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H^+, CH_3^+ and R_3Si^+ Carborane Reagents: When Triflates Fail

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CONSPECTUS

For decades, triflic acid, methyl triflate and trialkylsilyl triflate reagents have served synthetic chemistry well as clean, strong electrophilic sources of H^+, CH_3^+ and R_3Si^+ respectively. However, a number of weakly basic substrates are unreactive towards these reagents. In addition, triflate anion can express undesired nucleophilicity towards electrophilically activated substrates.

In this Account, we describe methods that replace triflate-based electrophilic reagents with carborane reagents. Using carborane anions of type $CHB_{11}R_5X_6^-$ (R = H, Me, X; X = Br, Cl) – members of a class of notably inert, weakly nucleophilic anions – instead of triflate significantly increases the electrophilicity of these reagents and shuts down subsequent nucleophilic chemistry of the anion. Thus, H(carborane) acids cleanly protonate benzene, phosphabenzene, C_{60} etc. while triflic acid does not. Similarly, CH_3(carborane) reagents can methylate substrates that are inert to boiling neat methyl triflate, including benzene, phosphabenzenes, phosphazenes, and the pentamethylhydrazinium ion which forms the dipositive ethane analogue, $Me_6N_2^{2+}$. Methyl carboranes are also surprisingly effective in abstracting hydride from simple alkanes to give isolable carbocation salts e.g. *t*-butyl cation.

Trialkylsilyl carborane reagents, R_3Si(carborane), abstract halides from substrates to produce cations of unprecedented reactivity. For example, fluoride is extracted from freons to form carbocations, chloride is extracted from $IrCl(CO)(PPh_3)_2$ to form a coordinatively-unsaturated iridium cation that undergoes oxidative addition with chlorobenzene at room temperature, and silylation of *cyclo*-$N_3P_3Cl_6$ produces a catalyst for the polymerization of phosphazenes that functions at room temperature. Although currently too expensive for widespread use, carborane reagents are nevertheless of considerable interest as specialty reagents for making reactive cations and catalysts.

1. Introduction

Chemists often reach for triflic acid, methyl triflate (or a Me_3O^+ Meerwein oxonium salt) and trimethylsilyl triflate when strongly electrophilic sources of H^+, Me^+ and Me_3Si^+ are required. Over the last half century, these triflate reagents have replaced their corresponding halides (e.g. HCl, MeI and Me_3SiI) in a wide variety of applications.

The success of triflate reagents is due to the lower basicity and chemical inertness of the triflate anion ($CF_3SO_3^-$) relative to halides. Triflate is a better leaving group in the reagent and is less likely to interfere as a nucleophile in subsequent chemistry of the electrophilically activated substrate. The triflate anion also lends useful solubility to compounds, particularly in coordination compounds of both main group and transition metal elements, thereby promoting cation-like reactivity.[1] Finally, triflic acid is available on a tank car scale, making triflate reagents affordable.

SUPPORTING INFORMATION: Synthetic procedures for commonly used carborane reagents. This is available free of charge at http://pubs.acs.org.

Triflate reagents now find themselves in a position related to halide reagents 50 years ago. Many weakly basic molecules (e.g. benzene, C_{60}, phosphabenzenes, phosphazenes, Xe, etc.) are not protonated, alkylated or silylated by triflate reagents, or if they are, their cationic products react in unwanted ways with the triflate nucleophile. Traditionally, electrophilic reagents have been rendered more potent by the addition of a Lewis acid such as $AlCl_3$ in Friedel-Crafts-type chemistry, or SbF_5 in superacid chemistry. However, the addition of a Lewis acid can result in messy reaction conditions, the presence of halide can interfere with desired outcomes and excess Lewis acid can suppress the nucleophilicity of the substrate via adduct formation. In addition, SbF_5 is a potent oxidant. It decomposes many molecules and glassware is corroded when HF is produced from trace water.

Carborane reagents avoid most of these difficulties. Carborane acids protonate a number of weakly basic molecules that are not protonated by triflic acid. Moreover, the inertness of a carborane anion as the conjugate base means that ensuing nucleophilic or oxidative chemistry is suppressed. Methyl carboranes can react with molecules that are inert to boiling neat methyl triflate. Trialkylsilyl carboranes are able to silylate substrates that are unreactive towards trialkylsilyl triflates. Because they are expensive to produce, however, carborane reagents are not yet available for bulk use. Nevertheless, sufficient new organic and inorganic chemistry has been demonstrated with carborane reagents over the past few years to warrant an account of their potential as new specialty reagents for electrophilic chemistry.

The chemistry described in this account is possible because carborane anions of the type $CHB_{11}R_5X_6^-$ (R = H, Me, X; X = halogen) (Figure 1) are amongst the least basic and most chemically inert anions presently known.[2,3] Their exceptional stability derives from σ aromaticity in the icosahedral CB_{11} core. In addition, the delocalized negative charge is screened by a layer of halogen substituents. By all measures, they are weaker bases,[4] weaker nucleophiles and more weakly coordinating anions than triflate.[5] In main group and transition metal coordination chemistry, anions such as the perfluorinated tetraphenylborates (F_{20}-BPh_4^-) are often competitive with carborane anions as the most weakly coordinating anions,[6,7] and they are cheaper, but with potent hard electrophiles such as H^+, CH_3^+ and R_3Si^+, the corresponding reagents do not exist or are problematic to use. The acid $H(F_{20}\text{-}BPh_4^-)$, although predicted to be extremely strong,[8] cannot be prepared because the anion is unstable with respect to B-phenyl bond cleavage.[9] Only the much weaker dietherate acid, $[H(Et_2O)_2^+][F_{20}\text{-}BPh_4^-]$ is known.[10] There are no reports of $CH_3(F_{20}\text{-}BPh_4)$. $R_3Si(F_{20}\text{-}BPh_4)$ reagents[11] do not crystallize well for easy handling and may be unwittingly contaminated with silane in the form of the $[R_3Si\text{-}H\text{-}SiR_3]^+$ cation.[12]

The choice of a specific carborane anion for a particular reagent is made on the basis of inertness, basicity, solubility and ease of preparation. Typically, the parent carborane, $CHB_{11}H_{11}^-$, has to be at least hexa-halogenated at boron (in the 7-12 positions, antipodal to C at 1) to achieve the required level of inertness. Inertness increases with the extent of halogenation, presumably because halide substituents screen the negative charge and create an impervious layer that protects the CB_{11} core from chemical attack. Anion basicity decreases in the order I > Br > Cl > F which can be ascribed to decreasing polarizability of the halide. Thus, the *undeca*chloro reagent $R_3Si(CHB_{11}Cl_{11})$ is a stronger silylating reagent than the corresponding *hexa*chloro reagent, which is stronger than the corresponding *hexabromo* reagent. The fluorinated carborane[13] and borane[14] anions developed in the Strauss lab should give even stronger electrophilic reagents[15] but these anions are only available to those willing to work with F_2. The easiest carboranes to prepare are the hexa- and undeca-halo anions of the more conveniently used halogens. For the convenience of readers, the most commonly used synthetic procedures are gathered together in the Supporting Information along with typical NMR and IR characterization data. Salts of the undecachloro anion, $CHB_{11}Cl_{11}^-$,[16] have better solubility in chlorocarbon solvents than most other carborane anions which, together with its extreme inertness and good crystallizing ability, has made it a favorite in our laboratories. With the hexane-soluble permethylated carborane, unique electrophilic Li^+ chemistry has been developed in the Michl labs.[17,18]

2. Protonation

Anhydrous carborane acids, H(carborane), are prepared by treatment of solid trialkylsilyl carboranes with condensed HCl (Eq. 1).

$$R_3Si(carborane)_{(s)}+HCl_{(l)} \rightarrow H(carborane)_{(s)}+R_3SiCl_{(l)} \tag{1}$$

They are solids having bridged-proton linear chain structures (Fig. 2).[19] By a number of measures, they are the strongest Brønsted acids presently known, yet they are also the gentlest.[4] This seeming paradox can be understood by recognizing that carborane acids separate the protonating capability of an acid from the nucleophilicity and oxidizing capacity of its conjugate base in a manner not previously achieved. Nitric acid decomposes molecules because protonation activates them towards attack by the nitrate ion as a nucleophile and oxidant. This occurs to a much lesser extent with triflic acid, and even less so with carborane acids because of the exceptional inertness of their conjugate base anions.

Except in gas phase calculations,[20,8] the strength of 100% carborane acids cannot be quantified in the usual manner because they are solids not liquids. Nevertheless, we know that in dilute solution carborane acids are, at the very least, 100 times stronger than triflic acid because they protonate benzene whereas triflic acid does not.[4] Benzenium ion salts, $[C_6H_7^+][carborane^-]$, are formed and their remarkable stability allows these Wheland intermediates of electrophilic aromatic substitution to be studied by X-ray crystallography (Fig. 3).[9]

Another illustration of the strong-yet-gentle properties of carborane acids is their use in making the first cations of fullerenes.[21] While typical superacids such as HF/SbF_5 decompose fullerenes even at dry ice temperatures, carborane superacids protonate C_{60} at room temperature in o-dichlorobenzene solution to give isolable HC_{60}^+ salts. Novel solid state ^{13}C NMR methodology shows that the carbocation center has a 1,2 rather than 1,4 disposition to the site of protonation (Fig. 4).[22]

A more recent example is the protonation of the weakly basic P atom in a phosphabenzene to give an isolable salt (Fig. 5).[23] Although triflic acid is strong enough to protonate phosphabenzenes, the triflate anion reacts with the protonated product causing a rearrangement reaction, the driving force presumably being that of strong P-O bond formation. The carborane anion is a poorer nucleophile so the reaction is arrested at the protonation stage.

Carborane acids are so strong that limitations on their use are imposed by the properties of solvents. Dissolution appears to occur only in solvents that are protonated. Not only does the acidity become leveled down to that of $H(solvent)_n^+$ (typically $n = 1$ for arenes and $n = 2$ for O-atom donor solvents) but the stability of the acid depends on the stability of the protonated solvent. In the case of benzene, solubility is low but the acids have long term stability as $C_6H_7^+$ salts. $H(CHB_{11}Cl_{11})$ protonates *o*-dichlorobenzene but is stable only for ca. 2 hours at room temperature. Dichloromethane eliminates HCl and forms dialkylchloronium ions, even at subambient temperatures.[24] Carborane acids are stable in anhydrous SO_2 in the form of a proton disolvate, $H(SO_2)_2^+$, but with a boiling point of 10°C, liquid SO_2 is not so easy to handle. Carborane acids irreversibly leach water from glassware to form H_3O^+ or higher hydrated $H(H_2O)_n^+$ salts[25,26] so vigilance in drying solvents is important. Maintaining the effective concentration of water below ca. 5×10^{-4} M is difficult on a routine basis.

Carborane acids can be sublimed,[19] offering a way to overcome the problems of using solvents. Solventless reactions may allow exploitation of the full acidity of carborane acids and lead to protonation of bases hitherto unprotonated. Xenon is such a target.

3. Alkylation

Alkyl carboranes are synthesized by treatment of a triethylsilylium carborane with an alkyl triflate (Eq. 2).[27,28]

$$\mathrm{Et_3Si(carborane)+R(O_3SCF_3)} \rightarrow \mathrm{R(carborane)+Et_3Si(O_3SCF_3)} \tag{2}$$

An X-ray structure for R = *i*-Pr (Fig. 6) reveals alkylation of the carborane at the “lower” pentagonal belt (7-11 positions) but ^{1}H NMR for R = CH_3 shows that the structure is fluxional in solution with the R group also occupying the 12-position.[28] The ∠C-C-C in the *i*-propyl group is 116.5° indicating developing carbocationic character. Because of their high reactivity, the preparative reaction of alkyl carboranes is frequently carried out *in situ* with its intended substrate.

The electrophilicity of “methyl$^+$” carborane reagents was revealed to us in a rather startling manner. The most reactive reagent, $CH_3(CHB_{11}Cl_{11})$, was observed to react with hexane solvent while merely attempting to wash its crystals at sub-ambient temperatures. The product was the methyl-*cyclo*-pentyl carbocation. Indeed, tertiary carbocations are formed readily by the reaction of methyl carborane reagents with C_4 or higher hydrocarbons (Scheme 1).[29] *n*-Alkanes give rise to tertiary carbenium ions, presumably via facile 1,2 shifts.[30] The byproduct is methane. Since CD_3(carborane) produces exclusively CD_3H, the mechanism is one of hydride abstraction from the alkane. Carborane counterions add a new dimension of stability of carbenium ions allowing these reactive intermediates of hydrocarbon chemistry to be studied easily by X-ray crystallography at room temperature. The *t*-butyl cation was confirmed to be planar and its capacity to act as a C-H acid is indicated by methyl group H-bonding to the carborane anion (Fig. 7).[29]

Notable electrophilic alkylations with methyl carborane reagents involve methylation of the weakly basic N atom of phosphazenes,31 the weakly basic P atom of phosphabenzenes[23] and the synthesis of the long-sought hexamethylhydrazinium(2+) cation (Scheme 2).[32] The $Me_3N\text{-}NMe_3^{2+}$ ion is a rare case of stable dication formation with formal positive charges on adjacent atoms. Hydrazinium(2+) cations are calculated to be thermodynamically unstable with respect to “coulombic explosion”[33] but the N-N bond is sufficiently strong that kinetic stability at room temperature is achieved. Decomposition occurs because of their acidity rather than by bond homolysis.34

4. Silylation

Trialkylsilyl carboranes are prepared by hydride abstraction from a silane with trityl ion in a low-basicity arene solvent such as benzene or toluene (Eq. 3).

$$[\mathrm{Ph_3C^+}][\mathrm{carborane}]+\mathrm{R_3SiH} \rightarrow \mathrm{Ph_3CH+R_3Si(carborane)} \tag{3}$$

Structurally, they are covalent compounds (Fig. 8) but developing R_3Si^+ character is demonstrated by the long Si-Cl distance (2.32 Å) and the approach of the sum of the C-Si-C angle towards the sp^2 ideal of 360°. This angle is 351.9° in *i*-$Pr_3Si(CHB_{11}H_5Cl_6)$[35] and 354.4°

in $Me_3Si(CHB_{11}F_{11})$.[15] Although they are not free silylium ions, they react like silylium ions.[35] We have exploited their fierce electrophilicity and avidity for halide and triflate anion in producing carborane acids from HCl and methyl carboranes from methyl triflate.

Trialkylsilyl carboranes silylate many substrates that are inert to trialkylsilyl triflates. For example, they silylate phosphazenes at N to give $R_3Si(N_3P_3Cl_6)^+$ salts (Fig. 9).[31] More importantly, these silylated cations are catalysts for ring-opening polymerization (ROP) at room temperature in halocarbon solvents. Previous Lewis acid catalysis has only been achieved in a melt at 200 °C. Silylation makes the ROP reaction open to mechanistic study and potentially greater control of the polyphosphazene properties.

The potency of trialkylsilyl carboranes as halide abstractors is illustrated by their reaction with freons to give fluorocarbocations (Fig. 10).[37] This reactivity has been put to important catalytic use in the dehydrofluorination of fluoroalkanes with silanes.[38] No anion other than a carborane is inert enough to support this type of reactivity.

Trialkylsilyl carboranes are successful where silver carboranes fail in abstracting chloride ion from Vaska’s compound in arene solvents.[39] Replacement of chloride by a weakly coordinating carborane anion such as $CHB_{11}H_5Cl_6^-$ in $IrCl(CO)(PPh_3)_2$ promotes unusually facile oxidative addition of chlorobenzene, giving the coordinatively unsaturated $IrCl(CO)(C_6H_5)(PPh_3)_2]^+$ cation (Fig. 11). Similarly, trialkylsilyl carboranes abstract chloride from B(sub-phthalocyanine)Cl to give a rare example of a cationic boron Lewis acid, $B(sub\text{-}Pc)^+$ (Fig. 12).[40]

When the trialkylsilyl reagent utilizes one of the most weakly basic carborane anions, $CHB_{11}Cl_{11}^-$, silylation of weak Lewis bases such as *o*-dichlorobenzene is observed.[12] Silylation occurs at Cl rather than C (Fig. 13) to form a Cl-bound coordination compound (or silyl/aryl chloronium ion). Surprisingly, silylation of benzene has yet to be established even though silylated toluene[41] has become the textbook example for the structure of an arenium ion on the σ-π complex continuum.19

$Me_3Si(CHB_{11}Cl_{11})$ reacts with Me_3SiH to form the $[Me_3Si\text{-}H\text{-}SiMe_3]^+$ cation which has a linear hydride-bridged structure (Fig. 14).[12] This raises a caution about using excess silane in the preparative reaction of Eq. 3. With the weakest coordinating anions there is always the possibility of competition between the anion, solvent and excess silane for coordination to the R_3Si^+ moiety. The presence of the $[R_3Si\text{-}H\text{-}SiR_3]^+$ cation is most easily detected by its characteristic νSi-H band in the IR spectrum at ca. 1900 cm^{-1}.[12]

Finally, the preparative reaction for trialkylsilyl carborane formation has been used to generate the silylium moiety *in situ* and isolate the first X-ray crystallographically characterized example of a vinyl cation via intramolecular silylation of an alkyne (Scheme 1).[42] Vinyl character in this doubly β-silyl-stabilized cation is evident in the short $C^\alpha{=}C^\beta$ bond length of 1.221 Å (Fig. 15). In related chemistry, a rare example of an allyl cation has recently been isolated as a carborane salt.[43]

5. Conclusion

These examples of protonation, alkylation and silylation, where the corresponding triflate reagents fail, illustrate the greater electrophilicity of carborane reagents over their triflate counterparts. Although the increases in reagent strength for delivering H^+, R^+ and R_3Si^+ moieties to substrates have yet to be quantified by the methods of physical chemistry (the challenge lies in finding unreactive solvents and keeping them dry) they are clearly significant and useful. In the past, weakly basic substrates that are unresponsive to triflate reagents have been activated towards electrophiles by the use of Freidel-Crafts conditions or superacid media, i.e. Brønsted/Lewis acid mixtures involving $AlCl_3$ or SbF_5.[29] The presence of excess Lewis acid in these media has the advantage of mopping up errant nucleophiles (e.g. water) and increasing the reactivity of the electrophile (E^+) by decreasing the nucleophilicity of its counterion (e.g., converting SbF_6^- to $Sb_2F_{11}^-$ or $Sb_3F_{16}^-$). However, apart from being a difficult working medium, mixed Lewis/Brønsted superacids have another disadvantage which is poorly recognized. The Lewis acid can form an acid/base adduct with the substrate, suppressing its basicity and thereby making it much harder to add the E^+ electrophilic reagent. In other words, there is a competition for the substrate between the E^+ reagent and the Lewis acid in the medium and, as a consequence, the basicities of most weakly basic molecules have been significantly underestimated. This phenomenon was first recognized in the protonation of weak bases[2] and referred to as *basicity suppression* but there is every reason for it to apply to R^+ and R_3Si^+ electrophiles as well. This is a more subtle reason why carborane reagents are useful. They are strong electrophiles *and* Lewis acid free.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Biography

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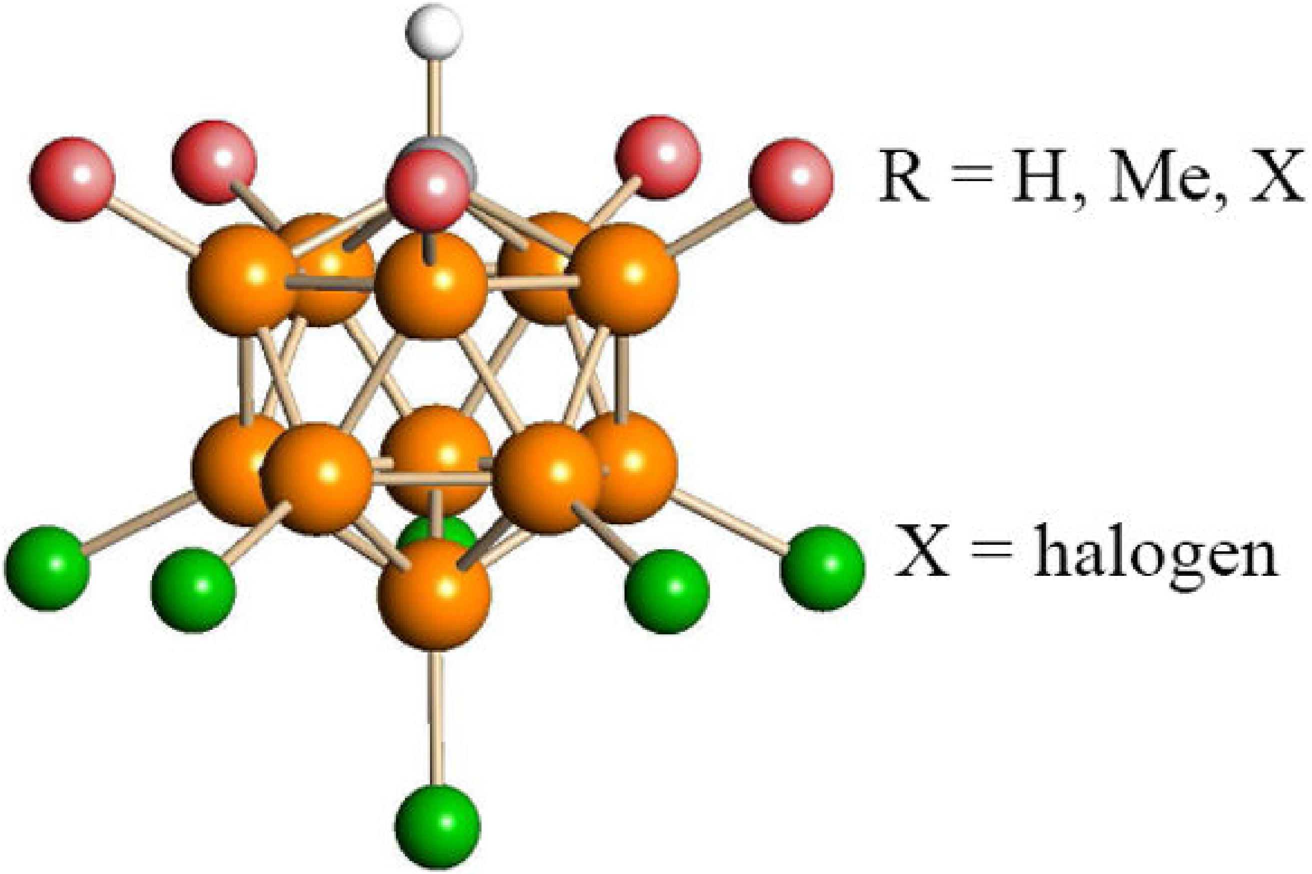


Fig. 1.
Carborane anions of the type $CHB_{11}R_5X_6^-$.

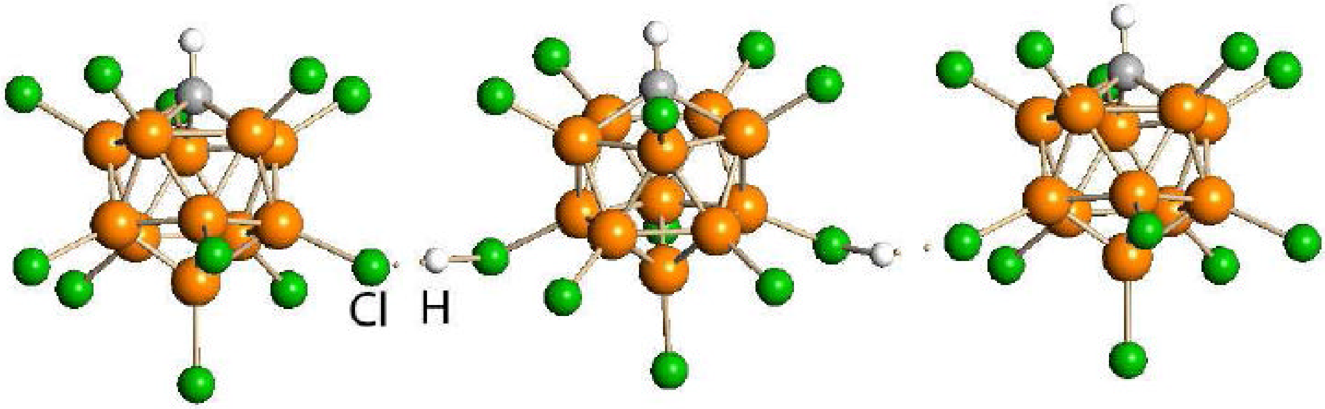


Fig. 2.

The proton-bridged linear-chain X-ray structure of H($CHB_{11}Cl_{11}$).

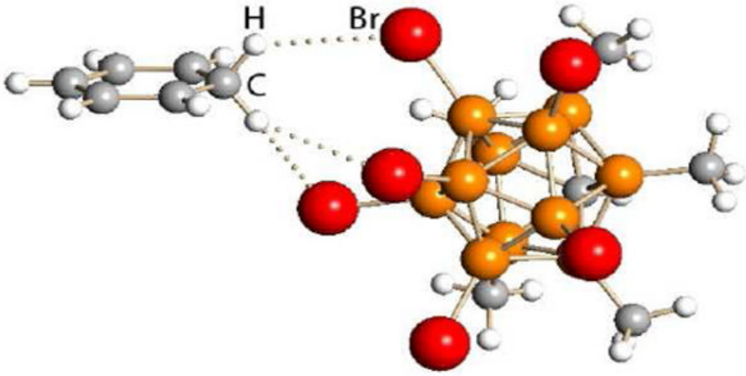


Fig. 3.
X-ray structure of the benzenium ion salt $[C_6H_7][CHB_{11}Me_5Br_6]$ showing H-bonding.

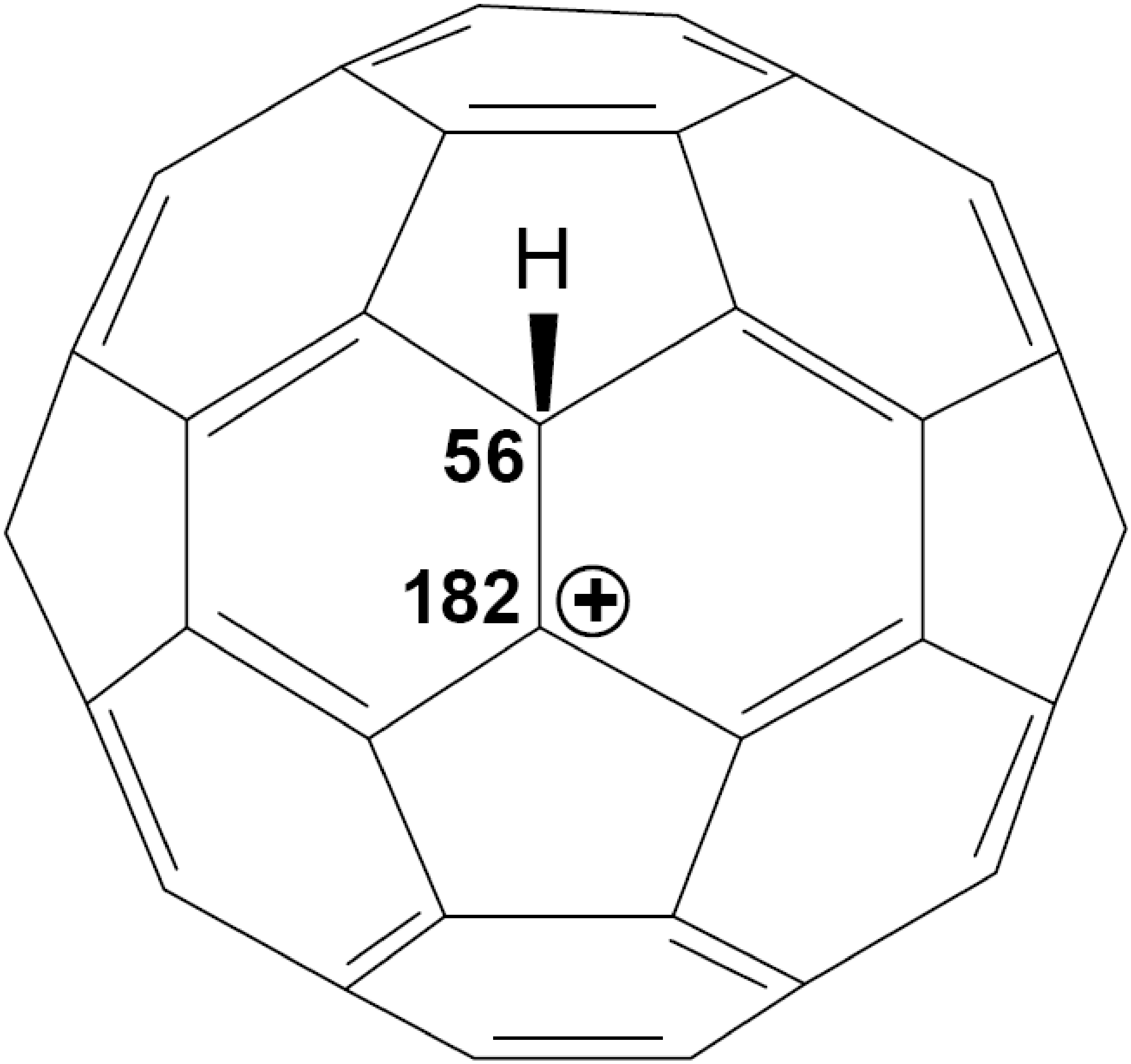


Fig. 4.
Structure of HC_{60}^{+} as determined by NMR showing key ^{13}C chemical shifts.

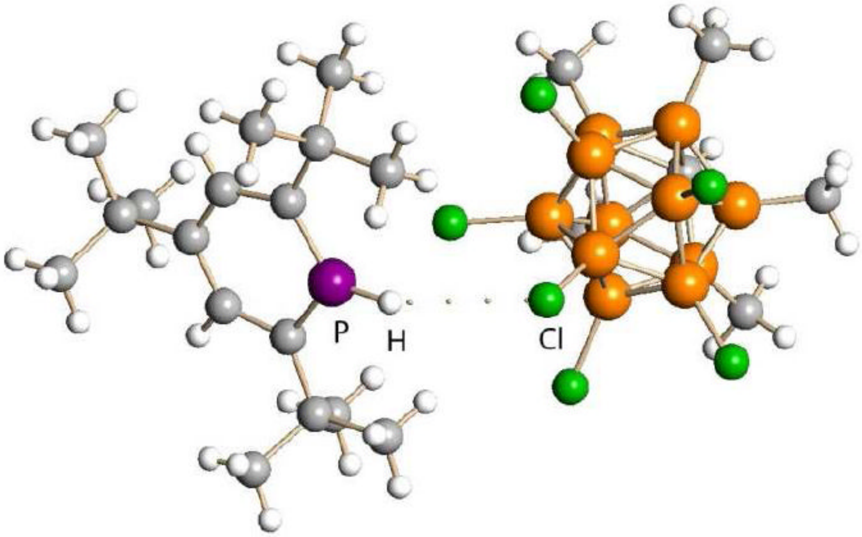


Fig. 5.

X-ray structure of a protonated phosphabenzene showing ion-pairing to the $CHB_{11}Me_5Cl_6^-$ anion via weak H-bonding.

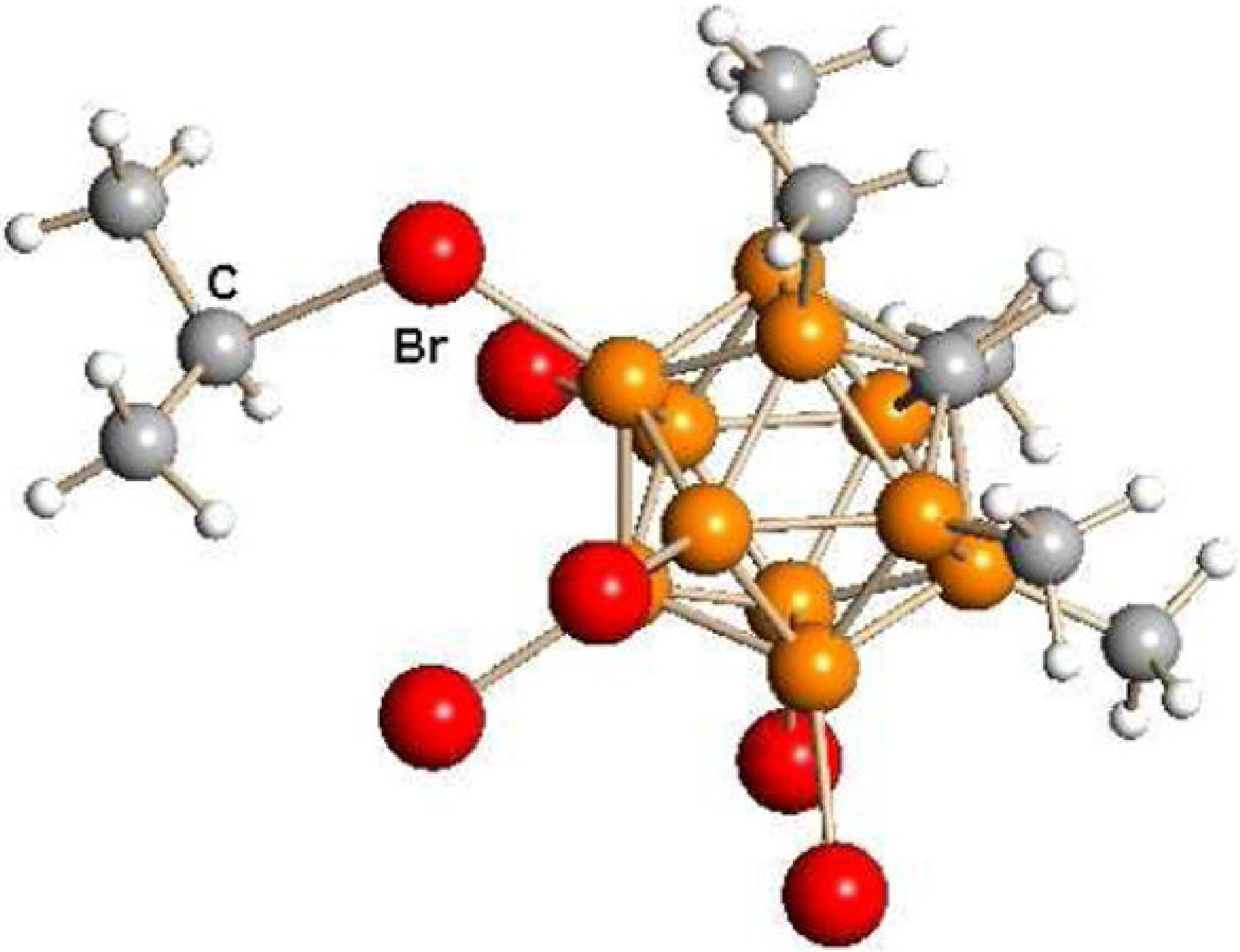


Fig. 6.

X-ray structure of *i*-Pr($CHB_{11}Me_5Br_6$) showing alkylation at the 7 position.

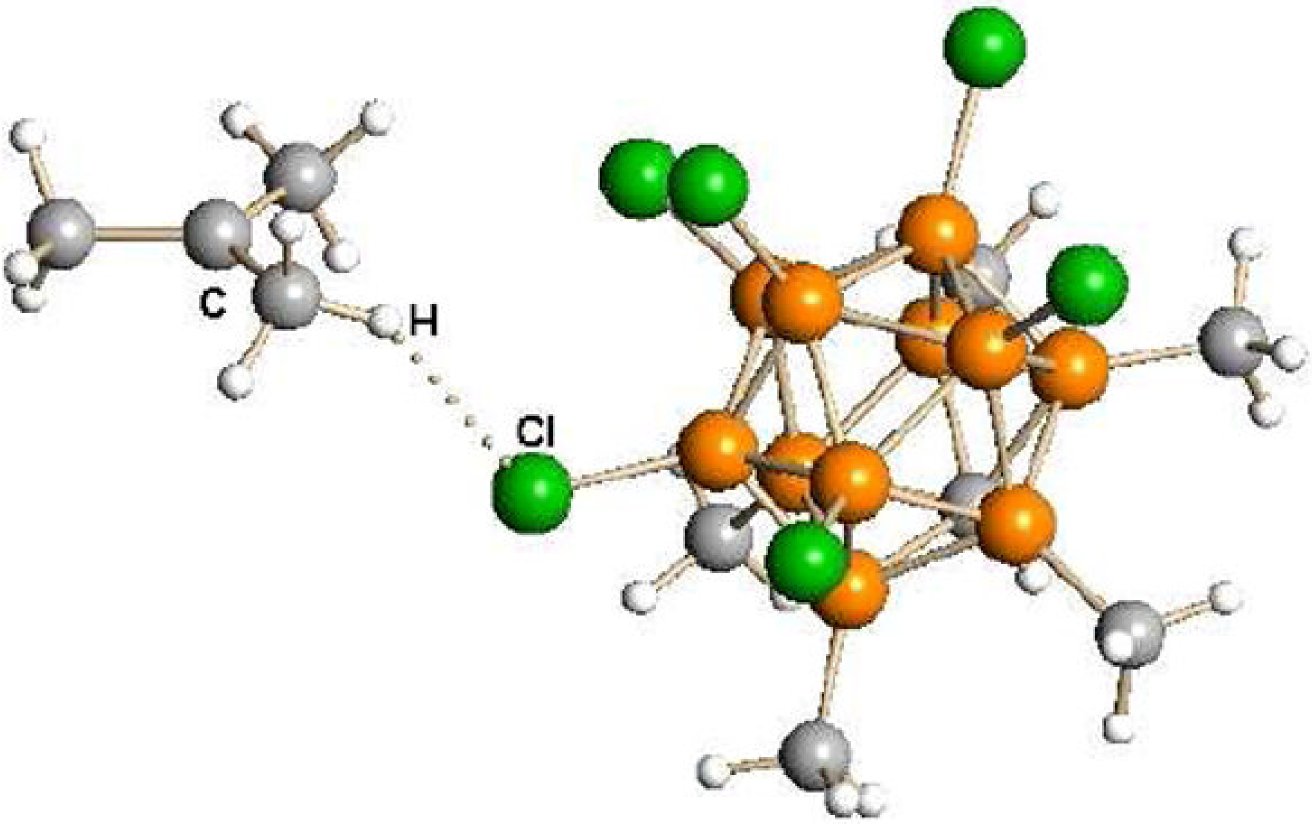


Fig. 7.

X-ray structure of *t*-butyl cation indicating H-bonding to $CHB_{11}Me_5Cl_6^-$ anion.

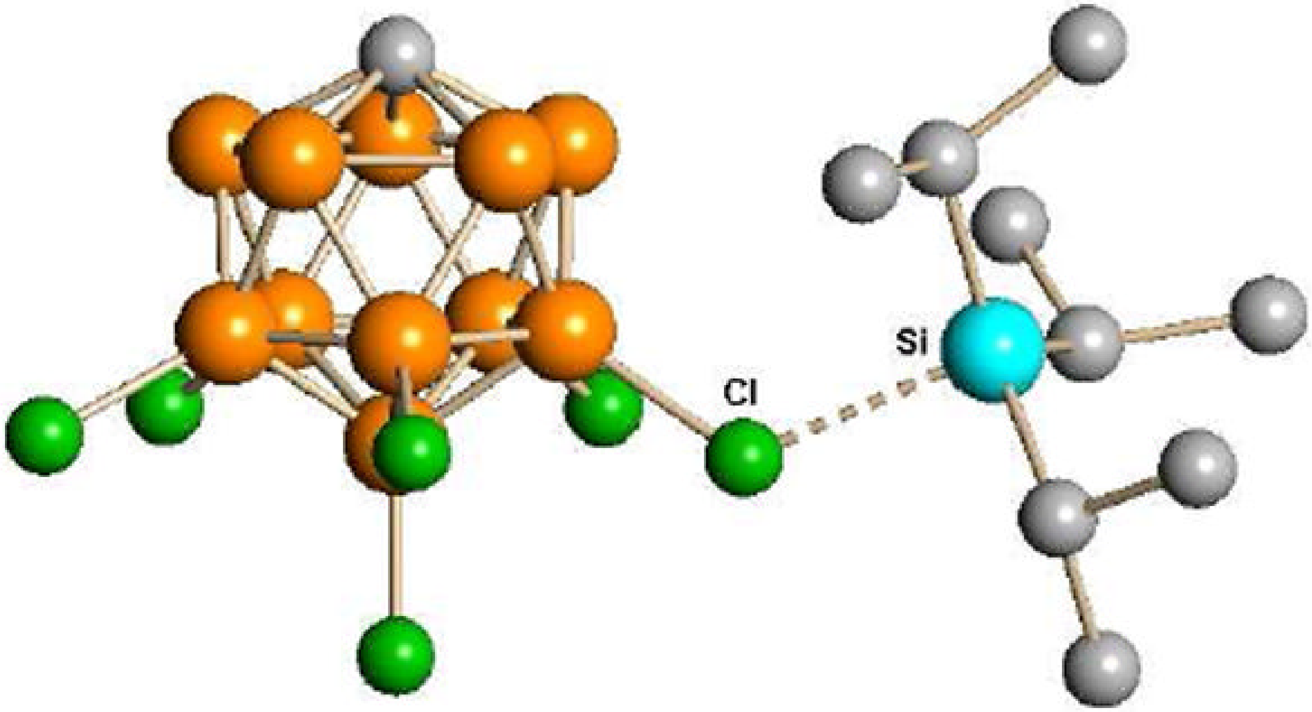


Fig. 8.

X-ray structure of *i*-$Pr_3Si(CHB_{11}H_5Cl_6)$ (H omitted) showing developing *i*-Pr_3Si^+ silylium ion character (Si---Cl = 2.32 Å; ΣC-Si-C = 351.9°).

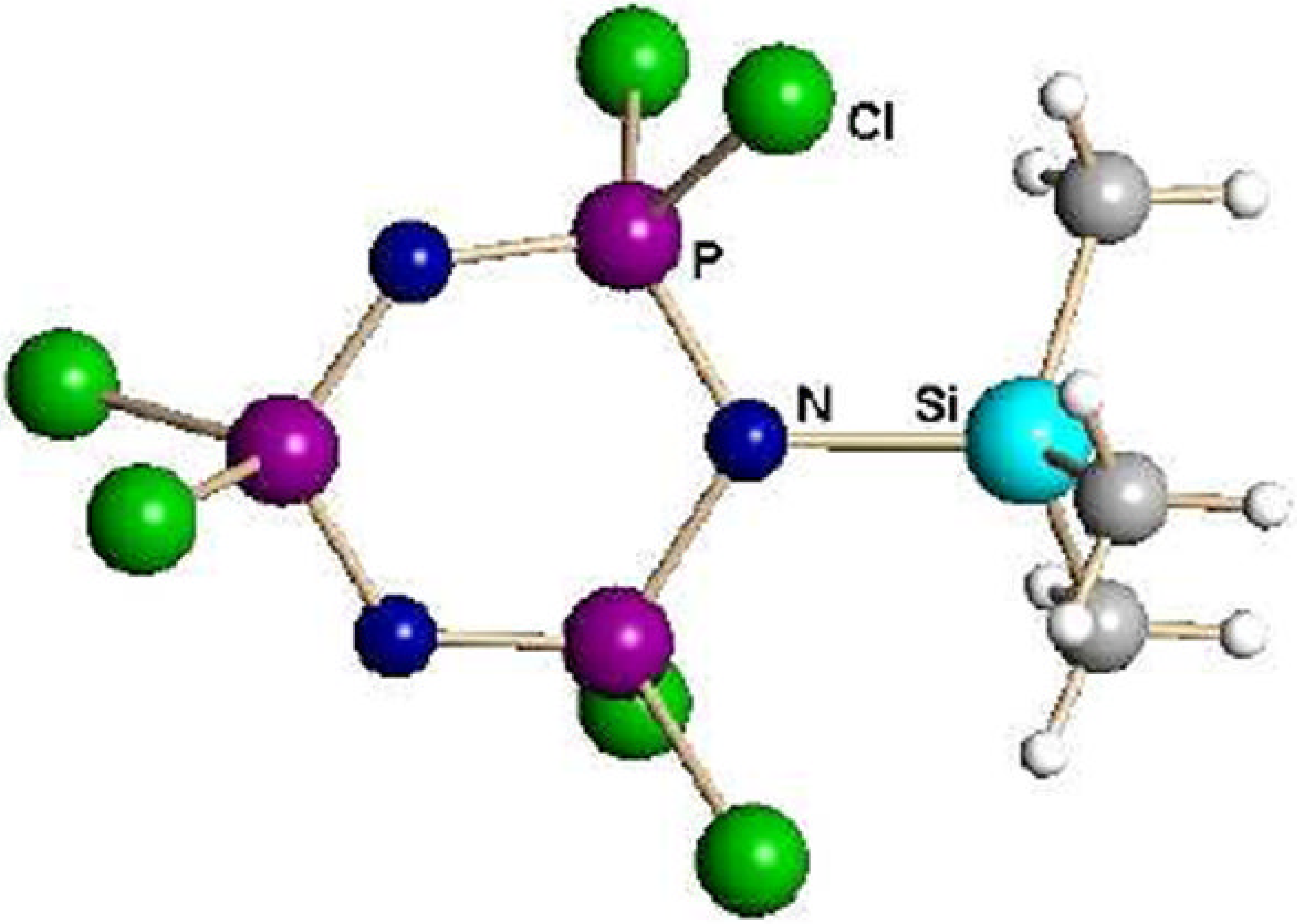


Fig. 9.

X-ray structure of the trimethylsilylated phosphazene cation as a carborane salt.

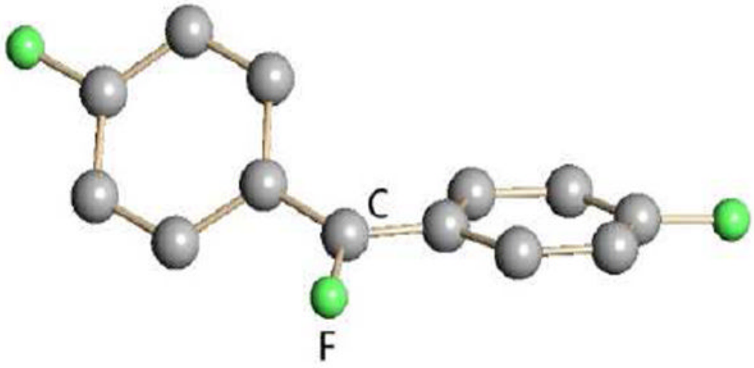


Fig. 10.
X-ray structure of the $CF(p\text{-}C_6H_4F)_2^+$ carbenium ion as a carborane salt.

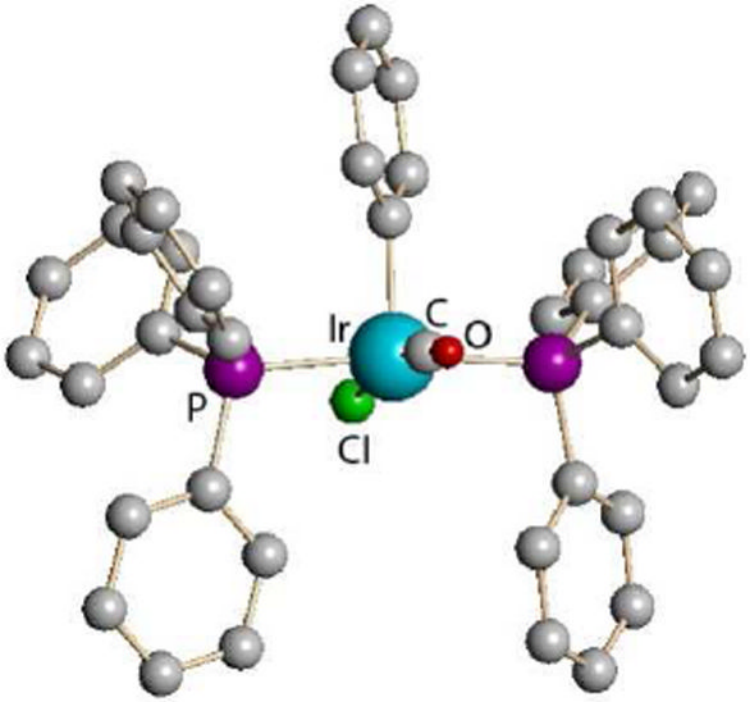


Fig. 11.
X-ray structure of the five-coordinate Ir(CO)Cl(Ph)(PPh$_3$)$_2$$^+$ cation as a carborane salt.

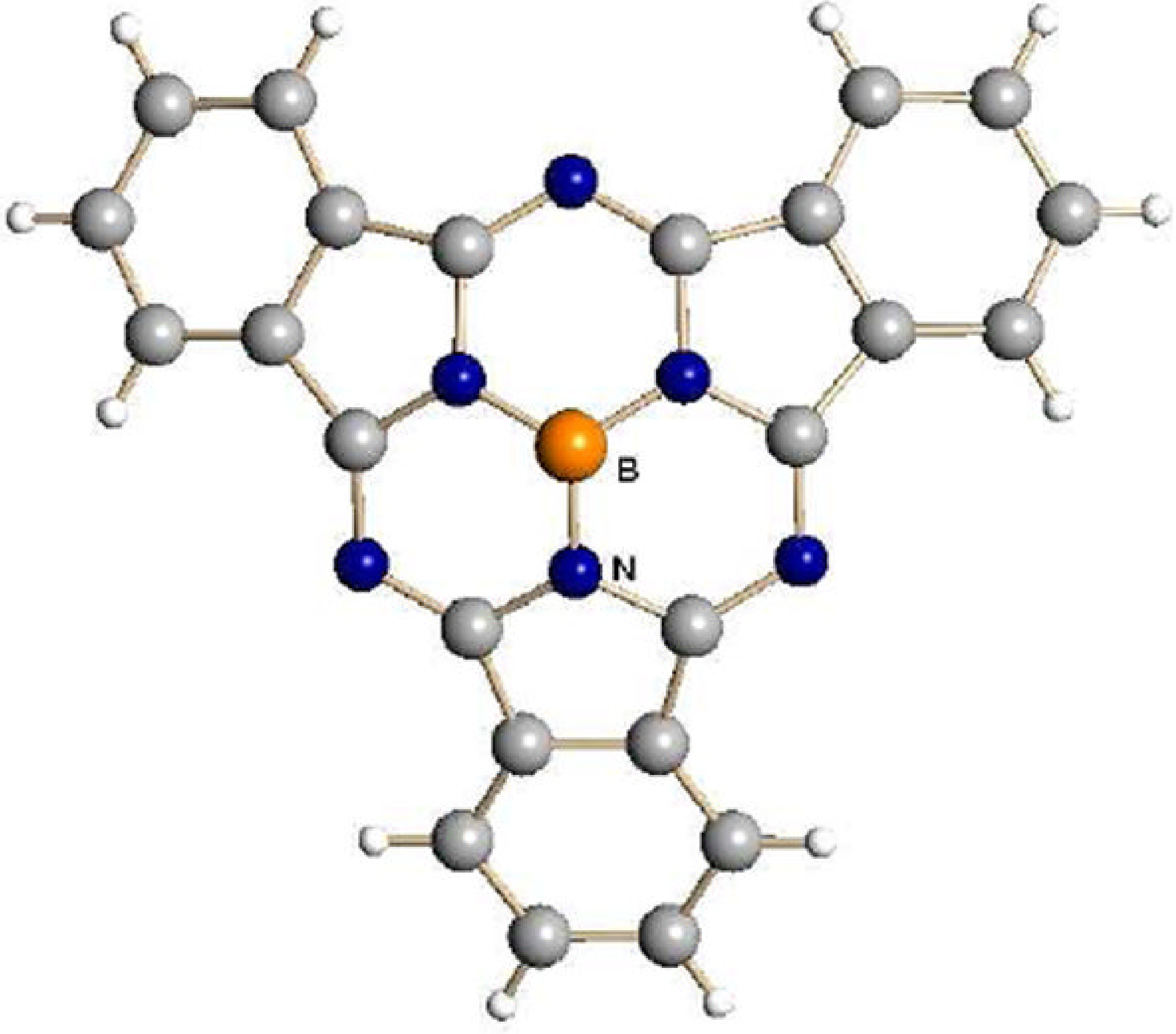


Fig. 12.
X-ray structure of the B(sub-phthalocyanine)$^+$ cation as a carborane salt.

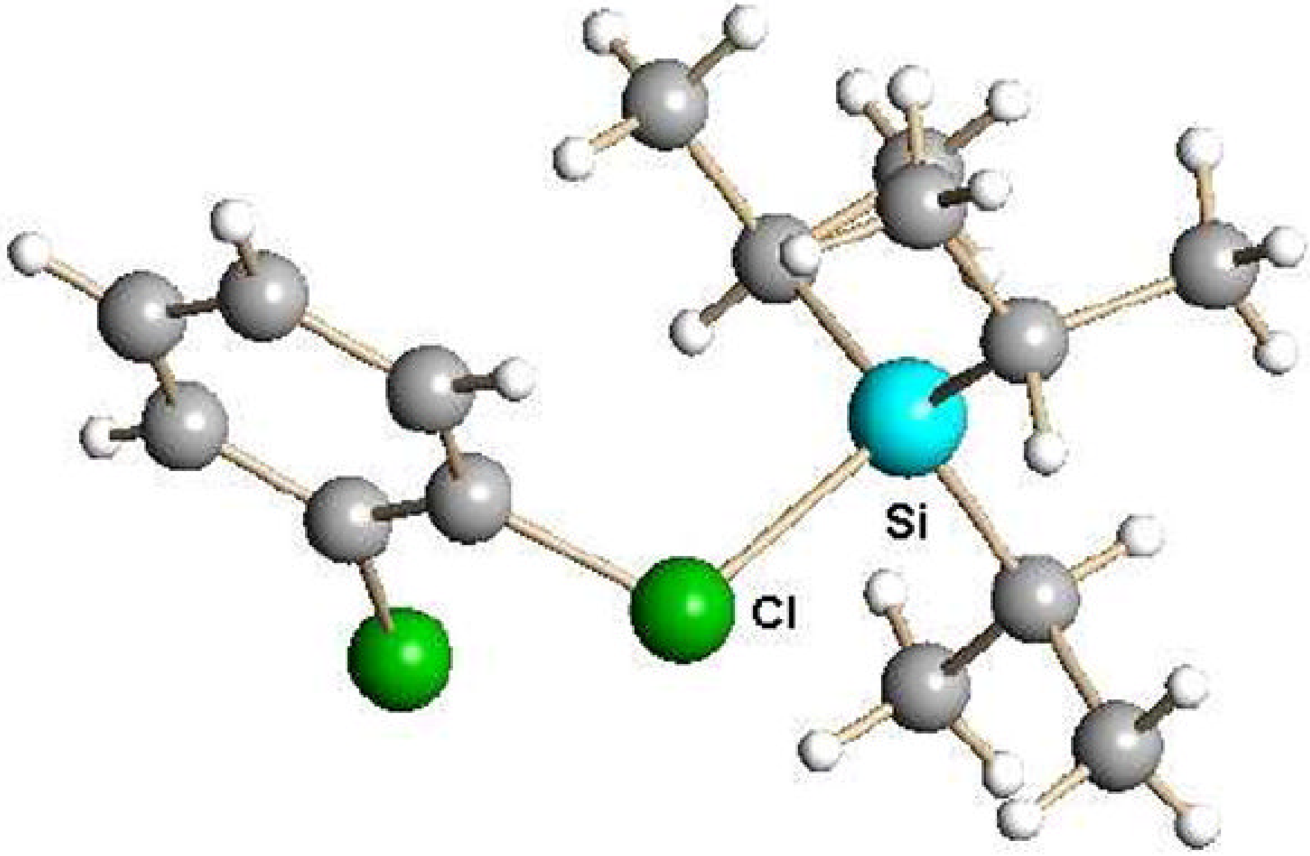


Fig. 13.
X-ray structure of the triethylsilylated *o*-dichlorobenzene cation as a carborane salt.

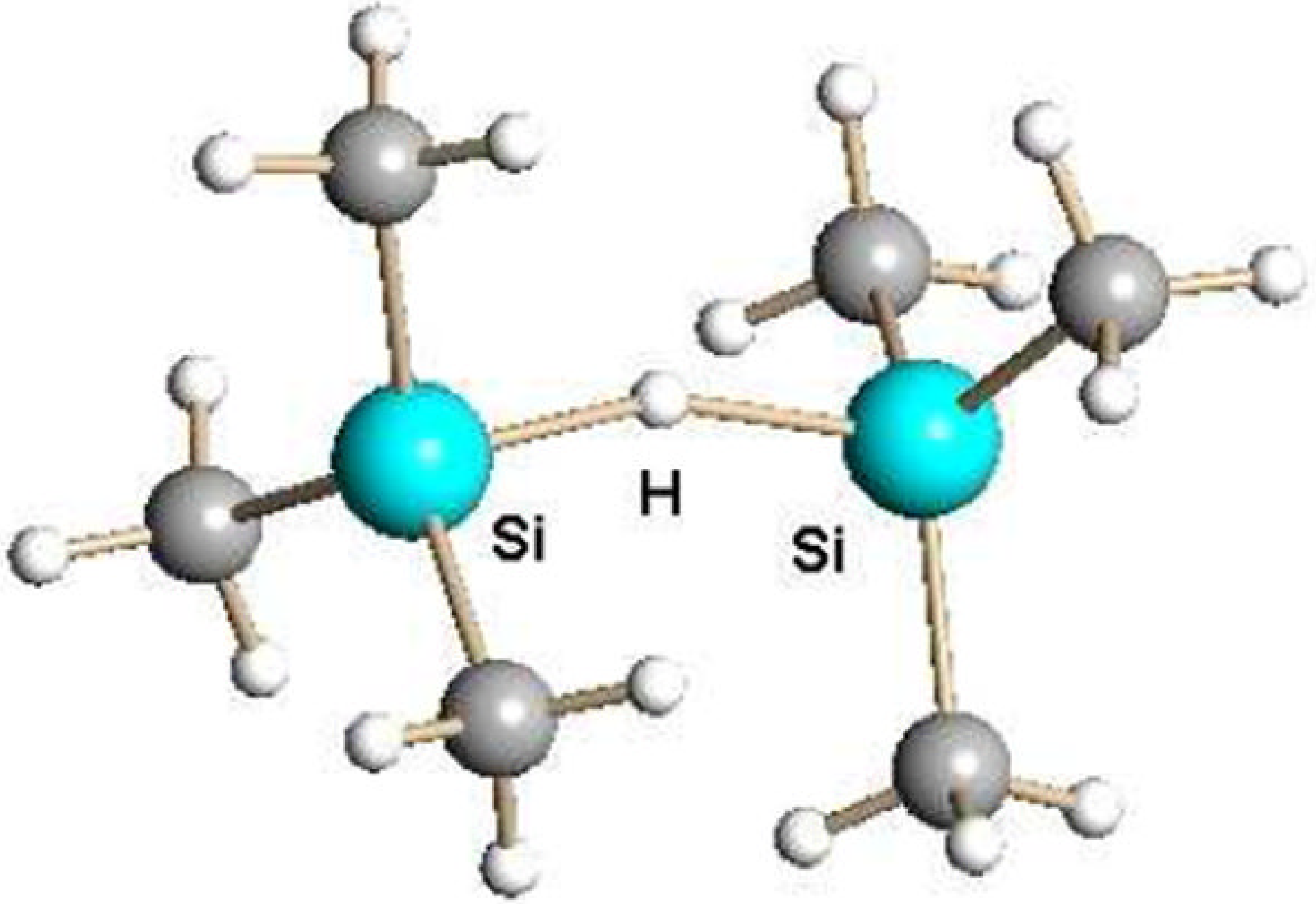


Fig. 14.
X-ray structure of the hydride-bridged silyl cation $Me_3Si\text{-}H\text{-}SiMe_3^+$ as a carborane salt.

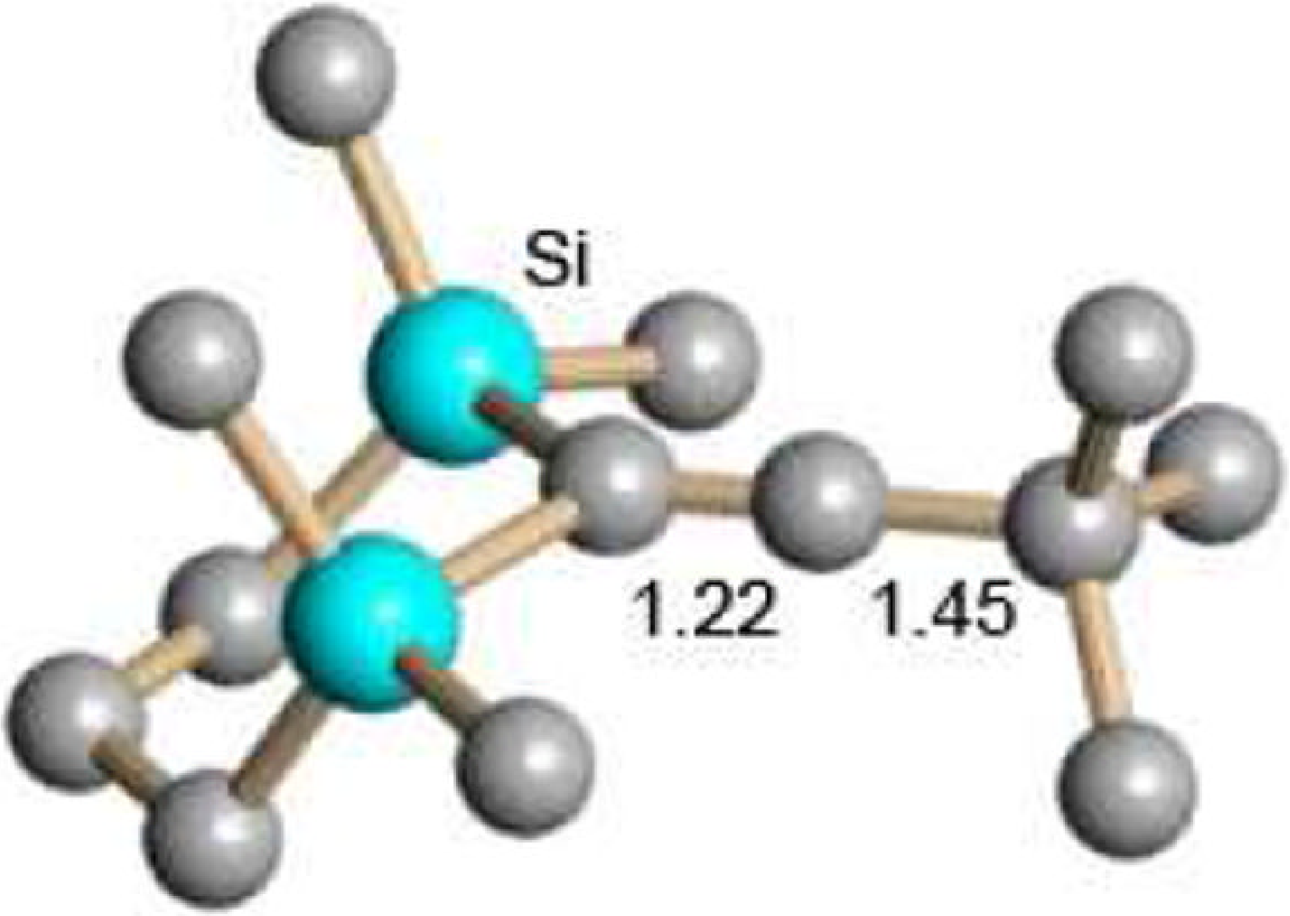
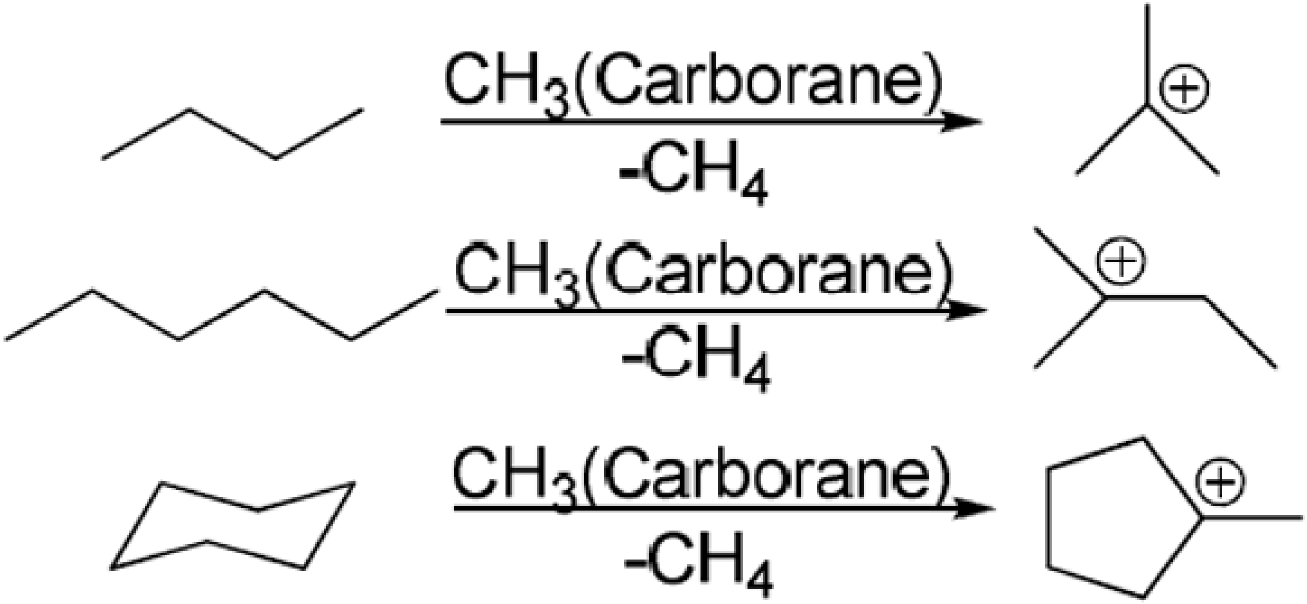
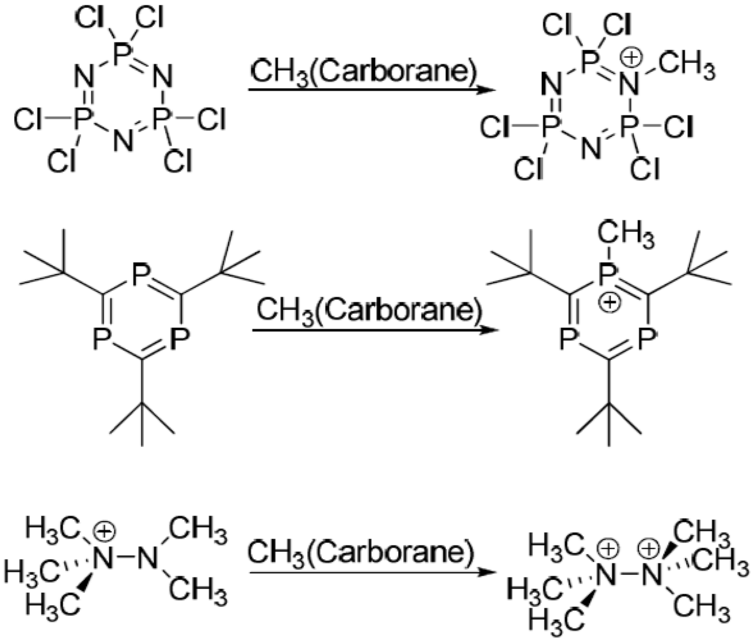


Fig. 15.
X-ray structure of a β-silyl stabilized vinyl cation ($CHB_{11}H_5Br_6^-$ carborane anion not shown).

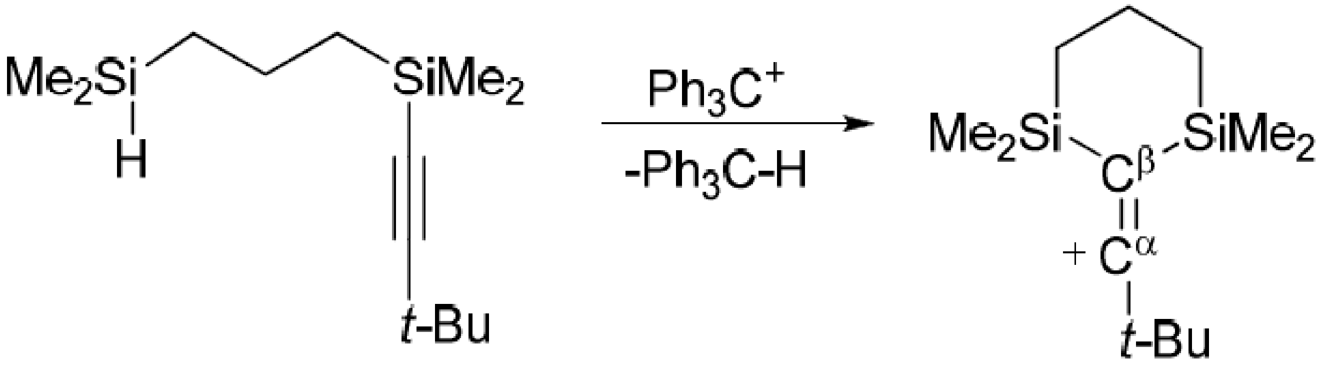


Scheme 1.

Formation of tertiary carbocations from alkanes.



Scheme 2.
Reactions of CH_3(carborane) with various weakly basic heteroatom substrates.



Scheme 1.
Synthesis of a stable vinyl cation (carborane anion omitted).