presence of H_2 could contribute to cometary activity at large heliocentric distances. Finally, the H_2 may also have significant effects on the chemistry associated with the gas and solid phases in these environments. Ultimately, the importance of frozen H_2 will depend on its ubiquity in space. Although difficult, the detection of the 4141-cm^{-1} H_2 feature along additional lines of sight, especially those having more normal, smaller column densities, is clearly of importance.

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19. Spectra were taken with CGS4, a cryogenic grating, two-dimensional InSb array spectrometer, capable of covering the 1- to 5-μm wavelength region at resolving powers between 200 and 20,000. These spectra of WL5 and a nearby comparison star (BS 5953) were obtained with a 150-groove-per-millimeter grating in second order, which provided a resolving power of ~1550 ($\Delta \upsilon$ = 2.7 cm^{-1} and $\Delta\lambda$ = 0.0016 μm, where λ is the wavelength). The wavelength setting of the grating was calibrated with a xenon emission-line lamp and is accurate to ~0.2 cm^{-1} (0.0001 μm; 1 SD). The total integration time on WL5 was 20 min. Individual 1-min integrations were normalized to the scan with the highest number of counts. None of the 19 individual integrations used in the coadded data had counts lower than 94% of the maximum integration period, and most were within 98 to 99% of the maximum. To calibrate flux and remove the effects of atmospheric absorption, we ratioed the spectrum of WL5 against that of BS 5953 (Fig. 1, A and B), which was assumed to have a K wave band magnitude of 3.12 and a blackbody temperature of 24,500 K. The spectrum of BS 5953 was taken directly before that of WL5, and the average air masses of the two observations agree to within 0.01 of an air mass. Despite this close agreement in air mass, small residual spectral features due to incomplete cancellation of atmospheric H_2O lines were apparent in the original ratioed data. These features were partially removed by the scaling of the comparison star data by a small factor before reduction. The base line given by the dashed line in Fig. 1B was then used to derive the optical depth plot given in Fig. 1C.
20. We thank the staff of UKIRT, which is operated by the Royal Observatory Edinburgh on behalf of the U.K. Science and Engineering Research Council, for its support of these observations. Supported also by National Aeronautics and Space Administration grants 452-33-93-03 (Origins of Solar Systems Program) and 199-52-12-04 (Exobiology Program).

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Closely Approaching the Silylium Ion (R_3Si^+)

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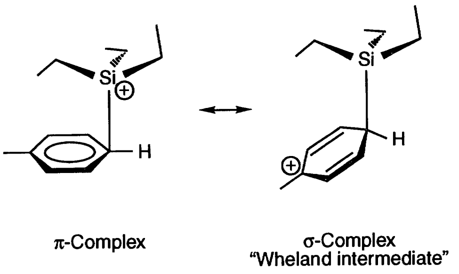
The crystal structure of the tri-isopropyl silyl species, *i*-$Pr_3Si(Br_6$-$CB_{11}H_6)$, where the brominated carborane Br_6-$CB_{11}H_6^-$ is perhaps the least nucleophilic anion presently known, has revealed the highest degree of silylium cation character (R_3Si^+) yet observed. The average C–Si–C angle is 117°, only 3° short of the planarity expected of a pure silylium ion (120°). This value compares to 114° recently reported for a toluene-solvated silyl cation, $[Et_3Si(toluene)]^+$ by Lambert and co-workers. The greater silylium ion character of *i*-$Pr_3Si(Br_6$-$CB_{11}H_6)$ versus [*i*-$Pr_3Si(toluene)]^+$ is also reflected in the larger downfield shift of the silicon-29 nuclear magnetic resonance, 109.8 versus ≤94.0 parts per million. The unusual bonding of toluene to R_3Si^+ in Lambert's compound is reinterpreted as a significant covalent π interaction.

There has been recent progress in the long search for a three-coordinate silicon cation (R_3Si^+, silylium ion) analogous to widely known carbocations (R_3C^+). Lambert *et al.* (*1*) have determined the crystal structure of the triethylsilyl cation with no coordination of the anion and weak coordination of the solvent (toluene). Indeed, the coordination of toluene with a long Si–C distance of 2.18 Å is unprecedented in silicon chemistry. It is not, however, unprecedented in silver chemistry. In a so-called η^1-benzene complex of silver(I), a similar π-complexation of an arene solvent molecule has been observed and structurally characterized (*2*). The silver ion in Ag(benzene)$(CB_{11}H_{12})$ sits almost directly over one carbon atom of the benzene ring at an Ag–C distance of 2.40 Å. This π-bonding distance is ~0.2 Å longer than typical Ag–C σ bonds (2.13 to 2.25 Å) (*3*). The 2.18 Å Si–C distance to toluene in $[Et_3Si(toluene)]^+$ (Et, ethyl) is ~0.3 Å longer than a typical average Si–C σ bond, ~1.87 Å (ranging from 1.80 to 2.03 Å) (*4*). We therefore conclude that the Si–C bond in $[Et_3Si(toluene)]^+$ is close to what should be expected for π-arene coordination to silicon.

The reality and significance of this covalent bonding is reflected in the pyramidalization of the triethylsilyl moiety. The average C–Si–C angle of the σ bonds in $[Et_3Si(toluene)]^+$ is 114°, well short of the 120° expected of a discrete sp^2 R_3Si^+ ion and is, in fact, comparable to other solvent-coordinated species such as [*i*-$Pr_3Si(acetonitrile)]^+$ (115°) (*i*-Pr, isopropyl) (*5*). Although there is good reason to expect planar R_3Si^+ to be readily deformable, particularly with bulky ligands like π-arenes, to suggest that covalent bonding may be absent and that the silicon is essentially three-coordinate (*1*, 6) overstates the case. Nevertheless, the structure has important novelty as a model for intermediates in electrophilic aromatic substitution, particularly since one might have expected a σ-type structure (known as a "Wheland intermediate") like that observed in the heptamethylbenzenium ion (*7*). Of the two idealized contributing resonance structures indicated below, a π-complex with sp^2 carbon and a σ-complex with sp^3 carbon, the best single description is as a π-complex.



π-Complex

σ-Complex
"Wheland intermediate"

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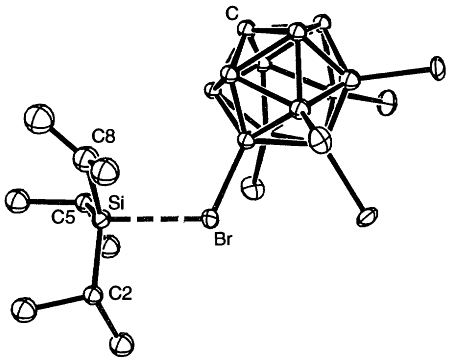

Fig. 1. Perspective view (ORTEP) of *i*-$Pr_3Si(Br_6$-$CB_{11}H_6)$. Bond distances (errors in last digits in parentheses): Si–Br = 2.479(9) Å (dashed); Si–C(2) = 1.860(27) Å; Si–C(5) = 1.908(27) Å; and Si–C(8) = 1.799(35) Å. Bond angles: C(2)–Si–C(5) = 120.2(12)°; C(2)–Si–C(8) = 111.2(14)°; and C(5)–Si–C(8) = 119.6(13)°.

The key dimension is the Si–C–C_{para} angle: 90° in the idealized π-complex and 125.3° in the idealized σ-complex. It is 94° for the analogous Ag–C–C angle in the silver-benzene complex, ~100° in Et_3Si-$(toluene)^+$, but is 124° for the corresponding C–C–C angle in the heptamethylbenzenium ion. This result suggests that the silicon-toluene bonding, although closer to the π formalism, is actually of some π/σ hybrid character. We also note that π bonding of both benzene to silver, and toluene to silicon, produces a barely detectable perturbation in the structure of the arene. The bonded carbon atom essentially retains its sp^2 planarity and, in contrast to the heptamethylbenzenium ion, which has sp^3 tetrahedrality, there is no significant alternation of the C–C bond lengths in the arene ring. As a consequence, the structure of the π-coordinated arene is not a particularly good indicator of the strength of a predominantly π-type of interaction.

We report the synthesis and characterization of an ionic-like tri-isopropylsilyl species having a very weak anion-cation interaction. By three important criteria—the average C–Si–C angle, the out-of-plane displacement of the silicon atom, and the ^{29}Si nuclear magnetic resonance (NMR) chemical shift—this species more closely approaches a free silylium ion than does its arene-coordinated counterpart.

The successful synthesis of R_3Si^+ in a condensed phase remains thwarted by reactivity toward the solvent (*1, 5, 8, 9*) or the counterion (*5, 8, 10, 11*). Not only is minimal nucleophilicity important but so is chemical inertness. In the choice of solvent, we have stayed with aromatic hydrocarbons. Although they express a nucleophilicity toward silicon, they are more chemically inert than halocarbons and are superior in dissolving the reagents. In our search for the least nucleophilic anion, we have found a possible candidate in the large 12-vertex frameworks of boron chemistry. The hexabrominated *closo*-carborane Br_6-$CB_{11}H_6^-$ (*12*) is larger than the previously introduced 10-vertex Br_5-$CB_9H_5^-$ (*5*) and hence is less nucleophilic. It has the added advantage of extremely high chemical stability. We find no evidence for bromide abstraction from Br_6-$CB_{11}H_6^-$ analogous to fluoride abstraction from fluorinated tetraphenylborates (*8, 9*). This property is particularly important, given the electrophilicity expected of R_3Si^+.

Equimolar treatment of *i*-Pr_3SiH with $[Ph_3C^+]$ [*closo*-7,8,9,10,11,12-Br_6-$CB_{11}H_6^-$] (Ph, phenyl) (*12*) in dry toluene gives a pale yellow solution from which *i*-$Pr_3Si(Br_6$-$CB_{11}H_6)$ can be isolated in good yield (*13*). Single crystals for x-ray diffraction were grown from toluene by *n*-hexane vapor diffusion (*14*). The molecular structure (Fig. 1) is qualitatively similar to that obtained with the 10-vertex carborane anion Br_5-$CB_{10}H_5^-$ (*5*) but we now have metrical accuracy that reliably reflects the developing cationic character at silicon. The average C–Si–C bond angle is 117.0°, more than two-thirds of the way from tetrahedral to trigonal planar. The Si atom is 0.30 Å out of the plane of its three bonded carbon atoms, ~0.1 Å less than in any previously reported trialkylsilyl structure. The weak binding of the anion is reflected in the long Si–Br bond of 2.479 ± 0.009 Å. This is 0.24 Å longer than a typical Si–Br bond (2.24 Å in Me_3SiBr) (*15*). A further probe of the ionic-like character of this species is to compare the coordinated B–Br bond length (2.05 ± 0.03 Å) to the other four noncoordinated bonds in the pentagonal belt of the anion (1.93 to 2.02 ± 0.03 Å). This result shows, at most, a marginal extension due to bonding to silicon and reflects a well-developed ionicity in the silicon-bromine interaction. These features, and the relatively small degree of pyramidalization at silicon, suggest that there is little in the way of bromonium ion character in this species, that is, little delocalization of positive charge onto the bromine atom.

The developing positive charge at silicon is reflected in the downfield ^{29}Si NMR chemical shift. Indeed, in the solid state, where there can be no ambiguity about anion versus solvent coordination, the chemical shift of 109.8 ppm downfield from tetramethylsilane is the largest yet observed for a tri-isopropylsilyl species. It is essentially matched by *i*-$Pr_3Si\{B(C_6F_5)_4\}$ at 107.6 ppm (*11*). We assume in this solvent-free species that the perfluorinated tetraphenylborate anion, the other most promising candidate for the least nucleophilic anion, is coordinated to the silicon via a fluorine atom or atoms. This has been structurally proven in a related ionic-like thorium species (*16*). The downfield shifts of both silyl species are attenuated by dissolution in toluene: 105 ppm for the Br_6-$CB_{11}H_6^-$ species and 94.0 ppm for the $B(C_6F_5)_4^-$ species (*5*). This result is consistent with partial solvent displacement of the anion according to the following equilibrium

$$i\text{-}Pr_3Si(\text{anion}) + \text{toluene} \rightleftharpoons [i\text{-}Pr_3Si(\text{toluene})]^+ + \text{anion}^-$$

Paradoxically, Br_6-$CB_{11}H_6^-$ dissociates less in toluene than does $B(C_6F_5)_4^-$ even though the ^{29}Si shifts of the bound species suggest that the carborane is slightly less nucleophilic toward silicon than the borate. This difference may simply reflect the role of solvation energy in the equilibrium. The aromatic $B(C_6F_5)_4^-$ anion is expected to be the better solvated anion in an aromatic solvent. The ^{29}Si shift of 94.0 ppm for $B(C_6F_5)_4^-$ system in toluene represents a maximum value for the toluene-coordinated species [*i*-$Pr_3Si(toluene)]^+$. This is because the equilibrium may not be biased completely to the right-hand side and the measured chemical shift will certainly be a weighted average of the anion-coordinated and toluene-coordinated species in solution. The low value for the toluene-coordinated cation reflects the greater pyramidalization of silicon or the greater electron density at silicon relative to the anion-coordinated species or both effects. This suggests that species with very weakly coordinated anions structurally approach a true silylium ion more closely than do their toluene-coordinated counterparts.

It is useful to view the present structure as an ionic-like species that lies along a continuum that ranges from four-coordinate covalent to trigonal-planar ionic. Ultimate success in achieving truly ionic three-coordination will require some combination of sterically more demanding and electronically more donating carbon substituents on silicon, a less nucleophilic solvent, and a more weakly coordinating anion. Alternatively, the σ-bonded carbon substituents on silicon can be replaced by heteroatoms capable of stabilizing the positive charge through π-donation. Tilley and co-workers have recently demonstrated this conclusively by using transition metal and thiolate substituents (*17*). The silylium ion character of the present anion-coordinated species is manifest in their highly electrophilic chemistry. The carborane species abstracts chloride from dichloromethane and fluoride from fluorobenzene but is stable in dry toluene for weeks. The perfluorinated borate species seems to be less stable, eventually decomposing to some *i*-Pr_3SiF.

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13. *i*-Pr_3SiH (20.1 mg, 0.127 mmol) was added to a suspension of $[Ph_3C^+][Br_6\text{-}CB_{11}H_6^-]$ (60.0 mg, 0.0698 mmol) in dry toluene (25 ml). The mixture was stirred at room temperature overnight to give a pale-yellow solution. *n*-Hexane vapor diffusion resulted in colorless crystals (35.5 mg, 66%). ^{11}B NMR (C_6D_6): −1.43 (s, 1B), −9.69 (s, 5B), and −20.06 (d, 5B). Elemental analysis: calculated for $C_{10}H_{27}B_{11}Br_6Si$, C, 15.52% and H, 3.52%; found, C, 15.59% and H, 3.57%.
14. The structure was solved by direct methods. Triclinic *P*1(bar), with unit cell parameters a = 11.124(8), b = 15.628(15), c = 8.000(9)Å, α = 94.96(8), β = 98.85(8), γ = 76.30(7)°, V = 1333(2) Å^3 for Z = 2 (errors in last digits in parentheses). Final factor R = 6.37% for 1296 reflections with $I > 3\sigma(I)$.
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Production of Perfluoroalkylated Nanospheres from Buckminsterfullerene

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Perfluoroalkylated nanospheres have been prepared by reaction of fullerenes with a variety of fluoroalkyl radicals. The latter are generated by thermal or photochemical decomposition of fluoroalkyl iodides or fluorodiacyl peroxides. Up to 16 radicals add to C_{60} to afford easily isolable fluoroalkylated derivatives. The monosubstituted radical adducts were detected by electron spin resonance in the early stages of the fluoroalkylation reactions. These spheroidal molecules are thermally quite stable, soluble in fluoroorganic solvents, chemically resistant to corrosive aqueous solutions, and more volatile than the parent fullerenes. Films of the sublimed material display properties typical for a perfluoroalkylated material.

Since the discovery of the large-scale synthesis of C_{60} (*1*), the fluorination of this molecule and the properties of $C_{60}F_n$ materials have aroused keen interest (*2*). There was the potential that unique, chemically resistant "fluorinated balls" would result that might have interesting physical properties (*3*). However, $C_{60}F_n$ compounds are unstable with respect to hydrolysis and readily lose fluoride ions, generating HF (*4*). We reasoned that perfluoroalkylation of C_{60} might provide the necessary stability against hydrolysis yet present a chemically resistant, fluorinated, hydrophobic surface to the external environment (*5*). High thermal stability might be expected for such materials because both perfluoroalkanes and C_{60} are exceptionally thermally stable.

We prepared such perfluoroalkylated nanospheres by adding perfluoroalkyl free radicals to C_{60}. These are generated by thermal or photochemical decomposition of radical precursors such as fluoroalkyl iodides, R_fI, and fluorodiacyl peroxides, R_f-C(O)O-O(O)C-R_f. We also report the electron spin resonance (ESR) detection of the radical species R_f-$C_{60}^{\cdot}$ formed in the early stages of these reactions by addition of a single fluoroalkyl radical to C_{60}. The behavior of these reaction intermediates is similar to that recently delineated for their hydrocarbon analogs (*6*). This similarity includes the tendency to form weakly bonded, dumbbell-shaped dimers R_f-C_{60}-C_{60}-R_f for which the dimer bond strength can be determined by ESR (*7*).

Heating C_{60} and excess perfluorohexyl iodide in 1,2,4-trichlorobenzene at 200°C with exclusion of oxygen produced after work-up a dark-brown glassy solid for which elemental analysis afforded the formula $C_{60}[(CF_2)_5CF_3]_{9.5}H_2$ (*8*). The electron-capture mass spectrum of this sample (*9*), facilitated by the remarkable volatility of the material, showed the addition of 6 to 12 perfluorohexyl groups to C_{60} (Fig. 1A). Although the relative intensity distribution varied somewhat for scans taken at different probe temperatures, the most intense peak always corresponded to 10 perfluorohexyl addends, consistent with the elemental analysis.

From ^{13}C nuclear magnetic resonance (NMR) spectra, evidence was obtained for an average of 8 to 10 perfluoroalkyl groups on each C_{60}. A broad resonance from 160 to 130 parts per million (ppm) was attributed to unreacted C=C double bonds on C_{60}; broad and sharp resonances from 125 to 105 ppm were assigned to perfluoroalkyl-group carbon resonances; finally, a broad resonance centered at 62 ppm was attributed to C_{60} carbons bearing perfluoroalkyl groups. The ratio of the intensity of this last resonance to that of the broad resonance between 160 and 130 ppm was about 6:1, appropriate for an average of 8 to 10 perfluoroalkyl substituents on each C_{60}. A very small extent of hydrogen incorporation was indicated by the expansion of each mass spectral peak. The expanded peak corresponding to C_{60} with 10 perfluorohexyl groups was simulated as a mixture of $C_{60}(R_f)_{10}^-$, $C_{60}(R_f)_{10}H^-$, $C_{60}(R_f)_{10}H_2^-$, $C_{60}(R_f)_{10}H_3^-$, and $C_{60}(R_f)_{10}H_4^-$ in the ratios 1.0:0.78:1.0:0.78:0.11 (Fig. 1A, inset). Consistent with this finding, ^1H NMR did show a broad resonance from 5.5 to 3.8 ppm, which we attribute to hydrogens on the C_{60} sphere. The ^{19}F NMR was more informative with resonances in the CF_2 chemical shift region and a single resonance in the CF_3 region (*10*).

Substantial coverage of C_{60} with fluoroalkyl groups can also be achieved at room temperature by photolysis of perfluoroalkyl iodides. For example, a saturated benzene solution of C_{60} with excess trifluoromethyl iodide was irradiated with ultraviolet light in a sealed quartz tube for 30 min. Electron-capture mass spectrometry showed addition of up to 13 CF_3 groups to C_{60} (Fig. 2A). Unlike the relative sharpness of the mass spectrum discussed above, each CF_3 adduct showed up as a cluster of masses, as wide as 30 mass units, indicating substantial hydrogen atom incorporation that progressively increased with the number of CF_3 groups. Negative-ion Fourier transform mass spectra (FTMS), expanded in the mass region appropriate for the addition of two and three CF_3 groups, peaked at compositions corresponding to $C_{60}(CF_3)_2H_3^-$ and C_{60}^--$(CF_3)_3H_4^-$ (Fig. 2A, inset). The peaks of all mass clusters were appropriately shifted toward higher masses when perdeuteriobenzene was used as the solvent. The hydrogen transfer from benzene most likely occurs in two steps: addition of $CF_3^{\cdot}$ radicals to benzene to yield a CF_3-substi-

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