Chemistry of the Carba-*closo*-dodecaborate(−) Anion, $CB_{11}H_{12}^-$

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1. Introduction

Polyhedral borane and carborane clusters are characterized by delocalized electron-deficient bonding, meaning that there are too few valence electrons for bonding to be described exclusively in terms of 2-center-2-electron (2c2e) bonds.[1,2] One characteristic of electron-deficient structures is the aggregation of atoms to form 3-center-2-electron (3c2e) bonds, which typically results in formation of trigonal faces and hypercoordination. The high connectivity of atoms in a cluster compensates for the relatively low electron density in skeletal bonds.[3] In drawing these polyhedral structures, it is common not to indicate the atoms at each vertex specifically. If no atom is indicated, it is assumed that the vertex contains a BH group. If the vertex contains a BH_2 group, only one of the hydrogens is shown explicitly, etc. Substituents other than H are always shown explicitly. If a vertex contains an atom other than B, such as C, the heteroatom and its hydrogens are both shown explicitly. We adopted this notation for the structural formulas shown in this review, but the reader should be warned that at times different conventions are used by other authors.

The three-dimensional deltahedral shapes typical of boron and carborane clusters are described by the terms closo, nido, arachno, and hypho. Closo refers to structures that are closed polyhedra with triangular faces, whereas nido clusters result by removal of one vertex. Likewise, arachno means two vertices and hypho means three vertices short of a closed polyhedron. Of interest presently are the closo clusters, which possess especially high thermal and chemical stability. The number of vertices n can range from 4 to 13.

The hypho, arachno, nido, and closo classes of structures are associated with degrees of hydrogenation. When a sufficient number of protons is added to neutralize all but two negative charges, the composition of these four forms is $B_nH_{n+6}^{2-}$, $B_nH_{n+4}^{2-}$, $B_nH_{n+2}^{2-}$, and $B_nH_n^{2-}$, respectively. Often the state of protonation is different, and the total charge

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Stefanie Körbe was born in 1974 in Bad Hersfeld, Germany, and studied Chemistry at the University of Göttingen, Germany. In 2001 she obtained her Ph.D. degree in Organic Chemistry with Professor Armin de Meijere at the University of Göttingen, where she was working on palladium-catalyzed cascade reactions. She then joined the group of Professor Josef Michl at the University of Colorado at Boulder for a postdoctoral position, working on the synthesis of carborane-containing polymers. Currently she is a postdoctoral researcher at the Institute of Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, where she continues to work on carboranes.

Peter Schreiber was born and raised outside of Chicago, IL. He obtained his B.S. degree from DePaul University in Chicago, IL, in 2000. He is currently finishing his Ph.D. degree at the University of Colorado, Boulder, under the direction of Professor Josef Michl. His thesis deals with the chemistry of the CB_{11} anion and some of its derivatives. Other research interests include hole-conducting polymers and proton-conducting membranes for fuel cells, batteries, and solar cells.

Josef Michl was born in 1939 in Prague, Czechoslovakia. He received his M.S. degree in Chemistry in 1961 under V. Horák and P. Zuman at Charles University, Prague, and his Ph.D. degree in 1965 under R. Zahradník at the Czechoslovak Academy of Sciences, also in Prague. He left Czechoslovakia in 1968. He did postdoctoral work with R. S. Becker at the University of Houston, with M. J. S. Dewar at the University of Texas at Austin, with J. Linderberg at Aarhus University, Denmark, and with F. E. Harris at the University of Utah, where he stayed and became a full professor in 1975 and served as chairman in 1979–1984. In 1986–1990 he held the M. K. Collie-Welch Regents Chair in Chemistry at the University of Texas at Austin, and he subsequently moved to the University of Colorado at Boulder. He is a member of the National Academy of Sciences, the American Academy of Arts and Sciences, the Czech Learned Society, and the International Academy of Quantum Molecular Science. Dr. Michl's current research interests are the development of a molecular-size "Tinkertoy" construction set for the assembly of giant molecules and surface-mounted molecular rotors, photophysics and photochemistry, chemistry of silicon, fluorine, and boron, preparation and study of reactive organic and organometallic molecules, and use of quantum chemical and experimental methods for better understanding the molecular electronic structure. He has been the Editor of *Chemical Reviews* since 1984.

on the molecule then adjusts accordingly. For example, the common electroneutral decaborane $B_{10}H_{14}$ and anion $B_{11}H_{14}^-$ belong to the nido class.

There is an even more oxidized class of polyhedral boranes, hypercloso, B_nH_n, but its members are rare and normally only stable when highly substituted with π-electron donors, e.g., B_4Cl_4. We shall see below that they more commonly occur as reactive intermediates.

In their stable redox form, deltahedral closo boranes thus have the formula $B_nH_n^{2-}$, and the 12-vertex icosahedral cluster, $B_{12}H_{12}^{2-}$, is the most common. Replacement of one or more vertex boron atoms with atoms of other elements leads to closo heteroboranes. Since CH is isoelectronic with BH^-, the anion $CB_{11}H_{12}^-$ and neutral species $C_2B_{10}H_{12}$ are *closo*-carboranes and enjoy special stability.

The $CB_{11}H_{12}^-$ anion **1**, interchangeably referred to as the monocarba-*closo*-dodecaborane(−) or monocarba-*closo*-dodecaborate(−) anion, is the subject of the present review. The 30 lines commonly drawn in the surface of its icosahedral structure (Figure 1) merely indicate connectivity between cage atoms and not 30 two-electron bonds. Only 13 pairs of valence electrons are available for delocalized cluster bonding. Roughly speaking, in each contributing resonance structure they make (3c2e) bonds in 13 of the 20 triangular faces of the icosahedron, leaving 7 faces empty. In contrast, the 12 radial lines represent 12 ordinary two-electron bonds to 12 substituents. Because most substituents are attached through atoms that are more electronegative than boron, the radial bonds are typically polarized toward the substituents, which therefore carry a significant part of the unit net negative charge in **1**. Most of the rest resides on carbon, the most electronegative atom in the cluster. A more detailed description of the electronic structure is provided in section 2.

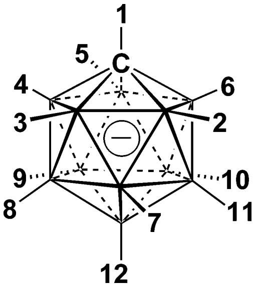


Figure 1. Vertex numbering in the CB_{11} icosahedron.

Since very modest beginnings 40 years ago and from the handful of derivatives that were known 20 years ago, the chemistry of **1** has grown tremendously. It is still possible to attempt to list all of its known derivatives **2**−**376** (Tables 1−3) in a single review (in Table 3 certain different salts of

Table 1. CB_{11} Anions with Five-fold Substitution Symmetry (cf. Figure 1)

	1	2−6	7−11	12		1	2−6	7−11	12
1[12]	H	H	H	H	**81**[23]	H	CF_3	F	F
2[13]	Me	H	H	H	**82**[23]	H	CF_3	CF_3	F
3[13]	H	Me	H	H	**83**[23]	H	F	CF_3	CF_3
4[13]	H	H	Me	H	**84**[23]	C_3H_5	F	CF_3	CF_3
5[14]	H	H	H	Me	**85**[23]	C_5H_9	F	CF_3	CF_3
6[13]	Me	Me	H	H	**86**[23]	H	CF_3	CF_3	CF_3
7[13]	Me	H	Me	H	**87**[24]	CF_3	CF_3	CF_3	CF_3
8[14]	Me	H	H	Me	**88**[19]	2-TMS-CH=CH	Me	Me	Me
9[13]	H	Me	Me	H	**89**[19]	2-Br-CH=CH	Me	Me	Me
10[13]	H	Me	H	Me	**90**[19]	$Me_{11}B_{11}C$-C=C	Me	Me	Me
11[13]	H	H	Me	Me	**91**[19]	$HC\equiv C$	Me	Me	Me
12[13]	H	Me	Me	Me	**92**[19]	TMS-$C\equiv C$	Me	Me	Me
13[13]	Me	H	Me	Me	**93**[25]	Ph-$C\equiv C$	H	H	H
14[13]	Me	Me	H	Me	**94**[19]	$Me_{11}B_{11}C$-$C\equiv C$	Me	Me	Me
15[13]	Me	Me	Me	H	**95**[26]	Ph	H	H	H
16[15]	Me	Me	Me	Me	**96**[27]	*p*-F-C_6H_4	H	H	H
17[16]	Et	H	H	H	**97**[27]	*p*-Cl-C_6H_4	H	H	H
18[13]	C_6H_{13}	H	H	H	**98**[27]	*p*-Br-C_6H_4	H	H	H
19[16]	$PhCH_2$	H	H	H	**99**[27]	*p*-I-C_6H_4	H	H	H
20[17]	CH_2OH	H	H	H	**100**[27]	*p*-C_6H_5-C_6H_4	H	H	H
21[17]	*i*PrCHOH	H	H	H	**101**[28]	Ph	Me	Me	Me
22[17]	X[a]	H	H	H	**102**[28]	3,4-Me_2-C_6H_3	Me	Me	Me
23[17]	PhCHOH	H	H	H	**103**[28]	2-biphenylenyl	Me	Me	Me
24[17]	X[b]	H	H	H	**104**[28]	2-naphthyl	Me	Me	Me
25[17]	$MeCHOHCH_2$	H	H	H	**105**[28]	*m*-NO_2-C_6H_4	Me	Me	Me
26[18]	1-(2-HOC_2H_4)	H	H	H	**106**[28]	*p*-NO_2-C_6H_4	Me	Me	Me
27[18]	1-(2-BrC_2H_4)	H	H	H	**107**[28]	*m*-CF_3-C_6H_4	Me	Me	Me
28[18]	1-(3-ClC_3H_6)	H	H	H	**108**[28]	*p*-CF_3-C_6H_4	Me	Me	Me
29[18]	1-(3-BrC_3H_6)	H	H	H	**109**[28]	*m*-CN-C_6H_4	Me	Me	Me
30[18]	1-(4-ClC_4H_8)	H	H	H	**110**[28]	*p*-CN-C_6H_4	Me	Me	Me
31[18]	1-(4-BrC_4H_8)	H	H	H	**111**[28]	*m*-CH_3-C_6H_4	Me	Me	Me
32[18]	1-(5-ClC_5H_{10})	H	H	H	**112**[28]	*p*-CH_3-C_6H_4	Me	Me	Me
33[18]	1-(5-BrC_5H_{10})	H	H	H	**113**[28]	*m*-Cl-C_6H_4	Me	Me	Me
34[18]	1-(6-ClC_6H_{12})	H	H	H	**114**[28]	*p*-Cl-C_6H_4	Me	Me	Me
35[18]	1-(6-BrC_6H_{12})	H	H	H	**115**[28]	*m*-Br-C_6H_4	Me	Me	Me
36[18]	1-(7-ClC_7H_{14})	H	H	H	**116**[28]	*p*-Br-C_6H_4	Me	Me	Me
37[18]	1-(7-BrC_7H_{14})	H	H	H	**117**[28]	*m*-I-C_6H_4	Me	Me	Me
38[18]	2-$PhCH_2Me_2N^+C_2H_4$	H	H	H	**118**[28]	*p*-I-C_6H_4	Me	Me	Me
39[18]	3-$PhCH_2Me_2N^+C_3H_6$	H	H	H	**119**[28]	*m*-MeO-C_6H_4	Me	Me	Me
40[18]	4-$PhCH_2Me_2N^+C_4H_8$	H	H	H	**120**[28]	*p*-MeO-C_6H_4	Me	Me	Me
41[18]	5-$PhCH_2Me_2N^+C_5H_{10}$	H	H	H	**121**[28]	*m*-Me_2N-C_6H_4	Me	Me	Me
42[18]	6-$PhCH_2Me_2N^+C_6H_{12}$	H	H	H	**122**[28]	*p*-Me_2N-C_6H_4	Me	Me	Me
43[18]	7-$PhCH_2Me_2N^+C_7H_{14}$	H	H	H	**123**[14]	H	H	H	Ph
44[19]	$Me_2N(CH_2)_2$	H	H	H	**124**[16]	H	H	H	C_6F_5
45[18]	C_6H_{11}	H	H	H	**125**[29]	Ph	H	H	Ph
46[20]	X[c]	H	H	H	**126**[13]	TIPS	H	H	H
47[21]	COOH	H	H	H	**127**[16]	Ph_3Si	H	H	H
48[14]	H	H	H	Et	**128**[13]	TIPS	H	Me	Me
49[14]	H	H	H	Bu	**129**[13]	TIPS	H	Et	Et
50[14]	H	H	H	C_6H_{13}	**130**[30]	$(C_6H_{12}O_2)B$	H	H	H
51[14]	H	H	H	$C_7H_6^+$	**131**[30]	$(C_6H_{12}O_2)B$	Me	Me	Me
52[13]	H	H	Et	Et	**132**[30]	$(C_6H_{12}O_2)B$	Me	Me	*p*-Br-C_6H_4
53[22]	H	Et	Et	Et	**133**[21]	NH_2	H	H	H
54[13]	H	Et	Me	Me	**134**[21]	NMeH	H	H	H
55[13]	C_6H_{13}	Me	Me	Me	**135**[12]	NMe_2	H	H	H
56[19]	$Me_3N^+(CH_2)_2$	Me	Me	Me	**136**[28]	N_3	Me	Me	Me
57[18]	2-$PhCH_2Me_2N^+C_2H_4$	Me	Me	Me	**137**[31]	X[d]	H	H	H
58[18]	3-$PhCH_2Me_2N^+C_3H_6$	Me	Me	Me	**138**[32]	$^-OHC{=}N^+(Me)$	H	H	H
59[18]	4-$PhCH_2Me_2N^+C_4H_8$	Me	Me	Me	**139**[32]	$^-OC(Ph){=}N^+(Me)$	H	H	H
60[18]	5-$PhCH_2Me_2N^+C_5H_{10}$	Me	Me	Me	**140**[33]	CH_3CONH	H	H	H
61[18]	6-$PhCH_2Me_2N^+C_6H_{12}$	Me	Me	Me	**141**[33]	X[e]	H	H	H
62[18]	7-$PhCH_2Me_2N^+C_7H_{14}$	Me	Me	Me	**142**[21]	NH_3^+	H	H	H
63[18]	2-BrC_2H_4	Me	Me	Me	**143**[21]	NH_2Me^+	H	H	H
64[18]	3-ClC_3H_6	Me	Me	Me	**144**[12]	NMe_2H^+	H	H	H
65[18]	3-BrC_3H_6	Me	Me	Me	**145**[12]	NMe_3^+	H	H	H
66[18]	4-ClC_4H_8	Me	Me	Me	**146**[32]	$HOCH{=}N^+(Me)$	H	H	H
67[18]	4-BrC_4H_8	Me	Me	Me	**147**[32]	$HOC(Ph){=}N^+(Me)$	H	H	H
68[18]	5-ClC_5H_{10}	Me	Me	Me	**148**[28]	1-$C_5H_5N^+$	Me	Me	Me
69[18]	5-BrC_5H_{10}	Me	Me	Me	**149**[32]	H	H	H	Me_3N^+
70[18]	6-ClC_6H_{12}	Me	Me	Me	**150**[16]	Ph_2P	H	H	H
71[18]	6-BrC_6H_{12}	Me	Me	Me	**151**[16]	$Ph_2P(OH)^+$	H	H	H
72[18]	7-ClC_7H_{14}	Me	Me	Me	**152**[21]	HO	H	H	H
73[18]	7-BrC_7H_{14}	Me	Me	Me	**153**[21]	MeO	H	H	H
74[18]	C_2H_3	Me	Me	Me	**154**[18]	CH_3COO	Me	Me	Me
75[18]	C_3H_5	Me	Me	Me	**155**[18]	HCOO	Me	Me	Me
76[18]	C_4H_7	Me	Me	Me	**156**[28]	CF_3CH_2O	Me	Me	Me
77[18]	C_5H_9	Me	Me	Me	**157**[28]	$(CF_3)_2HCO$	Me	Me	Me
78[18]	C_6H_{11}	Me	Me	Me	**158**[34]	H	H	H	X[f]
79[18]	C_7H_{13}	Me	Me	Me	**159**[34]	H	H	H	OH
80[16]	CF_3	H	H	H	**160**[35]	H	OH	OH	OH

Table 1. (Continued) CB_{11} Anions with Five-fold Substitution Symmetry (cf. Figure 1)

	1	2−6	7−11	12		1	2−6	7−11	12
161[36]	Me	Me	Me	OEt	**195**[29]	Ph	H	H	I
162[36]	Me	Me	Me	OMe	**196**[13]	TIPS	H	H	I
163[36]	Me	Me	Me	OH	**197**[44]	Me	H	Cl	Cl
164[21]	HS	H	H	H	**198**[44]	Me	H	Br	Br
165[21]	MeS	H	H	H	**199**[14]	Me	H	I	I
166[21]	Me_2S^+	H	H	H	**200**[40]	Me	F	F	F
167[21]	H	H	H	Me_2S	**201**[45]	Me	Cl	Cl	Cl
168[21]	H	H	H	X[g]	**202**[41]	Me	Br	Br	Br
169[37]	F	H	H	H	**203**[41]	Me	I	I	I
170[37]	Cl	H	H	H	**204**[46]	H	Me	Cl	Cl
171[37]	Br	H	H	H	**205**[46]	H	Me	Br	Br
172[37]	I	H	H	H	**206**[46]	H	Me	I	I
173[38]	H	H	H	F	**207**[13]	H	H	Me	I
174[21]	H	H	H	Cl	**208**[13]	TIPS	H	Me	I
175[21]	H	H	H	Br	**209**[13]	H	H	I	Me
176[21]	H	H	H	I	**210**[47]	H	Me	Me	I
177[21]	H	H	Cl	Cl	**211**[13]	H	Me	I	Me
178[21]	H	H	Br	Br	**212**[13]	H	I	Me	Me
179[39]	H	H	I	I	**213**[15]	Me	Me	Me	F
180[40]	H	F	F	F	**214**[47]	Me	Me	Me	I
181[41]	H	Cl	Cl	Cl	**215**[13]	Me	Me	I	Me
182[41]	H	Br	Br	Br	**216**[13]	Me	I	Me	Me
183[41]	H	I	I	I	**217**[13]	Me	Me	I	I
184[41]	Br	Br	Br	Br	**218**[48]	F	H	Me	Me
185[42]	Me_3N^+	H	H	I	**219**[48]	Cl	H	Me	Me
186[31]	X[d]	H	H	I	**220**[48]	Cl	Me	Me	Me
187[43]	NH_3^+	H	I	I	**221**[48]	Br	Me	Me	Me
188[43]	NH_3^+	I	I	I	**222**[48]	I	Me	Me	Me
189[14]	H	Br	Cl	Cl	**223**[49]	H	OH	Br	Br
190[14]	H	I	Cl	Cl	**224**[16]	H	H	H	X[h]
191[14]	H	Cl	Br	Br	**225**[16]	H	H	H	X[i]
192[14]	H	I	Br	Br	**226**[50]	NMe_3^+	H	H	X[i]
193[14]	H	Br	I	I	**227**[50]	NMe_3^+	X[i]	X[i]	X[i]
194[13]	Me	H	H	I					

[a] $MeCH{=}CHCHOH$. [b] 2-Furyl-CH(OH). [c] 3-I-Bicyclo[1.1.1]pent-1-yl. [d] 4-Pentylquinuclidinyl. [e] $HOCOCH_2CH_2CONH$. [f] $O(CH_2CH_2)O^+$. [g] $MeSCH_2S^+(Me)$. [h] CF_3COOHg. [i] CH_3COOHg.

Table 2. Low-Symmetry CB_{11} Anions (cf. Figure 1)

	compound		compound
228[51]	$2\text{-Ph-}CB_{11}H_{11}^-$	**248**[16]	$7,12\text{-}Cl_2\text{-}CB_{11}H_{10}^-$
229[51]	$2\text{-(}p\text{-}MeC_6H_4)\text{-}CB_{11}H_{11}^-$	**249**[16]	$7,12\text{-}Br_2\text{-}CB_{11}H_{10}^-$
230[51]	$2\text{-}Me_3N\text{-}CB_{11}H_{11}$	**250**[16]	$7,12\text{-}I_2\text{-}CB_{11}H_{10}^-$
231[52]	$2\text{-EtO-}CB_{11}H_{11}^-$	**251**[42]	$1\text{-}Me_3N\text{-2-Ph-8-}CH_2{=}CHCH_2\text{-}CB_{11}H_9$
232[51]	$2\text{-Cl}(CH_2)_4O\text{-}CB_{11}H_{11}^-$	**252**[42]	$1\text{-}Me_3N\text{-2-Ph-8-Br-}CB_{11}H_9$
233[51]	$2\text{-F-}CB_{11}H_{11}^-$	**253**[42]	$1\text{-}Me_2HN\text{-2-Ph-8-I-}CB_{11}H_9$
234[52]	$2\text{-Cl-}CB_{11}H_{11}^-$	**254**[53]	$7,9,12\text{-}F_3\text{-}CB_{11}H_9^-$
235[52]	$2\text{-Br-}CB_{11}H_{11}^-$	**255**[21]	$7,8,9,10,12\text{-}Cl_5\text{-}CB_{11}H_7^-$
236[16]	$7\text{-}C_6F_5\text{-}CB_{11}H_{11}^-$	**256**[57]	$1\text{-H-}7,12\text{-}Cl_2\text{-}CB_{11}Me_9^-$
237[32]	$7\text{-}H_3N\text{-}CB_{11}H_{11}$	**257**[50]	$1\text{-H-}CB_{11}H_9(HgOCOCF_3)_2^-$
238[32]	$7\text{-}Me_3N\text{-}CB_{11}H_{11}$	**258**[58]	$Rh(PPh_3)_2(7\text{-Et-}CB_{11}H_{11})$
239[53]	$7\text{-F-}CB_{11}H_{11}^-$	**259**[58]	$[Rh(PPh_3)_2(nbd)][7\text{-Et-}CB_{11}H_{11}]$
240[54]	$1\text{-}Me_2HN\text{-2-}i\text{}Pr_2NHCH_2\text{-}CB_{11}H_{10}$	**260**[58]	$Rh(PPh_3)_2(7\text{-}(CH_2{=}CH)\text{-}CB_{11}H_{11})$
241[55]	$1\text{-}Me_2N\text{-2-HS-}CB_{11}H_{10}^-$	**261**[58]	$[Rh(PPh_3)_2(nbd)][7\text{-}(CH_2{=}CH)\text{-}CB_{11}H_{11}]$
242[55]	$1\text{-}Me_2N\text{-2-}Me_2S\text{-}CB_{11}H_{10}$	**262**[58]	$[Rh(PPh_3)_2(1\text{-Me-}Et_3CB_{11}H_8]$
243[56]	$1\text{-}Me_2N\text{-7-}PhCH_2\text{-}CB_{11}H_{10}^-$	**263**[58]	$[Rh(PPh_3)_2(NCMe)_{2,3}][1\text{-Me-}Et_3\text{-}CB_{11}H_8]$
244[56]	$1\text{-}Me_3N\text{-7-}PhCH_2\text{-}CB_{11}H_{10}$	**264**[58]	$[Rh(PPh_3)_2(NCMe)_{2,3}][1\text{-Me-}Hex_3\text{-}CB_{11}H_8]$
245[55]	$1\text{-}Me_2N\text{-7-}Et_3N\text{-}CB_{11}H_{10}$	**265**[58]	$Rh(PPh_3)_2\text{-1-H-}Et_5\text{-}CB_{11}H_6$
246[38]	$2,12\text{-}F_2\text{-}CB_{11}H_{10}^-$	**266**[58]	$[Rh(PPh_3)_2(nbd)][1\text{-H-}Et_5CB_{11}H_6]$
247[53]	$7,12\text{-}F_2\text{-}CB_{11}H_{10}^-$		

the same anion are given separate numbers because we later need to refer to them individually) and list their NMR spectra in the Supporting Information, as we do presently, but only barely.

The primary reason for this explosion of interest in the chemistry of **1** is the chemical inertness of these delocalized anions. Suitably substituted, anions of this class are among the least nucleophilic and the most weakly coordinating of all known anions. Most are very stable even to the most aggressive reagents. They also can be extremely difficult to oxidize and highly lipophilic. This combination of properties makes them useful in applications as diverse as counterions for reactive cationic organometallic catalysts, electrolytes for nonaqueous solvents and electrical batteries, solubilizers of cations in organic solvents for solvent extraction of radionuclides, and catalysis of radical polymerization of alkenes to name just a few examples. They have been proposed for use in material science, medicine, and nanoscience.[4] They have only one disadvantage, and that is their cost. What is most needed at present is a high-yield one-step or two-step synthesis from cheap bulk chemicals. As we shall see in section 7, starting with bulk chemicals, at this time some

Table 3. Complexes of CB$_{11}$ Anions[a]

	compound		compound
267[59]	Ag(PPh$_3$)(**1**)	**322**[81]	Et$_3$Si(**178**)
268[59]	Ag(PPh$_3$)$_2$(**1**)	**323**[81]	*i*-Pr$_3$Si(**178**)
269[60]	[(IMes)$_2$Ag]$_2$[Ag$_2$(**1**)$_4$]	**324**[81]	*tert*-Bu$_2$MeSi(**178**)
270[61]	[Pd(dppp)(**1**)][**1**]	**325**[81]	*tert*-Bu$_3$Si(**178**)
271[62]	[(Cy$_3$P)$_2$Rh(C$_7$H$_8$)][**1**]	**326**[78]	Et$_2$Al(**178**)
272[62]	[(dppe)Rh(C$_7$H$_8$)][**1**]	**327**[59]	Ag(PPh$_3$)(**178**)
273[62]	[{(MeO)$_3$P}$_2$Rh(C$_8$H$_{12}$)][**1**]	**328**[59]	Ag(PPh$_3$)$_2$(**178**)
274[62]	[(Cy$_3$P)$_2$Rh(**1**)]	**329**[64]	[(Ph$_3$P)$_2$Rh(C$_7$H$_8$)][**178**]
275[62]	[{(MeO)$_3$P}$_2$Rh(**1**)]	**330**[64]	[(Ph$_3$P)(PPh$_2$-η^6-C$_6$H$_5$)Rh]$_2$[**178**]$_2$
276[62]	[(dppe)Rh(**1**)]	**331**[65]	[{Cp*Rh(μ_2-Cl)}$_3$(μ_3-Cl)][**178**]
277[63]	[Rh(cod)][η^2-**1**]	**332**[82]	[(PPh$_3$)$_2$Ir(COD)][**178**]
278[63]	[Rh(cod)(THF)$_2$][**1**]	**333**[82]	(PPh$_3$)$_2$Ir(H$_2$)(**178**)
279[64]	(Ph$_3$P)$_2$Rh(**1**)	**334**[82]	[(PPh$_3$)$_2$Ir(η^2-C$_2$H$_4$)$_3$][**178**]
280[64]	[(Ph$_3$P)$_2$Rh(C$_7$H$_8$)][**1**]	**335**[82]	[(PPh$_3$)$_2$Ir(η^2-C$_2$H$_4$)$_2$][**178**]
281[64]	[(Ph$_3$P)$_2$HRh(μ-H)(μ-Cl)$_2$RhH(PPh$_3$)$_2$][**1**]	**336**[83]	Fe(TPP)(**178**)
282[65]	[Cp*RhCl]$_2$[**1**]$_2$	**337**[68]	[MoCp(CO)$_3$I·Ag(**178**)]$_2$
283[66]	[Cp′$_2$Fe][**1**]	**338**[84]	[Cp″$_2$Sm(THF)$_2$][**178**]
284[67,68]	[MoCp(CO)$_3$(**1**)]	**339**[84]	[Cp″$_2$Er(THF)$_2$][**178**]
285[67,68]	[MoCp(CO)$_3$I·Ag(**1**)]$_2$	**340**[79]	[H(THF)$_2$][**178**]
286[68]	[MoCp*(CO)$_3$(**1**)]	**341**[85]	[H(*m*-xylene)][**178**]
287[66]	Cp$_2$Zr(PhCH$_2$)(**1**)	**342**[78]	Et$_2$Al(**179**)
288[66]	Cp′$_2$Zr(CH$_3$)(**1**)	**343**[39]	Ag(**179**)
289[66]	Cp$_2$Zr(CH$_3$)(**1**)	**344**[41]	Ag(**181**)
290[66]	Cp′$_2$ZrCl$_2$Ag(adduct)(**1**)[b]	**345**[41]	Ag(**182**)
291[66]	Cp*Zr(CH$_3$)$_2$(**1**)	**346**[86]	[H$_7$O$_3$][**182**]
292[69]	Cp$_2$Zr(η^2-C,N-{C=N-*tert*-Bu}CH$_3$)(**1**)	**347**[86]	[H(OEt$_2$)(H$_2$O)][**183**]
293[58]	Rh(PPh$_3$)$_2$(12-(CH$_2$=CH)(CB$_{11}$H$_{11}$)	**348**[87]	Ag(**189**)
294[58]	Rh(PPh$_3$)$_2$(12-Et-CB$_{11}$H$_{11}$)	**349**[86]	[H$_3$O·H$_2$O][**189**]
295[58]	[Rh(PPh$_3$)$_2$(nbd)][12-(CH$_2$=CH)-CB$_{11}$H$_{11}$]	**350**[86]	[H(DMF)(H$_2$O)][**189**]
296[58]	[Rh(PPh$_3$)$_2$(nbd)][12-Et-CB$_{11}$H$_{11}$]	**351**[87]	Ag(**190**)
297[70]	Ag(**12**)	**352**[87]	Ag(**191**)
298[71]	Ag(PPh$_3$)(**12**)	**353**[87]	Ag(**192**)
299[70]	Ag(P(C$_6$H$_{11}$)$_3$)(**12**)	**354**[65]	[{(L)$_4$Ag$_3$}{Ag(CB$_{11}$I$_5$Br$_6$)$_2$}(L)]
300[70]	Ag(P{3,5-Me$_2$C$_6$H$_3$}$_3$)(**12**)	**355**[87]	Ag(**193**)
301[70]	[(OEt$_2$)$_2$Ag(PPh$_3$)][**12**]	**356**[88]	(C$_5$H$_5$N)$_2$Ag(**193**)(C$_5$H$_5$N)
302[70]	Ag(PPh$_3$)$_2$(**12**)	**357**[44]	Ag(**197**)
303[72]	*trans*-[PtMe(*i*Pr$_3$P)$_2$][**12**]	**358**[44]	Ag(**199**)
304[72]	*cis*-[Pt(*i*Pr$_3$P)(*i*Pr$_3$PC(H)MeCH$_2$)(THF)][**12**]	**359**[89]	Ag(C$_6$H$_6$)(**200**)
305[57]	[(Ph$_3$P)$_2$Ir(C$_8$H$_{12}$)][**12**]	**360**[41]	Ag(**201**)
306[73]	[{CpMo(CO)$_3$I}·Ag]$_2$[**12**]	**361**[41]	Ag(**202**)
307[73]	[{CpMo(CO)$_3$}$_2$(μ-I)][**12**]	**362**[86]	[H$_3$O][**202**]
308[74]	[Cp$_2$ZrMe(12-μ-**12**)]	**363**[90]	Me(**204**)
309[75]	Me$_3$Ge(**16**)	**364**[90]	Me(**205**)
310[76]	*n*-Bu$_3$Sn(**16**)	**365**[90]	Et(**205**)
311[75]	Me$_3$Sn(**16**)	**366**[90]	*n*-Pr(**205**)
312[75]	Me$_3$Pb(**16**)	**367**[90]	*i*-Pr(**205**)
313[73]	[MoCp(CO)$_3$I·Ag(**175**)]$_2$	**368**[91]	*tert*-Bu(**205**)
314[73]	[MoCp(CO)$_3$(**175**)]	**369**[91]	2-methylbutyl(**205**)
315[77]	[*i*-Pr$_3$Si(*o*-Cl$_2$C$_6$H$_4$)][**177**]	**370**[91]	1-Me-*c*-C$_5$H$_8$(**205**)
316[77]	[Me$_3$Si-H-SiMe$_3$][**177**]	**371**[92]	[B(SubPc)][**205**]
317[78]	Et$_2$Al(**177**)	**372**[79]	[H(OEt$_2$)$_2$][**205**]
318[39]	Ag(**177**)	**373**[79]	[H(THF)$_2$][**205**]
319[79]	[H(OEt$_2$)(H$_2$O)][**177**]	**374**[79]	[H(OEt$_2$)(H$_2$O)][**205**]
320[79]	[H(OEt$_2$)$_2$][**177**]	**375**[85]	[H(mes)][**205**][c]
321[80]	[*p*-*i*-Pr-C$_6$H$_4$-I-C$_6$H$_4$Me][**178**]	**376**[57]	[A]$_2$[1-H-12-ClCB$_{11}$Me$_{10}$]$_2$

[a] A = (*i*-Pr$_3$P)$_2$Pt (μ-Cl); L = MeCN; IMes = 1,3-dimesitylimidazol-2-ylidene, (**1**) = coordinated **1**; [**1**] = **1** as counterion. [b] Ag coordinated through Ag−Cl−Zr. [c] Mes = mesitylene.

syntheses have reasonable yields in many steps while other have poor yields in as few as two steps. It is likely that this bottleneck can be overcome, but it has not happened yet.

Most prior reviews of CB$_{11}$H$_{12}^-$ chemistry concentrated on use of these anions as weakly coordinating anions[5−9] and their applications[4] more than on their chemical transformations.[10,11] In contrast, we focus on the properties and chemical transformations of **1** and its derivatives, and pay little if any attention to the chemistry of the counterions, interesting as it may be. We cover work published since the appearance of Štíbr's comprehensive review[10] until mid-2006 and only occasionally refer to earlier publications.

2. Electronic Structure

The bench chemist's understanding of the electronic structure of boron compounds is not as developed as the understanding of carbon compounds, and delightful surprises, intriguing puzzles, and unexpected reactivity are commonplace. For example, qualitative features of substituent effects on aromatic reactivity can be easily explained to a beginning student using a few simple concepts, whereas substituent effects on the reactivity of CB$_{11}$H$_{12}^-$ still are somewhat mysterious. The difference is primarily due to the fact that "arrow pushing" in resonance structures is not easily applicable to structures based on (3c2e) bonding and has not seen much use. Early on, electron distribution in electron-deficient molecules, such as **1**, was described using resonance structures in which the valence electrons were assigned to localized 2-center BH and BB and delocalized 3-center BHB and BBB bonds. Using this simple yet powerful approach, Lipscomb was able to describe bonding in numerous boranes and carboranes.[93] The disadvantage of this model is that it does not accurately describe the distribution of the BB and BBB bonds over the $3n - 6$ edges and $2n - 4$ faces of the polyhedron.[93] Additionally, the number of canonical resonance structures needed to describe the electronic structure accurately becomes staggering as the number of vertices increases.

An alternative approach, known as Wade's rules for electron counting,[1] alleviated some of these difficulties by assigning the electrons to the vertices of the polyhedron, not to edges or faces.[3] Each BH vertex contributes two electrons to the polyhedral cage because boron has three valence electrons and hydrogen one, and two of these four valence electrons are needed to make an ordinary sigma BH bond. For $B_{12}H_{12}^{2-}$, 26 electrons are available for cage bonding: 12 electron pairs provided by the 12 BH vertices and a 13th electron pair, which originates in the double negative charge. If a BH is replaced with a CH vertex, as in $CB_{11}H_{12}^{-}$, there are still 26 cage electrons but the dianion becomes a monoanion since a carbon nucleus carries 6 positive charges as apposed to boron's 5. Carboranes with two carbon vertices, as in $C_2B_{10}H_{12}$, are electroneutral.

A more quantitative description of bonding in boron clusters is provided by molecular orbital (MO) calculations. Each boron and carbon donates three hybrid or atomic valence orbitals to the polyhedral cage, and as in the description above, the fourth valence orbital is involved in a 2-center-2-electron exoskeletal bond to the substituent. Early semiempirical studies, by methods such as MNDO, EHMO, and AM1, have been reviewed by Štíbr,[10] and the methods continue to be used for qualitative studies.[94] They offered an improved description of the electronic structure but still did not provide intuitive insight into the electron counting rules proposed by Wade nor did they explain the preference for structures with trigonal faces. Such insight resulted from Stone's treatment of the problem using tensor surface harmonics.[95−97] This model is a three-dimensional analog of the perimeter model used by Platt[98] and Moffitt[99] to account for the optical properties of planar aromatics.

With the advent of greater computational power, ab initio and lately also density functional theory (DFT) calculations have become accessible. The structure, energies, dipole moments, atomic charges, and vibrational frequencies of many 10- and 12-vertex boranes and heteroboranes were examined.[100] The charge distribution was recalculated and the electrophile-induced nucleophilic substitution path characteristic of **1** briefly investigated in another early paper.[101] The structure of the Jahn−Teller-distorted radical of **1** and ionization potentials were predicted[102] and three-dimensional aromaticity, magnetic properties, and relative energies of isomers evaluated.[103] Very good agreement was found between the DFT calculated and observed structures of fluorinated derivatives of **1**, and bond strengths to substituents and other properties were evaluated.[104] Gas-phase acidity of $H^{+}CB_{11}(CF_3)_{12}^{-}$ (**187**) and related acids was calculated and discussed.[24,105] Even more recently, the reaction path that leads from $B_{11}H_{14}^{-}$ to **1** has been explored[106] and the properties of partially methylated anions and radicals computed.[13] The charge distribution in **1** and **16** and the electrostatic potential around them were calculated.[75] Electrostatic potential calculation was used to develop an interesting new concept for evaluation of anion basicity.[107] Electron distribution is sensitive to replacement of a hydrogen atom on the cage framework by another substituent,[108,109] especially the antipodal (most distant) one. Perhaps the most interesting manifestation of the "antipodal" effect was found in the chemical shift in the ^{11}B NMR of the antipodal boron atom.[110] The energies of three of the four $CB_{11}H_{11}$ isomers[101,104] and the properties of all four $CB_{11}Me_{11}$[36] isomers with a "naked" vertex were computed.

Increasingly, results of computations appear in experimental papers such as those on metal complexes containing derivatives of **1**,[70,75,111] and it will soon become very difficult to attempt a complete listing as we do here. After this very brief survey, we shall have an opportunity to refer to the results of ab initio and DFT calculations in more detail in appropriate locations throughout the text.

2.1. Aromaticity and Thermal Stability

Aromaticity is a fuzzy but very useful concept that originated in planar π-electron systems but has been generalized to many others. By the traditional criteria, including unconventional delocalized bonding, unusual stability, and the associated propensity to substitution as opposed to addition reactions, one immediately suspects that closo carboranes might exhibit 3-dimensional aromaticity. A more rigorous analysis left no doubt that **1** is aromatic, based on a consideration of energies (resonance and aromatic stabilization), geometries (bond length equalization and bond order indices), and magnetic properties (chemical shifts, magnetic susceptibility anisotropy and exaltation, and NICS, nucleus-independent chemical shift).[103] Magnetic properties of **1** are particularly telling, and large negative values of magnetic susceptibility exaltation (−153.48 ppm cgs, cf. −155.86 ppm cgs for the neutral *o*-carborane $C_2B_{10}H_{12}$) as well as large negative NICS values (−34.4 ppm at the center of the cage of **1**) were calculated.

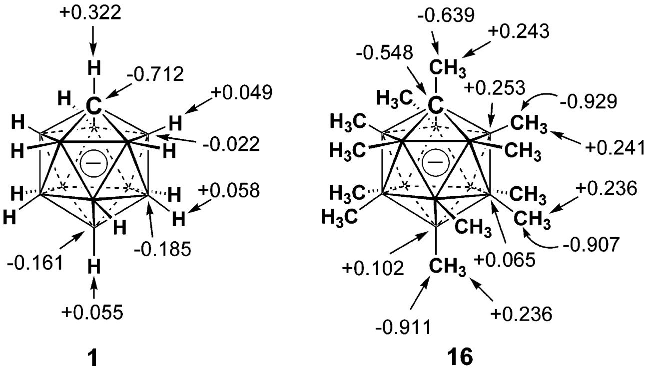
The thermodynamic stability of the closo carboranes is remarkable. It has been evaluated quantitatively using a structural-thermodynamic model[112] and found to be comparable to that of $B_{12}H_{12}^{2-}$. It has been stressed that overall carborane stability is a function of topographical charge distribution as well as connectivity.[113] Differential scanning calorimetry found nothing remarkable about the thermal properties of Cs^{+}**1** other than its great stability (water is eliminated at 137 °C and there is a phase transition at 291 °C).[114] No electrical conductivity was detected.

The exoskeletal bonds in **1** and its derivatives are calculated to be very strong.[104] The energies derived for the homolytic cleavage of the BH and BF bonds do not vary much as a function of position on the cluster and are about 103 and 155 kcal/mol, respectively, in position 2. For the other positions they are a little smaller but still within 2 kcal/mol the same. For heterolytic dissociation, the differences are larger, up to 12 kcal/mol, and this is due to the different stabilities of the isomers of the electroneutral ylide $CB_{11}H_{11}$, to be discussed in section 3.1.

2.2. Charge Distribution

All numerical calculations listed above agree that most of the calculated negative charge in **1** resides on the most electronegative atom in the cluster, the carbon in position 1, in contrast to earlier qualitative arguments based on reactivity and the structure of salts, which frequently refer to positions 7−12 as being the primary carriers of the negative charge in this anion. The exact values of the charges depend on the atomic charge definition used and the level of calculation, but the values of natural atomic charges computed in ref 75 for **1** and **16** and shown in Chart 1 are typical. In the same paper, the natural atomic charges were calculated for the ion pairs $Me_3Sn^+CB_{11}Me_{12}^-$ and $Me_3Ge^+CB_{11}Me_{12}^-$. There was little difference between the charge distributions in the free anion and in the salts, which indicates that the anion is not very polarizable. There was some charge transfer between ions in the ion pair, indicating a partial covalent character in the interaction. Cation−anion interactions are discussed in section 3.2.

Chart 1. Calculated Natural Atomic Charges in 1 and 16[75]



1 **16**

If the carbon of **1** is the carrier of much of its negative charge (Chart 1), why do crystal structures of salts invariably locate the positive counterion next to the antipodal position 12 or in one of the positions 7−11? We shall see in section 3.2 that solution NMR data also show unambiguously that these are the positions at which the cation preferentially resides.

The answer is provided in Figures 2 and 3, which show the anisotropy of the electrostatic potential calculated[75] for points on a sphere located at the center of the icosahedral anions **1** and **16** with a radius corresponding to a typical distances to a metal cation in the two cases. It is apparent that the lowest energy location for a cation is indeed in positions 7−12, although the same calculation yields the charge distribution shown in Chart 1, with most of the negative charge on the carbon in position 1. The authors actually recalculated the potential at the favored locations at the vertices from the point charges of Chart 1 using simple electrostatics and found an excellent agreement with the full-fledged evaluation from the ab initio calculation of the potential. The reason for the counterintuitive anisotropy of the electrostatic potential around anions **1** and **16** is actually quite simple. Because of the falloff of the potential of a charge with distance, the shape of the potential is dictated primarily by the distribution of charges on the surface and only to a much smaller degree by the charges inside, which are separated by the length of the bond to the substituent plus the van der Waals size of the substituent. It is therefore the strongly positive charge on the hydrogen or the methyl in position 1 that is responsible for making it relatively unfavorable to bring the counterion into the vicinity of vertex 1. In contrast, the hydrogens in positions 7−12 of **1** are approximately electroneutral and the methyl groups in these positions of **16** carry a net negative charge, making approach of a cation to these positions more favorable.

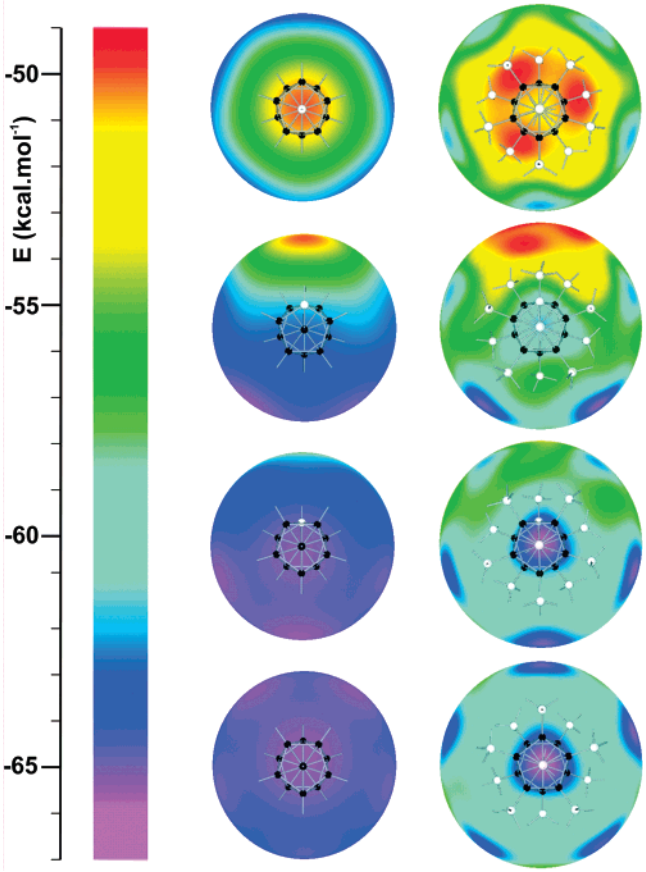


Figure 2. Electrostatic potential (B3LYP/6-31+G(d)) around **1** and **16**. The radii of the spheres are 5.2 and 5.7 Å, respectively, 2.5 Å from the hydrogen atoms (**1**) or methyl carbon atoms (**16**). Views along exocyclic bonds; from top to bottom, looking at positions 1, 2, 7, and 12.[75]

The charge distribution in the four $CB_{11}Me_{11}$ ylide isomers is of interest in connection with efforts to characterize their electronic structure.[36] These reactive intermediates are formed when one methide (methyl anion) is abstracted from the anion **16**, leaving a naked vertex in position 1, 2, 7, or 12. The distribution of natural atomic charges is similar as in **16**, except that there is a localized positive charge in the outward pointing radial orbital on the naked vertex, and the best description of the species in which the methyl is missing from vertices 2, 7, or 12 indeed is “boronium ylide”. When the naked vertex is located in position 1, the negative charge largely resides on the same atom as the positive charge, and the best single designation is “carbenoid”, even though the structure is intermediate between those of a carbenoid and an ylide. Its electronic structure is similar to that of the S_2 state of ordinary carbenes, with an unoccupied σ-type orbital and a doubly occupied π-type orbital on the carbon atom.

2.3. Molecular Orbitals

The molecular orbitals (MOs) of **1** have the form expected from Stone’s tensor harmonic bonding model,[95−97] and the correlation between I_h and C_{5v} point groups can be used to relate them to those of $B_{12}H_{12}^{2-}$. In the order of increasing energy, the occupied valence MOs of **1** are classified as a cluster bonding set (1−4), an exo bonding set (5−16), and a frontier set (17−25).

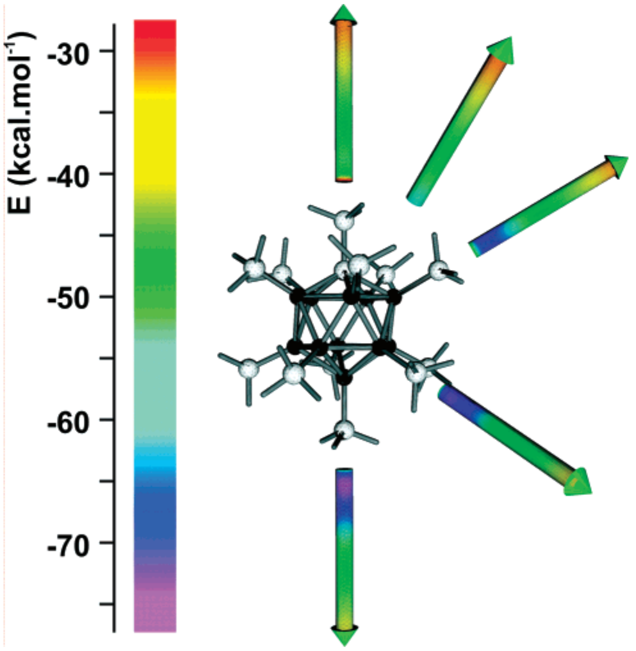


Figure 3. Electrostatic potential around **16**. The 5 Å long color-coded arrows are placed 1.2 Å above the carbon atom of methyl groups in positions 1, 2, 7, and 12. One arrow is placed between positions 1 and 2, showing that in this region the electrostatic potential is higher than that directly above the methyl group in position 1.[75]

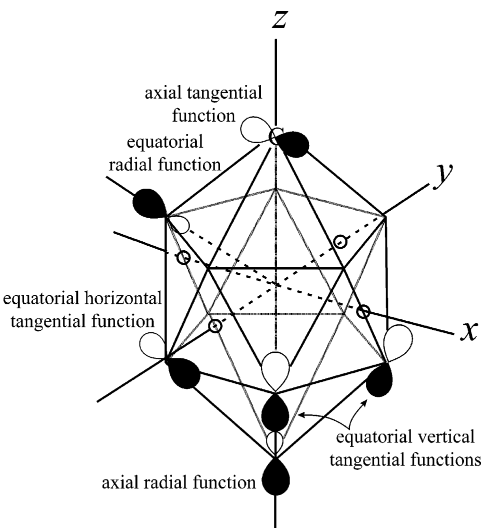


Figure 4. Definition of the cluster basis functions.

Stone's symmetry-adapted cluster basis set (Figure 4) is particularly appropriate for the display and discussion of the shape of these MOs and in a sense analogous to the familiar set of six carbon 2p_z orbitals ordinarily used to discuss the MOs of benzene. At each vertex, the basis set consists of two radial sp-hybridized AOs, one inward and one outward pointing, and two tangential orbitals represented by the remaining p orbitals. The 5-fold symmetry axis *z* passes through the axial vertices C(1) and B(12), and positions 2−11 are called equatorial. Tangential orbitals parallel with the *z* axis are referred to as vertical and those perpendicular to it as horizontal. Figure 4 does not show the radial orbitals that point inward since they primarily enter into the low-energy cluster bonding MO set that is of little interest in the present context but is of course essential for cluster stability.

Standard computer programs do not provide a description of the MOs of **1** and other clusters in terms of this symmetry-adapted cluster basis set but usually in terms of the standard Cartesian basis of p_x, p_y, p_z, and s valence atomic orbitals (AOs) on each vertex. Although it is possible to obtain a general qualitative idea of the location of nodal surfaces and the general shape of an MO from a graphic display, this does not enable any quantitative discussion, such as a comparison of the strength of an interaction with substituent orbitals in different positions. A freely available computer program[13] permits conversion of the commonly obtained results into the cluster basis set of Stone, starting with the valence portion of a density matrix available from all ab initio program packages. Figure 5[13] shows the frontier MO set of **1** derived from a DFT B3LYP/6-31G* or 6-31+G* calculation with similar results.

The nine frontier orbitals primarily bind the vertices of the cluster to each other and have only small contributions from the H 1s functions. The latter are not shown in Figure 5.

The HOMO degenerate orbital pair (4e_2) has no amplitude in the axial positions C(1) and B(12). It contains tangential amplitudes of nearly equal magnitudes on positions B(2)−B(6) and positions B(7)−B(11). In each member of the pair, large orbital coefficients concentrated on one side of the proximate pentagon formed by positions 2−6 are balanced by large orbital coefficients on the opposite side of the distal pentagon formed by positions 7−11. To a first order, this orbital set can only interact with valence orbitals of equatorial substituents that have π symmetry, primarily with their horizontal p functions. An example would be the lone pair orbitals on halogens or hydroxy groups.

The HOMO-1 orbital pair (5e_1) is concentrated on positions 7−12 and believed to be responsible for the antipodal effect. Its amplitude on B(12) is tangential and mirrored by a small contribution on C(1), while its amplitude in positions 7−11 resides on vertical tangential functions. This orbital, too, is susceptible to π-symmetry interaction with substituents, particularly in position 12.

These two pairs of MOs correlate with the quadruply degenerate HOMO of $B_{12}H_{12}^{2-}$ and are similar in energy. They are both susceptible to π-type (conjugative or hyperconjugative) interactions with substituents and should both be considered simultaneously in applications such as frontier orbital theory.

The members of the next pair of MOs (3e_2) again only have a nonzero amplitude in the equatorial positions 2−11 and now include both tangential and radial functions. The 6a_1 orbital consists of radial functions at C(1) and B(12) is concentrated on B(12). The 4e_1 orbitals are similar to the 5e_1 orbitals, but their amplitude resides mostly on positions 1−6.

The amplitudes of the MOs in the cluster basis set have been used for a quantitative treatment of substituent effects by perturbation theory, and it was found that the effect of methyl substitution on energies of the frontier MOs is quite accurately reproduced by a simple additive increment scheme.[13]

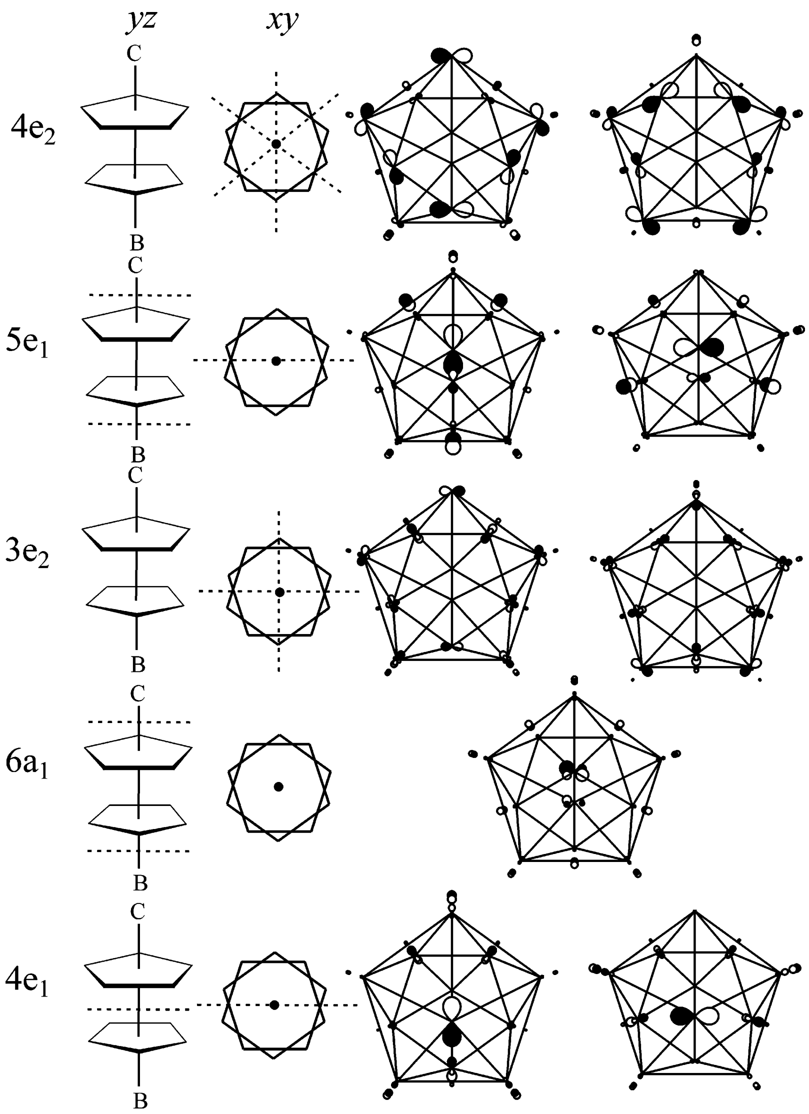


Figure 5. Occupied frontier MOs of **1**. The left column gives the orbital label. The next two columns show the nearly horizontal and nearly vertical nodal surfaces of the MO immediately to the right. Dashed lines represent the intersection of the nodal surfaces with the *yz* plane and *xy* plane. The next two columns are diagrams of the MOs viewed from C(1) to B(12).

3. Molecular Structure and Interaction with Cations

3.1. Free Anions, Radicals, and Ylides

The available X-ray structure examinations of the salts of **1** usually focus on cation−anion interactions and will be discussed in section 3.2. The calculated geometry of **1** is intermediate between those of $B_{12}H_{12}^{2-}$ and $C_2B_{10}H_{12}$.[115] Replacement of B by C in $B_{12}H_{12}^{2-}$ introduces two inequivalent B−B bonds, the longer B2−B3 (“latitudinal”) and the shorter B2−B7 (“meridional”). As B−B bonds become more distant from the C atom, their length becomes indistinguishable from that in $B_{12}H_{12}^{2-}$. The C−B and B2−B7 bond lengths are close to bond lengths in $C_2B_{10}H_{12}$; B2−B3 is shortened and C−H elongated in comparison with $C_2B_{10}H_{12}$.

The structure of the dodecamethyl anion **16** (Figure 6) is a slightly flattened sphere with a C(1)−B(12) diameter of 3.27 Å (B−B 3.39 Å), a methyl carbon diameter of 6.39 Å (6.56 Å), a methyl hydrogen diameter of 7.39 Å (7.56 Å), and a diameter with van der Waals radius of H of 9.79 Å (9.96 Å), comparable to C_{60} (10.7 Å).[15]

The X-ray structure of $[NMe_3H][1\text{-}Me\text{-}CB_{11}Cl_{11}]$ (**201**) shows the average B−Cl bond distance is 1.767 Å and the

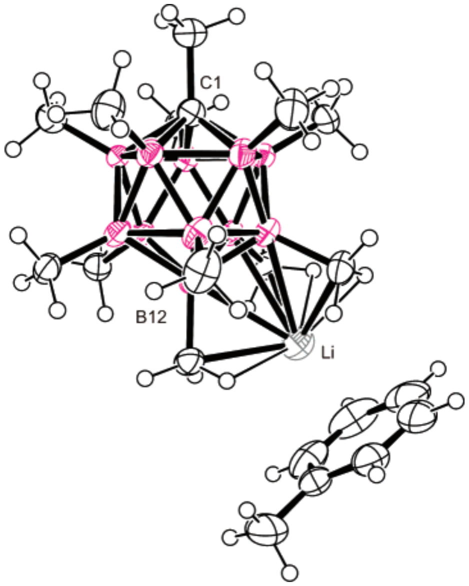


Figure 6. X-ray crystal structure of **16**.[116] (Reprinted with permission from ref 116. Copyright 1999 Collection of Czechoslovak Chemical Communications.)

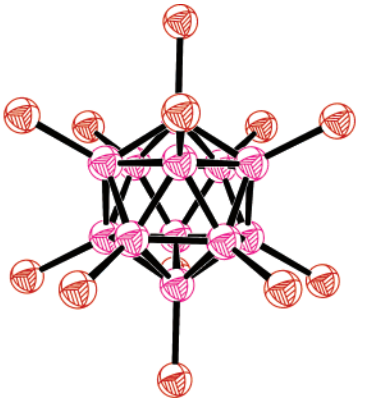


Figure 7. X-ray crystal structure of **184**.[41] (Reprinted with permission from ref 41. Copyright 1998 American Chemical Society.)

average diameter (Cl⋯Cl) is 6.942 Å, ranging from 6.937 to 6.947 Å. The anion is an almost a perfect sphere. When the van der Waals radius of Cl is included, the diameter is 10.442 Å.[45] Figure 7 illustrates the spherical nature of these anions on the case of the dodecabromo anion **184**.[41]

In the 1-H-(2−12)-F_{11} anion (**180**), the 2−6 B−F distances are shorter than the 7−12 B−F bond distances, in agreement with DFT calculations.[104] Increasing fluorine substitution removes electron density from bonding orbitals and results in longer and weaker bonds. The B(12)−F bond shortens from F_1 to F_{11} substitution, and B(7)−F shortens from F_6 to F_{11}. The cage edges become longer and the B(12)−F and B(7)−F bonds shorter.

In the X-ray structure of the 1-Me_2N-2-Me_2S zwitterion (**242**),[55] the carborate cage is little distorted from ideal icosahedron with a shorter cage C−N distance than in the 1-Me_3N anion. The X-ray structure of 2-Cl$(CH_2)_4$O-$CB_{11}H_{11}^-$ (**232**) shows a flattening of the C-capped pyramid relative to the B-capped ones.[51] The carbon vertex was identified, and the bonds to it were shorter than the bonds to any other vertex. The mean C−B bond length is 1.709 Å. The C(1)−B(2) bond is five standard deviations longer, 1.730 Å.

The structure of $CB_{11}Me_{12}^{\bullet}$ radical (Figure 8) is a perfectly symmetrical icosahedron, undoubtedly due to disorder. The average icosahedral edge length is 1.797(6) Å and the average length of the 12 cage atom−methyl carbon bonds 1.572(6) Å. Distances between opposite vertices are 3.417(9) Å, the distance between opposite methyl carbons is 6.561(8) Å, the distance between opposite hydrogen atoms is 7.54 Å, and the van der Waals radius inclusive average vertex to vertex diameter is 9.94 Å.[117]

The calculated structures of the four isomeric $CB_{11}Me_{11}$ ylides are an icosahedron flattened at the naked vertex.[36]

3.2. Anion–Cation Interactions

A large amount of work has been done on structural characterization of interactions between the anion **1** and its derivatives and their cation partners. Some of it pertains to the particularly interesting issue of a Lewis acid abstracting a hydride or methide group from a boron atom of the anion, thus triggering the electrophile-induced nucleophilic substitution (EINS) mechanism.

We collected the reports of structures of salts of the parent anion **1** in Table 4 and those of salts of its derivatives in Table 5.

3.2.1. Cations of Main Group Elements

Salts of halogenated derivatives of **1** with a solvated proton are discussed in section 6.1 in connection with a discussion of their weak basicity. In some of them, hydrogen bonding to the anion is observed. In **205**, each hydrogen atom of H_3O^+ binds to a bromine from the carborate anion.[118] Crystals of the free acid H($CB_{11}Cl_{11}$) of the undecachloro anion **181** were isolated and contain linear polymeric chains with proton bridges between chlorines located in the lower belt.[119]

The salts of alkali metals[41,45,87,116,120] tend to be ionic solids with little if any covalent cation−anion interaction. In the cesium salts of **177** and **178**[120] one Cs^+ cation is on a 2-fold axis, Cs(1), the other is disordered across the axis, Cs(2), and the Cs^+⋯Cl−B distances are long. The cesium cation on the 2-fold axis is surrounded by six carborate anions, with 10 Cs^+⋯Cl−B interactions ranging from 3.6815 to 4.0455 Å. In the X-ray structure of [Cs][1-H-$CB_{11}Br_5I_6$][THF] (**193**),[87] the cesium coordinates to four Br and four I atoms from three anions and to one oxygen from THF, with interatomic Cs⋯Br distances ranging from 3.699 to 4.085 Å and Cs⋯I from 3.872 to 4.260 Å. [Cs][1-H-$CB_{11}Br_{11}$] (**182**)[41] is another ionic salt, with Cs⋯Br distances from 3.708 to 3.757 Å.

Ammonium salts, such as [Me_3NH][1-H-$CB_{11}Cl_5Br_6$]·Me_3NHCl·H_2O (**191**), tend to be ionic as well. In [Me_3NH][1-Br-$CB_{11}Br_{11}$] (**184**),[41] the carbon and boron are indistinguishable, with a B−Br distance of 2.926 and 2.924 Å and a B−B distance of 1.781 and 1.784 Å. A compound consisting of isostructural cations and anions, [$H_3NCH_2C_2B_{10}H_{11}$][1-Et-$CB_{11}H_{11}$], does not show cation−anion interactions and does not form coordination polymers.[121]

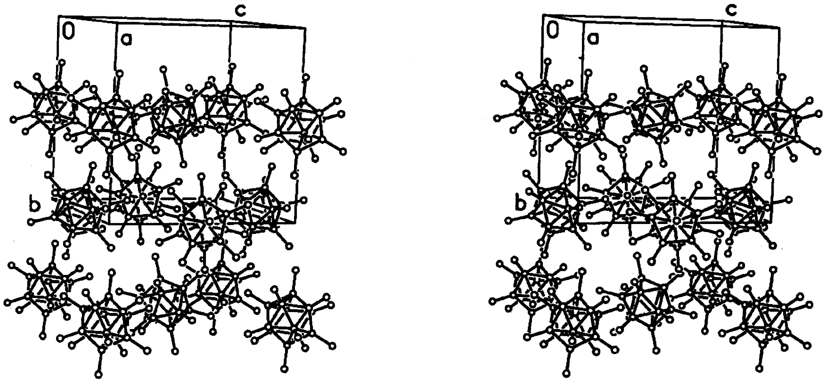


Figure 8. X-ray crystal structure of the radical **16r**.[117] (Reprinted with permission from ref 117. Copyright 1996 American Chemical Society.)

Table 4. Carborate Complexes of 1 and Their Binding Motifs[a]

complex	binding motif
267[59]	A
268[59]	B, each **1** bridges two Ag
269[60]	trigonal prism, **1** bridged dimer, four short, two long Ag−H−B interactions
270[61]	one **1** interacts with metal, second **1** acts as counterion
274[62]	C
277[63]	B
279[64]	B
282[65]	one **1** interacts with two B−H of lower belt
284[67]	A, four-legged piano stool
285[67]	D, ribbon of alternating cations and bridging anions
286[68]	D
287[66]	D
288[66]	D
291[66]	A
292[69]	D
$AgCB_{11}H_{12}\cdot 2C_6H_6$[125]	D, coordination to B−H(9)
[Ag(pyz)(**1**)][128]	3dim pillared checkerboard, 2dim sheets of Ag and **1**, pillared by pyz
$[Ag_4(NC(CH_2)_2CN)_5$(**1**)$_4]$[127]	coordination chain, two **1** coordinate to Ag, Ag connected by nitrile
$[Ag(NCCH_2CN)_2$(**1**)$]$[127]	coordination chain, ribbon motif with Ag−nitrile core and terminal **1**
$[Ag(CH_3CN)_2$(**1**)$]$[127]	2dim network, four long interactions of Ag to three different **1**
Fe(TPP)(**1**)[130]	D
$[(bpyH)_3(bpy)(CB_{11}H_{12})_3]$[132]	one-dimensional hydrogen-bonded ladder

[a] A: Coordination of the metal to B−H(7), B−H(8), and B−H(12). B: Coordination of the metal to B−H(12) and B−H(7). C: coordination of the metal to B−H(7) and B−H(8). D: Coordination of the metal to B−H(12).

X-ray structures of $M^+(\eta^6\text{-benzene})_2$ (M = Cs, Rb, K, Na) and $Li^+(\eta^6\text{-toluene})$ cations with anion **16** are of interest for interactions of the alkali metal cation with the aromatic π face.[116] For Cs^+, Rb^+, and K^+ the arene−cation distances exceed the van der Waals radii and anion−cation interactions are the dominant packing forces. The large cations keep the anions separated, and an arene is able to approach the cation closely. Crystal structures of Cs^+, Rb^+, and K^+ (and also Tl^+) salts show the metal cation η^6-sandwiched with two benzene molecules, for Na^+ the coordination is tetrahedral, and for Li^+ there are two different bonding motifs. In one, the Li^+ coordinates tetrahedrally to one toluene and three methyl groups of one anion (Figure 6). The methyl groups are pushed apart by the strength of the cation−anion attraction, and the Li^+ to methyl distance is significantly less the than the sum of the van der Waals radii. In the other motif, chains of half-occupied η^6-toluene−Li^+ complexes are on inversion centers between the anions, pinning the Li^+ against three methyl groups. Due to the very tight pinning, the Li salt of **16** shows unusual lipophilic properties to which we shall return in section 9. It is volatile and highly soluble in benzene (however, the solutions are conducting).

With **205** as the counterion, a borenium ion, $B(SubPc)^+$ (**371**, boron subphthalocyanine), has been isolated.[92] It forms cation/anion pairs, well separated from each other by solvate molecules. The boron of the cation coordinates to three bromine atoms of **205**. The borenium ion forms a stable oxo dimer in the presence of water, showing hydrogen bonds of protonated nitrogens to bromines of the carborate anion. The cation arranges in a ribbon-like structure, surrounded by the carborates.

Aluminum carborate complexes **317** and **326** have been isolated with **177** and **178** as counterions. The aluminum cation coordinates to the carborate anion via halogen substituents on B(7) and B(8).[78] Results from DFT calculations were in excellent agreement with the experimental data.[122]

As a new halide metathesis reagent, the thallium salt of **178** was prepared.[123] The thallium coordinates to the carborate via Br(7), Br(11), and Br(12). The X-ray structure of the $Tl^+(\eta^6\text{-benzene})_2$ cation with the anion **16** has already been mentioned above.[116]

The protonated toluene cation coordinates to **205** via weak H···Br bonds to lower belt positions of the carborate.[46] Similar complexes with benzene, *m*-xylene, mesitylene, and hexamethylbenzene have been synthesized. All of them show very weak interactions of the protonated arene with the lower belt bromines of **205**.[85] With Me^+**204** other alkyl cations, such as the *tert*-butyl, *tert*-pentyl, and methylcyclopentyl, have been prepared.[90] *tert*-Butyl$^+$**204** shows a weak interaction of a proton from the alkyl and a chlorine from the carborate cage.[91] The complex **367** shows coordination of the cationic carbon of the isopropyl to a bromine from the cage.[90]

During the search for a free silylium ion, many silylium carborate complexes were synthesized. In addition to crystal structures, an important criterion for silylium ion character is the ^{29}Si NMR shift. High silylium ion character is reflected in a large downfield shift. For a free silylium ion, the shift is expected to exceed 200 ppm. In complexes of the type trialkylsilyl **178** with Et (**365**), *n*-Pr (**366**), *i*-Pr (**367**), *tert*-Bu (**368**), and di-*tert*-Bu-Me (**369**), all compounds show only partial silylium ion character and the Si atom coordinates weakly to B−Br(7). Different counterions have been examined. From the hexahalogenated carborates, the one with **177** has the highest degree of silylium ion character, but no free silylium species was obtained.[39] With the undecachloro anion (**181**), the complex $Et_3Si(HCB_{11}Cl_{11})$ was isolated, with the carborate anion coordinated to the silicon via B−Cl(7).[77]

The structures of the amorphous salts of the trimethylplumbylium, trimethylstannylium, and trimethylgermylium cations with **16** showed an interesting progression from complexation toward actual reaction and from electrostatic toward covalent interaction.[75] The only solvents in which these extremely reactive cations could be formed (section 8.4.1) were alkanes, where solubility was inadequate for crystal growing. Structural characterization had to be done by a combination of extended X-ray absorption fine structure (EXAFS) measurements and DFT calculations. The EXAFS results were confirmed by comparison with the single-crystal

Table 5. Complexes of Substituted Carborates and Their Binding Motifs[a]

complex	binding motif
($C_6H_7^+$)(**205**)[85]	A
($MeC_6H_6^+$)(**205**)[46]	A
(*p*-$Me_2C_6H_5^+$)(**205**)[85]	A
($mesH^+$)(**205**)[85]	A
($Me_6C_6H^+$)(**205**)[85]	A
(*t*-Bu^+)(**204**)[91]	H^+ from alkyl to Cl−B from carborate
297[70]	B−Me(7,10‴,12″) and to B−Me(4′,8′,9′)
298[71]	B, longer interactions to B−Me(9′) and B−Me(12″)
299[70]	B-Me(12), longer interactions to B−Me(4′) and B−Me(8″)
300[70]	C
308[74]	D
309[75]	C or E, distorted tetrahedral
310[76]	F
311[75]	F
312[75]	trigonal bipyramidal, weak coordination of cation with Me from anion
313[73]	D and F, Ag_2I_2 core, two Mo fragments, coordination to two **175**
314[73]	D, pseudo-piano stool
317[78]	E, **177** less coordinating than **178** in complex **326**
318[134]	B−Cl(8,12) and B−Cl(10′,11′)
322[81]	B
323[81]	B
324[81]	B
325[81]	B
326[78]	E
327[59]	C, B−Br(11′), ribbon-like structure, Ag pseudo-trigonal planar
331[65]	Rh_3Cl_4 core, coordination to C−H, C−H of **178** eighth vertex of the cube
333[82]	E
337[68]	Ag_2I_2 core, Ag coordinates to B−Br(10,12), two Mo fragments trans oriented
343[134]	C, B−I(10′,11′)
(η^2-xylene)$_2$**344**[87]	four-coordinate Ag, propeller arrangement, B−Cl(9,10)
(η^1-mes)**345**(MeCN)[87]	distorted tetrahedral arrangement, B−Br(9,10)
(η^2-mes)$_2$**348**(mes)[87]	four-coordinate silver, B−Cl(8,12)
(η^1-mes)**352**(mes)[87]	distorted tetrahedral, coordination to two Br of one and one Br of another **191**
354[65]	Ag(1) σ bond to C(1), Ag(2) B−I(4) and B−Br(8), Ag(3) B−I and B−Br of each cage, zig-zag polymeric chain
356[88]	distorted tetrahedral, B−I(8,12)
(η^1-mesitylene)**357**[44]	distorted square-planar, bidentate coordination to two **197**
358[44]	distorted tetrahedral, B-I(7,12,9′,10′)
360[41]	Ag coordinates to six Cl from three **201**, **201** surrounded by six Ag, 3dim polymer
361[41]	1dim coordination polymer, Ag coordinates to three Br from two bridging **202**
367[90]	B
371[92]	C
Et_3Si(**181**)[77]	B
$Cu(CO)_2(1\text{-}PhCH_2CB_{11}F_{11})$[133]	η^2 coordination of Cu to benzene
(η^2-C_6H_6)Ag(**2**)[44]	B−H(8,9′)
Ag(**17**)[121]	B, B−H(10′,8″,9″)
[Ag(C_6H_6)][**173**][38]	coordination to two B−H of two **173**
[Ag(C_6H_6)][**175**][16]	D, coordination to three different **175**
Ag(**178**)[134]	C, Br(12) shared by two Ag
$[Ag(\mathbf{178})_2]^-$[136]	C, octahedral, coordination of Ag to two **178**
Ag(**198**)[44]	C, octahedral, Br(12) shared by two Ag
$LAg(1\text{-}Me\text{-}CB_{11}HBr_{10})$ [41]	five-coordinate propeller arrangement, two bidentate bridging anions
H(**181**)[119]	polymeric chains with proton bridges between Cl from lower belt
H_3O^+(**205**)[118]	each proton of H_3O^+ H bonded to Br of three different **205**

[a] A: weak H−Br bonds to the lower belt. B: Coordination of the metal to B−R(7). C: Coordination of the metal to B−R(7), B−R(8), and B−R(12). D: Coordination of the metal to B−R(12). E: Coordination of the metal to B−R(7) and B−R(8). F: trigonal bipyramidal, coordination to B−Me(2) and B−Me(9). L: (η^2-*p*-xylene); mes = mesitylene.

X-ray data obtained for *n*-Bu_3Sn^+**16**, whose solubility in pentane was sufficient for crystal growth.[76]

The structures develop in the Bürgi-Dunitz sense along the reaction coordinate for methide abstraction. The transfer of a methide anion from position 12 in **16** to the metal gradually changes from endothermic to approximately thermoneutral along the series, and for the Me_3Si^+ and Me_3C^+ cations, where it finally becomes highly exothermic, it apparently takes place. These combinations of ions are unstable, and the salts cannot be isolated (neopentane is formed from the *tert*-butyl cation, and the boronium ylide formed abstracts chlorine anions from the CH_2Cl_2 solvent). The progression in reaction energies is reflected in the structures, which start with weak complexation and proceed toward the transition state for methide transfer. The most weakly and primarily only electrostatically interacting cation, trimethylplumbylium, forms infinite chains with the anion **16**. It makes two equivalent and long coordination bonds to the methyl groups on two different anions located axially in a symmetric trigonal bipyramidal geometry. These weak interactions were not revealed in CP-MAS spectra of Me_3Pb^+**16**, which resembled those of Cs^+**16**, as did the solution spectra. The trialkylstannylium cations[75,76] still form infinite chains with trigonal bipyramidal geometry around the metal, but the interaction of Me_3Sn^+ with one of the axially located methyl groups is now stronger than the other (2.77 and 3.02

Å) and partially covalent in nature. CP-MAS NMR of solid Me_3Sn^+**16** showed evidence of cation coordination to a methyl group of **16**. In solution, the relative strength of the interaction of the Me_3Sn^+ cation with **16** and with the CD_2Cl_2 solvent was temperature dependent. Below −60 °C, interaction with the solvent was preferred, and above this temperature, interaction with the anion was favored.[75] Finally, according to the DFT calculation, the trimethylgermylium cation interacts with **16** strongly enough to be on the verge of being able to abstract a methyl group, and the interaction has a considerable covalent component. EXAFS was compatible with a highly pyramidal structure, a distorted tetrahedral geometry with three Ge−CH_3 bonds and one strong interaction to BCH_3(12), plus one or two additional weak interactions with BCH_3(7) and/or BCH_3(8). The reaction path reflected in this progression of gradually increasing covalent Me_3M^+ interaction with a methyl group on **16** as one proceeds up column 14 of the periodic table corresponds to a backside S_E2 substitution on the carbon of the methyl group and most likely provides a good picture of methide abstraction reactions in general.

A diorganotin compound with the parent **1** as a counterion has been reported as being of ionic nature in the solid state and in acetonitrile solutions.[124]

3.2.2. Transition Metal Cations

Many complexes of transition metals and carborates have been synthesized and studied. The most commonly used metal were silver, rhodium, zirconium, iron, and molybdenum, and a few complexes containing nickel, palladium, and titanium have also been isolated. In the solid complexes, the cation interacts with the carborate anion via different coordination motifs. In solution, these motifs may change or disappear. Synthesis of the carborate complexes is generally accomplished by metathesis reaction from silver, trityl, or “silylium” carborates.

Three types of solid-state structures are known: (i) coordination polymers, in addition, with an arene often also bound to the metal center; (ii) discrete molecules with carborate−metal interactions; (iii) discrete molecules with interactions of carborates and arenes.[60]

We start with salts of the parent anion **1**, which are generally dominated by interaction of the metal atom with its hydridic hydrogen atoms in positions 7−12. No coordination to H−B(2−6) has been observed.

The most popular metal cation for investigation was Ag^+, at least in part because it is a very convenient point of entry to the synthesis of salts of other metals. The first isolated silver salt of **1** was Ag^+**1**·$2C_6H_6$ in which one of the benzenes is η^1-coordinated to silver.[125] The carborate anions act as bridging ligands to form cation−anion chains through interactions with B−H(9) and B−H(12). Silver phosphine complexes **267** and **268** show similar 3c2e interactions.[59] In solution the complex has C_{5v} symmetry, and the $Ag(PPh)_3^+$ fragment is fluxional over the cage surface as seen by a significant upfield shift in the ^{11}B NMR compared to Ag^+**1**.[59,126] $[(PPh_3)_2Ag^+\mathbf{1}]_2$ (**268**) is dimeric in the solid state. Each carborate anion bridges two silver centers through one shorter and one longer Ag−H−B distance to BH(12) and BH(7).[59] With an *N*-heterocyclic carbene as a ligand, complex **269** has been prepared.[60] In the X-ray structure it shows two cations $[(IMes)_2Ag]^+$ and the anion $[Ag_2(\mathbf{1})_4]^{2-}$. The anionic fragment is a carborate-bridged dimer, each silver has four shorter and two longer Ag−H−B interactions, and the coordination geometry is trigonal prismatic. In solution, the Ag−H−B interactions are still present, as shown in an upfield shift in the ^{11}B NMR signal. The pattern of the NMR showed C_{5v} symmetry. The experimental data agreed with calculations.[60] Nitriles have also been used as ligands, and complexes with acetonitrile, malononitrile, and succinonitrile have been isolated.[127] Crystalline silver complexes with the N-bridging ligands pyz (pyrazine), bpy (2,2′-bipyridine), and bppz (2,5-bis(2-pyridyl)pyrazine) have been isolated and characterized. The structure of $[Ag^+(pyz)\mathbf{1}]$ contains sheets of a checkerboard arrangement; in the extended 3dim structure the sheets are pillared by pyz.[128]

The anion **1** stabilizes the $[Pd(L)]^{2+}$ cation in [Pd(dppp)(**1**)][**1**] (**270**), where one carborate is complexed with the cation while the second one acts as counterion.[61]

In the solid-state structure of rhodium complexes with cyclooctadiene,[63] nitrogen-containing ligands,[129] such as bisoxazoline, and phosphines,[62,64] the Rh coordinates to **1** through two 3c2e Rh−H−B bonds to B−H(7) and B−H(12) or B−H(7) and B−H(8), cf. Figure 9. In solution, the Rh fragment is fluxional over the cage, showing C_{5v} symmetry according to ^{11}B and ^1H NMR. An X-ray structure of the complex **274** shows coordination of **1** to the rhodium via B−H(7) and B−H(8). According to DFT calculations, the 7,8 isomer is only 1 kcal/mol higher in energy than the 7,12 isomer.[62] In the presence of $[Cp^*RhCl_2]_2$, the complex $[Cp^*RhCl]_2[\mathbf{1}]_2$ (**282**) was isolated.[65]

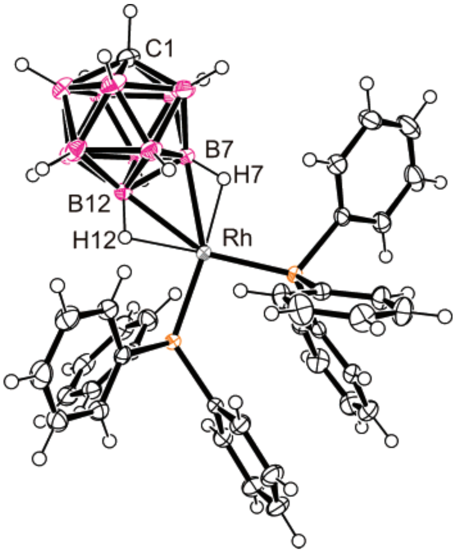


Figure 9. X-ray crystal structure of **279**.[64] (Reprinted with permission from ref 64. Copyright 2002 American Chemical Society.)

One of the first isolated iron complexes of **1** was Fe^+(TPP)**1**, where **1** binds to the iron via a Fe−H−B(12) bridge.[130] Zwitterionic molybdenum complexes $CpMo(CO)_3$(*x*-*μ*-H-**1**) (**284**) and $Cp^*Mo(CO)_3$(*x*-*μ*-H-**1**) (**286**) show interaction of the carborate cage and the Mo fragment in a 3c2e B−H−Mo bond in position B(12).[67,68] In solution, interactions of Ag and B−H of positions 12 and 7 are present. In the presence of $CpMo(CO)_3I$ the intermediate $[CpMo(CO)_3I{\cdot}Ag\mathbf{1}]_2$ (**285**) was isolated. It has a C_2 dimeric structure with the silver bound to the iodine of the $CpMo(CO)_3I$ fragment. The interaction again occurs via a 3c2e B−H−Mo bond in position B(12), resulting in a ribbon of alternating cation and bridging anions.

Zirconium-based olefin polymerization catalysts have been synthesized by silver salt metathesis reaction of Ag^+**1** with zirconium alkyls.[66] In $Cp_2Zr(\eta^2\text{-}CH_2Ph)$(**1**) (**287**), **1** is coordinated to Zr via B(12)−H−Zr. The solid-state structure is maintained in hydrocarbon solution, but in acetonitrile, the carborate is replaced. The complex $(C_5H_4Me)Zr(CH_3)$-(**1**) (**288**) shows the same B(12)−H−Zr coordination. The Cp^*ZrMe_2(**1**) (**291**) complex coordinates to Zr via three B−H−Zr bonds in a tridentate fashion (B7,8,12). In the Zr metallacycle $Cp_2Zr(\eta^2\text{-}C,N\text{-}C\{{=}N\text{-}tert\text{-}Bu\}CH_3)$(**1**) (**292**), the carborate is coordinated through position 12.[69] A similar titanium complex $Cp_2Ti(CH_2Ph)$(**1**) was synthesized, but it was too unstable for detailed characterization.[131]

During an attempted synthesis of a lanthanide carborate complex, a hydrogen-bonded complex [(bpyH)$_3$(bpy)(**1**)$_3$] was isolated.[132] It crystallized in a one-dimensional hydrogen-bonded ladder structure.

An even larger number of transition metal complexes with substituted derivatives of **1** is known. Most of these complexes contain halogenated carborane anions, and the metal cation interacts with one, two, or three of the halogen substituents in positions 7−12. Only a few examples of coordination to positions 2−6 are known. Salts of some metal cations with anions methylated in positions 7−12, such as **12** and **16**, tend to be unstable because of facile methide abstraction, but methyls in positions 1−6 appear to be much less reactive.

In $Cu(CO)_2(1\text{-}Bn\text{-}CB_{11}F_{11})$, Cu coordinates to the benzene ring and not to the fluorine atoms of the carborate.[133] The C-alkyl carboranes **2** and **17** form silver complexes $(\eta^2\text{-}C_6H_6)Ag$(**2**)[44] and Ag(**17**).[121] No coordination to B(12) was observed, presumably due to the electronic effect of the 1-alkyl group. Ag^+**12** salts are known and well characterized.[70,71] Ag^+**12** (**297**) is a closely associated salt with coordination to B−Me(7), B−Me(10‴), and B−Me(12″).[70] In the presence of the small triphenylphosphine as a ligand,[71] the silver cation interacts with three different carborate anions in two long and one short interaction. With a bulkier phosphine ligand, the interactions in the lattice can be suppressed, leaving only coordination to one carborate.[70,71] In solution, Ag ···Me−B interactions remain for all of these complexes and the metal fragment is fluxional over the lower belt.[70] According to DFT calculations the 12-coordinated isomer is 1.9 kcal/mol lower in energy than the 7 isomer and the 2 isomer is 6.2 kcal/mol higher. However, tridentate coordination of the phosphine fragment $[PPh_3Ag]^+$ to B-(7,8,12) is 1.9 kcal/mol more stable than the 12 isomer. The fluxional movement in solution possibly results from dynamic tridentate−monodentate−tridentate coordination. In the salt of the 12-bromo-substituted anion,$[Ag(C_6H_6)]$[**175**],[16] the silver ion interacts with three different carborate anions through Br−B(12). In the similar 12-fluoro complex,[38] the silver coordinates to two B−H hydrogen atoms of two carborate anions and no interaction between silver and fluorine is observed. Fluorine-containing anions seem to be generally more weakly coordinating than bromine-containing anions. Coordination of hexahalocarborate complexes with silver occurs to two different anions, and polymeric chains are formed.[88,134] The hexabrominated anion **178** was used in an attempted synthesis of the trityl salt.[135] In a similar complex $[(PPh_3)Ag(CB_{11}H_6Br_6)]$ (**327**), the silver is coordinated to the phosphine ligand and to three bromines from the same anion, Br(7), Br(8), and Br(12), and also has a weak interaction with a Br(11′) from another anion. This results in a ribbon-like structure in which the silver is pseudo trigonal planar coordinated.[59,126] As Figure 10 illustrates,

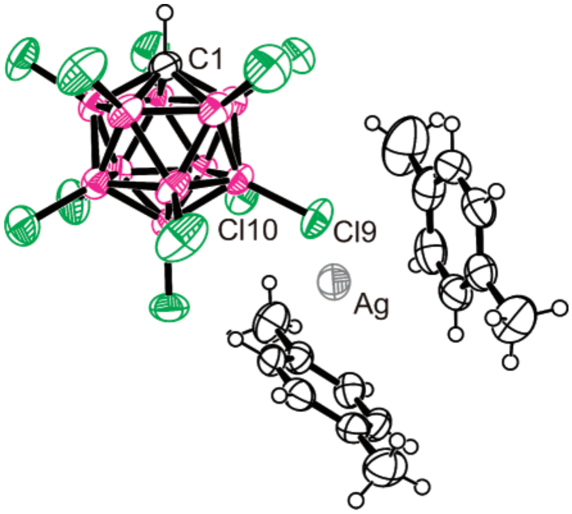


Figure 10. X-ray crystal structure of $(\eta^2\text{-xylene})_2$**344**.[87] (Reprinted with permission from ref 87. Copyright 2000 American Chemical Society.)

undecahalogenated anions do not coordinate to silver via the most electron-rich antipodal position but with halogens from the lower belt, possibly due to steric effects.[87] With **180** no coordination to the fluorine atoms occurred, and both cations and anions were free.[89] In all silver salts of 1-methylhexahalo and 1-methylundecahalo anions the metal coordinates to several halogens[44] (for more detail, see Table 5). Without coordination to solvent molecules, in $Ag(1\text{-}Me\text{-}CB_{11}Cl_{11})$ (**361**) the silver coordinates to six halogen atoms from three cages. Each anion is surrounded by six Ag ions, and the structure is the first example of a three-dimensionally polymeric structure for a silver salt of a carborate.[87] In the silver complex $Ag(1\text{-}Me\text{-}CB_{11}Br_{11})$ (**362**), the X-ray structure shows a one-dimensional coordinating polymer with the carborate anion acting as the bridging ligand.[41] In the silver complexes of the mixed halogenated anions **189**, **190**, **191**, **192**, and **193**, no coordination to the upper belt halogens was observed, regardless of the location of the softer base.[87] An argentate salt $[\{(CH_3CN)_4Ag_3\}\{Ag(CB_{11}I_5Br_6)_2\}(CH_3CN)]_n$ (**354**) was synthesized by deprotonation of $1\text{-}H\text{-}CB_{11}I_5Br_6^-$ and reaction with $AgNO_3$ and contains a σ bond between C(1) and the silver atom. A strong interaction of a second silver ion to an upper belt iodine atom in addition to coordination to one bromine of the lower belt and two nitrile ligands was present. The coordination to the upper belt iodines has been attributed to deprotonation at C(1) and the associated increased electron density in positions 2−6.[88]

An interesting trimeric complex $[\{Cp^*Rh(\mu_2\text{-}Cl)\}_3(\mu_3\text{-}Cl)][CB_{11}H_6Br_6]_2$ (**331**), obtained from 2 equiv of Ag^+[**178**] and $[Cp^*RhCl_2]_2$,[65] consists of an Rh_3Cl_4 core with the hydrogen of the C−H bond of one carborate ion completing the eighth vertex of the cube. The other carborate is distant. In solution, ^{11}B NMR shows an essentially free **178**. The iridium fragment of the complex $(PPh_3)_2Ir(H)_2(CB_{11}H_6Br_6)$ (**333**) coordinates to Br(7) and Br(8) of **178**.[82]

Reaction of $Ag(CB_{11}H_6Br_6)$ with Fe(TPP)Br led to formation of $Fe(TPP)[Ag(CB_{11}H_6Br_6)_2]$, consisting of free $Fe(TPP)^+$ and $[Ag(CB_{11}H_6Br_6)_2]^-$.[136] $Fe(TPP)(CB_{11}H_6Br_6)$ has been synthesized by oxidation of Fe(TPP) with $[N(C_6H_4Br)_3][CB_{11}H_6Br_6]$.[83] Addition of arene solvents led to formation of $Fe(TPP)(arene)^+$ and free anion.

The structure of the molybdenum complex $[CpMo(CO)_3I{\cdot}Ag(CB_{11}H_{11}Br)]_2$ consists of a central planar Ag_2I_2 core, two

Mo fragments, and two carborate anions. The carborate ligates in a bidentate manner via one Ag−Br−B interaction and one Ag−H−B(7) interaction.[73] In solution, no Ag−H−B interaction was observed; the ^{11}B NMR showed C_{5v} symmetry. Hydride abstraction from the trityl salt and CpMo(CO)$_3$H cleanly produces CpMo(CO)$_3$(CB$_{11}$H$_{11}$Br). In solution, two isomers are present with the Mo fragment coordinating through B−Br(12) and B−H(7). In the solid state only the interaction through B−Br(12) exists and the binding motif is a pseudo-piano stool. Similarly, in the presence of Ag(CB$_{11}$H$_6$Br$_6$) [CpMo(CO)$_3$I•Ag{CB$_{11}$H$_6$Br$_6$}]$_2$ (**313**) was isolated and found to have a similar binding motif.[68] The complex Cp$_2$Zr(Me)(HCB$_{11}$Me$_{11}$) (**308**)[74] has been described as having a linking Zr−CH$_3$−B(12) motif. The Zr−Me interaction is maintained in solution, and the metal fragment is fluxional among methyls in positions 7−12.

Anions **12** and **16** are attacked by many cationic transition metals and often produce complex mixtures of degradation products.[57] Such degradation was observed, for instance, with the [Cp(CO)$_3$Mo]$^+$ cation.[73] It occurs either during attempted synthesis of the salt in question or from a well-defined complex by solvent change. It most likely starts by methide transfer of the type discussed above in some detail with elements of group 14. This is then followed by trapping of the extremely reactive boronium ylide intermediate formed and further abstraction and trapping reactions that may ultimately lead to intractable mixtures. The metal fragment attaches to a chloride, hydride, or water residue. Evidence for this course of events is indirect but strong. When dissolved in CD$_2$Cl$_2$, the zirconium complex **308**[74] decomposes with formation of 1-H-CB$_{11}$Me$_{10}$Cl$^-$ and 1-H-CB$_{11}$Me$_9$Cl$_2$$^-$. Formation of 1-H-12-Cl-CB$_{11}$Me$_{10}$$^-$ was also observed from [(PCy$_3$)Re(CO$_4$)(CH$_2$Cl$_2$)]$^+$[1-H-CB$_{11}$Me$_{11}$]$^-$ in CD$_2$Cl$_2$ solution. The platinum complex *trans*-[PtMe(*i*Pr$_3$P)$_2$] [1-H-CB$_{11}$Me$_{11}$], synthesized from the radical 1-H-CB$_{11}$Me$_{11}$$^\bullet$ in CH$_2$Cl$_2$, forms 1-H-12-Cl-CB$_{11}$Me$_{10}$$^-$ when a second equivalent of the radical is added. Treatment with hydrogen in fluorobenzene leads to a mixture of products, and the main one has the methyl group in position 12 replaced by fluorophenyl. We can compare this with the above-discussed effect of the *tert*-butyl cation on **16** in CH$_2$Cl$_2$, which also leads to gradual replacement of methyl groups with chlorine atoms. We shall see in section 8.3.2 in more detail that these reaction products are indeed just those expected for the boronium ylide by abstraction of a chloride anion from the solvent or attack on an aromatic ring.

Several silver,[70,89] molybdenum,[68] copper,[133] and rhodium complexes[137] show no interaction between the cation and the carborate anion. Different cationic metal complexes of 1-alkyl-CB$_{11}$F$_{11}$$^-$ have been isolated, including Ag, Cu, and Rh derivatives.[89,138] No coordination of the cation to the fluorinated carborate was observed. Lanthanide complexes of **178** were unstable and decomposed easily.[84]

4. Spectroscopy

4.1. Nuclear Magnetic Resonance

For boron clusters, including **1**, 1-dimensional and especially 2-dimensional NMR spectroscopies are the most powerful and widely used tools for structure determination. A thorough but dated review is available.[139] Many empirical rules for chemical shifts values (δ) of boron were developed a long time ago.[140] Although nowadays NMR shifts can also be calculated quite reliably by quantum chemical methods,[141] few practicing boron chemists take advantage of it.

Among empirical rules applicable to the spectra of **1** and its derivatives, the vertex antipodal effect, summarized in a previous review,[139] is the most important. The rule states that the ^{11}B chemical shift of a skeletal boron atom is influenced most by the electron density of the atom located on the opposite side of the icosahedron. Partially positively charged atoms shift boron in the antipodal position to higher frequencies and partially negatively charged ones to lower frequencies.

An illustration of the effectiveness of π-electron donation is provided by the spectra of the 2-fluoro and 2-alkoxy derivatives of **1**.[51]

There have been relatively few systematic studies of the relation of the chemical shift of the atoms present in **1** as a function of substitution, and they have confirmed the general conclusions summarized earlier.[139] We note a report on the 1-halo anions,[37] which found that the shift increment $\Delta\delta$ relative to the parent **1** becomes more positive with increasing electronegativity of the halogen from I to F in the ipso position, whereas in the other positions the difference is much smaller and more negative with the more electronegative halogens. Among these, it is most pronounced for the antipodal position, where all the ^{11}B NMR shift increments are negative. It was concluded that the antipodal shift increments are dominated by π-electron donation from the lone pair and the ipso shift increments by σ-electron withdrawal, both increasing from iodine to fluorine. Shift increments in the other positions are influenced by both effects. The larger sensitivity of ^{13}C chemical shifts to substituent effects compared to ^{11}B shifts is general.

Attention has been paid to the electronic effect of methyl groups in boron clusters,[109] and intermolecular interactions with different Ge, Sn, Pb, and Zr salts of the highly methylated anions **12** and **16** have been accounted for noting the net negative charge on the methyl groups.

We attempted to collect the reported ^{11}B, ^{13}C, and ^{1}H chemical shifts in all known derivatives of **1** in tables provided in the Supporting Information in the hope that they will be useful for comparison with the spectra of anions that will be prepared in the future. The collection also permits more detailed statements about regularities in the chemical shifts than have been available up to now. None of them are particularly surprising, but they provide numerical values for substituent shifts to be expected.

Effects on ^{11}B chemical shifts are the best studied. Like most other substituents, including hydrogen, methyl groups in boron clusters have a net electron-withdrawing effect. Relative to hydrogen, however, methyl is a π-electron donor and has a small if any σ effect. An alkyl substituent in position 1 causes the shifts of B2−6 and B7−11 to become equal, and the signal of B12 is moved to higher field by up to 4 ppm, depending on the alkyl. The largest change was observed for the 1-methyl anion (**2**). Positions 2−6 and 7−11 are affected much less, about 2 ppm downfield. Hydroxy, amino, and halogen substituents also shift the signal of position 12 to higher field (up to −16.8 ppm for F), presumably again by their π-donor effect, while the shifts of borons 2−11 remain almost unchanged. For these, the π-donor and σ-acceptor influences of the substituent apparently cancel. A silyl or boryl substituent in position 1 shifts the signals of B2−6 and B7−11 slightly downfield, while B12 shows a large downfield shift by 5 ppm, and this is harder to understand since both ought to be weak π acceptors and σ donors.

A substituent in position 12 does not influence the signals of B2−6 and B7−11 significantly, but B12 shows a large downfield shift. With alkyl substituents, the shift is 2−4 ppm, and with hydroxy, fluorine, and amino groups it is ∼10 ppm. Higher alkylated carborates show a shift increment change on the ipso position by giving it a downfield shift. With halogens, the effect on the chemical shift in the ipso position increases from I (−17.9 ppm) to F (14.3 ppm). Changes in positions 2−11 are much smaller. Similar changes are observed for the hexahalogenated derivatives. In the perhalogenated compounds, an increase in the chemical shift of B12 is observed going from Br to F, but the iodo compound does not fit the pattern.

Effects on the CH proton shift can be noted as well. Its shift is mostly influenced by substituents in positions 2−6. The influence of the substituent in positions 7−11 is smaller, and that of the substituent in position 12 is very small. An alkyl substituent in positions 2−6 shifts the signal of the CH proton by ∼1 ppm to higher field. Electron-withdrawing substituents in **83** caused a downfield shift all the way to 5.76 ppm.

4.2. Electron Paramagnetic Resonance

Little has been done in this area. The neutral radical of **1**, $CB_{11}Me_{12}^{\bullet}$, shows an extremely broad EPR signal at $g = 2.0037(3)$.[117] The peak-to-peak width in the derivative signal is 37 G in solution and low-temperature glass. All attempts to saturate the EPR signal and obtain an ENDOR spectrum failed, even at 4 K. The lack of resolution, width of the signal, and fast relaxation are compatible with the presence of a large number of inequivalent proton and boron atoms in this presumably dynamic Jahn−Teller-distorted[102] structure, especially considering the presence of both ^{10}B and ^{11}B nuclei, both high spin.

The EPR spectrum of $1\text{-}CH_3\text{-}(CH_2)_5\text{-}CB_{11}Me_{11}^{\bullet}$ is similar and shows a broad signal without fine structure with a peak to peak width of 28 G.[23] The broad signal of $1\text{-H-}(2-6)\text{-}F_5\text{-}CB_{11}(CF_3)_6^{\bullet}$ has a peak to peak width of 45 G, and that of $1\text{-H-}(7-12)\text{-}F_6\text{-}CB_{11}(CF_3)_5^{\bullet}$ has over 80 G.[23]

4.3. Vibrational Spectroscopy

We are aware of a single thorough experimental and computational investigation of the vibrations of the parent anion **1**.[115] The anion belongs to the C_{5v} point symmetry group. There are 11 A_1 totally symmetric modes, 14 E_1 degenerate modes, both IR and Raman active, 12 E_2 modes, only Raman active, and 3 A_2 modes, neither Raman nor IR active. The experimental and calculated vibrational spectra are in good agreement. Replacement of B by C atoms in $B_{12}H_{12}^{2-}$ causes an increase in ν(BH) stretching frequencies, consistent with the shortening of B−H bonds. The ν(CH) stretch of $CB_{11}H_{12}^{-}$ lies slightly higher than that of $C_2B_{10}H_{12}$ and has lower intensity, compatible with a decrease in C−H bond polarity.

The IR spectrum of the radical of **1**, $CB_{11}Me_{12}^{\bullet}$, is similar to that of the Cs salt of **1**,[117] in accord with the similarity of their X-ray structures.

4.4. UV−Visible Spectroscopy

As noted in the discussion of aromaticity, the HOMO−LUMO gap in **1** is very large, and this anion is transparent down to nearly 200 nm. It is clearly only above 6 eV that singlet−singlet transitions of **1** occur, and they have not been investigated. The singlet absorption observed at longer wavelengths in certain derivatives of **1** is associated with the presence of absorbing substituents, such as aromatic rings. Although perturbation of their spectra by the carborate anion may be of interest, only one such case seems to have received detailed attention due to possible utility in nonlinear optical applications. This is the zwitterion $12\text{-}C_7H_6^{+}CB_{11}H_{11}^{-}$ (**51**),[14] whose absorption spectrum is close to that of the tropylium cation $C_7H_7^{+}$, shifted to longer wavelengths by the π-donor effect of the carborate anion. Both semiempirical[14] and ab initio[108] calculations have been done for this highly polar species with significant hyperpolarizability.[14]

Little is known about the triplet energy of the parent **1**, but an interesting observation has been made for its (7−12)-hexabromo derivative (**178**) and attributed to the “heavy-atom effect” of the bromine substituents on spin−orbit coupling.[142] This anion was investigated as its silver salt, but the authors argued that the cation did not affect the spectral properties. Absorption starts at 300 nm and shows a series of shoulders at shorter wavelength. The anion does not emit at room temperature, but in a 77 K glass it exhibits intense yellow phosphorescence with pronounced vibrational structure starting at 312 and peaking at 462 nm. This suggests that the lowest triplet state of this anion lies near 4 eV above the ground state, and that of parent **1** is presumably somewhat higher.

The radical forms of these carboranes represent the other extreme and absorb throughout the UV−visible and near IR regions, such that they appear black in the solid state and deeply colored in dilute solution, usually blue. The absorption and magnetic circular dichroism spectra of the stable permethylated radical **16r** have been reported.[117] Semiempirical (INDO/S) calculations confirmed the suspicion that the rich but unresolved absorption spectrum is due to transitions from doubly occupied MOs to the singly occupied MO.

5. Electrochemistry

The cyclic voltammetry of the cesium salt of parent **1** showed no wave up to the anodic limit of acetonitrile (2.4 V vs SCE; ∼2 V against ferrocene).[143] Due to the π-donor effect of the substituents, the permethylated anion **16** is much easier to oxidize and in this solvent yields a reversible wave at 1.6 V against Ag/AgCl (1.15 V against ferrocene).[15] Replacement of a methyl group by a fluorine atom (mixture of 7-F and 12-F substitution) increases the redox potential by 0.1 V.[117] The 1-H undecachlorinated anion shows no oxidation wave up to 2.0 V in acetonitrile.[45]

More recently, the electrochemical behavior of the parent **1** and all 15 of its symmetrically methylated derivatives **2**−**16** has been investigated in liquid SO_2.[13] Only **9**, **12**, **13**, **15**, and **16** exhibited reversible behavior and a few others showed faint indications of reversibility. It appears that the presence of two adjacent BH vertices in positions 7−12 makes the neutral radicals unstable, presumably due to dimerization.

The values of redox potentials were scattered widely from 1.1 to 2.2 V against ferrocene (**1**, **2**, and **5** gave no waves up to 2 V). Even the reversible redox potentials were in only fair agreement with the results of calculations at several levels of ab initio theory, including those that consider the expected Jahn−Teller distortion explicitly. All methods predicted the redox potentials to cluster around only three values, one for anions with no methyls in positions 2−11, a less positive one for those with five methyls in these positions, and a least positive one for those with 10. The experimental results also reflect the π-donor effect of the methyl groups but show more scatter. It is conceivable that the structures of some of the radicals are more significantly distorted away from C_{5v} symmetry than **16r**, whose X-ray structure is nearly indistinguishable from that of the anion **16**.[117]

6. Acidobasic Properties

There are two types of Brønsted acidity that need to be discussed: (i) Since **1** is an anion, it comes with a positive counterion, and this could be a proton or another Brønsted acid; (ii) the CH vertex in $CB_{11}H_{12}^-$ and its derivatives is Brønsted acidic as well, and its dissociation produces the salts of the dianion, $CB_{11}H_{11}^{2-}$. We shall take up the two types of acidity in this order.

6.1. Anion Basicity

The parent **1** and its derivatives are among the least coordinating anions known and, therefore, some of the least basic anions as well. Their conjugate acids are some of the strongest acids known. Some indication of their strength has been provided by calculations. DFT calculation of the proton affinity of the $CB_{11}(CF_3)_{12}^-$ anion **87**[24] gave a value of 252 kcal/mol, predicting the conjugate acid to be the strongest neutral Brønsted acid known. However, this number is ill defined since the geometry of the free acid (protonated anion) had to be assumed. An attempt to optimize it led to decomposition into HF and the ylide, $CB_{11}(CF_3)_{11}{}^-CF_2{}^+$. An even smaller proton affinity of 197 kcal/mol was found[105] using a semiempirical calculation (PM3), but the issue of free acid stability was not addressed. The latter authors also calculated the deprotonation energies of other substituted $CB_{11}X_{12}^-$ derivatives with the DFT method and found the order of acidity of dodecasubstituted carborate acids to be $CF_3 > F > CN > Cl > CF_3SO_2 > H$. Their investigation of possible protonation sites of $CB_{11}H_{12}^-$ (Figure 11) suggested that the most likely site is the hydrogen in position 12. Another stable structure is obtained with the protonated trigonal face formed by the borons in positions 7, 8, and 12. A BB edge protonated species did not correspond to a local minimum. A naked proton is so small that it could fit inside the CB_{11} framework; however, this structure did not prove to be stable either.

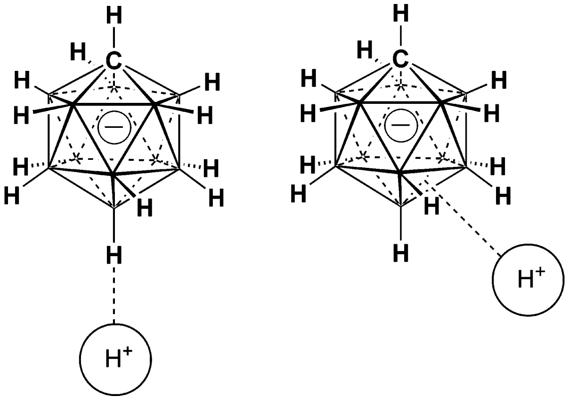


Figure 11. Protonation sites in **1**.[105]

An interesting concept for computational prediction and interpretation of anion basicity has been proposed recently.[107] The molecular electrostatic potential can be used to uniquely define a charge-neutral surface that encloses the anion in such a way that the net negative charge all lies outside and the inside charge integrates to zero. The value of the least negative minimum of the electrostatic potential on this surface provides information about the eagerness with which an outside proton will attach to the anion, i.e., about its basicity. In this fashion, the anions $1\text{-}HCB_{11}Cl_{11}^-$ (**181**) and **16** are found to be the least basic, followed by (7−12)-Br_6-$CB_{11}H_6^-$ (**178**) and others.

The free acids of dodecasubstituted $CB_{11}X_{12}^-$ anions have not been investigated experimentally, but those of several less substituted anions have been. The carborate acids are convenient Brønsted acids that are soluble in organic solvents. They are thermally stable, more so than "Brookhart's acid", $[H(OEt)_2][(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$.[144] One benefit to these carborate superacids is that a Lewis acidic medium (i.e., HF/SbF_5) is unnecessary, avoiding the concern of anion oxidation. Carborate acids are solids, and their strength cannot be measured using conventional Hammett acidity function (H_o). One attempt was made to use the $\Delta\delta$ mesityl oxide scale[145] to measure the acid strength of a series of hexa- and undecahalogenated CB_{11} acids in liquid SO_2.[146] This scale is based on the difference in ^{13}C NMR chemical shifts of the α- and β-carbon atoms of mesityl oxide, which increases upon protonation. All carborate acids were found to be stronger than all oxyacids, but relative acidities between carborates were difficult to establish because their acidities were leveled. Currently the best scale uses the ν(NH) IR frequencies of trioctylammonium salts of carborates.[118,147,148] It is based on the idea that the weaker the interaction between the conjugate base, CB_{11}^-, and proton, the stronger the acid. The ν(NH) frequencies probe the strength of the interaction. The weaker the carborate/cation interaction, the stronger the N−H interaction and higher the ν(NH) frequency. The IR measurements of trioctylammonium salts of derivatives of **1** were performed in CCl_4. Solvation effects were assumed to be negligible because of the strong structural similarities between carborate anions. Putting CH_3 groups into positions 2−6 only changed ν(NH) by 5−6 cm^{-1}, demonstrating that cations coordinate mostly to positions 7−12. The ranking for 7−12-hexahalo anions, Cl > Br > I, follows expectations based on the electronegativity and polarizability of each halogen. The authors found $H(1\text{-}HCB_{11}Cl_{11})$ to be the strongest known isolable acid, but they examined neither $H(CB_{11}F_{12})$[38] nor $H[CB_{11}(CF_3)_{12}]$.[149] They pointed out that the chemical stability of the free acid is an important factor, since acids such as HPF_6 would be considerably stronger but fall apart (in this case into HF and PF_5), and they emphasized that the robust nature of the aromatic skeleton **1** plays a key role. To this we would add that the electron-deficient nature of the carborate cluster is equally important, since in the end it is the ease of electrophilic abstraction of a halogen anion that determines whether the free acid falls apart and a hydrogen halide forms. It is much easier to abstract a halide anion from BF_4^- or similar anions, where the remaining fluorines provide electron density to the otherwise empty atomic orbital on boron, than from a halogenated **1**, where the empty orbital finds little solace.

Free carborate acids are prepared by reaction of the triethylsilylium salt with liquefied anhydrous HCl.[147] As mentioned in section 3.2, the ^{29}Si NMR shift of the silylium salt itself is a measure of coordination of the carborate anion and its cation as is its X-ray analysis.[150] The anion must be stable toward degradation and halogen abstraction by the Si center. Other considerations include the choice of solvent, Si substitution, and synthetic route.[151] X-ray structures provide C−Si−C bond angles, which indicate the amount of sp^2 character at the Si center. ^{29}Si NMR shifts also indicate how much "silylium" character is present. The assumption is that the more downfield the shift, the more positive the Si^+. However, chemical shifts are affected by anisotropy of the distribution of electrons around the nucleus and are not exclusively determined by charge. When the ^{29}Si chemical shift is plotted against the pyramidalization of the Si atom (for complete ionization, Si should be trigonal planar), the fit is not linear. ^{29}Si NMR shifts were given for a series of halogenated CB_{11} and CB_9 carborate salts.[152]

The coordinating ability of halogen substituents on the carborate anions decreases in the order I > Br > Cl > F. It is predicted that $1\text{-H-}CB_{11}F_{11}^-$ will be the strongest of these acids if coordination ability follows acidity.[152] Interestingly, ^{29}Si NMR measurement indicates that $1\text{-H-}CB_{11}H_5Cl_6$ is slightly less coordinating than $1\text{-HCB}_{11}Cl_{11}$; however, ν(NH) IR data suggest otherwise.[147,148] No explanation for this discrepancy is available.

Information about coordination strength of carborate anions has been used to develop stronger electrophilic reagents, such as a new class of alkylating reagents based on the halogenated carborates $R(CHB_{11}Me_5X_6)$, where R = Me, Et, *i*-Pr and X = Cl, Br.[90] NMR, IR, and X-ray structures show significant covalent interaction, but the carbon has cationic character (Figure 12). These reagents are stronger electrophiles than methyl triflate and more thermally stable than fluoroantimonate alkylating reagents.[90] The X-ray structure of $[C(CH_3)_3][1\text{-H-}CB_{11}H_5Br_6]$ showed well-defined cations and anions. These salts can be stored in a bottle indefinitely.[91]

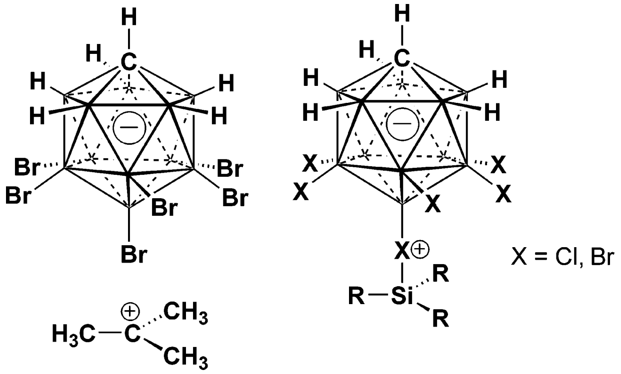


Figure 12. Hexahalogenated **1** as a weakly coordinating anion.[91]

Using a large non-nucleophilic counterion makes possible the isolation and characterization of stable crystalline hydronium salts with precisely defined hydration. Interesting results have been obtained for solvated acids and similar salts. The first example of a hydronium ion paired with a carborate was $[H_9O_4][CB_{11}H_6Br_6]$,[153] containing discrete $H_9O_4^+$ ions. The acid, $[H_3O][HCB_{11}Cl_{11}]$, displayed coordination of the H_3O^+ cation to three molecules of benzene (Figure 13).[154]

Several additional O-solvated H^+ species have been characterized, including $H(OEt_2)_2^+$ and $H(H_2O)(OEt)^+$.[79] X-ray structures of these $H(O\text{-donor})_2^+$ salts show a proton solvated by two solvent molecules. The experimental evidence (X-ray, IR) is consistent with an approximately centered proton yet with an indeterminate position. This type of cation is part of a class of hydrogen bonds that are short, strong, and low barrier (SSLB). These examples have proven to be some of the strongest H bonds to date.

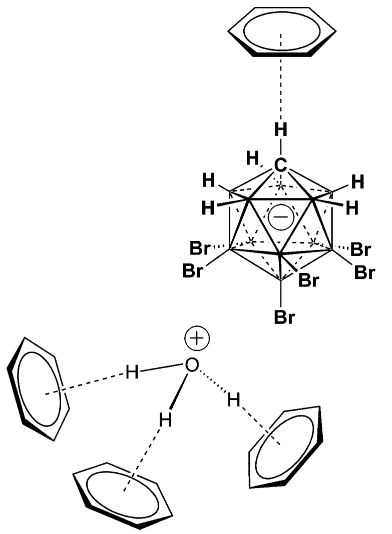


Figure 13. Coordination of H_3O^+ and **178** to benzene.[154]

Other solvated proton carborate salts include $[C_6H_7][CB_{11}H_6Cl_6]$, which is synthesized by adding benzene and HCl to a solution of $Et_3Si(CB_{11}H_6Cl_6)$.[85] $H[CB_{11}Br_5Cl_6]$ has been synthesized by heating $[H_3O{\cdot}H_2O][HCB_{11}Br_5Cl_6]$ (**349**) under vacuum.[86] $H[CB_{11}Br_5Cl_6]$ was not observed directly. Cyclohexene was added to the reaction vessel, stirred overnight, and then quenched with water to form cyclohexanol. The yield of the carborate acid was based on formation of cyclohexanol.[86]

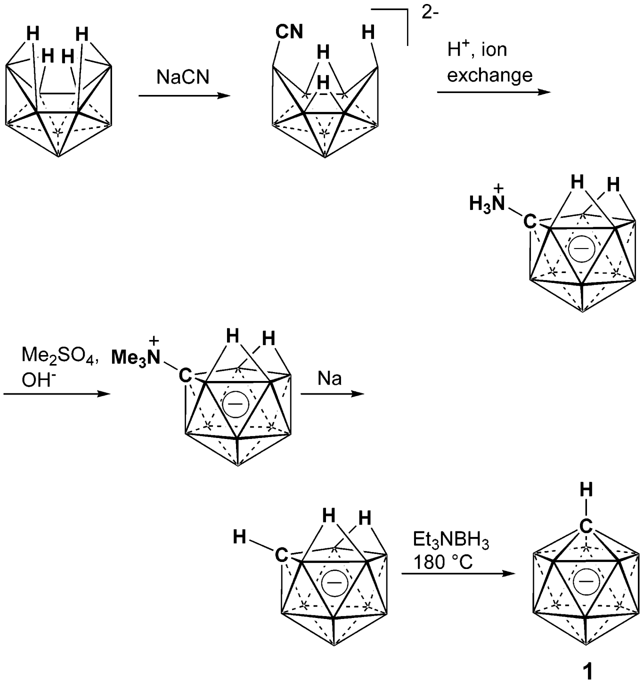
6.2. Anion Acidity

Although the acidity of the CH vertex of **1** and its derivatives is essential in their synthetic chemistry, only qualitative information is available in the literature. From synthetic work, it is known that halogenation in positions 2−6 makes the carbon vertex more acidic and that methylation anywhere on the cage reduces its acidity remarkably, such that it can no longer be deprotonated by any readily available base (see section 8.2.1). Very recently, simple titration experiments showed that in DMSO the pK_a of Li^+**1** is 21.7 and in cyclohexylamine it is 21.8, comparable to that of fluorene.[155] Substitution in the antipodal position 12 has a remarkable effect on the acidity of the CH vertex in **1**. For example, an iodine in position 12 (**176**) reduces it by nine orders of magnitude. A fluorine substituent in this position reduces the acidity even more, and the 12-fluoro derivative **173** is too weakly acidic for its pK_a to be measured in DMSO. A titration of a mixture of Li^+**173** and Li^+**176** with *n*-BuLi followed by ^{11}B NMR showed that in THF the fluorinated anion also is less acidic than the iodinated one, but the difference is small. Such a substantial decrease in CH acidity upon halogenation, especially fluorination, would be highly unusual in organic chemistry, and highlights the pronounced ability of the carborane cage to accept electron density from π-symmetry orbitals of substituents, which was already noted in section 5.

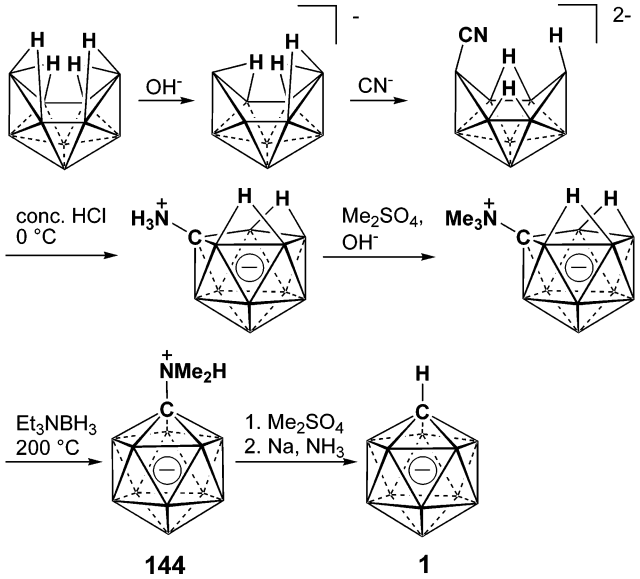
7. Synthesis

There are no known procedures for the preparation of **1** directly from small molecules. Its icosahedral skeleton has been synthesized only from boron clusters already containing at least 10 vertices. The conversion is accomplished by insertion of the missing one or two vertices, either one or two boron atoms into a CB_{10} or a CB_9 cluster, or a carbon

Scheme 1. Knoth's Synthesis of 1[156]



Scheme 2. Synthesis of 1 by the Group of Heřmánek[12]



atom into a B_{11} cluster. When the inserted vertex is BH or CH, the parent **1** is formed, and if it is BR or CR, where R is a substituent, a derivative of **1** is formed. This section is divided accordingly.

The mechanism of vertex insertion is probably rather complex, and little is known about it with certainty. Calculations of the reaction paths have been performed for both boron (AM1[42]) and carbon (DFT[106]) insertion.

7.1. Parent 1

7.1.1. Boron Insertion

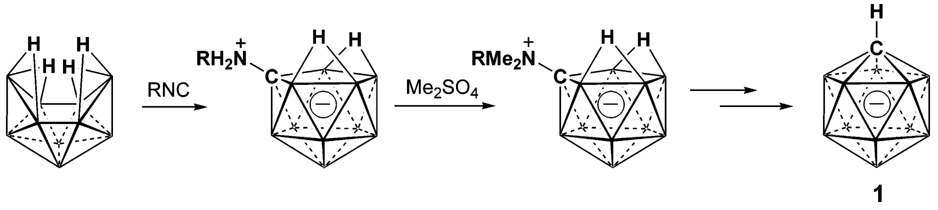
The initial preparation of **1** by Knoth[156] relied on the preparation of a CB_{10} precursor from the commercially available but expensive decaborane $B_{10}H_{14}$ (Scheme 1). Its reaction with sodium cyanide gives the 10-vertex arachno cluster $B_{10}H_{13}CN^{2-}$. Treatment with acid causes the carbon substituent to be incorporated into the polyhedral structure with formation of the 11-vertex nido cluster $CB_{10}H_{12}NH_3$. The amino group was then methylated with dimethyl sulfate to yield $B_{10}H_{12}CNMe_3$. The substituent was reduced off by reflux with sodium in THF, which produced a mixture of the desired nido salt $NaCB_{10}H_{13}$ and the dehydrogenated closo salt $NaCB_{10}H_{11}$, which were easily separated, because the former is much less soluble in THF. Heating of $CsCB_{10}H_{13}$ to 300−320 °C yielded a mixture of the cesium salts of $CB_{11}H_{12}^-$ (**1**) and $CB_9H_{10}^-$. Alternatively, heating in the presence of $BH_3{\cdot}NEt_3$ gave only the cesium salt of **1**.

A safer and more convenient modification of the synthesis was developed in the group of Heřmánek (Scheme 2).[12] Decaborane was deprotonated with sodium hydroxide to give $B_{10}H_{13}^-$ and only then treated with cyanide to form the arachno structure $B_{10}H_{13}CN^{2-}$, which was then converted to $CB_{10}H_{12}NH_3$ with concentrated HCl and methylated to Knoth's 11-vertex nido cluster 7-Me_3N-7-$CB_{10}H_{12}$. Now, the last vertex was inserted by heating with triethylamineborane at 180−200 °C, but one methyl group was lost from the nitrogen in the process and had to be reintroduce by another methylation with dimethyl sulfate. Finally, reduction with sodium in liquid ammonia split off the substituent and afforded **1**. This procedure is the basis of the commercial product available from the Katchem Company in Prague, Czech Republic. In a brief comment it has been noted that a similar synthesis has been accomplished in which the trimethylamine group was replaced by dimethyl sulfide and the triethylamineborane adduct by a tributylphosphine adduct.[157]

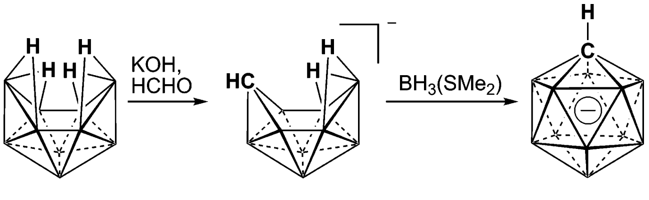
A further modification was introduced in an attempt to improve safety by avoiding the use of cyanide in the synthesis of 7-Me_3N-7-$CB_{10}H_{12}$,[158] taking advantage of an earlier observation that isocyanides react with decaborane similarly as cyanide and yield the mono-*N*-alkylated derivatives $B_{10}H_{12}CNH_2R$.[159] Reaction of decaborane with *tert*-butyl or cyclohexyl isocyanide, followed by deprotonation and alkylation, provided cyanide-free access to the nido intermediate needed for insertion of the last vertex (Scheme 3).

In an important recent advance, insertion of two BH vertices into the arachno $CB_9H_{14}^-$ anion in a one-pot reaction has been reported to afford **1** smoothly. Since the arachno anion is easily accessible from the decaborane $B_{10}H_{14}$ by Brellochs reaction with formaldehyde and base, this appears to be the best current route from *nido*-decaborane to **1**. It takes only two steps, and the overall yield is ~65% (Scheme 4).[120]

Scheme 3. Cyanide-Free Synthesis of 1 by the Group of Hughes[158]



Scheme 4. Synthesis of 1 by the Group of Kennedy[120]

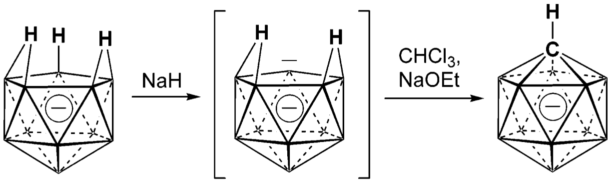


1

7.1.2. Carbon Insertion

It is tempting to insert the carbon vertex last because the 11-vertex nido precursor $NaB_{11}H_{14}$ is accessible in 50% yield in a one-step reaction from bulk chemicals, $NaBH_4$ and $BF_3 \cdot Et_2O$. This has indeed been accomplished[52] but in a poor yield, and there is considerable room for improvement (Scheme 5).

Scheme 5. Synthesis of 1 by the Group of Michl[52]



1

The stoichiometry of the insertion calls for use of a dihalocarbene or its functional equivalent, and the reported reaction used chloroform and a base (NaH for deprotonation of $B_{11}H_{14}^{-}$ to $B_{11}H_{13}^{2-}$ and sodium ethoxide for deprotonation of chloroform). It has not been proven that a carbenoid is actually involved in the process, but it appears likely. The presumed reaction path was explored with DFT calculations[106] and appears plausible. With bromoform, the 2-bromo derivative of **1** is formed as the main product, whereas iodoform acts only as an oxidant, yielding *closo*-$B_{11}H_{11}^{2-}$. This also is a side product in the reaction with the other haloforms but is easily removed. The reaction with chloroform is sensitive to reaction conditions and can yield a product contaminated with a few percent of the 2-choro and even the 2-ethoxy derivative of **1**. The reported yield of 40% has only been achieved on small scale, and on 5−50 g scale, a typical yield of pure **1** is usually only 20−25%.

7.2. Derivatives of 1

When the vertex that is being inserted in reactions that complete an icosahedron from a smaller cluster carries a substituent, or if a substituent is already present in the starting smaller cluster, or both, derivatives of **1** can be expected to form. Several syntheses of this type have indeed been described and provide an important complement to reactions that introduce a substituent into an already existing icosahedron. In particular, they usually lead to substitution in positions 1 and 2, whereas the latter have a tendency to place a substituent into positions 1, 7, and especially 12 (section 8). The results are summarized in Table 6.

7.2.1. Boron Insertion

The initially formed product in Heřmánek's synthesis of **1** carries a doubly methylated amino substituent in position 1 (Scheme 2). When the amine alkylation step is omitted, it carries a plain amino group, and when position 7 in the starting nido cluster carries a dimethyl sulfide instead of an amino substituent, the product is a derivative of **1** that carries a dimethylsulfide group in position 1.[21] A substituent in position 2 can be introduced through insertion of RBX_2 (X = Cl, F) into *nido*-7-$CB_{10}H_{10}^{3-}$. Such use of a functionalized boron derivative was demonstrated with R = Ph, *p*-Tol, F, $O(CH_2)_4Cl$, and NMe_3.[51] The 11-vertex nido precursor can carry substituents on other vertices. Insertion of $PhBCl_2$ into *nido*-4-I-7-Me_3N-7-$CB_{10}H_{11}$ yielded the 8-I-2-Ph-1-NMe_3 derivative of **1**.[42]

In a similar fashion, when two boron vertices are inserted from $Et_3N \cdot BH_3$ into the open hexagonal face of 6-Me_3N-*nido*-6-CB_9H_{11}, 1-NMe_2H-*closo*-$CB_{11}H_{11}$ (**144**) is formed, and when 6-H_3N-*nido*-6-CB_9H_{11} is used, 1-H_3N-$CB_{11}H_{11}$ (**142**) is formed, albeit in a poor yield.[160] Insertion of two boron vertices into the 6-Ph-*nido*-$CB_9H_{11}^{-}$, easily accessible in excellent yield from Brellochs reaction between benzaldehyde and *nido*-decaborane, offers an entry to 1-phenylated derivatives of **1**.[26] Reaction with 2 equiv of $BH_3(SMe_2)$ gives the 1-Ph anion (**95**) in good yield, whereas use of $BH_3 \cdot NEt_3$ gives a mixture with $PhCB_9H_9^{-}$. The anion 1,2-Ph_2-$CB_{11}H_{10}^{-}$ was obtained by insertion of $PhBX_2$.

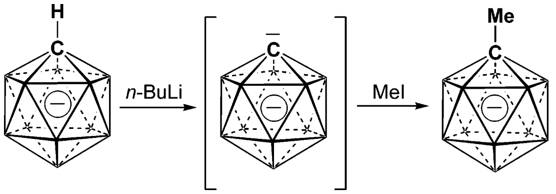
Although in these examples insertion of a boron vertex is regiospecific and yields the expected icosahedral product, rearrangements also have been observed. Thus, insertion into 8-$PhCH_2$-7-Me_3N-7-$CB_{10}H_{11}$ yielded the 1-Me_3N-7-benzyl-substituted anion (**244**),[56] and upon insertion of $Et_3N \cdot BH_3$ into a mixture of the isomeric disulfides 4,4′-(6,6′ and 4,6′)-S_2-(7-Me_3N-7-$CB_{10}H_{11}$)$_2$, the 1-Me_2N-2-HS-substituted **1** was formed.[55] Loss of a methyl from the amino nitrogen has precedent.[12] All three isomers of Me_3N-substituted **1** resulted from the thermal decomposition of *nido*-[7-$CB_{10}H_{13}$][$BH_2(NMe_3)$].[56]

Table 6. Synthesis of Substituted Carborates[a]

anion	synthesis	anion	synthesis
95[27]	$B_{11}H_{14}^{-}$, $PhCHCl_2$, NaH	**230**[b,52]	$B_{11}H_{14}^{-}$, $CHCl_3$, EtONa
95[26]	1. PhCHO, $B_{10}H_{14}$; 2. C	**231**[b,52]	$B_{11}H_{14}^{-}$, $CHCl_3$, EtONa
96[27]	$B_{11}H_{14}^{-}$, *p*-FC_6H_4-$CHCl_2$, NaH	**232**[51]	$CB_{10}H_{11}^{3-}$, $Me_2S \cdot BCl_3$, THF
97[27]	$B_{11}H_{14}^{-}$, *p*-ClC_6H_4-$CHCl_2$, NaH	**233**[51]	$CB_{10}H_{11}^{3-}$, $BF_3 \cdot OEt_2$
98[27]	$B_{11}H_{14}^{-}$, *p*-BrC_6H_4-$CHCl_2$, NaH	**234**[b,52]	$B_{11}H_{14}^{-}$, $CHCl_3$, EtONa
98[26]	1. *p*-BrC_6H_4-CHO, $B_{10}H_{14}$; 2. C	**235**[b,52]	$B_{11}H_{14}^{-}$, $CHBr_3$, EtONa
99[27]	$B_{11}H_{14}^{-}$, *p*-IC_6H_4-$CHCl_2$, NaH	**240**[54]	Li_2[7-Me_3N-7-$CB_{10}H_{10}$], *i*$PrNBCl_2$
100[27]	$B_{11}H_{14}^{-}$, *p*-C_6H_5-C_6H_4-$CHCl_2$, NaH	**241**[c,55]	S_2(7-Me_3N-7-$CB_{10}H_{11}$)$_2$, A
142[21]	7-H_3N-7-$CB_{10}H_{12}$, A	**242**[55]	**241**, Me_2SO
144[12]	7-Me_3N-7-$CB_{10}H_{12}$, A	**244**[56]	8-Ph-7-Me_3N-7-$CB_{10}H_{11}$, A
144[160]	6-(Me_3N)-6-CB_9H_{11}, A	**377**[42]	4-I-7-Me_3N-7-$CB_{10}H_{11}$, B
165[160]	7-Me_2S-7-$CB_{10}H_{12}$, A	**378**[201]	[7-Ph-7-$CB_{10}H_{12}$]$^{-}$, B
228[51]	$CB_{10}H_{13}^{-}$, B	**379**[161]	[7-*p*-MeC_6H_4-7-$CB_{10}H_{12}$]$^{-}$, B
230[51]	$CB_{10}H_{11}^{3-}$, $BCl_2(NMe_2)$, Me_2SO_4	**380**[51]	$CB_{10}H_{13}^{-}$, *n*-BuLi, (*p*-MeC_6H_4)BCl_2

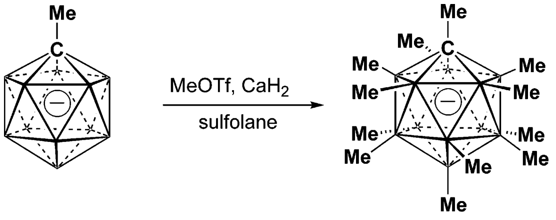
[a] A: $Et_3N \cdot BH_3$. B: *n*-BuLi, $PhBCl_2$. C: $BH_3 \cdot SMe_2$; **377** = 8-I-2-Ph-1-NMe_3-$CB_{11}H_9$; **378** = 1,2-Ph_2-$CB_{11}H_{10}^{-}$; **379** = 1-*p*-MeC_6H_4-2-Ph-$CB_{11}H_{10}^{-}$; **380** = 2-*p*-MeC_6H_4-$CB_{11}H_{10}^{-}$. [b] Side product in $CB_{11}H_{11}^{-}$ synthesis. [c] Mixture with **245**.

Scheme 6. Substitution on the Carbon Vertex[15]



1 **2**

Scheme 7. Substitution on Boron Vertices[15]



2 **16**

A different type of rearrangement was observed when i-Pr_2NBCl_2 was inserted into 7-Me_3N-*nido*-7-$CB_{10}H_{10}$.[54] A methyl group from the trimethylamino substituent inserted into the exoskeletal B−N bond to form a methylene link to a quarternized nitrogen atom, permitting strain associated with the proximity of two bulky substituents to be released, and the 1-Me_2N-2-i-Pr_2NHCH_2-substituted anion (**240**) was formed.

7.2.2. Carbon Insertion

When benzyl chloride $C_6H_5CHCl_2$ and substituted benzyl chlorides are used as precursors of substituted halocarbenes instead of chloroform, insertion into *nido*-$B_{11}H_{14}^-$ affords 1-aryl-substituted anions **1**.[27]

8. Reactions

8.1. Reactivity Patterns

Four fundamental types of reactions are known for the $CB_{11}H_{12}^-$ anion **1** and its derivatives: (i) substitution on the carbon vertex, (ii) substitution on one of the boron vertices, (iii) redox processes that involve removal of a delocalized electron from the cage or its addition to the cage, and (iv) transformations of substituents.

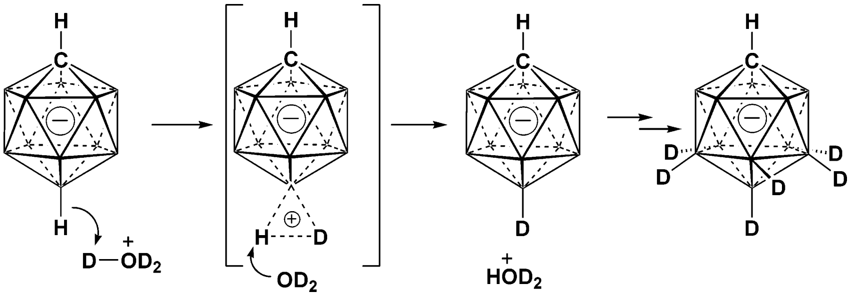
The C−H bond on the carbon vertex is weakly acidic, and we have noted in section 6 that strong bases such as n-butyllithium convert it to a carbanion or an organometallic derivative C−M. The B−H bonds at the other vertices are hydridic. Hence, all vertices are in principle amenable to attack by electrophilic reagents. When the carbon is deprotonated, it becomes by far the most nucleophilic vertex and electrophilic reagents attack there. When the carbon is not deprotonated, the B−H bond in position 12 is the most reactive toward electrophiles, with positions 7−11 not far behind. The B−H bonds in positions 2−6 are less nucleophilic.[162,163] The reactivity is strongly affected by cage substituents in ways that are currently not understood in much detail. In general, it appears that an alkyl substituent activates all positions and a halogen substituent activates distant positions and deactivates the adjacent ones. This could mean that the methyl substituent operates only by its π-donor effect, whereas halogens operate by a superposition of a long-range π-donor effect and a short-range acceptor σ-inductive effect, much as is the case on ordinary aromatic substrates. An illustrative example is provided by the exhaustive methylation of the 1-halo derivatives 1-X-**1**, X = F, Cl, Br, and I, with methyl triflate in sulfolane at room temperature to yield the 1-haloundecamethyl anions. When X = F, a hexamethylated anion is formed nearly quantitatively in 6 h and the reaction stops and never runs to completion. When X = Cl, hexamethylation is accomplished in 6 days and undecamethylation runs to completion in 18 days. When X = Br, undecamethylation takes 25 days, and when X = I, one needs to wait 42 days.[48] In the last two cases, there is not enough difference between the rate of methylation in positions 7−11 and positions 2−6 to allow the hexamethylated anion to accumulate.

In some derivatives, the acidity of the CH vertex is insufficient for deprotonation with a base, but when an iodine or bromine substituent can be introduced on the carbon first, lithium/halogen exchange can be effected by treatment with *tert*-butyllithium to produce the desired deprotonated organometallic derivative and proceed with electrophilic substitution.[48,164] Typical examples of introduction of substituents into the $CB_{11}H_{12}^-$ cage using electrophilic reagents are shown in Schemes 6 and 7.[15]

The mechanism of these substitutions has not been studied in detail. The reaction on the deprotonated carbon vertex probably proceeds in the same S_N2 way as on any ordinary carbanion, but the reactions on the boron vertices pose some unanswered questions. The initial association with the electrophile could occur on a triangular face, on an edge, or on a single B−H bond. Protonation on the hydrogen or on a triangular face is favored by calculations.[105] Addition of an electrophile presumably leads to an intermediate analogous the Wheland intermediate in electrophilic aromatic substitution. Its formation could represent the rate-determining step, or this could be the subsequent product-forming transfer of the originally attached BH proton to a base (Scheme 8).

The electrophilic substitution described so far can be easily directed exclusively to the deprotonated carbon vertex, but its selectivity on the boron vertices is not good. We shall see below that at times it is possible to perform monosub-

Scheme 8. Proposed Mechanism of Electrophilic Substitution on a Boron Vertex[163]



stitution in position 12, disubstitution in positions 7 and 12, or hexasubstitution in positions 7−12, but other specific substitution patterns are not easy to achieve.

Once a boron vertex is iodinated, it can be further selectively activated by a reaction with low-valent palladium catalysts to yield organometallic intermediates useful in Kumada coupling, which represents any important tool for introduction of carbon substituents. We shall describe in section 8.6 the complexity that was involved in the preparation of all 15 symmetrically methylated $CB_{11}H_{12}^-$ anions.[13] Specific synthesis of most of the vast number of unsymmetrically methylated ones would be a much harder proposition.

The anion **1** is so electron rich that in addition to performing substitution, an attacking electrophile can also abstract a hydride anion from a BH vertex to produce an electroneutral species $CB_{11}H_{11}$ that at least formally has the structure of a deprotonated hypercloso cation $CB_{11}H_{12}^+$ but reacts with simple nucleophiles as if it were an ylide, with a positive charge on the resulting "naked" boron vertex and the usual delocalized negative charge in the cluster cage.

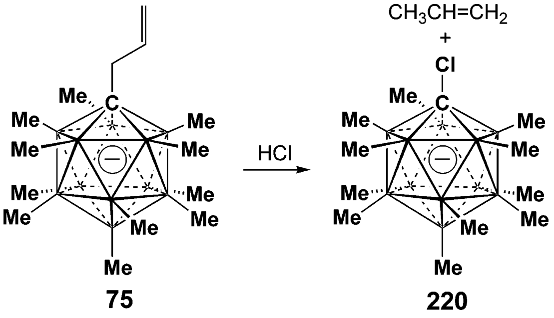
Calculations for such "boronium ylide" structures have been performed both for the parent $CB_{11}H_{11}$,[101,104] derived from **1** by hydride abstraction, and for $CB_{11}Me_{11}$,[36] derived from **16** by methide abstraction. The structures are an at least local and possibly global minimum on the potential energy surface. They are the most stable when the naked vertex is in position 12, somewhat (∼3−4 kcal/mol) less so when it is in one of the positions 7−11, and significantly (∼12 kcal/mol) less so in one of the positions 2−6, and these differences are the same in the parent and in the methylated series. The lowest triplet energies of the methylated species lie high above the lowest singlet, and triplets are not likely to intervene in thermal reactions. The calculated triplet excitation energy is lowest (16 kcal/mol) when the naked vertex is the carbon in position 1.[36]

It is not yet known whether the boronium ylide structure computed so far is indeed the most stable form of $CB_{11}H_{11}$ and other naked vertex reactive intermediates produced by hydride abstraction. Experimental efforts have so far been inconclusive, although the isomer of $CB_{11}Me_{11}$ with a naked B(12) vertex has been isolated as a powder at low temperature, and reactions of these species with aromatics suggest other possibilities.[36] All these ylides are extremely reactive toward nucleophiles, and their formation represents an "umpolung" of the normal reactivity of the CB_{11} cage.

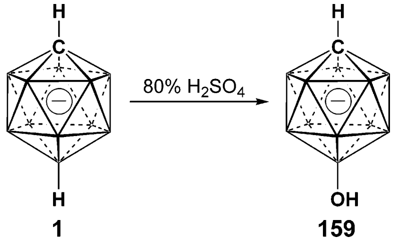
Thus, there are two distinct mechanisms for substitution, ordinary electrophilic substitution and the EINS (electrophile-induced nucleophilic substitution) process. Both are formally σ-bond metatheses. In electrophilic substitution, B−H + E−Nu is converted to B−E + H-Nu, and in EINS, B−H + E−Nu is converted to B−Nu + H−E.

Not surprisingly, abstracting a hydride from the carbon vertex is computed to be the hardest, but even the "carbonium ylide" can be produced easily when the cage is highly alkylated and a suitable leaving group is placed on the carbon.[18] This suggests that the actual structure of the $CB_{11}(CH_3)_{11}$ intermediate with a naked carbon vertex may be different from the one computed so far. DFT calculations[36] found a local minimum at a geometry with an approximately five-fold symmetry, fully 36 kcal/mol above the isomer with a naked boron atom in position 12. This need not be the absolute minimum, and the real optimum geometry of the species is perhaps different. When it reacts with simple nucleophiles, however, it behaves as if it had this structure (electroneutral analog of a carbocation, a formal ylide that can equally well be viewed as a carbenoid).

Scheme 9. Electrophile-Induced Nucleophilic Substitution on a Carbon Vertex[18]



Scheme 10. Electrophile-Induced Nucleophilic Substitution on a Boron Vertex.[34]



The generality of this "electrophile-induced nucleophilic substitution" (EINS) on boron vertices was recognized a long time ago by Heřmánek and his collaborators[162,163] and the analogous reactivity of the carbon vertex only much more recently.[18] In addition to hydride abstraction from a BH vertex and departure of a leaving group from the carbon vertex, access to this reaction path is provided by abstraction of a methyl group with a Brønsted or Lewis acid. For instance, $CB_{11}(CH_3)_{12}^-$ (**16**) reacts with the HF−pyridine adduct to yield a 70:30 mixture of the 12-fluoro- and 7-fluoro-substituted $CB_{11}F(CH_3)_{11}^-$ anions,[15] in analogy to the reaction of **1**, which yields the 12-fluoro-substituted $CB_{11}FH_{11}^-$ anion.[38] Similarly, **16** reacts with the *tert*-butyl cation in a chlorinated solvent to yield a mixture of partially methylated and partially chlorinated anions,[165] and also metal and metalloid cations can behave in this fashion (section 3.2). This reaction limits the utility of the parent and the alkylated CB_{11} anions as inert counterions.

Representative examples of EINS reactions are shown in Schemes 9 and 10.

Unlike its reactions with electrophiles and nucleophiles, reactions of the CB_{11} cage with radical reagents have not been explored much.

In addition to these three fundamental types of cage substitution processes, the CB_{11} cluster anion can also be oxidized to the delocalized cluster radical, which can subsequently transfer one of its substituents as a radical to a suitable substrate in a relatively poorly understood manner and yield the same hypercloso intermediate that occurs as an intermediate in EINS reactions.[36]

Reactions initiated by addition of an electron to the cage, or perhaps more accurately to a cage−substituent antibonding orbital, which ultimately lead to loss of the substituent, are also known.[12,13]

In sections 8.2 and 8.3, we shall consider specific cage substitution reactions that have been reported. In section 8.4, we shall deal with cage redox processes, in section 8.5, we shall deal with reactions that occur on the substituents, and in section 8.6, we exemplify the substitution chemistry on **1** by presenting a collection of multistep syntheses that led to all 15 symmetrically methylated CB_{11} anions.

8.2. Carbon Vertex Substitution

8.2.1. Electrophilic

Replacement Reactions. Deprotonation of the carbon vertex followed by treatment with an electrophile is one of the earliest known[156] and most frequently performed substitution reactions of **1** and its derivatives. Deprotonation of **1** is performed with a strong base, most commonly *n*-butyllithium. The reaction requires meticulous care and use of dry solvent and vessels if contamination of product with the reprotonated starting material is to be avoided. If the substituted product is stable to the reaction conditions, repetition of the procedure on the product mixture may be the fastest way to pure material.[166]

Attention often needs to be paid to the choice of counterion. Lithiation of the cesium salt of **1** in THF yields an insoluble cesium salt of the 1-lithio derivative, often rendering subsequent substitution difficult or impossible,[16,156b,167] although sometimes it still takes place.[17] Use of the NMe_3H^+ salt of **1** with 2 equiv of *n*-butyllithium yields the perfectly soluble lithium salt of the 1-lithio anion, but of course the NMe_3 byproduct has to be removed before the alkylating agent is added.

We noted in section 6.2 that the acidity of the carbon vertex varies remarkably with cage substitution, and this has important practical effects on substitution reactions. Especially strongly acidic derivatives of **1**, e.g., the undecafluorinated (**180**), are deprotonated with aqueous alkali hydroxide.[9,40] Deprotonation and alkylation of undecahalogenated[41] and (7−12)-hexahalogenated[44] derivatives generally pose no problem, whereas for the especially weakly acidic anions, such as the (7−11)-pentamethylated (**4**),[13] the (7−12)-hexamethylated (**11**),[48,168] or the undecamethylated (**12**)[18] anion, no base strong enough to remove the carbon vertex proton has yet been found.

However, access to the deprotonated species is still possible by halogen−metal exchange. The undecamethylated 1-iodo (**222**) and 1-bromo (**221**) anions are available[48] and have been converted with *n*-butyllithium or *tert*-butyllithium to the 1-lithio derivative of **12**.[164] The lifetime of this extremely strong base in THF is limited to a few hours but is sufficient for *ω*-alkenylation with $CH_2{=}CH\text{-}(CH_2)_{n-2}\text{-}OTos$ ($n = 3-7$)[164] and presumably for other electrophilic substitution reactions. Unfortunately, among the 1-halogenated (7−12)-hexamethylated anions only the chloro and fluoro derivatives are easily accessible,[48] and they do not undergo halogen−metal exchange, so this access to the deprotonated **11** currently remains blocked.

The problem with the low acidity of **4** and **11** has been solved in a less direct way. Introduction of iodine substituents often increases the acidity of the carbon vertex sufficiently for deprotonation with *n*-butyllithium, and after completed electrophilic substitution, the iodine substituent can be reduced off under Birch conditions.[13]

Although C-alkylation with ordinary alkylating agents has been a particular favorite, many other types of electrophilic substitution have been reported as well. Silylation is facile,[16] and temporary introduction of the bulky trisisopropylsilyl (TIPS) group has recently been used to block reactions at boron vertices 2−6.[13] The TIPS substituent was subsequently removed with fluoride. Other atoms that have been attached to the carbon vertex were boron,[30] phosphorus,[16] sulfur,[21] and copper.[40] Transient attachment of copper was used in the process of halogenation,[37] and of zinc, in Negishi coupling.[171] Halogenation was initially accomplished with *N*-halosuccinimides.[37] However, superior yields are obtained upon treatment of the deprotonated **1** with a 1,2-dihaloethane[48] or elemental iodine.[48] An *N*-fluoro reagent has been used for fluorination.[37] The initial hope that the 1-halogenated anions will serve as useful substrates for palladium-catalyzed coupling has not been fulfilled, and the unique synthetic value of the iodo and bromo derivatives is to provide access to deprotonated **12**.[164]

Addition Reactions. Addition of the deprotonated carbon vertex to double bonds and rings has been investigated much less. Additions to the carbonyl group of aldehydes,[17] including a porphyrine aldehyde,[169] and to carbon dioxide[21] have been reported (Scheme 11). We have not found reports of addition to ketones. Addition is also feasible with epoxides[17] and provided a higher yield route to anions with a 2-haloethylated carbon vertex[18] than 2-hydroxyethylation with a protected agent.[167] As we shall see below, the 2-haloethyl substituent affords an entry to nucleophilic substitution on the carbon vertex by Grob fragmentation.

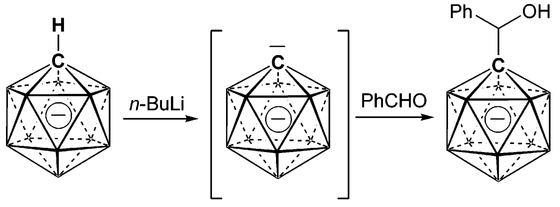
A summary of the known electrophilic substitution reactions on the carbon vertex is provided in Table 7.

Table 7. Electrophilic Substitution on the Carbon Vertex[a]

anion	conditions	anion	conditions
2[13]	**1**, A	**75**[18]	E, $n = 3$
17[16]	B, EtI	**76**[18]	E, $n = 4$
18[13]	B, HexBr	**77**[18]	E, $n = 5$
19[16]	B, $PhCH_2Br$	**78**[18]	E, $n = 6$
20[17]	C, R = H	**79**[18]	E, $n = 7$
21[17]	C, R = *i*-Pr	**80**[16]	B, CF_3I
22[17]	C, R = MeCH═CH	**126**[13]	B, TIPSCl
23[17]	C, R = Ph	**127**[16]	B, Ph_3SiCl
24[17]	C, R = 2-furyl	**130**[30]	B, *i*-PrOB($C_6H_{12}O_2$)
25[17]	B, propylene oxide	**150**[b,16]	B, Ph_2PCl
26[18]	B, oxirane	**164**[21]	B, S
27[18]	B, $Br-(CH_2)_2-Br$	**169**[37]	**1**, $(PhSO_2)_2NF$
28[18]	B, $Cl-(CH_2)_3-Cl$	**170**[37]	**1**, CuCl, NCS
29[18]	B, $Br-(CH_2)_3-Br$	**170**[48]	**1**, 1,2-$Cl_2C_2H_4$
30[18]	B, $Cl-(CH_2)_4-Cl$	**171**[37]	**1**, NBS
31[18]	B, $Br-(CH_2)_4-Br$	**171**[48]	**1**, 1,2-$Br_2C_2H_4$
32[18]	B, $Cl-(CH_2)_5-Cl$	**172**[37]	**1**, CuCl, NIS
33[18]	B, $Br-(CH_2)_5-Br$	**172**[37]	**1**, NIS, CuCl
34[18]	B, $Cl-(CH_2)_6-Cl$	**172**[48]	**1**, 1,2-$I_2C_2H_4$
35[18]	B, $Br-(CH_2)_6-Br$	**172**[48]	B, I_2
36[18]	B, $Cl-(CH_2)_7-Cl$	**197**[44]	**177**, A
37[18]	B, $Br-(CH_2)_7-Br$	**198**[44]	**178**, A
47[88]	B, CO_2	**200**[40]	**180**, NaOH, Me_2SO_4
63[18]	D, $Br-(CH_2)_2-Br$	**201**[41]	**181**, A
64[18]	D, $Cl-(CH_2)_3-Cl$	**202**[41]	**182**, A
65[18]	D, $Br-(CH_2)_3-Br$	**216**[13]	**212**, A
66[18]	D, $Cl-(CH_2)_4-Cl$	**381**[13]	**382**, A
67[18]	D, $Br-(CH_2)_4-Br$	**383**[9]	**180**, NaOH, Et_2SO_4
68[18]	D, $Cl-(CH_2)_5-Cl$	**384**[9]	**180**, NaOH, C_4H_9X
69[18]	D, $Br-(CH_2)_5-Br$	**385**[9]	**180**, NaOH, $ClCH_2X$
70[18]	D, $Cl-(CH_2)_6-Cl$	**386**[167]	B, I-$(CH_2)_2$OTBS
71[18]	D, $Br-(CH_2)_6-Br$	**387**[202]	Por, B
72[18]	D, $Cl-(CH_2)_7-Cl$	**388**[169]	Cu−Por, B
73[18]	D, $Br-(CH_2)_7-Br$	**389**[169]	Co−Por, B
74[18]	E, $n = 2$	**390**[40]	F

[a] A: *n*-BuLi, MeI. B: **1**, *n*-BuLi. C: **1**, *n*-BuLi, RCHO, H_2O. D: **221** or **222**, *n*-BuLi. E: **1**, *n*-BuLi, $CH_2{=}CH-(CH_2)_{n-2}-OTos$, $n = 2-7$. F: $[Cu(mesityl)]_n$, $N(n\text{-}Bu)_4Cl$, $[N(n\text{-}Bu)_4][1\text{-}H\text{-}(CB_{11}F_{11})]$; **381** = 1-Me-7-11-$Me_5$-2,3,12-$I_3$-$CB_{11}H_2^-$; **382** = 7−11-$Me_5$-2,3,12-$I_3$-$CB_{11}H_3^-$; **383** = 1-Et−$CB_{11}F_{11}^-$; **384** = 1-$C_4H_9$-$CB_{11}F_{11}^-$; **385** = 1-$ClCH_2$-$CB_{11}F_{11}^-$; **386** = 1-TBSO$(CH_2)_2$-$CB_{11}H_{11}^-$; **387** = Por-$CB_{11}H_{11}^-$; **388** = Cu-Por-$CB_{11}H_{11}^-$; **389** = Co-Por-$CB_{11}H_{11}^-$; **390** = $[N(n\text{-}Bu)_4]_2[CuCl(CB_{11}F_{11})]$; Por = 5,10,15,20-Tetraphenylporphyrin. [b] As mixture with **151**.

Scheme 11. Electrophilic Addition on a Carbon Vertex[17]



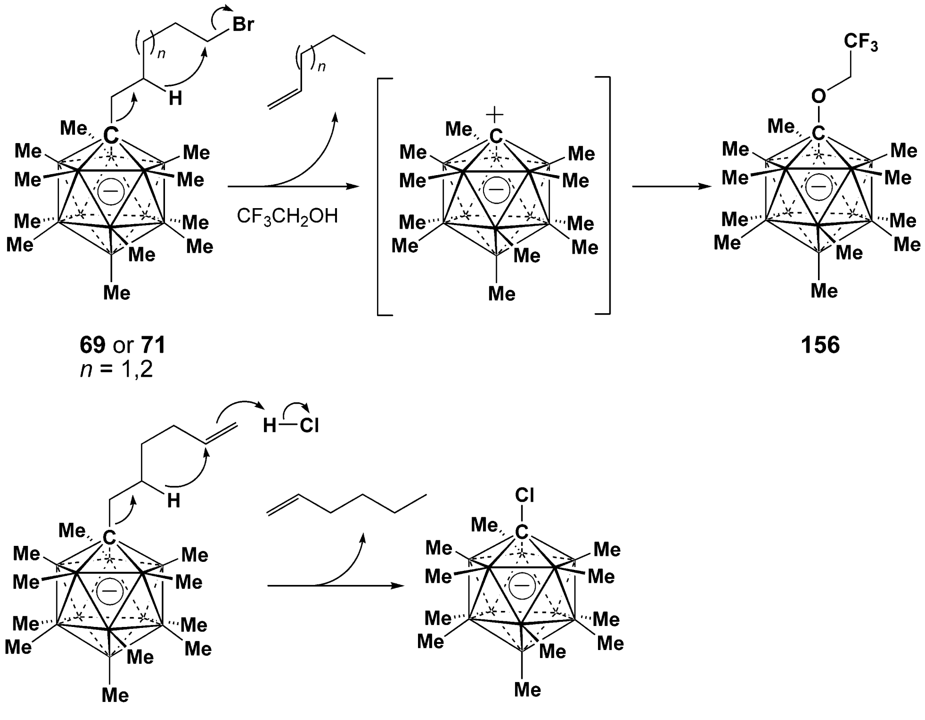
1 **23**

8.2.2. Nucleophilic

Nucleophilic reactions at the normally acidic carbon vertex may look improbable but were first reported a long time ago[21] and have recently received considerable attention.[18] They proceed through an as yet poorly characterized intermediate or intermediate mixture with a naked carbon vertex discussed in section 8.1. Their recent investigation involved some detective work that followed the bizarre observation that under solvolytic conditions certain 1-(ω-haloalkyl) derivatives of the undecamethylated anion **12** (1-Hal$(CH_2)_n$−$CB_{11}(CH_3)_{11}{}^-$) lose their alkyl chain in the form of a terminal alkene C_nH_{2n} and yield a product that can be viewed as an adduct of the ylide, $C^+B_{11}(CH_3)_{11}{}^-$, or carbenoid, $CB_{11}(CH_3)_{11}$, to one of the nucleophiles present. This happens only when $n = 2$, 5, or 6, and no reaction was observed under the same conditions when $n = 3$, 4, or 7, when the substituent at the carbon vertex was a plain alkyl group, or when the carborate anion was not methylated.[18] Isotopic labeling showed that the double bond in the terminal alkene produced is located at the end through which the carbon chain was attached to the carborate anion. The same products resulted when a 1-(ω-alkenyl) derivative of **12**(CH_2=$CH(CH_2)_{n-2}$-$CB_{11}(CH_3)_{11}{}^-$) was treated with acid but now only when $n = 3$, 6, or 7 and not when $n = 4$ or 5. The results were rationalized as due to a combination of a Grob fragmentation with an intramolecular hydride transfer that requires a five-membered or six-membered cyclic transition state (Scheme 12).[18]

Solvolysis is zero order in the nucleophile, demonstrating that the reactive intermediate leaves in the rate-determining step before the nucleophile becomes involved, and there is evidence that the solvolytic departure of the leaving group is simultaneous with the CC bond cleavage and formation of the intermediate.[18] These results are quite remarkable in that viewed as a substituent on an organic skeleton, the -$CB_{11}(CH_3)_{11}{}^-$ group behaves as a "superelectrofuge" that

Scheme 12. Grob Fragmentation and Hydride Transfer in an Electrophile-Induced Nucleophilic Substitution on a Carbon Vertex[18]

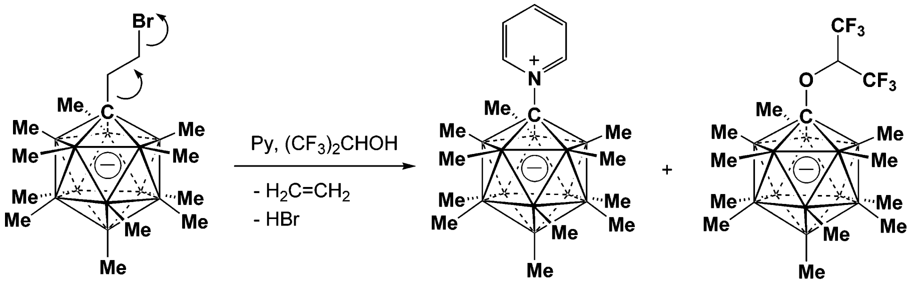


69 or **71**
n = 1,2

156

78 **220**

Scheme 13. Grob Fragmentation in an Electrophile-Induced Nucleophilic Substitution on a Carbon Vertex[28]



63 **148** **157**

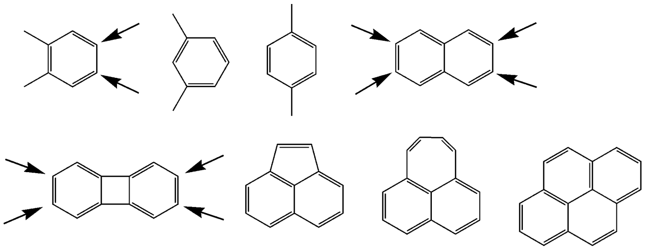
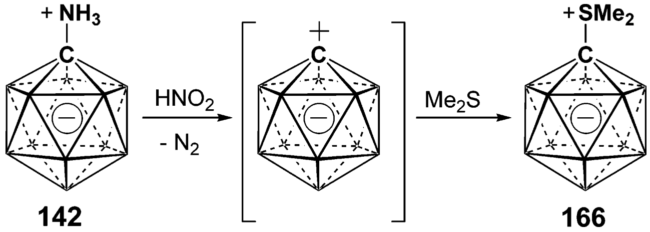


Figure 14. Aromatic substitution with the carbonium ylide generated from **63** or **157**: reactive sites in hydrocarbons.[28]

Scheme 14. Diazotization Entry in the Electrophile-Induced Nucleophilic Substitution Manifold[21]



is able to leave a carbon atom without taking with it the two electrons of the bond that held it in place, and to do so without assistance from a nucleophile. It is as if a proton left a carbon atom without assistance from a base or a silyl group left without assistance from a fluoride anion. Apparently, the assistance is provided internally by the delocalized electrons of the negative cage.

Replacement Reactions. In the presence of acetate, chloride, or hydride, the above reactions yield products in which the original carbon chain in position 1 has been replaced with an acetoxy group, chlorine, or hydrogen.[18] When Hal-CH_2CH_2-$CB_{11}(CH_3)_{11}^-$ is solvolyzed in $(CF_3)_2CHOH$ with an azide or pyridine, ethylene is lost and the expected substitution product, N_3-$CB_{11}(CH_3)_{11}^-$ (**136**), or the zwitterion, Py^+-$CB_{11}(CH_3)_{11}^-$ (**148**), is formed along with the solvent-trapping product, the ether $(CF_3)_2CHO$-$CB_{11}(CH_3)_{11}^-$ (**157**) (Scheme 13). In the absence of added nucleophiles, the ether is obtained in excellent yield, and in the presence of a trace amount of triflic acid, it can then itself serve as a source of $CB_{11}(CH_3)_{11}$. A similar result is obtained with CF_3CH_2OH as solvent,[28] and all these results fit perfectly the expectations one has for the carbonium ylide structure of the reactive intermediate $CB_{11}(CH_3)_{11}$. We shall see below that this is not always so in the case of addition reactions.

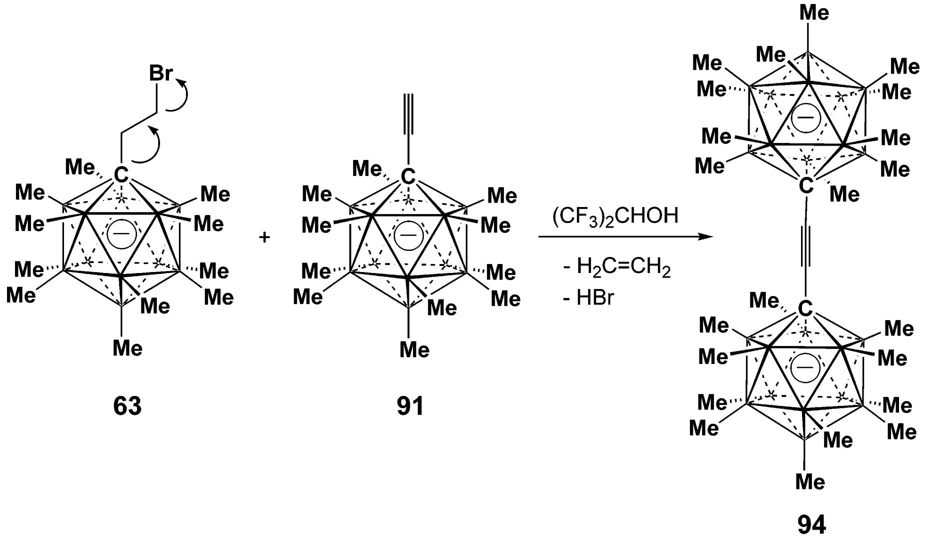
A substituent that promises useful access to the ylide intermediate even in the absence of methyl groups on the cage is the amino group, whose diazotization with nitrous acid leads to evolution of molecular nitrogen and generation of a naked vertex which is then trapped. The original observation was that treatment of the 1-amino derivative of **1** with nitrous acid in the presence of dimethyl sulfide afforded the zwitterionic 1-Me_2S derivative (**166**).[21] Addition of water resulted in formation of the 1-HO derivative (**152**),[21] and in the presence of Me_2NCHS the 1-Me_2NCHS-substituted product (**166**) was formed (Scheme 14).[170]

Addition Reactions. Double and triple bonds can also be used as traps. Thus, the 1-vinyl derivative of anion **12** yields **90** and the 1-ethynyl derivative yields **94**[19] (Scheme 15). This is as expected for the carbonium ylide structure of $CB_{11}(CH_3)_{11}$.

Addition of the naked carbon species to certain arenes proceeds with formation of 1-aryl derivatives of **12**, Ar-$CB_{11}(CH_3)_{11}^-$, and the reaction of $(CF_3)_2CHO$-$CB_{11}(CH_3)_{11}^-$ (**157**) with benzene in the presence of a small amount of triflic acid is essentially quantitative.[28] Other arenes, such as *m*-xylene and pyrene, do not react at all (Figure 14). Solvolysis of Hal-CH_2CH_2-$CB_{11}(CH_3)_{11}^-$ in the presence of a series of arenes revealed a curious reactivity pattern,[28] dominated entirely by steric effects and nearly oblivious to polar effects. Thus, in a competitive experiment, anisole and nitrobenzene showed similar reactivity. The same is true of the regioselectivity of the $CB_{11}(CH_3)_{11}$ reagent, and all monosubstituted benzenes examined, from *N*,*N*-dimethylaniline to benzonitrile, yielded comparable amounts of para and meta isomers and never any ortho isomer. The same meta/para product ratios were obtained when the solvolysis of $(CF_3)_2CHO$-$CB_{11}(CH_3)_{11}^-$ (**157**) served as the source of $CB_{11}(CH_3)_{11}$. The rule that has been deduced is that the substrate must contain at least one aromatic bond without ortho substituents, i.e., a -CHCHCHCH- subunit, and that the substitution occurs with roughly equal probability at either end of the bond to yield -CHC[$CB_{11}(CH_3)_{11}^-$]CHCH- and -CHCHC[$CB_{11}(CH_3)_{11}^-$]CH-.

This does not fit expectations for electrophilic aromatic substitution by a carbonium ylide at all. On the basis of the

Scheme 15. Electrophile-Induced Nucleophilic Addition on a Carbon Vertex[19]



reactivity pattern and deuterium isotope effects, a mechanism was proposed that involves a rate-determining 2 + 2 cycloaddition of one of the five CB edges of the $CB_{11}(CH_3)_{11}$ icosahedron across the central aromatic bond in the HCHCCHCH unit involved, followed by removal of a proton from the aromatic vertex to which the carbon of the cluster is attached and loss of the CB bond to the other aromatic vertex.[28] This type of reactivity does not follow from the standard formulation of the reactive intermediate $CB_{11}(CH_3)_{11}$ as a carbonium ylide, and one wonders whether it has one of its CB edges stretched and needs to be reformulated as a 1,2-biradicaloid analogous to benzyne. Possibly, this species can exist in two isomeric forms or it exists in only one form that can show both types of reactivity. At present, calculations are underway and the jury is still out.

8.2.3. Radical

Little is known about radical substitution on the carbon vertex. It is likely to be problematic since the free radical in position 1 can be expected to be an avid hydrogen-atom abstractor and likely to be quenched rapidly by BH bonds. Indeed, irradiation of the 1-iodo anion (**172**) with excess [1.1.1]propellane yields only a 17% yield of the insertion product and mostly the hydrogen abstraction product **1**.[20]

A reaction that is likely to proceed via free radicals is the thermal coupling of silver phenylacetylide with **172**, which proceeds in moderate yield.[25] The reaction failed for the permethylated analog **222**.

When the 1-lithio derivative of **12** obtained by lithium−halogen exchange was treated with allyl halides, a significant amount of **12** was formed along with the desired substitution product. Possibly, an electron transfer from 1-Li-$CB_{11}Me_{11}^-$ to the C-Hal takes place to produce the $^{\bullet}CB_{11}Me_{11}^-$ radical anion and an alkyl radical. The reactive radical anion then abstracts a hydrogen atom from the solvent or the alkyl radical. In the presence of allyl iodide, **12** is formed as a single product quantitatively.[164]

8.2.4. Palladium Catalyzed

Pd-catalyzed coupling of the carbon vertex to an arene carbon has met with limited success as well. Negishi coupling of the 1-ClZn-substituted anion **1** and its 12-phenyl analog (**123**) with iodoarenes afforded moderate yields of the expected 1-aryl derivatives, but an attempt to extend the reaction to the undecamethylated anion **12** failed, and all attempts to couple the 1-iodo anions **172** (11 H) and **222** (11 Me) with metalated arenes failed as well.[171] Several 1-aryl derivatives of **1** are nevertheless known. They have been prepared by including the aryl in an initial synthesis of the cluster anion, either by carbene insertion into the $B_{11}H_{14}^-$ anion[27] or by the Brellochs reaction,[26] as discussed in section 7.2. Many 1-aryl derivatives of the undecamethylated anion (**12**) have been prepared by nucleophilic substitution,[28] as discussed above.

The products obtained in radical and Pd-catalyzed coupling reactions are listed in Table 8.

Table 8. Radical and Palladium-Catalyzed Reactions on the Carbon Vertex[a]

anion	conditions
46[20]	**172**, [1.1.1]propellane, UV
93[25]	**172**, Ag^+R^-
95[171]	**1**, A, PhI

[a] A: *n*-BuLi, $ZnCl_2$, $[PdCl_2(PPh_3)_2]$; R^- = phenylacetylide.

Table 9. Summary of Substitution Reactions on the Carbon Vertex[a]

anion	conditions	anion	conditions
2[13]	**1**, A	**108**[28]	H, CF_3
17[16]	B, EtI	**109**[28]	H, CN
18[13]	B, HexBr	**110**[28]	H, CN
19[16]	B, $PhCH_2Br$	**111**[28]	H, CH_3
20[17]	C, R = H	**112**[28]	H, CH_3
21[17]	C, R = *i*-Pr	**113**[28]	H, Cl
22[17]	C, R = MeCH=CH	**114**[28]	H, Cl
23[17]	C, R = Ph	**115**[28]	H, Br
24[17]	C, R = 2-furyl	**116**[28]	H, Br
25[17]	B, propylene oxide	**117**[28]	H, I
26[18]	B, oxirane	**118**[28]	H, I
27[18]	B, $Br-(CH_2)_2-Br$	**119**[28]	H, MeO
28[18]	B, $Cl-(CH_2)_3-Cl$	**120**[28]	H, MeO
29[18]	B, $Br-(CH_2)_3-Br$	**121**[28]	H, Me_2N
30[18]	B, $Cl-(CH_2)_4-Cl$	**122**[28]	H, Me_2N
31[18]	B, $Br-(CH_2)_4-Br$	**126**[13]	B, TIPSCl
32[18]	B, $Cl-(CH_2)_5-Cl$	**127**[16]	B, Ph_3SiCl
33[18]	B, $Br-(CH_2)_5-Br$	**130**[30]	B, *i*-PrOB($C_6H_{12}O_2$)
34[18]	B, $Cl-(CH_2)_6-Cl$	**136**[28]	G, N_3
35[18]	B, $Br-(CH_2)_6-Br$	**148**[28]	G, C_5H_5N
36[18]	B, $Cl-(CH_2)_7-Cl$	**150**[c,16]	B, Ph_2PCl
37[18]	B, $Br-(CH_2)_7-Br$	**152**[21]	**142**, HNO_2, H_2O
46[20]	**172**, [1.1.1]propellane, UV	**154**[18]	G, CF_3COOAg
47[88]	B, CO_2	**155**[18]	G, HCOOH
63[18]	D, $Br-(CH_2)_2-Br$	**164**[21]	B, S
64[18]	D, $Cl-(CH_2)_3-Cl$	**166**[21]	**142**, HNO_2, Me_2S
65[18]	D, $Br-(CH_2)_3-Br$	**169**[37]	**1**, $(PhSO_2)_2NF$
66[18]	D, $Cl-(CH_2)_4-Cl$	**170**[37]	**1**, CuCl, NCS
67[18]	D, $Br-(CH_2)_4-Br$	**170**[48]	**1**, 1,2-$Cl_2C_2H_4$
68[18]	D, $Cl-(CH_2)_5-Cl$	**171**[37]	**1**, NBS
69[18]	D, $Br-(CH_2)_5-Br$	**171**[48]	**1**, 1,2-$Br_2C_2H_4$
70[18]	D, $Cl-(CH_2)_6-Cl$	**172**[37]	**1**, CuCl, NIS
71[18]	D, $Br-(CH_2)_6-Br$	**172**[37]	**1**, NIS, CuCl
72[18]	D, $Cl-(CH_2)_7-Cl$	**172**[48]	**1**, 1,2-$I_2C_2H_4$
73[18]	D, $Br-(CH_2)_7-Br$	**172**[48]	B, I_2
74[18]	E, *n* = 2	**197**[44]	**177**, A
75[18]	E, *n* = 3	**198**[44]	**178**, A
76[18]	E, *n* = 4	**200**[9]	**180**, NaOH, Me_2SO_4
77[18]	E, *n* = 5	**201**[41]	**181**, A
78[18]	E, *n* = 6	**202**[41]	**182**, A
79[18]	E, *n* = 7	**216**[13]	**212**, A
80[16]	B, CF_3I	**220**[18]	G, HCl
90[19]	**63**, **91**, $(CF_3)_2CHOH$	**381**[13]	**382**, A
93[25]	**172**, Ag^+R^- [b]	**383**[9]	**180**, NaOH, Et_2SO_4
94[19]	**63**, **74**, $(CF_3)_2CHOH$	**384**[9]	**180**, NaOH, C_4H_9X
95[26]	**1**, F, PhI	**385**[9]	**180**, NaOH, $ClCH_2X$
101[28]	G, C_6H_6	**386**[169]	B, I-$(CH_2)_2$OTBS
102[28]	G, 1,2-$Me_2C_6H_4$	**387**[169]	Por, B
103[28]	G, biphenylene	**388**[169]	Cu−Por, B
104[28]	G, naphthalene	**389**[169]	Co−Por, B
105[28]	H, NO_2	**390**[40]	J
106[28]	H, NO_2	**391**[170]	**142**, HNO_2, Me_2NCHS
107[28]	H, CF_3	**392**[9]	**180**, K

[a] A: *n*-BuLi, MeI. B: **1**, *n*-BuLi. C: **1**, *n*-BuLi, RCHO, H_2O. D: **221** or **222**, *n*-BuLi. E: **1**, *n*-BuLi, $CH_2{=}CH-(CH_2)_{n-2}-OTos$, *n* = 2−7. F: *n*-BuLi, $ZnCl_2$, $[PdCl_2(PPh_3)_2]$. G: **27**, $(CF_3)_2CHOH$. H: **27**, $(CF_3)_2CHOH$, $R-C_6H_5$, R shown in table. J: $[Cu(mesityl)]_n$, *n*-Bu_4NCl, [*n*-Bu_4N][1-H-($CB_{11}F_{11}$)]. K: *n*-BuLi, F-TEDA; **391** = 1-Me_2NCHS-$CB_{11}H_{11}$; **392** = $CB_{11}F_{12}^-$; Por = 5,10,15,20-Tetraphenylporphyrin. [b] R^- = phenylacetylide. [c] As mixture with **151**.

Table 9 contains the results of all reported substitutions on the carbon vertex of **1**.

8.3. Boron Vertex Substitution

8.3.1. Electrophilic

Substitution of a boron-bound proton with an electrophile is usually very facile, and occasionally, other kinds of substituents can be replaced as well. Alkylation and halogenation are the most common.

Deuteration. In room-temperature solution of **1** in D_2O containing a little DCl, the boron hydrogen atoms are rapidly replaced with deuterium atoms. In position 12 the process takes a few minutes and in positions 7−12 a few hours. Under these conditions, exchange in positions 2−6 was not observed.[163]

Alkylation. This reaction is usually performed with alkyl triflates in the presence of a base, commonly calcium hydride. Initially, 2,6-di-*tert*-butylpyridine was also used,[15] but an optimized version of the procedure uses only CaH_2 in sulfolane.[166] The base is needed to remove triflic acid. This byproduct reacts with the methylated anion, replacing a methyl group with the triflyloxy group in an EINS process, especially at elevated temperatures. Such interference from an EINS reaction when an electrophilic substitution is desired is relatively common but frequently can be minimized by a careful adjustment of reaction conditions.

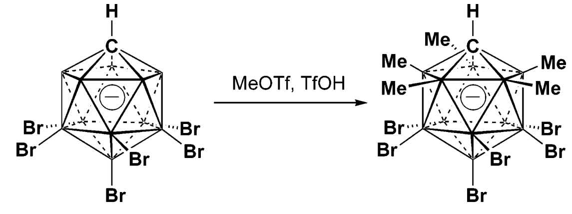
It is usually very difficult or impossible to avoid formation of complex mixtures of partially methylated derivatives unless the reaction is exhaustive and allowed to introduce the maximum number of alkyl groups possible. This is reminiscent of Friedel−Crafts alkylation of aromatics and presumably also caused by the hyperconjugative electron-donating effect of the alkyl groups, which activates the ring for further substitution.

The most common type of alkylation is methylation, which introduces 11 methyl groups into **1**, converting it into the undecamethylated anion (**12**).[13,71,172] Anions that carry a small substituent in position 1 are undecamethylated as well. Thus, **2** is converted into the dodecamethylated anion (**16**),[15] the first highly alkylated derivative of **1** described, and other alkyl and substituted alkyl derivatives[18] as well as a 1-dioxaborole derivative[30] are undecamethylated. The procedure is however limited by the extreme electrophilic reactivity of methyl triflate. It is not applicable to alkenyl-, alkynyl-, or aryl-substituted anions **1**, since the methyl triflate would methylate the double and triple bonds and aromatic rings also. For the synthesis of alkenyl[18]- and alkynyl[19]-substituted analogs, the unsaturated bond was masked and recovered after the methylation step.

Exhaustive methylation of the 1-bromo and 1-iodo derivatives of **1** yields the corresponding 1-haloundecamethyl anions **221** and **222** and offers a more direct synthetic route to the 1-alkenylated undecamethyl anions via Li/halogen exchange followed by alkylation with an alkenyl tosylate.[48] As mentioned in section 8.1, methylation of the 1-fluoro anion **169** stops after six methyl groups have been introduced into positions 7−12.[48] The 1-chloro anion (**170**) is exceptional in that it is possible to stop the reaction when the introduction of the first six methyls into positions 7−12 is complete, securing a good yield of the hexamethylated anion, and after a much longer time, the undecamethylated anion is formed in high yield.

When the substituent in position 1 is large, such as triisopropylsilyl (TIPS), positions 2−6 are sterically blocked, and it is then possible to keep them free and introduce methyl or ethyl substituents only in positions 7−12. The (7−12)-hexamethylated anion (**11**) has been subsequently pentaethylated in positions 2−6.[13]

Scheme 16. Electrophilic Substitution on Boron Vertices[46]



178 **205**

Methylation of anions that carry substituents in positions other than 1 has been investigated less but has been successful as well.[13] Even the strongly deactivated 7−12 hexahalogenated anions can be pentamethylated with methyl triflate in positions 2−6, but catalysis with triflic acid is required (Scheme 16).[13,46]

Xie et al. reported quantitative permethylation and perethylation of **1** under a different set of conditions,[22] heating to 200 °C with excess alkyl bromide in a sealed Pyrex tube for 5 days. With isopropyl bromide, a mixture of four to seven times alkylated product was obtained. In $(RO)_3PO$ solvent, the methylation or ethylation with RBr was reported to proceed at a lower temperature and faster. Use of methyl iodide caused partial halogenation of the cage. Unfortunately, these results are difficult to reproduce, and at least two laboratories failed to do so.[48,173]

Other carbon-based electrophiles have seen limited use. A reaction of the free acid of **1** with tropylium tetrafluoroborate yielded the12-substituted and 7-substituted products in a 95:5 ratio.[14] The resulting 12-substituted zwitterion **51** (“ousene”) has a large ground state dipole moment (11.25 D). Its nonlinear optical properties were mentioned in section 4.4.

A summary of results for the alkylation of boron vertices is provided in Table 10.

Table 10. Alkylation of Boron Vertices[a]

anion	synthesis	anion	synthesis
12[13]	**1**, A	**71**[18]	**35**, A
12[22]	**1**, MeBr	**72**[18]	**36**, A
16[13]	**2**, B	**73**[18]	**37**, A
16[13]	**2**, A	**124**[c,16]	**1**, *n*-BuLi, C_6F_5Br
51[14]	**1**,[b] $C_7H_7^+BF_4$	**128**[13]	**126**, A
53[22]	**1**, EtBr	**129**[13]	**126**, C
54[13]	**11**, C	**131**[30]	**130**, A
55[13]	**18**, A	**204**[46]	**177**, D
57[18]	**38**, A	**205**[46]	**178**, D
58[18]	**39**, A	**206**[46]	**179**, D
59[18]	**40**, A	**208**[13]	**196**, A
60[18]	**41**, A	**210**[13]	**176**, A
61[18]	**42**, A	**211**[13]	**209**, A
62[18]	**43**, A	**214**[13]	**194**, A
63[18]	**27**, A	**215**[13]	**211**, A
64[18]	**28**, A	**217**[13]	**199**, A
65[18]	**29**, A	**218**[48]	**169**, A, 6 h
66[18]	**30**, A	**219**[48]	**170**, A, 6 d
67[18]	**31**, A	**220**[48]	**170**, A
68[18]	**32**, A	**221**[48]	**171**, A
69[18]	**33**, A	**222**[48]	**172**, A
70[18]	**34**, A		

[a] A: MeOTf, CaH_2, sulfolane. B: MeOTf, 2,6-di-*tert*-butylpyridine, CaH_2. C: EtOTf, CaH_2, sulfolane. D: MeOTf, TfOH. [b] H_3O^+ salt. [c] Mixture with **236**.

Halogenation. Reaction of **1** and its derivatives with electrophilic halogenating agents, such as the elemental halogens themselves, follows the general reactivity patterns discussed for alkylation and is even more facile. The nature of the products does not indicate whether the reaction occurred by the electrophilic replacement of Scheme 8 or the EINS mechanism of Scheme 10, and this is generally not known. We shall list all electrophilic halogenations in this section without implying that the EINS mechanism is excluded for them.

Fluorination of **1** with elemental fluorine in liquid HF yields the undecafluorinated anion.[40] The *N*-fluoro reagent F-TEDA(1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]-octane bis(tetrafluoroborate)) showed little regioselectivity and produced mixtures of partially fluorinated anions.[53] For the preparation of partially fluorinated anions, the nucleophilic substitution with HF described below is preferable, and for a 2-fluoro anion insertion of $BF_3{\cdot}OEt_2$ into *nido*-7-$CB_{10}H_{13}^-$ has been used.[51] This was the very first fluorinated **1** to be prepared.

The fluorinated anions are generally stable to Et_3Al and aqueous acid. The 1-H-undecafluoro anion is only moderately stable to aqueous base, which gradually replaces its fluorines with hydroxy groups. Facile deprotonation of its carbon vertex and its alkylation[9,40] have been mentioned in section 8.2.1. The 1-methylundecafluoro derivative, which cannot deprotonate, is even less stable to aqueous base.

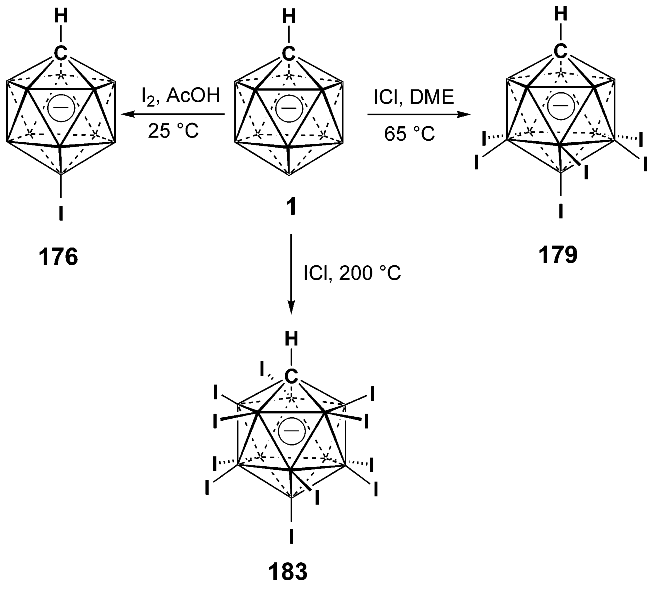
Chlorination of **1** with elemental chorine or *N*-chlorosuccinimide produces a mixture of partially (7−11 times) chlorinated anions,[45] and 12-chloro (**174**),[16] 7,12-dichloro (**248**),[16] (7,8,9,10,12)-pentachloro (**255**),[21] and (7−12)-hexachloro (**177**)[21] anions have been successfully isolated. The reactivity of the 1-methyl derivative **2** is sufficiently enhanced that its direct chlorination affords a high yield of the 1-Me undecachlorinated anion after 1 week in glacial acetic acid at 90 °C.[41,45] Methylation of the partially chlorinated mixture, followed by additional chlorination, yields the same product. Hexachlorination of **2** has also been accomplished.[44]

Exhaustive bromination with elemental bromine is difficult and under the conditions employed for chlorination produces mixtures of partially (8−10 times) brominated anions both from **1** and from **2**.[41] However, under suitable reaction conditions the 12-bromo (**175**),[16] 7,12-dibromo (**249**),[16] and (7−12)-hexabromo (**178**)[21] anions can be obtained. Use of bromine in triflic acid at 250 °C in a sealed tube for 2 days converted **2** into the 1-methylundecabrominated anion **202** as a single product in almost quantitative yield,[41] and hexabromination is possible as well.[44] Bromination of all of the boron vertices of **1** proceeded to completion in the presence of triflic acid, and under more forcing conditions its carbon vertex was brominated too.[41]

Iodination of **1** with elemental iodine takes place in position 12 and then, at higher temperature, also in position 7.[16,21] The 7,12-diiodo anion (**250**) was also formed when the 12-CF_3CO_2Hg-substituted anion (**225**) was treated with iodine.[16] The initially reported[21] conditions for the synthesis of the 12-iodo anion (**176**) have more recently been improved.[14] With ICl, the (7−12)-hexaiodo anion (**179**) is obtained[39] and under forcing conditions the (2−12)-undecaiodo anion (**183**) (Scheme 17).[41,43] Monoiodination[14,29] and hexaiodination[44] of **2** have been reported as well.

Iodination with ICl in the presence of triflic acid leads to interesting complications by providing an opportunity for a nucleophilic replacement of the iodine by chlorine. It converts **1** into the (2−12)-undecachloro anion (**181**) and **2** into a hexachloropentaiodo-substituted and even more highly chlorinated anions. Under the same reaction conditions, all iodines are exchanged for chlorines in the (2−12)-undecaiodo anion (**183**).[41]

Scheme 17. Monoiodination,[21] Hexaiodination,[39] and Undecaiodination[41] on Boron Vertices



All the halogenated anions and their 1-alkylated derivatives examined are thermally stable up to 250 °C and have good resistance to strong acids and, with the exception of highly fluorinated ones, also to bases.

Many additional substituted anions **1** have been halogenated as well. Undecasubstituted anions carrying one kind of halogen in positions 7−12 and another in positions 2−6 have been synthesized by halogenation of (7−12)-hexasubstituted anions.[87] Polymethylated anions with blocked positions 7−12 were polyiodinated in positions 2−6, and 1-triisopropylsilyl substituted **1** was iodinated in position 12 easily.[13] 1-Aryl-substituted anions are less reactive toward electrophilic halogenation. No bromination occurs on the aryl. Bromination yields first the (7,8,9,10,12)-pentabromo derivative and with more effort the (7−12)-hexabromo anion. Iodination occurs first in position 12,[29] then proceeds to the (7,8,9,10,12)-pentaiodo derivative, and finally to the (7−12)-hexaiodo anion. No halogenation in positions 2−6 was observed.[161]

The deactivated zwitterionic ammonio derivatives are much less reactive. Electrochemical chlorination in position 12 has been reported.[174] Iodination of the 1-Me_3N^+ derivative (**145**) was accomplished using iodine and $AlCl_3$.[42] Hexaiodination in positions 7−12 took place when the 1-H_3N^+ derivative (**142**) was treated with ICl in the presence of triflic acid.[43] In the absence of acid, the amino derivative was undecaiodinated successfully. The 12-iodination of 1-(4-pentylquinuclidinyl) zwitterion (**137**) required use of ICl.[31] In iodination of ammonio-substituted anions with sodium iodide and NCS in glacial acetic acid, less than 1 equiv of iodination reagent had to be used to avoid disubstitution, and mixtures of 12 and 7 substitution products were formed.[33]

Table 11 summarizes data available for the halogenation of boron vertices.

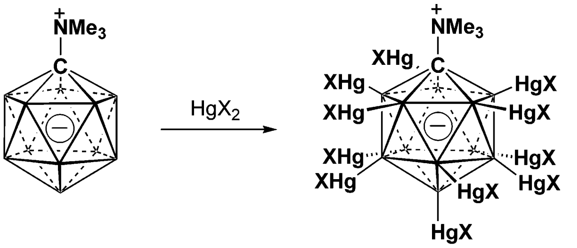
Miscellaneous. Mercuration of **1** in position 12 with $(CH_3COO)_2Hg$ or $(CF_3COO)_2Hg$ is facile. The CF_3COOHg substituent is easily removed again by heating or reduction with Zn and replaced with iodine upon treatment with I_2.[16] A doubly mercurated product has also been obtained. Under similar conditions, the less reactive 1-trimethylammonio derivative of **1** was monomercurated in

Table 11. Halogenation on Boron Vertices[a]

anion	synthesis	anion	synthesis
173[b,53]	**1**, F-TEDA	**198**[44]	**2**, Br_2, AcOH
174[16]	**1**, NCS, DMF	**199**[44]	**2**, DME, ICl
175[16]	**1**, NBS, DMF	**201**[45]	**2**, Cl_2, AcOH
175[16]	**1**, Br_2, K_2CO_3	**202**[41]	**2**, Br_2, TfOH
176[21]	**1**, I_2, KOH, H_2O[c]	**203**[41]	**2**, ICl
176[13]	**1**, I_2, AcOH	**207**[13]	**3**, ICl, DME
177[21]	**1**, AcOH, Cl_2	**212**[13]	**11**, ICl, DME
178[21]	**1**, AcOH, Br_2	**239**[b,53]	**1**, F-TEDA
179[39]	**1**, DME, ICl	**247**[b,53]	**1**, F-TEDA
180[40]	**1**, F_2/HF	**248**[16]	**1**, NCS, DMF
182[41]	**1**, Br_2, TfOH	**249**[16]	**1**, NBS, DMF
183[41]	**1**, ICl	**250**[21]	**1**, I_2, AcOH
184[41]	**1**, Br_2, TfOH	**250**[16]	**224**, I_2
185[42]	**145**, I_2, $AlCl_3$	**254**[b,53]	**1**, F-TEDA
186[31]	**137**, ICl, AcOH	**255**[21]	**1**, AcOH, Cl_2
187[43]	**142**, ICl, TfOH	**393**[b,53]	**1**, F-TEDA
188[43]	**142**, ICl	**394**[161]	**95**, Br_2, AcOH
189[87]	**177**, TfOH, Br_2	**395**[26]	**95**, Br_2, AcOH
190[87]	**177**, TfOH, I_2	**396**[161]	**95**, ICl, AcOH
192[87]	**178**, TfOH, I_2	**397**[161]	**98**, I_2, AcOH
193[87]	**179**, Br_2	**398**[41]	**2**, Br_2
194[14]	**2**, I_2, AcOH	**399**[41]	**2**, ICl, TfOH
195[29]	**95**, I_2, AcOH	**400**[45]	**1**, Cl_2, AcOH
196[13]	**126**, I_2, AcOH	**401**[13]	**207**, ICl, DME
197[44]	**2**, Cl_2, AcOH	**402**[33]	**141**, NCS, NaI
197[44]	**2**, NCS	**403**[33]	**140**, NCS, NaI

[a] **393** = 7,8,10,12-$F_4CB_{11}H_8^-$; **394** = 1-Ph-$CB_{11}H_5Br_6^-$; **395** = 1-Ph-7,8,9,10,12-$Br_5CB_{11}H_6^-$; **396** = 1-Ph-$CB_{11}H_5I_6^-$; **397** = 1-*p*-BrC_6H_4-12-I-$CB_{11}H_{10}^-$; **398** = 1-Me-$CB_{11}H_{11-x}Br_x^-$, mixtures of $x = 8-10$; **399** = 1-Me−$CB_{11}Cl_{11-x}I_x^-$, mixtures of $x = 3-5$; **400** = $CB_{11}H_{12-x}Cl_x^-$, mixtures of $x = 7-11$; **401** = 2,3,12-I_3-7,8,9,10,11-Me_5-$CB_{11}H_3^-$; **402** = 1-succinyl-12-I-$CB_{11}H_{10}^-$, mixture with 1-succinyl-7-I-$CB_{11}H_{10}^-$; **403** = 1-CH_3CONH-12-I-$CB_{11}H_{10}^-$, mixture with 1-CH_3CONH-7-I-$CB_{11}H_{10}^-$. [b] Mixture. [c] Less than 5% of **7**-isomer.

Scheme 18. Undecamercuration on Boron Vertices[50]



145 **227** X = $OCOCF_3$

position 12, but with a large excess of $Hg(CF_3COO)_2$ it was undecamercurated (Scheme 18).[50]

An unusual procedure for introduction of ethyl groups into **1** starts with its complex with the $(PPh_3)_2Rh^+$ cation.[58] When $(PPh_3)_2Rh(CB_{11}H_{12})$ is treated with an excess of ethylene, dehydrogenative borylation takes place and a mixture of $(PPh_3)_2Rh(x\text{-}C_2H_3\text{-}CB_{11}H_{11})$, x = 7, 12, is formed. Upon addition of H_2, hydrogenation takes place and $(PPh_3)_2Rh(x\text{-Et-}CB_{11}H_{11})$, a mixture of complexes of singly ethylated **1**, is produced. This can again react with ethene in another dehydrogenative borylation reaction. Running the cycle six times resulted in a single product, containing five ethyl groups on **1** in positions 4, 6, 8, 10, and 12. The regioselectivity seems to be dominated by steric effects, and further reaction is apparently prevented by steric hindrance. Starting with the analogous complex of **2**, $(PPh_3)_2Rh(1\text{-Me-}CB_{11}H_{11})$, a complex of 8,10,12-triethylated **2** was obtained. Similar results were obtained with 1-hexene, which reacted much more slowly, but few details were given.

8.3.2. Nucleophilic

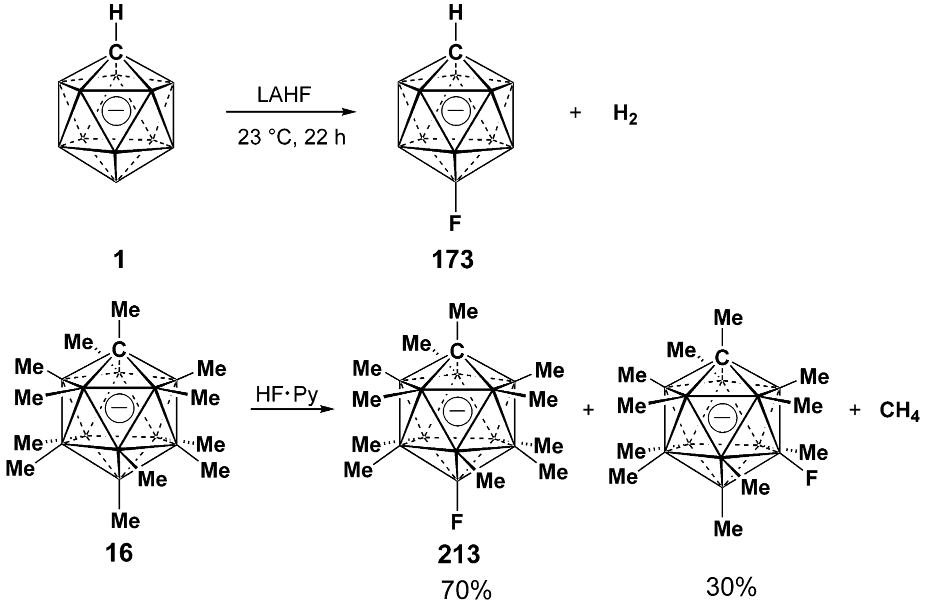
With the likely exception of some nucleophilic substitution reactions in which a strongly bound substituent such as a halogen is replaced by another, such as another halogen[41] or a hydroxyl,[9,40] nucleophilic substitution on boron occurs by the electrophile-induced nucleophilic substitution (EINS)[175,176] process in which a hydrogen or methyl group is replaced. On the one hand, it offers valuable synthetic procedures, and on the other hand, it sometimes interferes with electrophilic substitution and causes formation of mixtures. Activation of **1** with an electrophile E converts it into an electrophilic intermediate $CB_{11}H_{11}$ with a naked boron vertex that is then trapped with a nucleophile, and the process is general for many derivatives of **1**. Formally, at least, the three isomers of $CB_{11}H_{11}$ are deprotonated forms of the hypercloso cation $CB_{11}H_{12}^+$. They are isomeric with the carbonium ylide discussed in section 8.2.2 but are calculated to be much more stable. It is possible to raise similar doubts about their structure as was done for the carbonium ylide, but there is less motivation for doing so since the ylide structure now places a positive charge on boron and not on carbon and is not so disadvantaged.

The electrophilic intermediate results from abstraction by E of a cage substituent, such as H, including both electrons of its bond to the boron vertex. The order of reactivity of the vertices of **1** is the same as in ordinary electrophilic substitution, with 12 the most reactive, then 7−11, and finally 2−6. The most commonly used electrophile E is a proton. Other examples are alkylating agents, and elemental halogens may perhaps act in this fashion as well (E = Nu = Hal), but this is impossible to tell by inspection of product structures since in this case the two substitution mechanisms yield identical products. We have dealt with halogenation in section 8.3.1.

The electrophilic intermediate is normally immediately trapped with a nucleophile in a reaction that would be expected if its structure were that of a “boronium ylide”, with a positive charge on the naked boron vertex from which the ligand has been abstracted and a delocalized negative charge in the cage. This is the structure that is commonly drawn, and we use it in the present review. It is not known with certainty whether it is the actual geometrical structure of the intermediate. It is supported by DFT calculations for the three isomers of the parent $(CB_{11}H_{11})$[101,104] and the undecamethylated $(CB_{11}Me_{11})$[36] version, which optimized their structures to the expected geometries with approximate 5-fold symmetry around an axis containing the naked boron vertex. However, other low-energy minima may be present in the potential energy surface.

If one extrapolates from the properties of other deltahedral boranes,[177] it appears likely that in the absence of a nucleophile, the electrophilic intermediate dimerizes. Under the usual conditions for the EINS reaction, this process is highly unlikely since the concentration of the intermediate remains low at all times. A sterically hindered but nevertheless probably aggregated extremely reactive species $CB_{11}Me_{11}$ has however been isolated at low temperature.[36] Its structure was not established with certainty, but it gave the expected products with lone pairs of nucleophiles. Its reactions with aromatics were unusual and need to be investigated in more detail. A more detailed description of the isolated products is given in section 8.4.1, and a possible reaction mechanism is shown.

Scheme 19. Electrophile-Induced Nucleophilic Substitution on 1[38] and 16[15]



The proton is the most commonly used electrophile in EINS reactions. Thus, treatment of **1** with liquid HF at room temperature produces the 12-fluoro derivative (**173**) cleanly, and under forcing conditions polyfluorinated anions are formed, some of which have been isolated pure (Scheme 19).[38] Treatment with 80% sulfuric acid at elevated temperatures yields the 12-hydroxy anion (**159**).[34] Dimethyl sulfide can also serve as a trap for the boronium ylide, and in its presence, sulfuric acid converts the 1-phenyl anion (**95**) into a 2:1 mixture of 12- and 7-substituted dimethylsulfonium zwitterions.[161]

Methyl substituents can be replaced in strong acid as well. Reaction of **16** with anhydrous HF affords a 70:30 mixture of 12-fluoro and 7-fluoro undecamethylated anions (Scheme 19).[15]

Even replacement of iodines by chlorines in the presence of triflic acid takes place at high temperatures, and the (2−12)-undecachloro anion (**181**) is formed from the (2−12)-undecaiodo anion (**183**).[41] The mechanism of this substitution process is however unclear and could be associative instead of EINS. This is virtually certain to be the case in the replacement of fluorine with a hydroxyl in highly fluorinated anions **1** upon reaction with water.[9,40]

Electrophiles other than the proton will also induce the EINS process. Alkylating agents such as triflates, commonly used in electrophilic methylation (section 8.3.1), are best used at room temperature for the purpose, since at elevated temperatures triflyloxy derivatives are formed as vexing impurities. In the presence of dimethyl sulfate, dioxane reacts with **1** to yield a zwitterionic 12-dioxane derivative[34] in a process analogous to the above-listed reaction with dimethyl sulfide activated by sulfuric acid.[161]

In a strongly acidic medium, dimethylsulfoxide reacts with **1** and produces the zwitterionic compound 12-Me_2S-$CB_{11}H_{11}$ (**167**) as a mixture with 12-$MeSCH_2SMe$-$CB_{11}H_{11}$.[21] Under these conditions, it is not clear which acid is the activating electrophile. A cyclic sulfoxide afforded a poor yield of the 12-substituted zwitterionic product in an analogous reaction.[170]

Curiously, bare Li^+ cations induce EINS reactions, too.[30] At high temperature, anhydrous lithium salts of highly methylated derivatives of **1** react with benzene and its derivatives and their methyl groups are replaced with aryl groups with little meta/para selectivity, leading to product mixtures. This is reminiscent of the reactions of the isomeric carbonium ylide (section 8.2.2) and suggests that the boronium ylide, too, may react as a 1,2-biradicaloid. An anion carrying a dioxaborole ring on carbon was less reactive and gave a 12-substituted product and presumably methane. With a silylated aromatic, ipso substitution took place and tetramethylsilane was the byproduct (Scheme 20).

The typically undesired induction of EINS reactions by methide abstraction by other metal cations was already mentioned in section 3.2, which also described a Bürgi-Dunitz-type investigation of the reaction path for the methide transfer to a series of cations of elements of group 14.

A reaction whose mechanism could be EINS but could also involve radicals is the hydroxylation of boron vertices with hot 30% hydrogen peroxide. No explosions have been reported. Parent **1** has been converted to a moderate yield of the undecahydroxy anion (**160**) (Scheme 21),[35] which is unstable under the reaction conditions and degrades to boric acid. Similar pentahydroxylation of (7−12)-hexahalogenated anions[49] yielded anions that possessed high thermal stability in the presence of base and were stable in concentrated sulfuric acid at 100 °C for days.

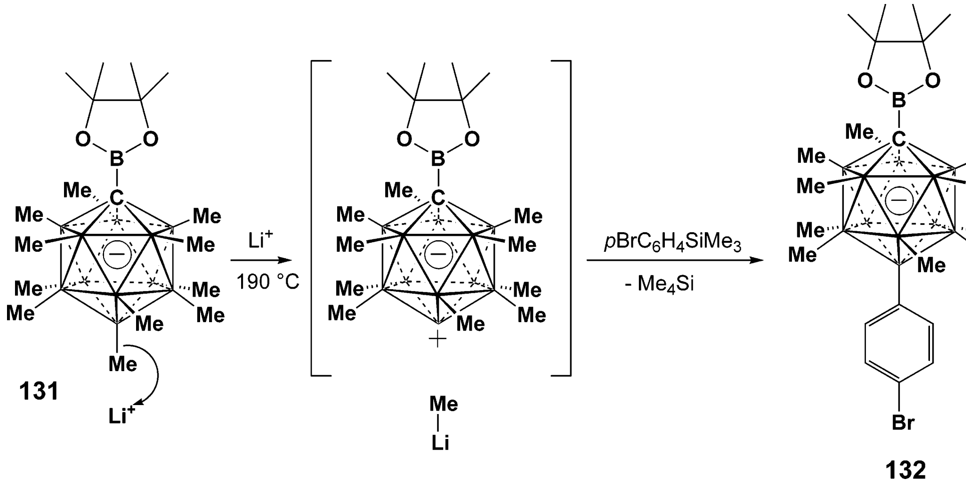
Nucleophilic substitution on boron vertices is summarized in Table 12.

Table 12. Nucleophilic Substitution on Boron Vertices[a]

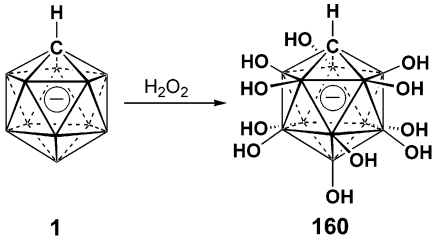
anion	synthesis	anion	synthesis
132[30]	**131**, *p*-$BrC_6H_4SiMe_3$	**191**[87]	**178**, TfOH, ICl
158[b,34]	**1**, Me_2SO_4, dioxane	**246**[38]	**1**, LAHF
159[34]	1, H_2SO_4, 175 °C, 5 h	**247**[d,38]	**1**, LAHF
160[35]	**1**, H_2O_2	**254**[38]	**1**, LAHF
167[c,21]	**1**, Me_2SO, H_2SO_4	**223**[49]	**178**, H_2O_2
173[38]	**1**, LAHF	**404**[21]	**95**, SMe_2, H_2SO_4
181[41]	**1**, ICl, TfOH	**405**[170]	**1**, A

[a] A: H_2SO_4, AcOH, *n*-C_5H_{11}-$CH(CH_2CH_2)_2SO$; **404** = 1-Ph-12-SMe_2-$CB_{11}H_{10}$ and 7-SMe_2-1-Ph-$CB_{11}H_{10}$; **405** = *n*-C_5H_{11}-$CH(CH_2CH_2)_2S$-$CB_{11}H_{11}$. [b] Side product 12-$O(CH_2CH_2)_2O$-(7−11)-$Me_5CB_{11}H_6$. [c] Mixture with **168**, 44% **167**, 23% **168**. [d] Mixture of isomers.

Scheme 20. Li^+-Induced Nucleophilic Substitution on a Boron Vertex[30]



Scheme 21. Perhydroxylation of Boron Vertices.[35]



8.3.3. Radical

We are not aware of studies in which radical substitution reactions on the boron vertices of **1** have been examined intentionally. As discussed in section 8.4, boron-based radicals may be involved in the Birch reduction of iodinated derivatives and especially, in the interfering methyl scrambling processes. Another process that possibly occurred by a radical mechanism is the attempted substitution of a bromine atom in bromopentafluorobenzene with deprotonated **1**.[16] Instead of the expected position 1, the C_6F_5 substituent entered positions 7 and 12. A plausible explanation is that electron transfer from the dianion of **1** to C_6F_5Br took place and the highly electronegative C_6F_5 radical was produced. It abstracted a hydrogen atom preferentially from the most hydridic sites on **1**, yielding a mixture of electropositive boron-based radicals in positions 7 and 12. These then performed radical aromatic substitution on C_6F_5Br, producing the observed products.

8.3.4. Palladium Catalyzed

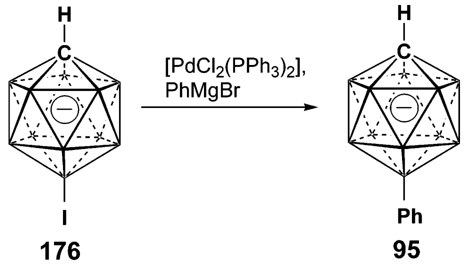
Pd-catalyzed coupling reactions have been important in the chemistry of **1** (Table 13). Following a demonstration of the feasibility of Kumada coupling between the 12-iodo derivatives of **1** and **2** and several alkyl and aryl Grignard reagents to yield 12-alkyl and 12-phenyl derivatives of **1** (Scheme 22),[14] the process has been used for the synthesis of many 12-substituted and 1,12-disubstituted anions.[161,178] In the 1-phenyl-(7−12)-hexaiodo anion, iodines in positions 7−11 can be replaced by an aryl but not the one in the sterically hindered position 12 (Figure 15).[29,178−180] The 1-amino-12-iodo-substituted anion (**185**) coupled with alkylzinc reagents in the presence of $(PPh_3)_4Pd$, but other coupling conditions failed.[170] The iodine in 8-I-2-Ph-1-Me_3N-1-$CB_{11}H_9$ (**377**) was replaced by allyl with allylmagnesium bromide in the presence of a palladium catalyst.[42]

Table 13. Pd-Catalyzed Coupling on B Vertices[a]

anion	synthesis	anion	synthesis
5[13]	**176**, A, MeMgBr	**251**[42]	**253**, B, $CH_2{=}CHCH_2MgBr$
8[13]	**194**, A, MeMgBr	**406**[161]	**396**, A, *p*-MeC_6H_4-MgBr
48[14]	**176**, A, EtMgBr	**407**[161]	**176**, A, $CH_2{=}CHCH_2MgBr$
49[14]	**176**, A, *n*-PrMgBr	**408**[178]	**397**, A, *p*-MeC_6H_4-MgBr
50[14]	**176**, A, *n*-PentMgBr	**409**[161]	**410**, A, *p*-MeC_6H_4-MgBr
123[14]	**176**, A, PhMgBr	**411**[42]	**377**, A, $CH_2{=}CHCH_2MgBr$
125[29]	**195**, A, PhMgBr	**412**[170]	**186**, RZnCl, Pd(0)

[a] A: $[PdCl_2(PPh_3)_2]$. B: $[Pd(PPh_3)_4]$; **406** = 1-Ph-12-I-7,8,9,10,11-$(MeC_6H_4)_5$-$CB_{11}H_5^-$; **407** = 1-Ph-12-(*trans*-CH=$CHCH_3$)-$CB_{11}H_{10}^-$; **408** = 1-*p*-BrC_6H_4-12-*p*-MeC_6H_4-$CB_{11}H_{10}^-$; **409** = 1-*p*-MeC_6H_4-C_6H_4-12-*p*-MeC_6H_4-$CB_{11}H_{10}^-$; **410** = 1-*p*-MeC_6H_4-12-I-$CB_{11}H_{10}^-$; **411** = 8-$CH_2{=}CHCH_2$-2-Ph-1-Me_3N-1-$CB_{11}H_9$; **412** = 12-I-1-(4-pentylquinuclidinyl)-$CB_{11}H_{10}$.

Scheme 22. Kumada Coupling on a Boron Vertex[14]



Substitution reactions on boron vertices are summarized in Table 14.

8.4. Cage Redox Processes

8.4.1. Oxidation and Reactions of Neutral Radicals

As described in section 5, one-electron oxidation of anions **1**−**16** to neutral radicals proceeds irreversibly in many cases, but for several highly substituted anions it is reversible.[13] In addition to the purely methylated radicals **9r**, **11r**, **12r**, **13r**, **15r**, and **16r**, also the 12-fluoroundecamethyl radical (**213r**) is formed reversibly[117] and is likely to be isolable. In general, it appears that a necessary condition for reversibility and presumably also for radical stability is the absence of two adjacent unsubstituted vertices in the 7−12 hemisphere. This condition need not be sufficient since **4r** and **7r** give less than perfectly reversible waves. Also, the rule has been derived for methylated radicals and need not apply to less inert substituents. The likely fate of those radicals that are insufficiently hindered is dimerization along the lines known for other deltahedral boranes,[177] but this has so far not been

Table 14. Summarized Substitution Reactions on B Vertices[a]

anion	conditions	anion	conditions	anion	conditions
5[13]	**176**, A, MeMgBr	**174**[16]	**1**, NCS, DMF	**218**[48]	**169**, B, 6 h
8[13]	**194**, A, MeMgBr	**175**[16]	**1**, NBS, DMF	**219**[48]	**170**, B, 6 d
12[13]	**1**, B	**175**[16]	**1**, Br_2, K_2CO_3	**220**[48]	**170**, B
12[22]	**1**, MeBr	**176**[g,21]	**1**, I_2, KOH, H_2O	**221**[48]	**171**, B
16[13]	**2**, C	**176**[13]	**1**, I_2, AcOH	**222**[48]	**172**, B
16[13]	**2**, B	**177**[21]	**1**, AcOH, Cl_2	**223**[49]	**178**, H_2O_2
48[14]	**176**, A, EtMgBr	**178**[21]	**1**, AcOH, Br_2	**224**[16]	**1**, $Hg(CF_3COO)_2$, MeCN
49[14]	**176**, A, *n*-PrMgBr	**179**[39]	**1**, DME, ICl	**225**[16]	**1**, $Hg(CH_3COO)_2$, MeCN
50[14]	**176**, A, *n*-PentMgBr	**180**[40]	**1**, F_2/HF	**226**[50]	**145**, $Hg(CF_3COO)_2$, MeCN
51[14]	**1**,[b] $C_7H_7^+BF_4$	**181**[41]	**1**, ICl, TfOH	**227**[50]	**145**, $Hg(CF_3COO)_2$, MeCN
53[22]	**1**, EtBr	**182**[41]	**1**, Br_2, TfOH	**239**[f,53]	**1**, F-TEDA
54[13]	**11**, D	**183**[41]	**1**, ICl	**246**[38]	**1**, LAHF
55[13]	**18**, B	**184**[41]	**1**, Br_2, TfOH	**247**[f,38]	**1**, LAHF
57[18]	**38**, B	**185**[42]	**145**, I_2, $AlCl_3$	**247**[f,53]	**1**, F-TEDA
58[18]	**39**, B	**186**[31]	**137**, ICl, AcOH	**248**[16]	**1**, NCS, DMF
59[18]	**40**, B	**187**[43]	**142**, ICl, TfOH	**249**[16]	**1**, NBS, DMF
60[18]	**41**, B	**188**[43]	**142**, ICl	**250**[21]	**1**, I_2, AcOH
61[18]	**42**, B	**189**[87]	**177**, TfOH, Br_2	**250**[16]	**224**, I_2
62[18]	**43**, B	**190**[87]	**177**, TfOH, I_2	**251**[42]	**363**, F, $CH_2{=}CHCH_2MgBr$
63[18]	**27**, B	**191**[87]	**178**, TfOH, ICl	**254**[38]	**1**, LAHF
64[18]	**28**, B	**192**[87]	**178**, TfOH, I_2	**254**[f,53]	**1**, F-TEDA
65[18]	**29**, B	**193**[87]	**179**, Br_2	**255**[21]	**1,** AcOH, Cl_2
66[18]	**30**, B	**194**[14]	**2**, I_2, AcOH	**266**[50]	**145**, $Hg(CF_3COO)_2$, MeCN
67[18]	**31**, B	**195**[29]	**95**, I_2, AcOH	**393**[f,53]	**1**, F-TEDA
68[18]	**32**, B	**196**[13]	**126**, I_2, AcOH	**394**[161]	**95**, Br_2, AcOH
69[18]	**33**, B	**197**[44]	**2**, Cl_2, AcOH	**395**[26]	**95**, Br_2, AcOH
70[18]	**34**, B	**197**[44]	**2**, NCS	**396**[161]	**95**, ICl, AcOH
71[18]	**35**, B	**198**[44]	**2**, Br_2, AcOH	**397**[161]	**98**, I_2, AcOH
72[18]	**36**, B	**199**[44]	**2**, DME, ICl	**398**[4]	**2**, Br_2
73[18]	**37**, B	**201**[45]	**2**, Cl_2, AcOH	**399**[41]	**2**, ICl, TfOH
123[14]	**176**, A, PhMgBr	**202**[41]	**2**, Br_2, TfOH	**400**[45]	**1**, Cl_2, AcOH
124[c,16]	**1**, *n*-BuLi, C_6F_5Br	**203**[41]	**2**, ICl	**401**[13]	**207**, ICl, DME
125[29]	**195**, A, PhMgBr	**204**[46]	**177**, E	**402**[33]	**141**, NCS, NaI
128[13]	**126**, B	**205**[46]	**178**, E	**403**[33]	**140**, NCS, NaI
129[13]	**126**, D	**206**[46]	**179**, E	**404**[21]	**95**, SMe_2, H_2SO_4
131[30]	**130**, B	**207**[13]	**3**, ICl, DME	**405**[170]	**1**, G
132[30]	**131**, *p*$BrC_6H_4SiMe_3$	**208**[13]	**196**, B	**406**[161]	**396**, H
158[d,34]	**1**, Me_2SO_4, dioxane	**210**[13]	**176**, B	**407**[161]	**176**, A, $CH_2{=}CHCH_2MgBr$
159[34]	**1**, H_2SO_4	**211**[13]	**209**, B	**408**[178]	**397**, H
160[35]	**1**, H_2O_2	**212**[13]	**11**, ICl, DME	**409**[161]	**410**, H
167[21]	**1**, Me_2SO, H_2SO_4[e]	**214**[13]	**194**, B	**411**[42]	**377**, A, $CH_2{=}CHCH_2MgBr$
173[38]	**1**, LAHF	**215**[13]	**211**, B	**412**[170]	**186**, RZnCl, Pd(0)
173[f,53]	**1**, F-TEDA	**217**[13]	**199**, B		

[a] A: $[PdCl_2(PPh_3)_2]$. B: MeOTf, CaH_2, sulfolane. C: MeOTf, 2,6-di-*tert*-butylpyridine, CaH_2. D: EtOTf, CaH_2, sulfolane. E: MeOTf, TfOH. F: $[Pd(PPh_3)_4]$. G: H_2SO_4, AcOH, *n*-C_5H_{11}-$CH(CH_2CH_2)_2SO$. H: $[PdCl_2(PPh_3)_2]$, *p*-MeC_6H_4MgBr. [b] H_3O^+ salt. [c] Mixture with **236**. [d] Side product 12-$O(CH_2CH_2)_2O$-(7−11)-$Me_5CB_{11}H_6$. [e] Mixture with **168**, 44% **167**, 23% **168**. [f] Mixture. [g] Less than 5% of **7**-isomer.

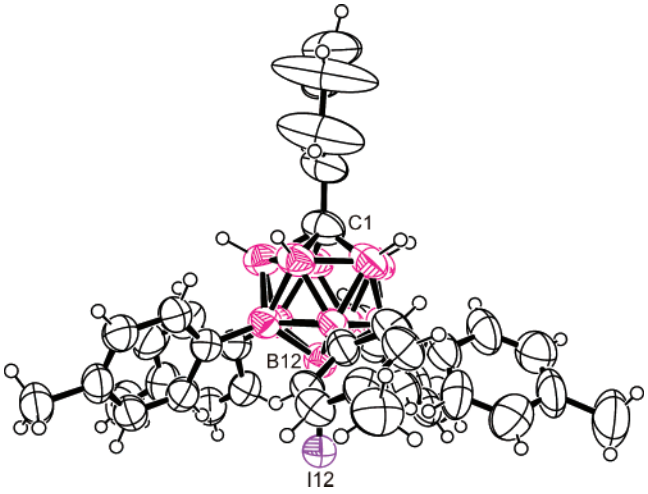


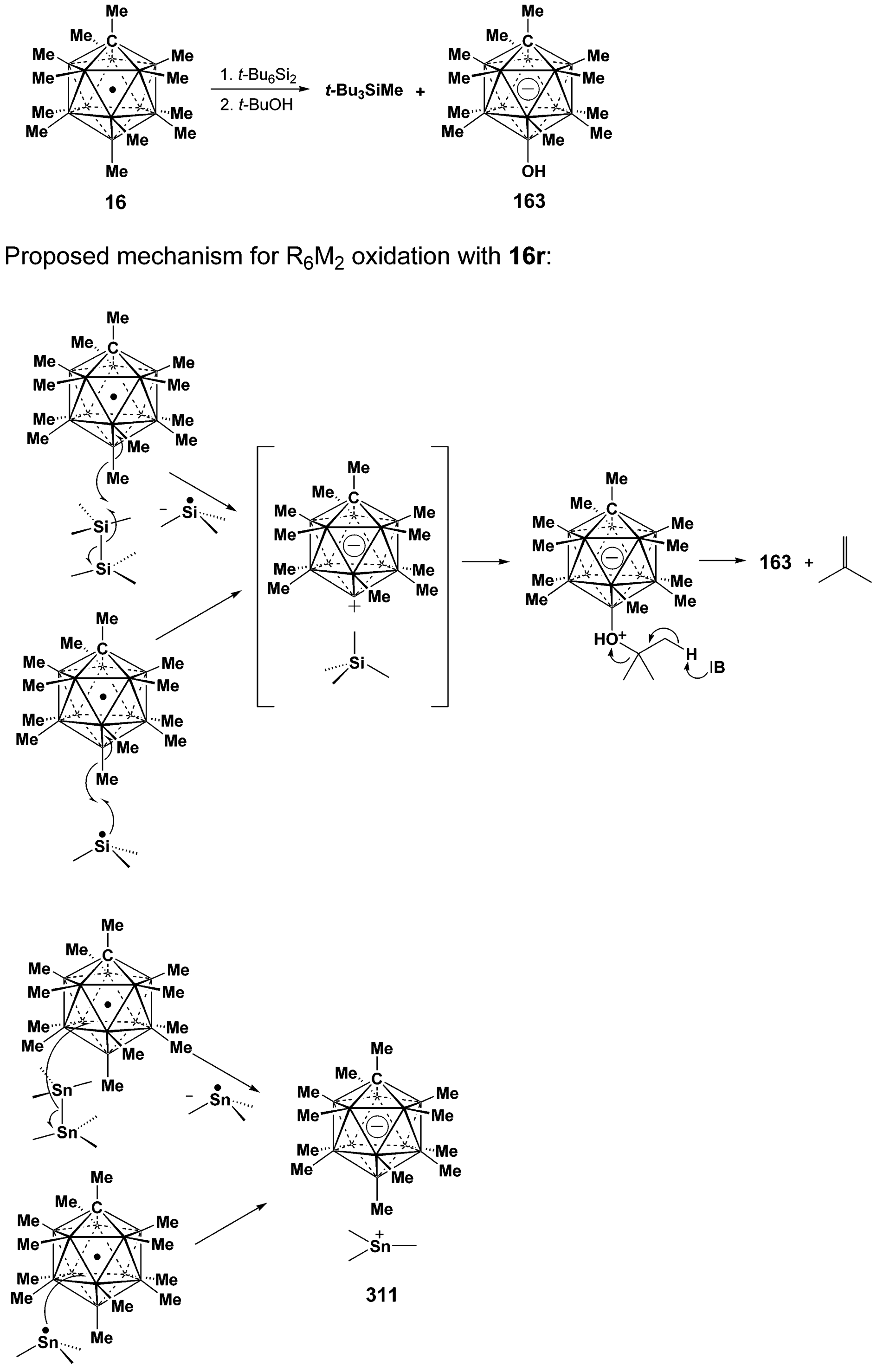
Figure 15. X-ray crystal structure of $[1\text{-Ph-}CB_{11}H_5\text{-12-I-7,8,9,10,11-}(p\text{-Tol})_5]^-$.[161] (Reprinted with permission from ref 161. Copyright 2002 Collection of Czechoslovak Chemical Communications.)

examined for **1** and its derivatives. The biradical **94r** was obtained by oxidation of **94** using PbO_2 and trifluoroacetic acid.[19] The biradical is isolable and stable at room temperature and even in air for a few hours, but prolonged exposure to the atmosphere destroys it.

Other radicals of this class have only been reported in a recent dissertation[23] but promise to have interesting properties. One-electron oxidation of 1-hexyl-$CB_{11}Me_{11}$ (**55**) gave a radical similar to **16r** but with enhanced solubility in alkanes. Solutions of the deeply colored radicals 1-H-(2−6)-F_5-$CB_{11}(CF_3)_6^{\bullet}$ (**83r**) and 1-H-(7−12)-F_6-$CB_{11}(CF_3)_5^{\bullet}$ (**81r**) were obtained by oxidation of the anions with AgF_2^+(solv) or NiF_3^+(solv) in liquid HF and extracted into perfluorohexane. Their solutions in Teflon vessels are not stable at temperatures above −60 °C, and the parent anions are regenerated. It is not clear whether the solvent or Teflon serves as the reductant. According to DFT calculations, the oxidative strength of 1-H-(2−6)-F_5-$CB_{11}(CF_3)_6$ (**83**) is nearly identical to PtF_6, probably the strongest electroneutral oxidant known. The radicals $HCB_{11}(CF_3)_{11}^{\bullet}$ (**86r**)[23] and $CB_{11}(CF_3)_{12}^{\bullet}$ (**87r**)[24] are calculated to be even stronger, but the respective anions are not oxidized with AgF_2^+(solv) and NiF_3^+(solv); besides, their unpredictably explosive nature makes work with them unpleasant.

In the present section, we address the chemistry of the only one of these radicals that has been reported in detail, the permethylated **16r**.[117] Its X-ray structure is very similar

Scheme 23. Radical-Mediated Entry into the EINS Manifold[180]



to the structure of **16** itself. It is a strong oxidant, at 1.27 V against Ag/AgNO$_3$ in acetonitrile[117] (ferrocene, 0.09 V) comparable to Ce(IV) at neutral pH, but soluble in alkanes and other nonpolar solvents. Relation of the redox potentials of other substituted anions of **1** to their structure is discussed in section 5. DFT calculations for the radicals **1r** and **16r** have been published,[102] and the optimized geometries display the expected Jahn–Teller distortion. Their computed electron affinity exceeds that of fluorine, and the methyl groups are calculated to facilitate electron detachment by 0.87 eV.

The black radical **16r** is accessible by both electrochemical and chemical (PbO$_2$/CF$_3$COOH) oxidation.[117] In the crystalline state it can be handled in air for an hour or so but is oxidized completely in a few days. Its deep blue solutions are however decolorized in a few minutes when air is bubbled through them. It oxidizes many aromatic amines and hydrocarbons to stable solutions of radical cations. Oxidation of [Fe(CO)$_2$Cp$_2$]$_2$ yielded the cation Fe(CO)$_2$Cp$^+$.

Oxidation of metal–metal and metal–carbon bonds of Ge, Sn, and Pb (Sn and Ge, R$_6$M$_2$; and Pb, R$_3$M-R) gave the salt of the metal-based cation R$_3$M$^+$ and the anion **16**,[75,76] apparently via initial formation of a cation radical, followed by dissociation of the metal–metal bond to give the R$_3$M$^+$ cation and a R$_3$M$^\bullet$ radical. The radical is then oxidized in a second step to the cation or it could dimerize. The product is an R_3M^+/**16** ion pair characterized by EXAFS in which the metal-based cation has a partly ionic and partly covalent interaction with the methyl group in position 12 of the anion, as if it were about to perform a backside S_E2 substitution on the methyl carbon (section 3.2).

When oxidation of the Si–Si bond in R_6M_2 is attempted, the reaction yields different products.[36] A methyl radical is transferred from position 12 in the radical **16r** to a silicon atom with formation of $MeSiR_3$. Trapping experiments yielded no indication that free Me_3Si^+ is formed. The other product presumably is the $R_3Si^\bullet$ radical, which then apparently abstracts a methyl group from another molecule of **16r** to give more $MeSiR_3$ (R = Me, *t*-Bu). A common rationalization of all these reactions was proposed as outlined in Scheme 23, which recognizes the different strengths of the carbon–metal and metal–metal bonds as one proceeds down a column of the periodic table. It is based on initial partial electron transfer from the metal–metal bond to **16r** and concurrent cleavage of the metal–metal bond with the departure of the $R_3M^\bullet$ radical and interaction of the other metal atom with the methyl group in position 12, in which the now positively charged metal atom attempts to perform an S_E2 substitution on the carbon of the methyl group. Since the methyl–metal interaction strength varies as $Me_3Pb^+ < Me_3Sn^+ \ll Me_3Ge^+ < Me_3Si^+$ the outcome varies as well. The Me_3Pb^+ metal cation is far from successful, Me_3Sn^+ does a little better, Me_3Ge^+ nearly succeeds, and with Me_3Si^+ the methide abstraction actually succeeds and a boronium ylide is formed directly. Hence, free Me_3Si^+ is never generated. The Me_3C^+ cation would undoubtedly succeed as well, but it cannot be prepared by oxidation of a C–C bond with **16r**. However, when it is prepared independently by reaction of the Ag^+ salt of **16** with a *tert*-butyl halide, it indeed abstracts a methyl group from **16** to yield a boronium cation, which then abstracts a chlorine atom from a chlorinated solvent (cf. section 3.2.1).

When *tert*-Bu_6Si_2 is used instead of Me_6Si_2, formation of *tert*-$BuSiMe_3$ proceeds already at −80 °C; the boronium ylide can be isolated as a solid stable up to about −60 °C and treated with nucleophiles at a later time. Reaction with ethanol or diethyl ether gives the 12-ethoxy-substituted anion (**161**) in excellent yields, methanol forms the 12-methoxy anion (**162**), and *tert*-butyl alcohol affords the 12-hydroxy anion (**163**) as the main product along with traces of the 12-*tert*-butoxy anion. The acidic medium presumably caused a loss of isobutylene. Other nucleophiles gave mixtures of alkyl-substituted anions and some anion **15** by hydride transfer. When carbon monoxide was used as a nucleophile, followed by treatment with methanol, a mixture of the 12-methoxycarbonyl and 12-methoxy anion **162** resulted, together with some **15**. In the presence of dimethylaminosulfur trifluoride, a fluorine was added to the cage, while benzene and pyridine gave $CB_{11}Me_{11}C_6H_5^-$ and $CB_{11}Me_{11}C_5NH_5^-$, respectively. However, these products were formed in mixtures, as fluorine, phenyl, and pyridyl substituents ended up not only in position 12 but also in one or even two others. This suggested that the structure of the reactive intermediate is not as simple as usually postulated for the boronium ylide and/or that rearrangements can occur during the trapping with Me_2NSF_3 and aromatics. The matter will clearly require additional investigation. An attempt to prepare a soluble form of the boronium ylide for NMR spectroscopy starting with a 1-hexyl analog of the radical **16** was not successful, and the solid-state NMR spectra obtained were not very informative. The actual structure or structures of the boronium ylide remain in doubt.

The radical 1-H-$CB_{11}Me_{11}^\bullet$ (**12r**) has been used for a one-electron oxidation of *cis*-[$PtMe_2$(*i*$Pr_3P)_2$] to the salt of *trans*-[PtMe(*i*$Pr_3P)_2]^+$ with **12** with loss of methane.[71]

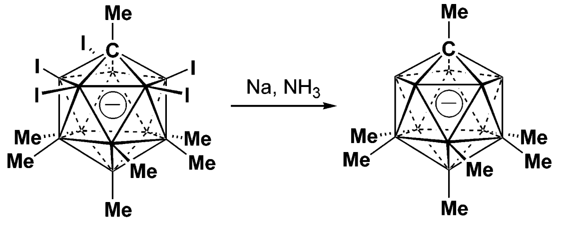
8.4.2. Reduction

Reduction of **1** and its derivatives would produce a radical or even a nido carborate but is generally difficult. However, it is possible when suitable substituents are present and can lead to cleavage of the cluster–substituent bond. It is questionable to what degree the added electron is actually delocalized into the cluster and how much it resides in the antibonding orbital of the cluster–substituent bond, but for a lack of a better location we treat these reactions here.

Reductive removal of substituents from **1** under Birch conditions has considerable synthetic importance. Removal of a trimethylammonio group is an essential step in one of the most important syntheses of **1**,[12] and it has been used elsewhere as well.[21,158]

The other substituent that is readily removed under these conditions is iodine (Scheme 24), and the process has allowed its use as a blocking group in numerous instances.[13] Under certain conditions, transfer of methyl groups between cluster cages has been noted. This complication needs to be prevented in synthetic applications, but the process in itself is intriguing and deserves to be investigated. To avoid its occurrence, it has been found best to dissolve sodium in liquid ammonia with THF as a cosolvent containing a small amount of methanol. A solution of the carborate salt in THF is then added, making sure that the blue color of the solution persists during the reaction.[13]

Scheme 24. Reductive Removal of Iodo Substitutents[13]



216 **13**

Cage redox processes are summarized in Table 15.

Table 15. Cage Redox Processes

anion	synthesis	anion	synthesis
1[12]	**145**, Na, NH_3	**15**[13]	**214**, Na, NH_3
3[13]	**206**, Na, NH_3	**12r**[71]	**12**, PbO_2, CF_3COOH
4[13]	**207**, Na, NH_3	**16r**[117]	**16**, PbO_2, CF_3COOH
6[13]	**217**, Na, NH_3	**55r**[23]	**55**, PbO_2, CF_3COOH
7[13]	**381**, Na, NH_3	**81r**[23]	**81**, K_2NiF_6, HF, BF_3
9[13]	**210**, Na, NH_3	**83r**[23]	**83**, K_2NiF_6, HF, BF_3
10[13]	**211**, Na, NH_3	**94r**[19]	**94**, PbO_2, CF_3COOH
13[13]	**216**, Na, NH_3	**213r**[117]	**213**[a,b]

[a] Mixture of 70% 12-F- and 30% 7-F-$CB_{11}Me_{11}^-$. [b] Electrochemical oxidation.

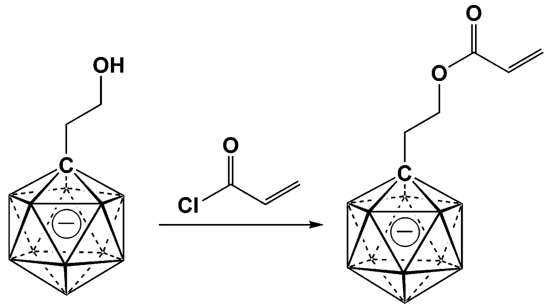
8.5. Reactions at Position α to the Cage

Reactions that take place at sites distant from the position at which the anion **1** is attached can be expected to proceed as usual and do not call for particular attention in this review. We only cover reactions that take place on atoms attached directly to one of the carborate anion vertices. These are analogous to the benzylic positions of organic chemistry and do not seem to have a simple name in the case of borane clusters. Here, we shall refer to them as positions α, with the understanding that atoms in a chain attached to cluster vertex *n* would be labeled α(*n*), *β*(*n*), *γ*(*n*), etc., proceeding outward.

We note that at times the reactivity at relatively remote sites can still be affected significantly by the carborate anion present, especially if it is a highly lipophilic polyalkylated one. Thus, it has been noted that the dehydrobromination of 1-(*ω*-bromohexyl) derivatives of **12** under standard conditions (*tert*-BuOK/*tert*-BuOH), which occurs on positions *ϵ* and *ζ*, is very much slower than that of 1-bromohexane.[18] Since the dehydrobromination proceeds well with DBU in benzene, the suspicion is that micelles form in the more polar solvent and hinder access of the base to the reaction site.

A carborate with a polymerizable chain for attachment onto a polymer matrix has been synthesized for use in ion-selective electrodes by attaching a protected alcohol to the carbon atom (see chapter C-centered subst.). The protection group was removed under standard deprotection reaction with acid and a polymerizable chain was attached by addition of acryloyl chloride (Scheme 25).[167]

Scheme 25. Substitution on a Distant Site[167]



26 **412**

For another polymerizable carborate, a permethylated carborate with an alkenyl chain was synthesized.[18] Since direct methylation of an carborate with an olefin is not possible under the established conditions, the double bond had to be masked. In a long synthesis sequence, first an *ω*-haloalkyl chain with 2−7 carbons was attached to the carbon atom and then converted to an ammonium salt with dimethylbenzylamine. After methylation of the boron vertices, the double bond was unmasked by a Hoffmann-elimination with MeLi. Since the 1-halo derivatives of **1** have become available, a shorter route can now be used.[164] During this work, it was noted that the lithium salt of the alkenyl-substituted undecamethylated carborate anions oligomerized spontaneously in air,[164] and this led to the discovery of Li$^+$-catalyzed radical polymerization of terminal alkenes discussed in section 9.2.2.

Table 16 summarizes reactions taking place on a substituent.

8.5.1. Electrophilic

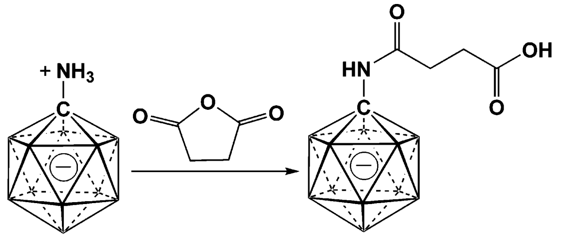
A lone pair on an atom in the α position to the cluster cage of **1** serves as a base and a nucleophile, and its strength is enhanced by the presence of the negative charge on the anion. Thus, an amino substituent on **1** is normally protonated, making the compound an electroneutral zwitterion. When the weak NH acid **142** (pK_a = ∼6) is deprotonated and the lone pair made available, it can react with electrophiles. Alkylation is performed commonly, and conversion of an ammonio to a trimethylammonio substituent on **1** was reported a long time ago.[21] Cyclization to the quinuclidine-substituted anion (**137**) was achieved by treatment with 1-bromo-3,3-bis(2-bromoethyl)octane.[31] Reaction with acetic or succinic anhydride results in formation of an amide (Scheme 26).[33]

Table 16. Reactions on a Substituent[a]

anion	synthesis	anion	synthesis
26[167]	**386**, HCl	**74**[18]	**57**, MeLi
27[18]	**26**, NBS, PPh$_3$	**74**[164]	**63**, LiTMP
38[18]	**27**, PhCH$_2$NMe$_2$	**75**[18]	**58**, MeLi
39[18]	**28**, PhCH$_2$NMe$_2$	**75**[164]	**65**, LiTMP
39[18]	**29**, PhCH$_2$NMe$_2$	**76**[18]	**59**, MeLi
40[18]	**30**, PhCH$_2$NMe$_2$	**76**[164]	**67**, LiTMP
40[18]	**31**, PhCH$_2$NMe$_2$	**77**[18]	**60**, MeLi
41[18]	**32**, PhCH$_2$NMe$_2$	**77**[164]	**69**, LiTMP
41[18]	**33**, PhCH$_2$NMe$_2$	**78**[18]	**61**, MeLi
42[18]	**34**, PhCH$_2$NMe$_2$	**78**[164]	**71**, LiTMP
42[18]	**35**, PhCH$_2$NMe$_2$	**79**[18]	**62**, MeLi
43[18]	**36**, PhCH$_2$NMe$_2$	**79**[164]	**73**, LiTMP
43[18]	**37**, PhCH$_2$NMe$_2$	**413**[167]	**26**, A

[a] A: Acryloyl chloride; **413** = $H_2C{=}CHC(O){-}O{-}(CH_2)_2{-}CB_{11}H_{11}^-$.

Scheme 26. Electrophilic Substitution in α(1) Position[33]



142 **141**

Methylation of a sulfur lone pair in 1-methylthio-substituted **1** has also been reported.[21] This type or reaction probably also occurred when the 1-phenyl-12-S$^+$Me$_2$ derivative of **1** was refluxed in THF to produce a compound in which one of the methyl groups on the sulfur atom was replaced with the residue -(CH)$_4$OH, clearly originating in the solvent. One can guess that the original sulfonium salt probably first methylated one of the nucleophiles present, perhaps a BH vertex or even a solvent oxygen, and the sulfur lone pair then performed an S$_N$2 substitution on the α carbon atom of a solvent molecule.[161]

An oxidative demethylation of **144** was observed in a reaction with iodine under basic conditions. In the presence of formaldehyde, the 1-hydroxymethylene derivative (**146**) was isolated, which then was hydrolyzed with acid to give **143** (Scheme 27).[32]

Reactions involving electrophilic substitution on a substituent are collected in Table 17.

8.5.2. Nucleophilic

An electrophilic center in the α position to the cluster cage of **1** is activated by the same factor that makes the vertex acidic, and this is neatly exemplified by the ease with which a TIPS substituent is removed from the carbon vertex 1. Whereas it is removed by warm water from the relatively acidic parent **1**, removal of TIPS from the much less acidic vertex 1 of polymethylated derivatives required heating with CsF at 270 °C or heating to 75 °C with wet TBAF in DMF (Scheme 28).[13]

Scheme 27. Oxidative Demethylation[32]

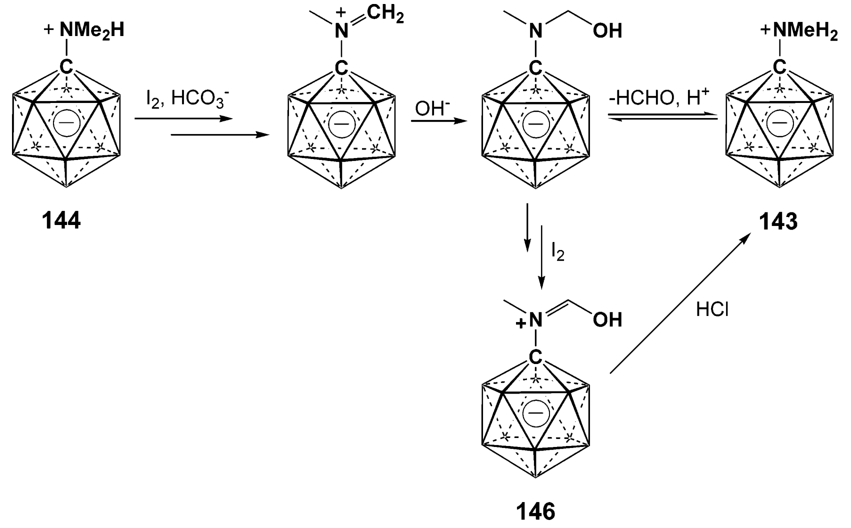


Table 17. Electrophilic Substitution on a Substitutent[a]

anion	synthesis	anion	synthesis
133[21]	**142**, pK_a 6.0	**141**[33]	**142**, C
134[21]	**143**, pK_a 6.5	**143**[32]	**144**, I_2
135[21]	**144**, pK_a 5.7	**145**[21]	**144**, Me_2SO_4
137[31]	**142**, A	**414**[21]	**404**, THF
140[33]	**142**, B		

[a] A: 1-Bromo-3,3-bis(2-bromoethyl)octane, K_2CO_3/18-crown-6, MeCN. B: Acetic anhydride, MeCN. C: Succinic anhydride, MeCN. D: Acryloyl chloride; **414** = 12-SMe$(CH_2)_4$OH-1-Ph-$CB_{11}H_{10}$.

Scheme 28. Nucleophilic Substitution in α(1) Position[13]

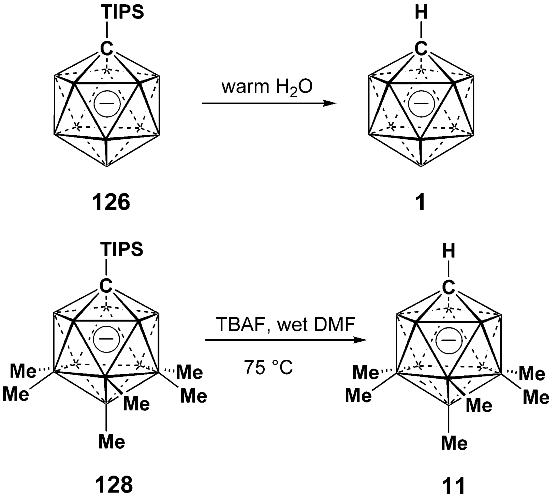


Table 18. Nucleophilic Substitution on a Cage Substituent.

anion	synthesis
1[13]	**126**, H_2O
11[13]	**128**, CsF
52[13]	**129**, CsF
207[13]	**208**, TBAF

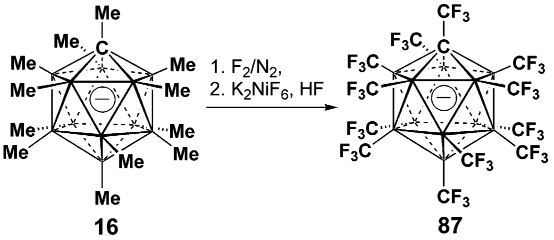
Nucleophilic substitution reactions on a substituent are collected in Table 18.

8.5.3. Radical

Radical halogenation might be expected to replace the hydrogen atoms in methyl substituents on **1**, but only results for fluorination have been published so far. Perfluorination converts methyl into trifluoromethyl groups and thus converts electron-donor into electron-acceptor substituents. This has been of interest in connection with efforts to make **16** into a more weakly nucleophilic anion and **16r** into a stronger oxidant.

The $CB_{11}(CF_3)_{12}^-$ anion (**87**) has been synthesized starting with **16**[24] and fulfilled its promise as a weakly coordinating anion that is hard to oxidize, but it is treacherously explosive. The synthesis was performed in two steps. Fluorination of **16** with 10% F_2/N_2 in the presence of silica as HF scavenger produced a mixture of anions containing 8−18 CF_3 groups, and full fluorination was achieved subsequently with K_2NiF_6/HF in 25% overall yield (Scheme 29). The latter reagent cannot be used in the first step because of the sensitivity of **16** to acid-induced loss of methyl groups. The perfluorinated anion is thermally stable at least to 250 °C and destroyed with Na in NH_3 but not with strong acids or bases. Unfortunately, its salts are shock-sensitive and unpredictably explosive. The products of the explosive decomposition are primarily BF_3 and soot. The driving force is the much higher energy of the BF bond (154 kcal/mol) compared with the CF bond (115 kcal/mol). A likely additional factor is steric crowding of the 12 CF_3 groups on the icosahedron. DFT calculations provided a value of 2358 kcal/mol for the heat of combustion of **87** and a heat of explosion of 1385 kcal/mol, which is more per gram than for TNT. The calculated crowding energy in this anion is 144 kcal/mol, comparable with the strain energy in cubane.

Scheme 29. Radical Substitution in α Positions[24]



A recent dissertation[23] described the synthesis of the less crowded 1-H-(2−6)-F_5-$CB_{11}(CF_3)_6^-$ (**83**) and 1-H-$CB_{11}(CF_3)_{11}^-$ (**86**) anions by first partial fluorination of the methylated anions 1-H-$CB_{11}H_5Me_6^-$ (**11**) and 1-H-$CB_{11}Me_{11}^-$ (**12**), respectively, followed by F_2 in anhydrous HF at 200 psi. The anion 1-H-(2−6)-$(CF_3)_5$-$CB_{11}F_6^-$

Table 19. Radical Halogenation on a Substituent[a]

anion	synthesis
81[23]	**206**, B
82[23]	1. **210** A; 2. B
83[23]	1. **11**, A; 2. B
86[23]	1. **12**, A; 2. B
87[24]	1. **16**, A; 2. K_2NiF_6, HF

[a] A: F_2/N_2. B: F_2, HF, 200 psi.

Table 20. Summarized Reactions on a Substitutent[a]

anion	synthesis	anion	synthesis
11[13]	**128**, CsF	**77**[164]	**69**, LiTMP
26[167]	**386**, HCl	**78**[18]	**61**, MeLi
27[18]	**26**, NBS, PPh_3	**78**[164]	**71**, LiTMP
38[18]	**27**, $PhCH_2NMe_2$	**79**[18]	**62**, MeLi
39[18]	**28**, $PhCH_2NMe_2$	**79**[164]	**73**, LiTMP
39[18]	**29**, $PhCH_2NMe_2$	**81**[23]	**206**, B
40[18]	**30**, $PhCH_2NMe_2$	**82**[23]	1. **210**, A; 2. B
40[18]	**31**, $PhCH_2NMe_2$	**83**[23]	1. **11**, A; 2. B
41[18]	**32**, $PhCH_2NMe_2$	**86**[23]	1. **12**, A; 2. B
41[18]	**33**, $PhCH_2NMe_2$	**87**[24]	1. **1**, A; 2. C
42[18]	**34**, $PhCH_2NMe_2$	**133**[21]	**142**, pK_a 6.0
42[18]	**35**, $PhCH_2NMe_2$	**134**[21]	**143**, pK_a 6.5
43[18]	**36**, $PhCH_2NMe_2$	**135**[21]	**144**, pK_a 5.7
43[18]	**37**, $PhCH_2NMe_2$	**137**[31]	**142**, D
52[13]	**129**, CsF	**140**[33]	**142**, E
74[18]	**57**, MeLi	**141**[33]	**142**, F
74[164]	**63**, LiTMP	**143**[21]	**144**, I_2
75[164]	**65**, LiTMP	**145**[21]	**144**, Me_2SO_4
75[18]	**58**, MeLi	**207**[13]	**208**, TBAF
76[18]	**59**, MeLi	**413**[167]	**26**, H
76[164]	**67**, LiTMP	**414**[21]	**404**, THF
77[18]	**60**, MeLi		

[a] A: F_2/N_2. B: F_2, HF, 200 psi. C: K_2NiF_6, HF. D: 1-Bromo-3,3-bis(2-bromoethyl)octane, K_2CO_3/18-crown-6, MeCN. E: acetic anhydride, MeCN. F: succinic anhydride, MeCN. H: acryloyl chloride.

(**81**) was prepared by fluorination of 1-H-(2−6)-Me_5-$CB_{11}I_6^-$ (**206**) at 200 psi with F_2 in HF. The iodine substituents were replaced by fluorines under the reaction conditions. The 1-H-12-F-$CB_{11}(CF_3)_{10}^-$ anion (**82**) was prepared from either 1-H-12-F-$CB_{11}Me_{10}^-$ or 1-H-12-I-$CB_{11}Me_{10}^-$ (**210**) under the high-pressure fluorination conditions. Salts of the anions with only five or six CF_3 groups are still flammable, but all attempts to cause them to explode failed. They may therefore represent practical candidates for inert anions.

Radical halogenation reactions on a substituent are collected in Table 19, and Table 20 provides an overall summary.

8.6. Multistep Synthesis: 15 Symmetrically Methylated CB_{11} Anions

The degree of complexity that the synthetic chemistry of **1** and its derivatives has reached recently is illustrated in Scheme 30, which shows the synthetic paths employed in the synthesis of all 15 of its symmetrically methylated derivatives,[13] combining many of the reactions that have been discussed in section 8.

9. Applications

9.1. As Weakly Coordinating Anions

There is considerable need for weakly coordinating anions for numerous applications. Perhaps the most appreciated is the need for inert counterions in the preparation of extremely reactive cations, especially stronger Brønsted acids, stronger oxidants, and cationic catalysts.

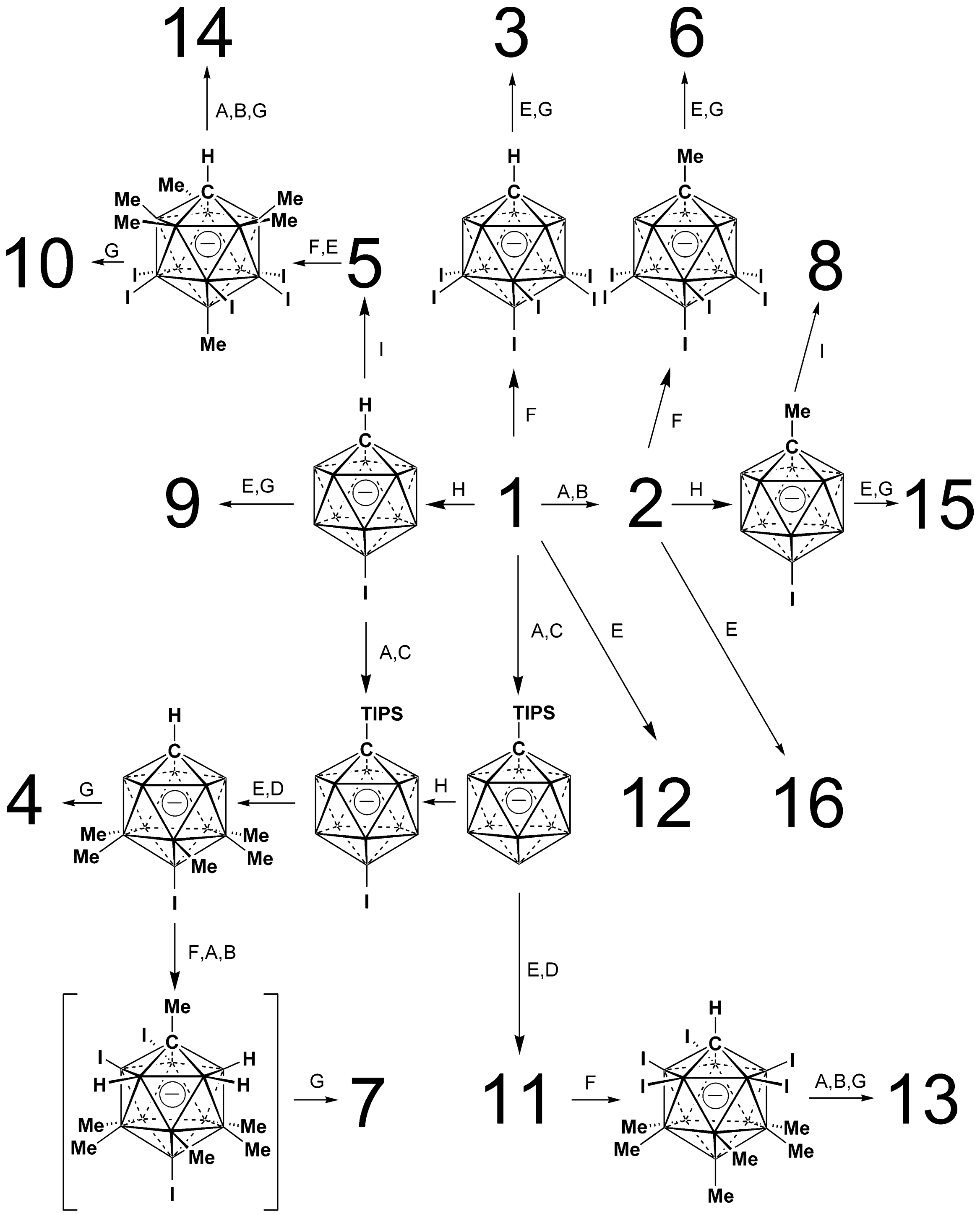
Weakly coordinating anions[5,7−9] are bulky anions with a low overall charge, preferably −1, highly delocalized over the entire anion. At best weakly basic sites, low nucleophilicity, and stability are additional important criteria. The anion **1** is only weakly coordinating and fulfils most of the requirements, but as we saw in section 3.2, its hydridic hydrogens coordinate quite readily, especially those in positions 7−12. Their hydridic nature poses an even more serious limitation in that many cationic electrophiles are able to abstract a hydride anion (section 8.3.2). For instance, the trityl salt cannot be prepared.

A remedy[5] is to replace the offending hydrogens, particularly those in positions 7−12, with substituents that offer no basic sites but resist abstraction. The first choice was the halogens, which however carry lone pairs, and these are weakly basic and nucleophilic. Their basicity is a function of the choice of the halogen, with fluorine being the obvious champion,[8,9] and of the residue to which the halogen is attached. If there is no residue and the halogen atom is in the form of the halide anion, it is actually quite nucleophilic, whereas on a group such as methyl, it is only weakly nucleophilic. In this respect, halogens in positions 7−12 of **1** are intermediate, and one might be concerned about their suitability. We have already seen in section 3.2 that polyhalogenated derivatives of anion **1** coordinate with some reactive cations, such as silylium and aluminum, but below we shall briefly mention many cases in which they have been used very successfully to stabilize others.

Thus, an optimal solution has not yet been found, and perhaps use of **180**[40] or anions with mixed fluoro and trifluoromethyl substitution[23] will be the answer. They have not seen much use so far because they are best prepared only with elemental fluorine, which few laboratories are equipped for. Replacement of hydrogens with methyl groups, which looked promising because their ionization potential is high and they have no lone pairs, did not provide the answer, since the methide anion is just as prone to abstraction as hydride.[36] Instead of providing a superior weakly coordinating anion, work with **16** provided information on the course of the methide abstraction reaction.[36,75] It also yielded another benefit, in that such highly alkylated anions turned out to be extremely lipophilic, and we address this issue in section 9.2. Mixed halogenated and methylated carborate anions have also been synthesized[46] and combine the advantages of both substituents. The halogens provide the needed inertness, and the methyl groups increase solubility in nonpolar solvents. Use of persubstitution with trifluoromethyl groups was thwarted by the explosive nature of this otherwise perfect anion.[24]

We next briefly mention the numerous instances in which derivatives of **1** have been used successfully as weakly coordinating anions. One of the most striking advances that they made possible is the generation and isolation of extremely strong yet extremely stable new superacids. A large number of these compounds of the general structure of $[H(\text{solvent})_x][1\text{-R-}CB_{11}X_5Y_6]$ (R = H, Me; X = Me, Cl, Br, I; Y = Cl, Br, I) have been developed in the laboratory of Reed.[181] The new superacids are crystalline and have been used for the delivery of protons to organic solvents and isolation of reactive cations (fullerenes, protonated arenes, carbocations). They have excellent thermal stabilities (to over 150 °C).

Scheme 30. Preparation of the 15 Symmetrically Methylated Anions 2−16[13] [a]



[a] A: *n*-BuLi; B: MeI; C: TIPS-Cl; D: F^-; E: MeOTf; F: ICl; G: Na; H: I_2; I: MeMgBr/[Pd].

A reaction of the new superacid $H(CB_{11}H_6X_6)$ (X = Cl, Br) with C_{60} yielded $[HC_{60}^+][CB_{11}H_6Cl_6^-]$, and protonated arenes were prepared, which themselves are crystalline superacids.[182] The arenium salts consist mostly of discrete cations and anions, but some interaction of the acidic proton of the arene with the bromines of the carborate is present. Salts of alkyl cations (Me, Et, *i*-Pr) with the $(HCB_{11}Me_5Br_6)$ anion (**205**) are covalent and contain bromonium ions, but they are immensely strong alkylating agents,[46,90] stronger than alkyl triflates. Methylation of benzene produced the toluenium ion. The new methylating agent can abstract a hydride from hydrocarbons to form methane and a carbocation, such as the *tert*-butyl cation.[91] A stable vinyl cation has also been isolated.[183]

Synthesis of the radical cations $C_{60}^{\bullet+}$ and $C_{76}^{\bullet+}$ required a strong enough weakly nucleophilic oxidant, and triarylaminium radical cations have been found satisfactory.[184] The counterion was again $CB_{11}H_6Br_6^-$ (**178**). Similarly, with the radical cation of hexabromo(phenyl)carbazole and $[Ag(CB_{11}H_6Cl_6^-)_2]$ as the counterion the dimer $(C_{59}N)_2$ was oxidized to the $C_{59}N^+$ cation.[185,186]

The weakly coordinating carborate anions seemed to be promising for the synthesis of a free silylium ion,[187] and many different combinations of substituents on the anion and cation have been tried. Reactions $[Ph_3C^+][CB_{11}H_6X_6]$ with R_3SiH ($X = Cl, Br, I$; $R = Et$, *tert*-Bu, *i*-Pr, *tert*-Bu_2Me) led to $R_3Si(CB_{11}H_6X_6)$ with different degrees of silylium ion character. The first isolated free silylium ion was $[Mes_3Si][HCB_{11}Me_5Br_6]$.[187] Other unusual silicon species have been isolated, such as a protonated silanol, *tert*-$Bu_3Si(OH_2)^+$, and a linear $[R_3Si\text{-}H\text{-}SiR_3]^+$ cation.[187]

9.2. As Solubilizing Anions

The permethylated anion **16** is amazingly lipophilic and solubilizes many cations in weakly polar or nonpolar solvents that they normally avoid. Anions carrying longer alkyl chains are even more effective in this regard. The solubility is useful in various applications, e.g., in electrochemistry and for use of iodonium salts as photoacid generators.

9.2.1. Large Cations and Ion Exchange Membranes

In a study of "extended viologens" with up to 10 positive charges, **16** was by far the best out of 8 different anions tried when it came to solubility in moderately polar solvents such as ethers.[188]

Iodonium salts of **178** are good photoacid generators for catalyzing cationic polymerizations of epoxy silicones.[80]

The dodecamethylated carborate **16** has been used as an lipophilic additive to polyaniline membranes to suppress their pH sensitivity.[189] Probably due to its water solubility, the carborate slowly leaches from the membrane. In another study, the use of **1** did not give promising results due to leaching into the aqueous phase,[190] and with **178** leaching was observed after 2 h. The undecabrominated carborate anion **182** showed less leaching than the normally used tetraphenylborate.[191] In another examination of undecahalogenated carborate anions,[94] the undecaiodinated carborate anion $HCB_{11}I_{11}^-$ (**183**) formed the weakest ion pairs and was superior to the other carborates.

In an effort to prepare a cation exchanger covalently attached to the polymeric backbone, a derivative of **1** with a polymerizable group has been synthesized and copolymerized with acrylates.[167] This polymer with a grafted carborate proved to be a suitable cation exchanger, and the carborate is a useful replacement of the common tetraphenylborate derivatives.

The hexabromocarborate anion (**178**) was used as anionic additive in Ag^+ ion-selective electrodes and outperformed the commonly used tetrakis(4-chlorophenyl)borate, reducing Hg^{2+} interference by 6 orders of magnitude.[192]

9.2.2. Metal Cations

The lithium salt of **16** can be used as a supporting electrolyte for cyclic voltammetry in benzene.[193] It has a wide potential window, limited by oxidation of $CB_{11}Me_{12}^-$ (**16**) at $+$ 0.7 V and reduction of Li^+ at -2.0 V. The electrical conductivity of the solution of Li^+**16** depends strongly on the water content, and water is apparently needed to break up ion pairs.

There has been considerable interest in using weakly coordinating anions in catalytic active complexes. They could have the ability to move to the side, allowing the substrate to coordinate to the metal but still remaining available for stabilization of the active intermediate. Carborate-containing silver catalysts with phosphine ligands showed high activity as catalysts for hetero-Diels–Alder reactions,[59] and a similar complex with an *N*-carbene ligand was used for the same purpose.[60] Zirconium-based catalysts were used for olefin polymerization,[66] and a Zr-metallacycle catalyzed the conversion of alkynes and alkenes to ketones.[69] Rhodium catalyst found application in the conversion of arylboronic acids to aldehydes[129] and in the hydrogenation of olefins.[64] An iridium complex with **178** as counterion has been used in the room temperature and pressure hydrogenation of internal alkenes.[82] Even sterically hindered alkenes were hydrogenated in very good yields. An aluminum carborate showed high efficiency as a catalyst for the polymerization of cyclohexene oxide.[78]

The lithium cation is well known as catalyst for pericyclic reactions, and the solution of the lithium salt of **16** in benzene is a much more effective catalyst than the usual solution of lithium perchlorate in diethyl ether.[194] The presence of a trace amount of water is necessary for the catalytic activity, and it is apparently needed to break up ion pairs. However, if the amount of water is excessive the activity is reduced, presumably due to hydration of the Li^+ cation.

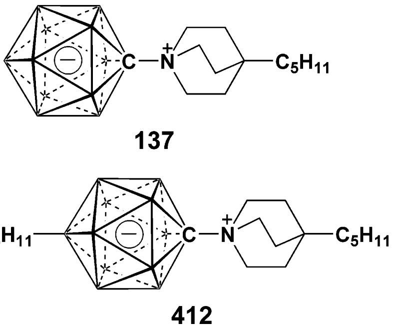
A possibly practically important application of Li^+**16** is catalysis of radical polymerization of alkenes, alkadienes, and alkynes at ambient pressure.[195] When an alkenyl chain is attached to the carbon atom of an otherwise permethylated carborate, the Li^+ salt acts as its own catalyst.[164]

9.2.3. Miscellaneous

A number of alkali metal cyclotriveratrylene (CTV) complexes that included carborate anions have been prepared.[196] The bowl-shaped CTV acts as ligand for alkali metals and forms two-dimensional networks. These networks stack together through $\pi-\pi$ interactions, and the carborate anion occupies the hydrophobic methyl-lined cavities.

The parent carborate **1** was used in $[M\subset[2.2.2]\text{cryptate}][CB_{11}H_{12}]\ [Ni(TMTAA)]_3$ ($M = K^+, Na^+$), another host–guest assembly.[197]

Carborate anions have been used in the synthesis of new liquid crystals with high-temperature mesophases due to the presence of strong molecular dipole moments (Figure 16).[31,170] Carborate-containing mesogens show a preference for formation of nematic phases and can be used to suppress smectic phases in mixtures.



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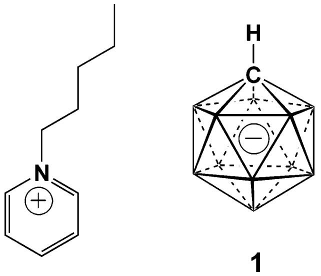
412

Figure 16. Liquid crystal derivatives of **1**.[31]

Ionic liquids are salts that are liquid at or near room temperature. In the development of new types of ionic liquids, carborates can serve as counterions.[198] The carborates used were C-alkylated anions $1\text{-}RCB_{11}H_{11}^-$ ($R = H$, Me, Et, Pr, Bu) and B-halogenated anions, $CB_{11}H_6X_6^-$ ($X = Cl$, Br). When the C(1) vertex is not alkylated, the melting point is higher. Substitution on the boron cage does not significantly influence the melting points. The pyridinium salt of the parent $[N\text{-pentylpyridinium}]^+$**1** has a melting point of 19 °C (Figure 17). The ionic liquid has been used as a solvent



1

Figure 17. Ionic liquid based on **1**.[199]

for Pd-catalyzed dehalogenation reactions. Debromination was complete after less than 10 h, and dechlorination in the ionic liquid was more regiospecific (o:m:p = 95:4:1) than in THF (40:40:10).[199] A picolinium ionic liquid, [*N*-pentyl-4-picolinium]$^+$**1**, with a melting point of 16 °C was used as a solvent for acetonylation reactions, and enhanced yields and higher regioselectivity were observed.[200]

There have also been attempts to develop medical applications of **1**. In boron neutron capture therapy (BNCT) for cancer, **1** combines the advantages of $B_{12}H_{12}^{2-}$ and $C_2B_{10}H_{12}$. It is water soluble and also can undergo substitution reactions on the carbon atom. Only the complicated synthesis presently hinders its practical use.[201] Substituted radioiodinated *closo*-CB_{11} derivatives of **1** showed a faster blood clearance time than the nido derivatives.[33] Substitution and radioiodination occur fast on derivatives of **1**, and a radioiodinated succinylated aminocarborate showed promise for use as a pendent group for the radioiodination of biomolecules. Carboranylporphyrines are highly potent compounds for human malignant cells and their sublines.[169] The Cu complex is toxic to many malignant cells in low concentration, kills human tumor cells resistant to apoptotic stimuli, but is inert for nonmalignant human skin fibroplasts, and only at higher concentration is it toxic to fibroplasts (Figure 18).

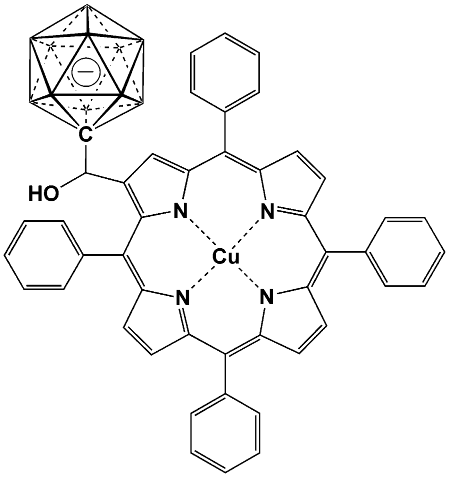


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Figure 18. Copper porphyrin derivative of **1**.[169]

A theoretical approach to the use of carborates in medicine has been reported, too. Interaction of carborates with biomolecules by formation of dihydrogen bonds has been calculated.[202] With the calculations in mind, this may result in explaining specific inhibition of proteases by carborates and in the more distant future allow the design of new carborate-containing drugs. Calculations showed that the largest stabilization was obtained from interaction of the carborate with ARG and GLY-SER.

10. Acknowledgments

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11. Supporting Information

Tables of NMR shifts. This material is available free of charge via the Internet at http://pubs.acs.org.

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