Approaching the Silylium (R_3Si^+) Ion: Trends with Hexahalo (Cl, Br, I) Carboranes as Counterions

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Abstract: A systematic investigation has been made into the degree of silylium ion character in species of the type i-Pr_3SiY where Y^- is a weakly coordinating hexahalo-carborane anion, X_6-$CB_{11}H_6^-$, with X = Cl, Br, I. By X-ray crystal structural criteria such as the average C−Si−C angle (117.3(4)°, 117.0(13)°, and 115.6(9)° for X = Cl, Br, I, respectively) and the downfield ^{29}Si chemical shift (115, 110, and 97 ppm for X = Cl, Br, I, respectively) the hexachloro-carborane anion is the least coordinating. Thus, the "ion-like" species i-$Pr_3Si^{\delta+}(Cl_6$-$CB_{11}H_6)^{\delta-}$ becomes the closest structural approach to date to a condensed phase silylium ion. With the aid of *ab initio* molecular orbital theory and silicon chemical shift calculations we address the question of how much silylium ion character this species represents. From structural, energetic, and NMR criteria (where expectation values for the condensed phase ^{29}Si chemical shifts are revised downward) we conclude that i-$Pr_3Si^{\delta+}(Cl_6$-$CB_{11}H_6)^{\delta-}$ may have >50% silylium ion character.

Introduction

The long-sought silylium ion, R_3Si^+, analogous to well-known carbenium ions (R_3C^+), remains a challenging synthetic problem in condensed media.[1] It has become an essential part of the search for the least coordinating anion,[2] an occasion to reconsider the designation of any solvent as "non-nucleophilic", and a continuing illuminator of carbocation chemistry by virtue of the differences between carbon and silicon electrophiles. It is also a fertile confluence for experiment and theory[3] because the well-recognized gas-phase existence and stability of R_3Si^+ contrasts so markedly with its elusive nature in condensed phases.

The successful synthesis of R_3Si^+ in condensed media will require progress toward (a) a noncoordinating anion, (b) a noncoordinating solvent, and (c) the optimal choice of substituent R. We have recently explored the relative merits of branched chain alkyl substituents and found an optimum at R = *iso*-propyl, unexpectedly better than *tert*-butyl because of C−H hyperconjugation.[4] The choice of solvent has a number of practical considerations: workable solubility, chemical inertness, and the rare combination of high dielectricity and low donicity. Toluene[5] is sufficiently nucleophilic to be silylated by Et_3Si^+ and dichloromethane is subject to chloride ion abstraction.[6] In this paper, we explore two new weakly coordinating anions which allow systematic observation of the degree of silylium ion character in species of the type $R_3Si^{\delta+}Y^{\delta-}$. The anions are the hexachloro and hexaiodo carboranes of the 7,8,9,10,11,12-X_6-*closo*-$CB_{11}H_6^-$ type (X = Cl, I) which systematically bracket the hexabromo anion, Br_6-$CB_{11}H_6^-$, currently the least coordinating anion for the silylium ion by structural and ^{29}Si NMR shift criteria.[7] Counter to expectations from size considerations and hard cation/soft anion incompatibility, we find that the hexachloro carborane, not the hexaiodo carborane, is the least coordinating to i-Pr_3Si^+.

Results and Discussion

Synthesis. Of the three carborane anions chosen for systematic study, X_6-$CB_{11}H_6^-$ (X = Cl, Br, I), the hexachloro and hexabromo are reported species,[8,9] prepared by the treatment of $CB_{11}H_{12}^-$ with excess halogen. With iodine, however, exhaustive iodination of $CB_{11}H_{12}^-$ leads only to the 7,12-*di*iodo species.[8] The electrophilicity of iodine can be enhanced by using the mixed halogen ICl. Accordingly, we find that treatment of $Cs^+CB_{11}H_{12}^-$ with excess ICl in acetic acid or dimethoxyethane leads to good yields of the hexaiodo anion:[10]

$$CB_{11}H_{12}^- + \text{excess ICl} \rightarrow 7,8,9,10,11,12\text{-}I_6\text{-}CB_{11}H_{12}^- + HCl$$

The high symmetry of the 7,8,9,10,11,12 regioselective pattern

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[⊥] Née Janet Hillary.

[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1996.

(1) Lambert, J. B.; Kania, L.; Zhang, S. *Chem. Rev.* **1995**, *95*, 1191−1201. For the purposes of the present paper, R_3Si^+ refers to a species with three Si−C bonds. Three-coordinate silicon in a cationic species with two Si−C bonds and bonding to a transition metal (i.e., having silylene character) are now well characterized: see ref. 22.

(2) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927−942.

(3) See for example: (a) Schleyer, P. v. R.; Buzek, P.; Müller, T.; Apeloig, Y.; Siehl, H. U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1471−1473. (b) Olson, L.; Ottosson, C.-H.; Cremer, D. *J. Am. Chem. Soc.* **1995**, *117,* 7460−7479 and references therein.

(4) Xie, Z.; Bau, R.; Benesi, A.; Reed, C. A. *Organometallics* **1995**, *14*, 3933−3941.

(5) (a) Lambert, J. B.; Zhang, S.; Stern, C. L.; Huffman, J. C. *Science* **1993**, *260*, 1917−1919. (b) Lambert, J. B.; Zhang, S.; Ciro, S. M. *Organometallics* **1994**, *13*, 2430−2443.

(6) Kira, M.; Hino, T.; Sakurai, H. *J. Am. Chem. Soc.* **1992**, *114*, 6697−6700.

(7) Reed, C. A.; Xie, Z.; Bau, R.; Benesi, A. *Science* **1993**, *262*, 402−404.

(8) Jelínek, T.; Plešek, J.; Hermánek, S.; Stíbr, B. *Collect. Czech. Chem. Commun.* **1986,** *51*, 819−829.

(9) Xie, Z.; Jelínek, T.; Bau, R.; Reed, C. A. *J. Am. Chem. Soc.* **1994**, *116*, 1907−1913.

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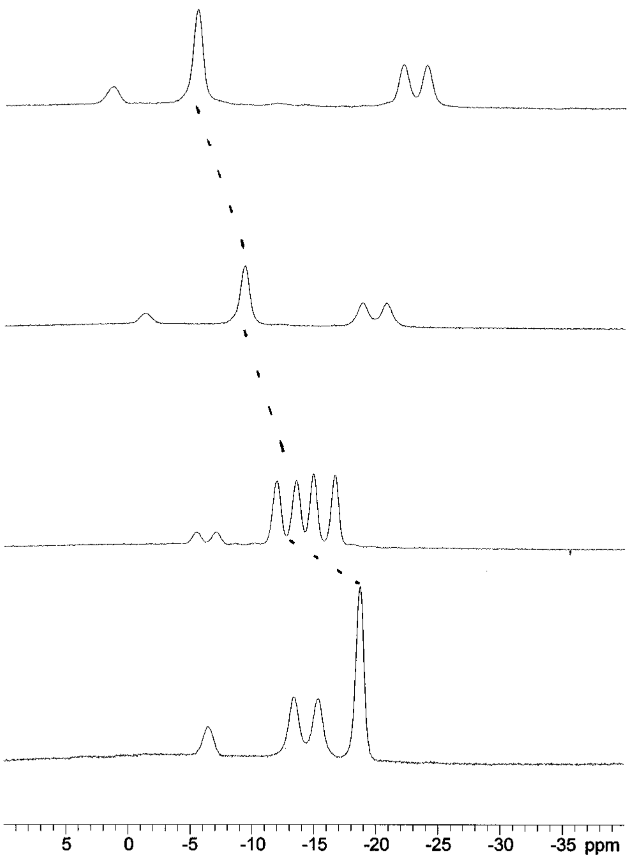

Figure 1. Correlation diagram for the ^{11}B NMR spectra of $Cs(X_6\text{-}CB_{11}H_6)$ in d_6-acetone, X = Cl (top), Br, H, I (bottom).

of electrophilic substitution is clearly established by ^{11}B NMR spectroscopy (see Figure 1) and is understood chemically as a consequence of the dipolar charge distribution within the CB_{11} cage. The B−H bond in the 12-position, antipodal to carbon, is the most electron rich, followed by the adjacent 7−11 pentagonal belt. The comparison of ^{11}B NMR spectra for the four anions $X_6\text{-}CB_{11}H_6^-$ with X = Cl, Br, H, I shows potentially interpretable trends in chemical shifts but, at this time, we note only that the correlated ordering places H between Br and I and that the 7−11 resonance is the most sensitive to substitution. This contrasts with the "antipodal effect" in cage-substituted heteroboranes where the largest shift is often at the farthest site of substitution.[11] The ^{13}C chemical shifts of the hexahalo anions follow the same trend: Cl < Br < H < I at 32.0, 41.7, 51.4, and 56.8 ppm, respectively.

The reaction of choice for the synthesis of silyl species of the type $i\text{-}Pr_3Si(X_6\text{-}CB_{11}H_6)$ is the treatment of tri-*iso*-propylsilane with the trityl salt of the carborane in toluene.

$$i\text{-}Pr_3SiH + [Ph_3C^+][X_6\text{-}CB_{11}H_6^-] \xrightarrow{\text{toluene}} i\text{-}Pr_3Si(X_6\text{-}CB_{11}H_6) + Ph_3CH$$

The new X = Cl and I species were isolated as pale yellow microcrystalline materials for solid state ^{29}Si NMR investigation and as single crystals for X-ray structure determination. The solid state is favored over solution for the investigation of the properties of these species not only for the practical reason of low solubility but also because comparative data might be complicated by coordination of solvent to the silicon center. We also wanted to see if, all else being equal, there was a correlation between the two most widely used experimental criteria of developing silylium ion character, namely, downfield ^{29}Si chemical shifts and the geometric approach of silicon toward planarity. As discussed below, this correlation is observed.

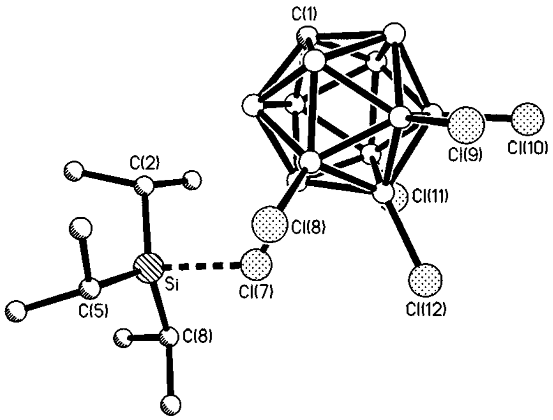

Figure 2. Perspective view of $i\text{-}Pr_3Si(Cl_6\text{-}CB_{11}H_6)$.

Table 1. Summary of Key Geometrical Parameters for $i\text{-}Pr_3Si(X_6\text{-}CB_{11}H_6)$

parameter	X = Cl	X = Br[a]	X = I
Si−X (Å)	2.323(3)	2.479(9)	2.661(6)
$B-X_{coord}$ (Å)	1.88(1)	2.05(3)	2.22(2)
$B-X_{non\text{-}coord}$ (Å)[b]	1.77−1.82(1)	1.93−2.02(3)	2.15−2.18(2)
Si−X−B (deg)	122.6(3)	114.7(7)	110.3(5)
C−Si−C (deg)	115.4(4)	111.2(14)	112.9(10)
	117.4(4)	119.6(13)	113.2(9)
	119.0(4)	120.2(12)	120.7(9)
$C-Si-C_{ave}$ (deg)	117.3(4)	117.0(13)	115.6(9)
ΣC−Si−C (deg)	351.8(4)	351.0(13)	346.8(9)
Si out of C_3 plane (Å)	0.307	0.300	0.400
$Si-C_{ave}$ (Å)	1.848(9)[c]	1.86(2)	1.883(21)

[a] Data from ref 4. [b] From pentagonal belt only. [c] Individual Si−C distances: 1.846(9), 1.848(10), 1.850(8) Å.

X-ray Structures. A perspective view of the crystal structure of $i\text{-}Pr_3Si(Cl_6\text{-}CB_{11}H_6)$ is shown in Figure 2. It is representative of all three hexahalo-carborane structures with tri-*iso*-propyl substituents. The key features to note about these structures are the absence of solvates, an essentially undistorted anion, and as we have now come to expect,[4] coordination of the anion to silicon via a halogen atom from the 7−11 pentagonal belt. The 12-halo atom is expected to be the most basic but is apparently sterically less accessible.

The key geometrical parameters of the three hexahalocarboranyl silanes are given in Table 1. The Si−X bonds are all about 0.25 Å longer than normal Si−X bonds,[12] indicative of the weakly coordinating nature of the anions and the developing ionic character $i\text{-}Pr_3Si^{\delta+}(X_6\text{-}CB_{11}H_6)^{\delta-}$. The Si−X−B angles decrease as the size of the halogen increases. This reflects the approximate van der Waals approach of B−H bonds of the anion to *iso*-propyl groups on silicon. The flexibility of this angle suggests that the Si−X interaction has little covalence, a conclusion also drawn from the minimal extension of the coordinated B(7)−X bond relative to a comparable noncoordinated bond, i.e., B(8−11)−X (see Table 1).

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(10) Preliminary communication: *Phosphorus Sulfur Silicon Relat. Elem.* **1994**, *93*, 485. This reaction has been independently investigated by Janoušek, Z.; Grüner, B.; Trammell, M.; Michel, J. *Abstracts of Papers*, 209th National Meeting of the American Chemical Society, Anaheim, CA, 1995; American Chemical Society: Washington, DC, 1995; ORG 315. Iodination of neutral carboranes has also been reported recently: Zheng, Z.; Jiang, W.; Zinn, A. A.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1995**, *34*, 2095−2100.

(11) Bühl, M.; Schleyer, P. v. R.; Havlas, Z.; Hnyk, D.; Hermánek, S. *Inorg. Chem.* **1991** *30*, 3107−3111.

(12) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds;* Patai, S., Rappoport, Z., Eds.; Wiley-Interscience: New York, 1989; Vol. 1, pp 227−303.

The pyramidalization at the R_3Si moiety is a good structural indicator of developing silylium ion character inasmuch as the closer the approach to sp^2 planarity, the closer the approach to a true silylium ion. Notably, the hexa*chloro* compound has the most silylium ion character of the three species. Its average C−Si−C angle is 117.3(4)°, the closest approach to date to the desired value of 120°. Alternatively, the sum of the C−Si−C angles is 351.8(4)°, about 8° short of the desired 360°. The displacement of Si from the plane of the three attached carbon atoms is 0.30 Å.[13]

The average Si−C distance of 1.848(9) Å in the chloro species is short, as expected for developing three coordination. Typical Si−C bonds in four-coordinate silanes are at least 1.87 Å.[12] A statistically meaningful comparison can be made to the hexaiodo compound where the average is 1.883(21) Å. The longer distance in the hexaiodo species is consistent with a more strongly coordinated anion. The value of 1.848(9) Å in the hexachloro compound can also be compared to the calculated values of 1.857 (HF/6-31G*),[14] 1.855 (HF/6-31G**), 1.854 (B3LYP/6-31G*), and 1.856 Å (B3LYP/6-31G**) for the fully cationic Et_3Si^+ moiety and 1.870 (HF/6-31G*) and 1.870 Å (B3LYP/6-31G*) for the analogous i-Pr_3Si^+ cation. That the calculated values for the free ions are actually ***longer*** than the experimental value in the anion-coordinated species raises the question of whether i-$Pr_3Si^{\delta+}(Cl_6\text{-}CB_{11}H_6)^{\delta-}$ more closely approaches full ionicity than might otherwise be apparent. It also raises the question of experimental error and how far such comparisons should be taken in the absence of an error estimate for the theoretical value, where accuracy to four significant figures is overly optimistic.[15] The range of reported values for the tri*methyl*silylium ion, Me_3Si^+, is 1.837−1.847 Å at an HF/6-31G* or better level of theory.[3b,14,16,17] Our own calculations of the molecular structure of Me_3Si^+ give values of 1.846 (HF/6-31G*), 1.838 (MP2/6-31G*), and 1.844 Å (density functional B3LYP). Considering this range of calculated values and the effect of the substituent (Me, Et, i-Pr), a reasonable expectation for the Si−C bond length in i-Pr_3Si^+ would be >1.857(9) Å. This is within one standard deviation of the experimental value of 1.848(9) Å in i-$Pr_3Si(Cl_6\text{-}CB_{11}H_6)$. Nevertheless, one might have expected the experimental value to have been on the long rather than the short side of the anion-free calculated value. A thermal motion analysis of the X-ray data revealed that librational motion corrections to the experimental bond lengths would amount to no more than 0.003 Å.[18]

In order to obtain a calibration for the expected change in Si−C distance as a function of developing silylium ion character we have performed a reaction coordinate calculation (HF/6-31G*) to follow the structure of Me_3SiCl as the Si−Cl bond length is varied from the equilibrium value of 2.095 Å to the essentially nonbonding distance of 3.5 Å. The results are plotted in Figure 3. They reveal that Si−C distance is a moderately sensitive guide to developing silylium ion character. The essential coincidence of the experimental value in i-$Pr_3Si(Cl_6\text{-}CB_{11}H_6)$ with the minimum estimate for i-Pr_3Si^+ suggests a very much closer approach to the free silylium ion than is suggested by the Si−Cl distance. In other words, the Si···Cl bond with the chlorocarborane is apparently a rather different and much weaker interaction than that with a chloride ion. This is quite understandable; the valency needs of chlorine in the former are met by covalent bonding to boron. This suggests that the Si···Cl distance in i-$Pr_3Si(Cl_6\text{-}CB_{11}H_6)$ is not a particularly good criterion by which to assess silylium ion character.

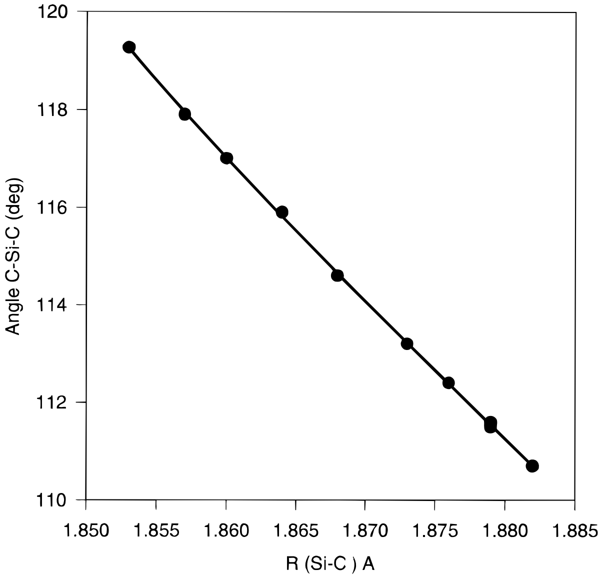

Figure 3. Plot of calculated C−Si−C bond angle versus Si−C distance in Me_3SiCl.

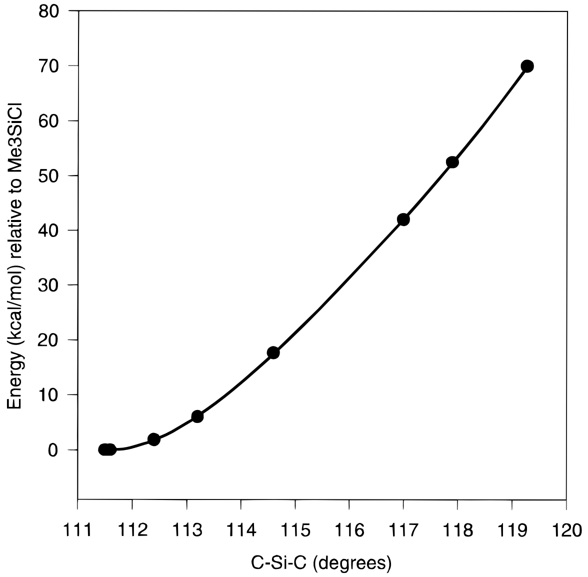

Figure 4. Plot of calculated total energy of Me_3SiCl versus C−Si−C angle.

Of further interest in these Me_3SiCl calculations is the plot of energy versus C−Si−C angle as the molecule is gradually ionized to Me_3Si^+ and Cl^-. As shown in Figure 4, early deformation from the equilibrium C−Si−C angle of 111.5° is not particularly difficult. However, the energy involved in charge separation rises rather steeply as the angle approaches 120°. We note that at a C−Si−C angle of 117.3°, that found experimentally in i-$Pr_3Si(Cl_6\text{-}CB_{11}H_6)$, $Me_3Si^{\delta+}Cl^{\delta-}$ is energetically >65% ionized along its trajectory to the 3.5 Å Si···Cl nonbonding limit. This model suggests that i-$Pr_3Si(Cl_6\text{-}CB_{11}H_6)$

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(13) The trend in out-of-plane displacements in Table 1 is slightly out of line with the other trends because the uniquely short (hyperconjugated) Si−C bond in the hexabromo compound contracts the basal plane. See ref. 4.

(14) Cremer, D.; Olsson, L.; Ottosson, H. *J. Mol. Struct. (Theochem)* **1994**, *313*, 91−109.

(15) Comparison of experimental versus calculated bond lengths in cations at the 3-21G level reveals a systematic overestimate of the calculated value, perhaps due to an underestimation of hyperconjugation. See: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986**;** p 219.

(16) Olah, G. A.; Rasul, E.; Heiliger, L.; Bausch, J.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1992**, *114*, 7737−7742.

(17) Maerker, C.; Kapp, J.; Schleyer, P. v. R in *Organosilicon Chemistry*; Auner, N.; Weis, J., Eds.; VCH: Weinheim, 1996; pp 329−359.

(18) Program THMA14, Trueblood, K. N., University of California at Los Angeles, March 1993.

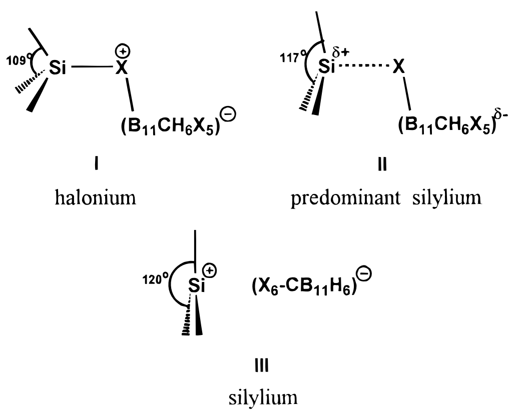

Figure 5. Representations of halonium (**I**) versus silylium ion (**III**) character.

has developed ~65% silylium ion character and corroborates the indication of substantial i-Pr_3Si^+ character that was deduced from the short Si−C distances.

Silylium versus Halonium Ion Character. Finding the ordering Cl < Br < I for the least coordinating hexahalo carborane anions to i-Pr_3Si^+ is unexpected on electrostatic grounds. The largest anion, I_6-$CB_{11}H_6^-$, might have been expected to be most weakly bound. However, as indicated above, the Si−X−B angle is flexible and becomes progressively more acute as the Si−X bond length increases. Thus, the boron cage as a whole is not as far displaced from the trialkylsilicon moiety as might be implied by the increasing Si−X distances. The ordering is also unexpected on the basis of hard−soft acid−base considerations. The softest anion, the hexaiodo, might be expected to bind most weakly to i-Pr_3Si^+, an acid which must be classified as hard.[19] The explanation for the ordering probably lies in the relative contribution of halonium ion character to the structure, i.e., the degree of covalence in the Si−X bond. Figure 5 shows idealized structural and electronic representations of a halonium ion (**I**) and a silylium ion (**III**). The present species are electronic and structural hybrids of these two representations. Silylium ion character is predominant as judged by the closer approach of the silicon geometry to planarity than to tetrahedrality. Since iodonium ions are more stable than bromonium ions, than chloronium ions[20] (this follows the order of first ionization potentials of the halogens), the iodo species will have the most halonium ion character and the most covalence in its Si−halogen bond. The chloro species will have the least halonium ion character and consequently the most silylium ion character.

^{29}Si NMR. A marked downfield ^{29}Si chemical shift is the most widely used criterion of silylium character. The earliest projections for Me_3Si^+ were in the range 225−275 ppm.[21] These were based on empirical correlations of ^{29}Si and ^{13}C shifts in isostructural silicon and carbon compounds and may still be the most appropriate expectation values for condensed phase experiments. Some extension of this range (in either direction) would be reasonable to accommodate substituents other than methyl. It is pertinent to note here that a 311 ppm shift has been reported for an essentially planar, three-coordinate, cationic silicon species having two methyl substituents and a (multiple) bond to ruthenium.[22] The first theoretical calculation of the ^{29}Si shift for Me_3Si^+, using the IGLO method, gave a value of 35l ppm.[23] Subsequent IGLO calculations[14,16,17] have given similar values of around 355 ppm. A more recent report gives an estimate of 385 ± 20 ppm based on the change in calculated ^{29}Si chemical shift for SiH_3^+ upon the inclusion of correlation effects using the GIAO-MP2 method.[3b] Our own estimate of the ^{29}Si chemical shift is 354 ppm using the GIAO method and 382 ppm using SOS-DFPT (which includes some correlation effects). Our comparable calculations for Et_3Si^+ are 371.2 (GIAO) and 415.6 ppm (SOS-DFPT), respectively, and for i-Pr_3Si^+ are 342.3 (GIAO) and 371.0 ppm (SOS-DFPT), respectively, from geometries optimized at the HF/6-31G* level.

How relevant are these "gas-phase" values to expectation values for R_3Si^+ in condensed media? First, we note that even at the highest levels of published theory, there is a 17−30 ppm downfield discrepancy between the calculated and experimental values for the Me_3C^+ carbocation.[24] Either theory overestimates the downfield shift (possibly by underestimating hyperconjugative stabilization) or solvent/anion effects have a compensating upfield shift in condensed media. Support for the latter explanation comes from Cremer and co-workers,[3b] who have very recently investigated this phenomenon by modeling both the specific and general effects of solvents in IGLO-type calculations. An energy-minimized solvated carbocation of the type $Me_3C(OH_2)_2^+$ (C−O = 2.72, 2.87 Å) is shifted 13 ppm upfield relative to Me_3C^+ at the HF 6-31G* level. This value can apparently be shifted further upfield if overall dielectricity is added to the calculation. Silylium ions are found to be much more sensitive than carbenium ions to the effects of solvent because of more facile electron donation from solvent to silicon.[3b] The dielectricity effect of a noncoordinating solvent is estimated to be no more than 20 ppm for Et_3Si^+. However, solvents with Gutmann donor numbers $D < 1$, at van der Waals distance from silicon, are calculated to shift δ ^{29}Si values upfield by as much as 170 ppm. In other words, a realistic expectation value for i-Pr_3Si^+ in condensed media could be as low as 220 ppm vs TMS. Solvents with $D = 1−10$ (nitrobenzene is 4.4, acetonitrile is 14.4, for example)[25] are calculated to give rise to further decreases of up to 110 ppm because of specific, albeit weak, covalent bonding of the solvent to silicon in species of the type $R_3Si(Solv)_{1or2}^+$. These results are consistent with those of Schleyer and co-workers[17] who, for example, have shown that the 3.08 Å approach of an argon atom to Me_3Si^+ lowers the ^{29}Si shift by 62 ppm and the 2.46 Å approach of the Br atom of methyl bromide to Me_3Si^+ lowers it by 145 ppm, i.e, to a value of only 102 ppm vs TMS.

The above considerations create an improved context in which to evaluate the ^{29}Si shifts of the present compounds. Instead of having the solvent interactions explored in these calculations, we have interactions with weakly coordinating anions. The experimental δ ^{29}Si values are 115, 110, and 97 for the hexachloro, hexabromo, and hexaiodo-carborane species, respectively. We note that the values were obtained in the solid state by CPMAS techniques on the identical materials to those characterized by X-ray crystallography to ensure that there is no ambiguity about the nature of the species under consideration. The most important observation about these data is that the downfield trend correlates very well with the ordering of increasing silylium ion deduced from X-ray crystallography, i.e.,

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[19] Schwarz, H. In *The Chemistry of Organic Silicon Compounds, Part 1*; Patai, S.; Rappoport, Z., Eds.; Wiley-Interscience: New York, 1989; pp 445−510.

[20] Olah, G.; Prakash, S. G. K.; Sommer, J. *Superacids;* Wiley-Interscience: New York, 1985; pp 193−206.

[21] Olah, G. A.; Field, L. *Organometallics* **1982**, *1*, 1485−1487.

[22] Grumbine, S. K.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116,* 5495−5496.

[23] Kutzelnigg, W.; Fleischer, U.; Schindler, M. In *NMR; Basic Principles and Progress;* Diehl, P., Fluck, E., Gunther, H., Kosfeld, R., Selling, J., Eds; Springer-Verlag: New York, 1989; Vol. 23, p 228.

[24] Sieber, S.; Buzek, P.; Schleyer, P. v. R.; Koch, W.; Carneiro, J. W. d. M. *J. Am. Chem. Soc.* **1993**, *115,* 259−270.

[25] Gutman, V. in *New Pathways in Inorganic Chemistry*; Ebsworth, E. A. V.; Maddock, A. G., Sharpe, A. G., Eds.; Cambridge University Press: Cambridge 1968; pp 65−86.

Cl > Br > I. Also, the chloro and bromo structures, and their shifts, are more similar to each other than the bromo is to the iodo. In other words, the NMR data corroborate conclusions drawn from the X-ray data and together provide consistent qualitative criteria for identifying silylium ion character.

We now address the question of how much silylium ion character the ^{29}Si chemical shift of 115 ppm in *i*-$Pr_3Si(Cl_6\text{-}CB_{11}H_6)$ represents.

The Degree of Silylium Ion Character. Classical carbenium ions show little interaction with their anions.[26,27] There is a clear demarcation between ionic/planar carbon in $[Me_3C][Sb_2F_{11}]$ and covalent/tetrahedral carbon in Me_3CCl. In carbon chemistry, sp^3 hybridization and sp^2 hybridization (plus hyperconjugation) are apparently quite distinct wells on the potential energy surface. The present work supports the idea that silicon is quite different. There is an apparent continuum of increasing ionicity as the anion becomes less coordinating, i.e., there is a "silicon valley" linking the covalent/tetrahedral and ionic/trigonal-planar forms. This creates something of a difficulty in defining precisely what might properly constitute a silylium ion in condensed media because it is always going to be a matter of degree.

Theoretical criteria for distinguishing covalence from ionicity have been devised and applied to the problem of solvent interaction with silylium ions.[3b] Experimental criteria will depend upon the parameter that is chosen, its boundary conditions, and how the parameter scales along the continuum.[28] For example, the 117.3° value for the mean C−Si−C angle in *i*-$Pr_3Si(Cl_6\text{-}CB_{11}H_6)$ is 75% of the way along the tetrahedral to trigonal-planar trajectory. On the other hand, the 0.30 Å out-of-plane displacement of the Si atom represents only 52% progress. As indicated earlier, energetically our calculations on Me_3SiCl show that at a C−Si−C angle of 117.3°, we have ca. 65% Me_3Si^+ character (see Figure 7). On the other hand, the Si−Cl distance of 2.32Å in *i*-$Pr_3Si(Cl_6\text{-}CB_{11}H_6)$ is only ca. 20% of the extension from covalent (ca. 2.05 Å)[12] to van der Waals contact (ca. 3.29 Å).[3b] Pauling-type bond order calculations[1] place the covalency of the Si−X bond in the present componds at ca. 0.3 but, as indicated earlier, the Si−X bond length is a poor criterion of silylium ion character. On the other hand, the silicon−carbon bond length is sufficiently short in *i*-$Pr_3Si(Cl_6\text{-}CB_{11}H_6)$ that it suggests nearly complete ionization to a silylium ion.

To help answer the question of how much silylium ion character is reflected in a 115 ppm ^{29}Si chemical shift, we have studied the variation in calculated chemical shift in Me_3SiCl as a function of the Si−Cl reaction coordinate. At each fixed Si−Cl distance the geometry was fully optimized (HF/6-31G*) and the ^{29}Si chemical shifts were calculated using either the GIAO method or SOS-DFPT. The variation of δ (^{29}Si) as a function of Si−Cl distance, C−Si−C angle, and charge on the chlorine atom is shown in Figures 6−8. The two methods show qualitatively similar trends but differ somewhat with respect to the details of the slopes and the endpoints (by up to 25 ppm). Neither geometrical parameter, i.e., neither Si···Cl bond distance nor C−Si−C angle, correlates linearly with δ, but Si···Cl does so roughly. As a function of charge separation in $Me_3Si^{\delta+}\cdots Cl^{\delta-}$, the ^{29}Si chemical shift follows the complex function shown in Figure 8, portions of which might be considered roughly linear.

The 115 ppm ^{29}Si chemical shift of *i*-$Pr_3Si(Cl_6\text{-}CB_{11}H_6)$ is between 36 and 52% of the way between TMS and our expectation values for *i*-Pr_3Si^+ in condensed media (ca. 220−320 ppm). In the $Me_3Si\cdots Cl$ calculations, fully half of the 388 ppm downfield shift of gas-phase Me_3Si^+ is erased before the Cl^- ion approaches any closer than van der Waals distance (ca. 3.3 Å, see Figure 6). This favors a yardstick with 220 ppm as its upper limit thereby leading to the proposal that the 115 ppm shift of *i*-$Pr_3Si(Cl_6\text{-}CB_{11}H_6)$ represents about a 50% approach to the ionicity expected for a condensed-phase silylium ion. This is somewhat at odds with the use of 2l0 ppm as the cutoff point below which there is "total loss of silylium ion character" in solvated species.[29] However, inconsistencies such as this are inevitable, given that silylium ion character is definition dependent. We favor definitions based on experimental observables within chemically reasonable continua and note that the approximately 50% silylium ion character favored by the above NMR analysis is consistent with the 50 to 75% deduced earlier from various structural and energetic criteria.

With ~50% silylium ion character and with a Si−Cl distance much shorter than the van der Waals contact, it would of course

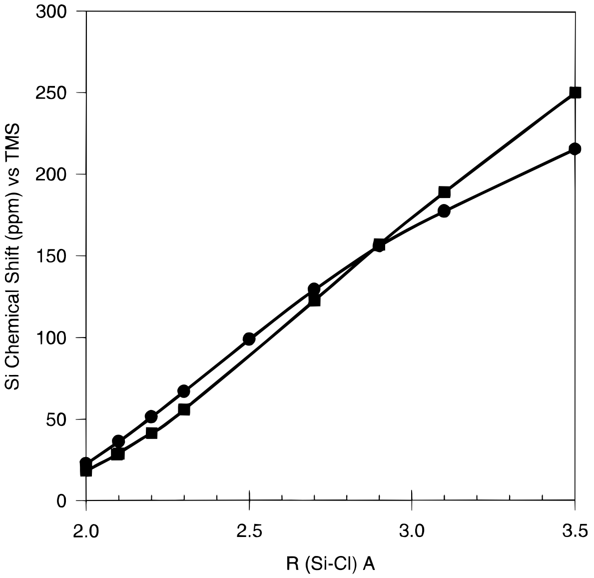

Figure 6. Plot of calculated ^{29}Si chemical shift versus Si···Cl distance in Me_3SiCl (●) by density functional and (■) GIAO methods.

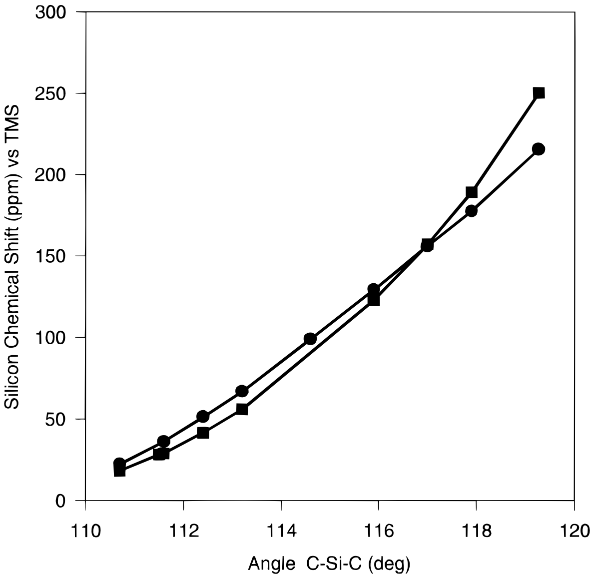

Figure 7. Plot of calculated ^{29}Si chemical shift versus C−Si−C angle in Me_3SiCl (●) by density functional and (■) GIAO methods.

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(29) See Table 10 in ref 3b.

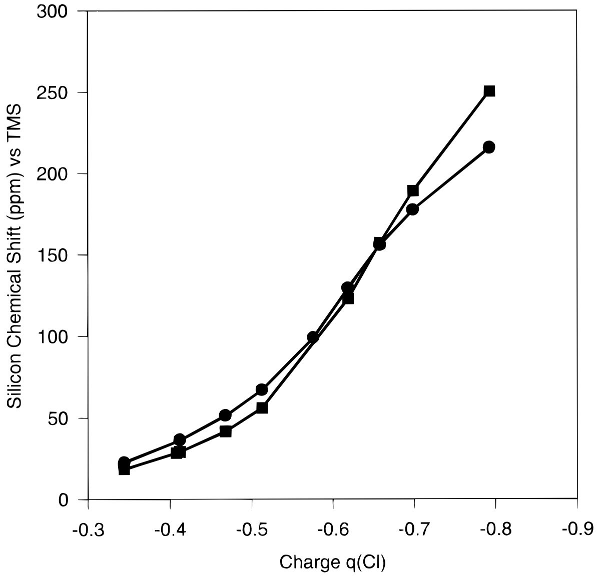

Figure 8. Plot of calculated ^{29}Si chemical shift versus charge (q) on the chlorine atom for Me_3SiCl as the Si−Cl bond is ionized (●) by density functional and (■) GIAO methods.

be inappropriate to call $i\text{-}Pr_3Si(Cl_6\text{-}CB_{11}H_6)$ a silylium ion. However, the term "silylium ion-like" and the acknowledgment of quite significant partial charges, $i\text{-}Pr_3Si^{\delta+}(X_6CB_{11}H_6)^{\delta-}$, seems most appropriate. This is especially relevant to viewing the chemistry of these species. They react like silylium ions. With traces of water[30] they give $[i\text{-}Pr_3Si(OH_2)]^+$, with siloxanes they react analogously to give trisilyloxonium ions,[31] and with both aliphatic and aromatic chlorocarbons they give chlorosilanes.[6,32] In aromatic substitution, their solution-phase electrophilicity has yet to be exploited synthetically along the lines that gas-phase experiments indicate might be possible.[33] To date, silylation of benzene is reported to proceed with yields of <2%.[34]

Experimental Section

General experimental conditions were as previously described.[9]

Cs(*closo*-7,8,9,10,11,12-I_6-$CB_{11}H_6$). Cesium 1-carbaundecaborane (0.5g, 1.81 mmol) was dissolved in dimethoxyethane (5 mL) and heated at 65 °C with iodine monochloride (4.0g, 24.6 mmol) overnight. After cooling to room temperature, the reaction mixtue was diluted with additional solvent (20 mL) and the excess ICl titrated away by dropwise addition of a saturated aqueous solution of sodium sulfite. Addition of water (100 mL) to the pale yellow solution and cooling to ice temperature yielded a white precipitate which was washed thoroughly with iced water and recrystallized from methanol by addition of saturated aqueous CsCl solution (1.2 g, 65%). ^{11}B NMR (86.7 MHz, DME, $BF_3{\cdot}OEt_2$ external) δ −6.3 [s, 1B, B(12)], −14.4 [d, 5B, J_{BH} = 166 Hz, B(2−6)], −18.7 [s, 5B, B(7−11)]. Connectivities from 2-D $^{11}B-^{11}B$ NMR (160.5 MHz, $(CD_3)_2CO$, $BF_3{\cdot}OEt_2$ external): B(12) [B(7−11)]; B(2−6) [B(7−11)]; B(7−11) [B(12), B(2−6)].

Ag(*closo*-7,8,9,10,11,12-I_6-$CB_{11}H_6$). This silver salt was prepared from the above cesium salt and silver nitrate in a manner similar to that described previously for the hexabromo analogue.[9] Yield 85%. ^1H NMR (500 MHz, CD_3CN) δ 2.4−3.6 [m, B−H], δ 3.4 [s, C-H]; ^{11}B NMR (86.7 MHz, CH_3CN, $BF_3{\cdot}OEt_2$ external) δ −6.0 [s, 1B, B(12)], −14.1 [d, 5B, J_{BH} = 165 Hz, B(2−6)], −18.7 [s, 5B, B(7−11)]. Connectivities from 2-D $^{11}B-^{11}B$ NMR (160.5 MHz, CD_3CN, $BF_3{\cdot}OEt_2$ external): B(12) [B(7−11)]; B(2−6) [B(7−11)]; B(7−11) [B(12), B(2−6)].

Table 2. Summary of Data and Intensity Collection Parameters for $i\text{-}Pr_3(X_6\text{-}CB_{11}H_6)$

	X = Cl	X = I
formula	$C_{10}H_{27}B_{11}Cl_6Si$	$C_{10}H_{27}B_{11}I_6Si$
molecular wt	507.0	1055.7
cryst syst	monoclinic	orthorhombic
space group	$P2_1/c$	$Pbca$
a, Å	8.993(1)	18.367(5)
b, Å	26.685(2)	15.732(4)
c, Å	10.437(1)	20.794(7)
β, deg	98.32(1)	
V, Å^3	2478.3(5)	6008(3)
Z	4	8
calcd density ($g{\cdot}cm^{-3}$)	1.359	2.334
radiation (λ, Å)	Cu Kα(1.54178)	Mo Kα (0.71073)
abs coeff (mm^{-1})	6.744	6.244
temp (K)	153	223
scan type	$2\theta-\theta$	$2\theta-\theta$
index ranges	$-1 \le h \le 9$ $-1 \le k \le 27$ $-10 \le l \le 10$	$-1 \le h \le 18$ $-1 \le k \le 15$ $-1 \le l \le 20$
no. of indep reflns	2676	3215
no. of obsd reflns ($F > 4.0\sigma(F)$	2247	2165
no. of params refnd	253	148
final R indices	6.71	4.66

[Ph_3C](*closo*-7,8,9,10,11,12-I_6-$CB_{11}H_6$). The above silver salt (0.30g, 0.30 mmol) in acetonitrile (10 mL) and triphenylbromomethane (0.096g, 0.30 mmol) in toluene (3 mL) were heated under reflux in the dark for 1 week. The cooled solution was filtered through a fine frit and the orange solution reduced in volume under vacuum until orange crystals began to form. The solution was cooled to −30 °C to complete crystallization and the product collected by filtration, washing with cold toluene and then hexane (0.24 g, 70%). ^1H NMR (360 MHz, $(CD_3)_2CO$) δ 7.72 and 7.68 [dd, 6H, *meta*], 7.86 [t, 6H, *ortho*], 8.25 [t, 3H, *para*]; ^{13}C NMR (90.6 MHz, $(CD_3)_2CO$) δ 69.2 [*carborane*-C], 127.5 [*para*- C], 128.2 [*meta* -C], 128.7 [*ortho*-C], 154.3 [*ipso*- C], 210.0 [Ph_3-*C*]; ^{11}B NMR (86.7 MHz, $(CD_3)_2CO$ $BF_3{\cdot}OEt_2$ external) δ −6.10 [s, 1B, B(12)], −14.0 [d, 5B, J_{BH} = 169 Hz, B(2−6)], −18.3 [s, 5B, B(7−11)].

***i*-Pr_3Si(*closo*-7,8,9,10,11,12-I_6-$CB_{11}H_6$).** To a slurry of the above trityl salt (0.05g, 0.044 mmol) in toluene (20mL) was added tri-*iso*-propylsilane (0.028 g, 0.18 mmol) and then the mixture was stirred for 1 week. After filtration through a fine frit, hexane diffusion over a period of 10 days led to pale yellow crystals suitable for X-ray diffraction and ^{29}Si CPMAS NMR (97 ppm).

Ag(*closo*-7,8,9,10,11,12,-Cl_6-$CB_{11}H_6$). This compound was prepared in an analogous manner to the hexabromo analogue[9] except that its greater solubility in water required solvent volumes to be substantially reduced. ^{11}B NMR (86.7 MHz, d_6-acetone, $BF_3.OEt_2$ external) δ 1.47 (s, lB), −5.34 (s, 5B), −22.95 (d, 5B, J_{BH} = 163 Hz). Anal. Calcd for $CH_6B_{11}Cl_6Ag$: C, 2.62; H, 1.32. Found: C, 2.48; H, 1.50.

[Ph_3C](*closo*-7,8,9,10,11,12,-Cl_6-$CB_{11}H_6$). This trityl salt was prepred in an analogous manner to the hexabromo analogue[9] and isolated as orange-yellow crystals (90%).

***i*-Pr_3Si(*closo*-7,8,9,10,11,12-Cl_6-$CB_{11}H_6$).** This compound was prepared in an analogous manner to the hexaiodo analogue above and isolated in 66% yield. Anal. Calcd for $C_{10}H_{27}B_{11}Cl_6Si$: C, 23.69; H, 5.37. Found: C, 23.21; H, 5.40. ^{29}Si NMR (CPMAS) 115.0 ppm.

X-ray Diffraction. Crystals of the two silyl carboranes were mounted in thin-walled glass capillaries using Paratone-N oil and diffraction data were collected as previously described.[4] Data were corrected for absorption using an empirical ψ-scan method. A summary of the collection parameters is given in Table 2. Further information is available as supporting information.

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Computational Methods. The molecular geometries of the alkyl silicon halides and silylium cations were fully optimized using the Hartree−Fock method, with 6-31G* basis set, implemented in the programs GAUSSIAN 90[35] and GAUSSIAN 92.[36] This has been reported to give satisfactory agreement with experimentally determined bonding lengths in a range of alkyl silicon species.[3b] In the case of the Me_3Si-Cl system the Si−Cl distance was systematically varied from the equilibrium position with full geometry optimizations of all other atom coordinates.

The silicon NMR chemical shifts were calculated by either the Sum-Over-States Density Functional Perturbation Theory (SOS-DFPT) method[37] or the Gauge-Independent Atomic Orbital (GIAO) method.[38] In both types of calculation the molecular geometries optomized at the HF/6-31G* level were used with the basis sets of Kutzelnigg and Schindler[23] (IGLOII basis set). SOS-DFPT and GIAO calculations were carried out either with a modified version of the program deMon[37] or with the program GAUSSIAN 94,[39] respectively. In both cases the shifts are referenced to those calculated for Me_4Si by each method.

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Supporting Information Available: Further details of the X-ray crystal structure determinations, tables of bond lengths, bond angles, anisotropic thermal parameters, calculated hydrogen atomic coordinates, final atomic coordinates, and atom-numbering schemes for the two structures (20 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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