

## PHOTOCHEMICAL REACTION OF POLYHEDRAL BORON COMPOUND WITH DIBROMOCARBENE

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**Abstract** — The photochemical reaction of phenyl(tribromomethyl)mercury with *nido*-decaborane gives a new boron cluster expanded compound. The two borons at the 6- and 9- positions in decaborane behave as electrophilic centers for the reaction with dibromocarbene. The first step in this reaction is the addition of two molar equivalents of dibromocarbene which is produced from phenyl(tribromomethyl)mercury to *nido*-decaborane. In the second step the unstable intermediate generates the product, 1,2-Br<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> through loss of H<sub>2</sub>.

### INTRODUCTION

The icosahedral carboranes, 1,2-, 1,7- and 1,12-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> are in general use as high-boron content materials; they are thermally stable and resistant towards acids.<sup>1</sup> Despite their cost, such properties make them suitable for various specialized applications. These include the incorporation of large concentrations of boron atoms in tumour-seeking drugs for boron neutron capture therapy (BNCT)<sup>2</sup>, and the synthesis of polymers for high temperature<sup>3</sup> or neutron shielding purposes<sup>4</sup> or for firing to form ceramics related to boron carbide.<sup>5</sup> It has been reported that a typical icosahedral carborane derivative is produced from the reaction of nitriles with decaborane.<sup>6</sup>



The reactions of neutral boron hydrides with nitriles have usually involved initial electrophilic addition at nitrogen and have resulted in the production of simple base adduct. In particular, we are interested in the development of new methods by which carbene insertion reactions to *cage*-caborane could be accomplished. We have now reported here this possibility and describe the synthesis and structure of a unique cage boron cluster having cage skeletal compound.

### MATERIALS AND METHODS

The reactions of decaborane with a precursor of dibromocarbene were performed in an inert atmosphere of argon or nitrogen. All solvents were distilled from appropriate drying agents under a nitrogen atmosphere prior to use. The chemical shifts of <sup>11</sup>B-NMR and <sup>1</sup>H-NMR were shown relative to external BF<sub>3</sub> · Et<sub>2</sub>O (<sup>11</sup>B) and residual <sup>1</sup>H in deuterated solvent. Melting points were measured using samples in sealed capillaries are uncorrected. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian XL-300 or VXR-500 or a Bruker AC 250 FT spectrometer. Infrared (IR) spectra were recorded on a Perkin-Elmer Series 1430 spectrophotometer or a Perkin-Elmer Series 1600 FT-IR spectrophotometer.

*Materials.* Decaborane, *nido*-B<sub>10</sub>H<sub>14</sub> was obtained from Aldrich Chemical Co. and sublimed prior to use. Phenylmercuric bromide was obtained from Aldrich Chemical Co. and was purified in diethylether and ethanol. Potassium *tert*-butoxide was purchased from Aldrich Chemical Co. and was used without further purification.

Sodium iodide was purchased from Tokyo Kasei Chemical Co. and was purified in the mixture of C<sub>2</sub>H<sub>5</sub>OH/H<sub>2</sub>O (1:1).

*Preparation of Phenylmercuric Bromide.* To a boiling solution of 78.25 g (0.1835 mole) of tetraphenyltin in 1.0 L of benzene that was stirred in a 2 L beaker on a magnetic stirrer hot plate, was added a hot solution of 180.2 g (1.0 mole) of mercuric bromide in 250 mL of tetrahydrofuran over a period of 2 min, during which time rapid precipitation of a white flaky solid produced. The mixture was stirred and heated for 5 min, then stirred without heating for 3 h. The mixture, the volume of which had been reduced to ca. 600 mL, was stored at 5°C overnight and filtered. The residue was washed with two 50 mL portions

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of benzene and dried in vacuum at 55°C for 4 h. This afforded 123 g (69%) of flaky, white phenylmercuric bromide, m.p. 283-285°C. The phenylmercuric bromide was used without further purification in the following reactions.

*Preparation of Phenyl(tribromomethyl)mercury.* Into a dry 1 L Morton flask, equipped with a high-speed stirrer, under an atmosphere of prepurified nitrogen were placed a mixture of 44.7 g (0.125 mole) of phenylmercuric bromide and 126.4 g (0.51 mole) of freshly distilled bromoform and 500 mL of benzene (freshly dried by molecular sieves). 9.75 g of solid potassium *tert*-butoxide was added with vigorous stirring and cooling in an ice bath, through a 2.5 cm diameter rubber connecting tube, over a 35 min period. The reaction mixture was stirred for an additional hour at 0°C and then the light yellow reaction mixture poured into 750 mL of distilled water. After standing for 7 h at 25°C, the mixture was filtered from 1.8 g of an off-white solid. The lower benzene phase of the filtrate was extracted with 250 mL of distilled water, while the aqueous phase was extracted with two 80 mL portions of benzene. The combined benzene phase and extracts were dried (MgSO<sub>4</sub>) for 4 h and rotary-evaporated at 25°C/20 torr to ca 125 mL. Filtration gave 29.8 g of a white, crystalline solid, m.p. 110-113°C (decomposed instantaneously after having partially melted). The yellow filtrate was concentrated to ca 25 mL, and the slow addition of 150 mL of *n*-hexane caused precipitation of a white and very fine crystalline solid, 26 g, m.p. 114-115°C. The filtrate from the latter was cooled to 0°C overnight and on filtration afforded 4.5 g of a cream-colored solid, m.p. 110-111°C (decomposed on melting); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 7.92(s, 5H) ppm. The total crude yield was 60.3 g (91%).

An analytical sample obtained in another preparation after four recrystallization from pentane/methylene chloride gave the material of m.p. 119-120°C (dec.); lit.<sup>7</sup> m.p. 98°C.

*Irradiation and Thermal Reaction of B<sub>10</sub>H<sub>14</sub> with Phenyl(tribromomethyl)mercury.* A 100 mL three-necked round-bottomed flask equipped with an additional funnel containing 25 mL of hexafluorobenzene, a reflux condenser, a nitrogen inlet/outlet tube, and a magnetic stirring bar was charged with 1.49 g (0.01 mole) of sodium iodide and 3.34 g (0.27 mole) of decaborane. A solution of 7.97 g (0.02 mole) of phenyl(tribromomethyl)mercury in 20 mL of carbon tetrachloride was added dropwise with stirring under nitrogen. The additional funnel containing the carbon tetrachloride solution of phenyl(tribromomethyl)mercury was shielded against light. During the addition, the reaction mixture was irradiated with a 350 W PHYWE high-pressure mercury lamp.

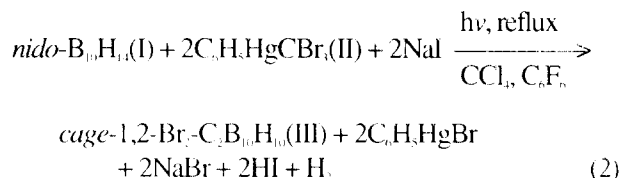
The solution became yellowish after ca 10 min of stirring with irradiation and slow evolution of gas was observed. The reaction mixture was irradiated continuously and heated to reflux under nitrogen for 20 h. In the course of run, a yellow precipitate formed. The residue obtained from the evaporation was extracted with hot benzene.

The precipitate was dried on a vacuum rotary evaporator and extracted with hot benzene and then cooled rapidly to

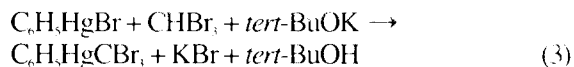
2°C. The product is very unstable at room temperature, however this is stable in methanol. The product was purified by flash column chromatography (10:1 and then 4:1 benzene/methanol) to give 2.81 g (82.7%) of a yellow solid: m.p. 74-76°C, <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ<sub>H</sub> 2.83(bs, 4,5,7,11 B-H), 2.01(bs, 8,9,10,12 B-H), 3.62(s, 3,6 B-H) ppm, <sup>11</sup>B-NMR (160.5 MHz, ref. BF<sub>3</sub> · Et<sub>2</sub>O, C<sub>6</sub>D<sub>6</sub>) δ<sub>B</sub> -2.79(bs, B 8,9,10,12), -1.04(bs, B 4,5,7,11), 8.10(bd, B 3,6) ppm, <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>) δ<sub>C</sub> 81.6 ppm.

## RESULTS AND DISCUSSION

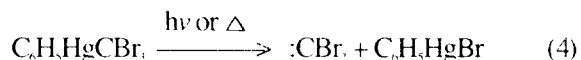
Irradiation of *nido*-decaborane(I) with phenyl(tribromomethyl)mercury(II) generated a new *cage*-compound III, which was isolated as an air sensitive, yellow solid product:



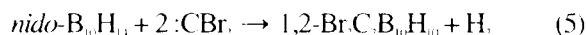
Dibromocarbene should be involved in this reaction. The dibromocarbene precursor, phenyl(tribromomethyl)mercury was generated as shown in Eq. (3).



Phenyl(tribromomethyl)mercury produces dibromocarbene easily in most cases of photolysis or thermal decomposition as shown in Eq. (4).



Eq. (1) shows that a *nido*-structure of B<sub>10</sub>H<sub>14</sub>(I) is expanded to the *cage*-structure of 1,2-Br<sub>2</sub>-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>(III). *nido*-B<sub>10</sub>H<sub>14</sub>(I) was expanded using a very reactive intermediate, :CBr<sub>2</sub> as shown in Eq. (5).



Reactive carbenes act as electrophiles, nucleophiles or ambiphiles.<sup>8</sup> Dihalocarbenes such as :CCl<sub>2</sub> and :CBr<sub>2</sub> seem to behave as electrophiles. However the relative reactivity and selectivity of dihalocarbenes depend on the intensity of light source and the temperature. It is known that the selectivity order of dihalocarbene based on the insertion reaction to the olefin showed as :CF<sub>2</sub> > :CCl<sub>2</sub> > :CBr<sub>2</sub> at 270 K,

however the order showed  $:\text{CBr}_2 > :\text{CCl}_2 > :\text{CF}_2$  at high temperature, 420 K.<sup>8</sup>

The yield of product III is influenced by irradiation and thermal conditions as shown in Table 1. Our results are contrary to the selectivity sequence of dihalocarbene which has been reported. The yield(%) increases with increasing reaction temperature as shown in Table 1. It seems to be caused by that B(6) and B(9) atoms in  $\text{B}_{10}\text{H}_{14}$  become more acidic centers comparing with other boron atoms<sup>9</sup> when a nucleophilic species ( $:\text{CBr}_2$ ) attacks to the *nido*-structure of  $\text{B}_{10}\text{H}_{14}$  closely as shown in Figure 1.

Two borons at 6- and 9- positions in decaborane might behave as electrophilic centers for reaction with dihalocarbenes, and then undergo intramolecular rearrangement to yield the expansion cluster compound.

Table 1. Yields of reaction of decaborane with dibromocarbene at various conditions

Conditions	Yield(%)	Relative yield
363K, $h\nu$	34 (20 h)	10.00
313K, $h\nu$	31 (20 h)	9.12
298K, $h\nu$	25 (20 h)	7.35
270K, $h\nu$	10 (20 h)	2.94
363K, (dark)	8 (72 h)	2.35
313K, (dark)	2 (72 h)	0.59
298K, (dark)	0 (72 h)	0.00
270K, (dark)	0 (72 h)	0.00

The observed formation of  $1,2\text{-Br}_2\text{C}_2\text{B}_{10}\text{H}_{10}$  as one product by the reaction of  $\text{B}_{10}\text{H}_{14}$  with a unique carbene was unexpected.

A reasonable reaction mechanism might be explained from this experimental results as shown in Figure 1.

The first step in this reaction is the addition of two molar equivalents of dibromocarbene produced from phenyl(tribromomethyl)mercury to *nido*- $\text{B}_{10}\text{H}_{14}$ , which then generates the product through loss of  $\text{H}_2$  as shown in Eq. (5).

The ten boron atoms of the *nido*-structure remain in a fixed state in their polyhedral arrangement before the cluster expansion.

The insertion of  $:\text{CBr}_2$  into *nido*- $\text{B}_{10}\text{H}_{14}$  probably proceeds through deprotonation of the acidic centers of B(9) and B(6) of *nido*- $\text{B}_{10}\text{H}_{14}$ , under the strong effect of lone electron pair of dibromocarbene.

After deprotonation, the cluster rearrangement from  $\text{I}_a$  to  $\text{I}_b$  occurs rapidly and then a new neutral bond between the two carbon atoms forms to give the final product, as shown in Figure 1.

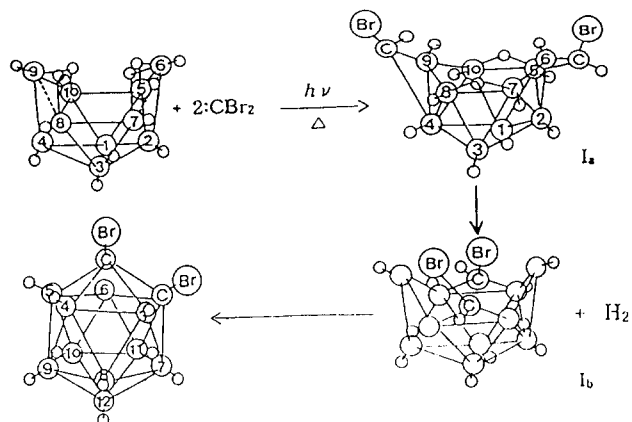


Figure 1. Proposed mechanism for formation of  $1,2\text{-Br}_2\text{C}_2\text{B}_{10}\text{H}_{10}$ .

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