Carborane acids. New "strong yet gentle" acids for organic and inorganic chemistry

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Icosahedral carborane anions such as $CHB_{11}Cl_{11}^-$ are amongst the least coordinating, most chemically inert anions known. They are also amongst the least basic, so their conjugate acids, H(carborane), are superacids (*i.e.* stronger than 100% H_2SO_4). Acidity scale measurements indicate that $H(CHB_{11}Cl_{11})$ is the strongest pure Brønsted acid presently known, surpassing triflic and fluorosulfuric acid. Nevertheless, it is also an extremely gentle acid—because its conjugate base engages in so little chemistry. Carborane acids separate protic acidity from anion nucleophilicity and destructive oxidative capacity in the conjugate base, to a degree not previously achieved. As a result, many long-sought, highly acidic, reactive cations such as protonated benzene ($C_6H_7^+$), protonated C_{60} (HC_{60}^+), tertiary carbocations (R_3C^+), vinyl cations ($R_2C{=}C^+{-}R$), silylium ions (R_3Si^+) and discrete hydronium ions (H_3O^+, $H_5O_2^+$ *etc.*) can be readily isolated as carborane salts and characterized at room temperature by X-ray crystallography.

Introduction

Acids and acid catalysis have been an important part of chemistry from its very beginnings. In the last half century, a superacidic medium (*i.e.* acidity greater than 100% H_2SO_4) has become widely recognized as a useful if still somewhat exotic environment to stabilize reactive cations (*e.g.* R_3C^+,[1] S_8^{2+},[2] HCO^+,[3] N_5^+,[4] $AuXe_4^{2+}$,[5] *etc.*).[6] It would be easy to think that acidity is a mature field, and that there is little left to be discovered.

However, the preparation of carborane acids[7] shows that traditional strong acids and superacids have significant limitations. Carborane acids differ from traditional superacids by bringing unexpectedly high superacidity to weakly basic organic solvents without the complicating necessity of adding a strong Lewis acid (*e.g.* SbF_5). They surpass triflic acid in terms of acid strength, low anion nucleophilicity and ease of crystallization of salts. They make it much easier to isolate long-sought, reactive cations and easier to stabilize the fleeting intermediates of acid catalyzed reactions.

Carborane acids are also leading to new conceptual thinking about superacidity. Carborane acids protonate weakly basic molecules more easily than expected, attaining superacidity without the addition of Lewis acid. This has led to the previously unrecognized concept of "basicity suppression" in traditional mixed Lewis/Brønsted superacids and suggests that the basicities of many weakly basic molecules (*e.g.* alkenes, Xe) have been significantly underestimated.

The title phrase "strong yet gentle" captures the essential value of carborane acids. They separate Brønsted (protic) acidity from oxidation and nucleophilicity in the conjugate base, in a manner not previously achieved. Typical strong acids and superacids have oxyanions (HSO_4^-, $CF_3SO_3^-$ *etc.*) or fluoroanions (BF_4^-, SbF_6^- *etc.*) as their conjugate bases and the oxidative capacity and nucleophilicity of these anions frequently conspire to decompose protonated molecules. The corrosiveness of oxyacids and fluoroacids is often the result of anion redox and nucleophile chemistry. The wise chemist chooses hydrochloric acid not nitric acid to clean a copper kettle, thereby saving the kettle from oxidative destruction by the nitrate anion. By contrast, icosahedral carborane anions of the type, $CHB_{11}R_5X_6^-$ (R = H, CH_3, Cl; X = Cl, Br, I, see Fig. 1), are amongst the least nucleophilic, least-redox active, most chemically inert anions of modern chemistry.[8]

As a result, their conjugate acids are very effective in protonating sensitive molecules without subsequent decomposition chemistry.

An added bonus is the tendency of salts of carborane anions to crystallize nicely. Thus, cations that had only been available for study in solution by spectroscopic methods at sub-ambient temperatures can now be crystallized, put in a bottle, and mounted on an X-ray diffractometer for detailed structural characterization.

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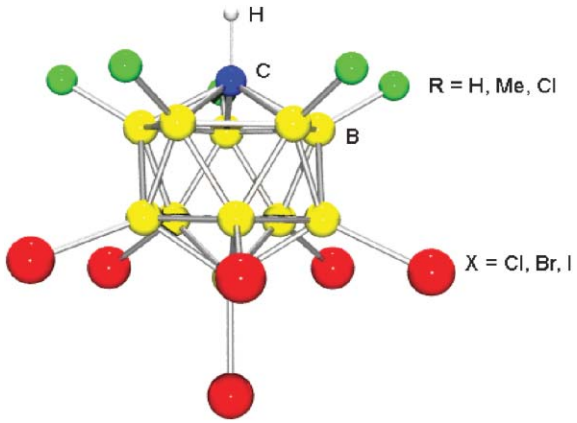

Fig. 1 The anions used as conjugate bases to carborane acids.

Carborane anions

The parent icosahedral carborane anion, $CB_{11}H_{12}^-$, was first synthesized by Knoth at Du Pont in 1967, at a time when industrial chemists were freer to pursue their curiosity.[9] The chemistry of $CB_{11}H_{12}^-$ lay fallow for a couple of decades while research on the neutral and dianionic isolectronic analogues, $C_2B_{10}H_{12}$ and $B_{12}H_{12}^{2-}$, took precedence. In the mid-1980s, the dedicated Czech boron group of Plešek, Štibr and Heřmánek reported an improved synthesis from decaborane[10] and showed that halogenation proceeded quite selectively to give 7,8,9,10,11,12-hexahalogenated anions, $CHB_{11}H_5X_6^-$ (X = Cl, Br; see Fig. 1).[11] Upon reading that anions of this type had an "…oral toxicity to rats roughly comparable to sodium chloride…"[12] we began to comprehend their extraordinary inertness and their potential as weakly coordinating anions.

While there have been periods of commercial availability, and there is a new synthesis available starting with sodium borohydride,[13] the same basic synthesis of the $CB_{11}H_{12}^-$ is still used today. It is not difficult to produce 7 g of the cesium salt from 10 g of decaborane starting material in about a week and the synthetic details are freely available at a website.[14]

The very weakly coordinating (*i.e.* weakly *Lewis* basic) nature of B-halogenated carboranes is illustrated by *i*-$Pr_3Si(CHB_{11}H_5Cl_6)$ which, structurally, is the closest approach to date to the long sought trialkylsilylium ion, R_3Si^+ (Fig. 2).[15] The anion is coordinated to silicon *via* a chloro substituent (from the 7 position on the carborane) indicating that the halide substituents are the most basic sites on the anion. The long Si···Cl bond, *ca.* 0.3 Å longer than a typical Si–Cl bond, has led to their description as "ion-like".[16] Although clearly not ionic, these silylium species react as though they were silylium ions, because the carborane anion is the leaving group *par excellence*.

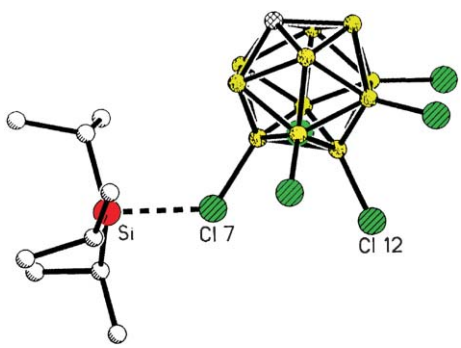

Fig. 2 X-ray structure of the *i*-$Pr_3Si(CHB_{11}H_5Cl_6)$, approaching an 'ion-like" state.[15] (H atoms have been omitted for clarity).

Synthesis and characterization of carborane acids

A strong Brønsted acid is typically prepared *via* the action of a strong Lewis acid on a weaker Brønsted acid. In the case of carborane acids, the extreme electrophilicity and halophilicity of silylium species, R_3Si(carborane),[16] (see Fig. 2) is exploited (eqn. (1)).

$$Et_3Si(carborane)_{(s)} + HCl_{(l)} \rightarrow H(carborane)_{(s)} + Et_3SiCl_{(g)} \quad (1)$$

The driving force for this reaction is the greater strength of the Si–Cl bond (*ca.* 113 kcal mol^{-1}) relative to that of HCl (103 kcal mol^{-1}). The acid is produced in essentially quantitative yield by stirring a slurry of the silylium starting material in liquefied anhydrous HCl at low temperatures. The volatile byproduct and excess HCl are simply removed by warming to room temperature under vacuum.

Carborane acids are moisture-sensitive, white solids with extremely high thermal stability. They sublime under vacuum at temperatures in the range 150–200 °C. The IR spectrum shows very little perturbation of the CB_{11} cluster bands relative to the silylium starting material so protonation of the anion must occur on the halogen substituents (red atoms X in Fig. 1) at the same positions (7–12) that coordination of R_3Si^+ and Ag^+ occurs. No band ascribable to a simple νX–H stretch is observed and, given the marked tendency of protons to be di-coordinate,[17] a polymeric structure with H^+ bridges between halogen substituents of the anions is proposed, similar to that observed in a number of Ag^+ salts of carboranes.[18]

Carborane acids are so strong that they protonate (or react with) almost every solvent. In liquid SO_2, one of the least basic solvents where good solubility is achieved (*ca.* 0.1 M), the extremely downfield-shifted ^1H NMR resonance of the acidic proton (20.4 ppm),[19] along with IR data,[20] suggest that complete ionization of $H(CHB_{11}Cl_{11})$ takes place. The nature of the proton is most likely the di-solvated cation, $H(SO_2)_2^+$.

Acid strength of carborane acids

The acidities of carborane acids cannot be measured in the conventional manner of an H_0 Hammett acidity function because carborane acids are solids not liquids. The comparison of the strengths of solid and liquid phase acids is a classic problem of physical chemistry. Gas phase acidities have been calculated for carborane acids, ranking them the strongest of any known isolable acid,[21] but it is presently not possible to translate gas phase ΔG data into measures of condensed phase acidity.

In liquid SO_2 solution, a fairly good solvent for carborane acids, the strength of carborane acids has been compared to some common mineral acids[19] using the $\Delta\delta$ mesityl oxide scale

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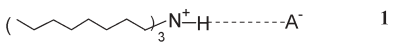
developed by Fărcaşiu.[22] This scale is based on the ^{13}C NMR chemical shift difference ($\Delta\delta$) between the C_α and C_β carbon atoms of mesityl oxide which increases with increasing protonation as eqn. (2) is shifted to the right hand side.

(2)

^{13}C NMR data for 0.15 M solutions of various acids and 0.10 M mesityl oxide are given in Table 1. It is immediately evident from their high chemical shift values that, as a class, carborane acids are stronger than conventional oxyacids. They easily outrank fluorosulfuric acid, the strongest known pure Brønsted acid on the H_0 acidity scale (−15.1), as well as triflic acid (H_0 = −14.1).

It is also evident from the data of Table 1 that whereas oxyacids only partially protonate mesityl oxide, carborane acids are strong enough to move eqn. (2) completely to the right hand side, *i.e.* their acidities are leveled. The $\Delta\delta$ value maximizes at *ca.* 84 ppm and the true measure of their acidity is not determined in this system. Though close to the limits of discrimination, the hexa-iodo carborane acid, $H(CHB_{11}H_5I_6)$, with a value of 83.3 ppm, does appear to be perceptibly weaker than its chloro and bromo counterparts.

In order to better discriminate between the acidities of different carborane acids, a new ranking of acidity has been developed, based on the *v*N–H frequencies of ammonium salts of their conjugate base anions.[19] The ranking is based on the influence of anion A^- on the N–H bond in a contact ion pair, **1**.



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The weaker the interaction of the base A^-, the stronger the N–H bonding, and the higher the *v*N–H frequency. Since *v*N–H frequencies (>3000 cm^{-1}) are energetically far removed from *v*H–A frequencies (<300 cm^{-1}), vibrational coupling or mass differences in A^- will have an insignificant effect on *v*N–H. Thus, *v*N–H frequencies should be a good measure of N–H bond strength. Since H-bonding is a predominantly electrostatic phenomenon, N–H bond strength should correlate strongly with A^- basicity, *i.e.* with HA acidity, at least for weakly basic anions. IR *v*N–H frequencies will decrease with increasing A^- basicity, correlating with HA acidity. In a constant solvation environment (CCl_4) within a series of isostructural anions, the correlation should be quite direct.

IR data for trioctylammonium carborane salts in CCl_4 solution are listed in Table 2. The strong dependence of *v*N–H on the nature of the anion indicates that contact ion pairs are formed.

The *v*N–H ranking brings out a number of features. (*a*) For each of the pairs of hexahalo carboranes $CHB_{11}H_5X_6^-$ (X = Cl, Br, I,) and their pentamethylated counterparts $CHB_{11}Me_5X_6$, the difference in *v*N–H values is 5 or 6 cm^{-1}. This consistency gives confidence in the scale, suggesting that the CCl_4 solvation environment remains constant over the series and that mass differences and steric effects have negligible influence. It is evident that small differences in anion basicity can be detected quite accurately and the scale should be useful for a much wider range of weakly coordinating anions. The scale is also predictive for new anions whose conjugate acids are unknown. (*b*) The ranking of the hexahalo carborane acids, $H(CHB_{11}H_5Cl_6) > H(CHB_{11}H_5Br_6) > H(CHB_{11}H_5I_6)$, makes sense on the basis of electronegativity and polarizability considerations for the halogen substituents. It is consistent with conceptually related deductions drawn from *v*C–H frequencies in benzenium ion salts having the same series of carborane counterions.[23] (*c*) The top ranking (*i.e.* least basic) carborane anion measured to date is the *undeca*chlorinated anion, $CHB_{11}Cl_{11}^-$. Thus, $H(CHB_{11}Cl_{11})$ can lay claim to the strongest isolable acid presently known.

Carborane acids are exceptionally strong acids because their anions are exceptionally weak bases. This arises from the large size of the anions, the delocalized nature of the negative charge in the CB_{11} cluster, and the shield of halide substituents. However, there is an equally important consideration for attaining high acidity. The anion must be chemically inert to protonation. The inertness of carborane anions arises from σ aromaticity within the CB_{11} icosahedral cage, a notable feature of boron cluster chemistry. The CB_{11} framework resists chemical disruption to a truly exceptional degree. There are anions that have lower basicity than carboranes, *e.g.* organofluoro anions such as $B(C_6F_5)_4^-$,[24] but their conjugate acids cannot be prepared because the anion decomposes at high acidity.[25] This is mirrored in the fact that traditional fluoroacids, commonly written as HBF_4, HPF_6, $HSbF_6$ *etc.*, are also non-existent compounds. They are unstable with respect to formation of HF and the corresponding neutral Lewis acid. The superacid commonly written "$HSbF_6$" is

Table 1 Acidity rankings on the ^{13}C $\Delta\delta$ mesityl oxide scale[19]

Acid	^{13}C $\Delta\delta$ (ppm)	H_0
$H(CHB_{11}Cl_{11})$	84.0 ± 0.1	[a]
$H(CHB_{11}H_5Cl_6)$	83.8 ± 0.1	[a]
$H(CHB_{11}H_5Br_6)$	83.8 ± 0.1	[a]
$H(CHB_{11}H_5I_6)$	83.3 ± 0.1	[a]
FSO_3H	73.8 ± 0.5	−15.1
CF_3SO_3H	72.9 ± 0.4	−14.1
$HN(SO_2CF_3)_2$	72.0 ± 0.4	[a]
H_2SO_4	64.3 ± 3.1[b]	−12.1
Mesityl oxide (unprotonated)	32.4 ± 0.1	

[a] H_0 values unavailable because acids are solids, not liquids. [b] Incomplete miscibility of H_2SO_4 in liquid SO_2 leads to higher error limits and possible underestimate of $\Delta\delta$.

Table 2 Acidity ranking based on *v*N–H in Oct_3NH^+ salts of carborane conjugate bases[19]

Conjugate base	*v*N–H/±1 cm^{-1}	$\Delta v/cm^{-1}$
[a]$CHB_{11}Cl_{11}^-$	3163	0
$CHB_{11}(CH_3)_{11}^-$	3156	7
[a]$CHB_{11}H_5Cl_6^-$	3148	15
$Co^{III}(C_2B_9H_8Cl_3)_2^-$	3145	18
$CHB_{11}(CH_3)_5Cl_6^-$	3143	20
$CHB_{11}H_{11}^-$	3129	34
[a]$CHB_{11}H_5Br_6^-$	3125	38
$CHB_{11}(CH_3)_5Br_6^-$	3120	43
[a]$CHB_{11}H_5I_6^-$	3097	66
$CHB_{11}(CH_3)_5I_6^-$	3091	72

[a] Denotes presently reported isolable acids

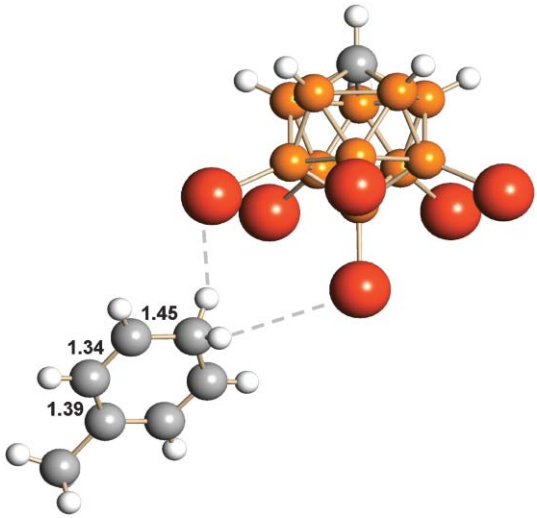


Fig. 3 X-ray structure of a carborane salt of protonated toluene (toluenium ion).[23]

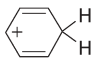
mostly a mixture of $[H(HF)_x][SbF_6 \cdot nSbF_5]$ ions in HF/SbF_5 solvent. $HSbF_6$ cannot be isolated as a pure Brønsted acid. Thus, present limits to acid strength are seen to be as much dependent on considerations of anion stability as anion basicity. This is an important consideration when contemplating how to synthesize even stronger acids than $H(CHB_{11}Cl_{11})$.

Protonated arenes

A demonstration of the strength of carborane acids is their ready protonation of benzene. Triflic acid does not protonate benzene[26] and the strongest known neat liquid acid, $HFSO_3$, (Hammett acidity function $H_0 = -15.1$) does so only to a very small extent.[27] Previously, mixed Brønsted/Lewis acids such as HF/SbF_5 were necessary to attain acidity high enough to protonate benzene, but this comes at a price. The presence of SbF_5 (in excess, or latently in SbF_6^- or $Sb_2F_{11}^-$ anions) limits the stability of the resulting benzenium ion to temperatures well below ambient. On the other hand, when a carborane acid is used, the resulting benzenium ion salt, $[C_6H_7^+][\text{carborane}^-]$, is stable to 150 °C! This demonstrates the 'strong yet gentle' qualities of carborane acids.

Protonated arenes are important as the intermediates of electrophilic aromatic substitution—so-called Wheland intermediates (even though they were proposed and characterized much earlier by Pfeiffer and Wizinger).[28] Surprisingly, they had not been characterized by X-ray crystallography except in a few cases with bulky and/or strongly electron-donating substituents.

Carborane salts of protonated simple arenes crystallize readily at room temperature making them amenable to structural characterization by X-ray crystallography. Single crystals of a benzenium ion salt were successfully grown[23] but the metrical accuracy of the X-ray structure suffered from disorder. Indeed, ^{13}C CPMAS NMR data indicate that the $C_6H_7^+$ ion is fluxional in the solid state even at dry ice temperatures. Rapid 1,2-shifts of the ring around the proton site in the crystal are likely. Nevertheless, the structure was unambiguously shown to be that of a σ complex, most simply written as resonance structure **2**.



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Protonated toluene as a $CB_{11}H_6Br_6^-$ salt leads to a high resolution structure (Fig. 3). The C–C bond lengths are consistent with structure **2** as the major contributing resonance form, with the formal positive charge at the tertiary (methylated) C atom. The shortest C–C distance is found in the formal double bond, the next shortest is the sp^2–sp^2 bond involving the formal carbocation centre, and the longest bond is to the sp^3 carbon atom.

There are weak H-bonding-type interactions of the protons on the sp^3 carbon atom with the halogen substituents on the carborane anion (dotted lines in Fig. 3) showing that these are the most acidic protons. In this sense, the positive charge in resonance form **2** is a little misleading.

The need for accurate X-ray structural data on the intermediates of electrophilic aromatic substitution arises because conventional wisdom on the structure of arenium ions has recently been challenged. In 1993, Lambert reported the structure of a silylarenium ion which did not conform to the structural expectations of a σ complex. The expected sp^3 character of the silylated carbon atom was only partially developed.[29] We offered an explanation for this structure and proposed that it should be viewed as neither a traditional σ complex, nor a π complex, but as a point along a σ–π continuum (Scheme 1).[15]

This viewpoint is gaining momentum with adoption and elaboration in recent reviews.[30,31] The structural results for various electrophiles towards arenes are summarized in Fig. 4.

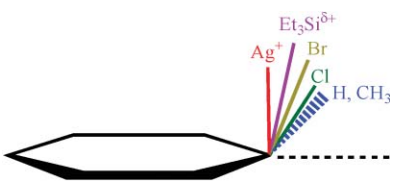
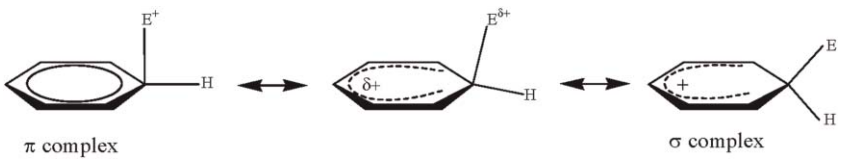


Fig. 4 Representation of the σ–π continuum of structures obtained upon addition of various electrophiles to arenes.[23]



Scheme 1 The σ–π continuum in arenium ion structures.

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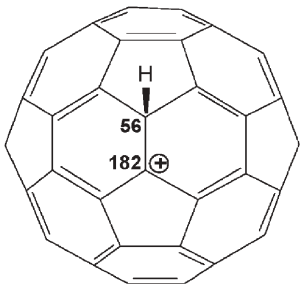
Protonated C_{60}

A more powerful illustration of the strong-yet-gentle characteristics of carborane acids is their protonation of fullerenes.[7] A decade of attempts to observe protonation of C_{60} with traditional strong and superacids had failed, even working at dry ice temperatures. This turned out not to be a problem of insufficient acid strength, but rather, a problem of oxidative/nucleophilic decomposition of the fullerene by the conjugate bases of the acids used. Even the usually non-oxidizing triflic acid was found to decompose C_{60}, possibly because of the presence of reducible impurities in the acid.

On the other hand, carborane acids such as $H(CB_{11}H_5Cl_6)$ cleanly and reversibly protonate C_{60} in dry halocarbon solvents.[7] The resulting $[HC_{60}^+][carborane^-]$ salt can be isolated in quantitative yield and characterized by novel solid state ^{13}C CPMAS methods[32,33] to have a 1,2-carbocation static structure, **3**. In solution, the appearance of a single sharp ^{13}C resonance indicates that the proton in the HC_{60}^+ cation is a true "globetrotter", rapidly sampling attachment to all 60 carbon atoms.



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These studies have allowed the basicity of C_{60} to be bracketed between that of xylene and mesitylene. Thus, fullerenes are not particularly difficult to protonate, but once protonated they are rather fragile. Carborane acids are more than strong enough to get the job done, but more importantly, they do not decompose the resulting cation.

Alkyl carbocations

The role of high acidity in the stabilization of alkyl cations such as *t*-buyl cation is evident from inspection of eqn. (3).

(3)

If the acid HA is not strong enough to move the equilibrium completely to the right hand side, carbocationic oligomerization would occur *via* successive additions of carbocations to *iso*-butene. Typically, a mixed Brønsted/Lewis acid such as "Magic Acid" ($HFSO_3/SbF_5$) having H_0 somewhere in the range -17 to -27 is used to stabilize *t*-butyl cation.[1] By contrast, carborane acids protonate alkenes and give rise to stable tertiary carbocations without the addition of a Lewis acid. However, this is not the method of choice to prepare stable salts. Instead, hydride extraction from an alkane is used.

Just as H(carborane) acids are stronger sources of H^+ than triflic acid, so alkyl carborane reagents, R(carborane), are stronger sources of alkyl$^+$ than alkyl triflates.[34] They are prepared by treatment of alkyl triflates with silyl carboranes, once again exploiting the high electrophilicity of cation-like silicon in R_3Si(carborane) species (eqn. (4)).

$$Et_3Si(carborane) + R(OTf) \rightarrow R(carborane) + Et_3Si(OTf) \quad (4)$$

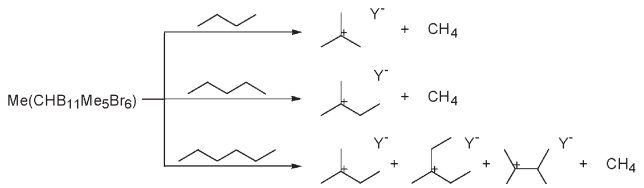
Known affectionately in our labs as "mighty methyl", $Me(CHB_{11}Me_5Br_6)$ is sufficiently electrophilic that it abstracts H^- from alkanes at or below room temperature.[35] Methane is eliminated and carbocations are formed (Scheme 2).

As expected, linear hydrocarbons rearrange to branched-chain products reflecting the higher thermodynamic stability of tertiary carbocationic centers over primary or secondary, and the ease of hydrogen or methyl 1,2 shifts in carbenium ions.[36] Microcrystalline $[R_3C][carborane]$ products produced this way at lowered temperatures are stable indefinitely at room temperature if kept dry and free of nucleophiles.

At -40 °C in dichloromethane or in liquid SO_2, solutions of tertiary carbocation salts are sufficiently long lived that single crystals can be grown. Two of the most interesting X-ray structures are those of the *t*-butyl cation and the *t*-pentyl (amyl) cation, the former because of its classic importance to the history of carbocations,[37] the latter because it gives information on the relative importance of C–C *versus* C–H bond hyperconjugation in carbenium ions.

Fig. 5 shows the structure of the *t*-butyl cation with $CHB_{11}Me_5Cl_6^-$ as counterion. As expected, the cation is planar at the sp^2 centre and the sp^2–sp^3 C–C bond lengths are short [ave. 1.442(4) Å]. The closest anion approaches to the cation involve C–H···Cl interactions to the methyl groups, not to the carbocationic centre, reflecting the high protic acidity of the *t*-butyl cation.

Fig. 6 shows the structure of the *t*-pentyl cation with $CHB_{11}Me_5Br_6^-$ as counterion. The small (25.8°) dihedral angle between the carbocationic plane and the C(1)–C(2)–C(3) plane indicates a preference for C–H over C–C bond hyperconjugative stabilization of the positive charge on the



Scheme 2 Formation of tertiary carbocations by reaction of a methyl carborane reagent with alkanes ($Y^- = CHB_{11}Me_5Br_6^-$).

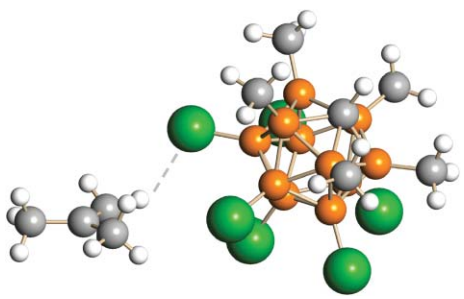


Fig. 5 X-ray structure of $[t\text{-butyl}][CHB_{11}Me_5Cl_6]$.[35]

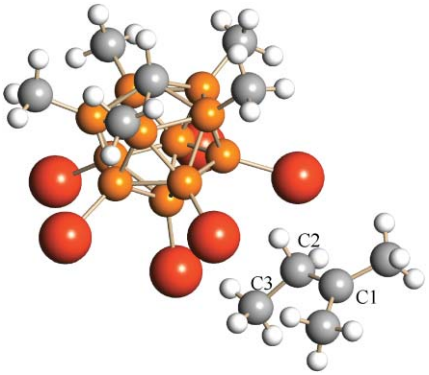


Fig. 6 X-ray structure of the *t*-pentyl (amyl) cation as a $CHB_{11}Me_5Br_6^-$ carborane salt. C_1 is the formal sp^2 cationic centre.[35]

carbenium ion centre. The C–C bond is *not* aligned with the vacant p orbital. This was not expected from ^{13}C NMR results in solution which better matched theory for the conformer having the C–C bond aligned (rather than perpendicular) with the vacant p orbital. However, theory at the MP4(SDTQ)6-31G**//MP2(FU)/6-31G* + ZPE level finds a negligible energy difference between the two idealized conformers. Evidently the torsional potential in the C^+–CH_2–CH_3 moiety is rather soft and crystal packing forces probably dictate the observed orientation, favoring C–H over C–C bond hyperconjugation.

The first X-ray structure of a vinyl cation, the two-coordinate unsaturated analogue of a carbenium ion, was recently obtained using a carborane as counterion.[38] The cation is stabilized by β-silyl substituents and the long C–Si distances to these substituents (1.95–1.98 Å) provide direct evidence of β–Si–C bond hyperconjugative stabilization of the positive charge on the sp carbon atom. The structure is shown in Fig. 7.

Silylium ions (R_3Si^+)

The existence and mechanistic importance of the carbenium ion (R_3C^+) in organic chemistry has inspired the long search for its elusive silicon counterpart, the silylium ion (R_3Si^+). The history of attempts to identify silylium ions in condensed media is quite checkered and full of controversy.[16] Suffice it to say, the Lewis basicity of counterions (and solvents) towards cationic silicon was seriously underestimated and the concepts used to stabilize carbenium ions, namely superacidity with fluoro counterions (*e.g.* SbF_6^-), did not translate well to silicon. The use of carborane anions and the perfluoro-tetraphenylborate ion, F_{20}-BPh_4^-, was necessary to solve the silylium ion problem.

Presently, the closest structurally-characterized approach to a tri*alkyl*silylium ion is *i*-$Pr_3Si(CHB_{11}H_5Cl_6)$, shown earlier in Fig. 2.[15] The average C–Si–C bond angle is 117.3°, closer to the sp^2 rather than the sp^3 ideal. Together with the long Si–Cl bond and the significantly downfield shifted ^{29}Si NMR resonance (115 ppm), this leads to the designation of these species as "ion-like".[16] The bonding between the R_3Si^+ cation and the carborane anion is weak and probably largely ionic. As illustrated in the synthesis of carborane acids (eqn. (1)) and alkyl carboranes (eqn. (4)), R_3Si(carborane) species show very potent Lewis acidity. Although they do not contain free silylium ions, they behave like free silylium ions.

Alum*en*ium "ion-like" species such as Et_2Al(carborane) (Fig. 8), show many similarities to R_3Si(carborane) species[39] and have a rich electrophilic catalysis chemistry.[40]

The Brønsted acidities of trialkylsilylium ion-like species have not been investigated in any depth but silylium ions are clearly less acidic than their superacidic carbenium ion counterparts. This can be deduced from the stability of the silylium ion-like species with the perfluoro-tetraphenylborate anion replacing the carborane in $R_3Si(F_{20}$-$BPh_4)$.[29] The F_{20}-BPh_4^- ion is unstable with respect to boron–aryl bond cleavage at acidities just above that of the mesitylenium ion,[25] which is *ca.* 10^9 less acidic than the benzenium ion.[41] To be stable, carbenium ions require comparable or greater acidity than that needed to make the benzenium ion, so silylium ion-like species must be at least *ca.* 10^9 weaker Brønsted acids than carbenium ions. The lower acidity of trialkylsilylium ion-like species relative to carbenium ions is likely due to a combination of charge compensation by the weakly coordinating anion, the higher electropositivity of Si, and the poorer delocalization of charge *via* hyperconjugation. The existence[29] of $Et_3Si(toluene)^+$ shows that Lewis acidity of the silicon centre is more important than Brønsted acidity of the C–H groups.

A truly three-coordinate sp^2 silylium ion was eventually isolated using bulky mesityl substituents on silicon.[42,43] As

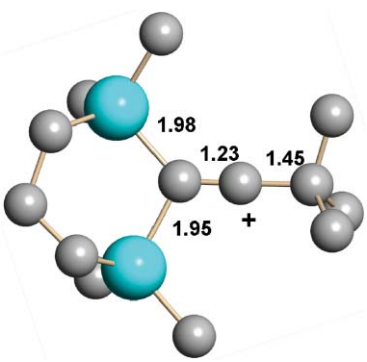


Fig. 7 X-ray structure of a vinyl cation stabilized with *t*-butyl and β-silyl groups.[38]

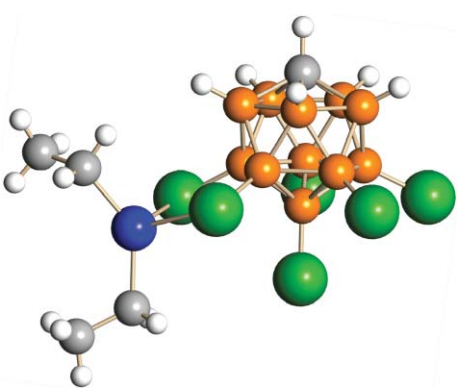


Fig. 8 X-ray structure of $Et_2Al(CHB_{11}H_5Cl_6)$ (C–Al–Cl = 136.6°).[40]

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with triaryl carbenium ions (*e.g.* trityl), acidity is relatively unimportant in the stabilization of triarylsilylium ions. Indeed, acid slowly cleaves the Si-mesityl bonds and protonated mesitylene can be isolated from the reaction mixture. Rather, it was the weakly coordinating properties of large counterions, F_{20}-BPh_4^- and carboranes, that were the key to stablizing the mesityl$_3$Si$^+$ cation. The superior crystallizing properties of carborane anions relative to F_{20}-BPh_4^- allowed the crystallographic characterization of this landmark structure (Fig. 9).

Hydronium ions (H_3O^+, $H_5O_2^+$ *etc.*)

Carborane acids pick up water from solvents and glassware with great avidity forming hydronium ion salts. This is expected for such strong acids with such "bare" protons, although, surprisingly, not all strong acids immediately protonate H_2O at the one equivalent level.[44] Protonation of water is very dependent on solvation energies and ion pairing effects so the acid strength of the H_3O^+ ion can vary by 12 orders of magnitude between water, benzene and BF_3 solvents.

Successive additions of 1 through 4 equivalents of water to carborane acids in benzene leads to isolable salts of H_3O^+, $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$ ions, respectively, most of which have not been available before as such discrete entities. They are of interest as the possible active protonating species in acid-catalyzed reactions in organic solvents since trace water is usually present. Somewhat surprisingly for the salt of a small cation, the hydronium ion salt $[H_3O][CHB_{11}Cl_{11}]$ has $>10^{-2}$ M solubility in benzene.[45] We have traced this to solvation of the H_3O^+ ion by three benzene molecules, as captured in the crystal structure shown in Fig. 10. The O–H bonds of the pyramidal H_3O^+ ion are H-bonded to the π face of benzene. This rationalizes the high solubility and there is a close analogy to Ag^+ where π complexation leads to good solubility of silver salts in arene solvents.

X-ray structural determinations of carborane salts of the $H_5O_2^+$ ion (Fig. 11)[45] and the $H_9O_4^+$ ion (Fig. 12)[46] show discrete structures of the two hydronium ions ("Zundel" and

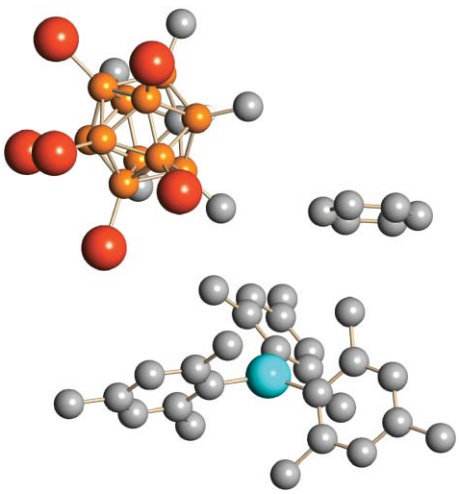

Fig. 9 Crystal structure of [mesityl$_3$Si][$CHB_{11}H_5Br_6$]·C_6H_6 showing the free, three-coordinate trimesitylsilylium cation, the well-separated carborane anion, and a benzene solvate molecule.[43]

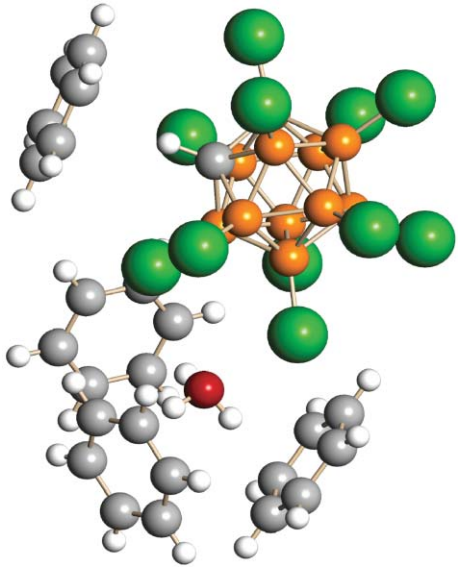

Fig. 10 X-ray structure of [H_3O·3benzene][$CHB_{11}Cl_{11}$]·benzene showing tri-solvation of H_3O^+ by benzene.[45]

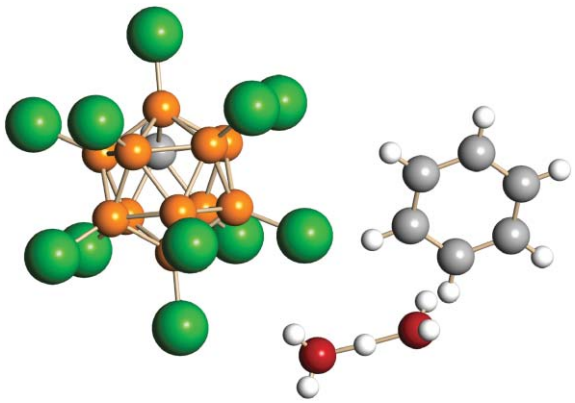

Fig. 11 X-ray structure of [H_5O_2][$CHB_{11}Cl_{11}$]·benzene showing the "Zundel-type" hydronium ion.[45]

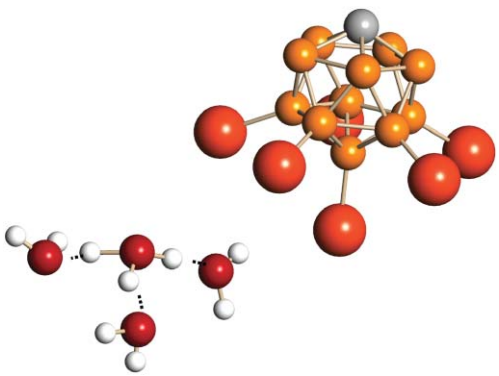

Fig. 12 X-ray structure of [H_9O_4][$CHB_{11}H_5Br_6$] showing tri-solvation of H_3O^+ by H_2O in the "Eigen-type" hydronium ion.[46]

"Eigen" type respectively) believed to be dominant in aqueous acid solution.

The $H_5O_2^+$ ion is of particular interest as a prototypical example of short, strong, low-barrier (SSLB) H-bonding where the position of H^+ is indeterminate within an interval between the two O atoms in the linear O···H···O bond. It is closely related to a number of structures of the solvated proton that have been isolated as [H(solvent)$_2$][carborane] salts.[17] It is not widely appreciated but linear *di*-solvation of H^+ is the rule when acids ionize in donor solvents. SSLB H-bonds give extra stability to these species and they have unusual and quite fascinating IR signatures.[17]

Relative acidities

The isolation of carborane acids and their use in stabilizing carbenium, arenium, fullerenium, silylium and hydronium ions allows a useful ordering of relative acidities to be constructed. The point of departure is the H_0 Hammett acidity scale for neat acids and the typically reliable relative acidities of arenium ions. For example, there are about 9 orders of magnitude difference in basicity between mesitylene and benzene.[41] These map onto each other approximately as illustrated in Fig. 13. The ability of carborane acids to protonate benzene easily places them at greater H_0 magnitude than -16. The observation that H_3O^+ and HC_{60}^+ can protonate mesitylene but not xylene, brackets their acidities in benzene between those of the mesitylenium and xyleneium ions.[23,20] The lack of evidence that trialkylsilylium ion-like species can protonate mesitylene suggests they have H_0 acidities below ~ -7. Traditional superacids stabilize *t*-butyl cations at H_0 values somewhere in the range -17 to -27 but a quantitative assessment of carbocation acidity has not been made because of the problem of oligomerization, and is complicated by the phenomenon of basicity suppression discussed below. Thus, the ability of carborane acids to stabilize tertiary carbenium ions such as *t*-butyl cation (*i.e.* protonate *iso*-butene) places them at magnitude greater than -17.

Basicity suppression

The highest attainable acidities (*e.g.* "Magic Acid", 1 : 3 $HFSO_3/SbF_5$) are generated by adding a strong Lewis acid to a strong Brønsted acid. The Lewis acid (*e.g.* SbF_5) binds to the conjugate base of the Brønsted acid (*e.g.* FSO_3^-) making the anion larger and more weakly basic, thus promoting ionization. However, the presence of the Lewis acid, often in large excess, may actually make it *more* difficult to protonate a substrate. If the Lewis acid forms an adduct with the substrate, the basicity of the substrate will be significantly lowered. Protonation of the substrate must then compete with Lewis adduct formation and several orders of magnitude more Brønsted acidity may be required. We call this phenomenon "basicity suppression" of the substrate and we suspect it is operative in the protonation of benzene and alkenes discussed above. It has not been recognized in the past and, thus, the basicities of many weakly basic molecules may have been systematically underestimated. Heretofore unprotonatable species such as Xe, whose intrinsic basicity has certainly been underestimated, might be protonated if a strong enough Brønsted acid can be prepared in the absence of a competing Lewis acid. Lewis acids are known from NMR data to interact quite strongly with Xe.[47]

Future prospects

Avoiding basicity suppression is one of the main reasons why stronger Brønsted-only acids are important. The prospects are good that tailoring the substituents on the CB_{11} cluster, such as the introduction of fluoro[48] or trifluoromethyl[49] groups, will lower the basicity of the anion without sacrificing chemical stability, and lead to even stronger acids than $H(CHB_{11}Cl_{11})$.

In preliminary experiments we have shown that carborane acids are strong enough to protonate alkanes. Applications of carborane acids to problems of hydrocarbon cracking chemistry are therefore likely. Indeed, many areas of acid catalysis may profit from the use of carborane acids, particularly where the conjugate base influences, or interferes with, the desired

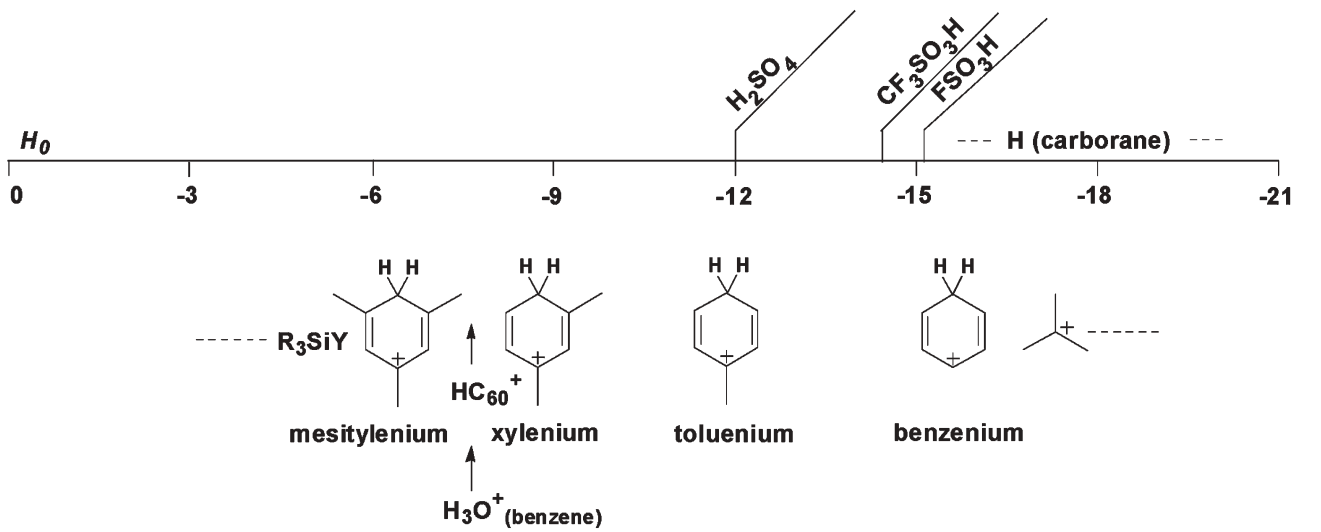

Fig. 13 Approximate relative acidities of protic species mapped onto the H_0 scale.

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chemistry. In general, the strong-yet-gentle properties of carborane acids should allow acid catalysis to proceed more cleanly, as well as allowing a distinction between Lewis and Brønsted acid processes to be made more definitively.

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