4830 *J. Am. Chem. Soc.* **1996,** *118,* 4830−4833

nido-Metalloborane Complexes: Synthesis and Structural Characterization of μ_2,η^4-Hexahydrodiboratotetrakis(*N,N′*-diarylformamidinato)ditantalum(III), Aryl = *p*-Tolyl and Phenyl. The First Structurally Characterized Complexes Containing the μ_2,η^4-$B_2H_6{}^{2-}$ Ligand

F. Albert Cotton,*[,†] Lee M. Daniels,[†] Carlos A. Murillo,*[,†,‡] and Xiaoping Wang[†]

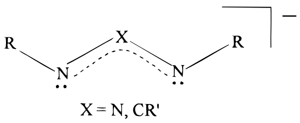
Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843-3255, and Department of Chemistry, University of Costa Rica, Ciudad Universitaria, Costa Rica

Received December 5, 1995[⊗]

Abstract: The *nido*-metalloborane complexes $Ta_2(\mu_2,\eta^4\text{-}B_2H_6)(DTolF)_4{\cdot}2Et_2O$, **1**, $DTolF^-$ = [(*p*-tolyl)NCHN(*p*-tolyl)]$^-$, and $Ta_2(\mu_2,\eta^4\text{-}B_2H_6)(DPhF)_4{\cdot}Et_2O$, **2**, $DPhF^-$ = [phenylNCHNphenyl]$^-$, are formed as the products of tantalum pentachloride with lithium borohydride followed by the addition of LiDTolF or LiDPhF. Complexes **1** and **2** are the first structurally characterized compounds in which two metal atoms that are bonded to each other are also bridged by an hexahydroborate ligand through four B−H−M three-center bonds in a symmetric bonding mode. The Ta−Ta distances are 2.725(1) Å in **1** and 2.728(1), 2.736(1) Å in **2**. Crystallographic data are as follows: compound **1**, $P\bar{1}$, $a = 15.197(3)$ Å, $b = 15.675(2)$ Å, $c = 16.449(6)$ Å, $\alpha = 102.50(1)°$, $\beta = 99.04(1)°$, $\gamma = 117.10(2)°$, and $Z = 2$; compound **2**, $P\bar{1}$ with $a = 11.547(5)$ Å, $b = 20.03(1)$ Å, $c = 24.934(8)$ Å, $\alpha = 107.60(1)°$, $\beta = 100.86(2)°$, $\gamma = 95.65(2)°$, and $Z = 4$. In these molecules there are two $ArNC(H)NAr^-$ ligand corrdinated in a chelating manner to each of two tantalum atoms. These two $Ta(DTolF)_2$ or $Ta(DPhF)_2$ fragments are united by a $Ta{=}Ta$ bond (ca. 2.73 Å), and a B_2H_6 unit lies across the bond forming two B−H−Ta bridge bonds to each tantalum atom. The $B_2H_6Ta_2$ moiety constitutes a B_2Ta_2 *nido*-metalloborane, formally similar to B_4H_{10}.

Introduction

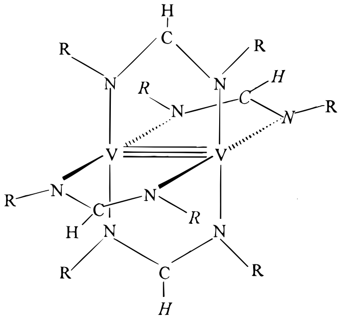
Over the past 20 years it has been found that nearly all of the transition metals can form dinuclear species in which there are metal−metal bonds, ranging from single bonds to quadruple bonds.[1] Among the most useful of ligands for prompting the formation of such bonds are those of the type **I**.



X = N, CR'

I

The work reported here was initiated with the hope of producing a ditantalum(II) analog of the recently reported vanadium compound, **II**, in which there is a triple bond between the vanadium(II) centers.[2] We recognized that in undertaking such a project, we had to deal with both favorable and unfavorable factors. The major positive factor specific to the element tantalum is that, in general, the tendency toward metal−metal bond formation increases markedly from the top to the bottom in any group (i.e., in the order Ta > Nb > V). The major negative factor specific to this particular case is that the oxidation state II is uncommon for tantalum and difficult to attain. A strong reducing agent would clearly be required.



R = p-tolyl

II

As one approach to the synthesis of the tantalum analog of II, we have employed tantalum(V) chloride with $LiBH_4$ as the reducing agent. We have also employed both Li[(*p*-tol)NC(H)N(*p*-tol)] and Li(PhNC(H)NPh) as ligand sources. In neither case was the intended product obtained, but instead the title compounds, equally interesting but in a different way, were prepared and characterized.

Experimental Section

General Procedures. All manipulations were carried out by employing standard Schlenk techniques or in a drybox under an atmosphere of argon. Solvents were refluxed over Na/K alloy/benzophenone. *N,N′*-Diphenylformamidine (HDPhF) and $LiBH_4$ were purchased from Aldrich and used as received. $TaCl_5$ was purchased from Strem Chemical, Inc. and resublimed before use. Di(*p*-tolyl)formamidine (HDTolF) was synthesized by high temperature condensation between toluidine and triethyl orthoformate in a slightly modified published procedure.[3] Single-crystal X-ray diffraction work was performed on a FAST area detector system at low temperature.

[†] Texas A&M University.

[‡] University of Costa Rica.

[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1996.

(1) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms,* 2nd ed.; Oxford University Press: Oxford, 1993.

(2) Cotton, F. A.; Daniels, L. M.; Murillo, C. A. *Inorg. Chem.* **1993**, *32*, 2881−2885.

(3) Roberts, R. M. *J. Org. Chem.* **1949**, *14*, 277−284.

S0002-7863(95)04087-X CCC: $12.00

Preparations of $Ta_2(\mu_2,\eta^4-B_2H_6)(DTolF)_4 \cdot 2Et_2O$ (1) and $Ta_2(\mu_2,\eta^4-B_2H_6)(DPhF)_4 \cdot Et_2O$ (2). To a mixture of $TaCl_5$ (0.72 g, 2 mmol) and $LiBH_4$ (0.30 g, 13 mmol) was added toluene (30 mL). The resulting green slurry was stirred at reflux temperature for 2 days to give a colorless solution and a black solid. The colorless toluene solution was removed by syringe, and the solid was dried under vacuum for 1 h. THF (15 mL) was then added to the solid while stirring, and a dark brown solution was formed. After 5 min of stirring at room temperature, the solution was cooled to −78 °C and stirred for 45 min. LiDTolF (4 mmol) in THF (15 mL) was introduced. The brown solution was stirred for 3 h and allowed to warm up slowly. Slow bubbling was observed during this period of time. The solvent was then evaporated under vacuum over a period of 16 h, and the residue was washed with hexanes (10 mL) (pale yellow solution). Benzene (30 mL) was added to the residue, and the dark brown solution obtained was stirred for 3 h and then heated to reflux for 1 h. After it cooled to room temperature, this solution was filtered, and the benzene solvent was removed from the filtrate under reduced pressure. The dark brown solid left was then extracted with diethyl ether (30 mL). A brown solution was obtained. It was filtered, and the volume of the filtrate was reduced to about 15 mL. After filtration, the ether solution was set in a freezer for 2 weeks. Crystals of **1** suitable for single crystal X-ray analysis were obtained in small amount (5%). More crystals of $Li_2(DTolF)_2(Et_2O)_2$ also grew in the solution, but further separation of **1** from the lithium salt was impossible because of their similar solubilities, and this prevented a successful elemental analysis. Complex **2** was prepared by a similar procedure, and it was crystallized as thin plates. Both compounds are very air-sensitive.

X-ray Crystallography for 1. Crystals grown at −15 °C were examined under a mixed layer of mother liquor and mineral oil in a small dish that was kept in a cold fritted funnel and flushed constantly by a stream of nitrogen. A suitable fragment cut from a rod-shaped crystal was mounted on the top of a glass fiber with grease and transferred immediately to a goniometer head under a nitrogen flow at −75 °C. The cell parameters were obtained from an auto-indexing routine and were refined with 250 strong reflections having $16° < 2\theta < 41°$. The cell parameters and triclinic system were confirmed by taking axial images. Details for data collection have been fully described elsewhere.[4] The structure of **1** was solved by the Patterson method.[5a] Only one ditantalum unit is found in the asymmetric unit. The structure was refined with the SHELXL-93 program.[5b] The least-squares refinement was performed so that all non-hydrogen atoms except those of the two disordered diethyl ether solvent molecules were treated anisotropically. The hydrogen atoms that bridge the B and Ta atoms as well as the terminal hydrogen atoms on the boron atoms were refined isotropically. The refinement converged with $R_1 = 0.055$ and $wR_2 = 0.119$ for 7182 reflections with $I > 2\sigma I$, and $R_1 = 0.078$ and $wR_2 = 0.134$ for all 9260 independent reflections. The highest peak in a final difference Fourier map, of height 2.2(2) e/Å, as well as the next six highest peaks were within 1.0 Å of the two tantalum atoms. Crystal data are listed in Table 1.

X-ray Crystallography for 2. Thin plate-shaped crystals, formed at −15 °C, were handled in the same way as for **1**. Unit cell parameters were refined with 250 reflections in the 2θ range 11.8−41.8°. After the metal atoms of the two ditantalum species in the asymmetric unit of the triclinic cell were found, the remaining non-hydrogen atoms were found by a combination of least-squares refinements on F^2 and differences Fourier syntheses using SHELXL-93. After all of the non-hydrogen atoms had been refined anisotropically, a difference Fourier synthesis revealed all of the hydrogen atoms, which were then included in the final full-matrix least-squares refinement. The hydrogen atoms that bridge boron and tantalum atoms were refined with distance constraints, while the terminal hydrogen atoms on the diborane unit were refined isotropically without restraints. The remainder of the hydrogen atoms were allowed to "ride" in ideal positions on the attached carbon atoms. For 14 579 unique reflections, the refinement converged with $R_1 = 0.072$ and $wR_2 = 0.131$. For the 11 744 reflections with $F_o^2 > 2\sigma(F_o^2)$, $R_1 = 0.051$ and $wR_2 = 0.114$. Crystal data are listed in Table 1.

Table 1. Crystal Data and Structure Refinement for $Ta_2(\mu_2,\eta^4-B_2H_6)(DTolF)_4 \cdot 2Et_2O$, **1**, and $Ta_2(\mu_2,\eta^4-B_2H_6)(DPhF)_4 \cdot Et_2O$, **2**

formula	$C_{68}H_{86}B_2N_8O_2Ta_2$ (1)	$C_{56}H_{60}B_2N_8OTa_2$ (2)
fw (g/mol)	1430.97	1244.64
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	15.197(3)	11.547(5)
b (Å)	15.675(2)	20.03(1)
c (Å)	16.449(6)	24.934(8)
α (deg)	102.50(1)	107.60(1)
β (deg)	99.04(1)	100.86(2)
γ (deg)	117.10(2)	95.65(2)
V (Å^3)	3255(1)	5324(4)
Z	2	4
D_{calc} (g/cm^3)	1.460	1.553
μ (mm^{-1})	3.409	4.154
wavelength (Mo K_α), Å	0.71073	0.71073
temp (K)	198(2)	195(2)
scan method	ω-scan/area det.	ω-scan/area det.
θ range for data collection	2.34−23.50°	1.74−23.50°
R indices,[a] R_1, wR_2[b]	0.055, 0.119	0.051, 0.114
R indices (all data), R_1, wR_2	0.078, 0.134	0.072, 0.131

[a] $I > 2\sigma(I)$. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_0^2) + (a \times P)^2 + b \times P]$, where $P = [\max(F_o^2 \text{ or } 0) + 2 \times (F_c^2)]/3$, $a = 0.0395$ and $b = 48.24$ for **1**; $a = 0.0329$, $b = 83.96$ for **2**.

Results and Discussion

Syntheses. The reduction of tantalum pentachloride with an excess of $LiBH_4$ in toluene at reflux temperature yields a black solid. In a previous reaction where only a 2:1 mol ratio was used, a light green solid was obtained at room temperature.[6] Edge-sharing bioctahedral ditantalum complexes with a "$Ta(\mu-Cl)_2Ta$" core were prepared from the green solid in polar solvents. When an excess of $LiBH_4$ was used, a black solid was obtained that partially dissolved in THF at low temperature to form a dark brown solution. After the lithium formamidinate was introduced to the tantalum solution, slow bubbling was observed. At this stage, presumably, the formation of the $B_2H_6^{2-}$ unit occurs:

$$2BH_4^- \rightarrow B_2H_6^{2-} + H_2(g) \tag{1}$$

Structural Results. The molecules of compounds **1** and **2** are homologous, differing only in the occurrence of tolyl groups in **1** and phenyl groups in **2** as the substituents on the nitrogen atoms of the amidinato ligands. For compound **1** there is one complete molecule in the asymmetric unit. It is depicted in Figure 1, and selected bond distances and angles are listed in Table 2. The amidinato ligands are chelating, which is one of their well-organized structural modes.[7] For compound **2** there are two entire molecules in the asymmetric unit, and they are depicted in Figure 2. Selected dimensions are presented in Table 3.

Since the three independently determined molecular structures, **1**, **2a**, and **2b**, are very similar, and since all three conform closely though not rigorously to C_2 symmetry, with the C_2 axis passing through the centers of the B−B and Ta═Ta bonds, we have assembled in Table 4 the important inner dimensions of the molecules, defined with reference to Figure 3. When the

---

(4) Bryan, J. C.; Cotton, F. A.; Daniels, L. M.; Haefner, S. C.; Sattelberger, A. P. *Inorg. Chem.* **1995**, *34*, 1875−1883.

(5) (a) Sheldrick, G. M. *SHELXS-86: A program for X-Ray Crystal Structure Determination*, University of Göttingen: Germany, 1986. (b) Sheldrick, G. M. *SHELXL-93: A program for Crystal Structure Refinement*, University of Göttingen: Germany, 1993.

(6) Babaian-Kibala, E.; Cotton, F. A. *Inorg. Chim. Acta* **1990**, *171*, 71−74.

(7) Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *133*, 219−300.

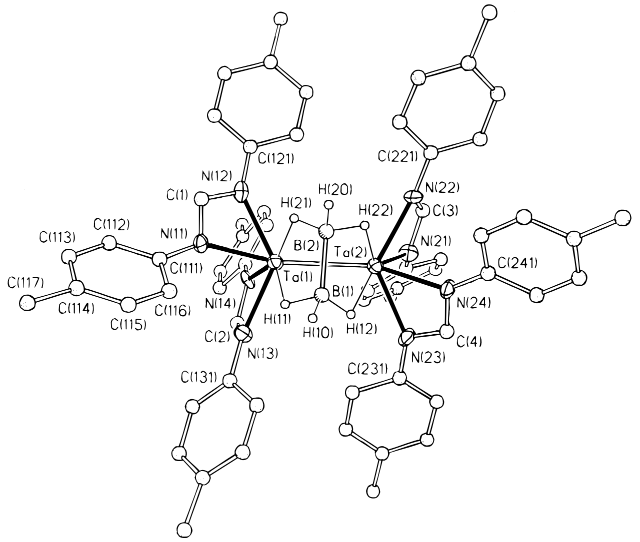


Figure 1. Perspective view of the $Ta_2(\mu_2,\eta^4\text{-}B_2H_6)(DTolF)_4$ molecule in **1** showing the atom labeling scheme. Atoms are drawn at 50% probability level. Hydrogen atoms except those bound to the boron atoms are omitted for clarity.

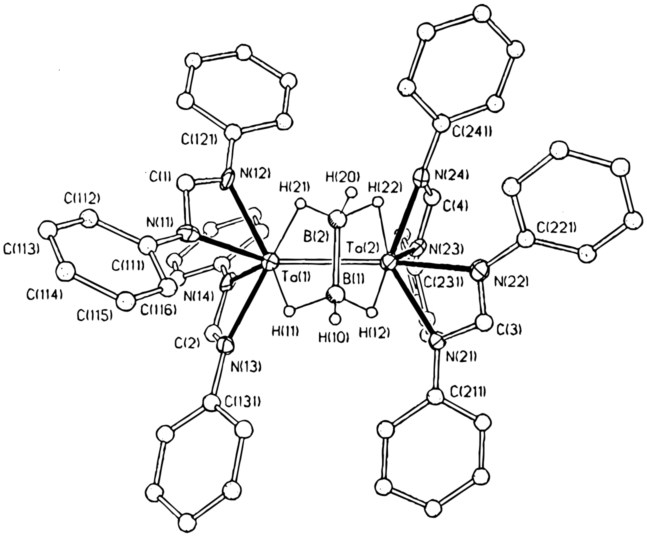
Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Ta_2(\mu_2,\eta^4\text{-}B_2H_6)(DTolF)_4\cdot 2Et_2O$, **1**

Ta(1)−Ta(2)	2.7251(11)	B(1)−B(2)	1.68(2)
Ta(1)−B(1)	2.497(13)	Ta(1)−B(2)	2.536(12)
Ta(2)−N(22)	2.220(8)	B(1)−H(10)	1.21(7)
N(11)−C(1)	1.324(13)	B(1)−H(11)	1.10(6)
B(2)−H(21)	1.09(6)	B(2)−H(20)	1.22(7)
Ta(1)−N(12)	2.197(9)	B(2)−H(22)	1.08(6)
Ta(1)−N(11)	2.226(8)	Ta(1)−H(11)	1.90(3)
B(1)−H(12)	1.13(5)	Ta(1)−N(13)	2.208(8)
Ta(2)−B(1)	2.485(13)	Ta(1)−N(14)	2.240(7)
Ta(1)−H(21)	1.89(3)	Ta(2)−H(22)	1.90(3)
Ta(2)−H(12)	1.91(3)	Ta(2)−N(21)	2.226(8)
Ta(2)−B(2)	2.466(12)	Ta(2)−N(23)	2.185(8)
Ta(2)−N(22)	2.220(8)	Ta(2)−N(24)	2.253(8)

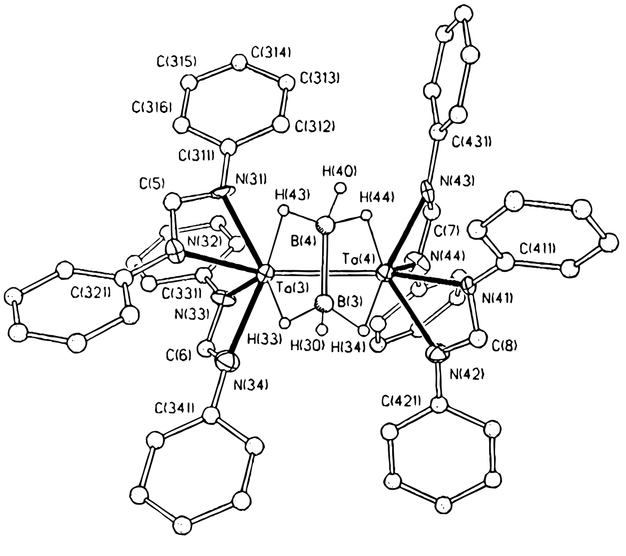
H(12)−B(1)−B(2)	115(2)	B(1)−H(11)−Ta(1)	110(4)
H(12)−B(1)−H(10)	113(5)	B(2)−H(21)−Ta(1)	114(4)
B(1)−H(12)−Ta(2)	107(3)	H(10)−B(1)−B(2)	120(5)
H(11)−B(1)−H(12)	104(6)	H(11)−B(1)−B(2)	107(4)
H(11)−B(1)−H(10)	95(5)	H(20)−B(2)−B(1)	123(4)
H(21)−B(2)−H(20)	108(5)	H(22)−B(2)−B(1)	103(4)
H(22)−B(2)−H(21)	121(8)	H(22)−B(2)−H(20)	97(5)
H(21)−B(2)−B(1)	106(4)	N(13)−Ta(1)−N(14)	58.7(3)
N(11)−Ta(1)−N(12)	59.7(3)	N(21)−Ta(2)−N(22)	59.5(3)
B(2)−H(22)−Ta(2)	109(4)	N(23)−Ta(2)−N(24)	59.7(3)

similarity of all three molecules is recognized, as emphasized in this table, it is appropriate to give average values for all three molecules, and this is done in the last column of Table 4.

The most interesting feature of this molecules is the central, ethane-like B_2H_6 unit that sits symmetrically over the Ta═Ta bond. This sort of structure has never before been subject to direct, metrical characterization, although its occurrence has been discussed on the bases of spectroscopic data on two occasions.[8,9] There have also been discussions of bridging H_2BHBH_2 and an unsymmetrical arrangement of B_2H_6[8,9] as well as the description of a B_2H_6 unit bonded through pairs of hydrogen atoms to three $Mn(CO)_n$ ($n = 3{,}4$) groups.[10] A related metal−boron bonding arrangement has been observed in $(\mu\text{-Br})(CO)_6(B_3H_8)Mn_2$.[11]



2a



2b

Figure 2. Perspective views of $Ta_2(\mu_2,\eta^4\text{-}B_2H_6)(DPhF)_4$ molecules **2a** and **2b** in **2** showing the atom labeling scheme. Atoms are drawn at 50% probability level. Hydrogen atoms except those bound to boron atoms are omitted for clarity.

Recently Onak and Shore *et al.*[12] have shown that the $B_2H_6^{2-}$ ion can exist in THF solution under reducing conditions.

In the molecules we report here, having an ethane-like B_2H_6 unit using four B−H bonds to form bridges to two Ta atoms, there is a formal similarity, as shown in Figure 4, between the $Ta(\mu_2,\eta^4\text{-}B_2H_6)Ta$ structure and the borane B_4H_{10}. The major differences are that in the present molecules the central B−B distance is about 1.70 Å, whereas in B_4H_{10} the B−B distance is 1.75 Å, and in B_4H_{10} the outer B atoms (corresponding to the Ta atoms) are not bound to each other. There is perhaps a closer similarity to B_4H_8, but this is known to occur only in a mass spectrometer.[13]

---

(8) (a) Jacobsen, G. B.; Anderson, E. L.; Housecroft, C. E.; Hong, F.-E.; Buhl, M. L.; Long, G. J.; Fehlner, T. P. *Inorg. Chem.* **1987**, *26*, 4040−4046. (b) Anderson, E. L.; Fehlner, T. P. *J. Am. Chem. Soc.* **1978**, *100*, 4606−4607. (c) Parry, R. W. *Phosphorus, Sulfur Silicon* **1994**, *87*, 177−191.

(9) (a) Ting, C.; Messerle, L. *J. Am. Chem. Soc.* **1989**, *111*, 3449−3450. (b) Ting, C.; Messerle, L. *Inorg. Chem.* **1989**, *28*, 171−173.

(10) Kaesz, H. D.; Fellmann, W.; Wilkes, G. R.; Dahl, L. F. *J. Am. Chem. Soc.* **1965**, *87*, 2753−2755.

(11) Chen, M. W.; Gaines, D. F.; Hoard, L. G. *Inorg. Chem.* **1980**, *19*, 2989−2993.

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

(13) Hollins, R. E.; Stafford, F. E. *Inorg. Chem.* **1970**, *9*, 877−889.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $Ta_2(\mu_2,\eta^4\text{-}B_2H_6)(DPhF)_4\cdot Et_2O$, **2**

Ta(1)−Ta(2)	2.7359(9)	B(1)−B(2)	1.68(2)
Ta(3)−Ta(4)	2.7283(14)	B(3)−B(4)	1.73(2)
B(1)−H(10)	1.05(11)	Ta(2)−B(1)	2.497(13)
B(1)−H(11)	1.16(8)	Ta(2)−B(2)	2.482(14)
B(1)−H(12)	1.08(7)	Ta(2)−H(12)	1.91(5)
B(2)−H(20)	1.14(10)	Ta(2)−H(22)	1.93(5)
B(2)−H(21)	1.07(7)	Ta(2)−N(21)	2.186(8)
B(2)−H(22)	1.17(8)	Ta(2)−N(22)	2.235(9)
B(3)−H(30)	1.05(12)	Ta(2)−N(23)	2.255(8)
B(3)−H(33)	1.07(8)	Ta(2)−N(24)	2.234(8)
B(3)−H(34)	1.23(8)	Ta(3)−B(3)	2.469(13)
B(4)−H(40)	1.19(12)	Ta(3)−B(4)	2.524(14)
B(4)−H(43)	1.22(8)	Ta(3)−H(33)	1.93(5)
B(4)−H(44)	1.06(8)	Ta(3)−H(43)	1.86(5)
Ta(1)−B(1)	2.487(13)	Ta(3)−N(31)	2.213(8)
Ta(1)−B(2)	2.516(13)	Ta(3)−N(32)	2.224(9)
Ta(1)−H(11)	1.90(5)	Ta(3)−N(33)	2.211(9)
Ta(1)−H(21)	1.90(5)	Ta(3)−N(34)	2.211(9)
Ta(1)−N(11)	2.242(9)	Ta(4)−B(3)	2.447(14)
Ta(1)−N(12)	2.225(9)	Ta(4)−B(4)	2.465(13)
Ta(1)−N(13)	2.228(8)	Ta(4)−H(34)	1.89(5)
Ta(1)−N(14)	2.215(8)	Ta(4)−H(44)	1.86(5)
Ta(4)−N(41)	2.264(8)	Ta(4)−N(43)	2.233(8)
Ta(4)−N(42)	2.218(8)	Ta(4)−N(44)	2.259(9)

B(1)−H(11)−Ta(1)	106(5)	H(34)−B(3)−B(4)	116(3)
B(1)−H(12)−Ta(2)	111(5)	H(40)−B(4)−B(3)	126(6)
B(2)−H(21)−Ta(1)	113(5)	H(40)−B(4)−H(43)	116(6)
B(2)−H(22)−Ta(2)	104(4)	H(43)−H(4)−B(3)	109(4)
B(3)−H(33)−Ta(3)	107(5)	H(44)−B(4)−B(3)	106(5)
B(3)−H(34)−Ta(4)	101(4)	H(44)−B(4)−H(40)	89(7)
B(4)−H(43)−Ta(3)	108(5)	H(44)−B(4)−H(43)	108(9)
B(4)−H(44)−Ta(4)	112(6)	N(11)−Ta(1)−N(12)	59.3(3)
H(10)−B(1)−B(2)	123(6)	N(13)−Ta(1)−N(14)	59.4(3)
H(10)−B(1)−H(11)	96(7)	N(21)−Ta(2)−N(22)	59.6(3)
H(10)−B(1)−H(12)	107(7)	N(24)−Ta(2)−N(23)	59.2(3)
H(11)−B(1)−B(2)	109(4)	N(31)−Ta(3)−N(32)	59.4(3)
H(12)−B(1)−B(2)	110(4)	N(33)−Ta(3)−N(34)	59.4(3)
H(12)−B(1)−H(11)	111(7)	N(41)−Ta(4)−N(42)	59.6(3)
H(20)−B(2)−B(1)	117(5)	N(43)−Ta(4)−N(44)	58.6(3)
H(20)−B(2)−H(22)	94(6)	H(21)−B(2)−H(20)	119(6)
H(20)−B(2)−Ta(1)	157(5)	H(21)−B(2)−H(22)	100(7)
H(21)−B(2)−B(1)	111(4)	H(22)−B(2)−B(1)	113(4)
H(30)−B(3)−H(33)	97(7)	H(30)−B(3)−B(4)	125(6)

Table 4. Core Dimensions (Å or deg) Averaged for C_2 Symmetry Molecule

	1	**2a**	**2b**	weighted av over **1**, **2a**, **2b**
Ta−Ta′	2.725(1)	2.736(1)	2.728(1)	2.730[3]
B−B′	1.68(2)	1.68(2)	1.73(2)	1.70[2]
B−Ta	2.52(1)	2.51(1)	2.50(1)	2.51[1]
B′−Ta	2.48(1)	2.49(1)	2.47(1)	2.48[1]
B−H1	1.08(6)	1.17(8)	1.07(8)	1.10[3]
H1−Ta	1.90(5)	1.92(5)	1.91(5)	1.91[5]
B′−H2	1.11(6)	1.08(7)	1.23(8)	1.13[5]
H2−Ta	1.90(5)	1.91(5)	1.86(5)	1.89[3]
Ta−N1	2.226(8)	2.214(9)	2.239(8)	2.227[7]
Ta−N2	2.209(8)	2.230(9)	2.221(9)	2.219[6]
Ta−N3	2.196(8)	2.242(8)	2.222(9)	2.22[1]
Ta−N4	2.247(8)	2.225(8)	2.235(9)	2.236[6]
N1−Ta−N2	59.6(5)	59.5(3)	59.5(3)	59.5[1]
N3−Ta−N4	59.2(3)	59.3(3)	59.5(3)	59.3[1]

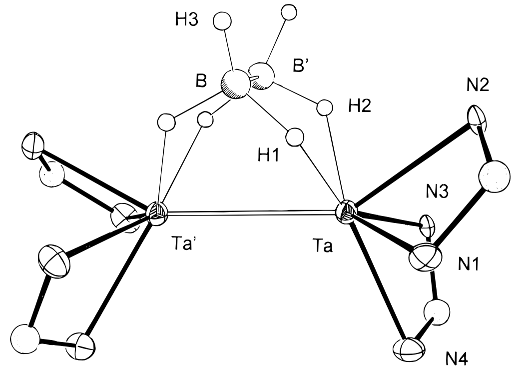


Figure 3. A view of the central portion of the molecules in **1** and **2** with a labeling scheme that allows comparison of the three independent molecules, as given in Table 4.

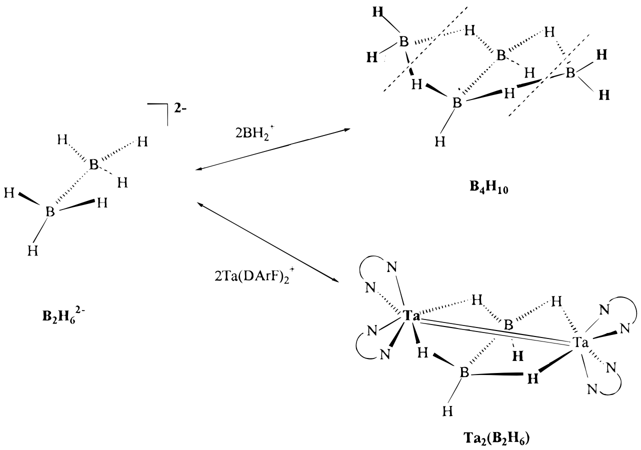


Figure 4. A schematic comparison of borohydrides B_4H_{10}, $B_2H_6^{2-}$, and the related *nido*-metalloborane.

Finally, it is appropriate to comment briefly on the electronic structure of these compounds, which can be formulated qualitatively as follows. We first regard the B_2H_6 unit as an ethane-like $B_2H_6^{2-}$ ion. On this basis, and with four formamidinium anions, the tantalum atoms are assigned the oxidation state +3. There are numerous dinuclear compounds of both Nb^{III} and Ta^{III}, most of which are edge-sharing or face-sharing bioctahedra. They have metal-to-metal distances in the range 2.6−2.8 Å and have been assigned[1] metal−metal bond orders of 2 although in some cases this may be a slight oversimplification.[14] In the present cases, where the Ta−Ta distances are about 2.73 Å and the compounds are diamagnetic, it again seems reasonable to propose that Ta═Ta bonds exist.

Acknowledgment. We are grateful to the National Science Foundation and the University of Costa Rica for support.

Supporting Information Available: Tables of crystal data, atomic coordinates, bond distances and angles, anisotropic displacement parameters, positional parameters of hydrogen atoms for structures **1** and **2** (29 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of this journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA954087D

---

(14) Cotton, F. A.; Feng, X.; Gütlich, P.; Kohlhaas, T.; Lu, J.; Shang, M. *Inorg. Chem.* **1994**, *33*, 3055−3063.