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be increased substantially in a number of ways. For example, difference spectroscopy (subtracting the double-quantum filtered spectrum of the unlabeled molecule or complex from that of the labeled molecule or complex[14]) or selective excitation of the ^{13}C label may be used to further enhance signals from the selected region relative to signals from outside of that region.

When applied to molecules with resolved or partially resolved ^{13}C MAS spectra, double-quantum filtering based on dipole–dipole couplings can provide information about internuclear distances without requiring isotopic labeling. A two-dimensional version of the technique described in this paper, analogous to the two-dimensional INADEQUATE technique used in solution NMR spectroscopy,[24,25] would reveal which pairs of resonances in the MAS spectrum arise from pairs of nuclei that are within a certain radius of one another, where the radius is determined by the parameters of the DRAMA sequence used to generate double-quantum coherences. Alternatively, the spectrum obtained by taking the difference between two one-dimensional double-quantum filtered spectra, one with selective inversion of a particular ^{13}C spin before preparation of double-quantum coherences and one without, will contain only resonances from nuclei that are within a certain radius of the inverted nucleus.

The practicality of any of the experiments outlined above depends critically on sensitivity considerations. In turn, this depends on the efficiency of the double-quantum filter. The fundamental obstacle to obtaining a filtering efficiency of unity is the orientation dependence of the dipole–dipole coupling contained in $F(\theta,\phi)$. In general, the maximum value of $E(\theta,\phi,n)$ occurs at different values of n for different values of θ and ϕ. One approach to achieving the maximum efficiency over a large range of coupling strengths at a single value of n, thereby increasing the maximum of $\bar{E}(n)$, is to construct composite DRAMA sequences in analogy to the composite sequences used by Barbara et al.[37] for broadband excitation of double-quantum coherences in nonspinning samples. An alternative approach is to carry out a numerical search[32] for DRAMA sequences that are somewhat more complicated than that in Figure 1b, using a computer to find values of pulse lengths, phases, and delays that maximize $\bar{E}(n)$. Both approaches are under investigation. As indicated in Figure 2, it is also important to evaluate the sensitivity of the sequences to resonance offsets and CSA. The decrease in $\bar{E}(n)$ with increasing offset and CSA width places limits on the spectral range and types of carbons to which the double-quantum filtering techniques can be successfully applied.

To get a quantitative estimate of the restriction imposed by sensitivity considerations on the size of the molecules that can be studied in double-quantum filtering experiments, we can begin with the conservative assumptions that the total sample size is limited to 100 mg and that it is possible to observe a resonance from no less than 10^{18} equivalent ^{13}C nuclei in an unfiltered, cross-polarized MAS experiment with an adequate signal-to-noise ratio in a single scan. In 10000 scans, it is then possible to detect the NMR signal from a single carbon site at natural abundance in a molecule with molecular weight up to about 60000. In a double-quantum filtering experiment in which a single site is labeled with the goal of obtaining the MAS spectrum of a region of the molecule localized around the labeled site, the upper limit on the molecular weight becomes about $60000\bar{E}(n)$. In a double-quantum filtering experiment on an unlabeled molecule intended to provide information about the approximate distances between nuclei that give rise to resolved resonances, the upper limit on the molecular weight is about $600\bar{E}(n)$. Of course, these limits are intended as order-of-magnitude estimates only, since the sensitivity depends on spin relaxation rates, the cross-polarization enhancement, the line widths, the field strength, the probe efficiency and filling factor, the sample temperature, etc. Nonetheless, the analysis presented above certainly indicates that double-quantum filtering can be successfully applied in structural studies of complex molecules.

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Computational Study of the Carboranylcarbenes 1-CH-1,2-$C_2B_3H_4$ and 1-CH-1,2-$C_2B_4H_5$

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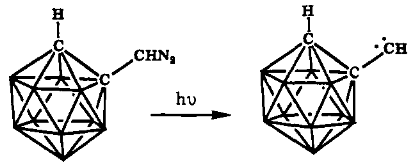
Abstract: Calculations are reported for the first two members of the carborane series, 1,2-$C_2B_3H_5$ and 1,2-$C_2B_4H_6$, with a carbene substituent at the 1-position. For the first member of the series, 1-CH-1,2-$C_2B_3H_4$, a singlet carbene attached to the cage causes a complete disruption of the cage structure. By contrast, the second member, 1-CH-1,2-$C_2B_4H_5$, is an energy minimum. On both potential energy surfaces, the global minimum is an expanded cage isostructural and isoelectronic with the next higher carborane. The relevance of the current work to the known chemistry of *o*-carboranylcarbene, 1-CH-1,2-$C_2B_{10}H_{11}$, is discussed.

Introduction

The overlap of carbene chemistry with carborane chemistry holds great potential for new and perhaps unexpected structures.[1-3] The reactive carbene center may donate a pair of electrons and insert into the carborane cage, may abstract a hydrogen atom forming an exocyclic carbon–carbon double bond, or may insert into a B–H bond forming a fused three-membered ring. Lastly, if the carbene center is attached by a flexible tether, a carbon-to-boron bridge can be formed.[3] Jones[1-3] has explored the carbene–carborane interface with the *o*-carboranylcarbene system (**1**) which is generated from a precursor diazo compound (**2**) by photolysis (eq 1).



2 **1**

(1)

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Table I. Total Energies (hartrees) of Species on the $C_3B_3H_5$ Potential Energy Surface at Various Levels of Theory

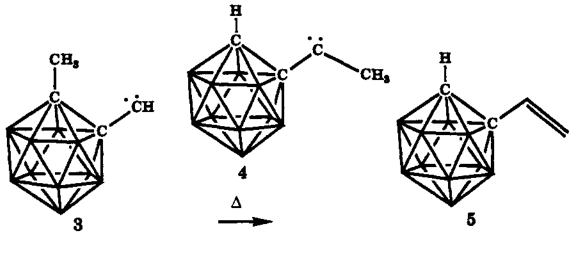
	sym	stat	HF/3-21G//3-21G	HF/6-31G*//3-21G	MP2/6-31G*//3-21G	ZPC//3-21G[a]	⟨S²⟩[b]
6	C_s	$^1A'$	−189.32510	−190.38585	−190.97334	48.20 (1)	
6′	C_1	^1A	−189.32699	−190.39070	−190.98610	48.50 (0)	
6″	C_1	^1A	−189.34664	−190.41227	−191.00565	48.63 (0)	
7	C_s	$^1A'$	−189.24812	−190.33387	−190.93893	46.47 (1)	
8	C_1	^3A	−189.30867	−190.38842	−190.97722	47.45 (0)	2.02 (2.00)
9	C_s	$^3A''$	−189.30646	−190.38685	−190.97623	46.98 (1)	2.03 (2.00)
10	C_s	$^3A''$	−189.30542	−190.38520	−190.97137	46.94 (1)	2.03 (2.00)
11	C_s	$^1A'$	−189.27594	−190.38761	−191.03726	49.98 (0)	
12	C_{2v}	$^1A_1$	−189.36321	−190.45617	−191.09647	50.16 (0)	
	sym	stat	HF/6-31G*//6-31G*	MP2/6-21G*//6-31G*	MP4/6-31G*//6-31G*	ZPC//6-31G*[a]	⟨S²⟩[b]
6	C_s	$^1A'$	−190.38668	−190.97457	−191.04942	47.47 (1)	
6″	C_1	^1A	−190.41443	−191.01156	−191.08896	48.35 (0)	
8	C_1	^3A	−190.39212	−190.98282	−191.05075	47.56 (0)	2.02 (2.00)
11	C_s	$^1A'$	−190.39487	−191.04468	−191.10908	50.77 (0)	
12	C_{2v}	$^1A_1$	−190.46535	−191.10691	−191.16955	50.92 (0)	

[a] Zero-point energy (kcal/mol). The value in parentheses is the number of imaginary frequencies. [b] Spin-squared values for triplets at the UHF/6-31G* level. The projected values are in parentheses.

The chemistry of **1** is similar to phenylcarbene in that the carbene adds stereospecifically to double bonds.[4] Since phenylcarbene is known to be a ground-state triplet,[5] the stereospecific addition to olefins implies that the singlet is in equilibrium with the triplet, because only the singlet carbene gives rise to stereospecific addition.

The EPR spectra of **1** and **3** have been observed[6] at temperatures as low as 5 K in frozen solutions which indicates that a triplet is either the ground state of *o*-carboranylcarbene (**1**) or lies at most only a few tenths of a kcal/mol above the singlet. On the other hand, the singlet cannot be much above the triplet since addition to double bonds occurs stereospecifically. It is also known that there is very little delocalization of the unpaired electrons into the carborane cage in the triplet.[6]

It was observed[1] that 2-methyl-*o*-carboranylcarbene (**3**) rearranged to 1-vinyl-*o*-carborane (**5**), probably through the intermediacy of the carbene **4** (see eq 2). The rearrangement of 1-methyl-*m*-carboranylcarbene to 1-vinyl-*m*-carborane was not observed, which suggests that the presence of a —CH=C=HC— unit could induce the formation of a 13-vertex cage as a low-energy intermediate or transition state for the rearrangement.[1]



(2)

In this regard, it is noteworthy that a current proposal for thermal isomerization of icosahedral carboranes is a 12-vertex nido intermediate.[7] The carbene substituent might actually stabilize the nido form by adding to the open face, thereby leading to a 13-vertex closo intermediate and a lower energy exchange pathway.

The 25-atom carboranylcarbene is too large to study with the computational methods necessary to achieve qualitatively correct results. Therefore, as models of the carborane-substituted carbene, we considered the first two members of the carborane series, 1,2-$C_2B_3H_5$ and 1,2-$C_2B_4H_6$, in place of 1,2-$C_2B_{10}H_{12}$ (*o*-carborane). The smaller carboranes are tractable computationally yet have directly bonded carbons as does *o*-carborane. In addition, the actual carbenes calculated here might be generated in the not too distant future.[8]

The goal of the present work is not to explore exhaustively the potential energy surface of the carboranylcarbenes. Even the first two members of the series are too complex to compute all decomposition and rearrangement pathways. Rather, aspects of structure and bonding in this new class of compounds will be studied. Of particular interest is a carborane geometry with a fused cyclopropene ring since there is NMR evidence for such a structure in the *o*-carboranylcarbene system.[9] Lastly, possible structures with a symmetric —CH=C=HC— unit will be evaluated as possible intermediates or transition states in the degenerate rearrangement which exchanges a cage carbon and the carbene carbon.

To the author's knowledge no calculations have been reported for any carboranylcarbenes or any derived structures.

Method

All calculations have been made by using the GAUSSIAN 88 program system.[10] Geometries have been optimized at the HF/3-21G (UHF/3-21G for open shell systems) level[11] and are available as supplementary material in *z*-matrix format. Single-point calculations were made at the MP2 level of electron correlation (frozen-core approximation) with the 6-31G* basis set. Selected geometries have been reoptimized at the HF/6-31G* level with electron correlation introduced at the MP4 level of theory (MP4/6-31G*//6-31G*). The effect of spin contamination has been projected out of the MP energies for open-shell species by the spin-projection method developed by Schlegel and co-workers.[12] Absolute energies, zero-point energies, and spin-squared values are given in Table I for $C_3B_3H_5$ species and in Table II for $C_3B_4H_6$ species, while $C_3B_3H_5$ geometries are given in Figure 1 and $C_3B_4H_6$ geometries are given in Figure 2. Geometric parameters are also given for the parent carboranes[13,14] (unnumbered) so that comparisons with the unperturbed carborane cages can be made. Vibrational frequencies have been calculated to characterize the nature of the stationary points and to make zero-point corrections (scaled by 0.9).

Relative energies in kcal/mol are given in Tables III and IV for $C_3B_3H_5$ and $C_3B_4H_6$ species, respectively. The values in parentheses represent the energy lowering obtained at the indicated level of theory when 6-31G* geometries are used rather than 3-21G geometries. The introduction of polarization functions (6-31G*) causes a contraction of the cage distances by about 0.04 Å compared to 3-21G geometries (Figures 1 and 2). The largest change in relative energies due to the level of geometry optimization is about 6 kcal/mol.

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Table II. Total Energies (hartrees) of Species on the $C_3B_4H_6$ Potential Energy Surface at Various Levels of Theory

	sym	stat	HF/3-21G//3-21G	HF/6-31G*//3-21G	MP2/6-31G*//3-21G	ZPC//3-21G[a]	$\langle S^2 \rangle$[b]
13	C_s	$^1A'$	-214.44288	-215.67789	-216.38770	58.06 (0)	
14	C_s	$^1A'$	-214.44153	-215.67442	-216.38475	57.98 (0)	
15	C_1	^3A	-214.47738	-215.70832	-216.39916	57.89 (0)	2.02 (2.00)
16	C_s	$^3A''$	-214.47629	-215.70780	-216.39920	57.56 (1)	2.03 (2.00)
17	C_s	$^3A''$	-214.47562	-215.70676	-216.39738	57.51 (1)	2.03 (2.00)
18	C_s	$^1A'$	-214.32098	-215.54715	-216.29649	54.76 (1)	
19	C_s	$^1A'$	-214.44184	-215.65134	-216.34271	57.45 (1)	
20	C_s	$^1A'$	-214.39279	-215.61352	-216.34189	57.19 (1)	
21	C_s	$^1A'$	-214.37886	-215.61363	-216.35195	56.98 (2)	
22	C_{2v}	$^1A_1$	-214.40388	-215.66951	-216.42384	59.39 (1)	
23	C_s	$^1A'$	-214.40574	-215.66374	-216.41120	59.40 (0)	
24	C_s	$^1A'$	-214.40986	-215.63736	-216.36964	59.58 (1)	
25	C_s	$^1A'$	-214.42764	-215.64070	-216.35904	59.14 (1)	
26	C_{2v}	$^1A_1$	-214.40870	-215.63372	-216.36706	57.05 (2)	
27	C_2	^1A	-214.46649	-215.69271	-216.40059	58.66 (0)	
28	C_{2v}	$^1A_1$	-214.48706	-215.73432	-216.46904	60.61 (0)	

	sym	stat	HF/6-31G*//6-31G*	MP2/6-31G*//6-31G*	MP4/6-31G*//6-31G*	ZPC//6-31G*[a]	$\langle S^2 \rangle$[b]
13	C_s	$^1A'$	-215.68185	-216.39132	-216.47079	58.68 (0)	
16[c]	C_s	$^3A''$	-215.71117	-216.40207	-216.47622	58.16 (1)	2.02 (2.00)
18	C_s	$^1A'$	-215.55549	-216.30361	-216.38164	55.25 (2)	
22	C_{2v}	$^1A_1$	-215.67520	-216.42727	-216.49797	60.93 (0)	
26	C_{2v}	$^1A_1$	-215.63791	-216.37528	-216.45372	57.77 (2)	
27	C_2	^1A	-215.69591	-216.40415	-216.48344	59.14 (0)	
28	C_{2v}	$^1A_1$	-215.74187	-216.47704	-216.54952	61.50 (0)	

[a] Zero-point energy (kcal/mol). The value in parentheses is the number of imaginary frequencies. [b] Spin-squared values for triplets at the UHF/6-31G* level. The projected values is given in parentheses. [c] The energy of the triplet optimized at the UHF/6-31G* level in C_1 symmetry (**15**) was -215.71190 hartrees, 0.4 kcal/mol lower in energy than the C_s symmetry triplet (**16**). Results at the UHF/3-21G level suggest that the C_s symmetry triplet would be more stable than the C_1 symmetry triplet at correlated levels.

Table III. Relative Energies (kcal/mol) of $C_3B_3H_5$ Species at 3-21G and 6-31G* Optimized Geometries

	//3-21G				//6-31G*[a]			
	HF/3-21G	HF/6-31G*	MP2/6-31G*	+ZPC[b]	HF/6-31G*	MP2/6-31G*	MP4/6-31G*	+ZPC[b]
6	0.0	0.0	0.0	0.0	0.0 (-0.5)	0.0 (-0.8)	0.0	0.0
6′	-1.2	-3.0	-8.0	-7.7				
6″	-13.5	-16.6	-20.3	-19.9	-17.0 (-1.4)	-23.2 (-3.7)	-24.8	-24.0
7	48.3	32.6	21.6	20.0				
8	10.3	-1.6	-2.4	-3.1	-3.4 (-2.3)	-5.2 (-3.5)	-0.8	-0.7
9	11.7	-0.6	-1.8	-2.9				
10	12.3	0.4	1.2	0.1				
11	30.8	-1.1	-40.1	-38.5	-5.1 (-4.6)	-44.0 (-4.6)	-37.4	-34.4
12	-23.9	-44.1	-77.3	-75.5	-49.4 (-5.8)	-83.0 (-6.6)	-75.4	-72.3

[a] The value in parentheses is the lowering of the total energy (kcal/mol) at the indicated level of theory when the calculation is performed at the 6-31G* geometry rather than the 3-21G geometry. [b] Zero-point energy corrections (scaled by 0.9) have been included.

Table IV. Relative Energies (kcal/mol) of $C_3B_4H_6$ Species at 3-21G and 6-31G* Optimized Geometries

	//3-21G				//6-31G*[a]			
	HF/3-21G	HF/6-31G*	MP2/6-31G*	+ZPC[b]	HF/6-31G*	MP2/6-31G*	MP4/6-31G*	+ZPC[b]
13	0.0	0.0	0.0	0.0	0.0 (-2.5)	0.0 (-2.3)	0.0	0.0
14	0.8	2.2	1.8	1.7				
15	-21.6	-19.1	-7.2	-7.4				
16	-21.0	-18.8	-7.2	-7.6	-18.4 (-2.1)	-6.7 (-1.8)	-3.4	-3.9
17	-20.5	-18.1	-6.1	-6.6				
18	76.5	82.0	57.2	54.2	79.3 (-5.2)	55.0 (-4.5)	55.9	52.8
19	0.6	16.7	28.2	27.7				
20	31.4	40.4	28.7	27.9				
21	40.2	40.3	22.4	21.4				
22	24.5	5.2	-22.7	-21.5	4.2 (-3.6)	-22.6 (-2.2)	-17.0	-15.0
23	23.3	8.9	-14.7	-12.5				
24	20.7	25.4	11.3	12.7				
25	9.6	23.3	18.0	19.0				
26	21.4	27.7	13.0	12.1	27.6 (-2.6)	10.1 (-5.2)	10.7	9.9
27	-14.8	-9.3	-8.1	-7.6	-8.8 (-2.0)	-8.0 (-2.2)	-7.9	-7.5
28	-27.7	-35.4	-51.0	-48.7	-37.7 (-4.7)	-53.8 (-5.0)	-49.4	-46.9

[a] The value in parentheses is the lowering of the total energy (kcal/mol) at the indicated level of theory when the calculation is performed at the 6-31G* geometry rather than the 3-21G geometry. [b] Zero-point energy corrections (scaled by 0.9) have been included.

It should be pointed out that the effect of polarization functions and electron correlation on relative energies can be quite large (>60–70 kcal/mol) particularly when comparing classical and nonclassical structures.[15] For that reason, while the 3-21G and 6-31G* basis sets are quite useful for locating stationary points, the number of imaginary frequencies determined from the force constant calculation may not provide an accurate picture of the "real" potential energy surface. A better picture of the surface can be obtained by optimizing a number of candidate structures at the HF/3-21G or HF/6-31G* levels and evaluating their energies at the MP2/6-31G* or MP4/6-31G* levels where the imaginary frequencies at the HF/3-21G and HF/6-31G* levels are

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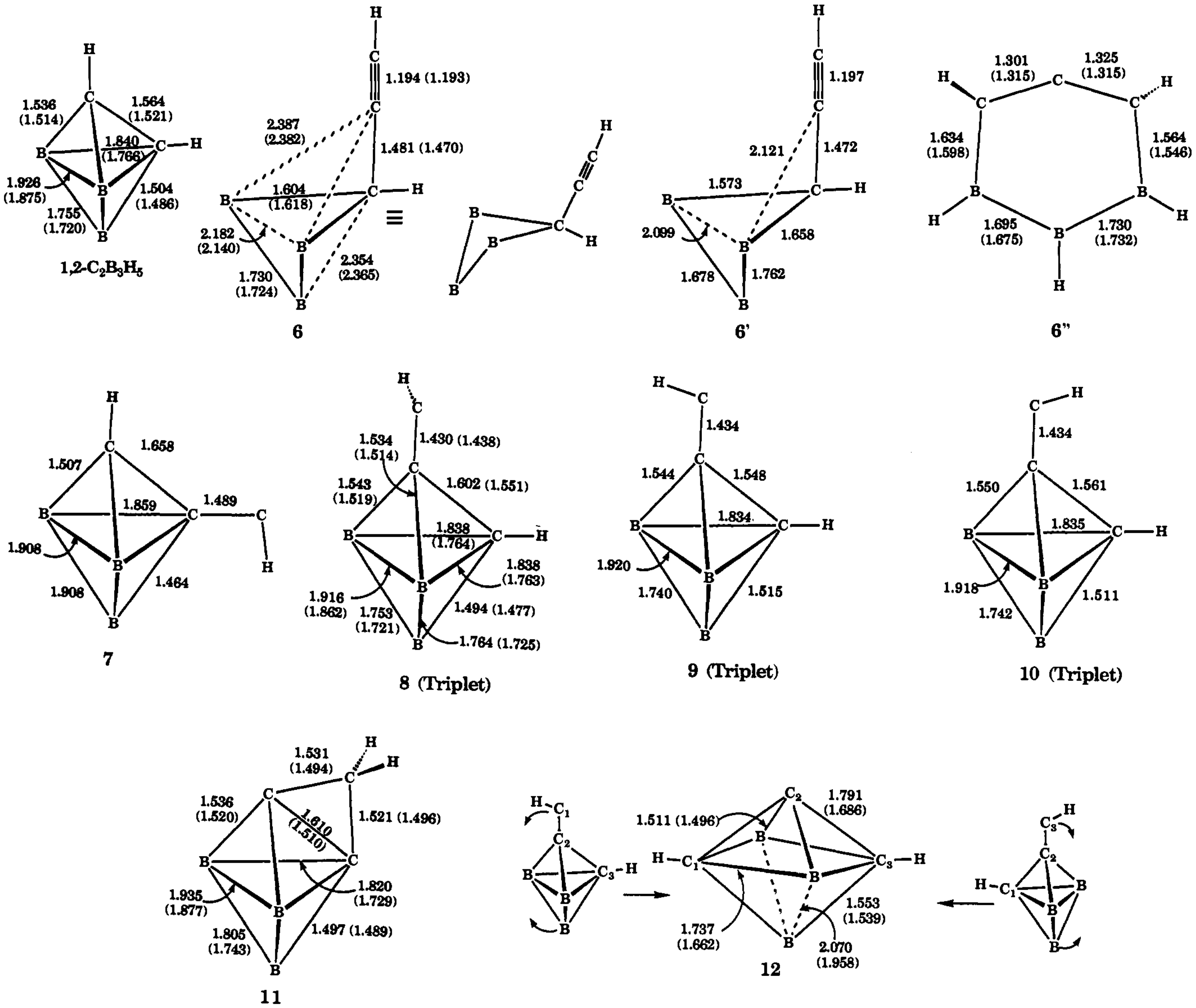

Figure 1. Selected geometric parameters at the HF/3-21G and HF/6-31G* levels (UHF/3-21G and UHF/6-31G* for open shell species) for 1,2-$C_2B_3H_5$[13] and $C_3B_3H_5$ species **6–12**. Hydrogens on carbons are shown explicitly, while each boron has one implicit hydrogen. Values in parentheses are at the HF or UHF/6-31G* level. All species are singlets except for **8–10** which are triplets.

very useful for locating new candidate structures. Of course, it would be better to evaluate geometries and vibrational frequencies at the MP2/6-31G* level. Unfortunately, the number of different candidate structures considered in the present survey would make geometry optimizations impractical at that level. However, in a limited comparison of known boron hydrides[16] and carboranes[17] structures at the HF/6-31G* and MP2/6-31G* levels, geometry differences were found to be in general small.

Results and Discussion

1-CH-1,2-$C_2B_3H_4$. The number of cage-bonding electrons in an *n*-vertex closo cage is given by Wade's rule[18] as $2n+2$, where each boron contributes two electrons and each carbon contributes three electrons. The initial optimization of 1-CH-1,2-$C_2B_3H_4$ revealed an unusual distortion of the carborane cage (**6**, Figure 1). Two cage electrons are diverted from cage bonding to form a triple bond with the carbene center. The resulting geometry is a puckered four-membered ring with an alkynyl substituent on one carbon. It appears that, at the level of theory used to determine geometries (HF/3-21G or HF/6-31G*), the energy gain by increasing the C–C bond order from one to three is greater than the energy loss caused by reduced multicenter bonding. It is interesting to note that conversion of the carboranylcarbene to the ethynyl compound (**6**) has a parallel in cyclopropylmethylene which can decompose to acetylene plus ethylene.[19]

Since **6** has one imaginary frequency at both the HF/3-21G and HF/6-31G* levels, full optimizations within C_1 symmetry were carried out. At the HF/3-21G level a structure (**6'**) was found which was 1.2 kcal/mol lower in energy than **6** (Table III). The lower symmetry is caused by a favorable interaction of the filled π orbital of the acetylenic group with the empty orbital on one boron (Figure 1). At the HF/6-31G* level, **6'** does not appear to be a local minimum, as **6** undergoes a much more radical rearrangement to a distorted cyclic allene system with near C_2 symmetry (**6"**). The six-membered ring, which is also a minimum at the HF/3-21G level, is formed when the terminal carbon of the acetylenic group inserts into a C–B bond of the four-membered ring. At the highest level, the energy of **6"** is 24.0 kcal/mol lower than **6** (Table III). The fact that the exocyclic carbene structure is not a minimum makes 1-CH-1,2-$C_2B_3H_4$ a poor model for *o*-carboranylcarbene. In the discussion below, energies are discussed relative to **6**, which is an artificial reference (since it is a

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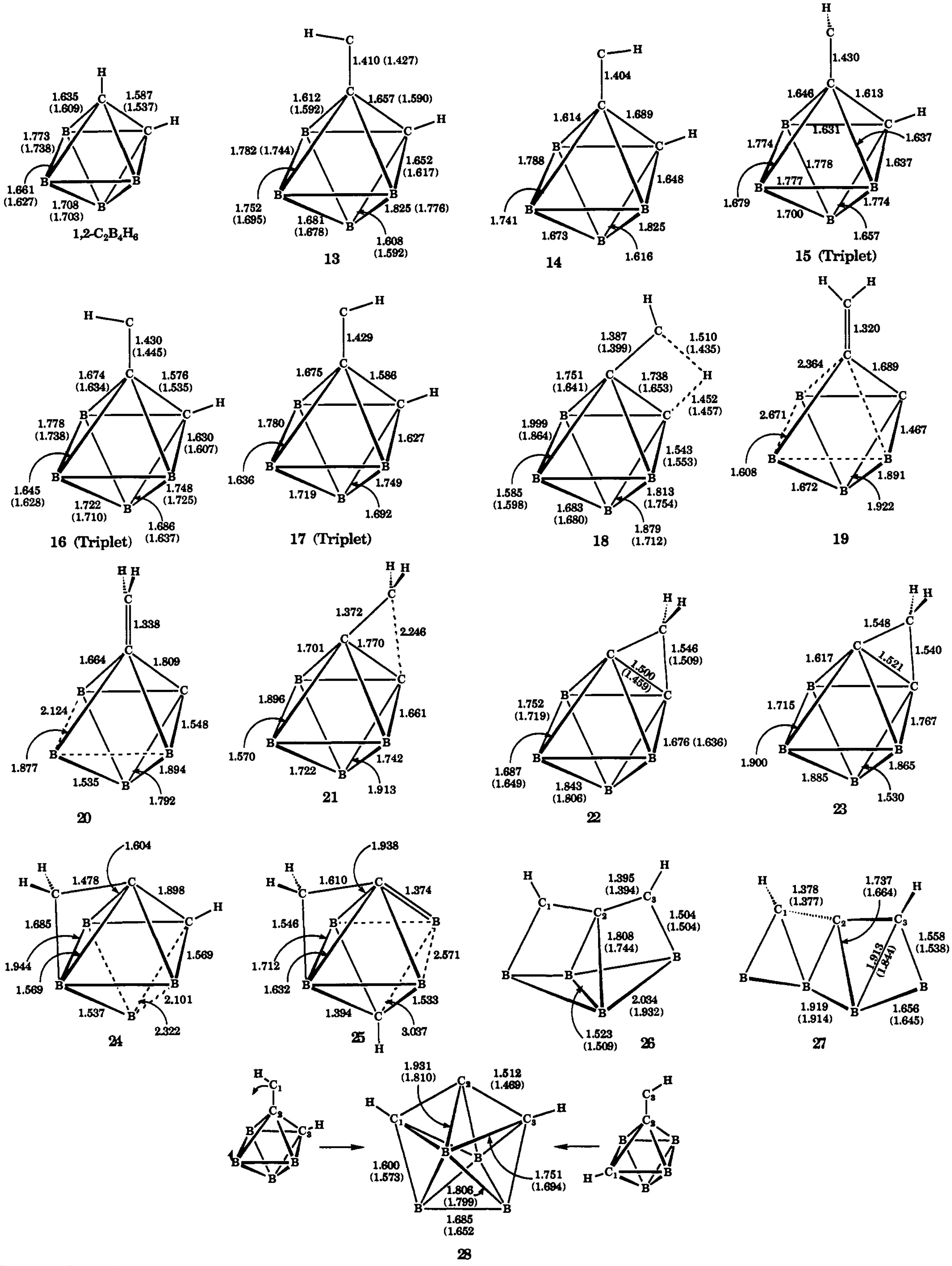

Figure 2. Selected geometric parameters at the HF/3-21G and HF/6-31G* levels (UHF/3-21G and UHF/6-31G* for open shell species) for 1,2-$C_2B_4H_6$[14] and $C_3B_4H_6$ species **13**–**28**. Hydrogens on carbons are shown explicitly, while each boron has one implicit hydrogen except in structure **24** and **25** where the boron which is contained in the three-membered ring does not have a hydrogen attached. Values in parentheses are at the HF or UHF/6-31G* level. All species are singlets except for **15**–**17** which are triplets.

transition state at both the HF/3-21G and HF/6-31G* levels).

The exocyclic carbene center was obtained when substitution occurred at the 2-position (**7**, 2-CH-1,2-$C_2B_3H_4$), but the energy is much higher than **6** (20.0 kcal/mol) at the MP2/6-31G*+ZPC level. Three structures were calculated for the triplet carbene (**8**–**10**) which differ in the torsion angle of the hydrogen attached to the carbene center. When the hydrogen is either trans (**9**) or cis (**10**) to the equatorial carbon, the structure is predicted to be a transition state (one imaginary frequency). A minimum is predicted for a structure of C_1 symmetry with a torsion angle of 91.3° (6-31G*) with respect to the cage carbon. The triplet is 0.7 kcal/mol more stable than **6** at the PMP4/6-31G*+ZPC//6-31G* level.

The next structure considered was a cyclopropene fused to a carborane cage (**11**). In *o*-carboranylcarbene (**1**) the structure could result from the insertion of carbene into the C–H bond.[20] In the model system, the presence of the fused three-membered ring does not excessively disturb the geometry of the 1,2-$C_2B_3H_4$ fragment as shown by the small differences between **11** and 1,2-$C_2B_3H_5$ (Figure 1). At the MP4/6-31G*+ZPC//6-31G* level, **11** is 34.4 kcal/mol more stable than **6**.

In *o*-carboranylcarbene (**1**), a process which exchanges the carbene carbon and a cage carbon must go through a transition state/intermediate in which the two exchanging carbons become equivalent.[1] A structure which meets this requirement in the model system is **12**, an approximate octahedron, which is calculated to be much more stable than **6**; in fact it is the apparent ground state. The stability is due to cage expansion to the next larger closo cage. The electron count still obeys Wade's rule for a closo cage because the central carbon has an exocyclically directed lone pair which leaves only two electrons for cage bonding. Since the bare carbon atom is isolobal[21] with a BH group, the cage $C_3B_3H_5$ has the same number of cage electrons as 1,6-$C_2B_4H_6$, a well-known closo carborane.[22] THe octahedral cage (**12**) is 72.3 kcal/mol more stable than **6** at the MP4/6-31G*+ZPC//6-31G* level.

An estimate of the stability of **12** can be made by calculating the exothermicity of eq 1 which compares the stability of a BH group incorporated into a cage relative to BH_3 with a bare carbon atom incorporated into a cage relative to singlet methylene (eq 3). The reaction is 22.7 kcal/mol exothermic at the MP4/6-31G*+ZPC//6-31G* level (20.4 kcal/mol at the MP2/6-31G*+ZPC//3-21G level) and appears to indicate that a carbon atom with an exocyclic lone pair can participate in multicenter bonding to the same extent as a BH group. The unsubstituted carbon in **12** could be considered inverted (since all atoms lie to one side) and therefore the center should be strained. However, as a vertex in a six-vertex closo cage, the unsubstituted carbon is required to contribute only two electrons to cage bonding, which can be done without introducing strain.

$$1,6\text{-}C_2B_4H_6 + :CH_2\ (^1A_1) \rightarrow \mathbf{12} + BH_3 \qquad (3)$$

While no pathways for the formation of **12** have been calculated, the large exothermicity suggests that the barrier might be low. If a carbene precursor of 1-CH-1,2-$C_2B_3H_4$ were deposited in a matrix and irradiated, **12** might be sufficiently stable to be observed.

1-CH-1,2-$C_2B_4H_5$. The next larger carborane in the series $C_2B_nH_{n+2}$ (n = 3–10) is n = 4 ($C_2B_4H_6$). Substituting a carbene at the apical position (**13** and **14**) does not lead to complete disruption of the cage as found for the n = 3 carborane. Rather, the C–C and the C–B distances in the molecular plane increase while the two remaining C–B distances decrease in comparison to the unsubstituted 1,2-$C_2B_4H_6$ carborane (Figure 2). The changes can be rationalized by realizing that the occupied lone pair on the carbene center will be in the molecular plane leading to a destabilizing 2c-4e interaction with the bonding electrons in the C–C and C–B bonds. Likewise, the empty p orbital on the carbene center will be perpendicular to the molecular plane leading to a stabilizing 2c–2e interaction with the bonding electrons in the two C–B bonds. The destabilizing interaction will lead to longer bonds, while the stabilizing interaction will lead to shorter bonds.

Two orientations of the carbene hydrogen were considered, either away from the 2-position carbon (**13**, trans) or toward the 2-position carbon (**14**, cis). The trans orientation is slightly favored at all levels (Table IV). At the highest level **13** is favored over **14** by 1.7 kcal/mol.

Three orientations were considered for the triplet carbene (**15**–**17**). At the lowest level, structure **15** is a minimum (no imaginary frequencies), while **16** and **17** are transition states (one imaginary frequency) for rotation about the carbene cage C–C bond. At the UHF/3-21G//3-21G level, the barriers are 0.6 kcal/mol over the trans transition state (**16**) and 1.1 kcal/mol over the cis transition state (**17**). At the PMP2/6-31G*+ZPC//3-21G level, the ordering of **15** and **16** are switched, which suggests that the true triplet minimum is the trans structure (**16**). For that reason only **16** was optimized at the UHF/6-31G* level. At the highest level (PMP4/6-31G*+ZPC//6-31G*), the triplet (**16**) is predicted to be 3.9 kcal/mol more stable than the singlet (**13**).

The calculated results for 1-CH-1,2-$C_2B_4H_5$ parallel the experimental EPR results[6] for *o*-carboranylcarbene. The triplet is the predicted ground state by 3.9 kcal/mol, and an inspection of spin densities in **16** indicates that there is little delocalization over the carborane cage. It should be pointed out that at the highest level of theory used in this study, the methylene (CH_2) singlet–triplet splitting is overestimated by 8.7 kcal/mol (17.7 kcal/mol, calc; 9.0 kcal/mol, exptl[23]). Therefore, improvements in the basis set and extent of electron correlation might reduce the singlet–triplet splitting or even change the predicted ground state of the carbene.

Since singlet carbenes are known to insert the C–H bonds,[4,24] the transition state was located (**18**) for insertion of the carbene carbon into the C–H bond of the cage carbon.[20] The breaking C–H bond is 1.457 Å, and the forming C–H bond is 1.435 Å. The barrier is 52.8 kcal/mol at the MP4/6-31G*+ZPC//6-31G* level. The large barrier indicates that a structure with an exocyclic double bond such as **19** or **20** would not be formed readily. At the HF/6-31G*//3-21G level, the eclipsed double bond (**19**) is over 30 kcal/mol more stable than the bisected double bond (**20**). At the MP2/6-31G*+ZPC//3-21G level, the two structures are separated by only 0.2 kcal/mol.

The attached double bond causes a large change in the cage geometry. The π bond causes an elongation of the two cage bonds that are coplanar with the π bond. The p orbital is engaged in forming the π bond and cannot effectively engage in cage bonding. The two cage bonds that are coplanar with the σ framework are shortened due to the availability of the sp^2 hybridized carbon to form 2c–2e bonds to boron.

The transition state (**21**) was located for the addition of the methylene to carbon forming a cyclopropenyl ring fused to the carborane cage (**22**). At the HF/3-21G//3-21G level, the activation barrier (**20** → **21** → **22**) is 8.8 kcal/mol (Table IV) and decreases to −6.5 kcal/mol at the MP2/6-31G*+ZPC//3-21G level. The methylene carbon-to-cage carbon distance in the transition state is 2.246 Å (Figure 2). The negative activation barrier at the higher level of theory indicates that structures **19** and **20** are not likely to exist and that a concerted pathway **13** → **22** would have a lower activation barrier on the MP2/6-31G* potential energy surface.

At the HF/3-21G//3-21G level, **22** is predicted to have one imaginary frequency. When the C_{2v} symmetry constraint is re-

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(20) It should be noted the CH insertion is *not* observed in the *o*-carboranylcarbene system. Zheng, G-x.; Jones, M., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 6487.

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moved (a plane of symmetry containing the three carbons of the fused cyclopropenyl ring was retained), structure **23** was obtained, which was 1.2 kcal/mol lower in energy at the HF/3-21G//3-21G level. The distortion from C_{2v} to C_s involved lengthening and shortening bonds which were related by symmetry in the C_{2v} carborane cage. At the MP2/6-21G*+ZPC//3-21G level, the distortion is unfavorable by 9.0 kcal/mol. For that reason, only the C_{2v} structure (**22**) was optimized at the HF/6-31G* level. At the highest level (MP4/6-31G*+ZPC//6-31G*), the fused-ring/cage system is predicted to be 15.0 kcal/mol more stable than the carboranylcarbene (**13**). Interestingly, there is NMR evidence for the existence of a fused-ring/cage compound formed from 1-CH-1,2-$C_2B_{10}H_{11}$ (**4**).[9]

Two alternative fused-ring/cage compounds were considered (**24** and **25**) where the three-membered ring contained one boron. The structures would result from carbene insertion into the B–H bond of 1-CH-1,2-$C_2B_4H_5$ (**24**) or the B–H bond of 1-CH-1,6-$C_2B_4H_5$ (**25**). It is known[3] that if the carbene is attached to *o*-carborane with a flexible tether, B–H insertion can occur to form carbon-to-boron *o*-carboranes.

The three-membered ring in **24** causes severe disruption of the cage as shown by the dotted lines (Figure 2), which indicate interactions which are weak or absent. Two B–B distances and one B–C distance have increased to 2.101 and 2.322 Å, respectively, and the energy is 34.2 kcal/mol higher than **22** at the MP2/6-31G*+ZPC//3-21G level.

While the 1,6-isomer of the $C_2B_4H_6$ carborane is predicted to be about 10 kcal/mol more stable than the 1,2-isomer,[14] in the fused ring/cage system, the 1,6-isomer (**25**) is 40.5 kcal/mol (MP2/6-31G*+ZPC//3-21G) less stable than the 1,2-isomer (**22**). There are large cage deformations (two B–B distances and one C–B distance have increased to 2.571 and 3.037 Å, respectively), while one C–B distance is predicted to be so short (1.374 Å) that it is indicated as a double bond in Figure 2.

The *o*-carboranylcarbene is known[1] to undergo the rearrangement shown in eq 2. It has been speculated[1] that the transition state/intermediate might be a 13-vertex cage in which the two C–H units are equivalent. While pathways for exchange have not been calculated in the model compound, 1-CH-1,2-$C_2B_4H_5$ (**13**), three structures (**26**–**28**) have been located with equivalent CH groups which is a prerequisite for the exchange transition state/intermediate.

The highest energy structure is **26**, which is 9.9 kcal/mol less stable than **13** and is characterized by two short C–C bonds (1.395, 3-21G; 1.394 Å, 6-31G*). The cage has an incorporated cumulene unit (C=C=C) which is expected to be strained since the C–H groups are in the same plane.[25] Reducing the symmetry from C_{2v} to C_2 and following the larger of two imaginary frequencies leads to **27**, which is 17.4 kcal/mol lower in energy than **26** due to relief of strain in the cumulene unit. Two B–B interactions have been broken, and the two CH group have become more orthogonal (Figure 2).

The lowest energy structure with equivalent CH groups is the pentagonal bipyramid (**28**), which is also the global minimum, 56.8 kcal/mol more stable than **26** and 46.9 kcal/mol more stable than **13**. In analogy to **12** which is the global minimum on the $C_3B_3H_5$ potential energy surface and isoelectronic to 1,6-$C_2B_4H_6$, **28** is the global minimum on the $C_3B_4H_6$ surface and isoelectronic with 2,4-$C_2B_5H_7$. An indicator of the stability of **28** can be seen by use of eq 4 which is 15.5 kcal/mol exothermic at the MP2/6-31G*+ZPC//3-21G level. As noted above for **12**, if the bare

$$2,4\text{-}C_2B_5H_7 + {:}CH_2\ (^1A_1) \rightarrow \mathbf{28} + BH_3 \qquad (4)$$

carbon atom contributes two electrons to cage bonding (isolobal with a BH group), **28** can be described as closo ($2n + 2$ cage electrons). In contrast to **26** and **27**, the C–C bonds in **28** are much longer (1.512 Å, 3-21G; 1.469 Å, 6-31G*), indicating cage bonding rather than an inverted carbon center or an incorporated cumulene unit. The expanded cage **28** could be formed from the carbene **13** by a simple carbene insertion into a C–B bond (see Figure 2).

The results of the first two members of the carboranyl carbene series suggest that the global minimum for a carbene attached to a small carborane may be the expanded cage. The most favorable expanded cage *might* be expected to have CH groups in the same location as in the known carboranes of the same cage size. However, more work is needed to confirm this suggestion.

The *o*-carboranylcarbene, 1-CH-1,2-$C_2B_{10}H_{11}$ (**1**), may be unique among carboranylcarbenes, in that a carbene attached to a 12-vertex cage may be more stable than the expanded 13-vertex cage due to the enhanced stability of the icosahedral cage. The 13-vertex expanded cage would then provide a low-energy pathway for exchange of carbene and cage carbons.

Lastly, it may be possible to direct the specific synthesis of new cage compounds by generating reactive groups such as carbenes directly attached to a cage smaller by one vertex. It is hoped that such synthetic strategies might be aided by theoretical calculations of heterosubstituted cage stabilities.[26]

Conclusion

A class of compounds, the carboranylcarbenes, has been studied computationally for the first time. A number of structures derived from a carbene substituted on carbon in the first two members of the carborane series 1,2-$C_2B_nH_{n+2}$ (n = 3, 4) have been optimized by ab initio methods. While the carbene center severely disrupts the first member of the carborane series 1-CH-1,2-$C_2B_3H_4$, a fused three-membered ring/cage system and a distorted octahedron are found to be stable.

When a carbene is substituted on the second member of the carborane series (1-CH-1,2-$C_2B_4H_5$), the resulting structure retains the carborane cage. The triplet carbene is predicted to be 3.9 kcal/mol more stable than the singlet carbene, but theoretical results on methylene indicate that higher level calculations might reduce the difference. While insertion into a C–H bond requires considerable activation, the resulting fused cyclopropenyl ring/cage product is 15.0 kcal/mol more stable than the carboranylcarbene (**13**). A pentagonal-bipyramidal structure (**28**) is found to be the global minimum, 46.9 kcal/mol more stable than **13**.

It is possible that features of the potential energy surface for 1-CH-1,2-$C_2B_4H_5$ may be similar to the potential energy surface of the larger carborane, 1-CH-2-CH_3-1,2-$C_2B_{10}H_{11}$, which has been studied experimentally. Several tentative predictions can be made for the larger members: (1) The singlet–triplet splitting is small. (2) Insertion into the C–H bond is accompanied with a substantial activation barrier. (3) The fused cyclopropenyl ring/cage system is more stable than the carbene. (4) The global minimum for the smaller carboranylcarbenes may be a cage expanded by one vertex. (5) For *o*-carboranylcarbene (**1**), the extra stability associated with the closo 12-vertex cage may reverse the stability of the carbene and expanded 13-vertex cage. The expanded cage, however, may provide a low-energy pathway for exchanging the carbene and cage carbons.

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Registry No. 12, 137007-09-1; **28**, 137007-10-4; 1,2-$C_2B_3H_5$, 23777-70-0; 1,2-$C_2B_4H_6$, 20693-68-9.

Supplementary Material Available: Z-matrices for species in Tables I and II (13 pages). Ordering information is given on any current masthead page.

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