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

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closo-6,7,8,9,10-Br_5-$CB_9H_5^-$ 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] teflates[4] and carboranes.[5] Exceptional chemical stability, large size and lack of lone pairs are the features that have made the 12-vertex *closo*-carborane $CB_{11}H_{12}^-$ 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 $CB_9H_{10}^-$ produces a new anion of exceptional inertness, low nucleophilicity and unusual solubility characteristics.

Treatment of Cs[CB_9H_{10}] with an excess of Br_2 in acetic acid leads to regiospecific 6,7,8,9,10-pentabromination in high yield [$^{11}B\{^1H\}$ (CD_3CN) δ 21.9 (B10), −11.8 {B(2–5) + B(6–9)}]. Metathesis with Ag(NO_3) gives the halide abstraction reagent Ag(Br_5-CB_9H_5). Treatment of this silver salt with Ph_3CBr in acetonitrile gives the useful hydride abstraction reagent [Ph_3C][Br_5-CB_9H_5], both in good isolated yield.

The definitive characterization of the long sought-after silylium ion (R_3Si^+) is one of the major extant synthetic challenges requiring an extremely weakly coordinating anion.

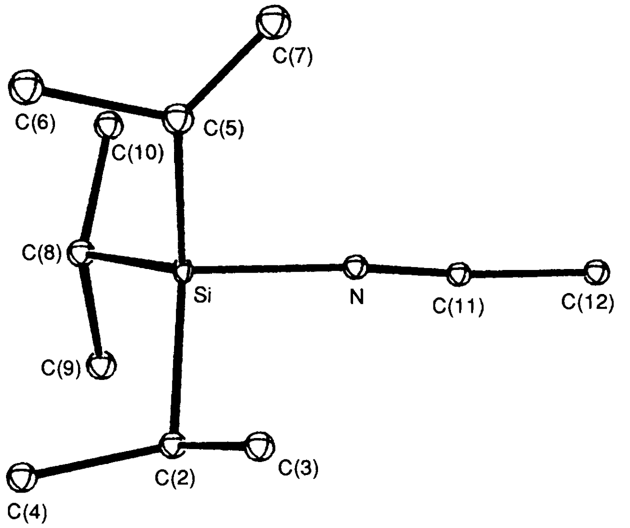

Fig. 1 A perspective view of the cation in $[\mathrm{Pr^{i}{}_{3}Si(MeCN)}]^{+}[\mathrm{Br_{5}\text{-}CB_{9}H_{5}}]^{-}$. Bond angles (°): C(2)–Si–C(5) 118.7(13), C(2)–Si–C(8) 112.9(12), C(5)–Si–C(8) 115.1(13), Si–N(1)–C(11) 175.2(23).

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 anion[9,10] *versus* solvent competition (diethyl ether,[11] acetonitrile, sulfolane) in four-coordinate species, eqn. (1). The

$$\mathrm{R_{3}Si(OClO_{3})} + \mathrm{Solvent} \rightleftharpoons \mathrm{R_{3}Si(Solv)^{+}} + \mathrm{ClO_{4}^{-}} \quad (1)$$

absence of three-coordinate silicon is indicated by the lack of significant downfield-shifted ^{29}Si NMR resonances.[12,13] Very recent work with the less coordinating anion tetrakis{3,5-bis(trifluoromethyl)phenyl}borate (TFPB) and the less nucleophilic solvent dichloromethane has revealed new problems.[11] Attempted formation of $[\mathrm{R_{3}Si}]$[TFPB] leads to fluoride abstraction from the anion and chloride abstraction from the solvent. We find that the new weakly coordinating anion $\mathrm{Br_{5}\text{-}CB_{9}H_{5}^{-}}$ is not only chemically stable to $\mathrm{R_{3}Si^{+}}$ formation conditions but also allows reactions to be carried out in an inert hydrocarbon solvent.

Treatment of stoichiometric amounts of the orange trityl salt of $\mathrm{Br_{5}\text{-}CB_{9}H_{5}^{-}}$ with $\mathrm{Pr^{i}{}_{3}SiH}$ in dry acetonitrile leads in 15 min to quantitative formation of $\mathrm{Ph_{3}CH}$ (^{1}H NMR δ 5.6) and the isolable, pale-yellow, solvent-coordinated salt $[\mathrm{Pr^{i}{}_{3}Si(MeCN)}][\mathrm{Br_{5}\text{-}CB_{9}H_{5}}]$. Single crystal X-ray analysis† reveals four-coordinate silicon with considerable trigonality (see Fig. 1). The Si atom is 0.41 Å out of the trigonal plane of the three bonded carbon atoms, about one third of the way from tetrahedral (0.64 Å) to trigonal planar. The average C–Si–C angle is 115.6(1.7)°, about halfway between tetrahedral and trigonal planar. By comparison to typical Si–N bond lengths (1.70–1.76 Å),[14] the Si–N distance of 1.82(2) Å might be considered long. However, it is short compared to 1.86 Å to pyridine in $[\mathrm{Me_{3}Si(pyridine)}]$I.[15] Together with Kira *et al.*'s recent results on silyloxonium ions[11] (diethyl ether-coordinated silicon cations) the stability of $[\mathrm{R_{3}Si(Solvent)}]^{+}$ cations explains most, if not all, of the ionicity of silyl perchlorates observed by Lambert and coworkers in acetonitrile and sulfolane.[7,8]

Treatment of $\mathrm{Pr^{i}{}_{3}SiH}$ with $[\mathrm{Ph_{3}C}][\mathrm{Br_{5}\text{-}CB_{9}H_{5}}]$ in a less nucleophilic solvent than acetonitrile *e.g.* toluene, produces (24 h) the unsolvated compound $\mathrm{Pr^{i}{}_{3}Si(Br_{5}\text{-}CB_{9}H_{5})}$, which

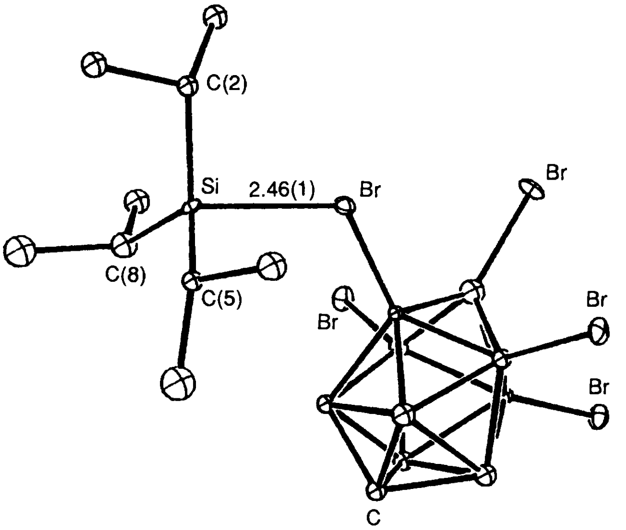

Fig. 2 A perspective view of $\mathrm{Pr^{i}{}_{3}Si(Br_{5}\text{-}CB_{9}H_{5})}$. Bond angles (°): Si–Br–B 119.8(11), C(2)–Si–C(5) 110.2(15), C(2)–Si–C(8) 120.5 (17), C(5)–Si–C(8) 116.8(16).

Table 1 ^{29}Si NMR resonances

Compound	Solvent	δ (SiMe$_4$)
$\mathrm{Pr^{i}{}_{3}Si(Br_{5}\text{-}CB_{9}H_{5})}$	[^{2}H$_8$]toluene	97.9
$\mathrm{Pr^{i}{}_{3}Si[B(C_{6}F_{5})_{4}]}$	[^{2}H$_8$]toluene	94.0
$\mathrm{Pr^{i}{}_{3}SiBr\text{-}AlBr_{3}}$[a]	[^{2}H$_8$]toluene	55.8
$\mathrm{Pr^{i}{}_{3}SiBr}$	[^{2}H$_8$]toluene	45.4
$[\mathrm{Pr^{i}{}_{3}Si(MeCN)}][\mathrm{Br_{5}\text{-}CB_{9}H_{5}}]$	[^{2}H$_2$]dichloromethane	37.2[b]
$[\mathrm{Pr^{i}{}_{3}Si(MeCN)}][\mathrm{Br_{5}\text{-}CB_{9}H_{5}}]$	[^{2}H$_3$]acetonitrile	33.8[b]
$\mathrm{Pr^{i}{}_{3}SiH}$	[^{2}H$_8$]toluene	12.1
$[\mathrm{Pr^{i}{}_{3}Si}]^{+}$ (estimated)	—	*ca.* 220[c]

[a] 3 equiv. $\mathrm{AlBr_{3}}$, presumably giving $\mathrm{Pr^{i}{}_{3}Si(BrAlBr_{3})}$. [b] The difference between dichloromethane and acetonitrile may reflect signal averaging with anion substitution of coordinated acetonitrile and/or additional acetonitrile coordination *e.g.* $[\mathrm{Pr^{i}{}_{3}Si(MeCN)_{2}}]^{+}$. [c] Estimated from $\mathrm{Me_{3}Si^{+}}$ (ref. 13) by applying a 30 ppm upfield correction for the Pr^{i} substituents.

has also been characterized by X-ray crystallography (see Fig. 2).‡ As expected from the reasonable toluene solubility, the carborane anion is directly bonded to silicon *via* a bromine atom. The average C–Si–C angle {115.8(2.0)°} and out-of-plane displacement (0.40 Å) reflect trigonality at silicon but these parameters are surprisingly *in*sensitive to the nature of the coordinated nucleophile. The average C–Si–C angle in each structure is statistically indistinguishable at current resolution and only a couple of degrees different from $\mathrm{Ph_{3}Si(OClO_{3})}$ {113.5(2)°}.[9] Nevertheless, partial ionicity in the coordinated $\mathrm{Br_{5}\text{-}CB_{9}H_{5}^{-}}$ structure is indicated by several features. The Si–Br distance is *ca.* 0.2 Å longer than a typical Si–Br bond (2.24 Å in $\mathrm{Me_{3}SiBr}$).[16] The coordinated B–Br bond {2.00(4) Å} shows no detectable extension relative to the others in the carborane anion {1.97(4)–2.05(4); average 2.00(4) Å}. The ^{11}B NMR is not reliably distinguishable from that of the free ion down to the solubility limit in toluene (−40 °C) suggesting intramolecular spinning of the coordinated anion *via* the four equivalent bromine substituents. This

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† The stucture was solved by heavy atom techniques after the bromine atoms were located from a detailed analysis of the Patterson map. Triclinic $P\bar{1}$, with $a = 12.876(12)$, $b = 14.111(9)$, $c = 8.550(4)$ Å, $\alpha = 90.76(5)$, $\beta = 92.91(6)$, $\gamma = 115.73(5)°$, $V = 1397$ Å^3 for $Z = 2$. Final factor $R = 6.5\%$ for 1213 non-zero reflections with $I > 3\sigma(I)$.

‡ The structure was solved by direct methods. Monoclinic $P2_1/n$ (No. 14), $a = 16.657(25)$, $b = 14.235(9)$, $c = 11.485(18)$ Å, $\beta = 109.80(11)°$, $V = 2562(5)$ Å^3 for $Z = 4$. $R = 7.98\%$ for 1269 reflections with $I > 4\sigma(I)$.

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.[7] The present situation is closer to ionic-like species such as $[Th(C_5Me_5)_2(Me)][B(C_6F_5)_4]$ where ^{19}F resonances are insensitive to fluorine coordination.[1] Indeed, $Pr^i_3Si[B(C_6F_5)_4]$, prepared by treatment of Pr^i_3SiH with $[Ph_3C][B(C_6F_5)_4]$ in toluene behaves in a very similar manner to $Pr^i_3Si(Br_5\text{-}CB_9H_5)$. The ^{29}Si resonance of $Pr^i_3Si(Br_5\text{-}CB_9H_5)$ is δ 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 *bona fide* three-coordinate cation. By comparison to more covalent species in Table 1, the ^{29}Si NMR data indicate that $Pr^i_3Si(Br_5\text{-}CB_9H_5)$ has about one third silylium ion character. This is the closest approach to date and suggests that $Br_5\text{-}CB_9H_5^-$ 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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