Reed et al. recently reported (6) the x-ray structure of the triisopropylsilyl species t-iPr3Si(Br6CB1_xH6), where the brominated carborane Br6CB1_xH6− obtained was considered to be the least nucleophilic anion now known, indicating the highest degree of silylum ion character (R3Si+) yet observed. Consideration of the x-ray structure (with Si-Br bond distance of 2.479 Å) and the relevant 79Si NMR shift of 109.8 ppm indicate however, that no R3Si+ species was observed, but one in which a single bromine atom was silylated, which resulted in a polarized silylboronium zwitterion. Apparently, this zwitterionic complex was so stable that it did not even react with the toluene from which it was isolated. A R3Si+ species with the “highest degree of silylum cation character...yet observed” (6, p. 402) could not display such behavior.

Previously we have called attention (4) to pitfalls with regard to reports of observation, and even of isolation, of “free” long-lived R3Si+ ions or species with a high degree of R3Si+ character that involves “nonnucleophilic” (or “least nucleophilic”) anions and aromatic solvents. Toluene and related 15-aromatic hydrocarbons (not unlike n-coordinating solvents such as sulfones, ethers, nitriles, ketones, and halogenated systems) are unsuitable for use in obtaining long-lived trivalent tricoordinated siliconium cations; they give instead tetracoordinated silylatedonium ions (or zwitterions). Lambert et al. (1) and Reed et al. (6) report significant new results and reliable x-ray structures of isolated silylated ionic complexes. However, both groups incorrectly assign their structures to R3Si+ species (free or closely approaching them). It is not thermodynamic, but kinetic instability in all known condensed phase systems that still renders long-lived trialkylsilyl cations elusive.

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**REFERENCES AND NOTES**
2. For similar calculations on p-trimethylsilyltoluenium ion see P. V. R. Schleyer, P. Buzek, T. Müller, Y. Apeloig, H.-U. Siehl, Angew. Chem. 105, 1558 (1993).

**Response:** We are in essential agreement with Pauling’s calculation and do not believe that it is in contradiction with our own conclusions (1). In our report (contrary to Pauling’s description of it), we were careful to make no claim for a “tricoordinate,” “free,” or “three-bonded” silyl cation. Instead, we state only that there was “distinct coordination to solvent” and elsewhere that there was “weakly coordinating toluene” at the fourth coordination site. The unprecedented, long Si-C distance between Et3Si and toluene and the planarity of toluene in an η1 situation indicate that there is only weak coordination between Si and toluene. We attributed the nonplanarity of the triethylsilyl group to this interaction. Pauling provides a quantitative expression for what we described as distant or weak coordination. The energetics of this interaction, as we more recently have determined experimentally, are more akin to noncovalent interactions such as H bonds or electrostatic attractions.

We take minor issue only with the bond distance Pauling uses for D(1.0), which he derived from the sum of the Si and C covalent radii of 1.94 Å (2). Actual experimental measurements of C-Si bond lengths in unstrained structures yield a range of about 1.81 to 1.87 Å, with a mean of 1.845 Å from 20 values (3). Long bonds (1.92 to 2.03 Å) have been found only when there are extremely large substituents around Si or C (3), which is not the case for the triethylsilyl-toluene system. The longest previously measured Si-C bond length, to our knowledge, is 2.03 Å in the extremely crowded four-membered ring [(t-Bu)2Si-(t- Bu)2Si-O-CPh2-] (4), hence our use of the descriptor “unprecedented” for the distance between Et3Si and toluene.

It is the increase from the normal value of C-Si of about 1.85 Å to the observed value of 2.18 Å that provides the appropriate measure of silyl cation character. If the more likely value for D(1.0) of 1.85 Å is used in Pauling’s equation, then the calculated value of n is 0.28. Thus the structure has 65 to 72% silylum ion character and is properly termed a silyl cation. By the same reasoning, the presence of three normal covalent bonds and one very weak fourth interaction indicates that the structure has more tricoordinate than tetracoordinate character. By contrast, the C-C distance in the σ complex of CH3 to an arenic cation by us (1) is 1.56 Å (5). This number is very close to the normal value of 1.54 Å in propane or adamantane (1) and corresponds to a bond order n of 0.93 and to essentially tetracoordination. We thank Pauling for providing this refinement, which enables us to specify more quantitatively the nature of the interaction between Si and toluene in our structure.

The comment by Olah et al. contains (i) a product study, (ii) theoretical calculations of geometry, (iii) theoretical calculations of chemical shifts, and (iv) comments on another recently published report by Reed et al. (6). We shall comment about the first three subjects in turn and shall defer to Reed et al. on the fourth.

The observation of (triethylsilyl)toluene is not relevant to an assessment of the extent of bonding between Si and toluene in the stable ion observed by us in solution and in the solid, as the same product would be expected both from the σ complex (arenium ion) that Olah et al. find in the gas phase by their calculations and from the distantly coordinated system that we observed in the solid. "Inconceivable" notwithstanding, there is firm evidence that these arenes do not react with triethysilylum in solution. Reed et al. (6) recrystallize their compounds from toluene without reaction. Both Olah and Reed maintain that the carborane ion is less nucleophilic than our borate. It does not follow then that the supposedly more closely bound (to anion) Si ion in our case is more likely to react with toluene. We have observed that toluene and other solvents exchange rapidly on the NMR time scale between bound and unbound states with the silyl cation (7). Thus triethylsilylum exhibits only one 29Si peak in a mixture of benzene and toluene, with a chemical shift intermediate between those in the pure solvents. A "reaction" as envisaged by Olah et al. would have led to two distinct σ complexes. In the system methyl-diisopropylsilylum tetraakis(pentafluorophenyl)borate, the isopropyl methyls are homotopic in the 1H and 13C spectra, again indicative of fast exchange. If the exchange of solvent on Si is dissociative rather than associative, as argued by both Boudjouk (8) and Tilley (9), an upper limit of about 15 kcal mol−1 may be placed on the barrier to dissociation of Si from toluene, for the given temperature and chemical shift difference. Such an observation does not support a "reaction," but again is more akin to the energetics of H bonds or electrostatic interactions.

With regard to theoretical calculations of geometry, there are appreciable and systematic differences between the gas phase geometry calculated by Olah et al. and the observed geometry in the solid. The calculations by Schleyer et al. (10) were at a higher level (MP2(fc)/6-31G* for the H3Si+ structure), but suffered from a similar
lack of agreement with the observed structure. (See figure 1 of the comment by Olah et al. for the numbering of atoms.) (i) The calculations indicate more pronounced alternation of bond lengths within toluene, 1.424/1.370/1.403 Å according to Olah et al. and 1.429/1.367/1.405 Å according to Schleyer et al., as opposed to 1.40/1.37/1.38 Å observed by us (I). (ii) The geometry around C4 is calculated to be rather different from that of sp2, as illustrated by Olah et al. The H attached to C4 is depicted as deviating significantly from the aromatic plane. Schleyer et al. (10) calculated the C3-C4-H angle to be 117°, whereas we observed it to be 120.5°. Neither group reports the extent of deviations of C4 from the plane of the remaining five atoms, but we expect that calculated deviations are significant, as in figure 1 of the comment by Olah et al. The observed toluene molecule, however, is essentially planar, the largest C-C-C-C dihedral angle being 1.7°. (iii) The calculations misplace the Si atom considerably with respect to the arene ring, as best illustrated by the Si-C4-C1 angle, calculated by Olah et al. to be 110.3°, calculated by Schleyer et al. to be 114°, and measured by us in the crystal to be 104°. In general, the calculations give a much tighter binding between Si and toluene, as might be expected for an ion-molecule complex in the gas phase. Thus the theoretical calculations lead to misinterpretation of the observed structure in the crystal.

The theoretical calculations of Olah et al. and Schleyer et al. indicate that the 29Si chemical shift reflects geometry more than positive charge density. The observed chemical shift of about 880 to 90 reflects the geometry of thetrialkylsilyl portion of the structure, which is well reproduced by calculation, but does not address the critical issues of the positive charge density on Si and the bond order between Si and the arene. The experimental values of chemical shift are perfectly reasonable for Si with low bond order to toluene and high positive charge density.

The operational definition of a silylum ion is that positive charge is predominantly on Si, whereas that of an arenium ion (σ complex) is that positive charge is found predominantly on the arene ring and its substituents. The distinction may be made by quantifying the bond order between Si and the para C of toluene and by quantifying the amount of positive charge on Si and toluene. As noted above, Pauling's equation estimates the Si-C bond order to be 0.28 to 0.35. Schleyer et al. (10) calculate the gas-phase Wiberg bond index to be 0.44 for the complex of benzene with H3Si+. The value should be lower for Me3Si+ and even lower in the condensed phase, so that modern theory is in fundamental agreement with Pauling's method which shows that there is only about a third of a bond between Si and toluene. Schleyer et al. calculate an association energy of about 30 kcal mol-1 between Me3Si+ and toluene in the gas phase, and a lower value should be observed in condensed phase, as indicated by fast exchange on the NMR time scale. Compared with a full C-Si bond dissociation energy of 90 kcal mol-1 (11), the calculated energies also suggest about a third of a covalent bond.

The amount of charge on atoms is a more difficult quantity to assess. Schleyer et al. (10) calculate the charge on Si in the gas-phase complex between Me3Si+ and toluene to be +0.71, leaving only a small amount of charge to be distributed over the atoms of toluene. For comparison, they calculate +0.43, in the neutral methylsilane. We have been able to assess the amount of charge in toluene experimentally by examining the 13C shifts in the solid (7). Introduction of positive charge into toluene in a σ complex of the type illustrated by Olah et al. should result in appreciable downfield movement of the chemical shift for C1/C3/ C5, upfield movement for C4, and downfield movement for CH3. In the solid state, however, all these resonances are essentially unchanged from those of free toluene. Thus experiment does not support the σ complex model. None of our observations, however, are in disagreement with the n, π complex model of Reed et al. (6), which is expected to have an undistorted, planar toluene ring and charge predominantly on Si.

In summary, theoretical calculations of bond order, theoretical calculations of charge density on Si, theoretical and experimental assessments of association energies (when differences between gas and condensed phase are taken into consideration), experimental determination of 13C chemical shifts of bound toluene, and observation of fast exchange on the NMR time scale all indicate that there is about a third of a covalent bond or less between Me3Si+ and toluene and that the preponderance of positive charge is on Si. Consequently, as we concluded in our report, triethyldisilane tetrakis(pentafluorophenyl)boration is best termed a silyl cation with weak coordination to toluene.

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REFERENCES

Response: The description of Et3Si(toluene)+ as a σ silylated arenium ion by Olah et al. [and by Schleyer et al. (1)] appears to arise from an emphasis on calculated structure in preference to observed structure and from the expectation that Si chemistry will closely follow C chemistry. It is becoming apparent however, that unlike carbenium ion (R3C)+ chemistry, that the silylum ion can be approached incrementally. Thus, Et3Si(toluene)+ is a hybrid of a π-complexed silyl cation and a σ-complexed arenium ion (Scheme 1). The legitimate polemic then becomes one of degree. We concur with Lambert et al. that the observed structure is consistent with a predominant contribution from a positively charged Si rather than C species. Theoretical calculations at the HF/6-31G* level produce a value for the critical Si-C-C para angle that is too large by about 6° to 10°, thereby conferring artifactual predominance of the arenium ion structure. Olah et al. and Schleyer et al. (1) state that Si hyperconjugation could explain the long Si-C distance (2.18 Å). Hyperconjugation contributes a further resonance form of the very type they discount, that is, one with ionic R3Si+ and no covalent bond.

In fact, it was the original description by Lambert et al. (2) of Et3Si(toluene)+ as a silylum ion where "covalent bonding is weak or absent" that first stirred controversy. Weak π bonding of toluene to Si seems currently to be the best single description of the structure. Certainly the search for a free R3Si+ ion must continue, but so must the search for better theory.

In a conceptually related manner, the
Response
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