The 2-D INEPT-INADEQUATE spectrum for **7** (Figure 2) is also irrefutable evidence for structural identification.[7] Note that **8** (Figure 3b) would show **a** connected to **b** and **b** connected to **c**. The spectrum clearly shows **a** directly bonded to both **b** and **c**, with two-bond coupling between **b** and **c** and three-bond coupling between **c** and **d**.[10,11]

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Note Added in Proof. While this work was in press two other groups published 2-D INADEQUATE NMR spectra of polysilicon compounds. See: Heugge, E.; Schrank, F. *J. Organomet. Chem.* **1989**, *362*, 11. Kuroda, M.; Kabe, Y.; Hashimoto, M.; Masamune, S. *Angew. Chem., Int. Ed. E*ngl. **1988**, *27*, 1727.

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(9) Only one set of three-bond couplings is observed for compound **1**. According to the Karplus relation, the magnitude of such a coupling depends on the dihedral angle between the Si exo to the ring and bond in the ring. Therefore, in the orientations of the rings in which an exo silicon is configured 90° to the ring silicons, the three-bond coupling would be diminished. MM2 calculations show dihedral angles near 90° for the couplings that do not appear.

(10) One-bond correlations, in 10^3 Hz(F1), for **7**: **a–d**, 0.3; **a–c**, −1.1; **a–b**, −0.6. Two-bond correlation: **b–c**, 7.3. Three-bond correlation: **d–c**, 8.7.

(11) The correlation for the three-bond coupling from **b** to **d** in **7** is not fully resolved because the intensity of signal **b** with respect to the other signals is so small. A peak at 8800 Hz (F1) and 3700 Hz (F2), although not shown in Figure 3, appears at lower levels on the contour plot, matching the peak at 8800 Hz (F1) and 4700 Hz (F2).

Borohydride B–H Activation and Dimerization by a Doubly Bonded, Early-Transition-Metal Organodimetallic Complex. Ditantalladiborane Syntheses as Models for Dehydrodimerization of Methane to Ethane

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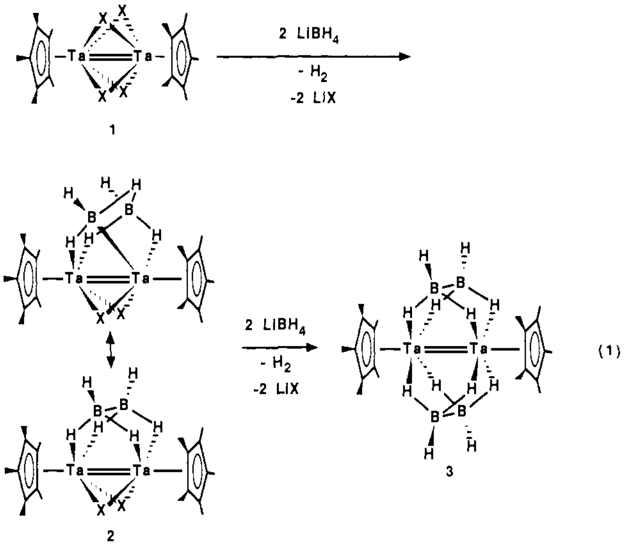
There is considerable interest in hydrocarbon C–H activation from the theoretical and organometallic perspectives,[1] particularly in discovering activation/functionalization pathways and bonding models for catalyst surface intermediates. The isoelectronic relationships[2] between hydrocarbons and boranes have led to studies of metallaboranes[3] as hydrocarbon–metal analogues;[3c] for example, distorted BH_4^- complexes are models for CH_4 coordination in the transition state for C–H activation.[4] Our discovery[5] of vinylic C–H activation by the Ta=Ta complexes $(C_5Me_4R)_2Ta_2(\mu\text{-}X)_4$[6] led us to examine reactivity toward B–H bonds. The reactions of BH_4^- with multiply bonded M–M compounds are unstudied,[7] particularly for the early transition metals;[8] hydroboration of M–C multiple bonds,[9] but not M–M multiple bonds, has been reported. We wish to report new complexes with hexahydridodiborate (diborane(2−), unknown as a free species) ligands derived from BH_4^- B–H activation and dehydrodimerization by a M=M group.

The reaction of 2 equiv of $LiBH_4$ with $(C_5Me_4R)_2Ta_2(\mu\text{-}X)_4$ (**1**: R = Me (Cp*), Et; X = Cl, Br) in ether yields the blue ditantalladiboranes $(C_5Me_4R)_2Ta_2(\mu\text{-}X)_2(B_2H_6)$ (**2**) in 30% isolated yield (eq 1).[10] Spectroscopic data are consistent with an unsymmetrical $B_2H_6^{2-}$ complex formulation for the major solution species; spectra are complicated by smaller amounts of three B-containing species (including **3**, vide infra). The ^1H NMR spectrum exhibits a single Cp* resonance, inequivalent BH_t resonances, and several unequal high-field multiplets (consistent with BHB and TaHB groups) for the major species from −80 to 25 °C. $^{11}B\{$selective $^1H\}$ NMR spectroscopy with resolution enhancement[11] shows that this species contains inequivalent borons ($\nu_{1/2}$ ~170 Hz before GRE) with H_t and partially resolved TaHB and BHB couplings (presumably[12] <80 Hz; the downfield resonance is an incompletely resolved quartet or double doublet, the other a triplet upon $\{H_t\}$). NMR data thus suggest a $(\mu\text{-}H)H_tB\text{-}H\text{-}BH_t(\mu\text{-}H)_2$ group[13] (with Ta–B bond) or TaB_2 face-bridging hydrides and rules out a TaHTa group. One solution species may be the symmetric $(\mu\text{-}H)_2H_tB\text{-}BH_t(\mu\text{-}H)_2$ isomer. The single Cp* resonance is presumed to be due to Ta–B/Ta–H–B exchange and a small Δδ for the inequivalent Cp* ligands.



The solid-state structure in a crystal from a **2b** mixture is shown in Figure 1. The structure[14] matches that proposed for the major solution species, with a Ta=Ta bond (2.839 (1) Å) bridged by two bromines and an unsymmetrical B_2H_6 group with long B···B separation (1.88 (3) Å) consistent with BHB bonding. The Ta···B distances (2.37 (2), 2.40 (2), 2.42 (2), 2.42 (2) Å) are in accord with three TaHB bridges and a Ta–B bond rather than four TaHB

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(14) Crystal data for **2b**: space group $P2_1/c$, $a = 10.935$ (5) Å, $b = 14.585$ (2) Å, $c = 15.967$ (8) Å, $\beta = 107.63$ (6)°, $V = 2427.04$ Å^3, $\rho_{calc} = 2.248$ g cm^{-3}, μ (empirical absorption, 0.62–1.00) = 165.03 cm^{-1}, reflections collected $(+h,\pm k,\pm l) = 9089$, observed $(I \geq 3\sigma(I)) = 5179$, unique reflections after averaging = 2414, atoms refined anisotropically except H(1)–H(5) (found, fixed), Cp* H atoms (one/Me found; others calculated, all fixed), and H(6) (calculated, fixed), $R = 0.0417$, $R_w = 0.0555$.

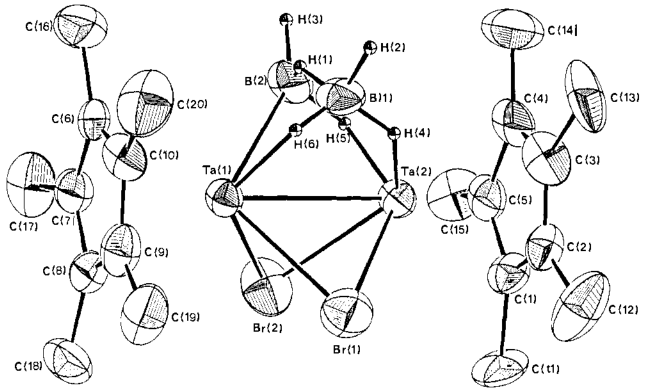

Figure 1. ORTEP diagram of the molecular structure of $(C_5Me_5)_2Ta_2(\mu\text{-}Br)_2(B_2H_6)$ (**2b**) viewed perpendicular to the Ta=Ta bond. Key bond distances (Å) and bond angles (deg) not given in the text are as follows: Ta(1)–Br(1), 2.649 (2); Ta(1)–Br(2), 2.641 (2); Ta(2)–Br(1), 2.627 (2); Ta(2)–Br(2), 2.645 (2); Ta(1)–Br(1)–Ta(2), 65.11 (5); Ta(1)–Br(2)–Ta(2), 64.99 (5).

bridges (a data set with lower σ's is needed to substantiate this) since a Ta^{III}–B distance can be estimated at 2.35 Å.[8,15] All non-Cp* hydrogens except H(6) were found during refinement, with H(6) calculated and placed between Ta(1)/B(1) because of the marginally longer Ta(1)···B(1) separation. Acute TaBrTa angles are consistent[8] with a Ta=Ta interaction. The Ta(1)=Ta(2) distance is in the single-bond range, whereas a double bond of $\sigma^2\delta^2$ configuration would be expected for $B_2H_6^{2-}$ bonded to a $Cp^*_2Ta(III)_2(\mu\text{-}X)_2^{2+}$ fragment. Metal-metal bond length-order correlations can be unreliable in complexes with bridging ligands, and M–M bonds lengthen substantially upon substitution of a μ-hydride by a μ-halide.[8,16] We ascribe the Ta=Ta lengthening to the $B_2H_6^{2-}$ ligand.

Addition of 4 equiv of $LiBH_4$ to **1** or 2 equiv to **2** results in halogen substitution, H_2 elimination, and formation of the violet $(C_5Me_4R)_2Ta_2(B_2H_6)_2$, **3**, in 60% yield (eq 1).[17] This complex has chemically equivalent C_5Me_4R groups, through which pass a mirror plane, and two ^1H resonances for BH_t and TaHB groups; a singlet is seen in the ^{11}B NMR spectrum. There is *no* NMR-detectable exchange between TaHB and BH_t hydrogens, with invariant chemical shifts between −83 and 95 °C. These data are consistent with symmetric bridging $(\mu\text{-}H)_2H_tB\text{-}BH_t(\mu\text{-}H)_2$ moieties.

The mechanism of formation of **2** and **3** has been probed in several ways. Reaction of excess $LiBH_4$ with a $Cp^*_2Ta_2Cl_4/(C_5Me_4Et)_2Ta_2Cl_4$ mixture yields $Cp^*_2Ta_2(B_2H_6)_2$ and $(C_5Me_4Et)_2Ta_2(B_2H_6)_2$ with no cross product $(C_5Me_4Et)Cp^*Ta_2(B_2H_6)_2$ by NMR, thus ruling out mononuclear intermediates. Kinetic studies by UV/vis show that both reactions in eq 1 are first-order in organoditantalum reactant and *zero-order* in $LiBH_4$.[18] The zero-order $[LiBH_4]$ dependence and near-zero ΔS^* for both reactions suggest that the organoditantalum reactants rearrange prior to BH_4^- reaction, perhaps by opening of two μ-halides.

Complexes with B_2H_6 ligands are rare.[13,19-22] $Fe_2(CO)_6(B_2H_6)$[13] possesses an unsymmetrical $(\mu\text{-}H)H_tBHBH_t(\mu\text{-}H)_2^{2-}$ group and Fe–B bond as shown by NMR. The byproduct $Cp^*_2Nb_2(B_2H_6)_2$ (4% yield), from synthesis[23] of $Cp^*_2Nb(BH_4)$, possesses a structure[22] analogous to **3** and presumably arises from reaction of BH_4^- with adventitious $Cp^*_2Nb_2Cl_4$ formed under the reducing conditions.

The dimetalladiboranes **2** and **3** are novel in several aspects: (1) they are obtained from BH_4^-, which shows that early metal dinuclear complexes can act as templates for B–H activation and BH_4^- oligomerization;[3a,24] (2) the isoelectronic relationships between BH_4^- and CH_4 and between the arachno anion $B_2H_6^{2-}$ and C_2H_6 suggest that the formation of **2** or **3** can serve as models for dehydrodimerization of CH_4 to H_3CCH_3 and that **2** and **3** are structural models[25] for C_2H_6 surface coordination; (3) they are novel examples of early-transition-metal metallaboranes with low boron content, an unexplored area (other than BH_4^- and Group 6 $B_3H_8^-$ complexes.[3b,26]).

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Supplementary Material Available: Tables of coordinates, thermal parameters, and bond lengths and angles (13 pages); listing of structure factors (9 pages). Ordering information is given on any current masthead page.

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(17) Characterization data for $Cp^*_2Ta_2(B_2H_6)_2$, **3**: Anal: Calcd for $C_{20}H_{42}B_4Ta_2$: C, 34.92; H, 6.11. Found: C, 34.85; H, 6.45. ^1H NMR (δ, 25°, C_6D_6): −10.5 (br, TaHB), 2.26 (s, Cp*), 4.4 (br, BH); at 75° (partial correlation time decoupling): −10.5 (br d, TaHB) and 4.28 (1:1:1:1 q, BH_t, $^1J_{BH} \cong 110$ Hz). ^{13}C NMR (δ, C_6D_6): 13.5 (s, C_5*Me*$_5$), 109.6 (s, *C*$_5$Me$_5$). ^{11}B NMR (δ, C_6D_6): −4.0. Mass spectrum (EI): *m/e* 688, M^+. IR (Nujol, cm^{-1}): 2417 (s, BH_t), 1784 (s, TaHB); 1800, 1328 for $LiBD_4$-derived product.

(18) Pseudo-first-order (in Ta_2, s^{-1}) rate constants and activation parameters: **1** → **2b** (24.7°): 3.04×10^{-4}, $\Delta H^* = 90.5$ (1.9) kJ mol^{-1}, $\Delta S^* = -8$ (6) J mol^{-1} K; **2b** → **3** (25.1°): 4.54×10^{-5}, $\Delta H^* = 83.1$ (5.8), $\Delta S^* = -49$ (19).

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Serial Radical Reactions of Enol Ethers: Ready Routes to Highly Functionalized C-Glycosyl Derivatives[1]

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Carbohydrate derivatives, because of their highly functionalized nature, have been favorite substrates for testing the viability of free-radical reactions for synthetic operations.[3-8] By corollary,

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