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Triethylsilyl Perfluoro-Tetraphenylborate, $[Et_3Si^+][F_{20}\text{-}BPh_4^-]$, a widely used Non-Existent Compound

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Abstract

The commonly used triethylsilyl per-fluoro-tetraphenylborate salt, $[Et_3Si^+][F_{20}\text{-}BPh_4^-]$, has been misidentified. As prepared, the cation is a hydride-bridged silane adduct $[R_3Si\text{-}H\text{-}SiR_3^+]$. Under favorable circumstances it can be an effective source of the triethylsilylium ion Et_3Si^+ but in the absence of a stabilizing base the potent electrophilicity of Et_3Si^+ decomposes the “inert” $F_{20}\text{-}BPh_4^-$ counterion.

Over the past decade, R_3Si^+ silylium ion chemistry has progressed from controversy over their existence[1–6] to an exploitation of their potent electrophilicity in stoichiometric reactions[7] and, most impressively, in catalytic chemistry.[8] These advances owe much to the availability of very weakly coordinating anions,[9,10] particularly carborane anions[7] and the perfluorinated tetraphenylborate anion[11] (abbrev. $F_{20}\text{-}BPh_4^-$ or $PFTPB^-$).

A frequently used reagent in this silylation chemistry is the so-called triethylsilyl perfluorotetraphenylborate salt $[Et_3Si^+][F_{20}\text{-}BPh_4^-]$, first reported by Lambert.[12,13] It is a versatile reagent for the abstraction of halide ions from transition metal complexes and from main group element compounds to give reactive, coordinatively unsaturated cations with $F_{20}\text{-}BPh_4^-$ counterions. As liquid clathrates or “swirls”, such salts have high effective solubilities in low dielectric solvents making them very suitable for cationic catalysis. The reagent is readily prepared by reaction of the trityl salt of the $F_{20}\text{-}BPh_4^-$ anion with triethylsilane, both starting materials being commercially available (Eq. 1).

$$Et_3SiH+[Ph_3C^+][PFTPB^-] \rightarrow [Et_3Si^+][PFTPB^-]+Ph_3CH \tag{1}$$

Given that all solvents, even those as weakly coordinating as benzene,[13] dichlorobenzene and liquid SO_2[14] coordinate to the Et_3Si^+ ion forming $[Et_3Si(solvent)]^+$ cations, $[Et_3Si^+][F_{20}\text{-}BPh_4^-]$ was prepared in the “absence” of solvent, or more correctly, using excess triethylsilane reagent as solvent.[13] Evaporation of the excess silane gave a white powder which was characterized by CPMAS NMR as $[Et_3Si^+][F_{20}\text{-}BPh_4^-]$. The lack of any detectable difference in the ^{19}F NMR of the anion between the presumed $[Et_3Si^+][F_{20}\text{-}BPh_4^-]$ and the corresponding trityl ion salt of $F_{20}\text{-}BPh_4^-$ led to the conclusion that the $F_{20}\text{-}BPh_4^-$ anion was not coordinated to silicon.[13] Lending some support to this ionic formulation is the more recent report of the X-ray crystal structure of the Me_3Si^+ moiety partnered with the most weakly coordinating carborane anion, the undeca-fluorinated $RCB_{11}F_{11}^-$ ion.[15] The sum of the three C-Si-C angles in the Me_3Si moiety in

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Supporting Information. Synthetic details and spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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$Me_3Si(RCB_{11}F_{11})$ is 354.4°, only ca. 6° short of the planarity expected for a Me_3Si^+ ion. The Si atom is 0.25 Å out of the plane of the three C atoms towards the carborane anion. While perhaps not strictly ionic, this compound is certainly ion-like.

However, during routine characterization of the presumed $[Et_3Si^+][F_{20}\text{-}BPh_4^-]$ salt we noticed that its ATR-IR spectrum contained an unanticipated strong absorption at ca. 1900 cm^{-1}. We had noticed this band earlier while characterizing the hydride-bridged disilyl cation $[Et_3Si\text{-}H\text{-}SiEt_3]^+$ as a $CHB_{11}Cl_{11}^-$ carborane salt and assigned it to $\nu_{as}SiHSi$.[14] Even the distinctive shape of the band was reproduced (see Fig. 1). It is immediately evident that the so-called silylium ion salt $[Et_3Si^+][F_{20}\text{-}BPh_4^-]$ salt is, in fact, isolated as a silane adduct thereof: $[Et_3Si\text{-}H\text{-}SiEt_3][F_{20}\text{-}BPh_4]$. Once again, the solvent is coordinated to the silylium ion (Eq. 2).

$$2Et_3SiH + Ph_3C[F_{20}-BPh_4] \rightarrow [Et_3Si-H-SiEt_3][F_{20}-BPh_4] + Ph_3CH \qquad (2)$$

The same result is obtained whether pure silane or a silane/hexane mixture is used as solvent, as long as at least 2 equiv. of silane are present. When the formation reaction is carried out with only one equivalent of Et_3SiH, ^1H NMR indicates that only half of the trityl ion is consumed. The reaction appears to be general. When trimethyl- and tri-*i*-propylsilane are substituted for triethylsilane, the products have the same characteristic IR band of a $[R_3Si\text{-}H\text{-}SiR_3]^+$ cation (see Supp. Info.). The products have the correct elemental analyses for $[R_3Si\text{-}H\text{-}SiR_3][F_{20}\text{-}BPh_4]$ salts. In addition, the presence of a displaceable equivalent of volatile silane was established by ^1H NMR for the isolated triethylsilane product by dissolving it in benzene and integrating $[Et_3Si(benzene)]^+$ against a hexamethylbenzene internal standard.

This finding offers a note of caution to those using so-called "$[Et_3Si][F_{20}\text{-}BPh_4]$" in synthesis.[16–33] When prepared using excess silane as the sole solvent (or when using excess silane mixed with a non-coordinating solvent for the Et_3Si^+ ion, e.g. an alkane) the isolated product will be $[Et_3Si\text{-}H\text{-}SiEt_3][F_{20}\text{-}BPh_4]$ not $[Et_3Si][F_{20}\text{-}BPh_4]$. Because of its higher molecular weight, stoichiometries in subsequent metathesis reactions may therefore be miscalculated. Fortunately, the "extra" equivalent of silane is usually displaced during a silylation reaction and escapes the reaction as an innocent volatile byproduct. Indeed, those[22–33] who pre-dissolve $[Et_3Si\text{-}H\text{-}SiEt_3][F_{20}\text{-}BPh_4]$ in a solvent that is coordinating to the Et_3Si^+ ion, e.g. arenes, ethers etc., will displace the silane forming $R_3Si(solvent)^+$ cations as the active silylating agents. Silane may be seen bubbling off.

These observations beg the question "Does $[Et_3Si][F_{20}\text{-}BPh_4]$ really exist?" The answer appears to be no. When a film of $[Et_3Si\text{-}H\text{-}SiEt_3][F_{20}\text{-}BPh_4]$ is deposited on the windows of an evacuable IR cell and pumped at 10^{-6} torr for 6 hours, no loss of intensity of the $\nu_{as}SiHSi$ band is observed, i.e., silane is not removed from the $[Et_3Si\text{-}H\text{-}SiEt_3]^+$ cation under high vacuum at room temperature. When heated under vacuum to 65 °C the colorless product turns black and tris(pentafluorophenyl)boron[34] is an identifiable sublimate. The cleavage of a pentafluorophenyl group from the $F_{20}\text{-}BPh_4^-$ anion is consistent with a growing number of reports that this anion is unstable towards strong electrophiles including H^+,[35] "naked" Ag^+,[36] and R_3Si^+.[17] Nevertheless, there is one report of $[Me_3Si][F_{20}\text{-}BPh_4]$ as a colorless solid with Mp. 137 °C, no IR band in the region expected for $\nu_{as}SiHSi$, and an acceptable C,H elemental analysis.[37] When we repeated the described synthetic procedure we observed only the formation of $[Me_3Si\text{-}H\text{-}SiMe_3][F_{20}\text{-}BPh_4]$.[38]

In summary, there is no evidence for the existence of $[Et_3Si][F_{20}\text{-}BPh_4]$. The "as prepared" material is the silane adduct $[Et_3Si\text{-}H\text{-}SiEt_3][F_{20}\text{-}BPh_4]$ and our attempts to remove the

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silane under vacuum lead to decomposition of the F_{20}-BPh_4^- anion. Only halogenated carborane anions are stable to the fierce electrophilicity of the Et_3Si^+ silylium ion.[7,15,39] A truly free trialkylsilylium ion exists only in the gas phase.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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ABBREVIATIONS

F_{20}-BPh_4^-	perfluorinated tetraphenylborate anion

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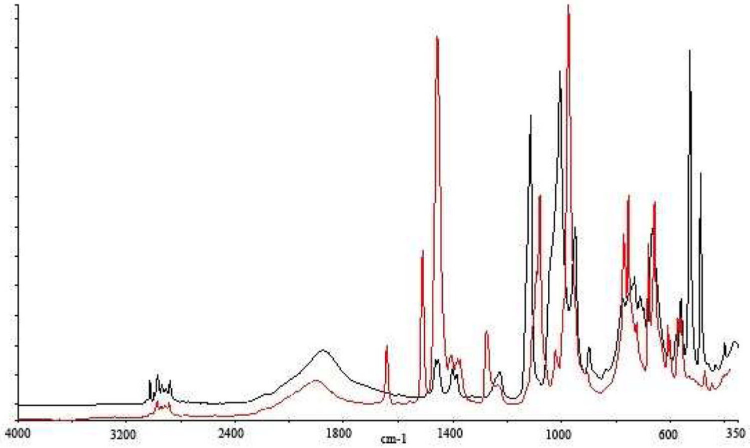

Fig. 1.

ATR IR spectra of $[Et_3Si\text{-}H\text{-}SiEt_3]^+Y^-$ for Y = F_{20}-BPh_4^- (red) and $CHB_{11}Cl_{11}^-$ (black) showing the distinctive ν_{as}SiHSi band near 1900 cm^{-1}.