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Optimizing the Least Nucleophilic Anion. A New, Strong Methyl⁺ Reagent

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The ideal weakly coordinating counterion for reactive cations would be the least nucleophilic, least basic, most inert anion available. It should also be inexpensive, have useful spectroscopic handles, and confer good solubility and crystallizing properties on its salts. Triflate anion, CF_3SO_3^- , has served chemistry well in this regard but larger size, absence of lone pairs, and extreme chemical inertness have recently made carboranes¹ or fluorinated tetraphenylborates the preferred choice for many applications.² These anions have led to the solution of the silylium ion problem,³ enhanced Lewis acid catalysis by Li^+ ion,⁴⁻⁶ new “strong-but-gentle” superacids,⁷ commercially viable olefin polymerization catalysts,⁸ new possibilities for electrolytes^{9,10} and ionic liquids,¹¹ and the isolation of new reactive cations such as $\text{C}_{60}^{+\bullet}$,⁷ Bu_3Sn^+ ,¹² $\text{Cu}(\text{CO})_4^+$,¹³ etc.

The perfluorinated tetraphenylborate anion is the preferred choice for price and solubility reasons but its salts frequently form liquid clathrates and fail to crystallize. The boron–phenyl bond is rather easily cleaved by strong Brønsted¹⁴ or Lewis¹⁵ acids. Halogenated carborane anions are much more inert than tetraphenylborates, their salts crystallize well, but they are more expensive and their salts less soluble. Permethylation of the icosahedral $\text{CB}_{11}\text{H}_{12}^-$ carborane to give $\text{CB}_{11}\text{Me}_{12}^-$ increases solubility dramatically, but at the cost of inertness.¹⁶ Trifluoromethyl groups can lead to explosive decomposition.¹⁷ We now show that mixed halogen and methyl substituents provide the golden mean. These new anions, 1-H- $\text{CB}_{11}\text{H}_5\text{X}_6^-$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) (Figure 1), meet all current benchmarks of inertness and, in addition to optimized handling characteristics, allow the preparation of a methylating agent stronger than methyl triflate.

By analogy to benzene, which is stabilized by π aromaticity and whose C–H bonds are subject to electrophilic substitution, carboranes are stabilized by σ aromaticity and their B–H bonds are susceptible to electrophilic substitution. Polarity of the CB_{11} cage directs halogenation of the icosahedral parent carborane, 1-H- $\text{CB}_{11}\text{H}_{11}^-$, first to the 12-position (antipodal to carbon) and then to the 7–11 positions of the “lower” pentagonal belt.^{18,19} Treatment of the 7,8,9,10,11,12-hexahalo derivatives, 1-H- $\text{CB}_{11}\text{H}_5\text{X}_6^-$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), with methyl triflate under conditions of elevated temperature and triflic acid catalysis¹⁶ leads cleanly to 2–5 pentamethylation (>80% yields).²⁰ The unique C–H bond is untouched by these conditions. The resulting anions, 1-H- $\text{CB}_{11}\text{Me}_5\text{X}_6^-$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) (Figure 1), have been characterized as cesium and tetramethylammonium salts.²⁰ All three Cs^+ salts have totally ordered crystal structures.²¹

Compared to their nonmethylated counterparts, salts of the pentamethylated anions have a number of advantages. Lower water solubility makes Ag^+ and alkali metal cation metathesis reactions more straightforward. Increased solubility in organic solvents and the presence of a sharp 15-proton NMR signal from the methyl groups at ~ 0 ppm, located conveniently upfield of most aliphatic resonances, allows rapid and accurate determination of cation/anion

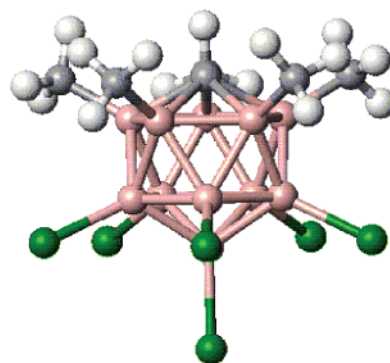


Figure 1. The 1-H-2,3,4,5,6-pentamethyl-7,8,9,10,11,12-hexahalo- CB_{11} carborane anions, 1-H- $\text{CB}_{11}\text{Me}_5\text{X}_6^-$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), used in this work.

Table 1. Selected ^{29}Si Chemical Shifts (ppm) for $i\text{-Pr}_3\text{SiY}$

compd	^{29}Si	conditions
$i\text{-Pr}_3\text{Si}(1\text{-H-CB}_{11}\text{H}_5\text{Br}_6)$	100	C_6D_6
$i\text{-Pr}_3\text{Si}(1\text{-H-CB}_{11}\text{H}_5\text{Cl}_6)$	103	C_6D_6
$i\text{-Pr}_3\text{Si}(\text{F}_{20}\text{-BPh}_4)^a$	108	solid state
$i\text{-Pr}_3\text{Si}(1\text{-H-CB}_{11}\text{H}_5\text{Br}_6)$	110	solid state
$i\text{-Pr}_3\text{Si}(1\text{-H-CB}_{11}\text{Me}_5\text{Br}_6)$	112	C_6D_6
$i\text{-Pr}_3\text{Si}(1\text{-H-CB}_{11}\text{Me}_5\text{Cl}_6)$	113	C_6D_6
$i\text{-Pr}_3\text{Si}(1\text{-H-CB}_{11}\text{Cl}_{11})^b$	114	d_8 -toluene
$i\text{-Pr}_3\text{Si}(1\text{-H-CB}_{11}\text{H}_5\text{Cl}_6)$	115	solid state
$i\text{-Pr}_3\text{Si}(1\text{-H-CB}_{11}\text{Br}_5\text{Cl}_6)^b$	116	solid state
$i\text{-Pr}_3\text{Si}(1\text{-Me-CB}_{11}\text{F}_{11})^c$	120	d_8 -toluene

^a Lambert, J. B.; Zhang, S. *J. Chem. Soc., Chem. Commun.* **1993**, 383.
^b Reference 23. ^c Ivanov, S. V.; Rockwell, J. J.; Polyakov, A. G.; Gaudinski, C. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. *J. Am. Chem. Soc.* **1998**, *120*, 4224.

ratios via ^1H NMR spectroscopy. Without methylation, lower solubility, quadrupole-broadened B–H resonances, and a single indistinct C–H resonance render the hexahalo carborane salts less amenable to NMR characterization. Illustrative of these points is the characterization of the silylium species, $i\text{-Pr}_3\text{Si}(\text{HCB}_{11}\text{Me}_5\text{Br}_6)$,²⁰ whose solubility in toluene (>20 mM) is more than an order of magnitude higher than the most soluble of the unmethylated analogues, $i\text{-Pr}_3\text{Si}(\text{HCB}_{11}\text{H}_5\text{Cl}_6)$,²² enabling collection of the ^{29}Si NMR spectrum in minutes.

In gaining these improved physical characteristics, none of the important chemical properties are lost. In terms of Lewis basicity, the pentamethylated anions are well placed in the group of least coordinating anions by the criterion of downfield ^{29}Si NMR shift¹ in silylium ion-like species ($i\text{-Pr}_3\text{Si}^{\delta+}(\text{Y}^{\delta-})$). As shown in Table 1, the ^{29}Si shifts of $i\text{-Pr}_3\text{Si}(1\text{-H-CB}_{11}\text{Me}_5\text{X}_6)$ are similar to those of their nonmethylated counterparts. One might have expected alkylation to inductively increase electron density on the CB_{11} cage, making the halide substituents more basic. However, this is not the case, mirroring the small effects seen with undecahalogenation.²³ Increased substitution may help screen access of cations to the

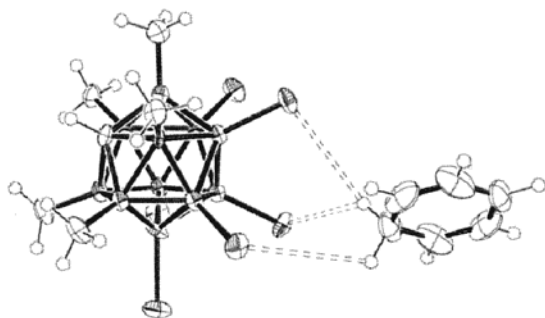


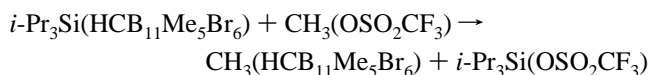
Figure 2. Perspective view of the cation and anion in the X-ray structure of $[\text{C}_6\text{H}_7][\text{HCB}_{11}\text{Me}_5\text{Br}_6]$. Thermal ellipsoids are at the 50% level. Dashed lines indicate weak H-bonding interactions (3.0–3.2 Å) of the acidic protons of the benzenium cation.

negative charge, which is largely confined to the CB_{11} framework by σ delocalization.

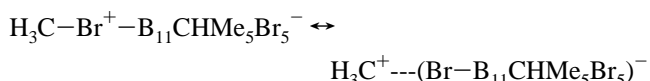
Stability toward strong Lewis acidity is echoed in corresponding inertness toward Brønsted acidity. As monitored by ^{11}B NMR, $\text{Cs}(\text{HCB}_{11}\text{Me}_5\text{Br}_6)$ is stable to boiling sulfuric acid/ethanol for >3 days and stable to neat triflic acid at room temperature indefinitely. More importantly, the conjugate acid $\text{H}(\text{HCB}_{11}\text{Me}_5\text{Br}_6)$ can be prepared.²⁰ Like its nonmethylated counterpart,⁷ it expresses superacidity greater than that of triflic acid. This is illustrated by the ready protonation of benzene and the isolation of single crystals of $[\text{C}_6\text{H}_7^+][\text{HCB}_{11}\text{Me}_5\text{Br}_6^-]$ for X-ray structure determination (see Figure 2).²⁰ Although the usefulness of C–C bond length data in the cation is limited by disorder, formulation is proven and we note that the anion shows none of the disorder commonly observed with dodecasubstituted carboranes. This salt is stable to >150 °C. Conferring this measure of stability on an arenium ion, where traditional anions such as SbF_6^- fail to stabilize them much above dry ice temperatures, illustrates the powerful effect of choosing a carborane as counterion.¹⁴

Oxidative stability is also noted. Whereas the dodecamethylated carborane is susceptible to oxidation at potentials greater than 1.2 V (vs Fc/Fc^+),²⁴ the pentamethyl hexahalo carboranes show no detectable CV redox processes within the operational window of dry dichloromethane (± 2.0 V vs Fc/Fc^+). This redox inertness makes them potentially useful alternatives to nonmethylated carboranes in stabilizing highly oxidized cations such as $\text{C}_{60}^{+\bullet}$.⁷

An additional bonus from optimizing the substituents on carborane anions is that they can be used to stabilize (and activate) the very reagents used to prepare them. Thus, while carbocations attack B–H bonds, replacement with B–Me and B–X bonds renders the anions inert to carbon electrophiles. For example, a “methyl⁺” reagent that is stronger than methyl triflate can be prepared by treatment of $i\text{-Pr}_3\text{Si}(\text{HCB}_{11}\text{Me}_5\text{Br}_6)$ with methyl triflate:²⁰



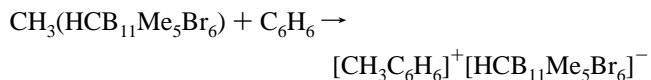
By structural analogy to $\text{R}_3\text{Si}(\text{HCB}_{11}\text{H}_5\text{X}_6)$, where the $\text{Si}^{\delta+}$ center is bonded to a halogen substituent at the 7 position of the carborane,²² the $\text{CH}_3^{\delta+}$ group is presumably bonded to a bromine substituent. $\text{CH}_3(\text{HCB}_{11}\text{Me}_5\text{Br}_6)$ can be formulated as a Zwitterionic bromonium ion:



Analysis by ^{13}C CPMAS NMR in a sample prepared from ^{13}C -enriched methyl triflate corroborates this formulation. The ^{13}C

resonance of the $\text{CH}_3^{\delta+}$ group appears downfield at 36.5 ppm, very similar to that in $[(\text{CH}_3)_2\text{Br}][\text{SbF}_6]$ (37.5 ppm).²⁵

The enhanced electrophilic methylating activity of $\text{CH}_3(\text{HCB}_{11}\text{Me}_5\text{Br}_6)$ relative to methyl triflate is illustrated by the stoichiometric conversion of benzene to protonated toluene:



This occurs at room temperature without catalysis by added acid. In contrast, methyl triflate shows insignificant reaction under the same conditions. The toluenium ion salt has been isolated and characterized with $^{13}\text{CH}_3$ group labeling.²⁰ This illustrates how reactive cations, previously viewed as intermediates (Wheland), can be “put in a bottle” and used as reagents when carboranes are used as counterions.

The present anions, $1\text{-H-CB}_{11}\text{Me}_5\text{X}_6^-$, come as close as any to the concept of a universal weakly coordinating anion. At or well above room temperature, they support superacidity, the potent Lewis acidity of the silylium ion and carbocations, and are anodically stable out to +2.0 V vs Fc/Fc^+ . They have convenient spectroscopic handles, they confer excellent solubility and crystallizing properties on their salts, and with the report of a new synthesis of the $\text{CB}_{11}\text{H}_{12}^-$ starting material that promises to decrease price significantly,²⁶ they should soon become much more accessible.

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Supporting Information Available: Synthetic, characterization, and X-ray structure details (pdf); crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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