Existence of *C*,3-Me_2-*closo*-1,2-$C_2B_3H_3$ Refuted by the *Ab Initio*/IGLO, GIAO-MP2/NMR Method. Attempted Repetition of the Synthesis

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The ^{11}B chemical shift assignment for the *closo*-carborane *C*,3-Me_2-1,2-$C_2B_3H_3$ structure (**1a** or **1b**) is refuted by *ab initio/*IGLO, GIAO/NMR evaluations. Attempts to reproduce the literature NMR data by examining the computed chemical shifts of many alternative structures failed. Rearrangement of the 1,2-$C_2B_3H_5$ isomer into the much more stable 1,5-$C_2B_3H_5$ is computed to involve only a modest energy barrier. Repetition of the thermal (but not the electric discharge) experiments failed to give a compound with the spectroscopic data reported earlier. The original experimental data remain unexplained. Nevertheless, the elimination of the *C*,3-Me_2-1,2-$C_2B_3H_3$ structural assignment removes the sole exception to four established structural patterns of *closo*-carboranes: (a) carbons tend to occupy sites with the lowest coordination, (b) carbons tend to be nonadjacent in the most thermodynamically stable *closo*-carboranes, (c) the ^{11}B NMR of boron atoms with exo-terminal alkyl groups are *always* found at lower field than those of otherwise identical boron atoms with exo-terminal hydrogens, and (d) exo-terminal $\delta(^1H)$'s normally parallel the $\delta(^{11}B)$ of the boron nuclei to which they are bound.

Introduction

Background. In pioneering work 30 years ago, Grimes employed electric discharge and flash reactions to obtain mixtures of intriguing carboranes.[1−4] *C*,3-Me_2-1,2-$C_2B_3H_3$ structures (**1a** and **1b** in Figure 1) were proposed for a product with $m/z = 90$ on the basis of NMR and IR spectroscopic evidence. One methyl group was believed to be attached to B(3), the other to carbon but the position was not clarified. Although this compound was included in several reviews subsequently,[3,5,6] the structural assignment (which is the subject of the present paper) received some skepticism very early. The preparation of a new carborane was not doubted, but the proposed structure was questioned, e.g.*"It would not be surprising to learn that the presumed closo-C,3-*Me_2*-1,2-*$C_2B_3H_3$ *has a different structure altogether"*.[5] In 1969, Grimes also identified "**1a** or **1b**" as a "significant component" of a mixture of carboranes which had been generated from the thermal reaction of B_5H_9 with HC≡CH, and supplied by Williams as part of a scientific exchange.[6] However, Williams' GLC analysis of a similar mixture[7] revealed only known methyl carborane derivatives. These included 2,3-Me_2-1,5-$C_2B_3H_3$, but no unidentified peaks were resolved. Unfortunately, no clarification of the issues, of special interest in several contexts, was achieved (the samples and the separation techniques were different) and the problem has not been reinvestigated since. However, with the passage of time the existence and structure of "*closo-C*,3-Me_2-1,2-$C_2B_3H_3$", **1a** or **1b**, seems to have become established in the cluster literature.[3,8]

NMR Analysis. Seen in a broader context, the NMR data[1,2] of "**1a** or **1b**" revealed three problems. A **major** ^{11}B NMR problem was that the resonance assigned to the B3 atom (attached to a methyl group in **1a** or **1b** (Figure 1)) was at *higher* field than the resonance of B4 (which only has a hydrogen substituent). The opposite relationship ($\delta^{11}B$ in BCH_3 at *lower* field than in BH) *had been previously observed in all other similar pairs of borons*.[9,10] Another **major** NMR problem has become evident more recently. Unlike the relationship found normally in the BH groups of other *closo*-carboranes,[11,12] the reported ^1H shieldings did not parallel the ^{11}B shieldings. In addition, the ^1H NMR chemical shifts of the methyl groups attached to boron and to carbon were reported to be almost the same. This is not impossible, but seems unlikely.

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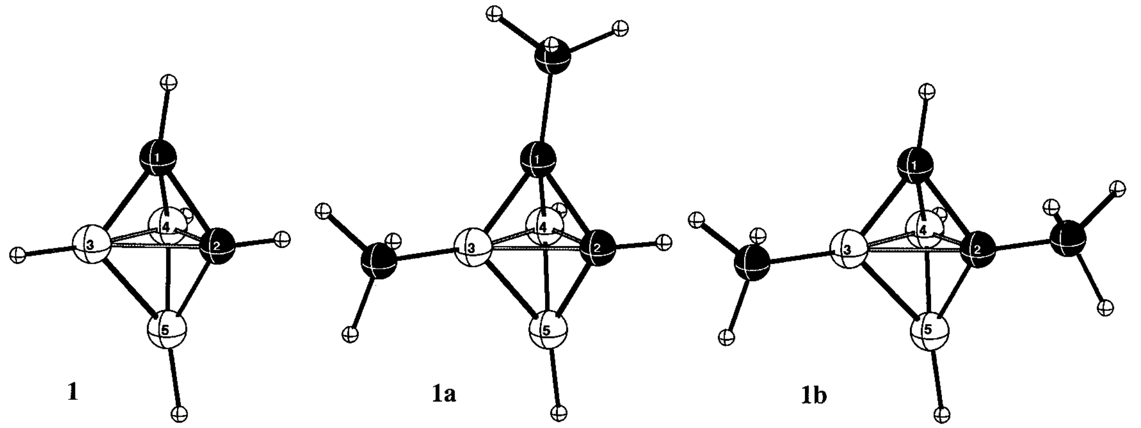
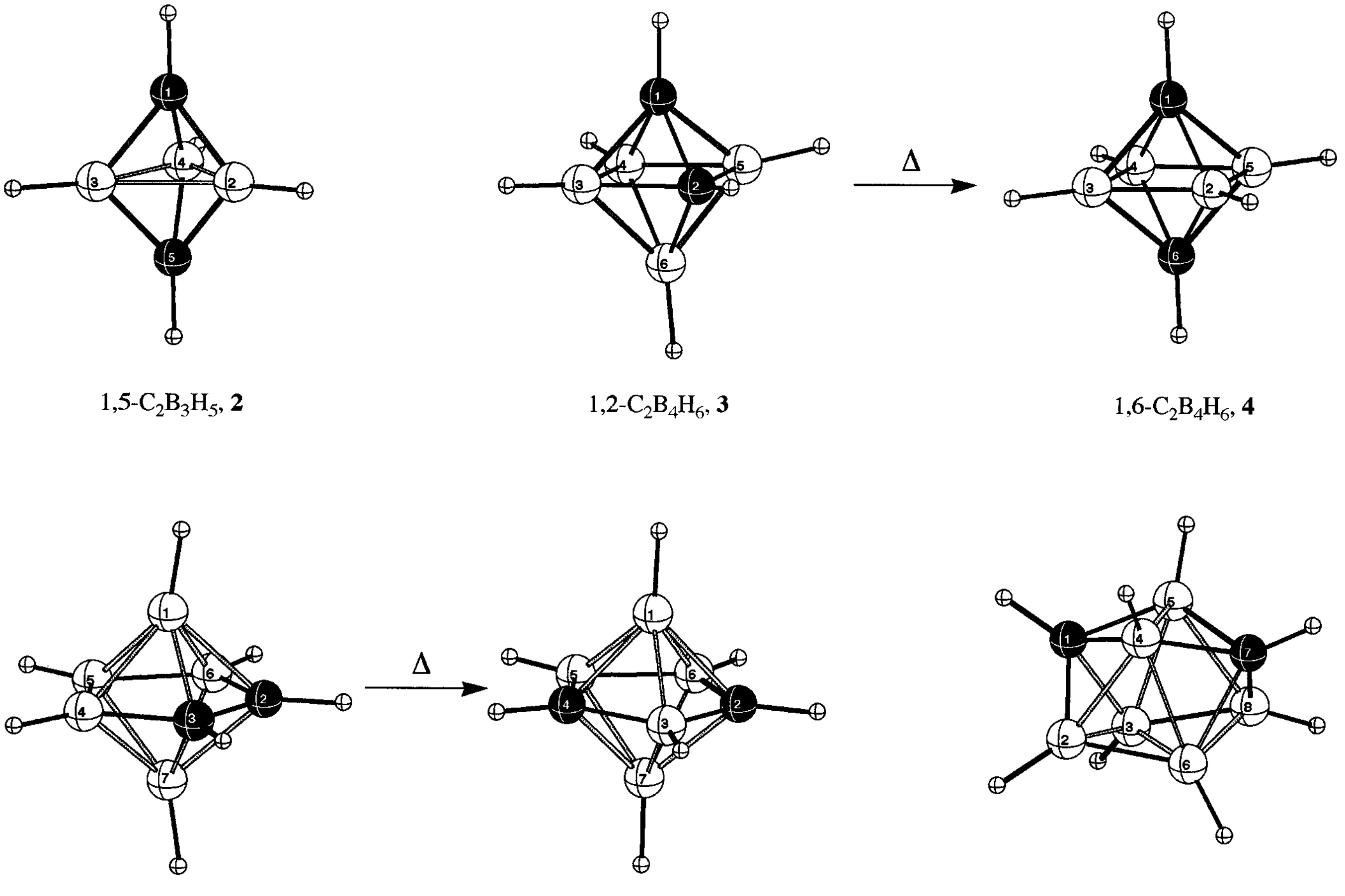


1 **1a** **1b**

Figure 1. The parent *closo*-1,2-$C_2B_3H_5$, **1**, and the two possible structures originally proposed for *closo*-C,3-Me_2-1,2-$C_2B_3H_3$, **1a** and **1b**, by Grimes et al.



1,5-$C_2B_3H_5$, **2** 1,2-$C_2B_4H_6$, **3** 1,6-$C_2B_4H_6$, **4**

2,3-$C_2B_5H_7$, **5** 2,4-$C_2B_5H_7$, **6** 1,7-$C_2B_6H_8$, **7**

Figure 2. *closo*-1,5-$C_2B_3H_5$, **2**. *closo*-1,2-$C_2B_4H_6$, **3**, rearranges into *closo*-1,6-$C_2B_4H_6$, **4**. *closo*-2,3-$C_2B_5H_7$, **5** rearranges into *closo*-2,4-$C_2B_5H_7$,**6**. *closo*-1,7-$C_2B_6H_8$, **7**.

Structural Analysis. When the first *closo*-carboranes (Figure 2) were discovered,[13−15] it was noted that (a) the carbon atoms tended to occupy the lowest connected vertices available and (b) if this is possible, the carbons also tended to be non-adjacent in the thermodynamically most stable isomers.[16] In contrast, the presumed 1,2-$C_2B_3R_5$ isomer ("**1a** or **1b**") did not rearrange on heating into a derivative of the 1,5-carborane-isomer, **2** (Figure 2) and even appeared to be more stable than similar derivatives of the 1,5-isomer, **2**.[17] McKee's computations confirmed that the *closo*-carborane isomer with the carbons separated, **2**, is thermodynamically more stable than the isomer with the carbons adjacent , **1** (Figure 1).[18]

The presumed *closo*-C,3-Me_2-1,2-$C_2B_3H_3$ assignment, **1a** or **1b**,[1−4] did not conform to either of these generalities, since (a) one of the carbon atoms was assigned to a highest connected vertex and (b) the two carbons were adjacent.[19] We could only

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cast doubt,[5] but had no proof. During the intervening decades numerous papers and reviews dealing with the structures of deltahedral clusters have been published and almost all accept and discuss *closo*-*C*,3-Me_2-1,2-$C_2B_3H_3$, **1a** or **1b**, as a compound of known composition and structure.[20]

The *ab initio*/IGLO, GIAO/NMR Method. As recently as the summer of 1987 it was correctly stated that no practicable theoretical method existed for computing ^{13}C, ^{11}B, and ^{1}H chemical shifts.[21] Within months Kutzelnigg and Schindler, using their IGLO program, were calculating ^{13}C chemical shifts, often with surprising accuracy.[22]

The Erlangen group demonstrated that even better agreement was achievable if high level *ab initio* optimized structures were employed for IGLO computations.[23−25] Early applications established the accurate geometries of (i. e. bond lengths and angles) *arachno*-B_5H_{11}[24a] and *arachno*-B_6H_{12}[25] for the first time. An extensive survey of boron compounds demonstrated the general superiority of computed over experimental geometries.[24]

Learning of these achievements at Erlangen, and having sought a definitive technique for almost 25 years, the Loker group subjected the putative *closo*-*C*,3-Me_2-1,2-$C_2B_3H_3$ structure, **1a** or **1b** (Figure 1) and several other problematic carboranes to similar *ab initio*/IGLO/NMR *"inquisitions"*.[26] Although the *closo*-$C_2B_6H_8$ structure in solution was quickly confirmed[27] and the correct conformer of the "carbon-apart" *nido*-$C_2B_6H_{10}$ selected,[28] the Loker group could find no *ab initio* evidence to support the assignments of **1a**, and/or **1b**. Similar conclusions had also been reached from preliminary computations on *closo*-1,2-$C_2B_3H_5$, **1**, at Erlangen.

This report chronicles the many computer intensive attempts at Erlangen to test alternative structures which might have chemical shift values similar to those reported.[1,2] Ultimately, this led to the repetition of some of the original experiments at Leeds, but the reported data for "**1a** or **1b**" were not reproduced. All three groups now conclude that the compound reported[1−4] to be *closo*-*C*,3-Me_2-1,2-$C_2B_3H_3$, "**1a** or **1b**", (Figure 1) was incorrectly identified. Instead, a derivative of the known *closo*-1,5-$C_2B_3H_5$, **2** (Figure 2) seems most likely to us.

Ab initio/IGLO and GIAO/NMR Calculations on Various Candidate Structures

Computational Details. All structures, optimized with the Gaussian 92/DFT program[29] first at the HF/6-31G* ab initio level, were confirmed to be minima by analytic frequency calculations. The geometries then were refined at MP2(fc)/6-31G*. Relative energies at this level were corrected for zero point vibrational energies (HF/6-31G*), scaled by 0.89.[30] Chemical shifts were computed at the SCF level with the IGLO program[31] employing Huzinaga basis sets:[32] DZ (double ζ) stands for 7s3p functions, contracted to [4111/21], for C and B and 3s functions, contracted to [21], for H. II′ designates 9s5p1d, contracted to [51111/311/1], for C and B together with a DZ description of H. The GIAO-MP2 electron correlated chemical shift computations as implemented by J. Gauss[33] and incorporated into the ACES II program package[34] were carried out using the dzp and tzp Ahlrichs basis sets[35] for C and B, which include one set of d polarization functions. H is described by a double ζ basis in both cases. ^{13}C chemical shifts were referenced to the experimental standard, tetramethylsilane (TMS). For ^{11}B, B_2H_6 served as a primary reference and δ (B_2H_6) = 16.6[36] was used for conversion to the experimental scale (i.e. relative to $BF_3{\cdot}O(CH_2CH_3)_2$).

Calculations on *closo*-$C_2B_3R_5$ Compounds. We first investigated the *closo*-$C_2B_3H_5$ parent system: McKee's earlier report that 1,2-$C_2B_3H_5$ (**1**) is thermodynamically much less stable than the 1,5-isomer (by 35.1 kcal mol^{-1}) is confirmed here.[37] Although **1** is a minimum, the computed *negative* ^{11}B IGLO chemical shift for B(2,3) disagrees drastically with the experimental data reported for the dimethyl compound (all the $\delta(^{11}B)$'s are quite positive, Table 1). However, the fit for 1,5-$C_2B_3H_5$ also is not entirely satisfactory with IGLO. We have shown previously that electron correlation has an important effect on the computed ^{11}B chemical shifts in this small strained carborane.[38] GIAO-MP2 gives values 11 ppm to higher field relative to the SCF value, and agrees with the measured ^{11}B NMR chemical shift to within 1.4 ppm. For 1,2-$C_2B_3H_5$, the GIAO-MP2 electron correlation effect is similar, also about 6.7−

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Table 1. Relative Energies and Chemical Shifts of *closo*-Dicarbapentaboranes

			chemical shifts				
compound	E_{rel}[a]	method[b]	^{13}C[c]		^{11}B[d]		
1,2-$C_2B_3H_5$ (**1**)	35.1	IGLO/DZ	64.5 (C1)	72.6 (C2)	−14.2 (B3,4)	27.6 (B5)	
		IGLO/II′	49.8 (C1)	63.7 (C2)	−13.0 (B3,4)	27.2 (B5)	
		GIAO−SCF/tzpdz	52.3 (C1)	67.3 (C2)	−11.5 (B3,4)	28.9 (B5)	
		GIAO−MP2/tzpdz	68.0 (C1)	52.1 (C2)	−21.9 (B3,4)	22.2 (B5)	
1,5-$C_2B_3H_5$ (**2**)	0.0	IGLO/DZ	97.0 (C1,5)		12.3 (B2−4)		
		IGLO/II′	90.9 (C1,5)		11.4 (B2−4)		
		GIAO−SCF/tzpdz	93.5 (C1,5)		13.1 (B2−4)		
		GIAO−MP2/tzpdz	105.5 (C1,5)		2.1 (B2−4)		
		experiment[e]	103.3 (C1,5)		3.5 (B2−4)		
1,3-Me_2-1,2-$C_2B_3H_3$ (**1a**)	41.7	IGLO/DZ	65.4 (C1)	82.5 (C2)	−8.5 (B3)	−11.2 (B4)	25.3 (B5)
2,3-Me_2-1,2-$C_2B_3H_3$ (**1b**)	40.5	IGLO/DZ	67.2 (C1)	89.6 (C2)	−4.0 (B3)	−7.5 (B4)	26.3 (B5)
“*C*,3-Me_2-1,2-$C_2B_3H_3$” (**1a** or **1b**)		experiment[f]			24.4 (B3)	26.0 (B4)	53.1 (B5)
1,2-Me_2-1,5-$C_2B_3H_3$ (**2a**)	6.9	IGLO/DZ	100.4 (C1)	89.4 (C5)	15.8 (B2)	13.3 (B3,4)	
		GIAO-SCF/tzpdz	104.7 (C1)	86.4 (C5)	17.3 (B2)	15.7 (B3,4)	
		GIAO-MP2/tzpdz	120.8 (C1)	97.5 (C5)	7.5 (B2)	5.2 (B3,4)	
		experiment[g]			8.3 (B2)	6.3 (B3,4)	
1,5-Me_2-1,5-$C_2B_3H_3$ (**2b**)	13.9	IGLO/DZ	103.1 (C1,5)		12.5 (B2−4)		
		GIAO-SCF/tzpdz	102.4 (C1,5)		13.1 (B2−4)		
		GIAO-MP2/tzpdz	117.8 (C1,5)		2.0 (B2−4)		
		experiment[g]			2.5 (B2−4)		
2,3-Me_2-1,5-$C_2B_3H_3$ (**2c**)	0.0	IGLO/DZ	96.7 (C1,5)		21.0 (B2,3)	17.3 (B4)	
		GIAO-SCF/tzpdz	88.9 (C1,5)		21.1 (B2,3)	17.6 (B4)	
		GIAO-MP2/tzpdz	100.6 (C1,5)		12.4 (B2,3)	8.9 (B4)	
		experiment[g]			13.1 (B2,3)	11.3 (B4)	

[a] In kcal mol^{-1}, at MP2(fc)/6-31G* + 0.89 ZPER(HF/6-31G*). [b] MP2(fc)/6-31G* optimized geometries were used in the computations. [c] In ppm relative to tetramethylsilane (TMS). [d] In ppm relative to $BF_3 \cdot OEt_2$. [e] Reference 38a. [f] Reference 1. [g] This work: coupling constants (*J*/Hz): **2a**, 182 (B3,4); **2b**, 186 (B2−4); **2c**, 180 (B4).

10.4 ppm (B5 and B3,4, respectively) to *higher* field. This increases the discrepancy of $\delta(^{11}B(3,4))$ and the experimental shifts, which are at much *lower* field.

Consequently, we investigated the dimethyl compounds, *closo*-$Me_2C_2B_3H_3$, as closer models. Again, the 1,2-dicarba isomers (**1a** and **1b**) are much higher in energy than the 1,5-isomers (**2a**−**c**). This is consistent with the empirical rule that the carbon atoms in the most stable carborane isomer tend to occupy low coordination, nonadjacent sites. Thus, **1a** and **1b** should isomerize into 1,5-isomers exothermically upon heating (provided, of course, that the barrier is low enough). The opposite was reported for **1a** or **1b** (evidently erroneously). The computed chemical shifts show that **1a** and **1b** do *not* violate the general rule: B3, which carries a terminal methyl group, *does* resonate at lower field than B4 (Table 1). Compared with the parent, the effect of the methyl groups is $\leq$+10 ppm (B3 in **1b**). While our present computational resources do not allow GIAO-MP2/tzpdz computations on **1a** or **1b**, neither can be responsible for the reported NMR data. Electron correlation effects are expected to be about as large as for the parent **1** (i.e. less than 10 ppm, in the *wrong* direction).

As mentioned above, *closo*-1,2-$C_2B_3R_5$ compounds (**1** and **1a** or **1b**) are expected to isomerize thermally into their 1,5-closo-isomers. We wondered whether *closo*-1,2-$C_2B_3H_5$ could survive the high energy conditions of Grimes' experiments and investigated the reaction path for the 1,2 to 1,5 rearrangement. On the HF/6-31G* potential energy surface there is an intermediate minimum **B** and two transition structures **A** and **C** connecting it with **1** and **2**, respectively (see Figure 8). However, the energetic and structural differences between **A**, **B**, and **C** are small. At the MP2 level, only a single transition structure resulted with a significantly higher barrier than at HF/6-31G* (28.9 vs 11.8 kcal mol^{-1}). (An optimization to a minimum at MP2 starting with **B** led to **1**.) Therefore, we also applied DFT (density functional theory) computations using the Becke3LYP combination of functionals. Both with the 6-31G* and the 6-311+G** basis sets, stationary points **A** (TS), **B** (MIN), and **C** (TS) were located. The reaction paths leading from **1** to **2** resemble the HF situation but with even smaller differences in energy (less than 0.5 kcal mol^{-1}) between **A**, **B**, and **C**. The barrier for the isomerization of **1** to **2**, about 20 kcal mol^{-1}, is between the HF and MP2 value and likely to be the most reliable estimation. The Becke3LYP relative energies are effectively identical with 6-31G* and 6-311+G** indicating a convergence with respect to the basis set size. The presence of three stationary points in the same region of the potential energy surface, minimum **B**, and *two* transition structures **A** and **C** at HF and Becke3LYP levels of theory may well be an artifact, but this is not significant. Whatever these details may be, **A** represents the effective transition state in the conversion of **1** into **2**. Hence, the estimated barrier for the isomerization of *closo*-1,2- (**1**) to *closo*-1,5-$C_2B_3H_5$ (**2**) via an open ring structure (**A** or **B**) is low (20 kcal mol $^{-1}$). This is a further argument against the claimed isolation of *closo*-*C*,3-Me_2-1,2-$C_2B_3H_3$, under the conditions employed.

The relative energies of methyl placements should also be considered. Boron sites are favored over carbon uniformely by ca. 7 kcal mol^{-1} in Me_2-1,5-$C_2B_3H_3$ (**2a** → **2c**, 6.9 kcal mol^{-1}; **2b** → **2a**, 7.0 kcal mol^{-1}, see Table 1). The same effect can be expected in the Me_2-1,2-$C_2B_3H_3$ isomers: the carbon methyl placements in **1a** or **1b** would be less stable than isomers with two B-Me groups (the extent can be evaluated by comparing the relative energies, e.g. **1a**−**1** = 6.6 kcal mol^{-1}).

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(38) (a) Schleyer, P. v. R.; Gauss, J.; Bühl, M.; Greatrex, R.; Fox, M. *J. Chem. Soc., Chem. Commun.* **1993**, 1766. (b) Bühl, M.; Gauss, J.; Hofmann, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1993**, *115*, 12385−12390.

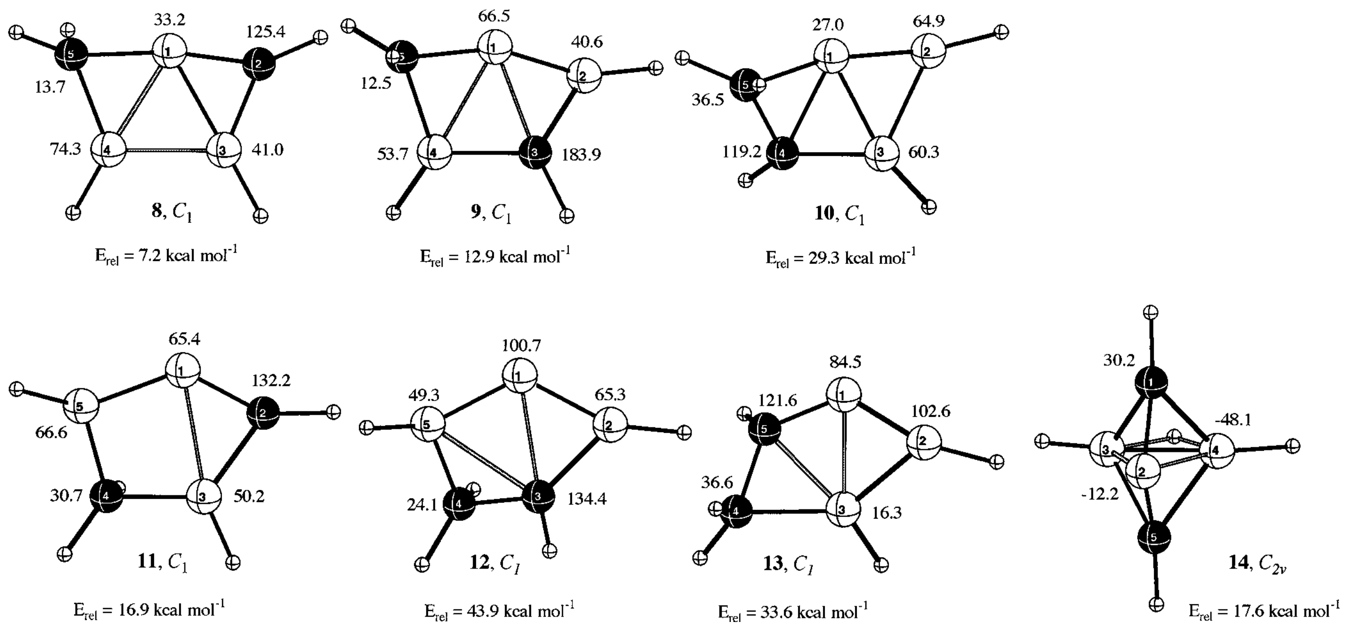
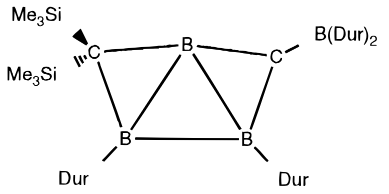


Figure 3. $C_2B_3H_5$ minima with a bare boron atom. Computed chemical shifts (IGLO/DZ//MP2(fc)/6-31G*) and energies (MP2(fc)/6-31G*) relative to *closo*-1,2-$C_2B_3H_5$ (**1**).

Searching for Alternatives. What is the correct structure, then? We first modeled two methyl groups by hydrogen atoms and searched the $C_2B_3H_5$ potential energy hypersurface extensively for low energy minima which would reproduce the reported NMR data reasonably well. Berndt et al. have reported a compound promising in this context:[39] a $C_2B_3H_5$ derivative with a trapezoidal heavy atom framework and a bare boron atom (**8a**). Considering the different substituents, the ^{11}B chemical shifts of **8a**, 23, 33, and 71 ppm, were not far from the 24.2, 26.0 and 53.1 ppm values reported for "**1a** or **1b**". Hence, we optimized the isostructural parent (**8** in Figure 3). It is only 7.2 kcal mol^{-1} higher in energy than *closo*-1,2-$C_2B_3H_5$, but the results of the chemical shift computations were discouraging: the signal at lowest field differs by more than 20 ppm (see Figure 3) and rules out **8** as a viable possibility. Neither computations with electron correlation (GIAO-MP2) nor adding methyl substituents[40] improved the δ(^{11}B) agreement significantly.



8a

Next, we examined other trapezoidal $C_2B_3H_5$ carboranes having a CH_2 group and a bare B atom, but with different substitution patterns from **8**. The optimized structures and computed chemical shifts (**9**−**13**) are shown in Figure 3. We also found a new closo minimum, **14**, with a bare B and a BHB hydrogen bridge. But none of these (**9**−**14**) reproduce Grimes' NMR data for "**1a** or **1b**". We next explored related structures with a bare carbon atom instead of a bare boron. Again, several minima were found (**15**−**19** in Figure 4), but none solved the puzzle. The rule that carbon atoms prefer to occupy separated, low coordination sites obviously is not only true for closo-systems, but also for the trapezoidal structures **8**−**13** and **15**−**19**.

Finally, we abandoned the assumption that two methyl groups were present and searched for $C_3B_3H_7$ minima with only one methyl substituent. Various starting geometries with partially classical (2c2e bonds) and nonclassical (multicenter bonds) structural moieties optimized to structures **21**−**25** in Figure 5. All these are relatively high in energy compared with *nido*-2,3,4-$C_3B_3H_7$, **20**.[41] Unexpectedly, **21** gives ^{11}B chemical shifts quite close to the data for "**1a** or **1b**". Therefore, **21** and its methyl derivatives, **21a**−**c** (Figure 6), were investigated further at GIAO-MP2 (see Table 2). For **21a**−**c** only the smaller dzpdz basis set could be used, but the results on **21** show that this level gives results not far from those with the better tzpdz basis set. Electron correlation is more important for ^{13}C (corrections up to 15 ppm) than for ^{11}B (less than 5 ppm). Our "best" alternatives to **1a** and **1b**, **21a** and **21c**, are only 8 and 6.8 kcal mol^{-1} higher in energy than **1a**, but the computed ^{11}B NMR data still differ by about 10 ppm, three times more than the acceptable error range at this level. (Structure **21b** is ruled out, because the methyl substituted boron was assigned the 24.4 ppm signal.) Since our extensive computational search failed to locate an entirely satisfactory structural alternative to "**1a** or **1b**", we hoped that repetition of the experiments with more modern techniques would give additional information.

Attempted Repetition of the "*closo-C*,3-Me_2-1,2-$C_2B_3H_3$" Synthesis

"*closo-C*,3-Me_2-1,2-$C_2B_3H_3$", "**1a** or **1b**", was reported to have been obtained from at least three different procedures: the electric-discharge-induced reaction of B_2H_6 with $HC\equiv CH$,[1,2] as well as the flash reactions of B_4H_{10} both with $MeC\equiv CH$,

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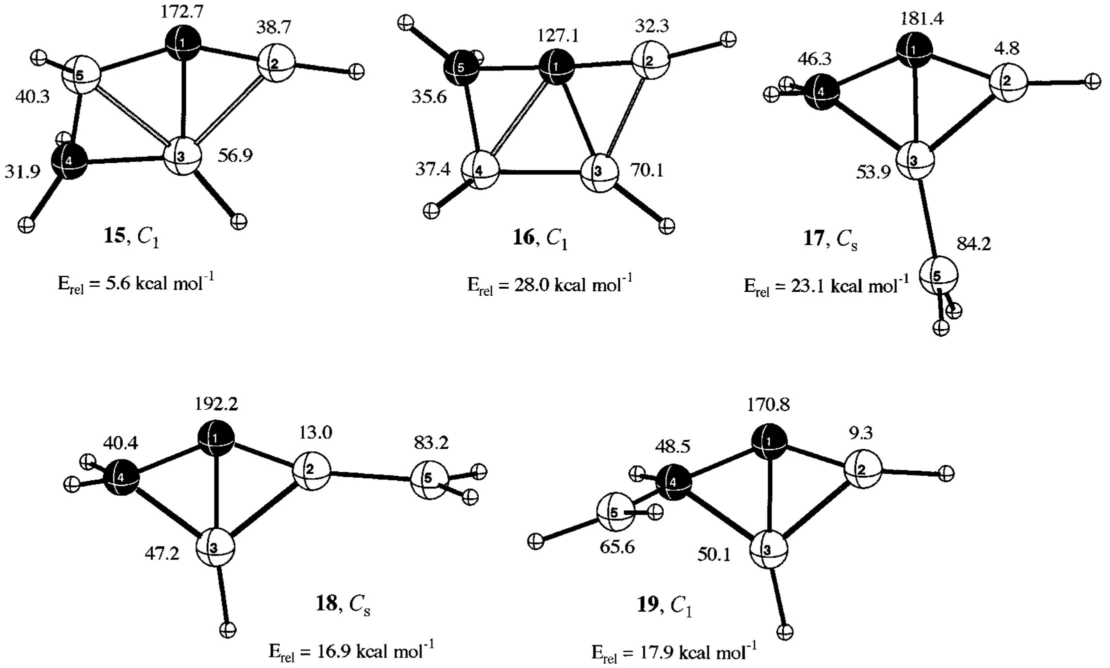
(39) Höfner, A.; Ziegler, B.; Hunold, R.; Willershausen, P.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30,* 594.

(40) IGLO(DZ)//HF/6-31G* gives 40.1 (B1), 38.9 (B3), and 73.5 (B4) for the 2,4-Me_2 derivative; 43.5 (B1), 40.2 (B3), and 77.0 (B4) for the 2,5-Me_2 derivative, and 51.5 (B1), 39.4 (B3), and 77.8 (B4) for the 5,5-Me_2 derivative. The energies relative to those of **1a** are −9.3, 2.3, and 6.6 kcal mol^{-1}, respectively. For **8**, GIAO-MP2/tzpdz (GIAO-SCF/tzpdz)//RMP2(fc)/6-31G* gives 89.2 (79.4) (B1), 35.3 (26.2) (B3), and 46.9 (38.0) (B4).

(41) Experimental chemical shifts of *nido*-2,3,4-$C_3B_3H_7$ are −55.2 (B1) and 0.1 (B5,6) (Fox, M. A.; Greatrex, R.; Nikrahi, A. *J. Chem. Soc., Chem. Commun.* **1996**, 175). For the 2-methyl derivative, values of −52.6 (B1) and −0.1 (B5,6) have been reported (Fox, M. A.; Greatrex, R. *J. Chem. Soc., Chem. Commun.* **1995**, 667). See also ref 24b.



15, C_1 E_{rel} = 5.6 kcal mol^{-1}

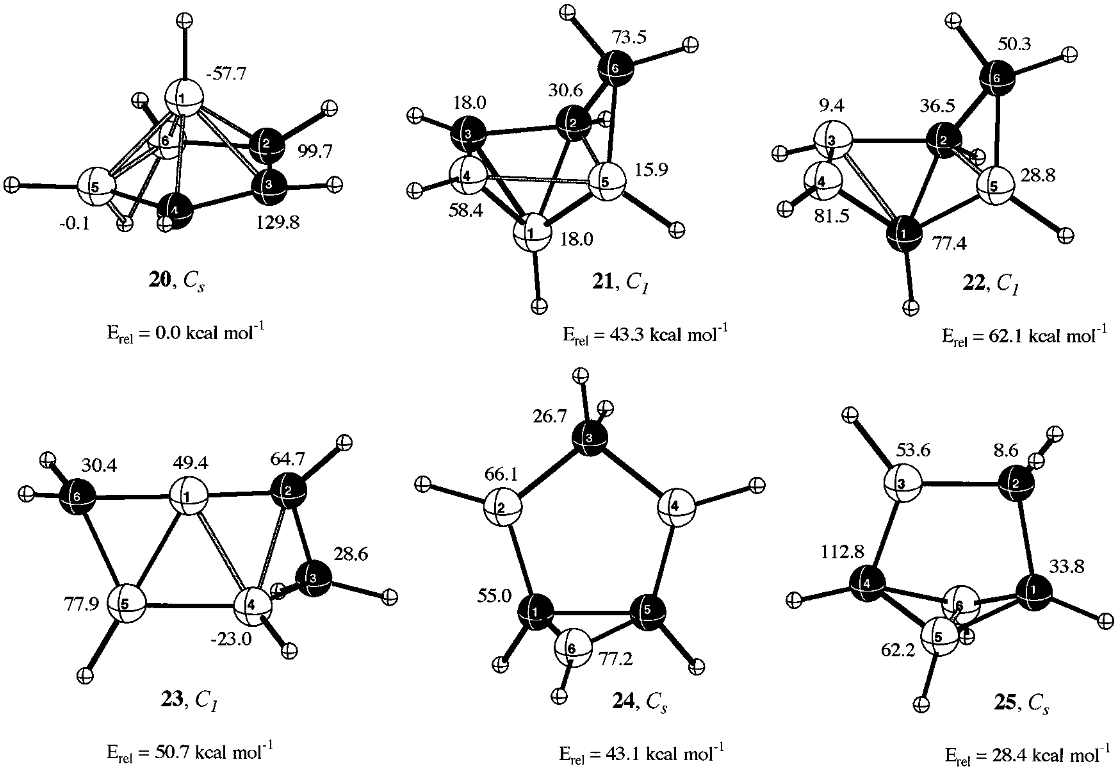
16, C_1 E_{rel} = 28.0 kcal mol^{-1}

17, C_s E_{rel} = 23.1 kcal mol^{-1}

18, C_s E_{rel} = 16.9 kcal mol^{-1}

19, C_1 E_{rel} = 17.9 kcal mol^{-1}

Figure 4. $C_2B_3H_5$ minima with a bare carbon atom. Computed chemical shifts (IGLO/DZ//MP2(fc)/6-31G*) and energies (MP2(fc)/6-31G*) relative to *closo*-1,2-$C_2B_3H_5$ (**1**).



20, C_s E_{rel} = 0.0 kcal mol^{-1}

21, C_1 E_{rel} = 43.3 kcal mol^{-1}

22, C_1 E_{rel} = 62.1 kcal mol^{-1}

23, C_1 E_{rel} = 50.7 kcal mol^{-1}

24, C_s E_{rel} = 43.1 kcal mol^{-1}

25, C_s E_{rel} = 28.4 kcal mol^{-1}

Figure 5. Some $C_3B_3H_7$ minima. Computed chemical shifts (IGLO/DZ//MP2(fc)/6-31G*) and energies (MP2(fc)/6-31G*) relative to *nido*-2,3,4-$C_3B_3H_7$ (**20**).

and with MeC≡CMe.[3,4] Separations of mixtures were carried out by GLC. Because of the difficulty of reproducing the conditions of such electric discharge reactions precisely, it was decided at Leeds to attempt to synthesize the desired compound by repetition of the flash reactions only. As an additional check, the thermal flash reaction of B_2H_6 with HC≡CH also was studied. However, we used a different separation technique than Grimes.

Standard high-vacuum systems fitted with greaseless O-ring taps and spherical joints (J. Young (Scientific Glassware) Ltd.) were used throughout. Typically 6 mmol of tetraborane(10), synthesized by a literature method,[42] and 6 mmol of alkyne (MeC≡CH (Cambrian Gases), MeC≡CMe (Lancaster Synthesis)) were condensed at −196 °C into a 650 mL round-bottomed flask and then warmed quickly by means of a heated oil bath. As the temperature approached 100 °C the gaseous mixture became cloudy and then suddenly flashed, giving tan solids which covered the walls of the reactor. The flask was then cooled to −196 °C and hydrogen removed by pumping. A

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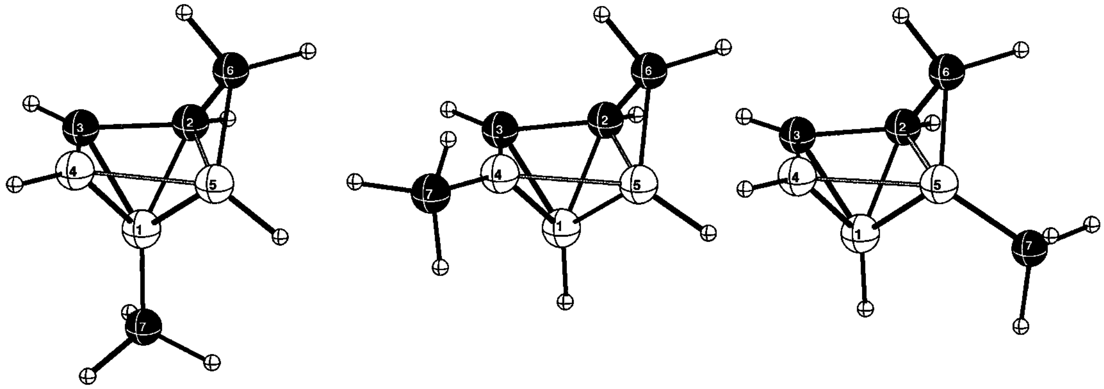
[42] Toft, M. A.; Leach, J. B; Himpsl, F. L; Shore, S. G. *Inorg. Chem.*, **1982**, *21*, 1952.

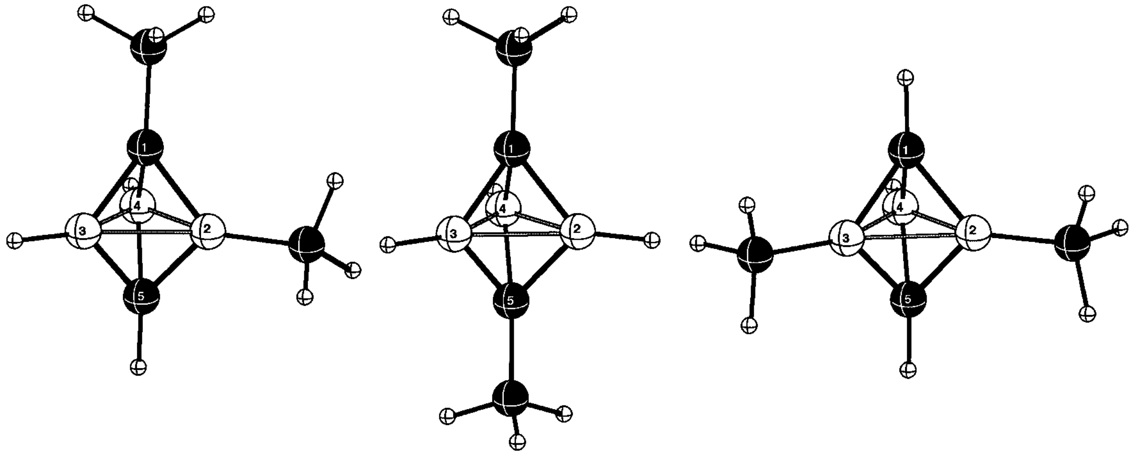


21a, C_1 $E_{rel} = 8.0$ kcal mol^{-1}

21b, C_1 $E_{rel} = 6.5$ kcal mol^{-1}

21c, C_1 $E_{rel} = 6.8$ kcal mol^{-1}

Figure 6. $C_4B_3H_9$ minima considered here. Energies (MP2(fc)/6-31G*) are relative to 1,3-$(CH_3)_2$-*closo*-1,2-$C_2B_3H_3$ (**1b**) (for computed chemical shifts see Table 2).



2a, C_s

2b, C_{2v}

2c, C_{2v}

Figure 7. $m/z = 90$ compounds, 1,2- (**2a**), 1,5- (**2b**) and 2,3-Me_2-*closo*-1,5-$C_2B_3H_3$ (**2c**), isolated from the attempted repetition of the "*closo-C*,3-Me_2-1,2-$C_2B_3H_3$" synthesis.

representative sample of the volatiles was then transferred to a resealable Young's NMR tube together with $CDCl_3$, and the remainder subjected to a cold-column fractionation. Species leaving the column were sampled continuously *via* a glass capillary of length 200 mm and internal diameter 0.1 mm (Jencons Scientific Ltd.) and monitored by means of a Kratos MS30 mass spectrometer fitted with an MSS data system. Volatile carborane fractions with mass cut-off at *m/z* 90 were accumulated from several runs of each of the three reactions and transferred to resealable Young's NMR tubes; ^{11}B and ^{1}H NMR spectra were recorded in $CDCl_3$ at 25 °C on a Bruker AM-400 instrument and the data are given in Table 1.

The 128 MHz ^{11}B NMR spectra of the *m/z* 90 fractions contained no peaks with the chemical shifts of 53.1, 26.0, and 24.4 ppm (converted to boron trifluoride etherate as reference) reported previously for "**1a** or **1b**". Minor peaks were present in the 20−60 ppm range, but none appeared as a doublet in the undecoupled spectrum and therefore did not arise from boron atoms bonded to hydrogen. These minor peaks are likely to be due to boron alkyls or other organoboron impurities. Considering all the products from the B_4H_{10}/MeC≡CH reaction by comparing the spectra of the representative samples, the major component in the *m/z* 90 fractions was estimated to constitute *ca*. 7% of the total volatile carborane fraction. For the B_4H_{10}/MeC≡CMe reactions, the major component was *ca*. 11%. The major components of these two reactions gave identical spectra and could not be due to "**1a** or **1b**". Indeed, the presence of a singlet of intensity two at 13.12 and a doublet of intensity one at 11.26 ppm ($J_{BH} = 183$ Hz) identified our major components to be 2,3-Me_2-1,5-$C_2B_3H_3$, **2c** (Figure 7).[7] This derivative was tentatively identified as a "trace product" by Grimes and coworkers in their reaction mixture.[2] In contrast, "**1a** or **1b**" was the major *m/z* 90 component but the reported yields (12 and 8%, respectively, for the MeC≡CH and MeC≡CMe reactions)[3] were similar to those found for **2c** here. Therefore, we raise the possibility that "**1a** or **1b**" and **2c** may be the same compound, although this does not explain the ^{11}B data reported in the early work. However, the 60 MHz ^{1}H NMR spectrum reported by Grimes et al. for "**1a** or **1b**" does show some similarity to the 400 MHz spectrum of **2c** recorded here. Thus, the reported shifts for the protons attached to carbon in "**1a** or **1b**", 4.50 and 0.30 ppm,[43] compare with our values for **2c** of 4.86 (intensity = 2, cage CH) and 0.40 (6, CH_3) ppm relative to tetramethylsilane.[44] The spectrum of **2c** has a peak of unit intensity at 4.14 ppm from a proton attached to boron, but the resonance at 1.9 ppm reported for "**1a** or **1b**" is not present. Isomers

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(43) 60 MHz ^{1}H, neat liquid at 298 K.

(44) 400 MHz ^{1}H, in $CDCl_3$ at 298 K.

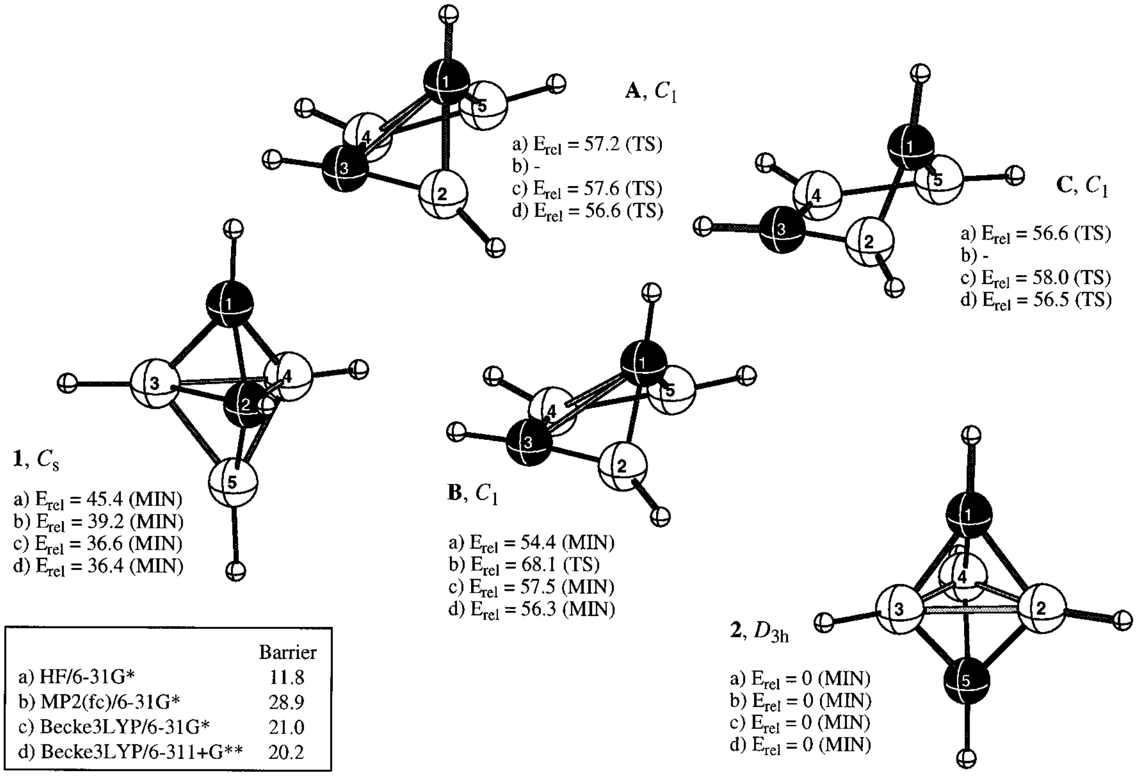

Figure 8. Reaction path leading from *closo*-1,2-$C_2B_3H_5$ (**1**) to *closo*-1,5-$C_2B_3H_5$ (**2**) and intermediate stationary points **A**, **B**, and **C** at various levels of theory.

Table 2. Relative Energies and Chemical Shifts of **21** and its *B*-Methyl Derivatives

			chemical shifts					
			$^{13}C^b$			$^{11}B^c$		
compound	$E_{rel}{}^a$	method^d	C2	C3	C6	B1	B4	B5
$C_3B_3H_7$ (**21**)		IGLO/DZ	30.6	83.8	73.5	18.0	58.4	15.9
		GIAO-SCF/dzpdz	24.2	74.7	68.3	21.8	57.0	17.9
		GIAO-MP2/dzpdz	34.7	87.0	82.8	21.0	52.3	15.3
		GIAO-SCF/tzpdz	25.0	78.0	69.3	24.2	60.3	18.5
		GIAO-MP2/tzpdz	36.0	92.5	85.8	23.3	55.8	15.7
1-Me-$C_3B_3H_6$ (**21a**)	8.0	IGLO/DZ	33.0	87.5	72.2	27.1	58.3	13.0
		GIAO-SCF/dzpdz	27.5	79.3	66.7	30.6	57.1	15.5
		GIAO-MP2/dzpdz	38.2	92.1	80.5	30.9	52.3	13.3
4-Me-$C_3B_3H_6$ (**21b**)	6.5	IGLO/DZ	25.3	75.5	66.6	14.6	62.6	15.6
		GIAO-SCF/dzpdz	19.0	67.9	62.1	19.2	62.0	18.2
		GIAO-MP2/dzpdz	27.4	79.3	75.1	18.8	59.1	15.6
5-Me-$C_3B_3H_6$ (**21c**)	6.8	IGLO/DZ	27.3	82.2	65.1	13.6	58.0	23.7
		GIAO-SCF/dzpdz	26.7	72.6	65.9	17.1	57.2	26.5
		GIAO-MP2/dzpdz	37.7	83.6	80.3	16.8	52.6	24.9
		experiment^e				26.0 (BH)	53.1 (BH)	24.4 (BMe)

[a] In kcal mol^{-1}, at MP2(fc)/6-31G* + 0.89 ZPE(HF/6-31G*) relative to *closo*-1,3-Me_2-1,2-$C_2B_3H_3$ (**1a**). [b] In ppm relative to tetramethylsilane (TMS). [c] In ppm relative to $BF_3{\cdot}OEt_2$. [d] MP2(fc)/6-31G* optimized geometries were used in the computations. [e] Reference 1.

2a and **2b** were also identified as minor components in the *m/z* 90 fractions from each of the two reactions (see Table 1).

Grimes believed he had observed a dimethyl-*closo*-1,2-$C_2B_3H_5$ derivative, "**1a** or **1b**", and was surprised by its thermal stability. If the product was **2c** instead, this behavior is easily understood. The 1,5-$C_2B_3H_5$ carborane arrangement is the most stable as is the placement of both methyl groups on boron atoms (see above and Table 1). Hence, **2c**, is not expected to rearrange even at high temperatures.

Conclusions

The *closo*-C,3-Me_2-1,2-$C_2B_3H_3$ structures, **1a** or **1b**, assigned to a compound with *m/z* = 90 by Grimes and co-workers, are ruled out. Not only are the energies of **1a** or **1b** much higher than those of other $C_4B_3H_9$ isomers, but the $\delta(^{11}B)$ chemical shifts reported for **1a** or **1b** are far from the values computed by IGLO and GIAO-MP2 methods. Furthermore, **1a** or **1b** should rearrange readily into more stable Me_2-1,5-$C_2B_3H_3$ derivatives.

Although a number of interesting structures were located in an extensive search for alternatives, none of these fit the early experimental NMR data either. These data remain unexplained. Attempted repetition of some of the original preparations, using thermal ("flash") routes (but not the electric discharge procedure), did give, as reported, *m/z* 90 compounds in low yield. However, the major component of this fraction was positively identified as 2,3-Me_2-1,5-$C_2B_3H_3$ (**2c**), rather than "**1a** or **1b**". As noted in the Introduction, this compound was also present in the mixture of carboranes from the thermal reaction of B_5H_9 with HC≡CH; Grimes also had claimed that this mixture contained *closo*-*C*,3-Me_2-1,2-$C_2B_3H_3$. However, as noted above, the separation techniques employed were not the same.

When added to the recent revelation by the Leeds group[45] that the putative *closo*-$C_3B_5H_7$,[46] whose structure also had been challenged,[27] was actually *closo*-2,3-$C_2B_5H_7$, **5**, (Figure 2) the regularities in the structural preferences and in the NMR spectra among the *closo*-carboranes and their alkyl derivatives are restored to their simple and uniform patterns. Thus, the demise of "**1a** or **1b**" eliminates the sole exception to each of the following generalizations: (i) carbon atoms tend to occupy lower coordination sites than boron atoms in the thermodynamically most stable *closo*-carboranes, (ii) isomers with adjacent carbons are less stable than those with the carbons separated, and (iii) the $\delta(^{11}B)$ of B-Me groups are *always* found at lower field than in their BH counterparts. We find computationally that *closo*-1,2-$C_2B_3H_5$ and its dimethyl derivatives also obey these rules, and, in addition, that methyl substitution on boron is favored over carbon by about 7 kcal mol^{-1}. The more recently recognized pattern, that exo-terminal proton shieldings normally parallel the shieldings of the boron nuclei to which they are bound, also is followed.

Acknowledgment. We thank Professor R. N. Grimes for extensive discussions and exchanges of information. He agrees that the theoretical findings reported herein are persuasive, but insists that the identity of the compound isolated in 1965 remains a mystery, as no alternative structure, or combination of structures, that accounts for the spectroscopic data has yet been proposed. He notes that boron-11 NMR spectra on this compound, acquired at the U.S. National Bureau of Standards Laboratories at the same time as those of eight other (noncontroversial) carborane products of the electric discharge reactions (refs 1 and 2), point to a species with three nonequivalent borons. He stresses that his electric discharge experiments were not repeated and that different separation techniques were employed here. We are grateful for financial support from the EPSRC, the DFG, and the Loker Hydrocarbon Institute. Thanks are also due to Professor G. A. Olah for his interest and encouragement.

Supporting Information Available: Cartesian coordinates of optimized geometries (11 pages). Ordering information is given on any current masthead page.

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(45) Fox, M. A.; Greatrex, R. *J. Chem. Soc., Dalton Trans.* **1994**, 3197.

(46) Thompson, M. L.; Grimes, R. N. *J. Am. Chem. Soc.* **1971**, *93*, 6677; Thompson, M. L.; Grimes, R. N. *Inorg. Chem.* **1972**, *11*, 1925.