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Low-Valent Ditantalum Complex $Ta_2(\mu\text{-}BH_3)(\mu\text{-dmpm})_3(\eta^2\text{-}BH_4)_2$: First Dinuclear Compound Containing a Bridging BH_3 Group with Direct Ta−B Bonds

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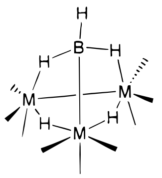
Abstract: The reduction of $TaCl_5$ with $LiBH_4$ in the presence of the bidentate ligand bis(dimethylphosphino)methane, dmpm, produces the novel BH_3-bridged ditantalum complex $Ta_2(\mu\text{-}BH_3)(\mu\text{-dmpm})_3(\eta^2\text{-}BH_4)_2$ (**1**) and the acid−base adduct $dmpm(BH_3)_2$ (**2**). Two crystalline forms of **1** were obtained, and their structures have been determined by X-ray crystallography. The unique feature of **1** is that the bridging borane is bound only to the ditantalum metal center, forming a simple metallaborane cluster, Ta_2B, with averaged Ta−Ta and Ta−B bond distances of 2.7792[5] and 2.307[9] Å, respectively; the averaged Ta−B separation for the axially coordinated BH_4^- groups, which are bound to the Ta atoms through hydrogen atoms, is ~0.2 Å longer than that of the bound BH_3 group. The μ-BH_3 group has one *exo*-hydrogen atom with a $B{-}H_{exo}$ distance of 1.10[8] Å. The distance between the *endo*-hydrogen atom and the boron atom is 1.23[8] Å. Each of the two *endo*-hydrogen atoms is also bound to a Ta atom with the Ta−H distance of 1.97[8] Å. Compound **1** represents the first example of a structurally characterized metallaborane complex containing a μ-BH_3 group bridging two metal centers. The structure of the air-stable compound **2** has also been determined; it shows a strong P to B dative bond with the P−B distance of 1.903(4) Å.

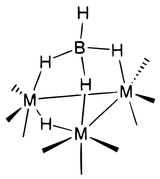
Introduction

The simplest monoborane, BH_3, forms donor−acceptor adducts of general formula $BH_3{\cdot}L$, where L = Lewis base;[1] the $L{\rightarrow}BH_3$ dative bond strength depends on the nature of the donor. For example, the dative bond in $BH_3{\cdot}THF$ is weak, and this adduct is often used as a borane source. When reacted with stronger bases such as phosphines, BH_3 forms more-stable complexes of the type $BH_3{\cdot}P$, where P = phosphine ligand. The phosphine adducts of BH_3 have been the subject of several spectroscopic[2] and X-ray crystallographic studies.[3] Conceivably, the Lewis base could be an electron-rich transition metal unit; i.e., one in which the metal atom is in a formally low oxidation state and thus one that contains *d* electrons available for bonding to a Lewis acid.[4] However, very few transition metal complexes containing BH_3 as an electron-accepting ligand are known. Examples are the group 7 and group 8 metal carbonyl anions $[H_3B{\leftarrow}M(CO)_nL]^-$, where M = Mn, Re, Co; L = CO, PPh_3; and n = 3, 4.[5] No X-ray structure of such a complex has been reported.

To our knowledge, direct coordination[6] of BH_3 to polynuclear metal-containing units is known only for trinuclear clusters of the type $M_3(CO)_6(\text{phosphine})_3(BH_3)(\mu\text{-}H)_2$,[7] and $M_3(CO)_9(BH_3)(\mu\text{-}H)_2$,[8] where M = Fe, Ru, and Os. The ruthenium cluster appears to exist in solution as two isomers, **Ia** and **Ib**. The former has a boron atom capping the Ru_3 triangle; it is directly bound to one Ru atom but indirectly, via hydrogen atoms bridging, to the other two Ru atoms. The second isomer (**Ib**) arises from the rearrangement of the bridging hydrogen atoms on the Ru_3B core. Consequently, the BH_3 group in **Ia** changes to a borohydride BH_4^- ion in **Ib** which caps the Ru_3 triangle through hydrogen atom bridges.



Ia



Ib

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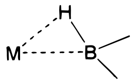
Formally, the BH_3 group can also be considered a 2-electron donor, in which a B−H σ bond is used to coordinate to a metal center forming the so-called "σ complexes." A few substituted monoborane σ complexes, namely, $Cp_2Ti(PMe_3)(HBcat)$ and $Cp_2Ti(HBcat)_2$, where HBcat = catecholborane, have been recently reported.[9] In $Cp_2Ti(PMe_3)(HBcat)$ the Ti, H, and B atoms form a triangle with a Ti−B bond length of 2.267(6) Å and a 3c−2e bond between the Ti−H−B atoms (**II**); the Ti−H bond distance is 1.61(5) Å. For $Cp_2Ti(HBcat)_2$, the Ti−B bond distance is 2.335(5) Å.



II

As a part of our interest in extending the chemistry of metal−metal-bonded compounds to low-valent tantalum, we used $LiBH_4$ as reducing agent to react with $TaCl_5$. The products isolated and the final oxidation states of the tantalum atoms from the reduction of $TaCl_5$ with $LiBH_4$ have turned out to be ligand-dependent and sensitive to subtle changes in reaction conditions. Previously we reported that μ_4,η^2-$B_2H_6^{2-}$ dianion bridged ditantalum(III) complexes[10] resulted from the reaction of $TaCl_5$ with $LiBH_4$ in the presence of arylformamidinate ligands, $[ArNC(H)NAr]^-$, where Ar = phenyl or tolyl. We also found that the reaction of potassium with crude $Ta_2(\mu_2\text{-}\eta^4\text{-}B_2H_6)(\mu\text{-DTolF})_4$ produces $[(B_2H_5)N(Tol)C(H)N(Tol)]Ta(\mu_2\text{-NTol})_2(\mu_2\text{-DTolF})_2Ta[(Tol)NC(H)N(Tol)B_2H_5]$, in which a new chelating ligand is formed by fusion of a B_2H_5 or a BH_3 unit to a $DTolF^-$ anion.[11] Cleavage of formamidinate ligands can produce the imido group $NTol^{2-}$ and several tantalum complexes containing cleaved formamidine ligands have been characterized.[12] In this paper we report the synthesis and structural characterization of a novel BH_3-bridged ditantalum compound, namely, $Ta_2(\mu\text{-}BH_3)(\mu\text{-dmpm})_3(\eta^2\text{-}BH_4)_2$ (**1**), where dmpm = bis(dimethylphosphino)methane. This compound was prepared by the reduction of $TaCl_5$ with $LiBH_4$ in the presence of dmpm, and isolated along with $dmpm(BH_3)_2$ (**2**). Compound **1** provides the first example of a bridging BH_3 complex to be crystallographically characterized in a dinuclear complex.

Experimental Section

Materials. All manipulations were performed under an atmosphere of argon by using standard Schlenk techniques. Solvents were purified by conventional methods and were freshly distilled under nitrogen prior to use. Tantalum(V) chloride and dmpm were purchased from Strem Chemicals, Inc. Lithium borohydride and $BH_3\cdot THF$ (1.0 M in THF) were purchased from Aldrich Chemical Co. Tantalum(V) chloride was resublimed before use, but other chemicals were used as received.

Physical Measurements. IR spectra were recorded on a Perkin-Elmer 16PC Fourier transform IR spectrophotometer as KBr pellets. ^{1}H and ^{13}C NMR spectral measurements were performed with a Varian Unity 300 spectrometer. The ^{1}H NMR spectra were recorded at 299.96 MHz; chemical shifts are referenced to trimethylsilane (0.00 ppm). ^{13}C NMR spectra were recorded at 75.43 MHz; chemical shifts were referenced to $CDCl_3$ (77.0 ppm). ^{31}P and ^{11}B NMR spectral measurements were performed with a Varian-200 broad band spectrometer. ^{31}P NMR spectra were recorded at 80.1 MHz, with an external 85% H_3PO_4 solution as standard (0.00 ppm). ^{11}B NMR spectra were recorded at 64.2 MHz, and chemical shifts were referenced to $BF_3\cdot$diethyl ether (0.00 ppm).

Preparation of $Ta_2(\mu\text{-}BH_3)(\mu\text{-dmpm})_3(\eta^2\text{-}BH_4)_2$ (1) and 1·toluene. A mixture of $TaCl_5$ (1.08 g, 3.0 mmol) and $LiBH_4$ (0.40 g, 18.4 mmol) was refluxed in toluene for 20 h to give a black suspension. After this suspension was cooled to ambient temperature, a black solid precipitated. The colorless supernatant liquid was removed with a syringe, and the solid was dried under vacuum. To the solid was added cold (−70 °C) THF (30 mL) and the mixture was stirred at that temperature for 30 min. Then a solution of dmpm (0.76 mL, 4.8 mmol) in THF (10 mL) was introduced into the mixture. The cooling bath was removed after 4 h and stirring was continued for 10 h at room temperature to give a purple solution. The THF solvent was then removed under vacuum and the remaining solid was first extracted with toluene (40 mL). Slow diffusion of hexanes (20 mL) into the toluene filtrate gave purple crystals of **1**·toluene. Yield 0.41 g, 30%. A second extraction with diethyl ether (40 mL) also produced a purple solution. After filtration, the volume of the ether solution was reduced to 20 mL, then layered with hexanes. Purple crystals of **1** were produced in 2 weeks, (yield 0.024 g, 2%). ^{1}H NMR δ 2.18 [t, 2H, PCH_2P, $J(^{31}P-^1H) = 8.7$ Hz], 2.09 (br m, 2H, PCH_2P), 1.73 (m, 2H, PCH_2P), 1.59, 1.36, 1.27 (36H, CH_3), −0.26 [br q, 8H, BH_4^-, $J(^{11}B-^1H) = 93.0$ Hz]. $^{31}P\{^1H\}$ NMR δ 4.52 (m), −7.32, −7.55 (s). $^{11}B\{^1H\}$ NMR δ −28.5 (br, s, BH_4^-), −33.5 (unresolved m, BH_3). IR (KBr pellet) 3449 (br, m), 2962 (m), 2924 (w), 2902 (m), 2376 (s), 2341 (sh, s), 2203 (w), 2122 (w), 2090 (w), 2052 (w), 1412 (m), 1345 (m), 1296 (m), 1262 (s), 1107 (s), 1066 (m), 930 (vs, br), 869 (m), 804 (m, br), 766 (w), 746 (w), 729 (w), 709 (m), 698 (m) 635 (m), 518 (br, w), 468 (w) cm^{-1}.

Preparation of $dmpm(BH_3)_2$ (2). A 1.0 M THF solution of BH_3 (1.0 mL, 1.0 mmol) was added to a solution of dmpm (80 μL, 0.50 mmol) in toluene (4 mL) at 0 °C. After having been stirred for 1 h, the resulting solution was layered with hexanes (6.0 mL) and placed at −30 °C. Slow diffusion of hexanes into the solution gave crystals of **2** (yield 0.075 g, 91%), mp 152−154 °C. ^{1}H NMR δ 1.18 [dq, 6H, BH_3, $J(^{11}B-^1H) = 95.4$ Hz, $J(^{31}P-^1H) = 10.8$ Hz], 0.989 [t, 2H, PCH_2P, $J(^{31}P-^1H) = 11.4$ Hz], 0.871 [d, 12H, $P(CH_3)_2$, $J(^{31}P-^1H) = 10.2$ Hz]. ^{13}C NMR δ 25.40 [t, PCH_2P $J(^{13}C-^{31}P) = 24.5$ Hz], 13.65 [d, $P(CH_3)_2$, $J(^{13}C-^{31}P) = 39.9$ Hz]. $^{31}P\{^1H\}$ NMR δ 5.28 [q, $J(^{31}P-^{11}B) = 58.1$ Hz]. $^{11}B\{^1H\}$ NMR δ −33.12 [d, $J(^{11}B-^{31}P) = 58.1$ Hz]. IR (KBr pellet) 3074 (vw), 2997 (w), 2980 (w), 2923 (m), 2913 (w), 2878 (w), 2587 (w), 2377 (vs), 2239 (s), 2276 (w), 2253 (m), 1426 (sh,w), 1418 (m), 1366 (w), 1304 (sh, w), 1296 (m), 1193 (m), 1148 (m), 1132 (m), 1078 (sh, w), 1067 (s), 941 (br, vs), 899 (m), 870 (s), 820 (m), 793 (m), 765 (m), 709 (m), 668 (m), 576 (m), 554 (w) cm^{-1}.

X-ray Structure Determinations. Geometric and intensity data for **1**·toluene and **2** were collected at −100 and −150 °C, respectively, with a Nonius CAD4-S diffractometer. Detailed procedures have previously been described.[13] Data for compound **1** were gathered at −60 °C with a Nonius FAST area detector system, utilizing the software program MADNES.[14]

Unit cell refinement for **1**·toluene and **2** utilized 25 high-angle reflections. In each case, the cell dimensions and Laue group were confirmed by axial images. All data were corrected for Lorentz and polarization effects. Three strong reflections measured periodically throughout the data collection for compounds **1**·toluene and **2** showed no significant decay. An empirical absorption correction based on six φ-scans was applied for **1**·toluene and **2**. For compound **1**, we used the program SORTAV[15] to correct for absorption.

In all structures, the positions of heavy atoms were found in direct methods E-maps by using the software solution program in SHELX-

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Table 1. Crystal Data and Structure Refinement for **1**, **1**·toluene, and **2**

compound	**1**	**1**·toluene	**2**
empirical formula	$C_{15}H_{53}B_3P_6Ta_2$	$C_{22}H_{61}B_3P_6Ta_2$	$C_5H_{20}B_2P_2$
formula weight	813.72	905.86	163.77
crystal system	monoclinic	orthorhombic	hexagonal
space group	$P2_1/c$	*P*nma	$P6_122$
a, Å	17.076(2)	16.308(1)	6.279(1)
b, Å	11.663(2)	16.086(1)	6.279(1)
c, Å	15.8577(8)	13.8755(7)	47.46(1)
β, °	99.257(8)	90	90
V, $Å^3$	3117.0(7)	3640.0(4)	1620.5(5)
Z	4	4	6
D_{calc}, g/cm^3	1.734	1.653	1.007
temperature, K	213(2)	173(2)	123(2)
reflections collected	12726	2700	1842
data/restraints/ parameters	4075/0/445	2438/6/262	708/0/79
final R indices [$I > 2\sigma(I)$], R1,[a] wR2[b]	0.032, 0.080	0.026, 0.067	0.033, 0.079
R indices (all data), R1, wR2	0.035, 0.082	0.038, 0.072	0.048, 0.083
goodness-of-fit[c] on F^2	1.087	1.051	1.195

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w = 1/\sigma^2(F_o^2) + (a \times p)^2 + b \times p$, $p = [\mathrm{Max}(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$. $a = 0.035$ and $b = 9.34$ for **1**; $a = 0.025$, $b = 26.93$ for **1**·toluene; $a = 0.033$ and $b = 0.60$ for **2**. [c] Quality-of-fit $= w(|F| - |F|)^2/(N_{obs} - N_{parameters})^{1/2}$.

TL.[16] Subsequent cycles of least-squares refinement followed by difference Fourier synthesis produced the positions of the remaining nonhydrogen atoms; they were refined anisotropically. Positions of hydrogen atoms were found and located from the final difference Fourier map. These hydrogen atoms, which are essential in defining the structures, were included and refined isotropically. Compound **2** crystallized in the chiral space group $P6_122$, which was confirmed by the program XPREP of the SHELXTL package. However, the absolute configuration of **2** could not be established from the Flack[17] parameter because of possible twinning of the crystal, as indicated by the structural refinement. Crystal data are given in Table 1.

Results and Discussions

The reaction of $TaCl_5$ with $LiBH_4$ at reflux temperature in toluene gave a black solid, which was then reacted with dmpm in THF at low temperature to give $Ta_2(\mu\text{-}BH_3)(\mu\text{-dmpm})_3(\eta^2\text{-}BH_4)_2$ (**1**) (eq 1). After removal of THF, the product was

$$2TaCl_5 + 10LiBH_4 + 3\text{dmpm} \xrightarrow{\text{THF}} Ta_2(\mu\text{-}BH_3)(\mu\text{-dmpm})_3(\eta^2\text{-}BH_4)_2 + 4H_2 + 10LiCl + 7BH_3{\cdot}\text{THF} \quad (1)$$

extracted with toluene. Crystals of **1**·toluene were obtained by slow diffusion of hexanes into its toluene solution at 0 °C.

The presence of BH_3 in the reaction mixture also led to the formation of a dmpm-borane adduct, namely, $\text{dmpm}(BH_3)_2$ (**2**). This was crystallized as a byproduct along with crystals of **1** from the toluene solution. Compound **1** is only slightly soluble in ether, from which we also obtained a small crop of nonsolvated crystals.

Compound **1** is sensitive to air and moisture; it burns immediately when exposed to air. In dichloromethane, it decomposes to form insoluble dark solids. The similarity in the solubility of **1** and **2** makes their separation difficult. Innumerable attempts to separate these two compounds by solvent extraction were also hampered by the great instability of solutions containing **1**; according to the NMR spectra, these attempts were all unsuccessful. The only method of separation that worked in our hands, and it is far from being completely satisfactory, was manual selection of the colorless crystals of **2** and separation from those of compound **1**, a painstaking process that must be done in a drybox. However, a small amount of **2** could always be detected by solution NMR (see below).

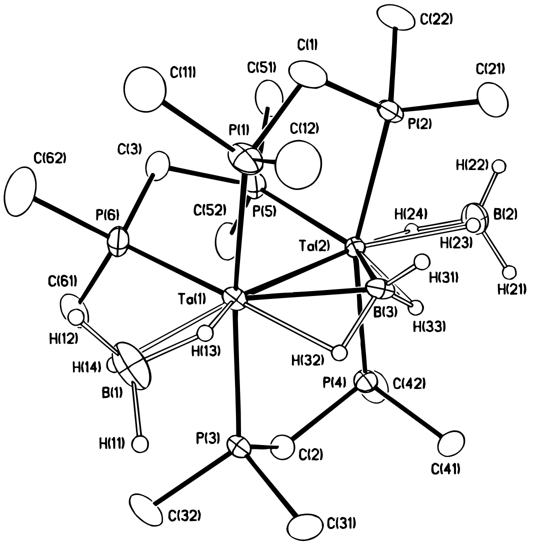

Figure 1. A perspective view of the molecular structure of **1**. Nonhydrogen atoms are represented by their 40% probability ellipsoids.

The structures of both crystalline forms of **1** have been determined by X-ray crystallography. For compound **1** there is one complete molecule in the asymmetric unit, and it is depicted in Figure 1. Selected bond distances and angles for **1** are listed in Table 2. Compound **1** consists of two Ta atoms joined by one BH_3 group and three dmpm ligands; each of the Ta atoms is also coordinated by an $\eta^2\text{-}BH_4^-$ anion located in the axial position. A drawing of the molecule of **1** in **1**·toluene is shown in Figure 2. Selected dimensions for **1**·toluene are presented in Table 3. It has crystallographically imposed C_s symmetry with a mirror plane passing through the methylene carbon atoms of the three bridging dmpm ligands and the boron atom of the bridging BH_3 group. The *trans*-dmpm ligands adopt a boat conformation with essentially identical Ta−P distances in the range of 2.567(2) to 2.580(2) Å. The bridging borane is trans to the third dmpm ligand at the equatorial position. Each axial BH_4^- anion coordinates to a Ta atom through two hydrogen atoms, H(11) and H(12), with Ta−H distances of 2.16(7) and 2.17(7) Å, respectively. The B(1)−Ta separation of 2.578(8) Å is comparable with the distances reported for complexes with (3c,2e) Ta−H−B linkages.[9,10] The bridging boron atom B(2) is symmetrically coordinated to both tantalum atoms with a B(2)−Ta distance of 2.306(8) Å, ∼0.26 Å shorter than the distance between the axial B(1) atom and the Ta atom for the borohydride units in which a Ta−H−B bond exists, and only ∼0.04 Å longer than those reported for the catecholborane complexes of titanium[8] mentioned earlier. The distance between the bridging boron and tantalum atoms in **1** is just slightly longer than those observed in complexes containing direct Ta−B bonds without hydrogen atom bridges. For example, the tantalaborane complex $Cp^*TaCl_2(B_4H_8)$ has a Ta−B bond distance of 2.249(12) Å;[18] and for both isomers of the η^1-boryl compound Cp_2-

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Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**

Ta(1)−Ta(2)	2.7708(5)	Ta(1)−B(1)	2.539(10)
Ta(1)−B(3)	2.304(9)	Ta(2)−B(2)	2.585(10)
Ta(2)−B(3)	2.312(9)	Ta(1)−H(13)	1.82(7)
Ta(1)−H(14)	2.25(8)	Ta(1)−H(32)	2.02(7)
Ta(2)−H(23)	2.04(8)	Ta(2)−H(24)	2.12(7)
Ta(2)−H(33)	1.86(10)	Ta(1)−P(1)	2.568(2)
Ta(1)−P(3)	2.583(2)	Ta(1)−P(6)	2.545(2)
Ta(2)−P(2)	2.545(2)	Ta(2)−P(4)	2.575(2)
Ta(2)−P(5)	2.572(2)	B(1)−H(11)	1.20(10)
B(1)−H(12)	1.13(13)	B(1)−H(13)	1.19(7)
B(1)−H(14)	0.99(8)	B(2)−H(21)	1.17(7)
B(2)−H(22)	1.03(12)	B(2)−H(23)	1.12(8)
B(2)−H(24)	1.16(7)	B(3)−H(31)	1.09(8)
B(3)−H(32)	1.28(7)	B(3)−H(33)	1.12(10)
B(3)−Ta(1)−B(1)	117.8(4)	B(3)−Ta(1)−P(1)	76.2(2)
B(3)−Ta(1)−P(6)	144.8(2)	P(6)−Ta(1)−P(1)	94.16(8)
B(1)−Ta(1)−P(1)	87.5(3)	B(3)−Ta(1)−P(3)	96.5(2)
B(1)−Ta(1)−P(3)	84.3(3)	P(6)−Ta(1)−P(3)	99.11(7)
P(1)−Ta(1)−P(3)	164.96(7)	P(1)−Ta(1)−Ta(2)	93.66(5)
H(32)−Ta(1)−Ta(2)	81(2)	B(1)−Ta(1)−Ta(2)	170.1(3)
B(3)−Ta(1)−Ta(2)	53.2(2)	P(2)−Ta(2)−P(5)	94.14(7)
P(6)−Ta(1)−Ta(2)	94.67(5)	P(2)−Ta(2)−P(4)	163.03(7)
P(3)−Ta(1)−Ta(2)	92.28(5)	B(3)−Ta(2)−P(4)	98.6(2)
H(33)−Ta(2)−B(3)	29(3)	P(5)−Ta(2)−P(4)	99.42(7)
B(3)−Ta(2)−P(2)	76.0(2)	B(3)−Ta(2)−B(2)	117.1(3)
B(3)−Ta(2)−P(5)	142.9(2)	P(5)−Ta(2)−B(2)	97.1(2)
H(33)−Ta(2)−B(2)	94(3)	H(33)−Ta(2)−Ta(1)	75(3)
P(2)−Ta(2)−B(2)	85.4(2)	P(2)−Ta(2)−Ta(1)	95.04(5)
P(4)−Ta(2)−B(2)	82.9(3)	P(4)−Ta(2)−Ta(1)	94.27(5)
H(23)−Ta(2)−Ta(1)	146(2)	H(31)−B(3)−H(33)	114(6)
B(3)−Ta(2)−Ta(1)	53.0(2)	H(33)−B(3)−H(32)	111(6)
B(2)−Ta(2)−Ta(1)	169.3(2)	H(33)−B(3)−Ta(1)	112(5)
H(31)−B(3)−Ta(2)	133(4)	B(3)−H(32)−Ta(1)	85(4)
H(32)−B(3)−Ta(2)	121(3)	B(3)−H(33)−Ta(2)	99(6)
H(31)−B(3)−H(32)	106(5)	H(33)−B(3)−Ta(2)	53(5)
H(31)−B(3)−Ta(1)	134(4)	Ta(1)−B(3)−Ta(2)	73.8(3)
H(32)−B(3)−Ta(1)	61(3)		

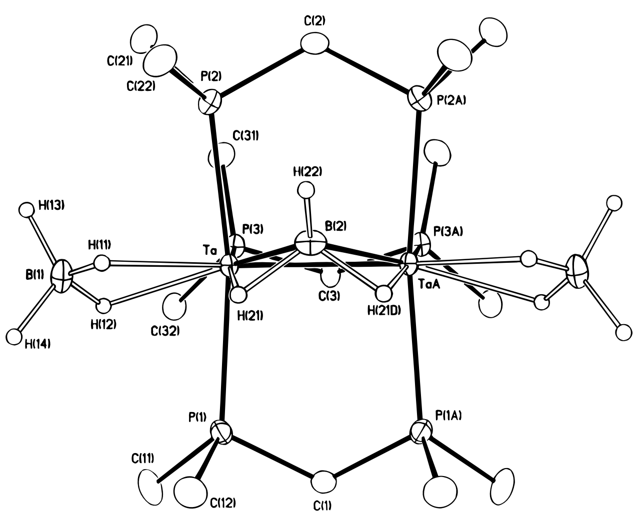

Figure 2. A perspective view of the molecular structure of **1** in **1**·toluene. Nonhydrogen atoms are represented by their 40% probability ellipsoids.

$TaH_2(BO_2C_6H_4)$, the Ta−B bond distances are 2.263(6) and 2.295(11) Å.[19]

Table 3. Selected Bond Distances (Å) and Angles (deg) for 1·toluene.

Ta−Ta[a]	2.7875(5)	Ta−H(11)	2.16(7)
Ta−B(1)	2.578(8)	Ta−H(12)	2.17(7)
Ta−B(2)	2.306(8)	Ta−H(21)	2.02(6)
Ta−P(1)	2.580(2)	B(1)−H(11)	1.09(7)
Ta−P(2)	2.569(2)	B(1)−H(12)	1.08(7)
Ta−P(3)	2.567(2)	B(1)−H(13)	1.23(6)
P(1)−C(1)	1.852(5)	B(1)−H(14)	1.24(6)
P(2)−C(2)	1.843(5)	B(2)−H(21)	1.29(6)
C(3)−P(3)	1.839(5)	B(2)−H(22)	1.11(8)
P(1)−C(11)	1.821(7)	P(2)−C(21)	1.835(7)
P(1)−C(12)	1.839(8)	P(2)−C(22)	1.833(8)
P(3)−C(31)	1.850(7)	P(3)−C(32)	1.833(7)
B(2)−Ta−B(1)	116.8(2)	B(2)−Ta−P(3)	143.3(2)
Ta−B(2)−Ta[a]	74.4(3)	B(2)−Ta−P(2)	75.3(3)
P(3)−Ta−P(2)	94.51(5)	P(3)−Ta−B(1)	97.2(2)
B(2)−H(21)−Ta	85(3)	P(3)−Ta−P(1)	99.23(5)
P(2)−Ta−B(1)	86.4(2)	B(1)−Ta−P(1)	83.4(2)
B(2)−Ta−P(1)	98.2(3)	B(2)−Ta−Ta[a]	52.8(2)
P(2)−Ta−P(1)	163.75(5)	P(2)−Ta−Ta[a]	94.40(3)
P(3)−Ta−Ta[a]	94.05(3)	P(1)−Ta−Ta[a]	93.25(3)
B(1)−Ta−Ta[a]	168.6(2)	Ta−B(2)−Ta[a]	74.4(3)
H(12)−B(1)−H(11)	108(7)	H(12)−B(1)−H(13)	115(6)
H(11)−B(1)−H(13)	110(5)	H(12)−B(1)−H(14)	105(7)
H(11)−B(1)−H(14)	98(6)	H(13)−B(1)−H(14)	119(6)
B(1)−H(11)−Ta	100(4)	B(1)−H(12)−Ta	100(4)
H(22)−B(2)−H(21)	108(4)	P(1)−C(1)−P(1)[a]	112.5(5)
H(21)−B(2)−H(21)[a]	108(5)	P(2)[a]−C(2)−P(2)	119.3(5)
H(22)−B(2)−Ta	133(2)	P(3)−C(3)−P(3)[a]	117.9(5)
H(21)[a]−B(2)−Ta	119(3)	B(2)−H(21)−Ta	85(3)

[a] Symmetry transformations used to generate equivalent atoms: x, $-y + 1/2$, z.

Table 4. Core Dimensions (Å or deg) Averaged for C_s Symmetry

compound	**1**	**1**·toluene	average
Ta−Ta′	2.7708(5)	2.7875(5)	2.7792[5]
Ta−B1	2.304(9) 2.312(9)	2.306(8)	2.307[9]
Ta−H1	2.02(7) 1.86(10)	2.02(6)	1.97[8]
B1−H1	1.28(7) 1.12(10)	1.29(6)	1.23[8]
B1−H2	1.09(8)	1.11(8)	1.10[8]
Ta−B1−Ta′	73.8(3)	74.4(3)	74.1[3]
Ta−H1−B1	85(4) 99(6)	85(3)	89[4]
H1−B1−H2	114(6) 106(5)	108(4)	109[6]
H1−B1−H1a	111(6)	108(5)	110[6]

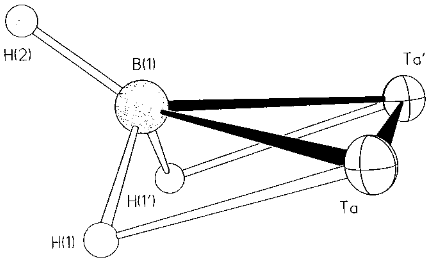

Figure 3. A view of the Ta_2B core in **1** and **1**·toluene with a labeling scheme that allows the comparison of the two independent molecules, as given in Table 4.

Both independently determined molecular structures of **1** are essentially the same and conform closely to C_s symmetry. Table 4 has the important inner dimensions of the molecules, defined with reference to Figure 3. The averaged values for both molecules are also listed in the last column of Table 4. The unique feature in **1** is that the boron atom from the borane group in the molecule is not bound to other elements except the ditantalum metal center, thus forming a simple metallaborane cluster with a Ta_2B core. As shown in Figure 3, the μ-BH_3 group has one *exo* hydrogen atom with an averaged B(1)−H(2) distance of 1.10[8] Å; the distance between the *endo* hydrogen atom and the boron atom is 1.23[8] Å. Each of the two *endo* hydrogen atoms is also bound to a Ta atom with the Ta−H(1) distance

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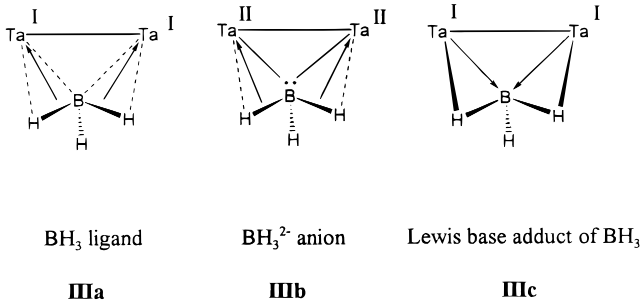
(19) Lantero, D. R.; Motry, D. H.; Ward, D. L.; Smith, III, M. R.; *J. Am. Chem. Soc*. **1994**, *116*, 10811−10812.

Scheme 1



of 1.97[8] Å. Compound **1** represents the first example of a structurally characterized compound with a μ-BH_3 group bridging two metal centers.

This type of symmetrically bridging μ-BH_3 group in a dimetal unit has not been observed before. As shown in Scheme 1, the bonding between the bridging BH_3 group and the tantalum metal centers in **1** may be described formally in one of three ways: as a ditantalum(I,I) compound containing a 4-electron-donor BH_3 ligand (**IIIa**); as a Ta_2(II,II) compound coordinated by a 6-electron-donor BH_3^{2-} dianion (**IIIb**); or as a Ta_2(I,I) complex (**IIIc**), in which there is donation of electrons from the low-valent Ta(I) atoms to the bridging boron atom. To be a 4-electron donor, the electron-deficient BH_3 group in (**IIIa**) must employ two B−H bonds to form two σ bonds to the Ta atoms. In **IIIb** there is formally a BH_3^{2-} anion, which is capable of existing only under very strong reducing conditions.[20] Thus neither **IIIa** nor **IIIb** is likely to be the best description of the structure of **1**. The bonding scheme in **IIIc**, which has been described as hyperconjugative interaction,[2b] includes donation of *d* electrons from the low-valent Ta(I) metal centers to the electron-deficient bridging BH_3 ligand. We believe this model provides the best qualitative explanation for the relatively short Ta−B bond lengths and the increase in the *endo* B−H bond distances coordinated to the Ta atoms, which are characteristic for metallaborane complexes.[21]

In terms of the isolobal analogy, the $Ta_2(BH_3)$ core has 12 electrons available for cluster bonding: 8 from 2Ta(I), 2 from $1BH_{exo}$, and 2 from $2H_{endo}$ atoms. Six pairs of electrons are consistent with a trigonal bipyramidal parent deltahedron. Thus, the 3 atom cluster core (2Ta + 1B) can be formulated as an *arachno*-metalloborane, which is isoelectronic with a known borane $[B_3H_8]^-$,[22] or as the hypothetical B_3H_9 molecule, for which Wade's rules predict a similar geometry. The difference between compound **1** and $[B_3H_8]^-$ or B_3H_9 is that the electrons in **1** can be used for metal−metal multiple bonding. In this case, a Ta═Ta double bond may exist, which is consistent with the Ta−Ta distance of ~2.78 Å observed in the solid-state structure and the diamagnetism of compound **1** in solution.

The $^{31}P\{^1H\}$ NMR spectrum of **1** at room temperature shows broad multiplets at 4.52 ppm and singlets at −7.32 and −7.55 ppm for the three bridging dmpm ligands. The $^{11}B\{^1H\}$ NMR indicates the presence of two kinds of boron atoms with chemical shifts of −28.5 and −33.5 ppm. The latter overlaps with the signals of **2**. The ^1H NMR spectrum of **1** has a broad quartet appearing as almost flat humps centered at −0.26 ppm, which can be assigned to the borohydride BH_4^- signals (J_{B-H} = 93.0 Hz). These are consistent with a fluxional behavior of the coordinated BH_4^- ions in solution. The exchange between the bridging and terminal hydrogen atoms in the coordinated BH_4^- ligands makes all the hydride signals equivalent on the NMR time scale. The ^1H NMR signals for the methylene protons of the bridging dmpm ligands appear as three multiplets centered at 2.18, 2.09, and 1.73 ppm. The signals for the methyl groups are found at 1.59, 1.36, and 1.27 ppm.

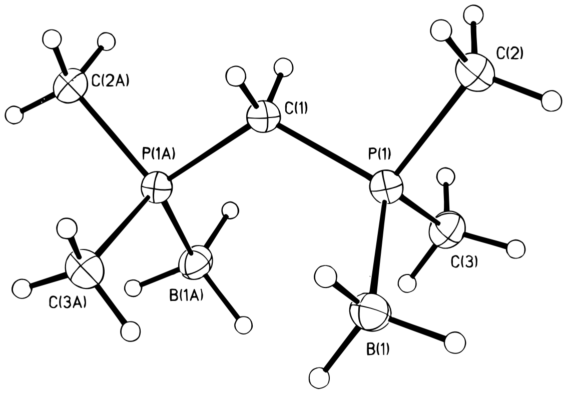
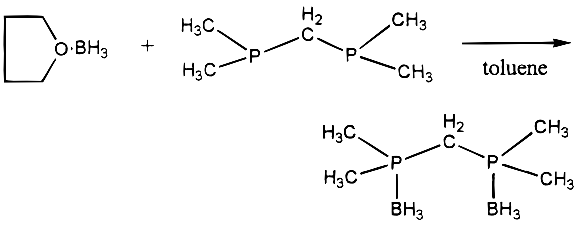


Figure 4. A drawing of the structure of **2**, showing the atom numbering scheme. Nonhydrogen atoms are represented by their 40% probability ellipsoids.

Table 5. Selected Bond Distances (Å) and Angles (deg) for **2**

P(1)−B	1.903(4)	P(1)−C(2)	1.797(3)
P(1)−C(1)	1.815(3)	P(1)−C(3)	1.796(4)
P(1)−C(1)−P(1A)	121.2(3)	C(3)−P(1)−C(1)	107.5(1)
C(2)−P(1)−C(1)	101.6(2)	C(2)−P(1)−C(3)	104.9(2)
C(1)−P(1)−B	116.2(1)	C(3)−P(1)−B	111.9(2)
C(2)−P(1)−B	113.7(2)		

Compound **2** was first isolated as a byproduct along with **1**. It is a simple borane phosphine adduct of the type $BH_3 \cdot L$, where L is a Lewis base. Compound **2** can also be independently prepared by adding two equivalents of $BH_3 \cdot THF$ in THF to a dmpm toluene solution (eq 2). It is noteworthy that **2** is air stable and melts at 152 °C; dmpm itself is air-sensitive and has a low melting point of −56 °C.[23]



(2)

A molecular drawing of **2** is shown in Figure 4. Selected bond distances and angles are listed in Table 5. Compound **2** crystallizes in the hexagonal space group $P6_122$. The molecule has crystallographically imposed C_2 symmetry with the two fold axis passing through the methylene carbon atom C(1). The P(1)−C(1) distance is 1.815(3) Å, and the distances between the methyl carbon atoms C(2) and C(3), and atom P(1), are 1.797(3) and 1.796(4) Å, respectively. The P(1)−B distance of 1.903(4) Å is comparable with those found in other compounds containing a P to B dative bond.[3]

The NMR data for **2** are consistent with the solid-state structure. The $^{31}P\{^1H\}$ NMR shows a broad quartet centered at 5.28 ppm with $J(^{31}P-^{11}B)$ = 58.1 Hz. The P−B coupling

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(20) Godfroid, R. A.; Hill, T. G.; Onak, T. P.; Shore, S. G. *J. Am. Chem. Soc.* **1994**, *116*, 12107−12108.

(21) Housecroft, C. E. *Boranes and Metalloboranes*, Ellis Horwood: Chichester, U.K. 1990.

(22) Mitchell, G. F.; Welch, A. J. *J. Chem. Soc., Dalton Trans*. **1987**, 1017−1025.

(23) Karsch, H. H.; Schmidbaur, H.*Z. Naturforsch. B Anorg. Chem. Org. Chem.* **1977**, *32*, 762−767.

constant is the same as that observed in the ^{11}B NMR, in which the ^{11}B signal appears as a doublet at −33.12 ppm. The ^{1}H NMR spectrum of **2** shows the methyl protons as a doublet at 0.87 ppm and the methylene protons as a triplet at 0.99 ppm [$^{2}J(^{31}\mathrm{P}-^{1}\mathrm{H}) = 11.4$ Hz]. The resonance of the coordinated borane appears as broad humps of doublets of quartet centered at 1.18 ppm [$J(^{11}\mathrm{B}-^{1}\mathrm{H}) = 95.4$ Hz, $^{2}J(^{31}\mathrm{P}-^{1}\mathrm{H}) = 10.8$ Hz].

Concluding Remarks

By using the robust dmpm ligand, the reduction of $TaCl_5$ with $LiBH_4$ produces the metallaborane compound **1**, in which the tantalum atom has a formal oxidation state of +1. The unique feature of this compound is the μ-BH_3 group bridging the ditantalum metal centers symmetrically to give a simple metallaborane complex. The Ta_2BH_3 core in **1** can be formulated as an *arachno*-tantalaborane with a Ta═Ta double-bond.

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Supporting Information Available: Tables of crystal data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and H coordinates (21 pages, print/PDF). CIF files are available online. See any current masthead page for ordering information and Web access instructions.

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