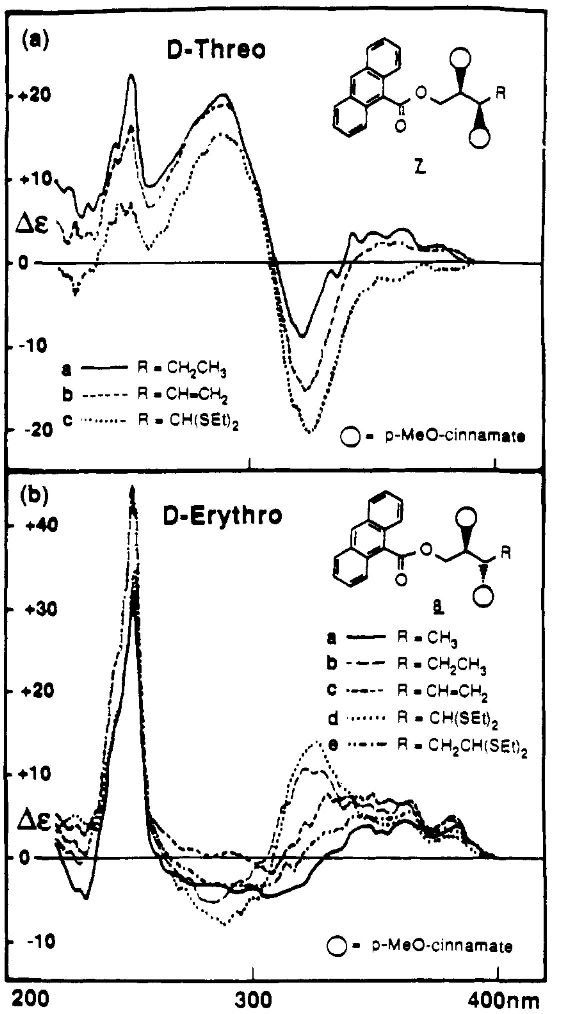

Figure 1. Circular dichroic spectra of "bichromophorically derivatized" 1,2,3-triols: Reference curves for empirical assignment of relative and absolute configuration.

gave the 1-*O*-(9-anthroate) 2,3-di-*O*-*p*-methoxycinnamates **7**.[25] The CD spectra[26] of these bichromophorically derivatized D-threo triols **7** are compared to the corresponding D-erythro derivatives **8**[27] in Figure 1. While both show positive Cotton effects at 253 nm indicating the *R* absolute configuration at C-2,[28] the magnitude of this Cotton effect in the erythro derivatives is roughly twice that in the threo derivatives. More dramatic differences between the two are seen at the 289 and 323 nm Cotton effects, which differ both in sign and magnitude. Variations within each group due to conformational differences (indicated by NMR coupling constants) are greatest when R is the bulky dithioacetal group (**7c** and **8d**, dotted lines).

The CD curves in Figure 1 may be used for empirical assignment of stereochemistry in 1,2,3-triols without any further understanding of the exciton coupling involved. We note, however, that they are in full accord with predictions based upon the recently demonstrated *pairwise additivity* of interchromophoric couplings.[10,11] CD curves of derivatives containing three or more chromophores can be accurately predicted by spectral summation of all two-chromophore subunits. Thus, these triol derivative spectra are accurately simulated by summation of the spectra corresponding to the 1,2- and 1,3-anthracene/cinnamate interactions and the 2,3-dicinnamate interaction,[29] indicating the nonempirical basis of the exciton chirality method.

This "bichromophoric" CD method has general applicability to a variety of hydroxylation patterns, including 1,3-polyols. We have completed an analogous study of 1,2,3,4-tetrols and 1,2,3,4,5-pentols and have found that up to four chiral centers can be assigned by this approach.[29] In addition to the exceptional ease with which this method can assign both relative and absolute configuration, it offers the distinct advantage of a minimal material requirement. The CD spectra are routinely recorded on 20 nmols or less, and the strongly fluorescent anthroate ester allows for derivatization and purification on a microscale (anthroate derivatives of hydroxysteroids have been prepared and chromatographed using fluorescent detection on μg quantities[22]). We are currently examining a range of applications to structural studies.

Acknowledgment. The studies have been supported by NIH Grant GM 34509.

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(25) Purified by flash chromatography (CH_2Cl_2, silica, 365 nm active). Partial ^1H NMR data (CD_3CN): **7a**, 5.58 (ddd, 3.3, 4.5, 6.6 Hz, 1 H, H-2), 5.30 (ddd, 4.5, 5.1, 7.8 Hz, 1 H, H-3), 4.93 (dd, 3.3, 12.0 Hz, 1 H, H-1), 4.75 (dd, 6.6, 12.0 Hz, 1 H, H-1′); **7b**, 5.74 (dd, 5.8, 6.0 Hz, 1 H, H-3), 5.64 (ddd, 3.3, 5.8, 6.6 Hz, 1 H, H-2), 4.96 (dd, 3.3, 12.1 Hz, 1 H, H-1), 4.77 (6.6, 12.1 Hz, 1 H, H-1′); **7c**, (ref 12).

(26) CD spectra were recorded from 420–220 nm on a Jasco 500A spectropolarimeter using a 1-cm cell at ambient temperature. Acetonitrile solutions were prepared which were 5–15 μM, the exact concentrations determined from the UV extinction coefficients: anthroate monocinnamates ϵ_{311nm} = 28 400; anthroate dicinnamates ϵ_{311nm} = 49 400. Prior to UV and CD measurements, derivatives were purified by HPLC (EtOAc/hexane 3:7, YMC 5 μm SiO_2 gel column).

(27) Partial ^1H NMR data (CD_3CN): **8a**, 5.54 (ddd, 3.7, 4.9, 6.4 Hz, 1 H, H-2), 5.33 (dq, 4.9, 6.5 Hz, 1 H, H-3), 4.95 (dd, 3.7, 12.1 Hz, 1 H, H-1), 4.87 (dd, 6.4, 12.1 Hz, 1 H, H-1′); **8b**, 5.55 (ddd, 3.6, 4.6, 6.5 Hz, 1H, H-2), 5.27 (ddd, 4.4, 4.6, 8.2 Hz, 1 H, H-3), 4.95 (dd, 3.6, 12.1 Hz, 1 H, H-1), 4.88 (dd, 6.5, 12.1 Hz, 1 H, H-1′); **8c**, 5.71 (dd, 4.9, 6.0 Hz, 1 H, H-3), 5.62 (dt, 4.9, 5.1 Hz, 1 H, H-2), 4.90 (d, 5.1 Hz, 2 H, H-1′s); **8d**, (ref 12); **8e**, 5.66 (ddd, 3.0, 4.2, 6.8 Hz, 1 H, H-3), 5.60 (ddd, 4.0, 4.2, 6.5 Hz, 1 H, H-2), 4.95–4.87 (m, 2 H, H-1′s).

(28) Configurational assignments (*R*,*S*): **7a**,**b** and **8d**, (2*R*,3*R*); **8a–c**,**e** and **7c**: (2*R*,3*S*). Note that (*R*,*S*) assignments vary with alkyl substituent within each stereochemical family.

(29) Wiesler, W. T.; Nakanishi, K., manuscript in preparation.

Use of 2-D INEPT-INADEQUATE ^{29}Si NMR To Determine Structures of Organosilicon Rings

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Recently, it was found that Lewis acid catalyzed rearrangement of permethylcyclosilanes, $(SiMe_2)_n$, leads to branched cyclosilanes.[1] In each case a single isomer is formed. For $(SiMe_2)_n$ (n = 6–9), the rearranged products were all trimethylsilyl-substituted cyclopentasilanes; for n = 10 to 12, the rearranged compounds were trimethylsilyl-substituted cyclohexasilanes. However, the NMR spectra did not allow unambiguous structural assignments in all cases.[2,3]

We report here the first use of 2-D INEPT–INADEQUATE ^{29}Si NMR spectroscopy to establish the structures of two of the rearranged cyclosilanes. Although the INEPT–INADEQUATE pulse sequence has been developed previously for ^{13}C NMR,[4] and

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(1) Blinka, T. A.; West, R. *Organometallics* **1986**, *5*, 128.

(2) Blinka, T. A.; West, R. *Organometallics* **1986**, *5*, 133.

(3) To determine the most likely structure according to steric energies, MM2 calculations were performed on the likely structures, but this approach was also inconclusive because the calculations predict only small differences in energies between the isomers. For the product from $(SiMe_2)_8$ the difference in energy between the two most likely isomers **1** and **2** is 0.33 kcal mol^{-1}. The actual product **1** is predicted to be the more stable one. The steric energy difference in the two possible isomers **7** and **8** from the rearrangement of $(SiMe_2)_9$ is 4.14 kcal mol^{-1}, with the actual product **7** again predicted to be more stable.[2]

(4) Sørensen, O. W.; Freeman, R.; Frenkiel, T.; Mareci, T. H.; Schuck, R. J. *J. Magn. Reson.* **1982**, *46*, 180.

0002-7863/89/1511-3447$01.50/0

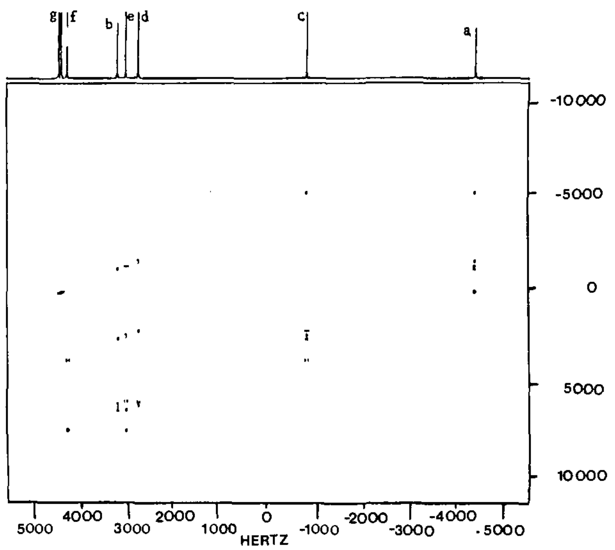

Figure 1. 2-D ^{29}Si–^{29}Si INEPT-INADEQUATE NMR spectrum of **1**.

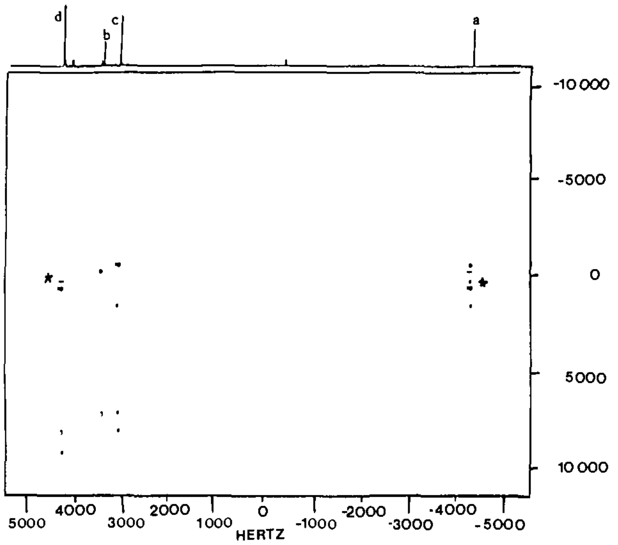

Figure 2. 2-D ^{29}Si–^{29}Si INEPT-INADEQUATE spectrum of **7**. Asterisks indicate quadrature images.

the 2-D INADEQUATE technique has been used in structural investigations of ^{13}C NMR and NMR of inorganic nuclei,[5] our experiments are apparently the first 2-D ^{29}Si–^{29}Si spectra to be reported and also represent the first use of 2-D INEPT-INADEQUATE NMR spectroscopy.[6]

In these spectra, the signal/noise ratio and the resolution are so good that correlations resulting from the smaller two-bond couplings, $^2J(^{29}\text{Si}-^{29}\text{Si})$ (8–17 Hz), and in special cases from ^3J are observable in the spectrum as well as correlations from the larger one-bond couplings (45–60 Hz). In the spectra displayed in Figures 1 and 2, the one-bond correlation appears as two dots since the large coupling is easily separated by the digital resolution chosen in the experiments. The longer range correlations appear as single dots because the resolution is insufficient to separate the scalar coupling that the peaks represent.

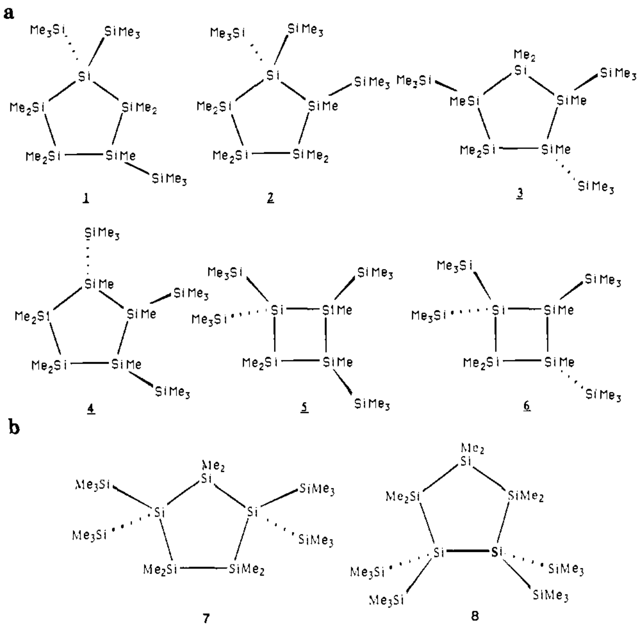

Figure 3. (a) The six possible isomers of Si_8Me_{16} that would have eight unique silicons in the NMR spectrum. (b) The possible isomers of Si_9Me_{18} that would have four unique silicons in the NMR spectrum in the ratio 4:2:1:2.

In the AlCl$_3$ catalyzed rearrangement, $(Me_2Si)_8$ is transformed into one new compound that has eight signals in the ^{29}Si NMR spectrum. Of the possible isomers of $(Me_2Si)_8$, structures **1–6** would each have eight unique silicon atoms and so could give the observed NMR pattern (Figure 3a). As explained earlier,[2] the ^{29}Si NMR spectrum of the rearranged compound suggests that it contains both a tri- and a tetrasubstituted silicon atom and is, therefore, most consistent with **1** or **2**. Rearrangement of $(Me_2Si)_9$ gives a product having four ^{29}Si signals with the intensity ratio 4:2:1:2.[1] Two isomers **7** or **8** are consistent with this pattern (Figure 3b).

The 2-D INEPT-INADEQUATE spectrum of the product from $(Me_2Si)_8$ (Figure 1)[7] shows decisively that the structure is **1**. The one-bond connectivities[8] of silicons **a** to **b**, **b** to **c**, **c** to **d**, **d** to **e**, and **e** to **a** establish the five-membered ring. The positions of the exocyclic silicones **f**, **g**, and **g′** are evident from the connectivities, **g** and **g′** to **a** and **f** to **c**, showing the positions of attachment.

The structural assignment of **1** is further corroborated by the long-range coupling patterns.[8] Moreover, a three-bond coupling is observed from the single *exo*-trimethylsilyl to one of the silicons in the ring. This would be expected since the MM2 calculations indicate that for this structure the dihedral angle from **f** to **e** would be 22°.[9]

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[5] For a review of the INADEQUATE experiment, see: Buddrus, J.; Bauer, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 625–642. Also for a review of NMR experiments in two dimensions, see: Kessler, H.; Gehrke, M.; Griesinger, C. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 490–536. 2-D INADEQUATE has been used to elucidate the structure of tungstenates: Brevard, C.; Schimpf, R.; Tourne, G.; Tourne, C. M. *J. Am. Chem. Soc.* **1983**, *105*, 7059. Domaille, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 7677. Finke, R. G.; Rapko, B.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 2947.

[6] Spectra were recorded on a Bruker AM-360 (71.55 MHz for ^{29}Si) at 25 °C; **1**, 230 mg in 1.5 mL of CDCl$_3$, 10 mm sample tube; **7**, 90 mg in 0.5 mL of CDCl$_3$, 5 mm tube. Pulse sequence:

^{1}H: D5-90°-D6-180°-D6-90°-D7-180°-D7-DECOUPLE

^{29}Si: ---180°-D6-90°-D7-180°-D7-D2-180°-D3-90°-D0-135°-FID

Delay times: D5 = 3.0 s; D6 = $(1/4J_{Si-H})$ = 0.037 s; D7 = $(\Delta_{opt}/2J)$ = 0.01 s; D3 = $[(2n + 1)/4J_{Si-Si}]$ (n = 0) = 0.0044 s; D2 = $\{[(2n + 1)/4J_{Si-Si}]$ (n = 1)$\}$ – D7 = 0.0044 s; D0 = incremental delay; DS = 2; NS = 32: 32-Phase cycle. Experimental time = 16 h.

[7] The INEPT ^{29}Si {^{1}H} spectrum is projected on top. However, peak intensities, especially for **7**, do not correspond to the numbers of silicon atoms because of differences in polarization transfer. The previously reported[2] silicon-29 spectrum for **7** gives the correct 4:2:1:2 intensity pattern for **d**:**b**:**c**:**a**. The 2-D spectra are interpreted by the following algorithm: The two peaks in the horizontal F2 dimension (^{29}Si resonances set on an arbitrary scale) are correlated in the vertical F1 dimension by the frequency that corresponds to the sum of the individual frequencies on the F2 scale.

[8] One-bond correlations, in 10^3 Hz(F1), for **1**: **a–b**, –1.2; **b–c**, 2.1; **c–d**, 1.6; **d–e**, 5.5; **e–a**, –1.4; **g/g′–a**, –0.4; **f–c**, 3.2. Long-range correlations: two-bond, **a–c**, –5.5; **a–d**, –2.1; **c–e**, 2.2; **b–d**, 5.7; **b–e**, 6.0; Three-bond, **e–f**, 7.3.

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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]

Acknowledgment. This work is supported by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Contract No. F49620-86-C-0010 and a grant from the 3M Corp.

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. Engl.* **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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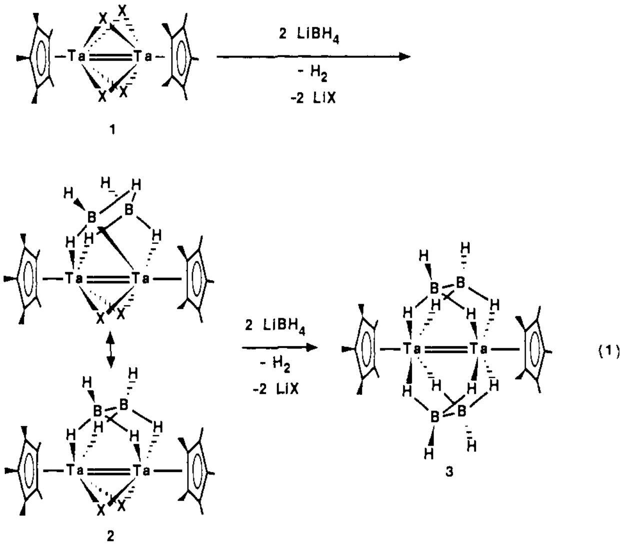
There is considerable interest in hydrocarbon C–H activation from the theoretical and organometallic perspectives,[1] particularly in discovering activation/functionalization pathways and bonding models for catalyst surface intermediates. The isoelectronic relationships[2] between hydrocarbons and boranes 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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(10) Data for $Cp^*{}_2Ta_2(\mu\text{-}Br)_2(B_2H_6)$, **2**: High-resolution mass spectrum: *m/e* 818.036. Calcd for $Ta_2C_{20}H_{36}{}^{79}Br_2{}^{11}B_2$, 818.033; $Ta_2C_{20}H_{36}{}^{79}Br^{81}Br^{10}B_2$, 818.038. ^1H NMR (δ, 25°, C_6D_6): −7.6, −7.1, −4.1 (m, BHB and TaHB of major, minor species), 2.27 (s, Cp*), 2.33 (s, Cp*, minor species), and 4.2, 7.2 (br, BH, BH_t'). ^{13}C NMR (δ, C_6D_6): 14.0 (s, C_5Me_5), 110.7 (s, C_5Me_5). ^{11}B NMR (δ, major isomer, $\{^1H\}$ of both B-H_t, C_6D_6): 18.8 and 10.5; minor isomer at −19.9. IR (Nujol, cm^{-1}): 2474 (s, BH_t), 1585 (s, TaHB or TaB_2H); 1817, 1734, 1120 for product from $LiBD_4$.

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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, β = 107.63 (6)°, V = 2427.04 Å^3, ρ_{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.

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