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Isolating fluorinated carbocations†

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Using carboranes as counterions, fluorinated benzyl-type carbocations such as $(p\text{-}FC_6H_4)_2CF^+$, $(p\text{-}FC_6H_4)(CH_3)CF^+$ and fluorinated trityl ions are readily isolated for X-ray and IR structural characterization.

The intermediacy of carbocations in electrophilic reactions of polyfluorinated compounds,[1] and the challenge of selective activation of fluorocarbons,[2,3] make the characterization of fluorinated carbocations important. The potential value of X-ray structural data as a complement to NMR characterization has been anticipated for some time[4] but only one report of X-ray studies has appeared. The cations $(m\text{-}CF_3\text{-}C_6H_4)(C_6H_5)CF^+$ and $(CH_3)_2CF^+$ were isolated at low temperature from superacid media and characterized as fluoroarsenate salts.[5] Given the ability of carborane counterions to stabilize carbocations such *t*-butyl cation for X-ray characterization at room temperature,[6] it is of interest to investigate whether carborane anions would confer comparable stability on fluorinated carbocations.

Fluoride ion abstraction from a fluorocarbon using a trialkyl-silyl carborane agent is a logical extension of successful chloride and triflate ion abstraction reactions with $R_3Si(carborane)$ in the formation of H(carborane) superacids from HCl and highly electrophilic alkylating reagents, R(carborane), from alkyl triflates, respectively.[7,8] Treatment of $p\text{-}F\text{-}C_6H_4\text{-}CF_3$ or CH_3CF_3 with $Et_3Si\text{-}(CHB_{11}I_{11})$ using fluorobenzene as a solvent effects immediate abstraction of fluoride at temperatures as low as $-25\,^\circ C$, as evidenced by the formation of Et_3SiF (^{19}F NMR 173.9 ppm). The highly reactive difluoro cations $p\text{-}F\text{-}C_6H_4CF_2^+$ and $CH_3CF_2^+$ are presumably formed but they apparently participate immediately in an electrophilic aromatic substitution reaction with the fluorobenzene solvent to form $(p\text{-}F\text{-}C_6H_4)_2CF^+$ ($\mathbf{1}^+$) and $(p\text{-}F\text{-}C_6H_4)(CH_3)CF^+$ ($\mathbf{2}^+$). These cations have been prepared previously for low temperature NMR characterization by fluoride abstraction from appropriate difluoromethyl precursors using SbF_5[9,10] and the arylation chemistry of fluoro carbocations has been studied extensively by Shteingarts.[1]

Single crystals of $[(p\text{-}F\text{-}C_6H_4)_2CF][CHB_{11}I_{11}]\cdot C_6H_5F$, **1**, and $[(p\text{-}F\text{-}C_6H_4)(CH_3)CF][CHB_{11}I_{11}]$, **2**, were grown from fluorobenzene solution at room temperature and $-20\,^\circ C$ respectively. Their X-ray structures[11] are shown in Figs. 1 and 2.‡ The cations are planar at their carbocationic centers having the sum of bond angles within experimental error of 360°. In contrast to the previously determined fluoroarsenate structures[5] where distances

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between the carbocationic C^+ atom and the anion F atoms (2.66–3.04 Å) are shorter than the sum of the van der Waals radii (3.17 Å),[12,13] there is no close approach of the carborane anion to the C^+ atom in **1** and **2**. The shortest $C^+\cdots I$ distance is 4.22 Å in **1** and 3.90 Å in **2** whereas the sum of the van der Waals radii is 3.68 Å.

The closest approach of the anion to the cation in **1** is indicated by three I atom contacts at 3.48, 3.55 and 3.72 Å with the F atom attached to the C^+ center. The triangular disposition of three
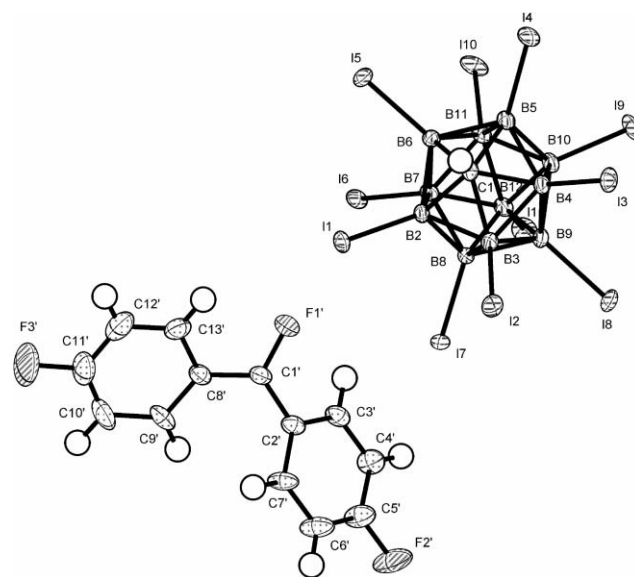

Fig. 1 Crystal structure of **1** (50% thermal ellipsoids). A C_6H_5F solvate molecule has been omitted for clarity.
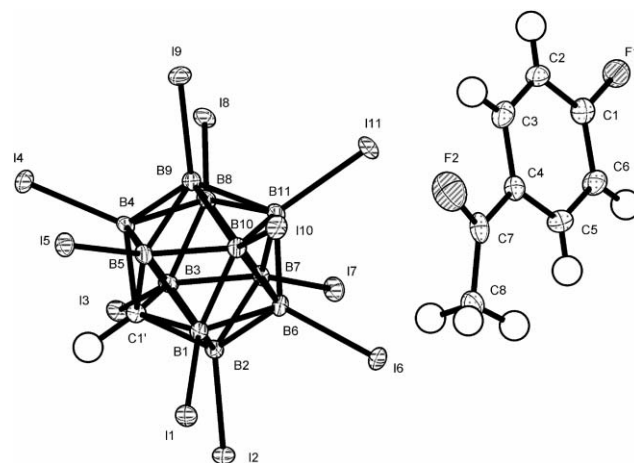

Fig. 2 Crystal structure of **2** (50% thermal ellipsoids).

halide atoms of a carborane anion towards a cation reflects the purely electrostatic nature of the interaction.[14]

The closest approach of the anion to the cation in **2** is indicated by two I atom contacts at 3.07 and 3.13 Å with H atoms of the CH_3 group. This is structural evidence for high acidity of the methyl group in this carbocation and is corroborated by IR spectroscopy. The νCH band is unusually broad and centered at very low energy (2750 cm^{-1}).

The sp^2 C$^+$–F bond lengths are 1.300(4) and 1.302(4) Å for **1** and **2** respectively, shorter than the average 1.342 Å for the sp^2 C–F bonds of the fluorobenzyl rings. This *ca.* 0.04 Å shortening must reflect the p_π ability of F to backbond into the formally empty 2p$_z$ orbital on the C$^+$ atom. The C$^+$–F bond lengths are within three standard deviations of those in the fluoroarsenate structures, 1.316(5) Å in [(*m*-CF$_3$-C$_6$H$_4$)(C$_6$H$_5$)CF][AsF$_6$] and 1.28(1) Å in the less precisely determined [(CH$_3$)$_2$CF][AsF$_6$],[5] indicating less dependence on ancillary substituents than might have been expected. Even though the present structures have better *R* factors than the fluoroarsenate structures, more structural data will be necessary to understand the effect of charge distribution of C–F bond lengths. The competing effects of (a) different types of cation–anion electrostatic interactions, (b) conjugative effects of aryl substituents, and (c) hyperconjugative effects of alkyl substituents in delocalizing the positive charge cannot be presently delineated.

The C$^+$–C$_6$H$_4$F bond length of 1.430(4) Å in **2**, as well as the average of 1.436(5) Å for the same bonds in **1**, is shorter than the C$^+$–CH$_3$ bond in **2** (1.460(5) Å), reflecting the better conjugative ability of the aromatic group to stabilize the carbocationic center. The dihedral angle between the carbocation C$_2$C$^+$F plane and the fluorophenyl group in **2** is 14.1° whereas those in the more bulky **1** are 36.7 and 20.2°. These low angles are a good structural indication that p_π conjugation is occurring.

The IR band associated with νCF for the C$^+$–F group in **1** and **2** appears as a sharp, strong absorption at 1155 and 1174 cm^{-1} respectively. To the best of our knowledge, this is the first report of νCF at a carbocationic center. The frequencies are higher than νCF in neutral aliphatic fluorocarbons (*ca.* 1100 cm^{-1}),[15] reflecting the double bond character arising from p_π(F) back donation to C$^+$.

The νCF bands associated with the *p*-F-phenyl groups in **1** and **2** deserve mention because they reflect charge density on the aryl ring. Frequencies increase in the order fluorobenzene < (*p*-F-C$_6$H$_4$)$_2$CF$^+$ < (*p*-F-C$_6$H$_4$)(CH$_3$)CF$^+$ < protonated *p*-fluorobenzene[16] with values of 1239, 1265, 1290 and 1308 cm^{-1} respectively, as expected from size-to-charge considerations.

While **2** slowly decomposes at room temperature, the (*p*-F-C$_6$H$_4$)$_2$CF$^+$ cation in **1** simply converts over several days in fluorobenzene to the (*p*-F-C$_6$H$_4$)$_3$C$^+$ trityl ion, detected by UV–vis spectroscopy some years ago.[17] Thus, all of the C–F bonds of the original trifluoromethyl group have been broken, two of them being converted to C–C bonds. In an analogous reaction using the more highly fluorinated substrate *p*-CH$_3$-C$_6$H$_4$-CF$_3$ with Et$_3$Si-(CHB$_{11}$Cl$_{11}$) in fluorobenzene as solvent, the new trityl ion (*p*-F-C$_6$H$_4$)$_2$(*p*-CH$_3$-C$_6$F$_4$)C$^+$ is formed. Single crystals of the carborane salts [(*p*-F-C$_6$H$_4$)$_3$C][CHB$_{11}$I$_{11}$]·1.5C$_6$H$_5$F, **3**, and [(*p*-F-C$_6$H$_4$)$_2$(*p*-CH$_3$-C$_6$F$_4$)][CHB$_{11}$Cl$_{11}$]·1.5C$_6$H$_5$F, **4**, were formed readily and the X-ray structures determined.‡[11]

The structures of the cations in **3** and **4** are generally similar to those of unfluorinated trityl ions and that in **4** is shown in Fig. 3.
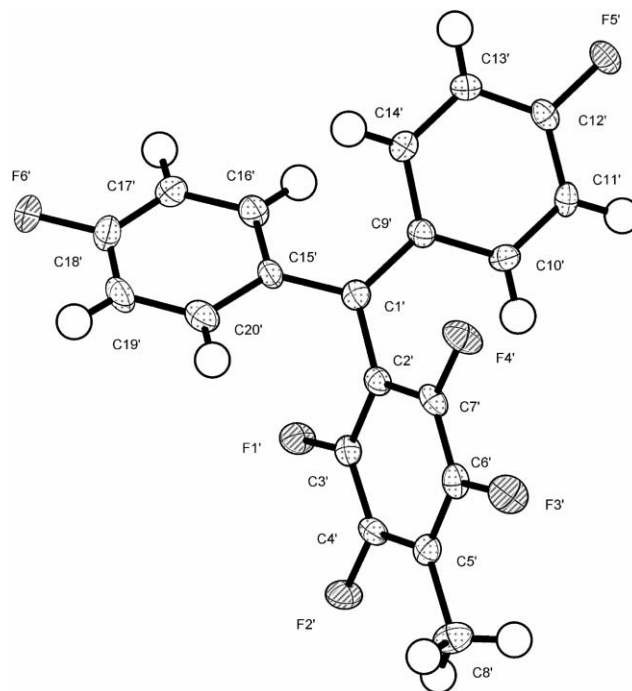

Fig. 3 Perspective view of the [(*p*-F-C$_6$H$_4$)$_2$(*p*-CH$_3$-C$_6$F$_4$)C]$^+$ cation in **4** (50% thermal ellipsoids).

They adopt propeller configurations with dihedral angles between the aryl groups and carbocation plane in the range 28–46°. However, unlike structures with fluoroanions,[18,19] there are no close approaches of anion atoms to the carbocationic C atom. With their large size and low charge density, carborane anions tend to yield cation structures in their most "free" or intrinsic state. One feature of **4** that appears to be significant is the long C$^+$–C$_{ipso}$ bond to the tetrafluorophenyl group (1.460(4) Å). This compares to the average of 1.436(5) Å for the fluorophenyl rings in the same cation, the average of 1.439(6) for the three fluorophenyl rings in **3**, and the average of 1.443(3) Å in the unfluorinated trityl salt with the BF[C$_6$F$_4$(C$_6$F$_5$)$_3$]$^-$ anion.[19] Short distances are observed between the *ortho* F atoms and the C$^+$ center (2.831 and 2.858 Å compared to 3.17 sum of the van der Waals radii for C and F), suggesting intramolecular stabilization of positive charge. This would diminish the necessity of p_π conjugative stablization of charge by the aryl group and lengthen the C$^+$–C$_{ipso}$ bond.

In summary, this work shows that the use of carborane counterions instead of those from traditional superacids (fluoroarsenates and fluorantimonates) allows the intrinsic stability of fluorinated carbocations to be demonstrated. Corrosive media such as AsF$_5$ or SbF$_5$ can be avoided and long lived fluorinated carbocations can be produced in common organic solvents. The good crystallizing properties of carborane salts allow single crystals to be readily grown for X-ray characterization and IR analysis. The limitation to stabilizing more highly reactive fluorinated carbocations is now the solvent, not the anion. Future work with carboranes in less nucleophilic solvents (*e.g.* SO$_2$, SO$_2$ClF) is anticipated to lead to the isolation of more highly fluorinated cations such as *di*fluoro carbocations (RCF$_2$$^+$).

Notes and references

‡ CCDC 629487–629490. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b617606b

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