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On Attempts at Generation of Carboranyl Carbocation

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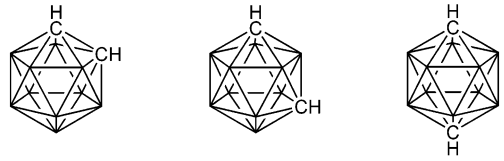
We have synthesized all three possible isomers of *C*-hydroxycarborane from the corresponding amines via diazotization. The *O*-protonated *C*-hydroxycarboranes were characterized using the NMR spectrum measurements. Attempts at generating of carboranyl carbocations were carried out by the solvolyses of *C*-tosylates and *C*-triflates, as well as by treatment with superacids. Anchimeric assistance of both homoconjugative and hyperconjugative substituents was also investigated, as demonstrated by a successful strategy devised for the solvolytic generation of a phenyl cation. However, we have not been able to chemically provide any evidence of carboranyl carbocations, although the carboranyl carbocation may be an intermediate in the decomposition of the *C*-carboranediazonium ion.

Introduction

The substitution reaction of both carbon and boron atoms in icosahedral *closo*-carborane cages has been extensively investigated. In dicarba-*closo*-dodecaborane-(12)s[1] (**1**) (hereafter, "carboranes"; see Chart 1), the electron density of the boron atoms is higher than that of the carbon atoms.[1,2] Thus, the electrophile reacts to the boron atoms in carborane cages.[1−4] The reaction at nucleophilic carbon atom in carborane cage has also been carried out; this reaction is the most important route for obtaining carborane derivatives.[1] Although the nucleophilic reaction at the boron atoms in carborane cages has also been reported,[5,6] the nucleophilic reaction at the carbon atoms has received surprisingly little attention.[7]

CHART 1. Three Possible Topological Isomers of Icosahedral Dicarba-*closo*-dodecaborane(12)[a]



1a **1b** **1c**

[a] Vertexes show the BH groups.

The icosahedral *closo*-carborane system is strongly stabilized by delocalizing three valence electrons of a carbon atom to the neighboring four or five C−B bonding orbitals.[1,2] Consequently, the carbon atoms in a carborane cage are extremely electron deficient.[1,2] Thus, if a cation center can be introduced at a carbon atom in a carborane cage, the carborane would no longer be expected to stabilize the icosahedral cluster cage.

On the other hand, it remains a matter of debate whether carborane cages have aromaticity and are therefore analogues of benzene.[8] In comparison with the benzenoid system, carbene and nitrene chemistries have demonstrated that the unpaired nonbonding electrons are not significantly delocalized in the carborane cage.[9] Nevertheless, many carborane compounds have been synthesized that mimic aromatic compounds.[10] The inductive as well as the resonance effects of carborane isomers on reactivity have also been studied.[11]

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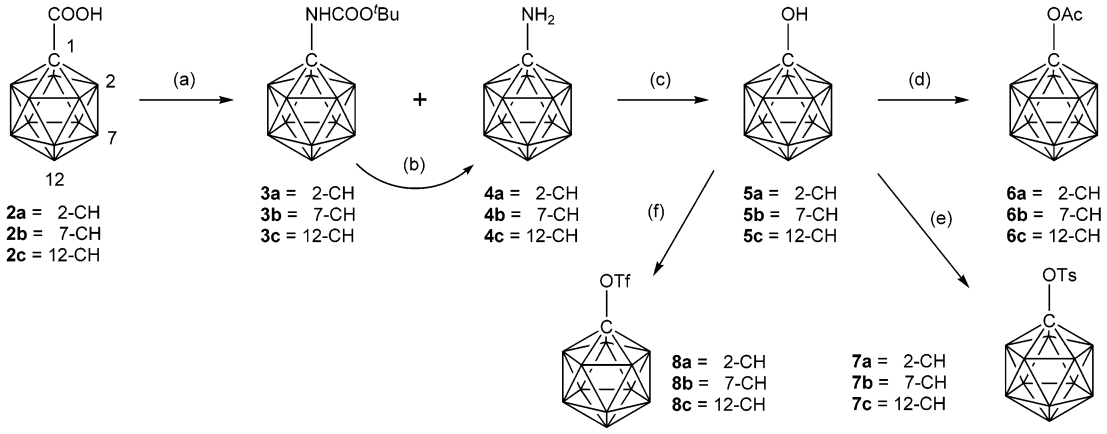
SCHEME 1. Synthesis of Three Positional Isomers of *C*-Hydroxycarborane and Derivatives[a,b]



[a] Reagents and conditions: (a) (1) $SOCl_2$, DMF, ref, 5 h, (2) Me_3SiN_3, PhMe, rt, 10 min then ref, 1 h, (3) *t*-BuOH, rt, 10 min then ref, 18 h; (b) CF_3COOH, CH_2Cl_2, rt, overnight; (c) (1) $NOBF_4$, CH_2Cl_2, −78 °C, 30 min, (2) water, rt, 3 h; (d) $(MeCO)_2O$, pyridine (for **5b** and **5c**),[45] 2 days; (e) *p*-$MePhSO_2Cl$, pyridine,[45] CH_2Cl_2, ref, 3 days; (f) $(CF_3SO_2)_2O$, pyridine,[45] rt, 1 h. [b]Vertexes show the BH groups, except for at a specified position, i.e., the number shows the position of the CH group (*o*-carborane cage at position 2, *m*-carborane cage at position 7, and *p*-carborane cage at position 12).

Therefore, we were interested in the electronic properties of the carbocation in a carborane system, since it was expected that clarification of the electronic structure would provide helpful information for the discussion of this type of system, provided that the cation is present.

C-Hydroxycarborane as a three-dimensional phenol has received little attention in the literature, although the preparation of all three isomers was completed in 1997.[12] To date, these derivatives have been synthesized by oxidation of the corresponding lithiocarboranes with peroxides[13,14] as well as with molecular oxygen.[15] The pK_a values of these isomers has been measured, and the acidity of *C*-hydroxy-*o*-carborane (**5a**) was found to be similar to that of benzoic acid; moreover, both *C*-hydroxy-*m*-carborane (**5b**) and *C*-hydroxy-*p*-carborane (**5c**) are as weakly acidic as phenol (Scheme 1).[12] Infrared spectra study have shown that the C═O stretching vibration of the corresponding acetate derivatives[14] (1790 cm^{-1} for the ortho isomer, and 1780 cm^{-1} for both the meta and the para isomers (see the results of the present study)) could be observed at a high frequency corresponding to that of phenyl acetate, rather than to the lower frequency of aliphatic acetate.

On the other hand, only one report of diazotization has been published to date; in that study, two *C*-hydroxycarboranes, i.e., **5a** and 1-hydroxy-7-methyl-1,7-carborane, were synthesized from the corresponding amines using nitrous acid.[7]

Here, we demonstrated the synthesis of all three topological isomers (**5**) of *C*-hydroxycarborane from the corresponding amines (**4**) via diazotization with three types of reagents: nitrosonium tetrafluoroborate ($NOBF_4$),[16] isoamyl nitrite, and sodium nitrate (Scheme 1).[17] We also attempted the solvolytic generation of a novel carboranyl carbocation, which may be a candidate for the reaction intermediate in the decomposition of *C*-carboranediazonium ion.

Results and Discussion

The *C*-Carboranediazonium Ion Is Similar to an Aliphatic Diazonium Ion. As shown in Scheme 1, the starting materials, *C*-aminocarboranes (**4**), were synthesized from the corresponding carboxylic acids (**2**) under Curtius conditions,[18,19] and the prepared isocyanates were successively treated with *tert*-butyl alcohol. This reaction

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TABLE 1. Method A for the Diazotization of 4

compd	$NOBF_4$ (equiv)	solvent[a] (M)	yield of **5** (%)
4a	1	CH_2Cl_2 (0.06)	13
4a	3	CH_2Cl_2 (0.20)	14
4a	3	CH_2Cl_2 (0.06)	31
4a	3	CCl_4 (0.06)[b]	20
4a	3	CH_3CN (0.06)[c]	13
4a	3	$(CH_3CH_2)_2O$ (0.06)	11
4b	3	CH_2Cl_2 (0.06)	24
4c	3	CH_2Cl_2 (0.06)	74

[a] Reaction was started at −78 °C. [b] At −20 °C. [c] At −45 °C.

TABLE 2. Conditions for the Diazotization of 4

compd	method[a]	*T* (°C)	yield of **5** (%)
4a	B	−25	37
4a	C	3	22
4b	B	−25	32
4b-HCl	C	3	22
4c	B	−25	29
4c	B	−50	13
4c	B	−78	NR[b]
4c-HCl	C	3	28

[a] Method B: 2.1 equiv of trifluoroacetic acid, CH_2Cl_2, rt, 10 min, 1.5 equiv of isoamyl nitrite, specified temperature, 1 h, and then water. Method C: 3 equiv of $NaNO_2$, H_2SO_4, (concd HCl for **4a**), 3 °C, 2 h, rt, 1 day. [b] No reaction.

gave the corresponding carbamate (**3**) and the desired amine (**4**). The isolated carbamate was then hydrolyzed to obtain the desired amine.[19]We investigated the diazotizations of **4** with three types of reagents: $NOBF_4$ (method A), isoamyl nitrite (method B), and sodium nitrate (method C) (Tables 1 and 2). However, using methods A and B, the corresponding *C*-carborananediazonium salt was not still isolated by decantation at −78 °C under a dry argon atmosphere. In the case of diazotization with $NOBF_4$ (method A), the hydrolysis following diazotization gave a complex mixture containing primarily the desired alcohol (**5**), and amine (**4**) was recovered as well as the corresponding carborane (**1**) (other byproducts were not identified). The addition of acetic acid instead of water to the reaction suspension gave the same mixtures and no acetate derivative was observed.[20] As shown in Table 1, both the concentration and the equivalent of $NOBF_4$ affected the yield of alcohol **5**. A solvent effect was also observed in this reaction. In the case of isoamyl nitrite (method B),[21] complex mixtures were obtained, together with additional byproducts such as the carborane dimer and *N*,*O*-dicarboranylhydroxylamine.

It remains unknown whether carboranes are aromatic or aliphatic. The present results indicated a similarity with the aliphatic diazonium ion[22] in terms of the instability of the compounds, i.e., the stabilization of the

(20) To a solution of **4** (20 mg) in dichloromethane-d_2 (or acetonitrile-d_3) (0.6 mL), arbitrary amounts of $NOBF_4$ were added at −78 °C. NMR measurements were initiated at −35 °C, and the temperature was raised gradually to 0 °C. No major changes in the chemical shifts were observed. Then, acetic-d_4 acid was added to the reaction mixture at −78 °C. NMR measurements were initiated at −35 °C, and the temperature was raised gradually to room temperature. However, after following this protocol, the acetate derivative was not identified. For acetolysis of benzenediazonium ion, see: Swain, C. G.; Sheats, J. E.; Harbison, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 783−790.

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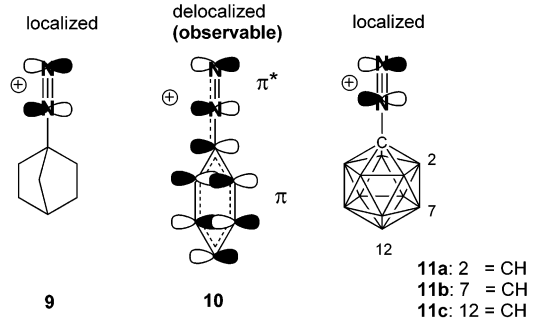

FIGURE 1. Homoconjugative interactions of an aromatic system (**10**) and weaker interactions of aliphatic (**9**) and carboranyl (**11**) systems.

TABLE 3. ^1H and ^{13}C NMR Chemical Shifts in TFSA and Magic Acid[a]

compd	solvent	^{13}C (ppm) ipso position	^{13}C (ppm) C−H	^1H (ppm) substituent
4a	$CDCl_3$	88.18	66.44	2.97
	TFSA	66.74	56.69	7.66
4b	$CDCl_3$	87.56	53.05	1.40−3.42
	TFSA	69.00	53.19	7.11
4c	$CDCl_3$	95.25	49.63	1.60−2.89
	TFSA	75.60	55.83	6.69
aniline[b]		146.7		2.5−5.0
N-protonated aniline[b]		128.6		6−9
5a	$CDCl_3$	98.62	62.94	4.76
	TFSA	93.69	59.95	no[d]
	Magic Acid	88.83	59.64	no[d]
5b	$CDCl_3$	101.48	51.67	3.23
	TFSA	95.70	50.58	no[d]
	Magic Acid	93.80	52.88	no[d]
5c	$CDCl_3$	108.32	48.15	3.03
	TFSA	101.99	48.60	no[d]
	Magic Acid	99.86	52.96	10.17[e]
8c	$CDCl_3$	105.08	53.74	
	Magic Acid	105.33	53.62	
phenol[b]		155.4		5.0−8.0
	(TFSA)[c]	(188.54)		(6.89)

[a] NMR spectra were measured at 30 °C. [b] Reference 26. [c] Protonation occurred at the para position (this study). [d] no = not observed. [e] *O*-Protonation was observed at −60 °C.

cation on the carborane cage did not occur as it does in the case involving the benzenediazonium ion, in which the π electrons of the aromatic system are known to delocalize to the diazonio group (homoconjugation) (Figure 1).

***N*- and *O*-Protonations in an Acidic Medium.** Three possible topological isomers of *C*-hydroxycarborane (**5**) were found to be very stable in a superacid medium, i.e., trifluoromethanesulfonic acid (TFSA), at 30 °C, as compared with the stability of phenol,[23] which rapidly protonates at the carbon at the para position and at an oxygen under the same conditions. As shown in Table 3, obvious changes ($CDCl_3$ vs TFSA) in the ^{13}C NMR chemical shifts at 30 °C, as well as shifts of both ^{11}B and ^1H NMR at 30 °C (data not shown), were not observed.[24] The reaction recovered the hydroxycarborane.

To compare this type of system with the benzenoid system, *C*-aminocarboranes (**4**) were dissolved in TFSA,

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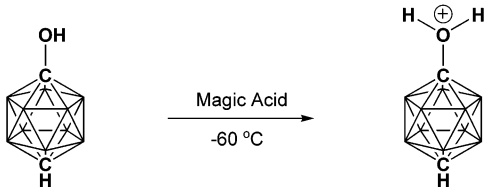

FIGURE 2. Direct observation of *O*-protonated *C*-hydroxy-*p*-carborane by ^{1}H NMR at −60 °C.

and the ^{13}C NMR chemical shifts were measured. The same tendency as that of *N*-protonated aniline was observed at the chemical shift of the ipso position carbon (shielding to upfield by 19−21 ppm in the case of the *C*-aminocarboranes and by 18 ppm in the case of aniline) (Table 3). In the ^{1}H NMR spectra, *N*-protonated ammonium protons were observed at around 7.0 ppm at 30 °C.

Then, the *C*-hydroxycarboranes (**5**) were dissolved in Magic Acid, SbF_5:FSO_3H = 1:1, and the ^{13}C, ^{11}B, and ^{1}H NMR spectra were measured at −60 and +30 °C.[25] In *C*-hydroxy-*p*-carborane (**5c**) at −60 °C, an *O*-protonated hydroxyl group was observed at 10.2 ppm (^{1}H NMR), relative to an external reference (0.0 ppm), i.e., capillaried tetramethylsilane in Magic Acid (Figure 2 and Supporting Information). While the *O*-protonated hydroxyl group of the other isomers was not directly observed, the ^{13}C NMR chemical shifts showed that both **5a** and **5b** also protonated in Magic Acid (8−11 ppm shielding to upfield) as well as in TFSA (5−6 ppm shielding to upfield). However, neither the carboranyl carbocation nor cage protonation were observed under these conditions.

Attempts at the Solvolytic Generation of Carboranyl Carbocations. None of the corresponding tosylate derivatives (**7**)[27] reacted with acetic acid in the presence or absence of 0.05 M sodium acetate at 120 °C for more than 24 h (the acetylated hydroxycarboranes (**6**) were prepared as authentic compounds). In the case of *p*-carboranyl triflate (**8c**), acetolysis, buffered with sodium acetate, did not proceed at 120 °C for 5 days. On the other hand, trifluoroethanolysis for the triflates (**8**) in the presence of 0.05 M potassium carbonate gave a sole product (**5**), which quickly dissociated at the S−O bond. The half-times of the reactions were 0.5 h at 10 °C in the case of **8a**, 1 h at 60 °C in the case of **8b**, and 5 h at 60 °C in the case of **8c**. The kinetic parameters are shown in Table 4.

Finally, the *p*-carboranyl triflate (**8c**) was dissolved in Magic Acid at −60 °C. No changes in the ^{13}C NMR chemical shifts were observed (Table 3). After 9 days at room temperature, the corresponding *O*-protonated alcohol was observed as the sole product. In contrast, it is already known that phenyl triflate under the same conditions gives multiple products via a *C*-protonated σ complex intermediate.[28]

These results showed that the carboranyl carbocations (**12**) are considerably unstable (e.g., the phenyl cation (**15a**), which was undetectable except under specific conditions).[29,30]

In the case of the phenyl cation (**15**), the vacant orbital and the aromatic π system are orthogonal and are therefore unable to interact directly.[32] The trigonal angle of the cation center also renders it difficult to rehybridize the sp^2 orbital in such a way as to reduce its s character. In this case, the phenyl cation was found to be stable when the substituents stabilized the vacant orbital of the cation by means of hyperconjugative interactions (**15b**) (Figure 3).[31]

In bridged bicyclic systems (**13** and **14**), on the other hand, **13** bearing the bridgehead vacant sp^3 orbital is the system wherein the hyperconjugation is dominant,[33] and **14** bearing the complete vacant p orbital is the system in which the homoconjugation (i.e., a three-center, two-electron interaction) is dominant (Figure 3).[34] These systems were shown to be more stable than **15**, and were detected by means of NMR observations in superacid medium, as well as by the reaction under solvolytic conditions.[33,34]

As shown in Figure 3, in the case of the carboranyl cation (**12**), the hexagonal carbon of the cation center is thought to have sp^3 character. However, since a triangle in the icosahedral architecture would be constructed by means of a three-center, two-electron interaction, the vacant orbital would be unable to interact with these valence orbitals in the same manner as that in the case of **13** (i.e., hyperconjugation). It seems that, in the series of **12**, three types of interactions would occur in terms of the arrangements and components of the cyclopropane-like skeletons (see the bold frame in Figure 3), which would lead to the individual properties of three topological carboranyl carbocations (**12a**−**c**). However, the vacant orbital would also have been unable to homoconjugate with the neighboring five cyclopropane-like Walsh orbitals in the same manner as that of **14**.[35] We noticed that the yield of *C*-hydroxy-*p*-carborane (**5c**) using method A was significantly higher than the yield of the other isomers (Table 2). It is therefore possible that the *p*-carboranyl carbocation is slightly more stable energeti-

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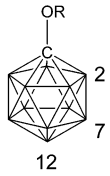
TABLE 4. Solvolysis Conditions of Unsubstituted *C*-Carboranyl Tosylates and Triflates



7: R = $-SO_2C_6H_5CH_3$
8: R = $-SO_2CF_3$
a: 2 = CH
b: 7 = CH
c: 12 = CH

compd	conditions	*T*(°C)	time(h)	products
7a	0.02 M in AcOD-d_3	120	48	No Reaction
7b	0.02 M in AcOH with 0.05 M NaOAc	120	24	No Reaction
7c	0.02 M in AcOH with 0.05 M NaOAc	120	24	No Reaction
8c	0.02 M in AcOD-d_3 with 0.05 M NaOAc-d_3	120	5 days	No Reaction
8a	0.026 M in CF_3CH_2OH with 0.05 M K_2CO_3	10	$T_{1/2}$ = 0.5 [a]	**5a**
8b	0.026 M in CF_3CH_2OH with 0.05 M K_2CO_3	60	$T_{1/2}$ = 1 [b]	**5b**
8c	0.026 M in CF_3CH_2OH with 0.05 M K_2CO_3	60	$T_{1/2}$ = 5 [c]	**5c**
8c	SbF_5 : FSO_3H = 1 : 1	rt [d]	9 days	**5c**

[a] k_1 (25 °C) = 1.84E−03, $\Delta H^{\ddagger}$ (kcal mol^{-1}) = 16.21, $\Delta S^{\ddagger}$ (cal K^{-1} mol^{-1}) = −16.64, $\Delta G^{\ddagger}$ (kcal mol^{-1}) = 21.17. [b] k_1 (25 °C) = 4.67E−06, $\Delta H^{\ddagger}$ (kcal mol^{-1}) = 20.70, $\Delta S^{\ddagger}$ (cal K^{-1} mol^{-1}) = −13.45, $\Delta G^{\ddagger}$ (kcal mol^{-1}) = 24.71. [c] k_1 (25 °C) = 8.66E−07, $\Delta H^{\ddagger}$ (kcal mol^{-1}) = 20.32, $\Delta S^{\ddagger}$ (cal K^{-1} mol^{-1}) = −18.05, $\Delta G^{\ddagger}$ (kcal mol^{-1}) = 25.71. [d] Room temperature.

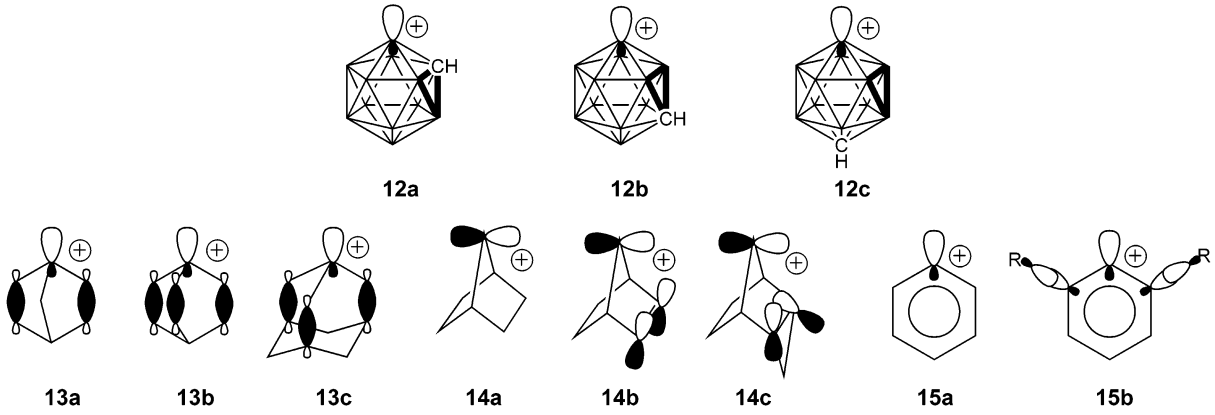


FIGURE 3. Carboranyl carbocations vs three types of cations in which hyperconjugation, homoconjugation, and weak interactions are dominant, respectively.

cally than the other carbocations.[36] In general, the carboranyl carbocation (**12**) was found to be similar to the phenyl cation (**15a**) with respect to the difficulty of generation (higher energy intermediate).[36] Moreover, a triplet state of the carboranyl carbocation would be impossible due to its high instability and the electron deficiency of the carborane cage.[37]

Stabilization of Intermediates by the Homoconjugative and Hyperconjugative Substituents. We also investigated the substituent effects on the stabilization of the carboranyl carbocation, as demonstrated by the phenyl cation chemistries.[38] A trimethylsilyl group was chosen as the substituent bearing the hyperconjugative stabilization effect.[31] The *tert*-butyl group also has a hyperconjugative effect and is potentially hydrogen-transferable when the cationic center is in the vicinity.[39] Both cyclopropyl and phenyl are strong homoconjugative assistance groups. A 4-methoxyphenyl group has an alternative effect in which the methoxy group stabilizes the localized carbocation.[40] As shown in Scheme 2, the *C*-substituted (*tert*-butyl (**16**), cyclopropyl (**18**), phenyl (**19**), and 4-methoxyphenyl (**20**)) *o*-carboranes were synthesized from the addition reaction[41] between the decaborane-bisacetonitrile complex and the substituted acetylene. *C*-Trimethylsilyl-*o*-carborane (**17**) was obtained by the reaction of *o*-lithiocarborane and trimethylsilyl chloride under low-concentration conditions.[42] *C*-Substituted-*C*′-hydroxy-*o*-carboranes (**21**−**25**) were synthesized by the oxidation reaction of the corresponding *C*-substituted *o*-lithiocarboranes with benzoyl peroxide. These *C*-hydroxy-*o*-carboranes were converted to *C*-triflates (**26**−**30**) and authentic acetates (**31**−**33**) by trifluoromethanesulfonic anhydride and acetic anhydride in the presence of pyridine, respectively.

Table 5 shows the results of the solvolyses of the *C*′-substituted *C*-carboranyl triflates. In the case of acetolysis in the absence of salt, *o*-carboranyl triflate (**8a**) was obtained from trimethylsilyl derivative (**27**) in a reaction carried out at 90 °C for 10 h. *tert*-Butyl (**26**) and 4-methoxyphenyl (**30**) derivatives gave a slight amount

(36) We conducted a preliminary investigation of the hydride affinities of carboranyl carbocations. The B3LYP/6-31G* method shows that the three topological carboranyl carbocations are more unstable than the phenyl cation (relative energy differences: 22 kcal/mol for **12a**, 19 kcal/mol for **12b**, 16 kcal/mol for **12c**).

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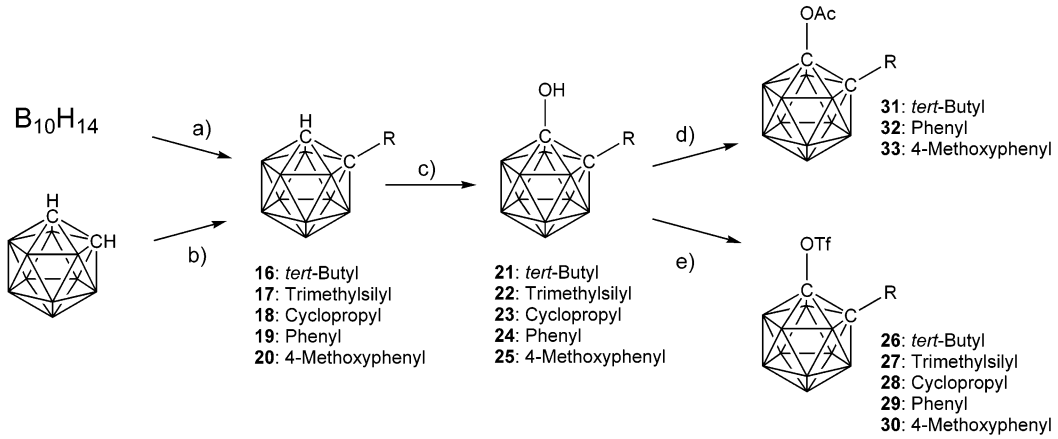
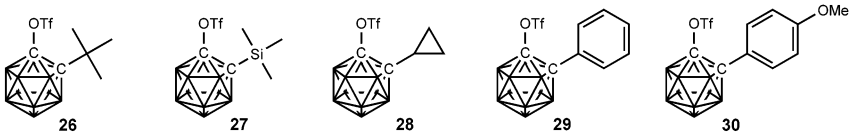
SCHEME 2. Synthesis of *C*′-Substituted *C*-Hydroxy-*o*-carboranes and the Corresponding Derivatives[a]



[a] Reagents and conditions: (a) (1) CH_3CN, ref, 2−3 h, (2) substituted acetylene, PhMe, ref, 2−3 h; (b) (1) *n*-BuLi, ether, −78 °C, 1 h, (2) $(CH_3)_3SiCl$, ether, −78 °C, 1 h; (c) (1) *n*-BuLi, ether, rt, 1−2 h, (2) $(PhCOO)_2$, ether, rt, overnight; (d) $(CH_3CO)_2O$, pyridine, rt, 30 min to 1 h; (f) $(CF_3SO_2)_2O$, pyridine, CH_2Cl_2, 30 min to 1 h.

TABLE 5. Solvolysis Conditions of the *C*′-Substituted *o*-Carboranyl Triflates



compd	conditions	*T* (°C)	time (h)	products
26	0.02 M in AcOD-d_3	120	26.5	**21**/**26** = 1:99
	0.02 M in AcOD-d_3 with 0.05 M NaOAc	120	24	**21**/**26** = 3:7, +multi
	0.02 M in CF_3CD_2OD	80	14.5	no reaction
	0.02 M in CF_3CD_2OD with 0.03 M K_2CO_3	30	0.5	**21**/**26** = 7:3
27	0.03 M in AcOH	90	10	**8a**/**27** = 8:1
	0.02 M in CF_3CH_2OH	80	5	no reaction
	0.02 M in CF_3CH_2OH with 0.03 M K_2CO_3	30	0.3	**22** + **5a**
28	0.02 M in AcOD-d_3 with 0.05 M NaOAc-d_3	120	17.5	**23**/**28** = 1:1
29	0.02 M in AcOD-d_3 with 0.05 M NaOAc-d_3	120	10.5	**24**/**29** = 1:1, +multi
	0.02 M in CF_3CH_2OH	80	10	no reaction
30	0.02 M in AcOD-d_3	120	26.5	**25**/**30** = 1:99
	0.02 M in AcOD-d_3 with 0.05 M NaOAc	120	24	**25**/**30** = 4:6, +multi
	0.02 M in CF_3CD_2OD	80	14.5	no reaction
	0.02 M in CF_3CD_2OD with 0.03 M K_2CO_3	30	0.5	**25**/**30** = 8:1

of the corresponding alcohol (**21** and **25**) in a reaction carried out at 120 °C for 27 h.

In the presence of sodium acetate, cyclopropyl derivative (**28**) gave the corresponding alcohol (**23**) cleaved at the S−O bond. The other derivatives, *tert*-butyl (**26**), phenyl (**29**), and 4-methoxyphenyl (**30**), gave primarily the corresponding alcohols (**21**, **24**, and **25**) with multiple products, among which the corresponding acetates were not observed (as compared with the authentic compounds, which were acetate derivatives (**31**−**33**)). In the case of *tert*-butyl derivative (**26**), the hydride shift product may have been obtained, but no corresponding CH proton was observed in the ^{1}H NMR spectra.

While in the case of trifluoroethanolysis, the reaction in the absence of salt did not proceed in all of the cases (**26**, **27**, **29**, and **30**), and the reaction in the presence of potassium carbonate occurred at the S−O bond, thus affording the corresponding alcohols (**21**, **22**, and **25**). Under these conditions, trimethylsilyl derivative (**27**) further reacted in the mixture, giving *C*-hydroxy-*o*-carborane (**5a**), which liberated the trimethylsilyl group.

These results suggested that carboranyl carbocations are highly unstable without assistance from both valence and nonbonding electrons on the carborane cages. All homoconjugative and hyperconjugative substituents failed to stabilize and/or generate the carboranyl carbocation under these solvolytic conditions.[43] When the present results are taken together with the results obtained for the diazonium ion, then it appears that carboranes are not similar to either aliphatic or aromatic systems (Figures 1 and 3).

(43) In the case of the phenyl cation, the bond shortening between the cation center and the adjacent carbon atoms has been predicted (1.33 Å for **15a** and 1.40 Å for benzene at the B3LYP/6-31G* level, respectively). See also ref 32. Similarly, the shortening of the C−C distance of *o*-carboranyl carbocation **12a** (1.59 Å) can be predicted at the B3LYP/6-31G* level, as compared with the parent **1a** (1.63 Å). In the case of carboranes, however, it seems that the abnormally long C−C distance, as well as its high degree of instability (ref 36), is not advantageous for stabilization by means of either homoconjugative or hyperconjugative substituents.

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(45) The syntheses of *C*′-unsubstituted *C*-hydroxy-*o*-carborane derivatives, i.e., acetate (**6a**), tosylate (**7a**), and triflate (**8a**), required precisely one equivalent of pyridine; however, the syntheses in the case of both *m*- and *p*-carboranes were carried out in an excess of pyridine.

Summary

We demonstrated here the marked electron deficiency of carborane cages and we discussed the preliminary expectations for the carbocation in this type of system. However, we were unable to provide chemical evidence in support of our expectations, although the carboranyl carbocation may be an intermediate in the decomposition of the carboranediazonium ion.

Experimental Section

Method A. 1,2-Dicarba-*closo*-dodecaborane(12)-1-alcohol (5a). A solution of **4a** (500.0 mg, 3.15 mmol) in dichloromethane (25 mL) was added to a suspension of nitrosonium tetrafluoroborate ($NOBF_4$) (1.14 g, 9.74 mmol) in dichloromethane (25 mL) at −78 °C (dry ice−acetone bath) under an argon atmosphere. After 30 min, the dry ice−acetone bath was removed, and the reaction suspension was stirred for an additional 30 min. Water (15 mL) was added to the suspension, which was then stirred for 3 h. The heterogeneous reaction mixture was extracted twice with dichloromethane, and the dichloromethane solution was washed with brine. The dichloromethane solution was dried over anhydrous sodium sulfate (Na_2SO_4) and concentrated under reduced pressure to give a crude product (626.6 mg). The crude product was chromatographed on silica gel with a mixture of *n*-hexane and dichloromethane (1:3) and then with a mixture of *n*-hexane and ethyl acetate (1:1). Removal of the solvent of the eluate gave the desired product as a light-yellow solid in a 31.4% yield (158.1 mg). Recrystallization from the mixture of *n*-hexane and dichloromethane gave **5a** as a white powder (mp 225−228 °C). ^{1}H NMR δ ($CDCl_3$): 1.20−3.20 (10H, m), 3.97 (1H, s), 4.76 (1H, s, br). ^{13}C NMR δ ($CDCl_3$): 62.94, 98.62. ^{11}B NMR δ ($CDCl_3$): −14.53 (2B, d, 177.4), −12.18 (7B, d, 156.8), −3.78 (1B, d, 168.5). IR ν_{max} (KBr) cm^{-1}: 3500, 3050, 2575, 1225, 1110, 1065, 1000, 715. HRMS: calcd for $C_2H_{12}O(^{10}B)_2(^{11}B)_8$ 160.1892, found 160.1885 (−0.7 mmu).

1,7-Dicarba-*closo*-dodecaborane(12)-1-alcohol (5b). As described for the preparation of **5a**, **5b** (chromatographed on silica gel with a mixture of *n*-hexane and dichloromethane (1:2)) (24.2% yield) was synthesized from **4b** as a colorless prism (recrystallized from the mixture of *n*-hexane and dichloromethane) (mp 293 °C). ^{1}H NMR δ ($CDCl_3$): 1.40−3.70 (10H, m), 2.84 (1H, s), 3.23 (1H, s). ^{13}C NMR δ ($CDCl_3$): 51.67, 101.48. ^{11}B NMR δ ($CDCl_3$): −15.86 (5B, d, 180.2), −13.12 (2B, d, 153.9), −11.31 (2B, d, 162.8), −4.60 (1B, d, 149.6). IR ν_{max} (KBr) cm^{-1}: 3200, 3025, 2600, 1395, 1205, 1130, 1065, 1000, 930, 900, 720. HRMS: calcd for $C_2H_{12}O(^{10}B)_2(^{11}B)_8$ 160.1891, found 160.1857 (−3.4 mmu).

1,12-Dicarba-*closo*-dodecaborane(12)-1-alcohol (5c). As described for the preparation of **5a**, **5c** (chromatographed on silica gel with a mixture of *n*-hexane and dichloromethane (1:2)) (74.2% yield) was obtained from **4c** as a colorless prism (recrystallized from the mixture of *n*-hexane and dichloromethane) (mp 148 °C). ^{1}H NMR δ ($CDCl_3$): 1.20−3.30 (10H, m), 2.44 (1H, s), 3.03 (1H, s). ^{13}C NMR δ ($CDCl_3$): 48.15, 108.32. ^{11}B NMR δ ($CDCl_3$): −17.30 (5B, d, 168.5), −13.11 (5B, d, 168.70). IR ν_{max} (KBr) cm^{-1}: 3225, 2600, 1390, 1200, 1130, 1055, 1000, 970, 795, 720. HRMS: calcd for $C_2H_{12}O(^{10}B)_2(^{11}B)_8$ 160.1891, found 160.1871 (−2.0 mmu).

Method B. To a solution of **4** (238.5 mg, 1.5 mmol) in dichloromethane (10 mL) was added TFA (2.1 equiv, 0.24 mL, 3.15 mmol) under an argon atmosphere. The resulting white suspension was cooled to specified temperatures, and isoamyl nitrite (1.5 equiv, 0.3 mL, 2.25 mmol) was added dropwise to the reaction suspension (vigorous bubbling was observed at over −25 °C). After the mixture was stirred for 1 h, water (5 mL) was added to the reaction mixture and the mixture was then vigorously stirred. The resulting light-yellow solution was extracted twice with ethyl acetate, and the ethyl acetate solution was dried over anhydrous $MgSO_4$. The ethyl acetate solution was concentrated in vacuo to give the crude products. The crude products were separated by chromatography on silica gel with the same solvent as that used for method A. Removal of the solvent of the eluate gave the desired product, and we obtained the additional compounds from the reaction with **4c**.

1,12-Carborane dimer was purified by recrystallization from methanol as a white powder (mp 237 °C (sublime)). LRMS: 286 (M^+). HRMS: calcd for $C_4H_{22}(^{10}B)_4(^{11}B)_{16}$ 286.3728, found 286.3712 (−1.6 mmu).

***N*-1,12-Carboranyl-*O*-1,12-carboranylhydroxyamine** was purified by recrystallization from methanol as a light-yellow powder (mp 214−215 °C). ^{1}H NMR δ ($CDCl_3$): 2.29 (20H, quad, 156.5, br), 2.60 (1H, s), 2.80(1H, s), 8.03 (1H, s). ^{11}B NMR δ ($CDCl_3$): −17.67 (5B, d, 175.9), −16.37 (5B, d, 171.6), −14.09 (5B, d, 153.9), −13.58 (5B, d, 170.1). IR ν_{max} (KBr) cm^{-1}: 3400, 3025, 2600, 1720, 1200, 1140, 1050, 970, 730. LRMS: 317 (M^+).

Method C. Sodium nitrate (55.5 mg, 0.80 mmol) was added to a suspension of **4a** (50.0 mg, 0.31 mmol), concentrated hydrochloric acid (conced HCl) (1 mL), and sulfuric acid (2 mL) for a period of 5 min at 3 °C. After then being stirred for 2 h at 3 °C, the suspension was additionally stirred overnight at room temperature. The reaction suspension was poured into water and the crude product was extracted twice with dichloromethane. The dichloromethane solution was dried over anhydrous Na_2SO_4 and evaporated in vacuo. The crude products were separated by chromatography on silica gel using the same solvent as that used for method A. Removal of the solvent of the eluate gave **5a** as a white powder in a 22.1% yield (11.1 mg). The other primary product was **1a** (9.0 mg, 19.9%), and **4a** (17.7 mg, 35.4%) was recovered.

Both **5b** (22.4% yield) and **5c** (28.1% yield) were synthesized from the corresponding **4-HCl** without concd HCl in the reaction mixture. **1b** (50.0%) and **1c** (45.7%) were isolated as byproducts from the reactions with **4b-HCl** and **4c-HCl**, respectively.

1-Acetoxy-1,2-dicarba-*closo*-dodecaborane(12) (6a). A solution of **5a** (129.5 mg, 0.81 mmol) in acetic anhydride (1 mL) was stirred for 30 min at 3 °C. After being stirred for 3 days at room temperature, the reaction mixture was poured into water and extracted twice with dichloromethane. The dichloromethane solution was washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated in vacuo, and the resulting residue was chromatographed on silica gel with a mixture of *n*-hexane and dichloromethane (1:2). Removal of the solvent of the eluate gave **6a** as a white powder (mp 57−59 °C) in a 33.1% yield (54.2 mg). ^{1}H NMR δ ($CDCl_3$): 0.80−3.40 (10H, m, br), 2.11 (3H, s), 4.76 (1H, s, br). LRMS: 202 (M^+). HRMS: calcd for $C_4H_{14}O_2(^{10}B)_2(^{11}B)_8$ 202.1997, found 202.2025 (+2.8 mmu). IR ν_{max} (KBr) cm^{-1}: 2575, 1790, 1365, 1225, 1175, 1115, 1060, 1005, 940, 720.

1-Acetoxy-1,7-dicarba-*closo*-dodecaborane(12) (6b). As described for the preparation of **6a**, **6b** (chromatographed on silica gel with a mixture of *n*-hexane and dichloromethane (1:1)) (73.5% yield) was synthesized from **5b** in the presence of excess amounts of pyridine, giving a white powder (mp 59−60 °C). ^{1}H NMR δ ($CDCl_3$): 0.80−4.00 (10H, m, br), 2.03 (3H, s), 2.84 (1H, s, br). LRMS: 202 (M+). HRMS: calcd for $C_4H_{14}O_2(^{10}B)_2(^{11}B)_8$ 202.1997, found 202.1992 (−0.5 mmu). IR ν_{max} (KBr) cm^{-1}: 3050, 2650, 2600, 1780, 1360, 1185, 1140, 1065, 1005, 720.

1-Acetoxy-1,12-dicarba-*closo*-dodecaborane(12) (6c). As described for the preparation of **6b**, **6c** (78.6% yield) was synthesized from **5c** as a white powder (mp 59−60 °C). ^{1}H NMR δ ($CDCl_3$): 1.30−3.40 (10H, quad, 167.4), 1.91 (3H, s), 2.64 (1H, s, br). LRMS: 202 (M^+). HRMS: calcd for $C_4H_{14}O_2(^{10}B)_2(^{11}B)_8$ 202.1997, found 202.1963 (−3.4 mmu). IR ν_{max} (KBr) cm^{-1}: 3050, 2600, 1780, 1360, 1185, 1165, 1050, 1000, 970, 725.

1,2-Dicarba-*closo*-dodecaboran(12)-1-yl Tosylate (7a). A solution of **5a** (20.0 mg, 0.13 mmol), tosyl chloride (TsCl) (33.3 mg, 0.18 mmol), and a catalytic amount of pyridine in

dichloromethane (1 mL) was stirred overnight at room temperature under an argon atmosphere. The reaction mixture was poured into water, and the crude product was extracted twice with dichloromethane. The dichloromethane solution was washed with brine and dried over anhydrous Na_2SO_4. The concentration of the solvent gave a residue (58.1 mg). The obtained residue was chromatographed on silica gel with a mixture of *n*-hexane and dichloromethane (4:1). Removal of the solvent of the eluate gave **7a** as a white powder (mp 84−85 °C) in a 12.7% yield (5.0 mg). ^{1}H NMR δ ($CDCl_3$): 0.80−3.40 (10H, m, br), 2.50 (3H, s), 4.26 (1H, s, br), 7.41 (2H, d, 7.9), 7.80 (2H, d, 8.6). LRMS: 314 (M^+). HRMS: calcd for $C_9H_{18}O_3S(^{10}B)_2(^{11}B)_8$ 314.1980, found 314.1985 (+0.5 mmu).

1,7-Dicarba-*closo*-dodecaboran(12)-1-yl Tosylate (7b). As described for the preparation of **7a**, **7b** (35.8% yield) was synthesized from **5b** in the presence of excess amounts of pyridine. **7b** was isolated by chromatography on silica gel with a mixture of *n*-hexane and dichloromethane (4:1) as a white powder (mp 83 °C). ^{1}H NMR δ ($CDCl_3$): 1.20−3.80 (10H, m, br), 2.47 (3H, s), 2.84 (1H, s, br), 7.36 (2H, d, 8.5), 7.75 (2H, d, 8.5). LRMS: 314 (M^+). HRMS: calcd for $C_9H_{18}O_3S(^{10}B)_2(^{11}B)_8$ 314.1980, found 314.1958 (−2.2 mmu).

1,12-Dicarba-*closo*-dodecaboran(12)-1-yl Tosylate (7c). As described for the preparation of **7b**, **7c** (27.9% yield) was synthesized from **5c**, giving a white powder (mp 81 °C). ^{1}H NMR δ ($CDCl_3$): 1.20−3.20 (10H, m, br), 2.45 (3H, s), 2.59 (1H, s, br), 7.33 (2H, d, 8.0), 7.67 (2H, d, 8.5). LRMS: 314 (M^+). HRMS: calcd for $C_9H_{18}O_3S(^{10}B)_2(^{11}B)_8$ 314.1980, found 314.1976 (−0.4 mmu).

1,2-Dicarba-*closo*-dodecaboran(12)-1-yl Triflate (8a). To a solution of **5a** (20.0 mg, 0.13 mmol) in dichloromethane (1 mL) was added trifluoromethanesulfonic anhydride (TFSAA) (0.5 mL). An adequate amount of pyridine (ca. 0.3 mL) was added dropwise to the reaction mixture for a period exceeding 1 h. (Due to the decomposition of TFSAA, excess amounts of pyridine were needed. However, the amount of pyridine had to be prepared at less than 1 equiv.) The resulting suspension was poured into water, and the crude product was extracted twice with dichloromethane. The dichloromethane solution was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The obtained residue was chromatographed on silica gel with a mixture of *n*-hexane and dichloromethane (2:1). Removal of the solvent of the eluate gave **8a** as a white viscous material in a 44.9% yield (16.4 mg). ^{1}H NMR δ ($CDCl_3$): 1.20−3.30 (10H, m, br), 4.25 (1H, s). ^{11}B NMR δ ($CDCl_3$): −14.45 (2B, d, 171.6), −12.37 (4B, d, 177.3), −11.40 (2B, d, 153.9), −8.73 (1B, d, 157.0), −3.40 (1B, d, 150.9). LRMS: 292 (M^+), 143 (M^+ − 149). HRMS: calcd for $C_3H_{11}O_3F_3S(^{10}B)_2(^{11}B)_8$ 292.1384, found 292.1374 (−1.0 mmu).

1,7-Dicarba-*closo*-dodecaboran(12)-1-yl Triflate (8b). As described for the preparation of **8a**, **8b** (69.6% yield) was synthesized from **5b** in the presence of excess amounts of pyridine, giving a colorless liquid. ^{1}H NMR δ ($CDCl_3$): 1.25−3.85 (10H, m, br), 2.97 (1H, s). LRMS: 292 (M^+), 143 (M^+ − 149). HRMS: calcd for $C_3H_{11}O_3F_3S(^{10}B)_2(^{11}B)_8$ 292.1384, found 292.1375 (−0.9 mmu).

1,12-Dicarba-*closo*-dodecaboran(12)-1-yl Triflate (8c). As described for the preparation of **8b**, **8c** (73.4% yield) was synthesized from **5c**, giving a colorless liquid. ^{1}H NMR δ ($CDCl_3$): 1.25−3.34 (10H, m, br), 2.71 (1H, s). ^{13}C NMR δ ($CDCl_3$): 53.74, 105.08, 117.67 (q, 319.7). ^{11}B NMR δ ($CDCl_3$): −17.22 (5B, d, 167.2), −13.93 (5B, d, 173.0). LRMS: 292 (M^+), 143 (M^+-149). HRMS: calcd for $C_3H_{11}O_3F_3S(^{10}B)_2(^{11}B)_8$ 292.1384, found 292.1392 (+0.8 mmu).

2-*tert*-Butyl-1,2-dicarba-*closo*-dodecaborane(12) 1-Alcohol (21). To a solution of **16** (500.0 mg, 2.5 mmol) in dry ether (20 mL) was added a 1.6 M solution of *n*-butyllithium (*n*BuLi) (in *n*-hexane) (1.6 mL, 2.5 mmol) for a period of 5 min at 3 °C under an argon atmosphere. After being stirred for 1 h at room temperature, a solution of benzoyl peroxide (25% wet; 484 mg, 1.5 mmol) in dry ether (20 mL), which was dried by 3 Å molecular sieves, was added dropwise to the reaction suspension for a period of 10 min at room temperature. The white suspension was stirred overnight at room temperature. The suspension was poured into ice-cooled 5% HCl and was extracted twice with ethyl acetate. The ethyl acetate solution was washed with aqueous sodium hydrogen carbonate solution (aq $NaHCO_3$) and brine, successively. The ethyl acetate solution was dried over anhydrous $MgSO_4$. The concentration of the solvent gave a colorless residue (216.7 mg, 80.1%). The residue was chromatographed on silica gel with a mixture of *n*-hexane and dichloromethane (2:1) and then with a mixture of *n*-hexane and ethyl acetate (2:1). Removal of the solvent of the eluate gave **21** as a colorless wax (mp 68−70 °C) (202.3 mg). ^{1}H NMR δ ($CDCl_3$): 1.10−3.50 (10H, m, br), 1.36 (9H, s). ^{13}C NMR δ ($CDCl_3$): 32.94, 38.50, 90.61, 103.50. ^{11}B NMR δ ($CDCl_3$): −13.78 (2B, d, 148.2), −12.80 (2B, d, 153.9), −11.25 (3B, d, 164.2), −10.589 (2B, d, 115.8), −5.56 (1B, d, 134.9). LRMS: 216 (M^+). HRMS: calcd for $C_6H_{20}O(^{10}B)_2(^{11}B)_8$ 216.2518, found 216.2494 (−2.4 mmu).

2-*tert*-Butyl-1,2-dicarba-*closo*-dodecaboran(12)-1-yl Triflate (26). To a solution of **21** (50.0 mg, 0.24 mmol) and TFSAA (1 mL) in dichloromethane (5 mL) was added pyridine (0.5 mL) for 5 min at room temperature under an argon atmosphere. After being stirred for 1 h, the resulting orange suspension was poured into ice−water, and the crude product was extracted with *n*-hexane twice. The *n*-hexane solution was washed with brine and dried over anhydrous Na_2SO_4. Removal of the solvent gave a colorless residue, and the residue was chromatographed on silica gel with *n*-hexane. Removal of the solvent of the eluate gave **26** as a colorless liquid in a 64.1% yield (51.7 mg). ^{1}H NMR δ ($CDCl_3$): 1.40 − 3.70 (10H, m, br), 1.37 (9H, s). LRMS: 348 (M^+), 199 (M^+ − 149). HRMS: calcd for $C_7H_{19}O_3F_3S(^{10}B)_2(^{11}B)_8$ 348.2020, found 348.1994 (−1.6 mmu).

1-Acetoxy-2-*tert*-butyl-1,2-dicarba-*closo*-dodecaborane-(12) (31). To a solution of **21** (25.5 mg, 0.12 mmol) in acetic anhydride (1 mL) was added a catalytic amount of pyridine (5 drops) at 3 °C. After being stirred for 1 h at room temperature, the reaction mixture was poured into ice−water and extracted twice with *n*-hexane. The *n*-hexane solution was washed with brine and dried over anhydrous Na_2SO_4. Removal of the solvent gave a colorless residue, which was then chromatographed on silica gel with a mixture of *n*-hexane and dichloromethane (2:1), giving **31** as a colorless prism (mp 84−86 °C) in a 77.7% yield (23.7 mg). ^{1}H NMR δ ($CDCl_3$): 1.31 (9H, s), 2.13 (3H, s), 1.20−3.80 (10H, m, br). LRMS: 258 (M^+). HRMS: calcd for $C_8H_{22}O_2(^{10}B)_2(^{11}B_2)_8$ 258.2623, found 258.2628 (+0.5 mmu).

2-Trimethylsilyl-1,2-dicarba-*closo*-dodecaborane(12) 1-Alcohol (22). As described for the preparation of **21**, **22** (chromatographed on silica gel with a mixture of *n*-hexane and ethyl acetate (2:1)) (30.1% yield) was obtained from **17** as a colorless prism (mp 115−117 °C). ^{1}H NMR δ ($CDCl_3$): 0.31 (9H, s), 1.20−3.30 (10H, m, br). ^{13}C NMR δ ($CDCl_3$): −0.29, 74.24, 102.63. ^{11}B NMR δ ($CDCl_3$): −12.59 (2B, d, 179.6), −11.05 (5B, d, 152.5), −10.27 (2B, d, 129.1), −2.51 (1B, d, 148.2). LRMS: 232 (M^+). HRMS: calcd for $C_5H_{20}OSi(^{10}B)_2(^{11}B)_8$ 232.2287, found 232.2282 (−0.5 mmu).

2-Trimethylsilyl-1,2-dicarba-*closo*-dodecaboran(12)-1-yl Triflate (27). As described for the preparation of **26**, **27** (64.3% yield) was synthesized from **22** as a colorless liquid. ^{1}H NMR δ ($CDCl_3$): 0.35 (9H, s), 1.20−3.50 (10H, m, br). LRMS: 364 (M^+), 215 (M^+-149). HRMS: calcd for $C_6H_{19}O_3F_3SiS(^{10}B)_2(^{11}B)_8$ 364.1779, found 364.1810 (+3.1 mmu).

2-Cyclopropyl-1,2-dicarba-*closo*-dodecaborane(12) 1-Alcohol (23). As described for the preparation of **21**, **23** (chromatographed on silica gel with a mixture of *n*-hexane and ethyl acetate (4:1)) was obtained from **18** as a colorless liquid. ^{1}H NMR δ ($CDCl_3$): 0.75−0.93 (4H, m), 1.00−3.20 (10H, m, br), 1.68 (1H, dddd, 13.4, 8.4, 8.2, 5.1). ^{11}B NMR δ ($CDCl_3$): −13.96 (2B, d, 132.0), −13.44 (2B, d, 162.8), −11.52 (3B, d, 175.9, br), −10.28 (2B, d, 184.7), −6.77 (1B, d, 165.6). LRMS: 200 (M^+).

HRMS: calcd for $C_5H_{16}O(^{10}B)_2(^{11}B)_8$ 200.2204, found 200.2189 (−1.5 mmu).

2-Cyclopropyl-1,2-dicarba-*closo*-dodecaboran(12)-1-yl Triflate (28). As described for the preparation of **26**, **28** (69.8% yield) was synthesized from **23** as a colorless liquid. ^{1}H NMR δ ($CDCl_3$): 0.82 (2H, dddd, 7.1, 7.1, 5.9, 4.8), 0.98 (2H, dddd, 8.2, 8.2, 7.6, 4.1), 1.2−3.8 (10H, m, br), 1.66 (1H, dddd, 8.4, 8.4, 5.1, 5.1). LRMS: 332 (M^+). HRMS: calcd for $C_6H_{15}O_3F_3S(^{10}B)_2(^{11}B)_8$ 332.1695, found 332.1704 (+0.7 mmu).

2-Phenyl-1,2-dicarba-*closo*-dodecaborane(12) 1-Alcohol (24). As described for the preparation of **21**, **24** (chromatographed on silica gel with a mixture of *n*-hexane and ethyl acetate (8:1) and then with a mixture of dichloromethane and methanol (8:1)) was synthesized from **19** as a colorless wax (mp 75−77 °C). ^{1}H NMR δ ($CDCl_3$): 1.00−3.70 (10H, m, br), 7.39 (2H, dddd, 7.7, 7.1, 1.8, 1.6), 7.46 (1H, dddd, 7.2, 7.1, 2.2, 1.3), 7.72 (2H, dd, 7.5, 1.5). ^{13}C NMR δ ($CDCl_3$): 83.84, 103.73, 128.57, 130.37, 131.09. ^{11}B NMR δ ($CDCl_3$): −13.68 (2B, d, 143.7), −11.15 (7B, d, 148.0), −5.01 (1B, d, 149.4). LRMS: 236 (M^+). HRMS: calcd for $C_8H_{16}O(^{10}B)_2(^{11}B)_8$ 236.2204, found 236.2204 (+0.0 mmu).

2-Phenyl-1,2-dicarba-*closo*-dodecaboran(12)-1-yl Triflate (29). As described for the preparation of **26**, **29** (52.5% yield) was synthesized from **24** as a colorless wax (mp 27 °C). ^{1}H NMR δ ($CDCl_3$): 1.20−3.80 (10H, m, br), 7.43 (2H, t, 8.1), 7.51 (1H, t, 7.5), 7.70 (2H, d,7.5). LRMS: 368 (M^+), 219 (M^+ − 149). HRMS: calcd for $C_9H_{15}O_3F_3S(^{10}B)_2(^{11}B)_8$ 368.1697, found 368.1712 (+1.5 mmu).

1-Acetoxy-2-phenyl-1,2-dicarba-*closo*-dodecaborane-(12) (32). As described for the preparation of **31**, **32** (68.2% yield) was obtained from **24** as a white powder (mp 96 °C). ^{1}H NMR δ ($CDCl_3$): 1.20−3.80(10H, m, br), 1.76 (3H, s), 7.38 (2H, dddd, 7.9, 7.9, 1.5, 1.5), 7.46 (1H, dddd, 7.5, 7.5, 1.3, 1.3), 7.65 (2H, ddd, 7.3, 1.8, 1.8). IR ν_{max} (KBr) cm^{-1}: 2520, 2510, 1805, 1480, 1440, 1420, 1365, 1145, 1065, 1025, 1005, 935, 855, 790, 755, 720, 685. LRMS: 278 (M^+). HRMS: calcd for $C_{10}H_{18}O(^{10}B)_2(^{11}B)_8$ 278.2310, found 278.2262 (−4.8 mmu).

2-(4′-Methoxyphenyl)-1,2-dicarba-*closo*-dodecaborane-(12) 1-Alcohol (25). As described for the preparation of **21**, **25** (chromatographed on silica gel with a mixture of *n*-hexane and dichloromethane (2:1) and then with a mixture of dichloromethane and methanol (8:1)) was synthesized from **20** in a 78.5% yield. Colorless needles (mp 168 °C) were obtained. ^{1}H NMR δ ($CDCl_3$): 1.20−3.50 (10H, m, br), 3.83 (3H, s), 6.88 (2H, ddd, 8.8, 3.3, 2.0), 7.63 (2H, ddd, 9.0, 3.5, 2.0). ^{13}C NMR δ ($CDCl_3$): 55.52, 84.14, 103.12, 113.97, 122.34, 132.62, 161.10. ^{11}B NMR δ ($CDCl_3$): −13.74 (2B, d, 145.1), −11.17 (7B, d, 174.5), −5.21 (1B, d, 174.5). LRMS: 266 (M^+). HRMS: calcd for $C_9H_{18}O_2(^{10}B)_2(^{11}B)_8$ 266.2310, found 266.2321 (+1.1 mmu).

2-(4′-Methoxyphenyl)-1,2-dicarba-*closo*-dodecaboran-(12)-1-yl Triflate (30). As described for the preparation of **26**, **30** (61.4% yield) was synthesized from **25** as a colorless liquid. ^{1}H NMR δ ($CDCl_3$): 1.10−3.80 (10H, m, br), 1.37 (9H, s). LRMS: 398 (M^+), 249 (M^+-149). HRMS: calcd for $C_{10}H_{17}O_4F_3S(^{10}B)_2(^{11}B)_8$ 398.1803, found 398.1799 (−0.4 mmu).

1-Acetoxy-2-(4′-methoxyphenyl)-1,2-dicarba-*closo*-dodecaborane(12) (33). As described for the preparation of **31**, **33** (67.7% yield) (mp 113−115 °C) was synthesized from **25** as a colorless prism. ^{1}H NMR δ ($CDCl_3$): 1.79 (3H, s), 3.83 (3H, s), 1.20−3.90 (10H, m, br), 6.87 (2H, d, 9.0), 7.56 (2H, d, 9.0). HRMS: calcd for $C_{11}H_{20}O_3(^{10}B)_2(^{11}B)_8$ 308.2415, found 308.2397 (−1.8 mmu).

General Procedure of Acetolysis. A 0.027 M solution of **7** (or **8c**) (0.016 mmol) in 99.5% deuterated d_4-acetic acid (or 99.7% acetic acid) (0.6 mL) in the presence or absence of 0.05 M sodium acetate (or 99% deuterated NaOAc-d_3) was sealed in an NMR tube. The reaction mixture was heated at 120 °C for specified times.

A 0.02 M (or 0.03 M) solution (0.6 mL) of triflate (**26**−**30**) (0.012 mmol) in acetic acid (or 99.5% deuterated AcOD-d_3) (0.6 mL) in the presence or absence of 0.05 M NaOAc-d_3 was sealed in an NMR tube. The reaction mixture was heated under specified conditions and the ^{1}H NMR spectra were measured. The chemical shifts were compared with those of authentic compounds. The reaction mixture was poured into 5% HCl and extracted twice with dichloromethane. The dichloromethane solution was dried over anhydrous Na_2SO_4 and concentrated in vacuo for comparison with the authentic compounds.

General Procedure of Trifluoroethanolysis. In the presence or absence of 0.03 M K_2CO_3, a 0.02 M solution of triflate (**26**−**30**) (0.012 mmol) in distilled trifluoroethanol (TFE) (or 99.5% deuterated TFE-d_3) (0.6 mL) was sealed in an NMR tube. The reaction mixture was heated under specified conditions. The reaction mixture was poured into water and extracted with dichloromethane. The dichloromethane solution was dried over anhydrous Na_2SO_4 and concentrated in vacuo for the comparison with an authentic compound by ^{1}H NMR.

Kinetic Procedure. In the presence of potassium carbonate (0.05 M), a 0.026 M solution of **8** (5.0 mg, 0.017 mmol) in TFE (0.57 mL) and 99.96% deuterated toluene-d_8 (0.1 mL) was sealed in an NMR tube and was frozen at −78 °C until ^{11}B NMR measurement. The reaction mixture was then heated with an external VT system for arbitrary durations. **8a**: 5.2 ± 0.1 °C, 9.7 ± 0.1 °C, 40.9 ± 0.1 °C. **8b**: 50.7 ± 0.1 °C, 60.6 ± 0.1 °C, 70.7 ± 0.1 °C. **8c**: 60.6 ± 0.1 °C, 65.8 ± 0.1 °C, 70.7 ± 0.1 °C.

General Procedure for Acidic Conditions in TFSA. A solution of 20 mg of **4** (or **5**) in distilled TFSA (0.7 mL) was prepared in a drybox under an argon atmosphere and sealed in an NMR tube. The solution was frozen at −78 °C until NMR measurements. The ^{1}H NMR (at 30 °C) and ^{13}C NMR (at −25 °C and 30 °C) spectra were measured and the peak of TFSA was referenced (10.46 ppm for ^{1}H and 114.7 ppm for ^{13}C) after the NMR was tuned with acetone-d_6. The chemical shifts of ^{11}B NMR (at 30 °C) referenced the peak of 15% $BF_3{\cdot}Et_2O$ (0.0 ppm) in $CDCl_3$ (v/v).

General Procedure for Acidic Conditions in Magic Acid (SbF_5/FSO_3H = 1:1). A solution of **5** (or **8c**) (20 mg) in cooled Magic Acid (0.6 mL) was prepared in a drybox under an argon atmosphere. After sampling in an NMR tube, the tube was sealed and the solution was frozen at −78 °C until the NMR measurements were carried out.

^{1}H NMR (at −60 and +30 °C) and ^{13}C NMR (at −60, −30, 0, and +30 °C) spectra were measured after the NMR was tuned with acetone-d_6, and the chemical shifts were measured with respect to the external reference of capillaried TMS (0.0 ppm) in Magic Acid. The chemical shifts of ^{11}B NMR (at −60, +30 °C) referenced the peak of 15% $BF_3{\cdot}Et_2O$ (0.0 ppm) in $CDCl_3$ (v/v).

Supporting Information Available: Part of the Experimental Section, the NMR (^{1}H, ^{11}B, and ^{13}C) spectra of **5c** in Magic Acid, and the ^{1}H or ^{13}C NMR spectra of newly obtained compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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