A New Weakly Coordinating Anion: Approaching the Silylium (Silicenium) Ion

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closo-6,7,8,9,10-Br₅-CB₉H₅⁻ is a new, chemically robust, soluble, weakly coordinating anion; it has been used to develop more cationic character in a trialkyl silicon moiety than has been conclusively demonstrated to date.

The quest for the least coordinating anion has recently led to an exploration of fluorinated tetraarylborates,¹,² polyoxometallates,³ teflates⁴ and carboranes.⁵ Exceptional chemical stability, large size and lack of lone pairs are the features that have made the 12-vertex closo-carborane CB₁₂H₁₂⁻ very useful in this regard. Derivatization via electrophilic substitution makes it even larger and more chemically inert.⁶ We now find that bromination of the 10-vertex closo-carborane CB₉H₁₀⁻ produces a new anion of exceptional inertness, low nucleophilicity and unusual solubility characteristics.

Treatment of Cs[CB₉H₁₀] with an excess of Br₂ in acetic acid leads to regiospecific 6,7,8,9,10-pentabromination in high yield [¹¹B{¹H} (CD₃CN) δ 21.9 (B10), -11.8 (B(2-5) + B(6-9))]. Metathesis with Ag(NO₃) gives the halide abstraction reagent Ag(Br₅-CB₉H₅). Treatment of this silver salt with Ph₃CBr in acetonitrile gives the useful hydride abstraction reagent [Ph₃C][Br₅-CB₉H₅], both in good isolated yield.

The definitive characterization of the long sought-after silylium ion (R₃Si⁺) is one of the major extant synthetic challenges requiring an extremely weakly coordinating anion.
In condensed media, the problem is one of thwarting coordination of both solvent and anion. Recent studies with perchlorate as counterion\(^7\)\(^8\) are best interpreted in terms of coordination of both solvent and anion. Recent studies with problems.

Treatment of stoichiometric amounts of the orange trityl salt of \(\text{Br}_{5}\)-carborane with \(\text{Pri}_{3}\text{SiH}\) in dry acetonitrile leads in 15 min to quantitative formation of \(\text{Ph}_{3}\text{CH}\) (1H NMR \(\delta 5.6\)) and solvent-coordinated salt \(\text{[Pri}_{3}\text{Si-(MeCN)}\text{]}^{+} \text{[Br}_{5}\text{-carborane}}\) with \(\text{Pri}\) substituents. The structure was solved by direct methods. Monoclinic \(\text{P2}_1/n\) (No. 14) with \(a = 12.876(12)\), \(b = 14.111(9)\), \(c = 8.580(4)\) \(\text{Å}\), \(\alpha = 90.76(5)\), \(\beta = 92.91(6)\), \(\gamma = 115.73(5)\)\(^\circ\), \(V = 1397\) \(\text{Å}^3\) for \(Z = 2\). Final factor \(R = 0.5\%\) for 1213 non-zero reflections with \(I > 3\sigma(I)\).

Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>(\delta (\text{SiMe}_{3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{[Pri}<em>{3}\text{Si-(MeCN)}\text{]}^{+} \text{[Br}</em>{5}\text{-carborane}})</td>
<td>(\text{[Ph}<em>{3}\text{C]}^{+} \text{[Br}</em>{5}\text{-carborane}})</td>
<td>97.9</td>
</tr>
<tr>
<td>(\text{[Pri}_{3}\text{Si-(MeCN)}\text{]}^{+} \text{[B(\text{CF}<em>3)</em>{2}]})</td>
<td>(\text{[Ph}_{3}\text{C]}^{+} \text{[B(\text{CF}<em>3)</em>{2}]})</td>
<td>55.8</td>
</tr>
<tr>
<td>(\text{[Pri}<em>{3}\text{Si-(MeCN)}\text{]}^{+} \text{[B}</em>{4}\text{Br}_{10}^{+}})</td>
<td>(\text{[Ph}<em>{3}\text{C]}^{+} \text{[B}</em>{4}\text{Br}_{10}^{+}})</td>
<td>45.4</td>
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<tr>
<td>(\text{[Pri}<em>{3}\text{Si-(MeCN)}\text{]}^{+} \text{[Br}</em>{5}\text{-carborane}})</td>
<td>(\text{[Ph}<em>{3}\text{C]}^{+} \text{[Br}</em>{5}\text{-carborane}})</td>
<td>37.2</td>
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<tr>
<td>(\text{[Pri}_{3}\text{Si-(MeCN)}\text{]}^{+} \text{[B(\text{CF}<em>3)</em>{2}]})</td>
<td>(\text{[Ph}_{3}\text{C]}^{+} \text{[B(\text{CF}<em>3)</em>{2}]})</td>
<td>33.6</td>
</tr>
<tr>
<td>(\text{[Pri}<em>{3}\text{Si-(MeCN)}\text{]}^{+} \text{[B}</em>{4}\text{Br}_{10}^{+}})</td>
<td>(\text{[Ph}<em>{3}\text{C]}^{+} \text{[B}</em>{4}\text{Br}_{10}^{+}})</td>
<td>12.1</td>
</tr>
</tbody>
</table>

\(\text{[Pri}_{3}\text{Si-(MeCN)}\text{]}^{+} \text{[Br}_{5}\text{-carborane}}\) has also been characterized by X-ray crystallography (see Fig. 2).\(^4\) As expected from the reasonable toluene solubility, the carborane anion is directly bonded to silicon \(\text{via}\) a bromine atom. The average \(\text{C-Si-C}\) angle is 95.8 (2.0\(^\circ\)) and out-of-plane displacement (0.40 \(\text{Å}\)) reflects trigonality at silicon but these parameters are surprisingly insensitive to the nature of the coordinated naphthyl. The average \(\text{C-Si-C}\) angle in each structure is statistically indistinguishable at current resolution and only a couple of degrees different from \(\text{Ph}_{3}\text{Si(OCIO}_{3})_{3}\) (113.5(2)\(^\circ\)).\(^9\) Nevertheless, partial ionicity in the coordinated \(\text{Br}_{5}\)-carborane- \(\text{Si}^{+}\) structure is indicated by several features. The \(\text{Si-Br}\) distance is ca. 0.2 \(\text{Å}\) longer than a typical \(\text{Si-Br}\) bond (2.24 \(\text{Å}\) in \(\text{Me}_{3}\text{SiBr}\)).\(^16\) The coordinated \(\text{Br}_{5}\)-carborane \(\text{[Br}_{5}\text{-carborane}}\) (2.00(4) \(\text{Å}\)) shows no detectable extension relative to the others in the carborane anion (1.97(4)-2.05(4); average 2.00(4) \(\text{Å}\)). The 1\(\text{B}\) NMR is not reliably distinguishable from that of the free ion down to the solubility limit in toluene (~40 \(\text{°C}\)) suggesting intramolecular spinning of the coordinated anion \(\text{via}\) the four equivalent bromine substituents. This

\(\text{[Pri}_{3}\text{Si-(MeCN)}\text{]}^{+} \text{[Br}_{5}\text{-carborane}}\)

is formed by intermolecular interactions (see Fig. 2).

The structure was solved by direct methods. Monoclinic \(\text{P2}_1/n\) (No. 14) with \(a = 16.657(25)\), \(b = 14.235(8)\), \(c = 11.485(18)\) \(\text{Å}\), \(\beta = 110.80(11)\)\(^\circ\), \(V = 2562(5)\) \(\text{Å}^3\) for \(Z = 4\). \(R = 7.98\%\) for 1269 reflections with \(I > 3\sigma(I)\).

Atomic coordinates, bond lengths and angles, and thermal parameters for both compounds have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.
contrasts with silyl perchlorates where $^{35}$Cl NMR indicates asymmetry of bound oxygen.\(^1\) The present situation is closer to ionic-like species such as $[\text{Th(C}_5\text{Me}_5)_2(\text{Me})][\text{B(C}_6\text{F}_5)_4]$ where $^{19}$F resonances are insensitive to fluorine coordination.\(^1\) Indeed, $\text{Pri}_3\text{Si}[\text{B(C}_6\text{F}_5)_4]$, prepared by treatment of $\text{Pri}_3\text{SiH}$ with $[\text{Ph}_3\text{C}][\text{B(C}_6\text{F}_5)_4]$ in toluene behaves in a very similar manner to $\text{Pri}_3\text{Si}(\text{Br}_5\text{-C}_9\text{H}_5)_2$. The $^{29}$Si resonance of $\text{Pri}_3\text{Si}(\text{Br}_5\text{-C}_9\text{H}_5)_2$ is $\delta$ 97.9, the most downfield yet observed for a tri-isopropyl-substituted silicon species in toluene solvent. However, it is still $>100$ ppm upfield of that expected for a \textit{bona fide} three-coordinate cation. By comparison to more covalent species in Table 1, the $^{29}$Si NMR data indicate that $\text{Pri}_3\text{Si}(\text{Br}_5\text{-C}_9\text{H}_5)_2$ has about one third silylium ion character. This is the closest approach to date and suggests that $\text{Br}_5\text{-C}_9\text{H}_5^-$ is presently the least coordinating anion for cationic silicon. Its inertness to bromide extraction by the strongly electrophilic silicon centre is notable and suggests applications with other coordinatively unsaturated cations.

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References