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### Authors

Nava, Matthew  
Reed, Christopher A

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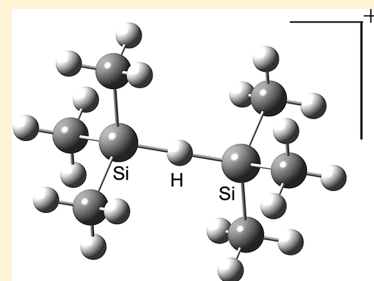
# Triethylsilyl Perfluoro-Tetraphenylborate, $[\text{Et}_3\text{Si}^+][\text{F}_{20}\text{-BPh}_4^-]$ , a Widely Used Nonexistent Compound

Matthew Nava and Christopher A. Reed\*

Center for *s* and *p* Block Chemistry, Department of Chemistry, University of California, Riverside, California 92521, United States

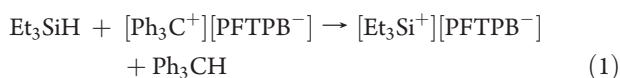
Supporting Information

**ABSTRACT:** The commonly used triethylsilyl perfluoro-tetraphenylborate salt,  $[\text{Et}_3\text{Si}^+][\text{F}_{20}\text{-BPh}_4^-]$ , has been misidentified. As prepared, the cation is a hydride-bridged silane adduct  $[\text{R}_3\text{Si}-\text{H}-\text{SiR}_3^+]$ . Under favorable circumstances it can be an effective source of the triethylsilylium ion  $\text{Et}_3\text{Si}^+$ , but in the absence of a stabilizing base the potent electrophilicity of  $\text{Et}_3\text{Si}^+$  decomposes the “inert”  $\text{F}_{20}\text{-BPh}_4^-$  counterion.

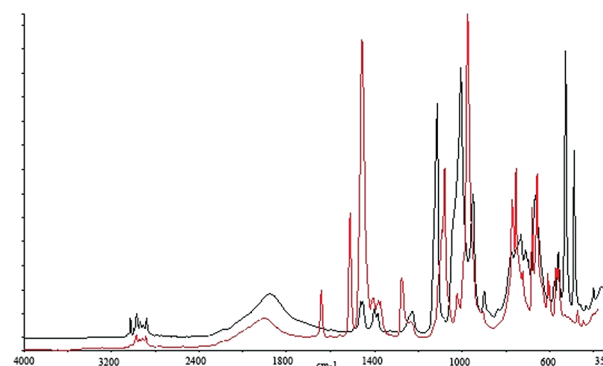


Over the past decade,  $\text{R}_3\text{Si}^+$  silylium ion chemistry has progressed from controversy over their existence<sup>1–6</sup> to an exploitation of their potent electrophilicity in stoichiometric reactions<sup>7</sup> and, most impressively, in catalytic chemistry.<sup>8</sup> These advances owe much to the availability of very weakly coordinating anions,<sup>9,10</sup> particularly carborane anions<sup>7</sup> and the perfluorinated tetraphenylborate anion<sup>11</sup> (abbreviated  $\text{F}_{20}\text{-BPh}_4^-$  or  $\text{PFTPB}^-$ ).

A frequently used reagent in this silylation chemistry is the so-called triethylsilyl perfluorotetraphenylborate salt  $[\text{Et}_3\text{Si}^+][\text{F}_{20}\text{-BPh}_4^-]$ , first reported by Lambert.<sup>12,13</sup> 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  $\text{F}_{20}\text{-BPh}_4^-$  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  $\text{F}_{20}\text{-BPh}_4^-$  anion with triethylsilane, both starting materials being commercially available (eq 1).



Given that all solvents, even those as weakly coordinating as benzene,<sup>13</sup> dichlorobenzene, and liquid  $\text{SO}_2$ ,<sup>14</sup> coordinate to the  $\text{Et}_3\text{Si}^+$  ion forming  $[\text{Et}_3\text{Si}(\text{solvent})]^+$  cations,  $[\text{Et}_3\text{Si}^+][\text{F}_{20}\text{-BPh}_4^-]$  was prepared in the “absence” of solvent, or more correctly, using excess triethylsilane reagent as solvent.<sup>13</sup> Evaporation of the excess silane gave a white powder, which was characterized by CPMAS NMR as  $[\text{Et}_3\text{Si}^+][\text{F}_{20}\text{-BPh}_4^-]$ . The lack of any detectable difference in the  $^{19}\text{F}$  NMR of the anion between the presumed  $[\text{Et}_3\text{Si}^+][\text{F}_{20}\text{-BPh}_4^-]$  and the corresponding trityl ion salt of  $\text{F}_{20}\text{-BPh}_4^-$  led to the conclusion that the  $\text{F}_{20}\text{-BPh}_4^-$  anion was not coordinated to silicon.<sup>13</sup> Lending some support to this ionic formulation is the more recent report of the X-ray crystal structure of the  $\text{Me}_3\text{Si}^+$  moiety partnered with the most



**Figure 1.** ATR IR spectra of  $[\text{Et}_3\text{Si}-\text{H}-\text{SiEt}_3]^+\text{Y}^-$  for  $\text{Y} = \text{F}_{20}\text{-BPh}_4^-$  (red) and  $\text{CHB}_{11}\text{Cl}_{11}^-$  (black) showing the distinctive  $\nu_{\text{as}}\text{SiHSi}$  band near  $1900\text{ cm}^{-1}$ .

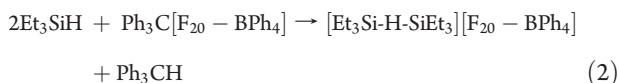
weakly coordinating carborane anion, the undeca-fluorinated  $\text{RCB}_{11}\text{F}_{11}^-$  ion.<sup>15</sup> The sum of the three C–Si–C angles in the  $\text{Me}_3\text{Si}$  moiety in  $\text{Me}_3\text{Si}(\text{RCB}_{11}\text{F}_{11})$  is  $354.4^\circ$ , only ca.  $6^\circ$  short of the planarity expected for a  $\text{Me}_3\text{Si}^+$  ion. The Si atom is  $0.25\text{ \AA}$  out of the plane of the three C atoms toward the carborane anion. While perhaps not strictly ionic, this compound is certainly ion-like.

However, during routine characterization of the presumed  $[\text{Et}_3\text{Si}^+][\text{F}_{20}\text{-BPh}_4^-]$  salt we noticed that its ATR-IR spectrum contained an unanticipated strong absorption at ca.  $1900\text{ cm}^{-1}$ . We had noticed this band earlier while characterizing the hydride-bridged disilyl cation  $[\text{Et}_3\text{Si}-\text{H}-\text{SiEt}_3]^+$  as a  $\text{CHB}_{11}\text{Cl}_{11}^-$  carborane salt and assigned it to  $\nu_{\text{as}}\text{SiHSi}$ .<sup>14</sup> Even the distinctive shape of the band was reproduced (see Figure 1). It is immediately evident that the so-called silylium ion salt  $[\text{Et}_3\text{Si}^+][\text{F}_{20}\text{-BPh}_4^-]$  is, in fact,

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isolated as a silane adduct thereof:  $[\text{Et}_3\text{Si}-\text{H}-\text{SiEt}_3][\text{F}_{20}\text{-BPh}_4]$ . Once again, the solvent is coordinated to the silylium ion (eq 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 1 equiv of  $\text{Et}_3\text{SiH}$ ,  $^1\text{H}$  NMR indicates that only half of the trityl ion is consumed. The reaction appears to be general. When trimethyl- and triisopropylsilane are substituted for triethylsilane, the products have the same characteristic IR band of a  $[\text{R}_3\text{Si}-\text{H}-\text{SiR}_3]^+$  cation (see Supporting Information). The products have the correct elemental analyses for  $[\text{R}_3\text{Si}-\text{H}-\text{SiR}_3][\text{F}_{20}\text{-BPh}_4]$  salts. In addition, the presence of a displaceable equivalent of volatile silane was established by  $^1\text{H}$  NMR for the isolated triethylsilane product by dissolving it in benzene and integrating  $[\text{Et}_3\text{Si}(\text{benzene})]^+$  against a hexamethylbenzene internal standard.

This finding offers a note of caution to those using so-called “ $[\text{Et}_3\text{Si}][\text{F}_{20}\text{-BPh}_4]$ ” in synthesis.<sup>16–33</sup> When prepared using excess silane as the sole solvent (or when using excess silane mixed with a noncoordinating solvent for the  $\text{Et}_3\text{Si}^+$  ion, e.g., an alkane), the isolated product will be  $[\text{Et}_3\text{Si}-\text{H}-\text{SiEt}_3][\text{F}_{20}\text{-BPh}_4]$  not  $[\text{Et}_3\text{Si}][\text{F}_{20}\text{-BPh}_4]$ . 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<sup>22–33</sup> who predissolve  $[\text{Et}_3\text{Si}-\text{H}-\text{SiEt}_3][\text{F}_{20}\text{-BPh}_4]$  in a solvent that is coordinating to the  $\text{Et}_3\text{Si}^+$  ion, e.g., arenes and ethers, will displace the silane, forming  $\text{R}_3\text{Si}(\text{solvent})^+$  cations as the active silylating agents. Silane may be seen bubbling off.

These observations beg the question, “does  $[\text{Et}_3\text{Si}][\text{F}_{20}\text{-BPh}_4]$  really exist?” The answer appears to be no. When a film of  $[\text{Et}_3\text{Si}-\text{H}-\text{SiEt}_3][\text{F}_{20}\text{-BPh}_4]$  is deposited on the windows of an evacuable IR cell and pumped at  $10^{-6}$  Torr for 6 h, no loss of intensity of the  $\nu_{\text{as}}\text{SiHSi}$  band is observed; that is, silane is not removed from the  $[\text{Et}_3\text{Si}-\text{H}-\text{SiEt}_3]^+$  cation under high vacuum at room temperature. When heated under vacuum to 65 °C, the colorless product turns black and tris(pentafluorophenyl)boron<sup>34</sup> is an identifiable sublimate. The cleavage of a pentafluorophenyl group from the  $\text{F}_{20}\text{-BPh}_4^-$  anion is consistent with a growing number of reports that this anion is unstable toward strong electrophiles including  $\text{H}^+$ ,<sup>35</sup> “naked”  $\text{Ag}^+$ ,<sup>36</sup> and  $\text{R}_3\text{Si}^+$ .<sup>17</sup> Nevertheless, there is one report of  $[\text{Me}_3\text{Si}][\text{F}_{20}\text{-BPh}_4]$  as a colorless solid with mp 137 °C, no IR band in the region expected for  $\nu_{\text{as}}\text{SiHSi}$ , and an acceptable C,H elemental analysis.<sup>37</sup> When we repeated the described synthetic procedure, we observed only the formation of  $[\text{Me}_3\text{Si}-\text{H}-\text{SiMe}_3][\text{F}_{20}\text{-BPh}_4]$ .<sup>38</sup>

In summary, there is no evidence for the existence of  $[\text{Et}_3\text{Si}][\text{F}_{20}\text{-BPh}_4]$ . The “as prepared” material is the silane adduct  $[\text{Et}_3\text{Si}-\text{H}-\text{SiEt}_3][\text{F}_{20}\text{-BPh}_4]$ , and our attempts to remove the silane under vacuum led to decomposition of the  $\text{F}_{20}\text{-BPh}_4^-$  anion. Only halogenated carborane anions are stable to the fierce electrophilicity of the  $\text{Et}_3\text{Si}^+$  silylium ion.<sup>7,15,39</sup> A truly free trialkylsilylium ion exists only in the gas phase.

## ■ ASSOCIATED CONTENT

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

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [chris.reed@ucr.edu](mailto:chris.reed@ucr.edu).

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