

The infrared spectrum (Nujol mull) of the solid included absorptions at 2519 (s), 2048 (s), 1940 (s), 1022 (w), 982 (w), and 948 (m) cm^{-1} .

Analytical data and solution infrared absorptions in the carbonyl region for the π -(3)-1,2-dicarbollymolybdenum and -tungsten carbonyl derivatives are given in Tables XVI and XVII.

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The Reconstruction of the 1,2-Dicarboclovododecaborane(12) Structure by Boron-Atom Insertion with (3)-1,2-Dicarbollide Ions

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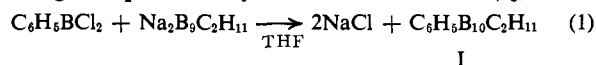
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Abstract: A series of (3)-1,2-dicarbollide ions were employed with phenylboron dichloride or ethylboron dichloride to reconstitute the 1,2-dicarboclovododecaborane(12) icosahedron. This boron insertion reaction yields B-substituted 1,2-dicarboclovododecaborane(12) derivatives which were further degraded to 6-substituted (3)-1,2-dicarboclovododecaborane(12) ions. The latter ions were converted to the corresponding (3)-1,2-dicarbollide ions which were employed in subsequent insertion reactions and in the formation of a representative transition metal derivative.

Previous reports of the chemistry of the (3)-1,2-dicarbollide ion¹⁻⁷ and its carbon-substituted derivatives have dealt with the formation of transition metal complexes which resemble the π -bonded metallocenes. We now wish to amplify our earlier report⁸ of the reaction of the (3)-1,2-dicarbollide ion with phenylboron dichloride which led to the first synthesis of B-aryl derivatives of the 1,2-dicarboclovododecaborane(12) system by boron-atom insertion. The only previously reported derivatives of 1,2-dicarboclovododecaborane(12) which bear an organic substituent on boron were 8- and 9-ethyl-1,2-dicarboclovododecaborane(12) which were obtained as a mixture from the reaction of 1- and 2-ethyldecaborane(14) with acetylene and not separated.⁹

Results and Discussion

Phenylboron dichloride and the (3)-1,2-dicarbollide ion reacted in tetrahydrofuran (THF) solution to produce 3-phenyl-1,2-dicarboclovododecaborane(12) (I) according to eq 1. The yields of I were 80–85%, while



(1) M. F. Hawthorne, D. C. Young, and P. A. Wegner, *J. Am. Chem. Soc.*, **87**, 1818 (1965).

(2) M. F. Hawthorne and R. L. Pilling, *ibid.*, **87**, 3987 (1965).

(3) M. F. Hawthorne and T. D. Andrews, *Chem. Commun.*, 443 (1965).

(4) M. F. Hawthorne and T. D. Andrews, *J. Am. Chem. Soc.*, **87**, 2496 (1965).

(5) P. A. Wegner and M. F. Hawthorne, *Chem. Commun.*, 861 (1966).

(6) L. F. Warren and M. F. Hawthorne, *J. Am. Chem. Soc.*, **89**, 470 (1967).

(7) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *ibid.*, **90**, 879 (1968).

(8) M. F. Hawthorne and P. A. Wegner, *ibid.*, **87**, 4392 (1965).

(9) T. L. Heying, J. W. Ager, Jr., S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *Inorg. Chem.*, **2**, 1089 (1963).

the recovery of sodium chloride based upon the above equation was quantitative. Other B-phenyl derivatives of substituted 1,2-dicarboclovododecaborane(12) were prepared in analogous reactions. The 1,2-dimethyl-(3)-1,2-dicarbollide and the 1-phenyl-(3)-1,2-dicarbollide ions reacted with phenylboron dichloride to produce 3-phenyl-1,2-dimethyl-1,2-dicarboclovododecaborane(12) (II) and 1,3-diphenyl-1,2-dicarboclovododecaborane(12) (III) in 55 and 38% yield, respectively. A B-ethyl derivative, 3-ethyl-1,2-dicarboclovododecaborane(12) (IV), was formed in 49% yield from ethylboron dichloride and the (3)-1,2-dicarbollide ion.

The preparation of compounds I–IV illustrated that the insertion reaction was successful using the (3)-1,2-dicarbollide ion and its carbon-substituted derivatives with both aryl- and alkylboron dichlorides. The B-phenyl-substituted derivatives (I–III) were sublimable, white crystalline solids, while the B-ethyl derivative was a viscous liquid. The B-substituted derivatives, in general, have physical properties comparable to those of the corresponding B-unsubstituted 1,2-dicarboclovododecaborane(12) derivatives.

The characterization data for I–IV are presented in Table I. An osmometric molecular weight determination of I was in good agreement with theory (calculated 220, found 227). The infrared spectra of I–IV contained B–H stretching bands in the 2550–2580- cm^{-1} region of the infrared spectrum. Compounds I, II, and III contained absorption bands characteristic of a monosubstituted phenyl ring near 700 cm^{-1} while I, III, and IV contained an absorption band due to the carbonyl carbon–hydrogen stretch at 3000 cm^{-1} .

The ¹H nmr spectra of I–IV presented in Table II confirmed their formulation as B-substituted 1,2-dicarboclovododecaborane(12) derivatives. Integration of these spectra proved that the original substituents on the carbon atoms of the precursor (3)-1,2-dicarbollide ion

Table I. Elemental Analyses

Compound	C, %		H, %		B, %		N, %	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
1,2-Dicarbaclvododecaborane(12) Derivatives								
3-Phenyl (I)	43.65	43.61	7.28	7.46	49.20	49.13
3-Phenyl-1,2-dimethyl (II)	48.40	48.67	8.06	8.46	43.60	43.64
1,3-Diphenyl (III)	56.69	56.47	6.80	6.99	36.51	36.82
3-Ethyl (IV)	27.85	28.33	9.36	9.57	62.79	62.62
3,6-Diphenyl (VIII)	56.69	56.98	6.80	7.14	36.51	36.56
3,6-Diphenyl-1,2-dimethyl (IX)	59.25	59.18	7.41	4.37	33.34	33.13
Tetramethylammonium (3)-1,2-Dicarbadodecahydroudecaborate(-1) Derivatives								
6-Phenyl (V)	50.84	50.81	9.91	10.05	34.40	34.68	4.95	4.91
6-Phenyl-1,2-dimethyl (VI)	54.00	54.34	10.30	10.66	31.20	31.17	4.51	4.55
6-Ethyl (VII)	40.74	40.52	11.98	12.10	41.33	41.10	5.95	5.86
(CH ₃) ₄ N[(C ₆ H ₅ B ₉ C ₂ H ₁₀) ₂ Co] ^a (X)	43.63	43.62	7.70	7.54	35.41	35.65	2.55	2.87

^a Anal. Calcd: Co, 10.71. Found: Co, 10.54.

Table II. ¹H Nmr Spectra Determined at 60 Mc/sec Relative to Tetramethylsilane

Compound	Solvent	Cage C-H, ppm (wt)	Cage C-CH ₃ , ppm (wt)	B-C ₆ H ₅ , ppm (wt)	B-C ₂ H ₅ , ppm (wt)	(CH ₃) ₄ N, ppm (wt)
1,2-Dicarbaclvododecaborane(12) Derivatives						
3-Phenyl (I)	CCl ₄	-3.54 (1.00)	...	-7.41 ^a (2.38)
3-Phenyl-1,2-dimethyl (II)	Cl ₂ C=CHCl	...	-1.80 (1.20)	-7.41 ^a (1.00)
1,3-Diphenyl (III)	CCl ₄	-4.18 (1.00)	...	-7.10 (8.20) ^b
3-Ethyl (IV)	CS ₂	-2.38 (1.00)	-0.80 (2.56)	...
3,6-Diphenyl (VIII)	CCl ₄	-3.67 (1.00)	...	-7.41 ^a (4.09)
3,6-Diphenyl-1,2-dimethyl (IX)	CCl ₄	...	-1.65 (1.00)	-7.53 ^a (1.63)
Tetramethylammonium (3)-1,2-Dicarbadodecahydroudecaborate(-1) Derivatives						
6-Phenyl (V)	CH ₃ NO ₂	-2.08 (2.06)	...	-7.55 (2.11)	...	-3.18 (11.72)
6-Phenyl-1,2-dimethyl (VI)	CH ₃ NO ₂	...	-1.13 (1.26)	-6.86 ^a (3.14)	...	-3.18 (2.76)
6-Ethyl (VII)	C ₆ H ₅ N	-2.07 (1.00)	-1.07 (2.41)	-3.28 (5.83)
(CH ₃) ₄ N[(C ₆ H ₅ B ₉ C ₂ H ₁₀) ₂ Co] (X)	C ₆ H ₅ N	-4.26 (1.99)	...	-7.67 (1.92)	...	-3.35 (5.83)

^a Multiplet centered at reported ppm. ^b Phenyl groups bonded to boron and carbon atoms.

were present in I-IV in the expected ratios. This result requires the phenyl or ethyl substituent group of I-IV be bonded, as expected, to a boron atom in the 1,2-dicarbaclvododecaborane(12) icosahedron. The ¹H nmr spectra of I-III contained a resonance of relative area 5 due to a phenyl group while the presence of a broad ethyl group resonance of relative area 5 was observed in the ¹H nmr spectrum of IV.

The ¹¹B nmr spectra of I-IV at 32 Mc/sec have no definitive structural significance. The expected singlet resonance due to the substituted boron atom of I-IV was not clearly observed. However, the ¹¹B nmr spectra of I and IV are very similar, and it is likely that these two derivatives bear their respective organic substituents in the same position.

The (3)-1,2-dicarbollide ion has been shown by X-ray diffraction studies¹⁰ of its metal complexes to have a vacant 3 position. Since I-IV are completed icosahedra, the organic moiety is most likely bonded to the 3-boron atom in the product. The remote possibility that the position of the phenyl or ethyl group substituents is shifted through a rearrangement of the formed icosahedral 1,2-dicarbaclvododecaborane(12) is unlikely since the rearrangement of 1,2-B₁₀C₂H₁₂ derivatives has not been observed¹¹ to take place below 400°. Based upon these assumptions and the behavior of the boron-substituted carborane derivatives toward bases

(10) See ref 7 for a summary of X-ray diffraction results.

(11) D. Grafstein and J. Dvorak, *Inorg. Chem.*, **2**, 1128 (1963).

(*vide infra*), I-IV have been formulated as 3-substituted 1,2-dicarbaclvododecaborane(12) derivatives represented in Figure 1.

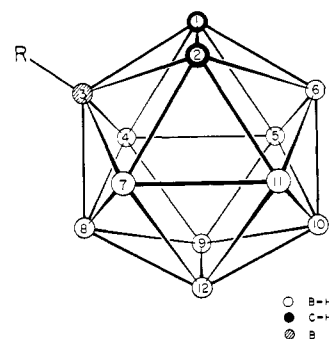


Figure 1. Schematic drawing of 3-substituted 1,2-dicarbaclvododecaborane(12) derivatives.

Alkoxide ions^{12,13} or amines^{14,15} such as piperidine degrade 1,2-dicarbaclvododecaborane(12) derivatives to form the corresponding (3)-1,2-dicarbadodecahydro-

(12) R. A. Wiesboeck and M. F. Hawthorne, *J. Am. Chem. Soc.*, **86**, 1642 (1964).

(13) M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, *ibid.*, **90**, 862 (1968).

(14) L. I. Zakharin and V. N. Kalmin, *Tetrahedron Letters*, 407 (1965).

(15) M. F. Hawthorne, P. A. Wegner, and R. C. Stafford, *Inorg. Chem.*, **4**, 1675 (1965).

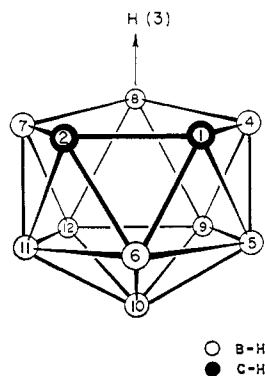
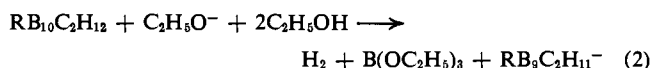


Figure 2. Schematic drawing of proposed (3)-1, 2- $B_9C_2H_{12}^-$ ion.

undecaborate(-1) ions, (3)-1,2- $B_9C_2H_{12}^-$, by removal of one of the equivalent 3- or 6-boron atoms¹⁶ which are nearest neighbors of the two carbon atoms (Figure 2). Having presumably obtained 3-substituted 1,2-dicarboclovdodecaborane(12) derivatives, it was of interest to examine the course of the base degradation reaction^{12,13} with these materials. On an *a priori* basis, one would expect either of the boron atoms (substituted 3- or unsubstituted 6-) which are nearest neighbors of the two carbon atoms to be removed by the action of the base. Accordingly, compounds I, II, and IV were examined in their reaction with ethanolic hydroxide ion at the reflux temperature. In each case, degradation proceeded smoothly in accord with eq 2 ($R = \text{phenyl or ethyl}$), and no phenyl or ethyl boronic acids or their derivatives were observed among the products. The



fact that the organic substituent attached to boron remains within the product anion strongly suggested that the 6-boron atom¹⁷ is removed from the 3-substituted 1,2-dicarboclovdodecaborane(12).

The tetramethylammonium salts of 6-phenyl-(3)-1,2-dicarbododecahydroundecaborate(-1) (V), 6-phenyl-1,2-dimethyl-(3)-1,2-dicarbododecahydroundecaborate(-1) (VI), and 6-ethyl-(3)-1,2-dicarbododecahydroundecaborate(-1) (VII) were employed for characterization purposes. The analytical data pertinent to V-VII are presented in Table I and agree with the proposed formulation of the salts. The infrared spectra of V and VI contained absorption bands attributable to a monosubstituted phenyl ring at 700 cm^{-1} , while those of V and VII contained an absorption due to the carboranyl carbon-hydrogen stretching at 3000 cm^{-1} . The B-H stretching bands of V-VII were in the $2500\text{--}2520\text{ cm}^{-1}$ region.

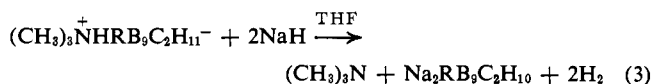
The 1H nmr spectra of V-VII presented in Table II also support the formulation of these species as substituted $B_9C_2H_{12}^-$ derivatives. The integration ratios obtained from the three spectra indicated one tetra-

(16) The numbering system employed in this and previous papers (ref 7 and 13) of this series has arbitrarily named the resulting product ion as though the 3-boron were removed exclusively. This point is illustrated by the numbering system assigned to the $B_9C_2H_{12}^-$ ion shown in Figure 2, and the two carbon atoms thus remain at positions 1 and 2 and the "hole" is denoted by the prefix (3)-.

(17) Using our previously employed numbering system, these ions could be identified as either 3-substituted (6)-1,2- or 6-substituted (3)-1,2-dicarbododecahydroundecaborate(-1) ions. For consistency, we will employ the latter designation throughout this paper.

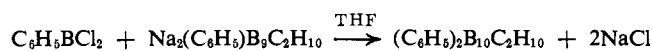
methylammonium group per B_9 unit, thus confirming a charge of -1 for the anion. These data also proved the presence of two equivalent carboranyl carbon substituents (H for V, VII; CH_3 for VI) as well as a phenyl (V, VI) and ethyl (VII) group bonded to a boron atom. The resonances of the carboranyl carbon hydrogen atoms in V and VII were in the same region of the spectrum (*ca.* -2 ppm relative to tetramethylsilane) as the carboranyl hydrogen atoms found in the (3)-1,2- $B_9C_2H_{12}^-$ ion.¹³ This fact, plus the equivalence of the carboranyl carbon atom substituents, are in complete agreement with the assigned structures.

The ^{11}B nmr spectra of V-VII at 32 Mc/sec were generally uninformative and consisted of badly overlapped doublets. However, in all three examples, a doublet was discerned at high field centered at $36.5\text{--}37\text{ ppm}$ (relative to $BF_3O(C_2H_5)_2$) with $J \sim 155\text{ cps}$. The ^{11}B nmr spectra of V and VII were remarkably similar in all respects, and this fact points to a gross similarity in structure. The 6-substituted (3)-1,2- $B_9C_2H_{12}^-$ ions (V-VII) should contain the unique hydrogen^{7,13} (Figure 2) present in the boron unsubstituted (3)-1,2- $B_9C_2H_{12}^-$ ions. As in the case of the parent ion,⁷ this hydrogen atom could be removed as a proton to form 6-substituted (3)-1,2-dicarbollide ions. Accordingly, the trimethylammonium salts of V and VI were allowed to react with sodium hydride in tetrahydrofuran (THF) to form $RB_9C_2H_{10}^{-2}$ derivatives (eq 3). The 6-substituted (3)-1,2-dicarbollide ions were



not isolated but generated *in situ* and employed in further reactions.

The (3)-1,2-dicarbollide ions generated from V and VI reacted with phenylboron dichloride to form compounds of the composition $(C_6H_5)_2B_{10}C_2H_{10}$ and $(C_6H_5)_2B_{10}C_2H_8(CH_3)_2$ which were assigned the structures 3,6-diphenyl-1,2-dicarboclovdodecaborane(12)

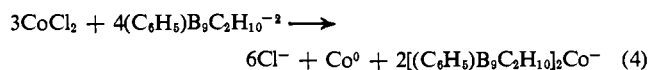


(VIII) and 3,6-diphenyl-1,2-dimethyl-1,2-dicarboclovdodecaborane(12) (IX), respectively. The analytical results (Table I) are in agreement with the above formulation of VIII and IX. The infrared spectra of VIII and IX contained absorptions due to a monosubstituted phenyl ring (700 cm^{-1}). The 1H nmr spectra of VIII and IX (Table II) indicated that the compounds contained two phenyl rings per carborane nucleus which were not bonded to carbon atoms, but to boron atoms.

Since VIII and IX most likely contain substituents at positions of 1,2-dicarboclovdodecaborane(12) which are attacked by base,¹²⁻¹⁵ the degradation reaction^{12,13} was again examined. Piperidine was chosen as the degradation reagent since it has been shown to be more effective^{14,15} in reactions of this type than is hydroxide ion in ethanol. Both VIII and IX were heated at the reflux temperature in piperidine solution for a 1-week period. In each case, VIII and IX were recovered unchanged. Under equivalent conditions, boron unsubstituted derivatives of 1,2-dicarboclovdodecaborane(12) are quantitatively converted to the corresponding $B_9C_2H_{12}^-$ derivatives.¹⁴

The resistance of VIII and IX to base degradation and the specific removal of the unsubstituted 6-boron atom of I, II, and IV by ethanolic hydroxide ion appear to be manifestations of the same phenomena. It is quite likely that steric requirements are paramount in determining the course of the base reaction of both the B-mono- and B,B'-disubstituted derivatives. Since the base must attack the carborane nucleus from the front side it is not unreasonable to suggest that substituted 3- and/or 6-boron atoms are protected by steric repulsion of the substituent and attacking base.

The 6-phenyl-(3)-1,2-dicarbollide ion derived from V was allowed to react with anhydrous cobaltous chloride to form the bis(π -6-phenyl-(3)-1,2-dicarbolly)cobalt(III)(-1) ion (X) which was isolated as its yellow tetramethylammonium salt (eq 4). The analytical data



(Table I) and infrared spectrum of tetramethylammonium X support its proposed formulation. The absorption due to a monosubstituted phenyl ring is present in the infrared spectrum at 700 cm^{-1} . The ^1H nmr spectrum of tetramethylammonium X (Table II) contains resonances associated with a tetramethylammonium cation, two phenyl groups bonded to boron atoms, and four carboranyl carbon hydrogen units. The formation of X proves that substitution at the 6 position does not interfere with the formation of transition metal complexes of the dicarbollide ion.

The ^1H nmr spectra of IV-VII and X are presented in Table II. In the ^1H nmr spectrum of IV, the broad resonance of weight 2.0 at -2.38 ppm was assigned to the two carboranyl carbon hydrogen atoms, while the broad resonance of weight 5.0 at -0.80 ppm was assigned to the ethyl group protons. In the ^1H nmr spectrum of VII, besides the resonances due to the tetramethylammonium protons (weight 12.0) at -3.28 ppm and the two equivalent carboranyl carbon hydrogen atoms at -2.07 ppm (weight 2.0), a single broad resonance (weight 5.0) at -1.07 ppm was assigned to the ethyl group protons. In the spectra of both IV and VII, the ethyl group resonance was broad ($\sim 7\text{ cps}$) and symmetrical and fine structure was absent. The chemical shifts of the methylene and methyl protons are coincident or nearly coincident, and the protons of these two groups have been decoupled. This type of phenomenon has previously been observed for ethyldiborane,¹⁸ ethylboron difluoride,¹⁹ and other substituted boranes and diboranes.¹⁸ The decoupling of the methylene and methyl group protons has been interpreted in terms of relaxation by the quadrupole moment of the ^{11}B nucleus.¹⁹ The chemical shift difference between the two sets of protons in an ethyl group bonded to a boron atom has been interpreted in terms of the hybridization of the boron atom and the electronic effects of other substituents upon the substituted boron atom.¹⁹ In the ^1H nmr spectra of IV and VII, the quadrupole moment of the ^{11}B nucleus undoubtedly has a predominant role in the severe decoupling of the methyl and methylene protons of the substituent ethyl group. Since the interpretation of the chemical shift difference between methyl and methylene protons of ethyl groups

bonded to boron atoms is based upon simple systems containing only one or two boron atoms, it would be improper to apply this interpretation to the substituted boron atoms of IV and VII which are in complex environments.

The ^1H nmr spectra of V and X are as expected except that the phenyl group in both compounds presents two sets of resonances; a broad, weakly structured resonance of weight 2 near -7.60 ppm and a multiplet of weight 3 near -7.30 ppm . The resonance near -7.60 ppm is severely decoupled, and it is likely that in the ^1H nmr spectra of V and X the same phenomenon which perturbs the ethyl group resonances of IV and VII also perturbs the substituent phenyl group resonances. Lindner and Onak²⁰ report in a study of alkyl-substituted boron derivatives that the decoupling and broadening effect is sharply decreased past the β position of the alkyl chain. In V and X, the *ortho* protons of the phenyl ring are β protons relative to the boron atom to which the phenyl group is attached. Therefore, the broad resonance of weight 2 at -7.60 ppm has been assigned to the *ortho* protons of the phenyl ring, while the multiplet of weight 3.0 at -7.30 ppm has been assigned to the *meta* plus the *para* protons of the phenyl ring.

Finally, it should be noted that the ^{11}B nmr spectra of I-IX did not clearly exhibit the singlet resonance due to the presence of substituted boron atom(s). This is not surprising as at the magnetic field strengths used the observable chemical shift difference of the nonequivalent boron atoms in 1,2-dicarboclovododecaborane(12) derivatives are comparable to the ^{11}B -H J values. The singlet resonance due to aryl or alkyl substitution at a boron atom would be clearly observed only if it were shifted away from the other boron resonances and this condition did not prevail.

Experimental Section

Materials and Methods. The trimethylammonium salts of (3)-1,2- $\text{B}_9\text{C}_2\text{H}_{12}^-$ and its 1,2-dimethyl and 1-phenyl derivatives were prepared as described elsewhere.¹⁸ Phenylboron dichloride was purchased from the Alpha Chemical Co. Ethylboron dichloride was kindly donated by the American Potash and Chemical Co. Tetrahydrofuran was distilled from lithium aluminum hydride and stored under nitrogen. Sodium hydride as a 56% dispersion in mineral oil was obtained from Metal Hydrides, Inc. Osmometric molecular weight determinations employed benzene solvent and 1-phenyl-1,2-dicarboclovododecaborane(12) as a standard.

Infrared spectra were determined using Perkin-Elmer Model 137 and Beckman Model IR-5 spectrophotometers. The ^1H nmr spectra were obtained using a Varian A-60 spectrometer and the ^{11}B nmr spectra with a Varian HA-100 spectrometer. Vapor phase chromatography was carried out using an Aerograph Model A-350-B gas chromatograph equipped with a 10-ft Apiezon L column. For preparative purposes, the Apiezon L column was 0.25 in. in diameter, while for analytical purposes it was $1/8$ in. in diameter.

General Procedure for the Insertion Reaction. 3-Phenyl-1,2-dicarboclovododecaborane(12) (I). The procedure for the formation of tetrahydrofuran solutions of the various dicarbollide ions and the addition of RBCl_2 (R = ethyl and phenyl) to these solutions is general for the insertion reaction. This general procedure is illustrated with the preparation of 3-phenyl-1,2-dicarboclovododecaborane(12) (I).

A tetrahydrofuran solution of $\text{Na}_2\text{B}_9\text{C}_2\text{H}_{11}$ was prepared in a 300-ml, three-necked, round-bottom flask equipped with a condenser, magnetic stirring bar, nitrogen bubbler, and pressure-equalized addition funnel. Sodium hydride (1.51 g, 0.063 mole; 2.70 g of a 56% dispersion in mineral oil) was washed twice with 30 ml of tetrahydrofuran to remove the mineral oil and was then

(18) H. H. Lindner and T. Onak, *J. Am. Chem. Soc.*, **88**, 1890 (1966).

(19) T. C. Coyle and F. G. A. Stone, *ibid.*, **83**, 4138 (1961).

(20) H. H. Lindner and T. Onak, *ibid.*, **88**, 1890 (1966).

immediately transferred with a total of 90 ml of tetrahydrofuran into the reaction flask. A solution of 5.0 g (0.0259 mole) of $(\text{CH}_3)_2\text{NHB}_9\text{C}_2\text{H}_{12}$ ¹⁸ dissolved in 75 ml of tetrahydrofuran was placed in the addition funnel and added to the sodium hydride. After the addition, the reaction mixture was stirred at the reflux temperature under nitrogen for 3 hr. Nearly complete removal of trimethylamine was achieved by passing a stream of nitrogen over the reaction solution and out through the condenser during the final 30 min of the reflux period. After the reaction mixture had cooled to ambient temperature and the excess sodium hydride had separated, the supernatant tetrahydrofuran solution of $\text{Na}_2\text{B}_9\text{C}_2\text{H}_{11}$ was ready for use.

Phenylboron dichloride (4.50 g, 0.0283 mole) was weighed and transferred into a 50-ml single-necked, round-bottom flask in a glove box under a nitrogen atmosphere. The flask was sealed with a vacuum line adapter bearing a stopcock and a vacuum line, frozen with a Dry Ice-acetone bath, and evacuated to remove any traces of hydrogen chloride which might have arisen from hydrolysis of the boron dichloride. After evacuation, the flask was sealed by closing the stopcock of the adapter, and the phenylboron dichloride was allowed to warm to room temperature.

The tetrahydrofuran solution of $\text{Na}_2\text{B}_9\text{C}_2\text{H}_{11}$ was decanted under nitrogen from the excess sodium hydride into a 500-ml, single-necked, round-bottom flask equipped with a magnetic stirring bar. The 500-ml flask containing the dicarbollide solution and the stoppered and evacuated flask containing the phenylboron dichloride were attached to an alembic distillation column.²¹ The $\text{Na}_2\text{B}_9\text{C}_2\text{H}_{11}$ solution was attached to the distillation column as the receiver, and the phenylboron dichloride was arranged for distillation. The distillation column was attached to the vacuum line, and the $\text{Na}_2\text{B}_9\text{C}_2\text{H}_{11}$ solution was degassed and refrozen using liquid nitrogen as the coolant. The alembic apparatus was then sealed off from the vacuum line, the stopcock leading to the phenylboron dichloride was opened, and the dichloride was distilled into the frozen dicarbollide solution using a 90–100° water bath as the heat source. After distillation was complete, the reaction mixture melted and a white precipitate began to form. The reaction mixture was stirred for 2 hr *in vacuo* at ambient temperature. The reaction mixture was then removed from the vacuum line and heated to reflux under nitrogen for 3 hr. The mixture was then cooled and filtered through a layer of Celite (filter aid). The Celite was washed twice with 20-ml portions of tetrahydrofuran and the precipitate was discarded.

The tetrahydrofuran was removed from the filtrate using a rotary evaporator, mechanical pump, and heat from a steam bath, leaving an oil or semisolid residue. The majority of the oily residue was dissolved by 300 ml of refluxing heptane over a 1.5-hr period. The heptane solution was filtered through Celite, the precipitate discarded, and the heptane removed from the filtrate by rotary evaporation. The slightly air-sensitive, semisolid residue was dissolved in the minimum amount of methylene chloride and was purified by chromatography on a silica gel column using hexane (100 ml) and then 50:50 hexane-benzene as the eluents. The eluent solvent was removed, and the white crystalline product which remained was further purified by sublimation at 80° under high vacuum. The yield of product was 4.51 g (80%), mp 109–110°.

Preparation of 3-Phenyl-1,2-dimethyl-1,2-dicarbaclododecaborane(12) (II). $(\text{CH}_3)_2\text{NHB}_9\text{C}_2\text{H}_{10}(\text{CH}_3)_2$ (5.0 g, 0.0226 mole) and phenylboron dichloride (4.0 g, 0.0252 mole) were employed using the initial procedure described above for the preparation of 3-phenyl-1,2-dicarbaclododecaborane(12). Upon removal of the solvent from the reaction mixture filtrate by rotatory evaporation a light yellow semisolid residue remained. This residue was crystallized from methanol to yield an air-stable white product. Recrystallization twice more from methanol afforded an analytical sample. The yield of product was 3.1 g (55%), mp 158–159°.

Preparation of 1,3-Diphenyl-1,2-dicarbaclododecaborane(12) (III). $(\text{CH}_3)_2\text{NHB}_9\text{C}_2\text{H}_{11}(\text{C}_6\text{H}_5)$ (5.0 g, 0.0186 mole) and phenylboron dichloride (3.25 g, 0.0204 mole) were employed using the initial general procedure described above. The light yellow oil obtained by removal of the filtrate solvent was dissolved in 300 ml of refluxing heptane over a 0.5-hr period and the resulting solution filtered through Celite. The precipitate was discarded and the heptane was removed from the filtrate in the usual manner. The residue was dissolved in a minimal amount of methylene chloride and purified on a silica gel chromatographic column using 100 ml

of hexane and then 50:50 hexane-benzene as the eluents. The eluent solvent was removed, and the air-stable white product which remained was twice sublimed at 90° under high vacuum to yield 2.1 g (38%) of product, mp 105–106°.

Preparation of 3-Ethyl-1,2-dicarbaclododecaborane(12) (IV). $(\text{CH}_3)_2\text{NHB}_9\text{C}_2\text{H}_{12}$ (5.0 g, 0.0259 mole) and ethylboron dichloride (3.0 g, 0.0271 mole) were employed as described above. The solvent was removed from the reaction mixture filtrate by rotary evaporation and a light yellow oil remained. The oil was transferred into a 25-ml microalembic distillation flask²¹ with a minimal amount of methylene chloride. The alembic flask was charged with glass wool to prevent bumping of the solution, and the methylene chloride was pumped off at room temperature. The product, $(\text{C}_2\text{H}_5)_2\text{B}_9\text{C}_2\text{H}_{11}$, a clear, air-sensitive, viscous liquid of pungent odor, was distilled at 35–45° (10⁻⁴ mm) with a bath temperature of 80–90°. The product was further purified by a second alembic distillation. Based upon microanalytical vapor phase chromatography (Apiezon L column at –206°, injection at 240° and detector at 238°, flow rate of helium of 200 ml/min), the product was shown to be 97% pure. Analytical samples of $(\text{C}_2\text{H}_5)_2\text{B}_9\text{C}_2\text{H}_{11}$ were prepared by preparative vpc techniques. The column used for the preparative vpc was an Apiezon L column, and the conditions were the same as those used in the microanalytical work, yield 2.27 g (51%), mp 15–17°.

6-Substituted (3)-1,2-Dicarbaclododecaborate(–1) Ions. Three of the 3-substituted 1,2-dicarbaclododecaborane(12) derivatives (3-phenyl, 3-phenyl-1,2-dimethyl, and 3-ethyl) were degraded with base. The procedure for the base reaction was identical for all derivatives. This procedure will be demonstrated by the following example.

Preparation of 6-Phenyl-(3)-1,2-dicarbaclododecaborate(–1) (V). A solution of 5.0 g (0.895 mole) of potassium hydroxide in 75 ml of absolute ethanol was placed in a 300-ml, round-bottom, three-necked flask equipped with a mechanical stirrer, nitrogen bubbler, and reflux condenser. A solution of 5.0 g (0.0228 mole) of 3-phenyl-1,2-dicarbaclododecaborane(12) dissolved in 50 ml of absolute ethanol was then added to the reaction vessel, and the resulting solution was heated at the reflux temperature for 10 hr. After the reflux period was completed, the ethanol was removed by rotary evaporation. The white solid residue, consisting of potassium hydroxide and the potassium salt of the product, was dissolved in the minimum amount of 6 M hydrochloric acid, and the resultant solution was filtered through Celite. The Celite cake was washed with two 15-ml portions of water and discarded. A solution of 50% tetramethylammonium chloride was added to the clear filtrate to produce a white precipitate. This precipitate, $(\text{CH}_3)_4\text{N}(\text{C}_6\text{H}_5)_2\text{B}_9\text{C}_2\text{H}_{11}$, was separated by filtration and purified by recrystallization from ethanol-water. The yield of product was 5.50 g (86%), mp 132–133°.

Cesium or trimethylammonium cations could be substituted for tetramethylammonium as the precipitating counterion. Both of these salts could be purified by recrystallization from ethanol-water as in the case of the tetramethylammonium salt.

Preparation of 6-Phenyl-1,2-dimethyl-(3)-1,2-dicarbaclododecaborate(–1) (VI). 3-Phenyl-1,2-dimethyl-1,2-dicarbaclododecaborane(12) (4.4 g, 0.0178 mole) was degraded as described above to yield 4.2 g (76%) of the tetramethylammonium salt of product anion, mp 283–286° dec.

Preparation of 6-Ethyl-(3)-1,2-dicarbaclododecaborate(–1) (VII). 3-Ethyl-1,2-dicarbaclododecaborane(12) (3.5 g, 0.0204 mole) was degraded as described above to yield 3.6 g (75%) of the air-sensitive tetramethylammonium salt of product anion, mp 278–279° dec.

Preparation of the 6-Phenyl-1,2-dimethyl-(3)- and 6-Phenyl-(3)-1,2-dicarbollide Ions. Both 6-phenyl substituted anions were shown to form their respective dicarbollide ions upon reaction with sodium hydride. Since the procedure does not change upon variation of carbon substituents, the general method will be illustrated by the preparation of 6-phenyl-(3)-1,2-dicarbollide ion.

The 6-phenyl-(3)-1,2-dicarbollide ion was prepared in a 300-ml, three-necked, round-bottom flask equipped with a condenser, addition funnel, nitrogen bubbler, and magnetic stirring bar. Sodium hydride (0.895 g, 0.0374 mole, 1.50 g of a 56% dispersion in mineral oil) was washed twice with 20 ml of tetrahydrofuran to remove the mineral oil and then washed into the reaction vessel with a total of 50 ml of tetrahydrofuran. A solution of 4.0 g (0.0149 mole) of the trimethylammonium salt of I dissolved in 50 ml of tetrahydrofuran was carefully added from an addition funnel to the sodium hydride-tetrahydrofuran slurry. After the addition was complete, the reaction mixture was heated at the reflux temperature for 3 hr. Trimethylamine was removed from the solvent

(21) See M. F. Hawthorne, *et al.*, *Inorg. Syn.*, 10, 103 (1967), for a description of this apparatus.

by passing dry nitrogen over the solution and out through the condenser during the last 30 min of the reflux period. The mixture was then allowed to cool and the excess sodium hydride separated. The supernatant tetrahydrofuran solution of $\text{Na}_2(\text{C}_6\text{H}_5)_2\text{B}_9\text{C}_2\text{H}_{10}$ was then ready for further use.

Preparation of 3,6-Diphenyl-1,2-dicarbaclododecaborane(12) (VIII). The 6-phenyl-(3)-1,2-dicarbollide ion, prepared as described above, was allowed to react with 2.5 g (0.0157 mole) of phenylboron dichloride using the previously described insertion reaction procedure. The reaction mixture filtrate was concentrated in the usual manner to a yellow semisolid which was crystallized from methanol-water. The air-stable white product was collected, dried, and recrystallized twice from heptane as fluffy plates. The yield of product was 1.51 g (35%), mp 173.5–174.5°.

Preparation of 3,6-Diphenyl-1,2-dimethyl-1,2-dicarbaclododecaborane(12) (IX). The procedure for the synthesis of 3,6-diphenyl 1,2-dimethyl-1,2-dicarbaclododecaborane(12) (IX) was employed in the preparation of VIII. This procedure was followed using 3.00 g (0.0101 mole) of the trimethylammonium salt of II and 0.84 g (0.0126 mole) of phenylboron dichloride. After the reaction mixture filtrate had been evaporated, the resulting yellow oil was dissolved in a minimum amount of methylene chloride and purified by chromatography on a silica gel column. Hexane, 100 ml, and then 50:50 hexane-benzene were used as the eluents. After removal of the eluent, an air-stable white crystalline material remained. This residue was twice recrystallized from heptane or 75:25 heptane-benzene to yield analytically pure needles of IX. The yield of product was 0.70 g (22%), mp 214–216°.

Piperidine Reactions with 3,6-Diphenyldicarbaclododecaborane(12) Derivatives. Both VIII and IX were treated with piperidine as described below. A solution of 0.25 g (0.845 mmole) of 3,6-diphenyl-1,2-dicarbaclododecaborane(12) (VIII) dissolved in 3 ml of piperidine was heated at the reflux temperature under nitrogen for 1 week. The piperidine was removed *in vacuo* and a yellow semisolid resulted. The yellow residue was dissolved in 10 ml of

hot heptane and the solution filtered. No perceptible precipitate was obtained and the filtrate upon cooling to 0° yielded white crystals which were collected. A second crop was obtained upon concentration of the heptane solution. Based upon infrared spectral and melting point data (213–215°), the recovered material, 0.18 g (72%), was the starting material, 3,6-diphenyl-1,2-dicarbaclododecaborane(12). Identical results were obtained with IX.

Preparation of Bis- π -6-phenyl-(3)-1,2-dicarbollycobalt (III) (X). A tetrahydrofuran solution of 6-phenyl-(3)-1,2-dicarbollide ion was prepared in the previously described manner using 1.80 g (0.0067 mole) of the trimethylammonium salt of V and 0.0188 mole (0.80 g of a 56% dispersion in mineral oil) of sodium hydride. Anhydrous cobaltous chloride was prepared by heating its hexahydrate under vacuum at 120° over phosphorus pentoxide for 48 hr. The anhydrous cobaltous chloride (0.70 g, 0.0054 mole) was washed with 25 ml of tetrahydrofuran into a 300-ml, three-necked, round-bottom flask equipped with a mechanical stirrer, condenser, addition funnel, and nitrogen bubbler. The solution of 6-phenyl-(3)-1,2-dicarbollide ion in tetrahydrofuran was rapidly added from the addition funnel to the cobaltous chloride. The color of the reaction mixture immediately changed from blue to black as cobalt metal formed. After the addition was complete, the mixture was heated at reflux for 0.5 hr, cooled, and filtered through Celite. The Celite layer was washed twice with two 20-ml portions of tetrahydrofuran and discarded. The filtrate was concentrated to a dry solid in the usual manner. The yellow residue was dissolved in hot water and the resulting solution filtered through Celite. A 50% aqueous solution of tetramethylammonium chloride was added to the filtrate to produce a light yellow precipitate. The product was recrystallized three times as yellow needles from ethanol-water. The yield of product was 1.13 g (62%), mp 275–277°.

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Electron Spin Resonance Studies of Silicon Difluoride

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Abstract: Electron spin resonance studies of SiF_2 - SiF_4 mixtures condensed with various diluents over the range 20°K to room temperature show the presence of paramagnetic species, probably $(\text{SiF}_2)_n$ diradicals where $n = 2, 3, \dots$

Most of the gas-phase properties of the extremely stable, carbene-like molecule silicon difluoride have been established by mass spectrometric studies¹ and microwave,² infrared,^{3,4} and electronic spectral measurements.⁵ Little is known, however, about the reddish brown solid formed when SiF_2 is condensed at low temperatures.^{1,6} Upon warming to room temperature, the solid turns white and can be cracked to yield

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(2) (a) V. M. Rao, R. F. Curl, P. L. Timms, and J. L. Margrave, *J. Chem. Phys.*, **43**, 2557 (1965); (b) V. M. Rao and R. F. Curl, *ibid.*, **45**, 2032 (1966).

(3) V. M. Khanna, R. Hauge, R. F. Curl, and J. L. Margrave, submitted for publication in *J. Chem. Phys.*

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(5) V. M. Khanna, G. Besenbruch, and J. L. Margrave, *J. Chem. Phys.*, **46**, 2310 (1967).

(6) D. C. Pease, U. S. Patent 2,840,588, assigned to Du Pont, Wilmington, Del., June 24, 1958.

perfluorosilanes up to at least $\text{Si}_{16}\text{F}_{34}$. SiF_2 is comparatively unreactive in the gas phase, oxygen being the only molecule with which it combines rapidly,^{1,7} but many chemical reactions can be performed by the cocondensation of the species with a particular reactant at low temperatures. The majority of compounds⁸ formed in this way contain $(\text{SiF}_2)_n$ units where n ranges from 2 to at least 11. The low-temperature chemistry and reddish-brown color of condensed SiF_2 - SiF_4 mixtures suggest that polymeric species are present with unsatisfied valences; esr studies have been performed on the low-temperature form of SiF_2 and confirm the existence of unpaired electrons.

Experimental Section

A Varian V4500-10A esr spectrometer, with Fieldial Mark II field regulation and a multipurpose cavity operating in the TE_{102}

(7) G. E. Besenbruch and J. L. Margrave, unpublished work, 1966.

(8) J. C. Thompson and J. L. Margrave, *Science*, **155**, 669 (1967).