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A Study on the Reaction of Icosahedral Carborane with Carbenes

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The photolysis and thermal reaction of hexafluorobenzene solution of icosahedral dicarba-*closo*-dodecaborane and various carbenes have been shown to lead to the formation of four isomeric insertion products to icosahedral molecules. The results showed the carbene insertion reaction to 1,2-dicarba-*closo*-dodecaborane to occur at the positions of 4-, 5-, 7-, and 11-borons, 9-, and 12-borons 3-, and 6-borons and 8-, and 10-borons. The samples of 1,7-, and 1,12-dicarba-*closo*-dodecaborane with carbenes in hexafluorobenzene by photolysis showed no reaction. To find out the reactivities of carbenes to dicarba-*closo*-dodecaboranes, the total energies have been calculated and have been discussed the tendency for carbene insertion reactions to icosahedral carboranes.

Introduction

Dicarba-*closo*-dodecaborane compounds were shown to have the geometry of regular icosahedron with two carbon atoms at adjacent vertices¹. The reactivity and structure for many derivatives of those compounds have been reported². Among the icosahedron cage compounds, 1,2-, 1,7-, and 1,12-dicarba-*closo*-dodecaborane compounds containing alkyl, aryl, ether, haloalkyl and olefinic substituents can be prepared from decaborane with acetylenic compounds in the presence of Lewis bases^{3,4}. These reactions have been proved that protons are readily abstracted at room temperature from the carbon atoms with formation of the corresponding carboranyl anions under the influence of strong bases^{5,6}.

Electrophilic halogenation to the regular icosahedron cage has proven that 1-phenyl-1,2-dicarba-*closo*-dodecaborane in the presence of AlCl_3 results in preferential attack on the 1,2-dicarba-*closo*-dodecaborane cage⁷. Icosahedral dicarba-*closo*-dodecaborane compounds were described as superaromatics on the basis of extensive molecular orbital calculations⁸. It seems that these compounds have an extensive electron delocalized structure. But dicarba-*closo*-dodecaboranes were found to undergo aromatic substitution reactions⁹ and 1,2-dicarba-*closo*-dodecaboranylcarbenes showed thermal rearrangement reactions¹⁰ of typical phenylmethylene¹¹ and derivatives¹². Dicarba-*closo*-dodecaborane cages are polarized, therefore a carbene insertion reaction to those cages may be observed.

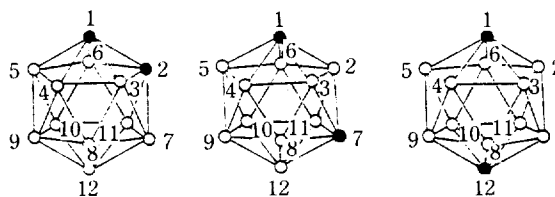
In order to investigate the reaction of carbene insertion to a polyhedral dicarba-*closo*-dodecaborane, the reactions of

three isomeric icosahedral dicarba-*closo*-dodecaboranes with various carbene insertions by photolysis and thermal reaction are reported below. The structure and reactivity of 1,2-, 1,7-, and 1,12-dicarba-*closo*-dodecaborane cages and various carbenes were also investigated from a calculation using the EHT-spd and CNDO/2.

Experimental

1,2-Dicarba-*closo*-dodecaborane(1,2-carborane), 1,7-dicarba-*closo*-dodecaborane (1,7-carborane) and 1,12-dicarba-*closo*-dodecaborane (1,12-carborane) from Olin Mathison Co. were recrystallized from benzene. Unless further purification is indicated, other materials were used as received from commercial sources. The photolysis was carried out by using PHYWE Mercury H-P Lamp CS 150W(I) and General Electric 275W Sun Lamp (II).

Gas chromatography was carried out by using an Shimadzu GC-RIA instrument employing $6' \times 1/6''$ 10% Carbowax



1,2(ortho)-Carborane 1,7(meta)-Carborane 1,12(para)-Carborane

Figure 1

20M on a 60/80 mesh Chromosorb P(A). 6'×1/6" 15% OV-17 Chromosorb 80/100 mesh W-HP (B), 4.5'×1/5" 20% Carbowax 20M on Chromosorb 60/80 mesh (C), and 6'×1/5" 15% OV-101 on a GAS-Chromosorb 60/80 mesh (D). GC/MS analyses were carried out using a Hewlett-Packard 5992 instrument employing SP2250 and OV101 column.

¹H NMR spectra were obtained by using a Varian EM390 spectrometer ¹¹B NMR spectra were recorded on a Varian HA-100 spectrometer. Infrared spectra were obtained by using a Perkin-Elmer 683 infrared spectrometer.

Insertion reaction of Methylene to Carboranes. 1,2-Carborane, 0.5g(3.47 mol) was dissolved in 7 ml of hexafluorobenzene. A Gaspar-Roth diazomethane generator¹³ was constructed in such a way that a stream of diazomethane carried by nitrogen could be bubbled into a 25 ml round bottom flask containing 1,2-carborane in hexafluorobenzene. The reaction flask was placed in a recirculating stream of ice water. The sample was photolyzed continuously using the lamp(II). The photolysis was conducted for 17 hours. During the reaction 21.5g(0.205 mol) of *N*-methyl-nitrosourea, 50 ml of 50% aqueous potassium hydroxide and 25 ml of decaline were used to generate diazomethane. The diazomethane generator and delivery glass tubing were shielded by aluminum foil. 1,7- and 1,12-carboranes were reacted with diazomethane in the same method and the samples were photolyzed using the lamp(II) for 20 hours. Gas chromatographic analysis on column, A at 220°C showed four products in the insertion to 1,2-carborane, but the reaction of 1,7- and 1,12-carboranes did not show any products. The first peak on the gas chromatogram of the insertion reaction of methylene to 1,2-carborane was 4-, 5-, 7-, and 11-B-methyl-1,2-carborane(4-B-a, 5-B-b, 7-B-c, 11-B-d); the yield of white powder, m.p.(127–129°C), 0.165g(30%); ¹H NMR(in CCl₄), δ 3.67–3.20(bs, 2H), 0.60–0.09(bs, 3H); ¹H NMR(in C₆D₆), δ 3.86–3.14(bs, 2H), 0.62–0.18(bs, 3H); ¹H NMR(in C₆D₆), δ 2.30–1.90(bs, 2H), 0.79–0.29(bs, 3H), ¹¹B NMR, δ (ppm, NaBH₄), -1.99(relative integrated area; 2) -6.13(1), -8.96(1.5), -13.74(1), -14.27(4), -17.34(2), IR(KBr), 3070, 2990, 2884, 2576, 1320, 1214, 1102, 1030, 725 cm⁻¹, mass spectrum, m/z (relative abundance), 158(M⁺, 100), 144[(M-CH₂)⁺] (58).

The second peak on the gas chromatogram of the insertion reaction of methylene to 1,2-carborane was 9-, and 12-B-methyl-1,2-carborane(9-B-e, 12-B-f); the yield of white powder, m.p.(134–136°C), 0.137g(25%); ¹H NMR(in C₆D₆), δ 2.46–2.0(bs, 2H), 0.78–0.22(bs, 3H), ¹¹B NMR, δ (ppm, NaBH₄), 5.24(relative integrated area; 1), -1.64(1.5), -9.02(4), -13.91(1.8), -15.51(1.8), -17.82(2), IR(KBr), 3060, 2948, 2908, 2508, 1325, 1220, 1157, 1035, 725 cm⁻¹, mass spectrum, m/z (relative abundance) 158 (M⁺, 100), 144[(M-CH₂)⁺] (60).

The third peak on the gas chromatogram of the insertion of methylene to 1,2-carborane was 8-, and 10-B-methyl-1,2-carborane(8-B-g, 10-B-h); the yield of white powder, m.p.(131–134°C), 0.099g(18%); ¹H NMR(in C₆D₆), δ 2.48–2.2(bs, 2H), 0.76–0.2(bs, 3H); ¹¹B NMR, δ (ppm, NaBH₄), 9.85(relative integrated area; 6), 8.94(5), -1.28(1.5), -5.30(2), -13.72(3.8), -17.93(2), IR(KBr), 3058, 2945, 2900, 2582, 1224, 1324, 1154, 1035, 725 cm⁻¹, mass spectrum, m/z (relative abundance), 158 (M⁺, 100), 144[(M-CH₂)⁺] (67).

The fourth peak on the gas chromatogram of the insertion of methylene to 1,2-carborane was 3-, and 6-B-methyl-1,2-carborane(3-B-i, 6-B-j); the yield of white powder,

m.p.(136–139°C), 0.055g(10%); ¹H NMR(in C₆D₆) δ 2.50–2.2(bs, 2H), 0.74–0.22(bs, 3H), ¹¹B NMR, δ (ppm, NaBH₄), -1.34(relative integrated area; 1), -6.61(1.7), -7.51(1), -11.56(2), -11.89(4), IR(KBr), 3068, 2995, 2885, 2575, 1325, 1215, 1100, 1032, 725 cm⁻¹, mass spectrum, m/z(relative abundance), 158(M⁺, 100) 144[(M-CH₂)⁺] (70).

Insertion Reaction of Difluorocarbene to Carboranes.

A precursor of difluorocarbene, phenyltrifluoromethylmercury was prepared by Seyferth's method¹⁴. Phenyltrifluoromethylmercury(7.97g, 0.023 mol), 1,2-carborane(0.0384g, 0.27 mol), sodium iodide 1.49g(0.01 mol) in 10 ml of carbontetrachloride and 15 ml of hexafluorobenzene were reacted by photolysis at 100°C for 74 hours using a lamp(I). The gas chromatographic analysis on columns C and D at 120°C showed four compounds.

4-, 5-, 7-, and 11-B-difluoromethyl-1,2-carborane(4-B-a, 5-B-b, 7-B-c, 11-B-d): the yield of yellow powder, m.p.(156–159°C), 0.0197g(38%), ¹H NMR(in C₆D₆), δ 3.70–3.58(bs, 2H), 5.20–4.98(bs, H), ¹¹B NMR, δ (ppm, NaBH₄), -2.01(relative integrated area; 1), -6.02(1.5), -8.83(1), -9.38(1), -13.58(6), -14.04(2), -16.43(2), mass spectrum, m/z(relative abundance), 195(M⁺, 100), 183[(M-BH₃)⁺] (36), 144[(M-CF₂)⁺] (65), 118[(M-B₂H₁₀)⁺] (24), 83 [(M-C₂B₁₀H₁₀)⁺] (55).

9-, and 12-B-difluoromethyl-1,2-carborane(9-B-e, 12-B-f): the yield of yellow powder, m.p.(152–154°C), 0.0135g(26%), ¹H NMR(in C₆D₆), δ 3.46–3.20(bs, 2H), 4.86–4.64(bs, H), ¹¹B NMR, δ (ppm, NaBH₄), 5.08(relative integrated area; 1), -1.63(2), -8.47(4), -13.81(1.5), -15.23(6), -17.85(2), mass spectrum, m/z(relative abundance), 195(M⁺, 100), 181[(M-BH₃)⁺] (49), 118[(M-B₂H₁₀)⁺] (26), 83[(M-C₂B₁₀H₁₀)⁺] (58).

8-, and 10-B-difluoromethyl-1,2-carborane(8-B-g, 10-B-h): the yield of yellow powder, m.p.(153–157°C), 0.0103g(20%), ¹H NMR(in C₆D₆), δ 3.18–3.16(bs, 2H), 4.66–4.48(bs, H), ¹¹B NMR, δ (ppm, NaBH₄), 5.21(relative integrated area; 1), -1.24(1.5), -8.88(4), -9.63(1), -13.61(6), -17.98(2), mass spectrum, m/z(relative abundance), 195(M⁺, 100), 181[(M-BH₃)⁺] (52), 144[(M-CF₂)⁺] (68), 118[(M-B₂H₁₀)⁺] (27), 83[(M-C₂B₁₀H₁₀)⁺] (54).

3-, and 6-B-difluoromethyl-1,2-carborane(3-B-i, 6-B-j); the yield of yellow powder, m.p.(151–155°C). 0.0052g(9%). ¹H NMR(in C₆D₆), δ 3.16–3.14(bs, 2H), 4.50–4.48(bs, H), ¹¹B NMR, δ (ppm, NaBH₄), -2.36(relative integrated area; 1), -7.37(4), -8.38(3.5), -12.74(6), -13.11(1), mass spectrum, m/z(relative abundance), 195(M⁺, 100), 181[(M-BH₃)⁺] (53), 144[(M-CF₂)⁺] (59), 118[(M-B₂H₁₀)⁺] (25), 83[(M-C₂B₁₀H₁₀)⁺] (55). The gas chromatographic analysis for the reaction products of 1,7- and 1,12-carboranes with difluorocarbene on the columns A,B and D at 180° and 200°C showed no peaks with retention time similar to 1,2-carborane.

Insertion Reaction of Dichlorocarbene to Carboranes.

The insertion reaction of dichlorocarbene to carborane was carried out on the thermal reaction. A 250 ml three-necked flask equipped with mechanical stirrer, nitrogen inlet tube and a syringe connector *n*-butyllithium(5.16 ml, 1.47 mol) storage was used and charged with bromotrichloromethane(0.99g, 4.99×10⁻³ mol), 1,2-carborane(0.72g, 4.99×10⁻³ mol) and 100 ml of ether. The contents were cooled to -23°C in a carbontetrachloride-dry ice bath under an atmosphere of dry nitrogen and then *n*-butyllithium was added in small portions over a 30 minute period. The reaction mixture was stirred for 40 minute while the flask was allowed to warm slowly to room

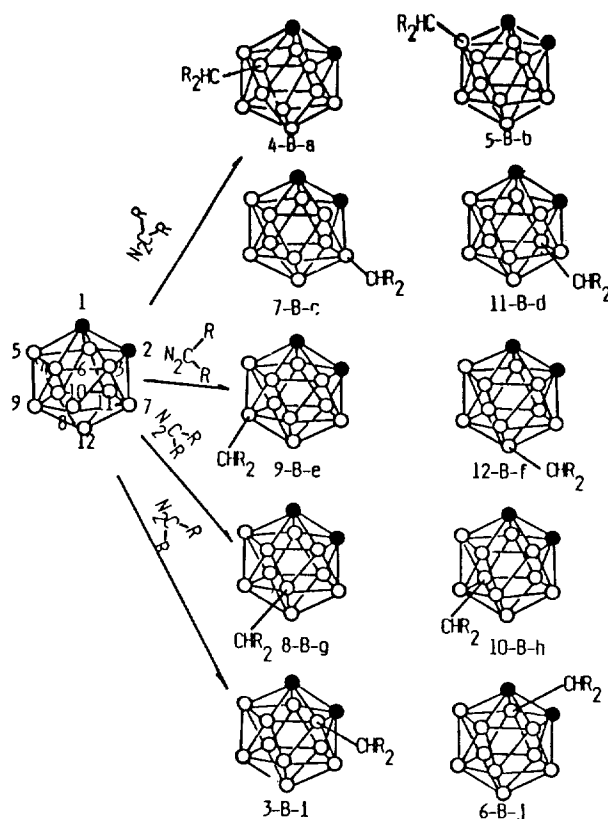


Figure 2

temperature. A gas chromatographic analysis on the columns C and D at 120°C showed the similar retention time as the previous photolysis products. But 1,7-, and 1,12-carboranes did not show any products in this dichlorocarbene insertion reaction.

4-, 5-, 7-, and 11-B-dichloromethyl-1,2-carborane(4-B-a, 5-B-b, 7-B-c, 11-B-d): the yield of white powder, m.p. (163–165°C), 0.374g(33%), ¹H NMR(in C₆D₆), δ 3.67–3.53(bs, 2H), 4.74–4.54(bs, H), ¹¹B NMR, δ (ppm, NaBH₄), -1.94 (relative integrated area; 1), -5.83(1.5), -8.80(1), -9.35(2), -13.55(2.5), -14.03(5), -16.40(3), mass spectrum, m/z(relative abundance), 227(M⁺, 100), 144[(M-CCl₂)⁺] (67), 118 [(M-B₉H₁₀)⁺] (24), 83[(M-C₂B₁₀H₁₀)⁺] (55).

9-, and 12-B-dichloromethyl-1,12-carborane(9-B-e, 12-B-f): the yield of white powder, m.p.(167–169°C), 0.272g(24%), ^1H NMR(in C_6D_6), δ 3.24–3.18(bs, 2H), 4.86–4.72(bs, H), ^{11}B NMR, δ (ppm, NaBH_4), 5.14(relative integrated area; 1), –1.59(1), –8.44(1.5), –13.73(2), –15.12(5), –17.74(3) (mass spectrum, m/z (relative abundance), 227 (M^+ , 100), 144[($\text{M}-\text{CCl}_2$) $^+$] (65), 118[($\text{M}-\text{B}_9\text{H}_{10}$) $^+$] (28), 83[($\text{M}-\text{C}_2\text{B}_{10}\text{H}_{10}$) $^+$] (55).

8-, and 10-B-dichloromethyl-1,2-carborane(8-B-g, 10-B-h): the yield of white powder, m.p.(159–162°C), 0.283g(25%), ¹H NMR(in C₆D₆), δ 3.14–3.12(bs, 2H), 4.91–4.88(bs, H), ¹¹B NMR, δ (ppm, NaBH₄), 5.26(relative integrated area; 1), -1.22(1), -8.71(2.5), -9.61(5), -13.57(3), -17.77(2), mass spectrum, m/z(relative abundance), 227(M⁺, 98), 144[(M-CCl₂)⁺] (72), 118[(M-B₉H₁₀)⁺] (21), 83[(M-C₂B₁₀H₁₀)⁺] (52).

3-, and 6-B-dichloromethyl-1,2-carborane(3-B-i, 6-B-j): the yield of white powder, m.p.(165–167°C), 0.091g(8%), ¹H NMR(in C₆D₆), δ 3.08–2.98(bs, 2H), 4.85–4.76(bs, 1H), ¹³B

NMR, δ (ppm, NaBH_4), -2.34(relative integrated area; 1), -7.35(2), -8.37(3), -12.51(5), -13.09(3), mass spectrum, m/z (relative abundance), 227(M^+ , 100), 144[($\text{M}-\text{CCl}_2$) $^+$] (62), 118[($\text{M}-\text{B}_9\text{H}_{10}$) $^+$] (25), 83[($\text{M}-\text{C}_2\text{B}_{10}\text{H}_{10}$) $^+$] (48).

Computational Details. MO calculations have been performed by using a program No. 256, 142 QCPE. Semi-empirical methods were performed by EHT-spd and CNDO/2. Calculations were done on an IBM 370-148 Type computer.

Results and Discussion

B-carbene inserted-1,2-carboranes were obtained by insertion reaction of various carbenes to 1,2-carborane. The ^{11}B NMR, ^1H NMR, IR spectra and mass spectral analysis corresponded with expected values^{15,16}, where those carbenes were inserted to 1,2-carborane icosahedron in the positions related to the 4-, 5-, 7-, and 11-borons, 9-, and 12-borons, 8-, and 10-borons, 3-, and 6-borons as shown in Figure 2. The ^{11}B NMR spectrum of 4-, 5-, 7-, and 11-B-methyl inserted-1,2-carborane exhibited two discernible doublets which were decoupled into singlets by selectively inserting the borons. By comparing the area of the resolved peak of the low field doublet of the ^{11}B NMR spectrum with the remainder of the spectrum, it was determined that the low-field doublet represents two-borons of the total ten, while the high-field doublet arises from all other borons which, therefore appear to be nearly equivalent.

Four singlet lines(-1.28, -5.30, -13.72, -17.93) and two doublets(8.94, 9.85) were observed in the ^{11}B NMR spectrum of 8-, and 10-B-methyl inserted-1,2-carborane which were due to the B-H and B-CH₃ bonds respectively. In 9-, and 12-B-methyl inserted-1,2-carborane four singlet lines(5.24, -1.64, -15.51, -17.82) and two doublets (-9.02, -13.91) were observed where occurred in the chemical shift and 3-, and 6-B-methyl inserted-1,2-carborane, one doublet(-11.89) and four singlet lines(-1.34, -6.61, -7.51, -11.56) were observed. These spectral data corresponded with the expected values from the results of an analogical inference by the literatures^{17,18}

The ^{11}B NMR spectra of dichloromethyl inserted-1,2-carboranes and difluoromethyl inserted-1,2-carboranes in which each boron-bonded hydrogen is replaced by CHCl_2 or CHF_2 are in accord with a low-field and high-field singlet equivalent to their methylene inserted-1,2-carborane.

Insertion of methylene, dichlorocarbene and difluorocarbene to 1,2-carborane produced 4-, 5-, 7-, and 11-B-carbene inserted-1,2-carborane with about 30–38% yield, 9-, and 12-B-carbene inserted-1,2-carborane about 24–27%, 8-, and 10-B-carbene inserted-1,2-carborane about 18–25% and 3-, and 6-B-carbene inserted-1,2-carborane about 8–10% yield. This result showed that carbene insertion reactions to 1,2-carborane undergo normal reactions with carbene cage acting as a strong electron withdrawing group¹⁹.

Throughout the reaction, polyehylene has produced partly forward yielding polymerization at ground state when the products of B-methyl inserted-1,2-carboranes also have been formed simultaneously. But the case of difluorocarbene and dichlorocarbene insertion reactions have not produced polymer of halocarbene at ground state. It may be conjectured that difluoro and dichloro carbenes favor the singlet carbene state²⁰ at ground state while methylene may favor the triplet state²¹. Lineberger²² has reported that a difference in energy of

Table 1. Atomic Charges and Frontier Orbital Energies for 1,2-Carborane by EHT, and CNDO/2

1,2-Carborane	Charges												Orbital Energy	
	B ₃	B ₆	B ₄	B ₅	B ₇	B ₁₁	B ₈	B ₁₀	B ₉	B ₁₂	C ₁	C ₂	HOMO	LUMO
EHT-Spd	0.543	0.542	0.321	0.319	0.338	0.341	0.0098	0.0995	0.0995	0.273	-0.0204	-0.344	-10.6643	-4.9209
CNDO/2	0.025	0.023	-0.003	-0.003	0.037	0.037	0.001	0.001	0.016	0.048	0.265	0.125	-0.466	0.1072
													(eV)	(a.u.)

Table 2. Atomic Charges and Frontier Orbital Energies for Carbenes by EHT, and CNDO/2

Carbenes (:CR ₂)	EHT-spd					CNDO/2				
	:C	Charges R	R	HOMO(eV)	LUMO(eV)	:C	Charges R	R	HOMO(a.u.)	LUMO(a.u.)
:CH ₂	-0.1724	0.0862	0.0862	-12.328	-11.4000	-0.024	0.012	0.012	-0.5543	0.0943
:CCl ₂	0.7421	-0.3711	-0.3711	-12.458	-11.2814	0.0791	-0.0395	-0.0395	-0.4979	-0.0204
:CF ₂	1.1757	-0.5858	-0.5858	-13.820	-10.4626	0.3387	-0.1694	-0.1694	-0.6085	0.0476

Table 3. Total Energies and Stability

Compounds	Total Energy		Stability by CNDO/2
	EHT-spd(eV)	CNDO/2(a.u.)	
1,2-C ₂ B ₁₀ H ₁₂	-768.9437	-65.4885	1
1,7-C ₂ B ₁₀ H ₁₂	-769.8329	-65.4877	2
1,12-C ₂ B ₁₀ H ₁₂	-767.7861	-65.4259	3

* bond length: B₃-B₆: 1.77 Å, B₃-B₄: 1.74 Å, B₃-C₂: 1.70 Å, C-C: 1.64 Å.

19.5 ± 0.7 Kcal mol⁻¹ was determined experimentally for the singlet and triplet of methylene. In a methylene insertion reaction, methylene tends toward singlet at ground state but the spin state may be reversible according to a change in the energy amount of irradiation. Davidson²³ has reported the effect of substitution on singlet-triplet energy gaps in dihalocarbenes. He showed that the change in ground state from triplet to singlet as one changes from CH₂ to CF₂ was the cause of a result of the greater electronegativity of fluorine. The electron-withdrawing property of fluorine stabilizes the non-bonding electrons in the σ orbital, which is doubly occupied in the singlet and only singly occupied in the triplet²⁴. Thus an electronegativity effect preferentially stabilizes the singlet²⁵.

The reaction of 1,2-carborane with halogen under FeX₃ or AlX₃ and the conformation of the calculated electronegativities of the cage atoms of 1,2-carborane have been reported by Schroeder *et al.*²⁶. The result of the calculations have shown that electrophilic attack first occurs at the positions of highest negative charge(9,12) followed by addition to the remaining borons in order of decreasing negative charge (8,10) and (4,5,7,11). In contrast to those propositions authenticated in the experiments and calculations, a counterargument runs along more traditional point of view and focuses not on electronegativity but upon the π -donating ability of elements such as fluorine.

To find out the reactivities of carbenes to 1,2-carborane the results of the calculation of atomic charges and frontier orbital energies for 1,2-carborane by EHT and CNDO/2 are

presented in Table 1.

The calculated atomic charges and frontier orbital energies for various carbenes by EHT and CNDO/2 are listed in Table 2.

It is conjectured that difluorocarbene insertion reaction to 1,2-carborane first occurs at the position of negative charge in preference to other carbene insertions to the positions 4,5 of 1,2-carborane from the charges in CNDO/2 calculations. The atomic charges of 1,2-carborane have shown that difluorocarbene insertion reaction occurs favourably in the positions 4,5 of 1,2-carborane in the same with experimental results however, the computations are not in accord with in the positions 8,9,10,12 of 1,2-carborane. But the experimental result and computations of EHT-spd and CNDO/2 are consistent with in the 9,12 positions of 1,2-carborane.

By population analyses and reactivities for icosahedral carborane, 1,2-carborane have more electronegative carbons on the molecules and borons have less than carbons²⁷. From atomic charges and nonsymmetry-equivalent overlap populations for 1,2-carborane, this molecule may be described as a composite of many resonance structure containing 3 normal B-B bonds and 10 central or open three-center BBB bonds.

Methylene, dichloro-, and difluoro-carbene insertion reactions to 1,2-carborane have been not followed the benzenoid system from the experimental result. In the case of insertion of methylene to the carborane cage to give a ring of expanded carboranes, it would similarly expect the addition of methylene²⁸ to benzene to produce a norcaradiene²⁹ but this reaction was not shown from the product analyses. No products with cage expanded structures were observed. It is possible that these species are formed but either reverted to starting materials or rearranged to the B-methyl compounds. A more likely explanation for the absence of a ring expanded product is that carbene is too reactive to react the internal carborane skeleton, and adds instead to the peripheral boron-hydrogen bonds.

There are two possibilities for carbene insertions to icosahedral carborane cage, a C-H bond, and a B-H bond. If the B-methyl compounds arise from a straightforward in-

Table 4. Atomic Charges and Frontier Orbital Energies for 1,7-Carborane and 1,12-Carborane

Compounds	Charges												HOMO	LUMO
	B ₂	B ₃	B ₅	B ₁₂	B ₄	B ₆	B ₈	B ₁₁	B ₉	B ₁₀	C ₁	C ₇		
1,7-C ₂ B ₁₀ H ₁₂														
EHT-spd	0.5449	0.5491	0.3093	0.4636	0.3116	0.3122	0.3553	0.1011	0.0995	0.01011	-0.2531	-0.5575	-10.6488	-4.8378
CNDO/2	0.0194	0.021	0.008	0.065	-0.006	-0.006	0.029	0.002	0.002	0.254	0.254	0.154	-0.4677	0.1445
														(a. u.)
1,12-C ₂ B ₁₀ H ₁₂														
EHT-spd	0.3036	0.3036	0.3036	0.3036	0.3036	0.3036	0.3036	0.3036	0.3036	0.3036	-0.2537	-0.2537	-10.6146	-4.9356
CNDO/2	-0.0004	-0.0004	-0.0004	-0.0004	-0.0004	-0.0004	-0.0004	-0.0004	0.0004	-0.0004	0.2633	0.2633	-0.4584	0.1588
														(a. u.)

Table 5. Relative Energy (Kcal. mol⁻¹) Components for Icosahedral Carborane by CNDO/2

Carborane	ΔE_T	$2\Sigma\epsilon_i$	E_{elec}	V_{ee}	V_{nn}
1,2-C ₂ B ₁₀ H ₁₂	-65.488454	-49.8282	-321.39676	271.56856	255.9083
1,7-C ₂ B ₁₀ H ₁₂	-65.427731	-49.7704	-321.21099	271.44059	255.72326
1,12-C ₂ B ₁₀ H ₁₂	-65.425892	-49.6216	-321.28715	271.66555	255.86216

$$* \Delta E_T = \Delta(2\Sigma\epsilon_i) + \Delta(V_{nn} - V_{ee}).$$

sertion into a B-H bond, the isomer formed should show a preference for the more electronegative borons. The methylene insertion reaction may be inserted first at the positions 4,5(CNDO/2) or 9,12 secondly it may be inserted at the positions 7,11, in due order 3,6 and 8,10 positions in view of the atomic charges. It is likely that the three adducts formed correspond to carbene insertion to the four chemical equivalent sets of borons. The C-H carbene insertion compounds were clearly absent in the experiment.

In the comparison of the reactivities of carbenes from Table 2, the atomic charge of carbon shows a negative charge in methylene while the positive charge of fluorine atom in difluorocarbene is higher either in EHT-spd or CNDO/2. This means difluorocarbene attacks the more electronegative boron atoms which are located a greater distance from carbon. This calculation is good in explaining the results of higher yield of difluorocarbene insertion product.

In increasing the frontier orbital energy, the orderings were LUMO: CCl₂<CF₂<CH₂ and HOMO: CF₂<CH₂<CCl₂ in CNDO/2 in Table 2. This is not in accordance with the prediction that electrophilic behavior of carbenes(CR₂) should be most strongly expressed³⁰ when R is most electronegative. Carbene insertion reaction is generally regarded as a particular kind of general acid-base type reaction and so the principle of hard and soft acids and bases applies equally to the reactions of electrophiles with nucleophiles³¹. Hard nucleophiles are generally those which are negatively charged and have relatively low-energy HOMOs while hard electrophiles are generally those which are positively charged and have relatively high energy LUMOs³². Thus a hard-hard interaction is fast because of a large Coulombic attraction. HOMO and LUMO energies in CNDO/2 of Table 2 shows those carbenes act as hard electrophiles with increasing the order of magnitude: CF₂>CCl₂>CH₂. They have a large Coulombic attraction in

atomic charges. Especially in the frontier orbital term³³, it was shown in a soft-soft reaction that HOMOs of nucleophile interacts with LUMOs of electrophiles with increasing the order of magnitude of the orbital term: CCl₂>CF₂>CH₂.

Population analyses and reactivities for three carborane isomers were reported³⁴ using a method devised by Mulliken³⁵, but it was faced a great number of less accessible parameters in even the simplest molecular orbital theory, and one could only vaguely conjecture the nature of the transition state in chemical reaction of carboranes. To find out the reactivities of carboranes, the calculated total energies and stability, the atomic charges and frontier orbital energies for 1,7-, and 1,12-carboranes and relative energy components for these icosahedral isomers are listed in Table 3, 4 and 5. The order stability magnitude has shown 1,2->1,7->1,12-carborane in CNDO/2. It is forecasted a good carbene insertion reaction occurs in the 4 and 6 positions of 1,7-carborane because these positions have a more negative charge than those of 1,2-carborane from Table 4. Although a sample of 1,7-carborane and methylene in hexafluorobenzene was allowed over 20 hours by photolysis and thermal reaction in the attempted carbene insertion reaction, the methylene only slowly polymerized to polyethylene, but 1,7-carborane remained unreacted. Like the same preceding method, difluoro-, and dichlorocarbene inserted to 1,7-carborane and also methylene, difluoro-, and dichlorocarbene inserted 1,12-carborane, but 1,7-, and 1,12-carborane remained unreacted. A contribution of total energy, ΔE_T is advantageous to electron occupied energy, $2\Sigma\epsilon_i$ while it is disadvantageous to steric effects, $-V_{ee}$, $+V_{nn}$ terms, therefore carbene insertion to 1,2-carborane is thought to occur more than in 1,7-, and 1,12-carboranes.

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