

A PHOTOCHEMICAL REACTION OF DECABORANE WITH TRIMETHYLSILYLDIAZOMETHANE

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Abstract — The reaction of decaborane with trimethylsilyldiazomethane gives 1,2-bis(trimethylsilyl)-1,2-carba-closo-dodecaborane(12). This compound is similar to the icosahedral cage structure of *o*-carborane. This formation of the first adduct proceeds through deprotonation of the acidic center of B(9) and B(6) by intermolecular attack by the lone electron pair of the carbene, :CHSiMe₃. The yield of product is influenced by irradiation and thermal conditions.

INTRODUCTION

The reaction of decaborane(14) with acetylenic compounds in the presence of Lewis bases has resulted to give members of a class of organoboranes.¹ A typical reaction of 1,2-dicarbocloso-dodecaborane(12), (C₂B₁₀H₁₂) and its thermal rearrangement have been reported by Heying *et al.*²⁻¹⁰ The structure of this compound shows a regular icosahedron with two carbo atoms at adjacent vertices¹¹ as shown in Figure 1.

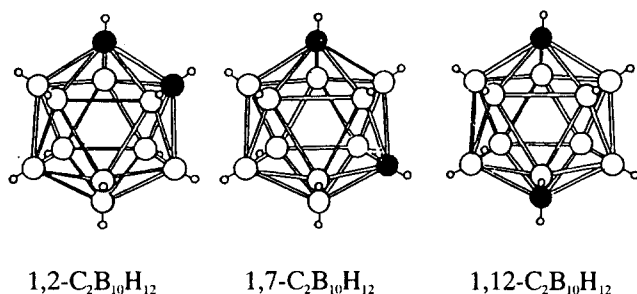


Figure 1. Structure of icosahedral carborane isomers.

Several groups¹²⁻¹³ have continuously discovered the new icosahedral *closo*-carborane isomers, 1,7-C₂B₁₀H₁₂ and 1,12-C₂B₁₀H₁₂ as shown in Figure 1. They are called *o*-carborane, *m*-carborane and *p*-carborane.

o-Carborane and its derivatives draw an interest in synthesis of new low molecular weight boron compounds for boron neutron capture therapy of cancer.¹⁴⁻¹⁶ The lipophilic clusters including *closo*-carborane derivatives have been synthesized for a useful medicine of boron neutron capture therapy¹⁷.

The formation of hexadecyl-*o*-carborane was synthesized by the reaction of 1-octadecyne and decaborane in the solution of acetonitrile and benzene.¹⁸ However, the yield was somewhat low (30%). A new medicine of boron neutron capture therapy was synthesized as a compound of 5-(1,2-dicarbocloso-dodecaborane(12)-1-yl)-2-aminopentanoic acid as a good receptor to bind the cancer cell selectively by using a alkylation approach to cage boron skeleton recently.¹⁹ The receptor compound is obtained *via* the reaction of alkylation of imidazolidine with a protected alkylsilyliodoalkylcarborane. Alkylsilylcarborane is a very important material for protecting reagent for the synthesis of receptor compounds.

After due consideration to the equivalency of electronic structure of a C-C and a Si-C unit, we synthesized the *closo*-species C₂B₁₀H₁₂ analogues and their silicon derivatives. From the photochemical and thermal reaction of trimethylsilyldiazomethane with decaborane, 1,2-bis(trimethylsilyl)-1,2-carba-closo-dodecaborane(12) was prepared and characterized.

MATERIALS AND METHODS

All manipulations for the reactions of trimethylsilyldiazomethane with decaborane were performed in an inert atmosphere of argon or nitrogen as described by Shriver.²⁰ All solvents were distilled from appropriate drying agents under a nitrogen atmosphere prior to use. NMR chemical shifts were shown relative to external BF₃·Et₂O (¹¹B), external Si(CH₃)₄ (²⁹Si), or residual ¹H in deuterated solvent.

Melting points were measured using samples in sealed capillaries and are uncorrected. Proton magnetic resonance (¹H-NMR) spectra were recorded on a Varian XL-400

spectrometer or a Bruker FT-300 MHz Aspect-300 spectrometer. Infrared absorption (IR) spectra were recorded on a Perkin-Elmer Model 683 grating spectrophotometer. Raman spectra were obtained using a Ramanov HG-2S spectrometer equipped with an ILA-2 Ar⁺ laser operating at 5145 Å as the exciting source. The exciting power was less than 100 mW.

Materials. Decaborane, *nido*-B₁₀H₁₄, was obtained from Aldrich and sublimed prior to use. Trimethylsilyldiazomethane (10% in hexane) purchased from Tokyo Kasei Kogyo Co. and purified by Hashimoto's method.²¹

Irradiation and thermal reaction of B₁₀H₁₄ with (CH₃)₃SiCHN₂. A 50 mL three-necked round-bottomed flask equipped with an additional funnel containing the toluene solution of trimethylsilyldiazomethane, a reflux condenser, a nitrogen inlet/outlet tube, and a magnetic stirringbar was charged with a solution of 0.500 g (4.1 mmol) of decaborane in 15 mL of dry toluene. A solution of 0.467 g (4.1 mmol) of (CH₃)₃SiCHN₂ in 5 mL of dry toluene was added dropwise with stirring under nitrogen. The additional funnel containing the toluene solution of trimethylsilyldiazomethane was shielded against the light. During the addition, the reaction mixture was irradiated with a Hanovia 450 W high pressure mercury lamp.

The solution became cloudy after *ca.* 5 min of stirring with irradiation and slow evolution of gas was observed. The reaction mixture was irradiated continuously and heated to reflux under argon for 10 h. In the course of run, white precipitate formed. The precipitate was filtered. The residue from the evaporation was extracted with two 10 mL portions of hot benzene. The precipitate was dried on a vacuum rotary evaporator and extracted with hot benzene and then cooled to 2°C. Purification by hot benzene gave 0.387 g of 1,2-bis(trimethylsilyl)-1,2-carba-*closo*-dodecaborane(12) as an amorphous white powder. Evaporation of the remaining benzene solution gave 0.42 g of white solid, identified as 6,9-(N₂CH₂SiMe₃)₂B₁₀H₁₂, on the basis of its ¹H and ¹¹B NMR and mass spectra. The solid that had precipitated during the reaction was sublimated at 80°C/0.5 Torr to give an additional 0.043 g of 1,2-bis(trimethylsilyl)-1,2-carba-*closo*-dodecaborane(12).

The total yield of 6,9-(N₂CH₂SiMe₃)₂B₁₀H₁₂ was 0.42 g (29.9%). The total yield of 1,2-bis(trimethylsilyl)-1,2-carba-*closo*-dodecaborane(12) was 0.43 g (37% yield, based on B₁₀H₁₄).

Characterization of 1,2-bis(trimethylsilyl)-1,2-carba-*closo*-dodecaborane(12). (a) Melting point (sealed capillary): 310-312°C; decomposition with gas evolution above 315°C. (b) Analysis: Calcd for C₈H₃₈B₁₀Si₂ (289.38 g/mol): C, 33.20; H, 10.02; Si, 19.41; B, 37.36. Found: C, 33.19; H, 10.03; Si, 19.40; B, 37.38 (c) Mass spectrometry (high resolution EI): C₈H₃₈¹¹B₁₀²⁸Si₂ (exact mass, 291.3092; observed mass, 291.3060); C₈H₃₈¹¹B₁₀²⁸Si³⁰Si (exact mass, 291.3092; observed mass, 291.3060); C₈H₃₈¹¹B₁₀²⁸Si³⁰Si (exact mass, 292.3092; observed mass, 292.3018); C₈H₃₈¹¹B₁₀²⁹Si³⁰Si (exact mass, 293.3092; observed mass, 293.3011); The peaks at the highest masses observed in the EI mass spectrum are at *m/z*=290 (25.8% relative

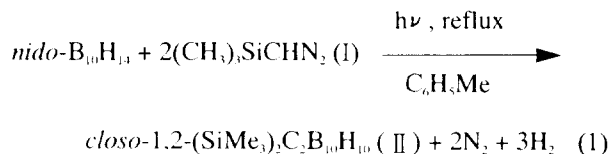
intensity), 296 (6.8) and 292 (1.2). (d) ¹H NMR spectrum (300MHz, CDCl₃) δ 0.053~1.22 (S, br, Si-Me₃); CD₂Cl₂, δ 0.69~1.28 (S, br, Si-Me₃), CDCl₃, 2.08~3.51 (several broad signals of B-H) ppm. (e) ²⁹Si NMR spectrum (99.34MHz, CDCl₃): proton-decoupled, at 45°C, δ⁻ -35.89 ppm. (f) ¹¹B NMR spectrum (ref. BF₃·Et₂O, 160.45 MHz, CDCl₃): at room temperature, δ_B⁻ -2.84 (d, B9,12), -1.23 (d, B8,10), 2.73 (S, B4,5,7,11), 8.12 (S, B3,6,) ppm.

Characterization of 6,9-(N₂CH₂SiMe₃)₂B₁₀H₁₂. (a) Melting point (sealed capillary): decomposition at 198-200°C with vigorous gas evolution. (b) Analysis: Calcd for C₈H₃₄B₁₀N₂Si₂: C, 27.40; H, 9.77; Si, 16.02; N, 15.98; B, 30.83. Found: C, 26.92; H, 9.75; Si, 15.98; N, 15.93; B, 30.54. (c) Mass spectrometry (high resolution EI): C₈H₃₄¹¹B₁₀¹⁴N₂²⁸Si₂ (exact mass, 352.3566; observed mass, 352.3528); C₈H₃₄¹¹B₁₀¹⁴N₂²⁸Si²⁹Si (exact mass: 353.3566; observed mass, 353.3524); The peaks at the highest masses observed in the EI mass spectrum at *m/z*=352(31.4% relative intensity) and 353 (8.9). (d) ¹H NMR spectrum (300 MHz, CDCl₃) δ -4.89 (S, br, 2H, BHB), 2.08~2.43 (several broad signals, BH), 0.048 (S, br, Si-Me₃), 1.96 (S, NBBH), 4.02 (S, br, NCH₂) ppm. (e) ²⁹Si NMR spectrum (99.34 MHz, CDCl₃): proton-decoupled, at 45°C -34.73 ppm. (f) ¹¹B NMR spectrum (ref. BF₃·Et₂O, 96.58 MHz), (CDCl₃): at room temperature, δ_B⁻ -52.24 (d, 1B), -18.71 (d, 2B), -12.37 (d, 2B), -3.78 (d, 1B) ppm.

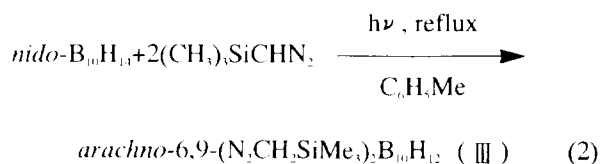
Calculation method. The standard procedure implemented in MOPAC version 6.0 program²² was used through in this work. Geometry of reactants product was fully optimized without any assumption, and characterized by confirming all positive eigenvalues in the Hessian (force constant) matrix.²³

RESULTS AND DISCUSSION

Irradiation of decaborane with trimethylsilyldiazomethane (I) generated *closo*-compound II, which was isolated as an air-stable, white solid product:



With the product (II), 6,9-(N₂CH₂SiMe₃)₂B₁₀H₁₂ (II) was formed concurrently as the minor component:



The yield of products II and III are varied with irradiation or thermal condition as shown in Table 1.

Table 1. Relative yields of reaction of decaborane with trimethylsilyldiazomethane

Product	Conditions	Yield (%)	Relative yield
II	383K, hν	37	1.00
	323K, hν	19	0.52
	293K, hν	5	0.14
	383K(dark)	0	0.00
III	383K, hν	34	1.00
	383K(dark)	34	1.00
	293K, hν	18	0.53
	293K(dark)	18	0.53

Irradiation of diazo compound (I) can lead to produce a reactive carbene intermediate as $(\text{Me}_3\text{SiCH:})$ but thermal reaction in dark room gives a less reactive azine intermediate as $\text{Me}_3\text{SiCH=N-N=CHSiMe}_3$.

Generally photochemical and thermal reaction of diazo compounds have been known to give different precursors. The thermal reaction of diphenyldiazomethane gives azine, while tetraphenylethylene is a major product under for photoreaction.²⁴

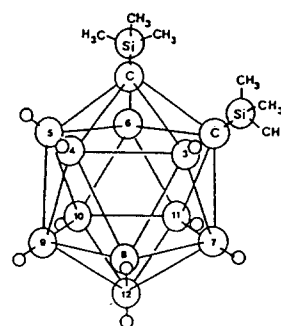
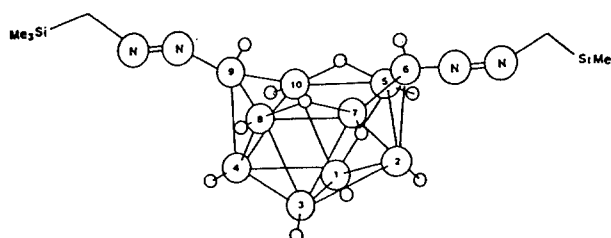
The compound, III was soluble only in solvents such as *N,N*-dimethylformamide and dimethyl sulfoxide. It melted with decomposition above 198°C. This results from weaker B-N bonding in the *arachno* structure. However, when *nido*- $\text{B}_{10}\text{H}_{14}$ was reacted with the diazo compound (I) with irradiation in toluene, white precipitate was formed after 10 h reflux. The structures of the reaction product II and III are shown in Figure 2.

The geometry-optimized MNDO calculation as shown in Table 2 suggest that the structure of II has a slightly distorted icosahedral structure.

Table 2. Intramolecular bond distances (Å) for II

Si(1) - C(1)*	1.856(1)	B(4) - B(9)	1.852(8)
Si(1) - C(3)	1.816(7)	B(4) - B(8)	1.788(1)
Si(1) - C(4)	1.814(7)	B(5) - B(6)	1.872(1)
Si(1) - C(5)	1.820(1)	B(5) - C(1)	1.738(1)
Si(2) - C(2)	1.856(1)	B(6) - B(11)	1.894(1)
Si(2) - C(6)	1.820(1)	B(7) - B(8)	1.755(8)
Si(2) - C(7)	1.816(6)	B(7) - B(11)	1.852(8)
Si(2) - C(8)	1.814(5)	B(8) - B(9)	1.831(5)
B(3) - C(2)	1.683(5)	B(8) - B(12)	1.867(7)
B(3) - B(4)	1.893(7)	B(9) - B(10)	1.867(7)
		C(1) - C(2)	2.316(4)

*Estimated standard deviations in the least significant figure are given in parentheses.

Closo-1,2-(SiMe₃)₂C₂B₁₀H₁₀Figure 2. *Arachno*-6,9-(N₂CH₂SiMe₃)₂B₁₀H₁₂ (III)

The C-C bond (2.316 Å) of II is longer than the C-C bond of *o*-carboranes (1.655 Å on the average).²⁵ The Si-C bond distances (1.827 Å, on the average) in II (Table 2) are very close to the results²⁶ of 1,2-dimethyl-1,2-disila-*closo*-dodecaborane(12). The B-B bond distances in II are very similar to the icosahedral cage structures of *o*-carboranes.

It is supported by the fact that C-Si bond distance is within the normal C-Si single bond range²⁷ and the bond angles about a pentagonal ring of B₅, B₄, B₅, B₆ and C₂ indicate a formal structure of cage compound (B(4)-B(3)-C(2) = 119.9(8)°; B(3)-B(4)-B(5) = 101.7(1)°; B(4)-B(5)-B(6) = 97.3(1)°) as shown in Table 3.

Table 3. Intramolecular bond angles °

B(4)-B(3)-C(2)	119.9(8)	B(9)-B(8)-B(12)	56.0(1)
B(3)-B(4)-B(5)	101.7(1)	B(5)-C(1)-Si(1)	122.5(7)
B(4)-B(5)-B(6)	97.3(1)	B(3)-C(2)-Si(2)	123.3(5)
B(4)-B(5)-C(1)	54.8(1)	C(1)-Si(1)-C(3)	111.7(2)
B(3)-B(4)-B(8)	62.1(2)	C(1)-Si(1)-C(5)	110.1(1)
B(4)-B(8)-B(9)	61.9(1)	C(1)-Si(1)-C(4)	112.5(2)
B(8)-B(9)-B(10)	106.2(9)	C(2)-Si(2)-C(8)	112.5(2)
B(4)-B(8)-B(7)	114.5(6)	C(2)-Si(2)-C(6)	110.0(2)
B(8)-B(7)-B(11)	108.8(6)	C(2)-Si(2)-C(7)	111.7(2)

° Angles are in degrees. Estimated standard deviations in the least significant figure are given in parenthesis.

Other bond angles of B-B-B and B-B-C in Table 3 are similar to the cage icosahedral compounds.²⁸ The ¹¹B NMR spectrum, taken in CDCl₃ solution, showed the four peaks at δ_B -2.84, -1.23, 2.73 and 8.12 ppm. The Si-Me₃ peak showed at δ 0.053 ~ 1.22 in the ¹H NMR spectrum of **II** in CDCl₃, moved downfield as the solvent polarity was changed: to 0.69~1.28 ppm in CD₂Cl₂. The IR spectrum of **II** was measured in the region 450 - 3500 cm⁻¹ and its Raman spectrum was also obtained in the region of 400 - 3600 cm⁻¹. The polarization measurements of Raman lines were carried out for its saturated solution in benzene. The results are given in Figures 3, 4 and Table 4.

Table 4. Vibrational spectrum of 1,2-bis(trimethylsilyl)-1,2-carba-*closo*-dodecaborane (**12**)

solid sample $\Delta\nu, \text{cm}^{-1}$	Raman		IR vacuum sublimation on cold target ν, cm^{-1}
	solution in benzene $\Delta\nu, \text{cm}^{-1}$	ρ	
152 m			
280 sh			
306 w	326	0.80	304 w
329 s			328 s
399 vs			399 s
449 w			448 s
503 m	504	0.12	503 w
550 m	552	0.62	
587 m			578 w
610 w			610 vw
645 m		p	659 w
686 w			689 w
716 s	713	0.03	718 m
758 w			752 sh
			759 m
773 w			775 w
792 w			793 vs
841 w			848 m
860 w			862 w
895 w			886 vs
920 w			916
924 s	923	0.27	922 vs
			957 w
1010 w			1010 vs
1260 w			1246 w
1392 w			1395 m
2547 s	2549	0.16	2548 vs
2556 vs			2564 vs
2913 m			2908 s
2942 m			
2994 w br			2991 w

Abbreviation: s=strong, sh=shoulder, w=weak, m=medium, vs=very strong

The most prominent features of the vibrational spectra of all cage *closo*-boranes are the $\nu(\text{BH})$ multiplet in the region 2490-2520 cm⁻¹ and the polyhedron "breathing" mode near 780 cm⁻¹. In the case of **II** the $\nu(\text{BH})$ medium bands show near

2548cm⁻¹ and the "breathing" mode at near 690 cm⁻¹, both features being markedly shifted to lower frequencies compared to *o*-carborane. The frequency shifts seem to be caused by weakening of molecular bonding in **II** as compared to that in *o*-carborane. The most intense band in the Raman spectrum is the strongly polarized at 2556 cm⁻¹, which corresponds to that of $\nu(\text{C-C})$ mode of metalloporphyrin²⁹. It seems reasonable to assign this line to the C(1)-C(2) stretching mode. However, this assignment is tentative and needs to be proved by a normal coordinate analysis.

The polarized Raman line at 923 cm⁻¹ seems to be the symmetrical stretch of the exo-polyhedral Si-C bands. This frequency lies in the usual range of Si-C bonds and is similar to that of the $\nu(\text{Si-C})$ mode in Si(CH₃)₄³⁰ and (CH₃)₃SiCl³¹. The formation of **II** as one product of the reaction of decaborane with a diazo compound (**I**) was unexpected and its reaction mechanism seems to be complicated. A reasonable interpretation of formation of **II** is under investigation. However, a reaction mechanism for the formation of **II** is proposed as follows. The first step in this reaction (eq.1) is the addition of two molar equivalent of **I**, a Lewis base, to *nido*-B₁₀H₁₄. Adduct **Ia** was generated through loss of H₂ and N₂ as

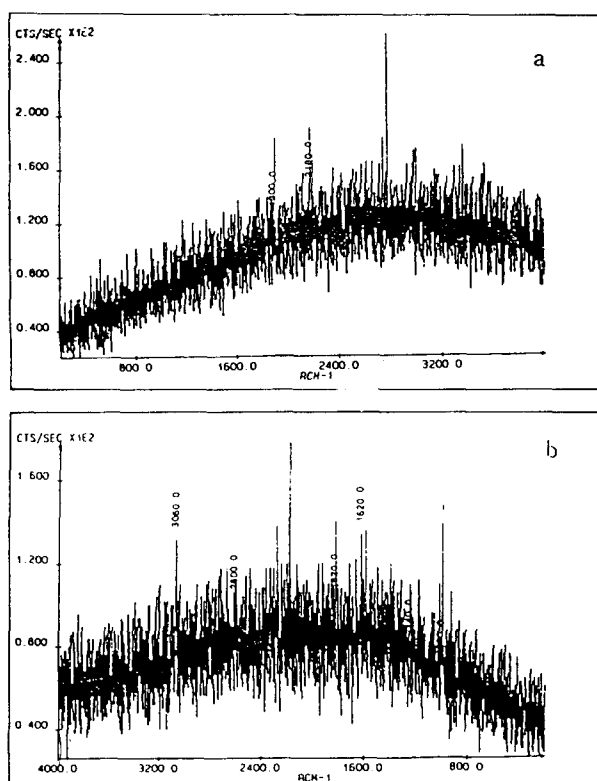


Figure 3. Raman spectra of 1,2-bis(trimethylsilyl)-1,2-dicarba-*closo*-dodecaborane. (a; solid sample, b; solution in benzene)

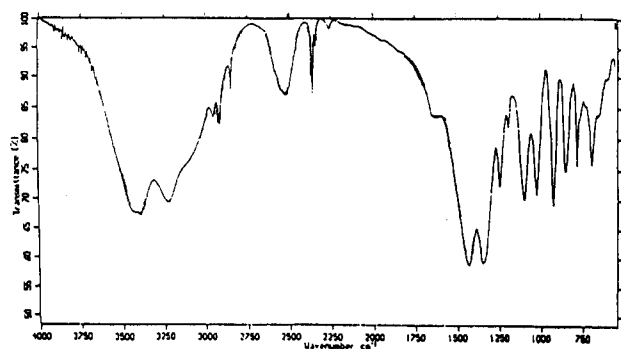
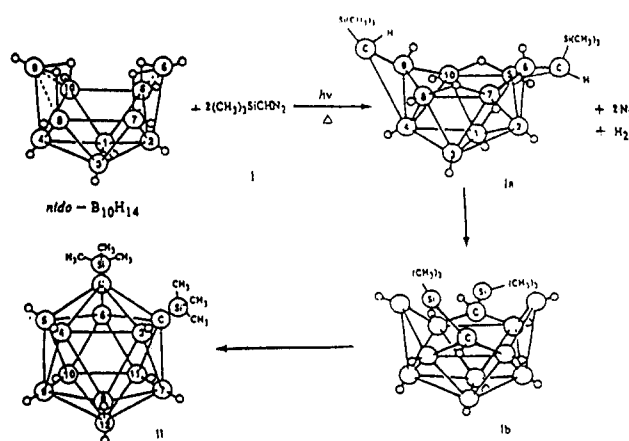


Figure 4. Infrared spectrum of 1,2-bis(trimethylsilyl)-1,2-dicarba-closo-dodecaborane.

shown in Scheme I. The ten boron atoms of *nido*-structure remain as fixed state in their polyhedral arrangement during this cluster expansion. The formation of Ia adduct proceeds through deprotonation of the acidic center of B (9) and B (6) by intermolecular attack of the lone electron pair of the carbene, :CHSiMe₃. Deprotonations of analogous Ia adduct have been reported by Hawthorne *et al.*^{10,32} Rapid rearrangement of neutral BBCHSiMe₃ bond from Ia occurs to produce Ib as depicted in Scheme 1.



Scheme 1.

As the final step which results in the formation of II, the two carbon centers make a new bond closely to form the final icosahedral compound.

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