 (2)	0.0557 (9)	0.0	0.0030 (8)	0.0
P1	0.103 (2)	0.090 (2)	0.074 (1)	0.0	-0.024 (1)	0.0
P2	0.082 (2)	0.108 (2)	0.096 (2)	0.0	-0.016 (1)	0.0
C1	0.090 (8)	0.14 (1)	0.17 (1)	0.0	-0.026 (7)	0.0
C2	0.19 (1)	0.140 (8)	0.115 (7)	-0.038 (6)	-0.037 (6)	0.009 (9)
C3	0.13 (1)	0.28 (2)	0.093 (7)	0.0	-0.039 (9)	0.0
C4	0.15 (1)	0.26 (1)	0.22 (1)	0.01 (2)	-0.02 (1)	0.120 (10)
B1	0.097 (10)	0.30 (2)	0.072 (8)	0.0	0.029 (7)	0.0
B2	0.127 (7)	0.101 (7)	0.124 (8)	0.017 (6)	0.008 (6)	-0.057 (8)
H	0.172 (7)					

Figure 1. ORTEP view of the molecular structure of $\text{Ti}(\text{BH}_4)_3(\text{PMe}_3)_2$.

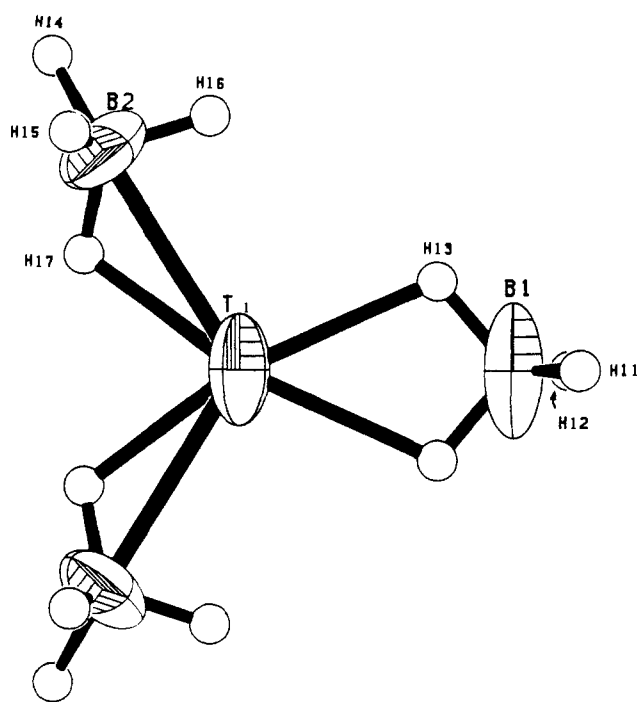
are obscured by the bidentate BH_4^- absorptions, and thus the bonding mode cannot be determined from the B-H stretching frequencies. However, an unusual low-frequency absorption at 517 cm^{-1} is present that is not characteristic of either bidentate or tridentate BH_4^- groups.¹⁶ In order to define the molecular structures of the $\text{Ti}(\text{BH}_4)_3(\text{PR}_3)_2$ species and particularly to establish the nature of the BH_4^- bonding modes, an X-ray crystallographic determination has been carried out. Surprisingly, the results reveal that two of the BH_4^- ligands adopt unprecedented side-on coordination geometries.

X-ray Crystal Structure of $\text{Ti}(\text{BH}_4)_3(\text{PMe}_3)_2$. Suitable crystals of $\text{Ti}(\text{BH}_4)_3(\text{PMe}_3)_2$ were grown from pentane solutions at -20°C . Crystal data are given in Table I, while final atomic coordinates and anisotropic thermal parameters are given with estimated standard deviations in Tables II and III. Bond lengths and angles are presented with their esd's in Table IV.

The structural analysis shows that $\text{Ti}(\text{BH}_4)_3(\text{PMe}_3)_2$ is monomeric in the crystal; a perspective view of the molecule is shown in Figure 1. The molecule possesses crystallographically imposed mirror symmetry, with the mirror plane passing through Ti, B1, H11, H12, P1, C1, H2, P2, C3, and H7. The titanium center adopts a distorted trigonal-bipyramidal geometry with equatorial BH_4^- groups and axial phosphines; the P-Ti-P angle is $170.27(9)^\circ$. Overall, the coordination geometry resembles that previously reported for $\text{Sc}(\text{BH}_4)_3(\text{thf})_2$.^{17,18} The methyl groups of the tri-

Table IV. Selected Bond Distances (\AA) and Angles (deg) for $\text{Ti}(\text{BH}_4)_3(\text{PMe}_3)_2$

Ti-P1	2.571 (3)	P1-Ti-P2	170.27 (9)
Ti-P2	2.539 (3)	P1-Ti-B1	85.5 (3)
Ti...B1	2.40 (1)	P1-Ti-B2	92.5 (2)
Ti-B2	2.27 (1)	P2-Ti-B1	84.8 (3)
Ti-H13	1.90 (6)	P2-Ti-B2	92.6 (2)
Ti-H17	1.73 (7)	H13-Ti-H13'	49 (3)
Ti...H14	3.27 (6)	H13-B1-H13'	100 (5)
Ti...H15	2.62 (7)	H11-B1-H12	115 (7)
Ti...H16	2.25 (7)	H17-Ti-B2	23 (2)
B1-H13	1.03 (7)	H17-B2-Ti	45 (4)
B1-H11	0.98 (8)	H14-B2-H15	98 (6)
B1-H12	1.02 (9)	H14-B2-H16	98 (5)
B2-H17	0.95 (6)	H14-B2-H17	126 (5)
B2-H14	1.06 (6)	H15-B2-H16	108 (6)
B2-H15	0.82 (6)	H15-B2-H17	108 (7)
B2-H16	0.99 (6)	H16-B2-H17	117 (6)
		Ti-H17-B2	112 (5)

Figure 2. View of $\text{Ti}(\text{BH}_4)_3(\text{PMe}_3)_2$ perpendicular to the equatorial plane. The axial PMe_3 groups have been deleted for clarity.

methylphosphine ligands are staggered with respect to the three tetrahydroborate ligands in the equatorial plane.

The Ti-P distances of $2.571(3)$ and $2.539(3)\text{ \AA}$ are the first Ti^{III} phosphine bond lengths to be determined. Comparisons with Ti^{I} , Ti^{II} , and Ti^{IV} trialkylphosphine complexes in the literature show that the Ti-P distances in these molecules do not change significantly with variations in the oxidation state of titanium, since all reported values lie in the range $2.58 \pm 0.07\text{ \AA}$. One of the three equatorial BH_4^- groups adopts a normal bidentate structure as expected from the IR results. The Ti-H13 distance of $1.90(6)\text{ \AA}$ and the Ti...B1 contact of $2.40(1)\text{ \AA}$ resemble the

(17) Lobkovskii, E. B.; Kravchenko, S. E.; Semenenko, K. N. *J. Struct. Chem. (Engl. Transl.)* 1977, 18, 312-314.

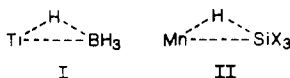
(18) Morris, J. H.; Smith, W. E. *J. Chem. Soc., Chem. Commun.* 1970, 245.

distances observed in another Ti^{III} tetrahydroborate, $\text{Cp}_2\text{Ti}(\eta^2\text{-BH}_4)^{19,20}$ where $\text{Ti-H} = 1.75$ (8) Å and $\text{Ti}\cdots\text{B} = 2.37$ (1) Å.

Undoubtedly the most remarkable feature of the structure is the unusual side-on bonding of two of the tetrahydroborate ligands. A view of the Ti-BH_4 bonding geometry viewed perpendicularly to the equatorial plane is given in Figure 2. The Ti-B2 distance of 2.27 (1) Å is 0.13 Å shorter than that to the normal bidentate BH_4^- ligand and would ordinarily be associated with a tridentate bonding mode such as that in $[\text{CpTi}(\eta^3\text{-BH}_4)\text{Cl}]_2$,^{21,22} where $\text{Ti}\cdots\text{B} = 2.17$ (1) Å. However, only one of the hydrogen atoms is strongly interacting with the titanium center, $\text{Ti-H17} = 1.73$ (7) Å. The next closest titanium-hydrogen contacts, $\text{Ti}\cdots\text{H16} = 2.25$ (7) Å and $\text{Ti}\cdots\text{H15} = 2.62$ (7) Å, are 0.52 and 0.89 Å more distant.

The unusual ligation mode of two of the BH_4^- groups is also evident from the torsion angles, which, interestingly, resemble those of unidentate tetrahydroborate ligands. Thus, the torsion angles $\text{Ti-H17-B2-H16} = -28$ (7)°, $\text{Ti-H17-B2-H14} = -151$ (5)°, and $\text{Ti-H17-B2-H15} = 94$ (7)° are very similar to the analogous $\text{Cu-H}_b\text{-B-H}_i$ torsion angles in $\text{Cu}(\eta^1\text{-BH}_4)(\text{PMePh}_2)_3$,^{23,24} of -27.9° , -157.9° , and $+90.0^\circ$.²⁵ However, the side-on tetrahydroborate ligand in $\text{Ti}(\text{BH}_4)_3(\text{PMe}_3)_2$ and the unidentate group in $\text{Cu}(\text{BH}_4)(\text{PMePh}_2)_3$ exhibit different internal angles at the bridging hydrogen: $\text{Ti-H17-B2} = 112$ (5)° vs $\text{Cu-H}_b\text{-B} = 121.7$ (4)°. The larger Cu-H-B angle results in a nonbonding $\text{Cu}\cdots\text{B}$ contact of 2.518 (3) Å^{23,24} that is much longer than the strongly bonding Ti-B2 contact of 2.27 (1) Å in the present compound. The fact that the M-H-B-H torsion angles in the Ti and Cu compounds are similar suggests that the side-on BH_4^- bonding mode observed in $\text{Ti}(\text{BH}_4)_3(\text{PMe}_3)_2$ can be thought of as a unidentate group that has been swung in toward the metal so as to bring the boron atom within bonding distance of the titanium center.

The nearest analogues to the side-on bonding mode, I, of the BH_4^- ligands in $\text{Ti}(\text{BH}_4)_3(\text{PMe}_3)_2$ are the manganese silyl complexes $\text{CpMn}(\text{CO})_2(\text{SiHR}_3)$,²⁶⁻³¹ which were first prepared by Graham in 1971 by photolysis of $\text{CpMn}(\text{CO})_3$ in the presence of a silane such as SiHCl_3 or SiHPh_3 . These molecules have been



shown by X-ray and neutron diffraction studies to possess a three-center $\text{Mn}\cdots\text{H}\cdots\text{Si}$ unit, II, that is remarkably similar to the $\text{Ti}\cdots\text{H}\cdots\text{B}$ unit described here, taking into account the relative sizes of Ti vs Mn and B vs Si. We will discuss below the factors that favor the adoption of these unusual geometries in such apparently different molecules.

Among transition-metal borane complexes, there are several cluster species that possess $\text{M}\cdots\text{H}\cdots\text{B}$ interactions that are somewhat similar to those in $\text{Ti}(\text{BH}_4)_3(\text{PMe}_3)_2$. The metallocarborane species $\text{Co}[(\text{B}_{10}\text{C}_2\text{H}_{10})_2]_2^-$ and $(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Rh}_2(\text{PPh}_3)_2$,^{32,33} the pentaborane compound $(\text{B}_5\text{H}_9)\text{Fe}(\text{CO})_3$,³⁴ and the butterfly cluster $\text{Fe}_4(\text{BH}_2)\text{H}(\text{CO})_{12}$,³⁵ all contain three-center $\text{M}\cdots\text{H}\cdots\text{B}$ units with direct M-B bonding. More recently, examples of unusual bridging geometries with short M-B contacts involving tetrahydroborate groups have been observed in the dimeric transition-metal complex $[\text{Ru}_2(\text{BH}_4)\text{H}_2(\text{tripod})_2]^+$ and the tetrahedral cluster $\text{Fe}_3(\text{BH}_4)\text{H}(\text{CO})_9$.^{36,37} Other examples of BH_4^- groups bridging between transition metals have been reported,³⁸⁻⁴¹ but in all cases it is difficult to assess the extent of direct bonding between the metal atom and boron. In any event, none of these molecules possesses a side-on B-H bonding mode closely analogous to that found in the $\text{Ti}(\text{BH}_4)_3(\text{PR}_3)_2$ system.

Reactivity of $\text{Ti}(\text{BH}_4)_3(\text{PMe}_3)_2$. The reaction chemistry of the titanium(III) tetrahydroborate complexes has been investigated, and the reaction with ethylene at 25 °C (15 atm) leads to small quantities of polyethylene. At higher temperatures, $\text{Ti}(\text{BH}_4)_3(\text{PMe}_3)_2$ decomposes to give $\text{BH}_3\cdot\text{PMe}_3$ and an insoluble titanium-containing material; accordingly, it is likely that the olefin polymerization activity reported for " $\text{Ti}(\text{BH}_4)_3$ " at 150 °C¹⁰ (20 atm) is a heterogeneous and not a homogeneous process.

No reaction of $\text{Ti}(\text{BH}_4)_3(\text{PMe}_3)_2$ is evident with carbon monoxide or pentamethylcyclopentadiene, while excess PMe_3 , trialkylamines, hydrogen, phenylacetylene, diphenylacetylene, lithium alkyls, and LiAlH_4 lead to the formation of intractable metal-containing products and variable amounts of $\text{BH}_3\cdot\text{PMe}_3$. Although loss of BH_3 as $\text{BH}_3\cdot\text{PMe}_3$ was evident in several of these reactions, titanium hydride products could not be detected; this behavior may be compared with similar zirconium, hafnium, niobium, and tantalum systems where metal hydrides can be generated by the addition of a Lewis base to a tetrahydroborate complex.⁴²⁻⁴⁵

Discussion

The molecular structures of the $\text{Ti}(\text{BH}_4)_3(\text{PR}_3)_2$ species have been shown to feature a three-center $\text{Ti}\cdots\text{H}\cdots\text{B}$ interaction that results in a side-on bonding mode for two of the BH_4^- ligands. Significantly, neither the d^0 analogue $\text{Sc}(\text{BH}_4)_3(\text{thf})_2$ ^{17,18} nor the high-spin d^2 analogue $\text{V}(\text{BH}_4)_3(\text{PMe}_3)_2$ ⁴⁶ possesses this structural feature. In fact, the latter molecule adopts a regular D_{3h} geometry with three bidentate BH_4^- groups occupying the equatorial sites of a pseudo-trigonal-bipyramid. In such a D_{3h} geometry, the d orbitals split into three sets: a doubly degenerate set at low energy (d_{xz}, d_{yz}), a doubly degenerate set at intermediate energy ($d_{xy},$

(19) Melmed, K. M.; Coucouvanis, D.; Lippard, S. J. *Inorg. Chem.* **1973**, *12*, 232-236.

(20) Mamaeva, G. I.; Hargittai, I.; Spiridonov, V. P. *Inorg. Chim. Acta* **1977**, *25*, L123-L125.

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

(22) Soloveichik, G. L.; Bulychev, B. M.; Semenenko, K. N. *Sov. J. Coord. Chem. (Engl. Transl.)* **1978**, *4*, 913-919.

(23) Kotal, C.; Grutsch, P.; Atwood, J. L.; Rogers, R. D. *Inorg. Chem.* **1978**, *17*, 3558-3562.

(24) Tagusagawa, F.; Fumagalli, A.; Koetzle, T. F.; Shore, S. G.; Schmitkors, T.; Fratini, A. V.; Morse, K. W.; Wei, C. Y.; Bau, R. *J. Am. Chem. Soc.* **1981**, *103*, 5165-5171.

(25) In contrast, normal bidentate tetrahydroborate ligands including the one in the present structure typically display $\text{M-H}_b\text{-B-H}_i$ torsion angles of 0°, +120°, and -120°; e.g., $\text{Ti-H13-B1-H13}' = 0^\circ$; $\text{Ti-H13-B1-H11} = +116$ (5)°, $\text{Ti-H13-B1-H12} = -116$ (5)°.

(26) Jetz, W.; Graham, W. A. G. *Inorg. Chem.* **1971**, *10*, 4-9.

(27) Harrod, J. F.; Gilson, D. F. R.; Charles, R. *Can. J. Chem.* **1969**, *47*, 2205-2208.

(28) Carre, F.; Colomer, E.; Corriu, R. J. P.; Vioux, A. *Organometallics* **1984**, *3*, 1272-1278.

(29) Schubert, U.; Ackerman, K.; Kraft, G.; Worle, B. Z. *Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 1488-1492.

(30) Schubert, U.; Kraft, G.; Walther, E. Z. *Anorg. Allg. Chem.* **1984**, *519*, 96-106.

(31) Kraft, G.; Kalbas, C.; Schubert, U. *J. Organomet. Chem.* **1985**, *289*, 247-256.

(32) Love, R. A.; Bau, R. *J. Am. Chem. Soc.* **1972**, *94*, 8274-8276.

(33) Baker, R. T.; King, R. E.; Knobler, C.; O'Con, C. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1978**, *100*, 8266-8267.

(34) Shore, S. G.; Ragaini, J. D.; Smith, R. L.; Cottrell, C. E.; Fehlner, T. P. *Inorg. Chem.* **1979**, *18*, 670-673.

(35) Fehlner, T. P.; Housecroft, C. E.; Scheidt, W. R.; Wong, K. S. *Organometallics* **1983**, *2*, 825-833.

(36) Rhodes, L. F.; Venanzi, L. M.; Sorato, C.; Albinati, A. *Inorg. Chem.* **1986**, *25*, 3335-3337.

(37) Vites, J. C.; Eigenbrot, C.; Fehlner, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4633-4635.

(38) Holah, D. G.; Hughes, A. N.; Maciaszek, S.; Magnuson, V. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1308-1309.

(39) Gilbert, T. M.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3508-3516.

(40) Green, B. E.; Kennard, C. H. L.; Smith, G.; James, B. D.; Healy, P. C.; White, A. H. *Inorg. Chim. Acta* **1984**, *81*, 147-150.

(41) Holah, D. G.; Hughes, A. N.; Hui, B. C.; Kan, C. T. *Can. J. Chem.* **1978**, *56*, 2552-2559.

(42) James, B. D.; Nanda, R. K.; Wallbridge, M. G. H. *Inorg. Chem.* **1967**, *6*, 1979-1983.

(43) Otto, E. E. H.; Brinzingler, H. H. *J. Organomet. Chem.* **1978**, *148*, 29-33.

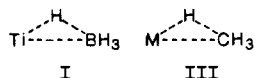
(44) Luekens, M. L.; Huffman, J. C.; Sattelberger, A. P. *J. Am. Chem. Soc.* **1985**, *107*, 3361-3363.

(45) Fryzuk, M. D.; Rettig, S. J.; Westerhaus, A.; Williams, H. D. *Inorg. Chem.* **1985**, *24*, 4316-4325.

(46) Jensen, J. A.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 4450-4451.

$d_{x^2-y^2}$), and a singly degenerate orbital at high energy (d_{z^2}). A high-spin d^2 system is a favorable electronic configuration for a D_{3h} geometry since the doubly degenerate (d_{xz}, d_{yz}) set is half-filled; however, a d^1 molecule should undergo a Jahn–Teller distortion to remove the orbital degeneracy. Although the exact nature of the distortion cannot be rationalized on this basis, the net effect is that there is a driving force in $Ti(BH_4)_3(PMe_3)_2$ to distort away from D_{3h} symmetry. As revealed by the crystallographic study, the observed distortion lowers the symmetry of $Ti(BH_4)_3(PMe_3)_2$ to a C_s geometry.

In order to explore why the side-on geometry is adopted in particular, comparisons can be made between this bonding mode, I, and one possible transition state for the activation of methane, III. In the case of methane, transition state III would clearly



lie along the pathway leading to oxidative addition of the CH_4 molecule. Although the formal distribution of electrons in the $Ti \cdots H \cdots B$ unit of $Ti(BH_4)_3(PMe_3)_2$ is somewhat less clear-cut, it is reasonable to suggest that the side-on BH_4^- ligands are frozen along a pathway that, taken to its limit, would also lead to oxidative addition. Of course, since the low-valent Ti^{III} center is incapable of a two-electron oxidation, the oxidative addition is arrested partway along the reaction coordinate.

In the structurally similar manganese silyl derivatives mentioned previously, oxidative addition is also inhibited, but in this case by the presence of electron-withdrawing carbonyl groups that stabilize the lower oxidation state. Furthermore, oxidative addition would convert a pseudooctahedral d^6 metal center to a seven-coordinate d^4 center with less ligand-field stabilization energy. These circumstances are also those that favor the formation of the recently discovered molecular hydrogen adducts of transition metals.^{47–53}

From a study of the relative reaction rates of $(C_5Me_5)Rh(PMe_3)$ with mixtures of linear alkanes, Bergman⁵⁴ has proposed that rearrangements of alkyl fragments in $(C_5Me_5)Rh(H)(R)(PMe_3)$ complexes to exclusively primary products proceed via an η^2 -alkane intermediate with a structure similar to the side-on BH_4^- group in $Ti(BH_4)_3(PMe_3)_2$. Further evidence of this intermediate was obtained from the kinetic isotope effects for oxidative addition vs reductive elimination. In other work, spectroscopic studies of the photolysis of transition-metal carbonyls in alkane solutions and matrices have provided direct evidence of alkane-solvated metal carbonyl intermediates such as $Cr(CO)_5(CH_4)$ and $Fe(CO)_4(CH_4)$.^{55–62} Similar interactions of metal atoms with alkanes

have been noted in the gas phase.⁶³ Indeed, while no alkane adducts of transition-metal complexes have been isolated as pure complexes, there is increasing evidence that they exist; unfortunately, none of these studies have been able to determine the exact mode of alkane coordination.

Although an extended Hückel calculation predicted that transition state III is less favorable than an “end-on” approach of methane due largely to steric repulsions,⁶⁴ we expect these steric constraints to be much less important in the present $Ti(BH_4)_3(PMe_3)_2$ system, partly because there is more room in the coordination sphere of a large titanium atom but also because the terminal hydrogens on the larger boron atom are farther from the metal center. A similar situation pertains in the manganese silyl derivatives. Both the titanium and the manganese complexes suggest that steric repulsions may *not* be sufficient to prevent the side-on approach of methane to a transition-metal center in all cases. Indeed, it is possible that the *productive* transition state leading to C–H bond activation of alkanes involves this kind of concerted process, in which the M–C and M–H bonds are formed simultaneously.

Experimental Section

All operations were carried out in vacuo or under argon with standard techniques. Solvents were distilled under nitrogen from sodium (toluene) or sodium benzophenone (pentane, diethyl ether, tetrahydrofuran) immediately before use. 1,2-Bis(dimethylphosphino)ethane,⁶⁵ PMe_3 ,⁶⁶ PEt_3 ,⁶⁶ and PMe_2Ph ⁶⁷ were prepared by modifications of literature routes; $LiBH_4$ (Strem) was used without purification, while $TiCl_4$ (Fisher) and $P(OMe)_3$ (Aldrich) were distilled prior to use. Ethylene (Airco) was purified by sequential passage through H_2SO_4 , KOH pellets, BTS catalyst (BASF), and 4-Å molecular sieves (Linde).

Microanalyses were performed by Josef Nemeth of the University of Illinois Microanalytical Laboratory. The IR spectra were recorded on a Perkin-Elmer 599B as Nujol mulls. The 1H NMR data were recorded on a Perkin-Elmer R-24B at 60 MHz, a Varian EM-390 at 90 MHz, or a General Electric QE 300 at 300 MHz. Chemical shifts are uncorrected for the paramagnetic shift of the solvent. Magnetic moments were determined in toluene by a modification of Evans' method.⁶⁸ Melting points were determined in closed capillaries under argon.

Tris(tetrahydroborato)bis(trimethylphosphine)titanium(III). To $TiCl_4$ (1.0 mL, 9.1 mmol) in diethyl ether (50 mL) was added dropwise a solution of $LiBH_4$ (0.91 g, 41.8 mmol) in diethyl ether (150 mL). After the addition was complete, the solution was stirred an additional 2 h and then concentrated to ca. 50 mL. After the solution was cooled to $-78^\circ C$ and filtered, PMe_3 (1.85 mL, 18.2 mmol) was added, causing the pale blue-green solution to turn bright blue. The solution was warmed to $0^\circ C$, the solvent was removed, and the residue was extracted with cold ($0^\circ C$) pentane (150 mL). The pentane extract was filtered, concentrated to ca. 100 mL, and cooled to $-20^\circ C$. Blue crystals of the complex were isolated, and several further crops of the crystals were obtained by concentration and cooling of the supernatant; yield 1.57 g (70%). Anal. Calcd: C, 29.5; H, 12.4; Ti, 19.6. Found: C, 29.3; H, 11.4; Ti, 17.8. Mp: $104^\circ C$ dec. 1H NMR (C_6D_6 , $25^\circ C$): δ -1.65 (s, fwhm = 325 Hz, PMe_3). 1H NMR (C_7D_8 , $-40^\circ C$): δ -2.33 (s, fwhm = 700 Hz, PMe_3). ESR (C_7H_8 , $25^\circ C$): $g_{iso} = 1.977$, $A(^{31}P) = 0.0025$ cm $^{-1}$. IR (Nujol, cm $^{-1}$): 2532 m, 2401 s, 2358 s, 2276 w, 2230 w, 2209 w, 2110 s br, 1433 w, 1420 m, 1355 m br, 1303 m, 1286 m, 1218 m br, 1136 s, 994 w, 945 s, 845 w, 736 m, 517 m br, 414 m br.

Tris(tetrahydroborato)bis(triethylphosphine)titanium(III). $Ti(BH_4)_3(PEt_3)_2$ was prepared from $TiCl_4$ (1.0 mL, 9.1 mmol), $LiBH_4$ (1.05 g, 48.2 mmol), and PEt_3 (4.0 mL, 27.1 mmol) in a manner analogous to the preparation of $Ti(BH_4)_3(PMe_3)_2$. Two crops of blue needles were obtained from pentane at $-20^\circ C$; yield 0.80 g (27%). Anal. Calcd: C, 43.8; H, 12.9; Ti, 14.6. Found: C, 41.9; H, 12.8; Ti, 14.8. Mp: $75^\circ C$.

(62) Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1974**, 2276–2285.

(63) Kafafi, Z. H.; Hauge, R. H.; Margrave, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 6134–6135.

(64) Saillard, J. Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006–2026.

(65) Burt, R. J.; Chatu, J.; Hussain, W.; Leigh, G. J. *J. Organomet. Chem.* **1979**, *182*, 203–206.

(66) Wolfsberger, W.; Schmidbauer, H. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 149–156.

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

(68) Evans, D. F.; Fazakerley, G. V.; Phillips, R. F. *J. Chem. Soc. A* **1971**, 1931–1934.

(47) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451–452.

(48) Upmacis, R. K.; Gadd, G. E.; Poliakoff, M.; Simpson, M. B.; Turner, J. J.; Wyman, R.; Simpson, A. F. *J. Chem. Soc., Chem. Commun.* **1985**, 27–30.

(49) Church, S. P.; Grevels, F. W.; Hermann, H.; Schaffner, K. *J. Chem. Soc., Chem. Commun.* **1985**, 30–31.

(50) Sweany, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 2374–2379.

(51) Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1986**, 794–795.

(52) Ashworth, T. V.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1976**, 705–706.

(53) Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581–5582.

(54) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332–7346.

(55) Turner, J. J.; Burdett, J. K.; Perutz, R. N.; Poliakoff, M. *Pure Appl. Chem.* **1977**, *49*, 271–285.

(56) Kelly, J. M.; Bent, D. V.; Hermann, H.; Schulte-Frohlinde, D.; Koerner von Gustorf, E. *J. Organomet. Chem.* **1974**, *69*, 259–269.

(57) Bonneau, R.; Kelly, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 1220–1221.

(58) Hermann, H.; Grevels, F. W.; Henne, A.; Schuffner, K. *J. Phys. Chem.* **1982**, *86*, 5151–5154.

(59) Welch, J. A.; Peters, K. S.; Vaida, J. *J. Phys. Chem.* **1982**, *86*, 1941–1947.

(60) Kelly, J. M.; Long, C.; Bonneau, R. *J. Phys. Chem.* **1983**, *87*, 3344–3349.

(61) Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4791–4800.

°C dec. ¹H NMR (C₆D₆, 18 °C): δ 1.04 (s, fwhm = 80 Hz, PEt). ESR (C₇H₈, 25 °C): $g_{\text{iso}} = 1.972$, $A(^{31}\text{P}) = 0.0025 \text{ cm}^{-1}$. IR (Nujol, cm⁻¹): 2530 m, 2414 s, 2374 s, 2283 w, 2236 w, 2218 w, 2118 s br, 1416 m, 1347 m br, 1259 m br, 1214 m br, 1126 s, 1038 m, 996 w, 767 m, 753 m, 731 w, 717 w, 690 w, 514 w br, 403 w br.

Tris(tetrahydroborato)bis(dimethylphenylphosphine)titanium(III), Ti(BH₄)₃(PMe₂Ph)₂ was obtained from TiCl₄ (1.0 mL, 9.1 mmol), LiBH₄ (0.97 g, 44.5 mmol), and PMe₂Ph (2.6 mL, 18.2 mmol) in a manner analogous to the preparation of Ti(BH₄)₃(PMe₃)₂. Crystallization from 1:1 diethyl ether/pentane at -78 °C gave blue prisms, yield 2.33 g (69%). Mp: 75 °C dec. Anal. Calcd: C, 52.1; H, 9.3. Found: C, 50.9; H, 9.7. ¹H NMR (C₆D₆, 18 °C): δ 8.32 (s, fwhm = 156 Hz, ortho H), 7.67 (s, fwhm = 56 Hz, meta H), 7.25 (s, fwhm = 37 Hz, para H), -1.24 (s, fwhm = 670 Hz, PMe₂). ESR (C₇H₈, 25 °C): $g_{\text{iso}} = 1.976$, $A(^{31}\text{P}) = 0.0023 \text{ cm}^{-1}$. IR (Nujol, cm⁻¹): 2530 m, 2410 s, 2370 s, 2300 w, 2230 w, 2215 w, 2115 s br, 1433 m, 1418 w, 1338 w, 1294 m, 1279 m, 1210 m br, 1120 s, 1100 sh, 1025 w, 995 w, 941 m, 914 m, 904 s, 869 m, 841 w, 826 m, 743 s, 708 m, 689 s, 515 m br, 483 m, 404 m br.

Tris(tetrahydroborato)bis(trimethyl phosphite)titanium(III), Ti(BH₄)₃[P(OMe)₃]₂ was obtained from TiCl₄ (1.0 mL, 9.1 mmol), LiBH₄ (1.0 g, 45.9 mmol), and P(OMe)₃ (2.2 mL, 18.6 mmol) in a manner analogous to the preparation of Ti(BH₄)₃(PMe₃)₂. Crystallization from diethyl ether at -78 °C gave blue prisms. The low thermal stability of this compound precluded obtaining reliable microanalytical data. IR (Nujol, cm⁻¹): 2525 m, 2410 s, 2375 s, 2345 sh, 2195 w, 2130 s br.

Tris(tetrahydroborato)[1,2-bis(dimethylphosphino)ethane]titanium(III), [Ti(BH₄)₃(dmpe)]_n was obtained from TiCl₄ (1.0 mL, 9.1 mmol), LiBH₄ (0.97 g, 44.5 mmol), and dmpe (3.0 mL, 18.2 mmol) in a manner analogous to the preparation of Ti(BH₄)₃(PMe₃)₂. The pale blue solid residue was washed with cold (0 °C) diethyl ether (3 × 50 mL) and dried under vacuum. The solid obtained contains significant amounts of LiCl. Mp: 190 °C dec. IR (Nujol, cm⁻¹): 2542 m, 2405 s, 2362 s, 2336 sh, 2249 w, 2217 w, 2107 s br, 1435 m, 1346 m, 1302 m, 1286 m, 1215 m, 1197 m, 1131 s, 1116 w, 1001 w, 949 s, 910 sh, 880 w, 835 w, 796 w, 741 m, 720 m, 527 w br, 405 w br.

Ethylene Polymerization Study. Ti(BH₄)₃(PMe₃)₂ (0.16 g, 0.7 mmol) in benzene (20 mL) was transferred to a glass Fisher-Porter bottle and cooled to -196 °C. The flask was evacuated, and ethylene (60 mmol) was condensed into the vessel. As the reactor warmed to room temperature, white solid began forming. The solution was stirred 6 h at room temperature and then was heated to 60 °C for 1 h. At this time all of the initial blue color had discharged. The white solid was collected by filtration, washed with dilute HCl and methanol, and air-dried.

Crystallographic Study. Dark blue single crystals of Ti(BH₄)₃(PMe₃)₂ were grown from pentane at -20 °C and were sealed in thin-walled glass capillaries under argon. A suitable crystal was transferred to the diffractometer, and standard peak searching and automatic indexing procedures revealed the orthorhombic cell. Least-squares refinement with 25 reflections yielded the cell dimensions given in Table I. Data were collected in one octant of reciprocal space (+*h*, +*k*, -*l*) with measurement parameters given in Table I. Systematic absences for 0*kl* (*k* + *l* ≠ 2*n*), and *hk*0 (*h* ≠ 2*n*) were consistent with space groups *Pnma* and *Pn2₁a*. Refinement in the centric space group *Pnma* proceeded after correcting for Lorentz,⁶⁹ polarization,⁶⁹ and absorption⁷⁰ effects; for the last, the maximum and minimum transmission factors were 0.848 and 0.781. The structure was solved by Patterson and Fourier methods.⁷¹ The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$ where $w = 4.85/[\sigma(F_o)^2 + (pF_c)^2]$.⁷² Analytical approximations to the scattering factors were used, and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion.⁷³ All non-hydrogen atoms were refined anisotropically, hydrogen atoms were independently refined with one common isotropic thermal parameter, and an empirical isotropic extinction parameter⁷⁴ converged to $1.4(3) \times 10^{-7}$.

Successful convergence was indicated by the maximum shift/error of 0.02 for the last cycle of least-squares refinement. Final refinement parameters are given in Table I. The final difference Fourier map had no significant features, with all peaks less than 0.4 e/Å³. Refinement of the proposed model in the acentric space group *Pn2₁a* did not significantly change the model or improve the fit of the data ($R_{wF} = 0.041$ on 200 variables); the acentric choice was rejected on the basis of a Hamilton *R* factor ratio test.⁷⁵ Despite a large crystal volume, the percentage of observed data at the 1.96σ level was somewhat low. This fact is attributable to the relative absence of heavy scatterers in general positions: The titanium atom, both phosphorus atoms, two of the six carbon atoms, and one of the three boron atoms all lie in the crystallographic mirror plane at *y* = 0.25. Nevertheless, sufficient data were obtained to prevent difficulties in the refinement procedure, and the data to variable ratio of 6.9:1 was judged to be quite acceptable.

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 BH₄⁻ geometry across the crystallographic mirror plane. Such a model might account for the short Ti-B2 contact 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 of the side-on BH₄⁻ groups, possess nearly isotropic thermal parameters and do not suggest that any disorder of the side-on BH₄⁻ groups is present. Furthermore, the positions of the hydrogen atoms on B2 are inconsistent 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, Ti-H17, observed. Overall, we consider that a disordered model can be rejected as inconsistent with the evidence.

Three crystals of Ti(BH₄)₃(PMe₃)₂ were examined in all, and full data sets were obtained for each; the results above were from crystal one. For crystal two (see supplementary material), the larger sample volume, 0.5 × 0.6 × 0.7 mm, resulted in a larger number of observed reflections, 901 with *I* > 2.58δ(*I*). The crystal was slightly twinned, and the mosaic spread was larger than for crystal one; however, no problems were encountered during data collection, and refinement of the data set proceeded smoothly to give a weighted residual of $R_{wF} = 0.057$. The refined parameters for crystal two, including hydrogen atom positions, were all within 1 esd of the parameters from crystal one, except *U*₁₁ and *U*₃₃ for Ti and *U*₃₃ for P1, which were within 2 esd's.

For crystal three (see supplementary material), data were collected in four octants to test the Laue group: (+*h*, +*k*, +*l*), (+*h*, +*k*, -*l*), (+*h*, -*k*, +*l*), and (-*h*, +*k*, +*l*). The 865 nonunique data measured gave an internal consistency index of $R_i = 0.067$ and confirmed the orthorhombic crystal habit. However, for this crystal the number of observed reflections was low: 552 with *I* > 2.58σ(*I*). This data set showed substantial crystal decay over the collection period, and data sets for the other two crystals were accordingly restricted to one octant.

The refinement parameters for crystal one were judged to be the most reliable since this sample exhibited the most precise cell constants, had the smallest mosaic spread, and showed the best agreement between *F*_o and *F*_c.

We were unable to obtain a useful data set at temperatures below room temperature because the crystals undergo a phase transformation at ca. -25 °C. Attempts were made to collect neutron diffraction data at the IPNS facility at Argonne National Laboratories. However, all crystals with suitably large sample volumes diffracted poorly and appeared to be severely twinned.

Acknowledgment. We thank the National Science Foundation (Grant CHE-85-21757) and the Office of Naval Research under their Young Investigator Award Program for support of this research. We also thank Dr. Arthur J. Schultz of Argonne National Laboratory and Charlotte Stern of the University of Illinois for their assistance. G.S.G. is the recipient of a Sloan Research Foundation Fellowship (1988-1990).

Supplementary Material Available: Descriptions of data sets on crystals two and three (7 pages); table of final observed and calculated structure factors for Ti(BH₄)₃(PMe₃)₂ (4 pages). Ordering information is given on any current masthead page.

(74) Zachariasen, W. H. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Gen. Crystallogr.* **1968**, *24*, 212-216.

(75) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502-510.

(69) Stout, G. H.; Jensen, J. H. *X-ray Determination, a Practical Guide*; Macmillan: New York, 1968; pp 195-200.

(70) Busing, W. R.; Levy, B. A. *Acta Crystallogr.* **1957**, *10*, 180-182.

(71) Software packages in use at the University of Illinois X-ray Crystallographic Laboratory include the following. SHELXS-86: Sheldrick, G. N. *Crystallographic Computing 3*; Sheldrick, G. N., Kruger, C., Goddard, R., Eds.; Oxford University: New York, 1985; pp 175-189. MULTAN 80: Mann, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; German, G.; Declercq, J.-P.; Woolfson, M. M. ORTEP-II: Johnson, C. K. *ORNL-3794*; Oak Ridge National Laboratory: Oak Ridge, TN, 1971.

(72) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197-210.

(73) *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch: Birmingham, England, 1974; Vol. IV.