Metal-Mediated Formation of Boron–Silicon Bonds. Synthesis and Characterization of η^1- and η^2-Silylborohydride Complexes of Tantalum

Qian Jiang, Patrick J. Carroll, and Donald H. Berry[*,1]

Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104–6323

The tantalum silyl complex $Cp_2Ta(PMe_3)(Si(t\text{-}Bu)_2H)$ (1, $Cp \equiv \eta^5\text{-}C_5H_5$) affects the activation of a B–H bond in amine–borane adducts $L\cdot BH_3$ (L = NEt_3, *N*-methylmorpholine), with formation of new B–Si bonds. The initial product is the silyl-substituted η^2-borohydride complex $Cp_2\text{-}Ta(\eta^2\text{-}BH_3(Si(t\text{-}Bu)_2H))$, 2. Treatment of 2 with PMe_3 initially produces the silyl-substituted η^1-borohydride complex $Cp_2Ta(PMe_3)(\eta^1\text{-}BH_3(Si(t\text{-}Bu)_2H)$, 3. Reaction of 3 with excess PMe_3 leads to complete displacement of the silylborohydride from the metal center and formation of $Me_3P\cdot BH_2(Si(t\text{-}Bu)_2H)$, 4. Compounds 2 and 3 are fluxional on the NMR time scale and undergo bridging–terminal hydride exchange. Both 2 and 3 have been structurally characterized by single-crystal X-ray diffraction methods: 2, $C_{18}H_{32}BSiTa$, monoclinic space group $P2_1/n$ (Z = 4) with a = 12.024 (2) Å, b = 7.952 (1) Å, c = 21.623 (2) Å, β = 105.13 (1)°, and V = 1996 (1) Å^3; 3, $C_{21}H_{41}BPSiTa$, monoclinic space group $P2_1/n$ (Z = 4) with a = 14.455 (2) Å, b = 8.102 (2) Å, c = 21.755 (3) Å, β = 107.56 (1)°, and V = 2429 (1) Å^3.

Introduction

Although transition metal complexes have long been used to promote the transformations of one organic molecule into another, the application of this approach to the synthesis and manipulation of main group inorganic compounds is a relatively recent advance.[2] Better known exceptions, such as the metal-catalyzed insertion of olefins into B–H and Si–H, have traditionally been driven by the desire to modify the organic fragment, rather than as means to prepare new main group inorganic or organometallic compounds. Recently, however, there has been a resurgence in interest in the chemistry of metal complexes containing main group inorganic ligands, both as intermediates in synthetic routes to main group compounds and for their fundamental chemistry. For example, metal-catalyzed routes to compounds containing B–B,[3] Si–Si,[4] B–C,[5] and Si–C[6] bonds have been reported in recent years. This contribution describes the formation of B–Si bonds through the productive activation and functionalization of B–H bonds by a tantalum silyl complex. Intermediate η^2- and η^1-silylborohydride complexes of tantalum have been isolated and structurally characterized, and the

trimethylphosphine adduct of the silylborate ultimately produced has been isolated.

The first molecular compounds containing covalent B–Si bonds, *B*-(triphenylsilyl)borazines, were reported independently by two groups in 1960.[7] Since that time, three types of covalent interactions between organoboron and organosilicon groups have been identified: silylboranes and silylborates containing 2-center, 2-electron B–Si bonds,[8] polyboranes or carboranes with bridging silyls (3-center, 2-electron bonds),[9] and polyborane or carborane compounds in which a silicon atom is completely incorporated into the cage framework.[10] Because all of the earliest known silylboranes contained at least one B–N bond, it was originally proposed that the presence of the amido group was necessary to ensure the stability of these compounds.[11] Although this does not now appear to be

(1) Alfred P. Sloan Fellow, 1990–1992.

(2) For an interesting overview, see: Fehlner, T. P., Ed. *Inorganometallic Chemistry*; Plenum: New York, 1992; and references therein.

(3) (a) Davan, T.; Corcoran, E. W.; Sneddon, L. G. *Organometallics* **1983**, *2*, 1693. (b) Wilczynski, R.; Sneddon, L. G. *Inorg. Chem.* **1982**, *21*, 1693. (c) Wilczynski, R.; Sneddon, L. G. *Inorg. Chem.* **1981**, *20*, 3955.

(4) For example: (a) Harrod, J. F.; Mu, Y.; Samuel, E. *Polyhedron* **1991**, *10*, 1239. (b) Tilley, T. D. In *The Silicon-Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991. (c) Nakano, T.; Nakamura, H.; Nagai, Y. *Chem. Lett.* **1989**, *83*. (d) Brown-Wensley, K. A. *Organometallics* **1987**, *6*, 1590. (e) Chang, L. S.; Corey, J. Y. *Organometallics* **1989**, *8*, 1885.

(5) (a) Corcoran, E. W.; Sneddon, L. G. *J. Am. Chem. Soc.* **1985**, *107*, 7446. (b) Corcoran, E. W.; Sneddon, L. G. *J. Am. Chem. Soc.* **1984**, *106*, 7793. (c) Marsalla, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1982**, *104*, 2361. (d) Rossetto, G.; Porchia, M.; Ossola, F.; Fischer, R. D. *J. Chem. Soc., Chem. Commun.* **1985**, *1460*.

(6) For example, see: (a) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 25. (b) Lappert, M. F.; Maskell, R. K. *J. Organomet. Chem.* **1984**, *264*, 217. (c) Procopio, L. J.; Berry, D. H. *J. Am. Chem. Soc.* **1991**, *113*, 4039.

(7) (a) Seyferth, D.; Kogler, H. P. *J. Inorg. Nucl. Chem.* **1960**, *15*, 99. (b) Cowley, A. H.; Sisler, H. H.; Ryschkewitsch, G. E. *J. Am. Chem. Soc.* **1960**, *82*, 501.

(8) (a) Haase, M.; Klingebiel, U.; Boese, R.; Polk, M. *Chem. Ber.* **1986**, *119*, 1117. (b) Biffar, W.; Nöth, H. *Chem. Ber.* **1982**, *115*, 934. (c) Biffar, W.; Nöth, H.; Schwerthoffer, R. *Liebigs Ann. Chem.* **1981**, *2067*. (d) Biffar, W.; Nöth, H. *Angew. Chem.* **1980**, *19*, 58. (e) Kirk, R. W.; Smith, D. L.; Airey, W.; Timms, P. L. *J. Chem. Soc., Dalton Trans.* **1967**, *89*, 1392. (f) Amberger, V. E.; Römer, R. Z. *Anorg. Allg. Chem.* **1966**, *345*, 1. (g) Nöth, H.; Höllerer, G. *Chem. Ber.* **1966**, *99*, 2197. (h) Nöth, H.; Höllerer, G. *Angew. Chem.* **1962**, *74*, 718. (i) Timms, P. L.; Ehlert, T. C.; Margrave, J. L.; Brinckman, F. E.; Farrar, T. C.; Coyle, T. D. *J. Am. Chem. Soc.* **1965**, *87*, 3819.

(9) (a) Gaines, D. F.; Iorns, T. V. *J. Am. Chem. Soc.* **1967**, *89*, 4249. (b) Gaines, D. F.; Iorns, T. V. *J. Am. Chem. Soc.* **1968**, *90*, 6617. (c) Calabrese, J. C.; Dahl, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 6042. (d) Savory, C. G.; Wallbridge, M. G. H. *J. Chem. Soc., Chem. Commun.* **1971**, *622*. (e) Savory, C. G.; Wallbridge, M. G. H. *J. Chem. Soc., Chem. Commun.* **1972**, *918*. (f) Thompson, M. L.; Grimes, R. N. *Inorg. Chem.* **1972**, *11*, 1925. (g) Tabereaux, A.; Grimes, R. N. *Inorg. Chem.* **1973**, *12*, 792.

(10) (a) Siriwardane, U.; Islam, M. S.; West, T. A.; Hosmane, N. S.; Maguire, J. A.; Cowley, A. H. *J. Am. Chem. Soc.* **1987**, *109*, 4600. (b) Schubert, D. M.; Rees, W. S.; Knobler, C. B.; Hawthorne, M. F. *Organometallics* **1990**, *9*, 2938. (c) Hosmane, N. S.; de Meester, P.; Siriwardane, U.; Islam, M. S.; Chu, S. S. C. *J. Chem. Soc., Chem. Commun.* **1986**, *1421*. (d) Seyferth, D.; Buchner, K.; Rees, W. S.; Davis, W. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 918.
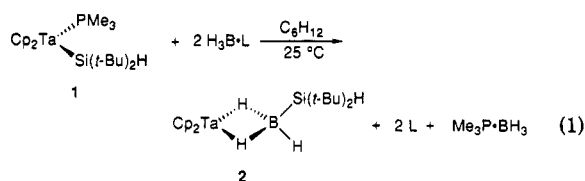
(11) Nöth, H. In *Progress in Boron Chemistry*; Pergamon Press: Oxford, U.K., 1970; Vol. 3, p 281.

© 1993 American Chemical Society

the case, it was only quite recently that organosilylborane compounds which lack B–N bonds were isolated.[12]

Our interest in the metal-mediated formation of B–Si bonds came about indirectly, as a result of on-going studies of a highly reactive tantalum silyl complex, $Cp_2Ta(PMe_3)$-$(Si(t$-$Bu)_2H)$ (1, $Cp \equiv \eta^5$-C_5H_5).[13] Compound 1 had been previously shown to react readily with arene C–H bonds to form tantalum aryls[14] and had been established as a key intermediate in the reaction of a tantalum alkylidene complex with $H_2Si(t$-$Bu)_2$.[15] Reactions of 1 with boranes were initially investigated with the hope that the boron compounds would function as phosphine "sponges", leaving the unsaturated tantalum silyl complex free to form the corresponding silylidene (or silylene) hydride complex by α-hydrogen elimination. The B–H bond functionalization reactions that resulted instead form the basis for this report.

Results and Discussion

Reaction of the tantalum(III) silyl complex Cp_2Ta-$(PMe_3)(Si(t$-$Bu)_2H)$ (1, $Cp \equiv \eta^5$-C_5H_5) with 2 equiv of an amine–borane adduct, $L\cdot BH_3$ (L = NEt_3, N-methylmorpholine (NMM)), in cyclohexane at ambient temperature results in the formation of the silyl-substituted η^2-borohydride complex $Cp_2Ta(\eta^2$-$BH_3(Si(t$-$Bu)_2H))$ (2), as shown in eq 1. Compound 2 has been isolated in 87% yield as a green, air-sensitive crystalline solid. The complex is also thermally sensitive and decomposes slowly in hydrocarbon solution to form an unidentified brown powder, even at –40 °C under N_2.

$$Cp_2Ta\overset{PMe_3}{\underset{Si(t\text{-}Bu)_2H}{\big\langle}} \quad + \ 2\ H_3B\cdot L \quad \xrightarrow[\ 25\ °C\ ]{C_6H_{12}}$$

1

$$Cp_2Ta\overset{H}{\underset{H}{\big\langle}}\overset{\cdots}{B}\overset{Si(t\text{-}Bu)_2H}{\underset{H}{\big\langle}} \quad + \ 2\ L \ + \ Me_3P\cdot BH_3 \quad (1)$$

2

The infrared spectrum of 2 exhibits a strong band at 2412 cm^{-1} characteristic of a terminal B–H stretching mode and two bands at 1688 and 1601 cm^{-1} for bridging B–H stretching modes, indicating a bidentate coordination of the silylborohydride ligand.[16] This is also consistent with the ^1H NMR spectrum observed at –70 °C in toluene, which shows resonances for the terminal B–H (δ 5.90) and the bridging hydrides (δ –16.16) in an integrated ratio of 1:2, in addition to resonances for inequivalent Cp rings (δ 5.07, 4.87), the tert-butyl groups (δ 1.15), and a Si–H group (δ 3.58). The room-temperature ^1H NMR spectrum, however, shows only singlets for the Cp, tert-butyl, and Si–H groups. The B–H resonances are in coalescence at this temperature and are not observed (vide infra). A broad singlet at δ 45 is observed in the $^{11}B\{^1H\}$ NMR spectrum at 25 °C. The shift of this resonance is rather downfield, but this cannot be attributed to the silyl group as a similar value is found in the unsubstituted derivative $Cp_2Ta(\eta^2$-$BH_4)$ (δ 47, vide infra).

(12) (a) Biffar, W.; Nöth, H.; Pommerening, H. *Angew. Chem., Int. Ed. Engl.* 1980, 19, 56. (b) Pachaly, B.; West, R. *Angew. Chem., Int. Ed. Engl.* 1984, 23, 454.

(13) Jiang, Q.; Carroll, P. J.; Berry, D. H. *Organometallics* 1991, 10, 3648.

(14) Berry, D. H.; Jiang, Q. *J. Am. Chem. Soc.* 1989, 111, 8049.

(15) Berry, D. H.; Koloski, T. S.; Carroll, P. J. *Organometallics* 1990, 9, 2952.

(16) For a general review of metal borohydride complexes, see: Marks, T. J.; Kolb, J. R. *Chem. Rev.* 1977, 77, 263.
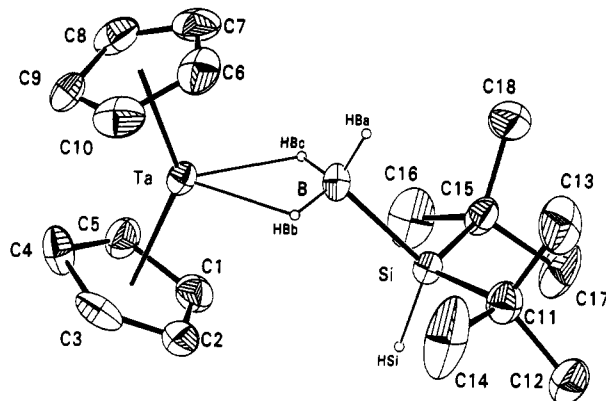
Figure 1. ORTEP drawing of $Cp_2Ta(\eta^2$-$BH_3(Si(t$-$Bu)_2H))$ (2), showing 30% probability thermal ellipsoids.

Table I. Summary of Structure Determinations of 2 and 3

	2	3
formula	$TaSiC_{18}BH_{32}$	$TaPSiC_{21}BH_{41}$
fw	468.30	544.38
cryst dimens (mm)	0.40 × 0.28 × 0.18	0.70 × 0.40 × 0.15
cryst class	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
Z	4	4
cell consts		
a (Å)	12.024 (2)	14.455 (2)
b (Å)	7.952 (1)	8.102 (2)
c (Å)	21.623 (2)	21.755 (3)
β (deg)	105.13 (1)	107.56 (1)
V (Å^3)	1996 (1)	2429 (1)
μ (cm^{-1})	54.96	45.88
D(calc) (g/cm^3)	1.56	1.49
F(000)	928	1096
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
θ range (deg)	2.0–27.5	2.0–27.5
scan mode	ω–2θ	ω–2θ
h,k,l colld	±15,–10,28	±18,–10,–28
no. of reflcns measd	5038	6234
no. of unique reflns	4565	5567
no. of reflcns used in refinement	3597 (>3.0σ)	4392 (>3.0σ)
no. of params	190	242
data/param ratio	18.9	18.1
R_1	0.034	0.031
R_2	0.063	0.039
GOF	2.140	1.292

Table II. Bond Distances (Å) in 2[a]

Ta–B1	2.331 (9)	C1–C5	1.39 (1)
Ta–C1	2.37 (1)	C2–C3	1.37 (2)
Ta–C2	2.42 (1)	C3–C4	1.44 (2)
Ta–C3	2.340 (8)	C4–C5	1.44 (1)
Ta–C4	2.321 (9)	C6–C7	1.39 (2)
Ta–C5	2.31 (1)	C6–C10	1.39 (1)
Ta–C6	2.40 (1)	C7–C8	1.37 (1)
Ta–C7	2.38 (1)	C8–C9	1.43 (1)
Ta–C8	2.35 (1)	C9–C10	1.41 (2)
Ta–C9	2.30 (1)	C11–C12	1.56 (2)
Ta–C10	2.33 (1)	C11–C13	1.54 (2)
Si–B1	2.02 (1)	C11–C14	1.47 (1)
Si–C11	1.92 (1)	C15–C16	1.56 (2)
Si–C15	1.907 (9)	C15–C17	1.53 (1)
C1–C2	1.39 (1)	C15–C18	1.51 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

The molecular structure of 2 as determined by a single-crystal X-ray diffraction study is shown in Figure 1. Crystallographic details are summarized in Table I, and selected bond distances and angles are listed in Tables II and III. Although the positions of the B–H hydrogens could not be refined, the geometrical relationship of the Ta, B, and Si atoms unequivocally supports the bidentate
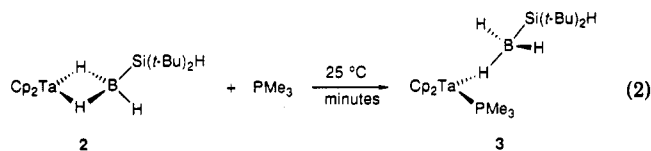
Table III. Selected Bond Angles (deg) in 2[a]

Cp1[b]–Ta–Cp2	139.9	C1–C5–C4	105.7 (9)
B1–Ta–C1	84.3 (3)	C7–C6–C10	109.1 (9)
B1–Ta–C2	89.0 (3)	C6–C7–C8	111.3 (8)
B1–Ta–C3	120.6 (4)	C7–C8–C9	103.7 (9)
B1–Ta–C4	141.7 (4)	C8–C9–C10	111.1 (8)
B1–Ta–C6	84.7 (4)	C6–C10–C9	104.6 (9)
B1–Ta–C7	86.1 (4)	Si–C11–C12	113.6 (8)
B1–Ta–C8	116.2 (3)	Si–C11–C13	113.5 (8)
B1–Ta–C9	139.6 (4)	Si–C11–C14	105.4 (7)
B1–Ta–C10	114.2 (4)	C12–C11–C13	107.8 (8)
B1–Si–C11	108.8 (4)	C12–C11–C14	106.5 (9)
B1–Si–C15	108.9 (4)	C13–C11–C14	110 (1)
C11–Si–C15	116.8 (4)	Si–C15–C16	106.5 (6)
Ta–B1–Si	134.4 (5)	Si–C15–C17	113.9 (7)
C2–C1–C5	111.8 (8)	Si–C15–C18	113.4 (8)
C1–C2–C3	106.4 (9)	C16–C15–C17	105.4 (9)
C2–C3–C4	110.1 (9)	C16–C15–C18	108.4 (9)
C3–C4–C5	106.0 (9)	C17–C15–C18	108.8 (8)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Cp1 and Cp2 refer to the C_5H_5 centroids.

configuration assigned on the basis of IR and NMR spectra. The tantalocene fragment displays a geometry typical for bent metallocene complexes. The boron atom is symmetrically situated in the center of the equatorial wedge at a Ta–B distance of 2.331 (9) Å. In addition, the silicon atom of the di-*tert*-butylsilyl group lies in the plane defined by the two ring centroids and tantalum and is oriented toward one Cp ring, exhibiting a Ta–B–Si angle of 134.4°. This geometry is consistent with a distorted tetrahedral environment at the boron atom consisting of two bridging hydrides, one terminal hydride, and a silyl group. In addition, the Ta–B separation is comparable to the metal boron distances observed in the related η^2-borohydride complexes $Cp_2Nb(\eta^2\text{-}BH_4)$ (2.26 (6) Å)[17] and $Cp_2Ti(\eta^2\text{-}BH_4)$ (2.37 (1) Å).[18] Another significant feature of this structure is the length of the B–Si bond. The bond distance of 2.02 (1) Å is in close agreement with the value of 2.05 estimated from the covalent radii of boron (0.88 Å) and silicon (1.17 Å).[19] The only other structurally characterized compound containing a 2-center 2-electron B–Si single bond is $t\text{-}BuN{\equiv}BSi(SiMe_3)_3$,[8a] in which the B–Si bond is adjacent to the N≡B triple bond. The relatively short B–Si bond length of 1.97 Å in this compound is consistent with the sp hybridization at boron. In contrast, a compound containing a three-center two-electron B–Si interaction, $B_5H_7I(\mu\text{-}SiMe_3)$,[9c] exhibits a substantially longer B–Si distance (2.32 (2) Å). The average B–Si distance found in cage complexes is 2.09 Å.[10]

Compound 2 reacts with PMe_3 within minutes at room temperature to yield the reddish brown complex Cp_2Ta-$(PMe_3)(\eta^1\text{-}BH_3(Si(t\text{-}Bu)_2H))$ (3), as shown in eq 2. The

(2)

2　　　　　　　　　　　　　　　**3**

room-temperature ^{1}H NMR spectrum of **3** exhibits a doublet ($J = 25$ Hz) at δ 0.93, assigned to a coordinated PMe_3 ligand. The spectrum also contains resonances for the Cp rings (δ 4.39, $J_{P-H} = 1.6$ Hz), the *tert*-butyl groups

Figure 2. ORTEP drawing of $Cp_2Ta(PMe_3)(\eta^1\text{-}BH_3(Si(t\text{-}Bu)_2H))$ (3), showing 30% probability thermal ellipsoids.

Table IV. Bond Distances (Å) in 3[a]

Ta–P	2.542 (1)	B1–HB1	1.32 (5)
Ta–B1	2.915 (5)	B1–HB2	1.02 (6)
Ta–C1	2.381 (5)	B1–HB3	1.18 (6)
Ta–C2	2.387 (6)	C1–C2	1.400 (9)
Ta–C3	2.352 (5)	C1–C5	1.41 (1)
Ta–C4	2.313 (6)	C2–C3	1.36 (1)
Ta–C5	2.337 (6)	C3–C4	1.43 (1)
Ta–C6	2.365 (6)	C4–C5	1.420 (8)
Ta–C7	2.410 (6)	C6–C7	1.370 (9)
Ta–C8	2.360 (6)	C6–C10	1.403 (9)
Ta–C9	2.290 (6)	C7–C8	1.38 (1)
Ta–C10	2.308 (6)	C8–C9	1.40 (1)
Ta–HB1	1.88 (5)	C9–C10	1.410 (9)
P–C19	1.824 (5)	C11–C12	1.529 (8)
P–C20	1.837 (6)	C11–C13	1.541 (7)
P–C21	1.820 (6)	C11–C14	1.533 (9)
Si–B1	2.030 (5)	C15–C16	1.54 (1)
Si–C11	1.920 (6)	C15–C17	1.510 (9)
Si–C15	1.938 (5)	C15–C18	1.50 (1)
Si–HSi	1.57 (6)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

(δ 1.44, s) and the proton bound to silicon (δ 3.75, br). In addition, a very broad doublet is observed at δ −5.4 for the three averaged B–H protons. The [11]B–H coupling is not resolved at this temperature.[20] Variable-temperature NMR studies of **3** and **2** will be discussed below. The infrared spectrum of **3** shows two terminal B–H stretching bands at 2395 and 2374 cm^{-1} and a single weak band at 1850 cm^{-1} for the bridging hydrogen, consistent with monodentate coordination of the silylborohydride ligand. The [11]B resonance of **3** is observed at δ −45, which is shifted ca. 90 ppm upfield from that of **2**. Chemical shifts in ^{11}B NMR spectra are influenced by many factors, and the origin of this large shift difference is not clear. One potentially significant difference between **2** and **3** is that the boron atom in **2** is held within the equatorial wedge and in close proximity to the d^2 metal center, whereas the boron in **3** is further away and can freely rotate with respect to the metal.

The molecular structure of **3** as determined by a single-crystal X-ray diffraction study is shown in Figure 2. Crystallographic details are summarized in Table I, and selected bond distances and angles are listed in Tables IV and V. The B–H hydrogens were located and refined.

(17) Kirilova, N. I.; Guser, A. I.; Struchkov, Y. T. *J. Struct. Chem. (Engl. Transl.)* **1974**, *15*, 622.

(18) Melmed, K. M.; Coucouvanis D.; Lippard, S. *Inorg. Chem.* **1973**, *12*, 232.

(19) Pauling, L. In *The Nature of the Chemical Bond*, 3rd ed.; Cornell University: Ithaca, NY, 1960; p 246.
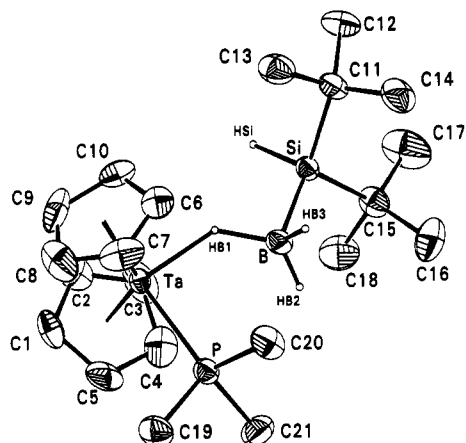
(20) (a) Anderson, J. A.; Astheimer, R. J.; Odom, J. D.; Sneddon, L. G. *J. Am. Chem. Soc.* **1984**, *106*, 2275. (b) Marks, T. J.; Shimp, L. A. *J. Am. Chem. Soc.* **1972**, *94*, 1542. (c) Grace, M.; Beall, H.; Bushweller, C. H. *J. Chem. Soc., Chem. Commun.* **1970**, 701.

Table V. Bond Angles (deg) in 3[a]

Cp1[b]–Ta–Cp2	136.8	C2–C3–C4	107.5 (5)
P–Ta–HB1	97.0 (2)	C3–C4–C5	107.5 (6)
Ta–P–C19	116.1 (2)	C1–C5–C4	107.2 (6)
Ta–P–C20	117.6 (2)	C7–C6–C10	108.6 (5)
Ta–P–C21	118.6 (2)	C6–C7–C8	109.7 (6)
C19–P–C20	101.3 (3)	C7–C8–C9	107.0 (6)
C19–P–C21	99.7 (3)	C8–C9–C10	108.4 (6)
C20–P–C21	100.3 (3)	C6–C10–C9	106.4 (6)
B1–Si–C11	112.6 (2)	Si–C11–C12	114.5 (4)
B1–Si–C15	109.8 (3)	Si–C11–C13	106.9 (4)
B1–Si–HSi	117.0 (2)	Si–C11–C14	111.8 (5)
C11–Si–C15	114.1 (2)	C12–C11–C13	106.7 (5)
C11–Si–HSi	104.0 (2)	C12–C11–C14	109.1 (5)
C15–Si–HSi	99.0 (2)	C13–C11–C14	107.4 (5)
Si–B1–HB1	96.0 (2)	Si–C15–C16	110.3 (4)
Si–B1–HB2	109.0 (3)	Si–C15–C17	114.8 (5)
HB1–B1–HB2	122.0 (4)	Si–C15–C18	106.6 (4)
HB1–B1–HB3	116.0 (4)	C16–C15–C17	108.8 (6)
HB2–B1–HB3	107.0 (5)	C16–C15–C18	107.2 (6)
C2–C1–C5	107.4 (6)	C17–C15–C18	108.9 (6)
C1–C2–C3	110.4 (7)	Ta–HB1–B1	131.0 (4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Cp1 and Cp2 refer to the C_5H_5 centroids.

The Ta atom resides at the center of a pseudotetrahedral environment consisting of two Cp ring centroids, the phosphorus atom, and the single bridging hydrogen atom of the silylborohydride group. The observed Ta–H–B angle is 131.0 (4)°, with accompanying Ta–H and B–H distances of 1.88 (5) and 1.32 (5) Å. Although these bond distances may not be reliable due to the uncertainties associated with locating hydrogen atoms in heavy-atom structures, it should be noted that the distance between the bridging hydrogen and the boron atom is longer than previously reported values for transition metal η^1-BH_4 complexes (1.123–1.170 Å, average = 1.144 Å).[21] The η^1-borohydride configuration is further confirmed by the Ta–B separation of 2.915 Å, which is dramatically longer than that in 2 (2.331 (9) Å). This value is the longest metal–boron distance reported for η^1-borohydride complexes. Previously reported values range from 2.44 (2) ((triphos)Cu(η^1-BH_4))[21e] to 2.876 Å ((CO)$_5$Cr(η^1-B_2H_4· 2PMe$_3$)).[22] The bulky silyl group in 3 is oriented so as to minimize interaction with the Cp rings and the trimethylphosphine ligand. The B–Si bond distance in 3 is 2.030 (5) Å, essentially the same as in 2.

Reaction of 3 with excess PMe$_3$ over hours at 25 °C leads to cleavage of the Ta–H–B bridge and displacement of a silylborane phosphine adduct, Me$_3$P·BH$_2$(Si(t-Bu)$_2$H) (4), from the metal center (eq 3). Compound 4 is a white

(3)
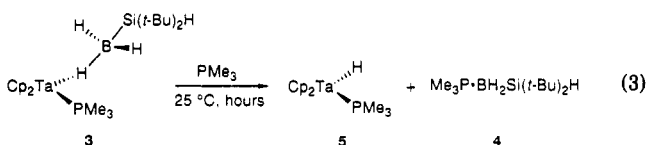
volatile solid with a melting range of 99–101 °C, which can be separated from the tantalum product Cp$_2$Ta(H)-(PMe$_3$)[23] (5) by fractional sublimation. The infrared

(21) (a) Takusagawa, F.; Fumagalli, A.; Koetzle, T. F.; Shore, S. G.; Schmitkons, T.; Fratini, A. V.; Morse, K. W.; Wei, C.-Y.; Bau, R. *J. Am. Chem. Soc.* **1981**, *103*, 5165. (b) Ghilardi, C. A.; Midollini, S.; Orlandini, A. *Inorg. Chem.* **1982**, *21*, 4096. (c) Fryzuk, M. D.; Rettig, S. J.; Westerhaus, A.; Williams, H. D. *Inorg. Chem.* **1985**, *24*, 4316. (e) Jensen, J. A.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 4450. (f) Edelstein, N. *Inorg. Chem.* **1981**, *20*, 299.
(22) Shimoi, M.; Katoh, K.; Ogino, H. *J. Chem. Soc., Chem. Commun.* **1990**, 811.
(23) Tebbe, F. N.; Parshall, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 3793.

spectrum of 4 displays three strong bands in the region of 2000–2500 cm^{-1}. Two bands at 2355 and 2340 cm^{-1} are assigned to the B–H stretching modes, and a sharp band at 2030 cm^{-1} is assigned to the Si–H stretch. The ^{1}H NMR spectrum of 4 consists of resonances for a Si–H group (δ 3.43, d, $^3J_{PH}$ = 9.6 Hz), equivalent *tert*-butyls (δ 1.34, s), and a PMe$_3$ ligand (δ 0.91, d, $^2J_{PH}$ = 10.6 Hz). The B–H protons are not observed in the ^{1}H NMR spectrum. However, a multiplet at δ –42 is observed in the ^{11}B NMR spectrum. This multiplet collapses to a doublet ($J_{^{11}B-^{31}P}$ = 61 Hz) in the proton-decoupled spectrum. Likewise, a 1:1:1:1 quartet exhibiting a 61-Hz coupling constant is observed at δ 0.91 in the ^{31}P{^{1}H} NMR spectrum.

Compound 4 is also formed by the slow disporportionation of 3 in solution at room temperature, which also produces 2 and 5 as shown in eq 4. The reaction probably

(4)
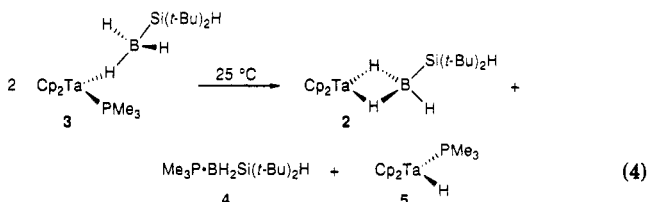
proceeds by an initial reversible PMe$_3$ dissociation from one molecule of 3, yielding 2 and free PMe$_3$. The subsequent reaction of free PMe$_3$ with another molecule of 3 generates 4 and 5, as observed in eq 3.

Although bonding in the Ta–H–B unit in 3 is most properly viewed as a delocalized, 3c–2e$^-$ bond, the reaction chemistry is best predicted by viewing it as a Ta–H bond acting as a two electron donor toward the electron-deficient boron center. The facile displacement of silylborane 4 from the complex, along with the unusually long bridging B–H bond distance, suggests that Cp$_2$Ta(PMe$_3$)(H) can be thought of as a weaker electron donor toward the silylborane fragment than is PMe$_3$. Related examples of complexes which have been described as Lewis acid adducts of transition metal hydrides include trialkylaluminum complexes of Cp$_2$M(H)$_3$ (M = Nb, Ta) and Cp$_2$-Nb(L)(H) (L = CO, PMe$_3$, C$_2$H$_4$).[24]

In contrast to the facile reaction of 1, treatment of less sterically hindered silyl complexes Cp$_2$Ta(PMe$_3$)(SiR$_3$) (SiR$_3$ = SiMe$_2$H, SiMe$_3$)[13] with BH$_3$·NMM results in no reaction after days at 25 °C. Under thermal (100 °C) or photochemical (350 nm) conditions, however, decomposition occurs, which may be due to the instability of the corresponding silylborohydride products under these more rigorous conditions. One of the decomposition products observed in these reactions is Cp$_2$Ta(η^2-BH$_4$) (6). Compound 6 has been independently prepared and isolated in high yield by the photolysis (350 nm) of Cp$_2$Ta(H)(PMe$_3$) (5) and BH$_3$·L (L = NEt$_3$) (eq 5). The ^{1}H NMR spectrum


(5)
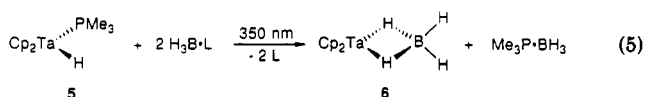
of 6 at 25 °C consists of a quartet centered at δ 6.46 (terminal B–*H*), a singlet at δ 4.87 (C$_5$*H*$_5$), and a broad signal at δ –16.0 (bridging *H*). The ^{11}B NMR resonance

(24) Tebbe, F. N. *J. Am. Chem. Soc.* **1973**, *95*, 5412.

Scheme I
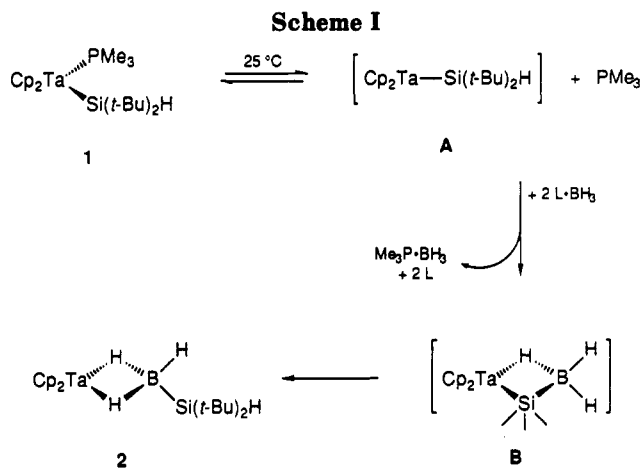
is located at δ 47, which is very close to that found for compound 2 (δ 45).

The overall transformations from silyl complex 1 to silylborane 4 and hydride complex 5 described in eqs 1–3 can be summarized as shown in eq 6, in which L represents
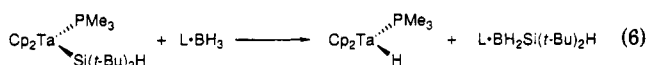
either amine or phosphine bases. The net reaction converts a borane adduct to a silylborane adduct, a productive B–H bond activation by 1. The reaction demonstrates the first example of the formation of a B–Si bond at a transition metal center.

A proposed mechanism for the formation of the B–Si bond is shown in Scheme I. Initial dissociation of the trimethylphosphine ligand from 1 generates the 16e⁻ intermediate A. Attack of BH₃·L on A leads to intermediate B, containing bridging silyl and hydride groups between boron and the metal. Exchange of a terminal hydrogen with the silyl group yields the observed product, 2.

Unlike the related compounds Cp₂Ta(PMe₃)(SiR₃) containing less bulky silyl ligands, 1 readily loses PMe₃ in solution at ambient temperature. Free PMe₃ is trapped as Me₃P·BH₃, thereby greatly increasing the effective concentration of intermediate A. The carbonyl complex Cp₂Ta(CO)(Si(*t*-Bu)₂H), which does not readily lose CO, is unreactive toward L·BH₃ at room temperature. Hence, direct attack of BH₃·L or BH₃ on the silyl ligand of the 18e⁻ phosphine complex seems unlikely. In addition, formation of 6 from 5 and L·BH₃ also does not proceed prior to photochemical generation of the analogous unsaturated tantalum intermediate.

Reaction of BH₃ or BH₃·L with the 16e⁻ intermediate A is the key step for the formation of the B–Si bond. Several examples of polyhedral borane compounds containing bridging silyl groups involved in 3-center 2e⁻ bonds have been reported.[9] In addition, intermediates similar to B have been proposed in the dealkylation reactions of Cp₂-UR (R = Me, Et)[5d] and Cp₂ZrMe₂[5c] with BH₃·L, which lead to the formation of bis(alkylborane). In these latter two reactions, however, the proposed alkyl-substituted borohydride complexes were not observed. It is also worth noting that electron-deficient intermediates with bridging silyl and hydride ligands such as B are quite analogous to those proposed in "σ-bond metathesis" processes in early transition metal complexes.[25]

As described previously, the bridging and terminal hydrogens in compound 2 are not observed by ¹H NMR at 25 °C, and an averaged signal for both bridging and terminal hydrogens is found for compound 3 at this temperature. These observations arise from rapid intramolecular exchange between the bridging and terminal hydrogens, a common phenomenon in transition metal borohydride complexes. The fluxional behavior of compounds 2 and 3 have been examined by variable-temperature NMR.

The ¹H NMR spectrum of 2 exhibits a broad peak centered at δ −8.70 at 380 K. This is the averaged resonance for the two bridging and one terminal hydrogens. As the temperature is decreased, this peak diminishes and two new signals at δ 5.90 and −16.16 for terminal (H$_t$) and bridging (H$_b$) hydrogens appear. Coalescence is observed at 313 ± 10 K ($\Delta G^{\ddagger}$ = 12.6 ± 0.4 kcal mol⁻¹). This is apparently the lowest activation barrier for fluxionality in Nb and Ta η^2-borohydride complexes: Cp₂Nb(η^2-BH₄) (14.6 kcal mol⁻¹ at 346 K);[16] Cp*₂Nb(η^2-BH₄) (16.4 kcal mol⁻¹ at 388 K);[26] CpCp*Ta(η^2-BH₄) (16.4 kcal mol⁻¹ at 298 K).[27] Within group 5, only Cp₂V(η^2-BH₄) has a lower barrier to bridge–terminal exchange ($\Delta G^{\ddagger}$ = 7.6 kcal mol⁻¹ at 186 K).[28]

Interestingly, the averaged proton NMR signal for the Cp ligands (δ 5.05) observed for 2 at room temperature decoalesces at 252 K to two sharp singlets at δ 5.07 and 4.87. The activation barrier for exchange is 12.4 kcal mol⁻¹, very similar to that obtained from the coalescence of the terminal and bridging hydrogens. Coalescence of the Cp signals reflects a process which can be thought of as the exchange of the two terminal sites on boron (B–H and B–Si). In contrast, coalescence of the boron hydride resonances reflects bridge–terminal hydride site exchange. These processes need not necessarily be related, a point made recently by Green and Wong.[27] These workers described a dynamic NMR study of the scrambling process in CpCp*Ta(η^2-BH₄) and concluded that the exchange most likely proceeds via an associative coordination of one of the terminal hydrogens, accompanied by a selective ring slippage of one of the η^5-C₅R₅ ligands. Exchange is completed by rotation of the η^3-BH₄ fragment followed by the specific dissociation of one of the original bridging hydrogens to the same terminal site. Interestingly, a key conclusion of Green's study is that direct exchange between the two terminal hydrogens in CpCp*Ta(η^2-BH₄) is negligible compared with that between bridging and terminal hydrogens. Thus, if the fluxionality of 2 follows Green and Wong's mechanism, a second process would be necessary to provide for the equilibration of Cp ring environments. However, the similarity of the activation barriers for bridge–terminal hydride exchange and Cp equilibration may indicate that both may occur via a common mechanism. Likely pathways leading to both types of exchange simultaneously include (a) dissociation

(25) See, for example: (a) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51–56. (b) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 425–437. (c) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 204–219. (d) Woo, J.-G.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 8043. (e) Tilley, T. D. *Comments Inorg. Chem.* **1990**, *10*, 37.

(26) Bell, R. A.; Cohen, S. A.; Doherty, N. M.; Threliel, R. S.; Bercaw, J. E. *Organometallics* **1986**, *5*, 972.

(27) Green, M. L. H.; Wong, L.-L. *J. Chem. Soc., Dalton Trans.* **1989**, 2133.

(28) Johnson, P. L.; Cohen, S. A.; Marks, T. J.; Williams, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 2709.

of a Ta–H interaction to generate a 16e⁻ η^1-silylborohydride complex (eq 7) and (b) association of a terminal hydride

$$(7)$$

$$(8)$$
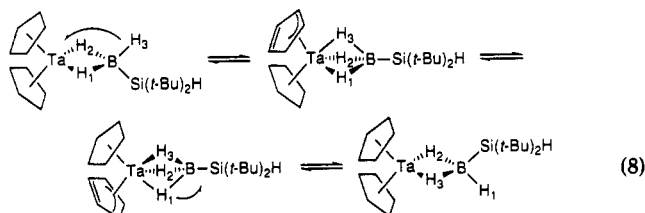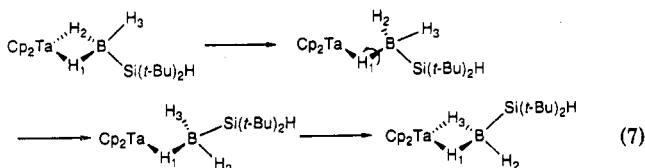
to yield an η^3-borohydride (eq 8). The latter is shown with concurrent slip of the Cp ring to η^3-bonding mode to avoid the intermediacy of an 20e⁻ species. The intermediate in eq 7, a 15e⁻ η^1-silylborohydride complex, would also be the key intermediate in the facile reaction of 2 with PMe₃ to form 3.

The variable-temperature ¹H NMR behavior of 3 is slightly different from that of 2. At room temperature, the complex exhibits a very broad resonance at δ –5.4 for the average chemical shift of H$_b$ and H$_t$. This resonance collapses to a sharp singlet when the ¹¹B resonance is decoupled. The averaged signal gradually decoalesces as the temperature is decreased, until two peaks at δ 0.2 (H$_t$) and δ –15.1 (H$_b$) are observed at 183 K. The activation barrier to bridge–terminal exchange is 8.3 ± 0.2 kcal mol⁻¹ (215 K). No other resonance exhibits splitting or broadening as the temperature is decreased.

Studies on the fluxional behavior of the bridging and terminal hydrogens in monodentate borohydride complexes are by far less extensive, for the simple reason that relatively few such complexes are known. In one study, Baker and Field[29] examined the facile bridging and terminal hydrogen exchange in Fe(H)(dmpe)₂(η^1-BH₄) (dmpe = 1,2-bis(dimethylphosphino)ethane) and found that the Fe–H ligand is not involved in the scrambling of the BH₄ protons. It was suggested that the "rapid reorganization of the bonding of the –H–BH₂ group in its coordination site" proceeds via a 20e⁻ bidentate species.

The mechanism for the hydrogen exchange in compound 3 is not straightforward. One obvious possibility, dissociation of the PMe₃ ligand, followed by an monodentate–bidentate equilibrium, can be immediately excluded as this would involve the intermediacy of 2, the barrier to fluxionality of which is >4 kcal/mol *higher* than in 3. Other mechanisms involving η^2-borohydrides are possible, providing 2 is not an intermediate. For example, association of one terminal hydride to yield an η^2-intermediate, with concurrent slip of the Cp ring from η^5 to η^3, is a feasible pathway (eq 9).

Experimental Section

General Considerations. All reactions and manipulations were carried out using either high vacuum line techniques or a glovebox under an atmosphere of prepurified N₂. Solvents were distilled over Na/Benzophenone ketyl before use. ¹H NMR

(29) Baker, M. V.; Field, L. D. *J. Chem. Soc., Chem. Commun.* **1984**, 996.

$$(9)$$
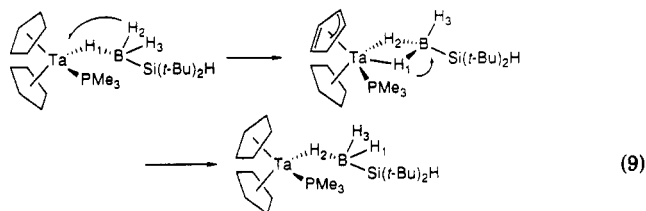
spectra were recorded on an IBM AC-250 NMR spectrometer. ¹³C NMR spectra were obtained on a Bruker AM-500 spectrometer equipped with a ¹H/¹³C dual probe. ³¹P NMR spectra were recorded on a Bruker AF-200 spectrometer with a broadband multinuclear probe. ¹¹B NMR spectra and variable-temperature ¹H{¹¹B} NMR spectra were obtained on a Bruker AF-200 spectrometer equipped with a broadband ¹H/¹¹B dual probe, Bruker temperature control unit, and a PTS 160 frequency synthesizer at 64.5 MHz. Benzene-d_6 was used as NMR solvent unless otherwise indicated. Toluene-d_8 was used as NMR solvent for variable-temperature experiments. The ¹H and ¹³C chemical shifts are referenced to TMS. ³¹P NMR spectra are referenced to external standard 85% H₃PO₄ and ¹¹B NMR spectra are referenced to external standard BF₃·OEt₂. Infrared spectra were obtained on a Perkin-Elmer 1430 spectrometer and calibrated against polystyrene films. High-resolution mass spectra were obtained on a VG Instrument ZAB-E spectrometer using chemical ionization. Cp₂Ta(L)(Si(t-Bu)₂H) (L = PMe₃, CO) was prepared as previously described.[13] The BH₃·N-methylmorpholine complex was purchased from Aldrich and used without further purification.

Preparation of Cp₂Ta(η^2-BH₃(Si(t-Bu)₂H)) (2). A solution containing 420 mg (0.79 mmol) of 1 and 520 mg (4.52 mmol) of BH₃·NMM in 30 mL of cyclohexane was stirred for 3 days at 25 °C. The resulting green solution was filtered, and all volatiles were removed under vacuum. The residue was held under vacuum for another 24 h to remove volatile solids (NMM, BH₃·PMe₃, BH₃·NMM). Recrystallization of the remaining solid from hexanes yielded green crystalline 2 (320 mg, 87% yield). ¹H NMR (25 °C): δ 5.02 (s, 10 H, C₅H₅), 3.57 (s br, 1 H, SiH), 1.15 (s, 18H, C(CH₃)₃). ¹³C{¹H} NMR (25 °C): δ 91.3 (C₅H₅), 19.04 (C(CH₃)₃), 39.36 (C(CH₃)₃). ¹¹B{¹H} NMR: δ 45.07. HRMS (m/e): calcd for C₁₈H₃₂BSiTa, 468.185; found, 468.186. IR (Nujol mull): 2412 (ν(B–H$_t$)), 2040 (ν(Si–H)), 1688 (ν(B–H$_b$)), 1601 cm⁻¹ (ν(B–H$_b$)).

Preparation of Cp₂Ta(PMe₃)(η^1-BH₃(Si(t-Bu)₂H)) (3). A solution of 2 (120 mg, 0.256 mmol) in 3 mL of benzene was cooled to –196 °C, and trimethylphosphine (0.50 mmol) was vacuum transferred onto the frozen solution. The mixture was allowed to warm to room temperature and stirred for 15 min. All volatiles were then removed under vacuum, and the residue was recrystallized from toluene/hexanes to yield 3 (65 mg, 47% yield) as reddish brown crystals. The mother liquors were then used in the synthesis of 4. Characterization data for 3 are as follows. ¹H NMR (25 °C): δ 4.39 (d, J_{PH} = 1.8 Hz, 10H, C₅H₅), 3.75 (br, 1 H, SiH), 1.44 (s, 18 H, C(CH₃)₃), 0.93 (d, J = 7.8 Hz, 9H, P(CH₃)₃), –5.0 (br, 3H, BH₃). ¹³C{¹H} NMR (25 °C): δ 87.11 (C₅H₅), 31.2 (CCH₃), 20.2 (d, ²J_{CP} = 27.8 Hz, PCH₃). ¹¹B{¹H} NMR (25 °C): δ –50. ³¹P{¹H} NMR (25 °C): δ –33.2. IR (Nujol mull): 2395 (ν(B–H$_t$)), 2374 (ν(B–H$_t$)), 2038 (ν(Si–H)), 1850 (br, ν(Ta–H$_b$)).

Preparation of Me₃P·BH₂SiH(t-Bu)₂ (4). The mother liquors containing 3 (calcd 0.135 mmol) from the previous synthesis were cooled to –196 °C, and 0.53 mmol of PMe₃ was vacuum transferred onto the frozen solution. The mixture was warmed to room temperature and stirred for 12 h. Volatiles were then removed under vacuum, and the residue was sublimed at room temperature onto a probe cooled to –78 °C to yield 4 as a white solid (24 mg, 77% yield based on calcd amount of 3). The temperature of the sublimation was increased to 45 °C, and orange red Cp₂Ta(H)(PMe₃) (5, 40 mg, 77% yield based on calcd amount of 3) was collected. The overall yield of both 3 and 5 based on 120 mg of 2 is 87%. Characterization data for of 4 are as follows. ¹H NMR: δ 3.43 (d, J_{PH} = 9.6 Hz, 1 H, SiH), 1.34 (s, 18H, C(CH₃)₃), 0.68 (d, J = 10.6 Hz, 9H, PCH₃). ¹³C{¹H} NMR: δ 30.5 (CCH₃),

13.3 (d, $^1J_{PC}$ = 39.2 Hz, PCH_3). $^{11}B\{^1H\}$ NMR: δ –42 (d, $^1J_{BP}$ = 61 Hz). $^{31}P\{^1H\}$ NMR: δ 0.91 (q, $^1J_{BP}$ = 61 Hz). HRMS (*m/e*): calcd for $C_{11}H_{30}BPSi$, 232.1947; found, 232.1913. IR (Nujol mull): 2355 (ν(B–H)), 2340 (ν(B–H)), 2030 (ν(Si–H)). Mp: 99–101 °C. Anal. Calcd for $C_{11}H_{30}BPSi$: C, 56.89; H, 13.02. Found: C, 56.10; H, 13.29.

Preparation of $Cp_2Ta(\eta^2\text{-}BH_4)$ (6). A solution containing $Cp_2Ta(H)(PMe_3)$ (5) (90 mg, 0.23 mmol) and $BH_3\cdot NEt_3$ (300 mg, 2.6 mmol) in 3 mL of toluene was photolyzed (350 nm) for 7 h at 15 °C. The solution was filtered, and all volatiles were removed under vacuum. The greenish residue was recrystallized from toluene/hexanes to yield 6 (66 mg, 87% yield). ^1H NMR: δ 6.46 (q, 2H, $^1J_{BH}$ = 118 Hz, B–H_t), 4.87 (s, 10H, C_5H_5), –16.0 (br, 2H, B–H_b). ^{11}B NMR: δ 47. IR (Nujol mull): 2438 (ν(B–H_t)), 2396 (ν(B–H_t)), 1740 (br, ν(B–H_b)), 1600 (br, ν(B–H_b)).

Structure Determinations of 2 and 3. General Crystallographic Procedures. Single crystals of suitable size were grown from toluene/hexanes at –35 °C and sealed in 0.5-mm thin-walled Pyrex capillaries in the glovebox, and the capillaries were mounted on the diffractometer. Refined cell dimensions and their standard deviations were obtained from least-squares refinement of 25 accurately centered reflections with $2\theta > 25°$. Crystal data are summarized in Table I.

Diffraction data were collected at 295 K on an Enraf-Nonius four-circle CAD-4 diffractometer employing Mo Kα radiation filtered through a highly oriented graphite crystal monochromator. The intensities of three standard reflections measured at intervals of ca. 80 reflections showed no systematic change during data collection. The raw intensities were corrected for Lorentz and polarization effects by using the program BEGIN from the SDP+ package.[30] Empirical absorption corrections based on ψ-scans were also applied.

All calculations were performed on a VAX 11/785 computer using the SDP+ software package.[30] The full-matrix least-squares refinement was based on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights (w) were taken as $4F_o^2/(\sigma(F_o^2))^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. Atomic scattering factors and complex anomalous dispersion corrections were taken from refs 31–33. Agreement factors are defined as $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$ and $R_2 = [\sum w\|F_o| -$

$|F_c\|^2/\sum w|F_o|^2]^{1/2}$. The goodness-of-fit is defined as GOF = $[\sum w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$, where N_o and N_p are the number of observations and parameters.

Solution and Refinement for 2. The coordinates of the tantalum and silicon atoms were obtained from three-dimensional Patterson maps. Analysis of subsequent difference Fourier maps led to location of the remaining heavy atoms. Refinement using anistropic Gaussian amplitudes followed by difference Fourier synthesis resulted in the location of most of the Cp hydrogens and at least one hydrogen on each methyl group. Peaks were also located at positions roughly corresponding to the hydrogen on silicon and one of the bridging boron hydrides, although their positions could not be successfully refined. All remaining hydrogen atoms were placed at idealized locations, and the positions of all hydrogens were optimized by using the program HYDRO.[30] Final refinement included anisotropic Gaussian amplitudes for all non-hydrogen atoms and fixed positions and fixed isotropic parameters for the hydrogen atoms. Structure refinement is summarized in Table I. Final positional parameters and Gaussian amplitudes for 2 are included in the supplementary material.

Solution and Refinement for 3. All heavy atoms were located by Patterson and difference Fourier methods as described above for 2. Refinement using anisotropic Gaussian amplitudes followed by difference Fourier synthesis resulted in the location of the hydrogen atoms on boron and silicon, most of the Cp hydrogens, and at least one hydrogen on each methyl group. All remaining hydrogen atoms were placed at idealized locations. Final refinement included anisotropic Gaussian amplitudes for all non-hydrogen atoms, isotropic Gaussian amplitudes for the B–H and Si–H atoms, and fixed positions and fixed isotropic parameters for the Cp and methyl hydrogen atoms. Structure refinement is summarized in Table I. Final positional parameters and Gaussian amplitudes for 3 are included in the supplementary material.

Supplementary Material Available: Tables of positional parameters and anisotropic thermal parameters for 2 and 3 (7 pages). Ordering information is given on any current masthead page.

OM9205307

(30) B. A. Frenz and Associates, Inc., College Station, TX 77840, and Enraf-Nonius, Delft, Holland.

(31) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(32) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3187.

(33) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1.