

# The Strongest Acid

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## About the Author

Chris Reed was born a *kiwi* to English parents in Auckland in 1947. He attended Dilworth School from 1956 to 1964 where his interest in chemistry was undoubtedly stimulated by being entrusted with a key to the high school chemical stockroom. Nighttime experiments with white phosphorus led to the Headmaster administering *six of the best*. He obtained his BSc (1967), MSc (1st Class Hons., 1968) and PhD (1971) from The University of Auckland, doing thesis research on iridium organotransition metal chemistry with Professor Warren R. Roper FRS. This was followed by two years of postdoctoral study at Stanford University with Professor James P. Collman working on *picket fence* porphyrin models for haemoglobin. In 1973 he joined the faculty of the University of Southern California, becoming Professor in 1979. After 25 years at USC, he moved to his present position of Distinguished Professor of Chemistry at UC-Riverside to build the Centre for *s* and *p* Block Chemistry.



His present research interests focus on weakly coordinating anions, weakly coordinated ligands, acids, silylium ion chemistry, cationic catalysis and reactive cations across the periodic table. His earlier work included extensive studies in metalloporphyrin chemistry, models for dioxygen-binding copper proteins, spin-spin coupling phenomena including paramagnetic metal to ligand radical coupling, a Magnetochemical alternative to the Spectrochemical Series, fullerene redox chemistry, fullerene-porphyrin supramolecular chemistry and metal-organic framework solids (MOFs).

His work has been recognized by Alfred P. Sloan, Camille and Henry Dreyfus Teacher-Scholar, John Simon Guggenheim and Senior Alexander von Humboldt Awards. He was the 2004 Awardee of the Richard C. Tolman Medal of the Southern California Section of the ACS. He is a Fellow of the Royal Society of Chemistry, the American Association for the Advancement of Science and the NZ Institute of Chemistry, has served on several Editorial Advisory Boards and been Guest Editor for *Accounts of Chemical Research* and *Heteroatom Chemistry*.

## Introduction

When people learn that we have made the world's strongest acid, they frequently ask: *Gee, what container do you keep it in? Doesn't it dissolve everything?* My answers: *Any old container will do* and *No, it is actually one of the gentlest acids known* inevitably disappoint. But the idea that an acid can be the *strongest yet gentlest* does intrigue those who are curious to learn more.

How can an acid be the strongest yet gentlest? It sounds like a contradiction. The answer lies in the way acid strength is defined. The strongest acid (HA) is simply the one that releases a hydrogen ion the easiest. Its anion A<sup>-</sup> is the least basic. Acid ionization in Eq. 1 moves furthest to the right hand side.



On the other hand, the *gentlest* acid is the least corrosive acid. Corrosiveness is associated with the chemistry of the anion. For example, an anion may act as a nucleophile as recognized when HF dissolves glass. The fluoride anion is a strong enough nucleophile towards silicon that it can break a protonated Si-O-Si bond. More often, the anion of a corrosive acid engages in complex redox chemistry. The

wise chemist chooses hydrochloric acid, not nitric acid, to dissolve limestone out of a copper kettle, thereby saving the kettle from oxidative destruction by the nitrate anion. All synthetic organic chemists have experienced the production of *black gunk* when their organic molecules decompose *via* complex protonation/redox chemistry in the presence of H<sub>2</sub>SO<sub>4</sub> – when all they really wanted was simple acid catalysis. Triflic acid has largely replaced sulfuric acid in acid-catalyzed organic chemistry these days because the triflate anion is less nucleophilic and less redox active than the bisulfate anion. As headlined in the first reporting on carborane acids *Acidity: It's a lot about anions*.<sup>1</sup>

## Synthesis of Carborane Acids

To make the strongest acid, one needs the least basic anion. This obvious requirement is not enough, however. The conjugate base anion must also be chemically stable towards H<sup>+</sup>. The perfluorinated tetraphenylborate anion, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>, a very popular weakly coordinating anion in transition metal chemistry,<sup>2</sup> is one of the least basic anions known but it is unsuitable for superacid chemistry because of acid cleavage of a B-C bond. The strongest acids attainable with this anion are those whose acidity is atten-

uated by relatively basic solvents such as diethyl ether<sup>2</sup> in  $[\text{H}(\text{Et}_2\text{O})_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  or mesitylene in the mesitylenium ion salt  $[\text{H}(\text{mesitylene})]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ .<sup>3</sup> The acidity of these cations is millions of times lower than that expected for the unsolvated (but non-existent) acid  $\text{HB}(\text{C}_6\text{F}_5)_4$ . Most chemists do not realize that fluoroanion acids commonly written as  $\text{HBF}_4$ ,  $\text{HSbF}_6$ , *etc.*, are also non-existent. The  $\text{BF}_4^-$  and  $\text{SbF}_6^-$  anions are unstable to  $\text{H}^+$  with respect to HF elimination and their acids only exist in forms such as  $\text{H}(\text{H}_2\text{O})_n^+\text{BF}_4^-$  and  $\text{H}(\text{HF})_n^+\text{SbF}_6^-$ .

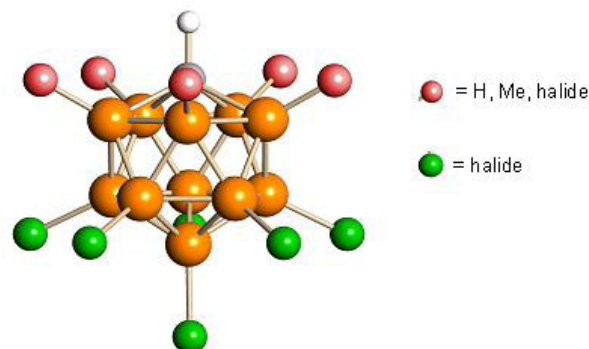
A convenient guide to anion basicity is the vNH scale,<sup>4</sup> which uses infrared spectroscopy to rank the H-bond acceptor ability of an anion in a trioctylammonium ion pair. The stronger the basicity of the anion  $\text{A}^-$  in the  $\text{Oct}_3\text{N}^+-\text{H}---\text{A}^-$  ion pair, the lower the NH stretching frequency. As shown in Table 1, this scale indicates that the conjugate acid of the  $\text{B}(\text{C}_6\text{F}_5)_4^-$  anion should be the strongest acid but, as discussed above, the anion is not sufficiently stable to withstand bare  $\text{H}^+$  acidity. The next most weakly basic classes of anions are the fluoroanions,  $\text{PF}_6^-$ ,  $\text{SbF}_6^-$ , *etc.*, and carboranes of the type  $\text{HCB}_{11}\text{X}_6^-$  ( $\text{X} = \text{H}$ , halide). As explained above, the pure conjugate acids of fluoroanions do not actually exist. We had been working with carborane anions as weakly coordinating, *i.e.* weakly Lewis basic, anions in transition metal and main group cation chemistry<sup>5</sup> and it became clear that we should start exploring their Brønsted ( $\text{H}^+$ ) basicity. The vNH scale made the clear prediction that the conjugate acids of carborane anions would be much stronger than familiar mineral acids  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{CF}_3\text{SO}_3\text{H}$ , *etc.*, including fluorosulfuric acid ( $\text{HSO}_3\text{F}$ ), which in the year 2000 was the strongest neat acid known.

**Table 1.** vNH anion basicity ranking in  $\text{Oct}_3\text{NH}^+$  ion pairs.

Conjugate base	vNH ( $\text{cm}^{-1}$ )	$\Delta v$	Comments re conjugate acid
$\text{B}(\text{C}_6\text{F}_5)_4^-$	3233	0	non-existent
$\text{EtCB}_{11}\text{F}_{11}^-$	3219	14	predicted strongest
$\text{PF}_6^-$	3191	42	non-existent
$\text{SbF}_6^-$	3175	58	non-existent
$\text{HCB}_{11}\text{Cl}_{11}^-$	3163	70	present strongest
$\text{HCB}_{11}\text{H}_5\text{Cl}_6^-$	3148	85	
$\text{BF}_4^-$	3133	100	non-existent
$\text{HCB}_{11}\text{H}_5\text{Br}_6^-$	3125	108	
$\text{HCB}_{11}\text{H}_5\text{I}_6^-$	3097	136	
$\text{N}(\text{SO}_2\text{C}_4\text{F}_9)_2^-$	3086	147	prev. strongest (gas)
$\text{ClO}_4^-$	3050	183	
$\text{FSO}_3^-$	3040	193	prev. strongest (liq)
$\text{CF}_3\text{SO}_3^-$	3030	203	

Carborane anions (Fig. 1) are weakly basic because they are large and the delocalized negative charge is masked by weakly basic substituents on boron, typically halides. The undecachloro  $\text{HCB}_{11}\text{Cl}_{11}^-$  anion has about the same basicity as a chloroalkane. The negative charge is delocalized over the icosahedral  $\text{CB}_{11}$  cage in bonding that is referred to as  $\sigma$  aromatic. The comparison to  $\pi$  aromaticity in benzene is a useful one. Just as planar benzene gains

stability from  $\pi$  aromaticity in 2D, icosahedral carboranes gain stability from  $\sigma$  aromaticity in 3D. In its chemistry, benzene resists disruption of its aromaticity and, similarly, carboranes resist disruption of the icosahedral  $\text{CB}_{11}$  core. But, since  $\sigma$  bonding is stronger than  $\pi$  bonding, carboranes resist disruption of their cores to an even greater extent than benzene. This is the origin of the legendary stability of carboranes (and the isoelectronic all-boron  $\text{B}_{12}\text{H}_{12}^{2-}$  ion). A paper stating that anions of this type had *...oral toxicity in rats roughly comparable to sodium chloride...*<sup>6</sup> made us acutely aware of the extraordinary inertness of the icosahedral boron framework and the potential of carborane anions as weakly basic anions.

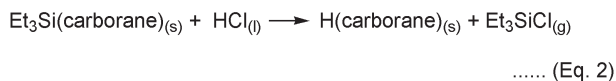


**Fig. 1.** Icosahedral carborane anions of the type  $\text{HCB}_{11}\text{R}_5\text{X}_6^-$  used as conjugate bases to carborane acids; orange = B, gray = C, white = H, green = halide, red = R (H, methyl or halogen).

The parent icosahedral carborane anion,  $\text{HCB}_{11}\text{H}_{11}^-$ , was first synthesized by Knoth at Du Pont in 1967, at a time when industrial chemists were free to pursue their curiosity.<sup>7</sup> The chemistry of  $\text{HCB}_{11}\text{H}_{11}^-$  lay fallow for a couple of decades while research on the isoelectronic neutral and dianionic analogues,  $\text{C}_2\text{B}_{10}\text{H}_{12}$  and  $\text{B}_{12}\text{H}_{12}^{2-}$ , took precedence. In the mid-1980s, the dedicated Czech boron group of Plešek, Štibr and Heřmánek reported an improved synthesis from decaborane and showed that halogenation proceeded quite selectively to give 7,8,9,10,11,12-hexahalogenated anions,  $\text{HCB}_{11}\text{H}_5\text{X}_6^-$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ; see Fig. 1).<sup>8</sup> While there is some commercial availability, and a new synthesis is available starting with sodium borohydride,<sup>9</sup> the same basic synthesis of the  $\text{HCB}_{11}\text{H}_{11}^-$  is still used in our labs today. Price is the greatest limitation to making  $\text{HCB}_{11}\text{H}_{11}^-$ , but is not too difficult to produce 7 g of the cesium salt from 10 g of decaborane starting material in about a week. We make the synthetic details readily available.<sup>10</sup> Undergraduates perform the synthesis in my labs as their initiation into research. The halogenation reactions present varying degrees of difficulty such that the hexabromo and undecachloro anions,  $\text{HCB}_{11}\text{H}_5\text{Br}_6^-$  and  $\text{HCB}_{11}\text{Cl}_{11}^-$ , are the most commonly used. Alkali metal salts of the  $\text{HCB}_{11}\text{Cl}_{11}^-$  anion are extraordinarily stable and can be heated to  $>400^\circ\text{C}$  without detectable decomposition.

The starting material for the synthesis of a carborane acid is the extremely strong Lewis acid,  $\text{Et}_3\text{Si}(\text{carborane})$ . Such trialkylsilyl carboranes are the silicon analogues of carbenium ions,  $\text{R}_3\text{C}^+$ , and because silicon is more electropositive than carbon and less stabilized by hyperconjugation, they are stronger electrophiles.<sup>11</sup> Structurally, they are not fully ionic, showing weak coordination to the

carborane anion. We call them *ion-like*. While they are not truly *free* silylium ions, they behave like silylium ions. Indeed, they are fierce electrophiles, abstracting chloride from anhydrous HCl to give the desired carborane acid in essentially quantitative yield (Eq. 2):

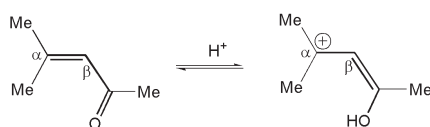


### Physical Properties of Carborane Acids

Carborane acids are colourless solids that are sublimable at *ca.* 150 °C under vacuum. They must be handled with strict exclusion of water and errant bases. The X-ray crystal structure of H(CHB<sub>11</sub>Cl<sub>11</sub>) reveals a linear polymeric chain with proton bridges between Cl atoms (Fig. 2).<sup>12</sup> The IR spectrum of H(HCB<sub>11</sub>Cl<sub>11</sub>) does *not* show νHCl vibrations expected for typical, *i.e.* asymmetric H-bonding. Instead, broad absorptions at *ca.* 1250 and 700 cm<sup>-1</sup> assigned to ν<sub>as</sub> ClHCl and δClHCl, respectively, are seen. These are signatures of symmetrical, or essentially symmetrical, H-bonding and are becoming increasing recognized as the expected mode of H-bonding for a relatively strongly acidic proton with linear two-coordination by identical bases.<sup>13</sup> The <sup>1</sup>H NMR spectrum of H(HCB<sub>11</sub>Cl<sub>11</sub>) in liquid SO<sub>2</sub> shows a highly downfield shifted peak at *ca.* 20 ppm assigned to the H(SO<sub>2</sub>)<sub>2</sub><sup>+</sup> ion. We suspect that carborane acids only dissolve in solvents that they can protonate and that the stable species in solution is typically a *two*-coordinate H(solvent)<sub>2</sub><sup>+</sup> ion. When chemists write H<sup>+</sup> as shorthand in a chemical equation, it is a very poor representation of the actual hydrogen ion species present.

Using the νNH scale (Table 1), H(HCB<sub>11</sub>Cl<sub>11</sub>) is currently the strongest acid that has been fully characterized. The scale indicates that the corresponding perfluorinated carborane acid would be even stronger. A preliminary report of its synthesis<sup>14</sup> as H(RCB<sub>11</sub>F<sub>11</sub>) (R = Me, Et) appeared in 2007, but no follow up paper has been published and the reported IR spectrum is inconsistent with what we expect by analogy to H(HCB<sub>11</sub>Cl<sub>11</sub>). We have repeated this work with some adjustments and produced a new material that has the expected IR spectrum of H(HCB<sub>11</sub>F<sub>11</sub>).<sup>15</sup>

In order to show that H(HCB<sub>11</sub>Cl<sub>11</sub>) is the strongest acid *in solution* we have employed the mesityl oxide method of Fărcașiu<sup>16</sup> to show that carborane acids are more ionized than mineral acids. This scale is based on the <sup>13</sup>C NMR chemical shift difference (Δδ) between the C<sub>α</sub> and C<sub>β</sub> carbon atoms of mesityl oxide whose averaged values increase with increasing protonation as Scheme 1 is shifted to the right hand side:



**Scheme 1.** Equilibrium protonation of mesityl oxide.

<sup>13</sup>C NMR data for 0.15 M solutions of various acids and 0.10 M mesityl oxide are given in Table 2. 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 oxyacid on the *H*<sub>0</sub> Hammett acidity scale (-15.1), as well as triflic acid (*H*<sub>0</sub> = -14.1). It is also evident from the data of Table 2 that, whereas oxyacids only partially protonate mesityl oxide, carborane acids are strong enough to move the protonation in Scheme 1 completely to the right hand side. The Δδ value maximizes at *ca.* 84 ppm indicating their acidities are levelled, probably at the acidity of H(SO<sub>2</sub>)<sub>2</sub><sup>+</sup>. The true measure of their maximum acidity is not determined in this system.

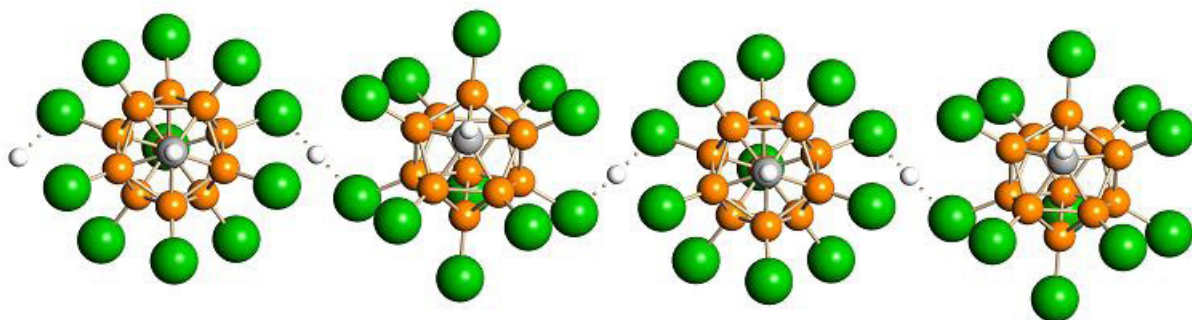
**Table 2.** Acidity rankings on the <sup>13</sup>C Δδ mesityl oxide scale.

Acid	<sup>13</sup> C Δδ (ppm)	<i>H</i> <sub>0</sub>
H(CHB <sub>11</sub> Cl <sub>11</sub> )	84.0 ± 0.1	<sup>a</sup>
H(CHB <sub>11</sub> H <sub>5</sub> Cl <sub>6</sub> )	83.8 ± 0.1	<sup>a</sup>
H(CHB <sub>11</sub> H <sub>5</sub> Br <sub>6</sub> )	83.8 ± 0.1	<sup>a</sup>
H(CHB <sub>11</sub> H <sub>5</sub> I <sub>6</sub> )	83.3 ± 0.1	<sup>a</sup>
FSO <sub>3</sub> H	73.8 ± 0.5	-15.1
CF <sub>3</sub> SO <sub>3</sub> H	72.9 ± 0.4	-14.1
HN(SO <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub>	72.0 ± 0.4	<sup>a</sup>
H <sub>2</sub> SO <sub>4</sub>	64.3 ± 3.1 <sup>b</sup>	-12.1
mesityl oxide	32.4 ± 0.1	

<sup>a</sup> *H*<sub>0</sub> acidity values unavailable because acids are solids, not liquids.

<sup>b</sup> Incomplete miscibility of H<sub>2</sub>SO<sub>4</sub> in liq. SO<sub>2</sub> leads to higher error limits and possible underestimate of Δδ.

In collaboration with Steve Kass, we have shown that H(HCB<sub>11</sub>Cl<sub>11</sub>) is easily the strongest of any isolable acid in the *gas* phase.<sup>17</sup> Compared to the former record holder (C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>)<sub>2</sub>NH with Δ*H*<sub>acid</sub><sup>o</sup> = 291 ± 2 kcal/mol, H(HCB<sub>11</sub>Cl<sub>11</sub>) has a gas phase enthalpy of deprotonation of only 241 ± 29 kcal/mol. The HCB<sub>11</sub>Cl<sub>11</sub><sup>-</sup> conjugate base was found by photoelectron spectroscopy to have a remarkably large electron binding energy (6.35 ± 0.02 eV), but the value for the (C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup> anion is even larger (6.5 ± 0.1 eV). Thus, it is the weak H-HCB<sub>11</sub>Cl<sub>11</sub> bond dissociation energy (calc. 70 kcal/mol) compared to the stronger BDE of H-N(SO<sub>3</sub>C<sub>4</sub>F<sub>9</sub>)<sub>2</sub> (calc. 127 kcal/mol) that accounts for the greater acidity of carborane acids.



**Fig. 2.** The X-ray structure of the carborane acid H(CHB<sub>11</sub>Cl<sub>11</sub>) (white = H, green = Cl, orange = B, gray = C).

Thus, in the solid state by the  $\nu\text{NH}$  scale, in solution by Fărcașiu's mesityl oxide scale, and in the gas phase by the measured enthalpy of proton loss,  $\text{H}(\text{HCB}_{11}\text{Cl}_{11})$  is the strongest acid. It will soon be surpassed by its fluorinated analogue  $\text{H}(\text{HCB}_{11}\text{F}_{11})$ .<sup>15</sup> Nevertheless, apparently stronger acidity can be obtained in solution in traditional superacid media when conventional acids are mixed with strong Lewis acids. One of the strongest is the so called Magic Acid, a 1:3 mixture of  $\text{HFSO}_3$  and  $\text{SbF}_5$ . The Lewis acid ( $\text{SbF}_5$ ) binds to the conjugate base of the Brønsted acid ( $\text{FSO}_3^-$ ) presumably making the anion larger and more weakly basic, thereby promoting ionization. These Brønsted/Lewis acid mixtures have been extensively studied by Gillespie and their acidities placed on a quantitative basis using the logarithmic Hammett  $H_0$  acidity scale.<sup>18</sup> The  $H_0$  scale can be viewed as an extension into non-aqueous media of the well known water-based pH scale (Fig. 3). The origin of the designation *superacid* is set arbitrarily to any acid whose  $H_0$  magnitude exceeds that of 100% sulfuric acid ( $H_0 = -12.1$ ). The approximate  $H_0$  acidities required to protonate various marker bases are indicated. Note that benzene is not protonated by the strongest mineral acid, *i.e.*  $\text{HFSO}_3$  at  $H_0 = -15.1$ , but since all basicity scales estimate *ca.*  $10^9$  basicity difference between mesitylene and benzene, an  $H_0$  acidity of *ca.*  $-17$  is judged necessary to protonate benzene. Carborane acids easily protonate benzene so their acidity is apparently greater than  $-17$  on the  $H_0$  scale.

As attractive as the  $H_0$  quantification of acidity is, it is conceptually problematic as a measure of the basicity of molecules. Consider, for example, the case of xenon which cannot be protonated even by the strongest Brønsted/Lewis mixture at  $H_0 = -30$ . Is Xe really a  $10^{18}$  weaker base than toluene? I doubt it. Here is why. The presence of a large excess of  $\text{SbF}_5$  in Magic Acid, essentially as solvent, means that Xenon will form a Lewis acid/base adduct,  $\text{Xe}:\rightarrow\text{SbF}_5$ . Indeed, Lewis acids are known from NMR data to interact quite strongly with Xe.<sup>19</sup> Lewis adduct formation will make Xe less basic and much more difficult to protonate. In other words, Brønsted protonation of Xe must compete with Lewis adduct formation. Several orders of magnitude more Brønsted acidity will be required to observe it. We have called this phenomenon *basicity suppression*.<sup>20</sup> It means that the basicities of all weakly

basic substrates have been systematically underestimated. Thus, heretofore unprotonatable species such as Xe might be protonated if a strong enough Brønsted acid can be prepared *in the absence of* a competing Lewis acid. This motivates us to make even stronger Brønsted-only acids. Indeed, once we have conclusively proved<sup>15</sup> the existence of  $\text{H}(\text{HCB}_{11}\text{F}_{11})$  we will try to protonate Xe.

### The Reactivity of Carborane Acids

Carborane acids have a number of advantages over traditional superacid media.<sup>20</sup> As crystalline solids rather than glass-dissolving viscous liquids, they are easily weighed and handled. Their acid strength surpasses all other pure Brønsted acids by at least a factor of 100, probably by much more. The absence of a Lewis acid such as  $\text{SbF}_5$  gives them their most important advantage over traditional superacid media: they are non-redox active, *i.e.* *gentle*, when it comes to protonating substrates. Fragile substrates readily can be protonated and isolated. Carborane salts tend to crystallize nicely making many protonated substrate cations amenable to single crystal X-ray characterization for the first time. Finally, since carborane anions interact extremely weakly with their cations, certain easily distorted cations such as  $\text{H}(\text{H}_2\text{O})_n^+$  can be crystallized to give structures that are more closely related to those in solution. This allowed us to find a surprising solution to one of the oldest unsolved problems in chemistry: the  $\text{H}_{13}\text{O}_6^+$  structure of  $\text{H}_{\text{aq}}^+$  in water.<sup>21</sup> The following protonation chemistry illustrates some of the key attributes of carborane acids.

To illustrate the *gentle* qualities of carborane acids, consider the protonation of  $\text{C}_{60}$ . A decade of attempts to observe protonation of  $\text{C}_{60}$  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  $\text{C}_{60}$ , possibly because of the presence of redox active impurities in the acid or the solvent. On the other hand, carborane acids such as  $\text{H}(\text{HCB}_{11}\text{H}_5\text{Cl}_6)$  cleanly and reversibly protonate  $\text{C}_{60}$  in dry *o*-dichlorobenzene solvents at room temperature.<sup>22</sup> The resulting  $[\text{HC}_{60}^+][\text{carborane}^-]$  salt was isolated in

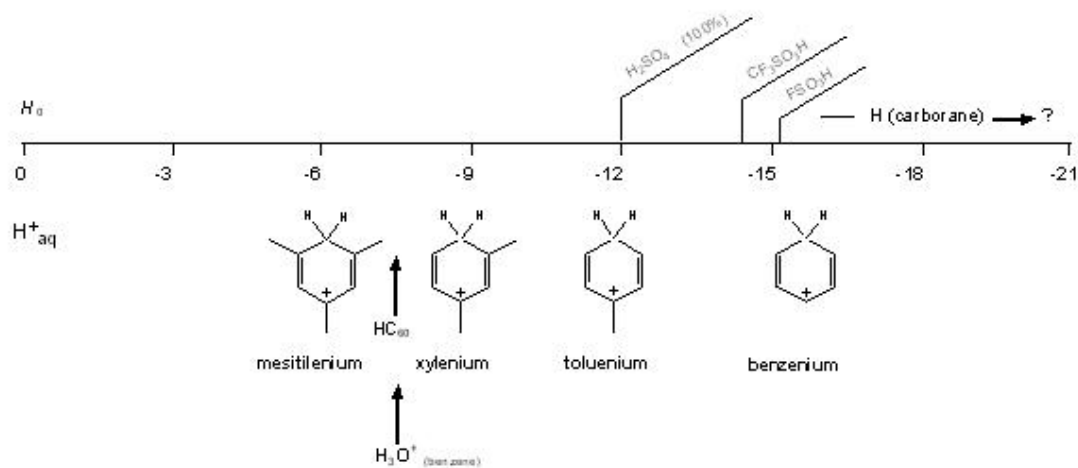
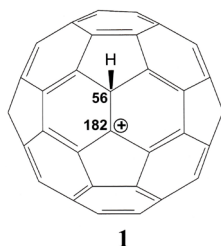
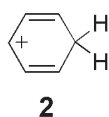


Fig. 3. Approximate relative acidities of protic species mapped onto the  $H_0$  scale.

quantitative yield and characterized by novel solid state  $^{13}\text{C}$  CPMAS methods to have a 1,2-carbocation static structure and the  $^{13}\text{C}$  assignments shown in **1**. In solution, the appearance of a single sharp  $^{13}\text{C}$  resonance indicates that the proton in the  $\text{HC}_{60}^+$  cation is a true *globetrotter*, rapidly sampling attachment to all 60 carbon atoms on the NMR timescale. These studies allowed the basicity of  $\text{C}_{60}$  to be bracketed between that of mesitylene and xylene. 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 are sufficiently gentle that they do not decompose the resulting cation.



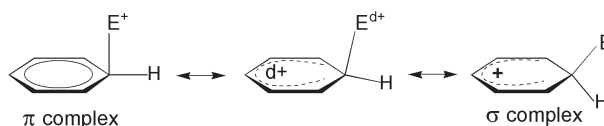
To illustrate the *strength* of carborane acids and *crystallizability* of their salts, consider the protonation of arenes such as benzene.<sup>3</sup> Protonated arenes are important as the intermediates of electrophilic aromatic substitution – the so called Wheland intermediates in organic textbooks, even though they were proposed and characterized much earlier by von Pfeiffer and Wizinger.<sup>23</sup> Triflic acid does not protonate benzene and the previously strongest known neat liquid acid,  $\text{HFSO}_3$ , ( $H_0 = -15.1$ ) does so to only a minimal extent. Olah<sup>24</sup> found that mixed Brønsted/Lewis acids such as  $\text{HF}/\text{SbF}_5$  were necessary to attain acidity high enough to protonate benzene, but this came at a price. The presence of  $\text{SbF}_5$  in excess, or latently in  $\text{SbF}_6^-$  or  $\text{Sb}_2\text{F}_{11}^-$  anions, limited the stability of the resulting  $\text{C}_6\text{H}_7^+$  benzenium ion to temperatures well below ambient. On the other hand, when a carborane acid is used to protonate benzene, the resulting benzenium ion salt,  $[\text{C}_6\text{H}_7^+][\text{carborane}^-]$ , is stable to 150 °C – like most regular organic molecules. This demonstrates both the strong and gentle qualities of carborane acids. Single crystals of a benzenium ion salt were successfully grown but the metrical accuracy of the X-ray structure suffered from disorder. Indeed,  $^{13}\text{C}$  CPMAS NMR data indicated that the  $\text{C}_6\text{H}_7^+$  ion was 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  $\sigma$  complex, most simply written as resonance structure **2**.



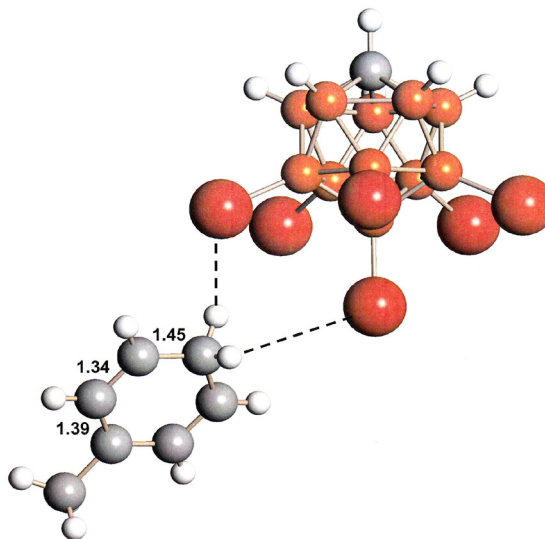
Protonated toluene as a  $\text{HCB}_{11}\text{H}_5\text{Br}_6^-$  salt led to a high resolution X-ray structure (Fig. 4). The C-C bond lengths are consistent with the structure **2** as the major contributing resonance form, with the formal positive charge *para* to the site of protonation. The shortest C-C distance (1.34 Å) 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 C-C bond is to the  $sp^3$  protonated carbon atom. As shown by the broken lines in Fig. 4, there are  $sp^3$  C-H bond H-bonding-type interactions of the cation with the halogen substituents on the carborane anion, revealing the most acidic protons. In this sense, the formal positive charge in the resonance form **2** is a little misleading.

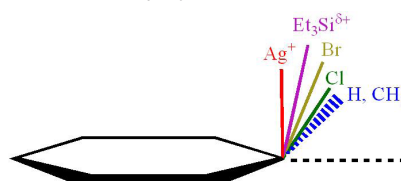
The need for accurate X-ray structural data on the intermediates of electrophilic aromatic substitution arises because conventional wisdom on the structure of arenium ions has been challenged recently. In 1993, Lambert reported the structure of a silylarenium ion which did not conform to the structural expectations of a  $\sigma$  complex. The expected  $sp^3$  character of the silylated carbon atom was only partially developed.<sup>25</sup> We have offered an explanation for this structure and proposed that it should be viewed as neither a traditional  $\sigma$  complex with  $sp^3$  carbon, nor a  $\pi$  complex with  $sp^2$  carbon, but as a point along a  $\sigma$ - $\pi$  continuum (Scheme 2).<sup>26</sup> This viewpoint has gained recognition with adoption and elaboration in reviews<sup>27</sup> but it has yet to be seen widely in textbooks. The structural results for various electrophiles towards arenes are summarized in Fig. 5. Electrophiles of the heavier elements, which engage less in  $sp^3$  hybridized bonding, show greater  $\pi$  character.



**Scheme 2.** The  $\pi$ - $\sigma$  continuum in arenium ion structures.



**Fig. 4.** X-ray structure and C-C bond lengths of protonated toluene as  $\text{HCB}_{11}\text{H}_5\text{Br}_6^-$  salt.



**Fig. 5.** The continuum of structures from  $\pi$  in  $\text{Ag}(\text{C}_6\text{H}_6)^+$  to  $\sigma$  in the  $\text{C}_6\text{H}_7^+$  ion.

## Conclusion

Carborane acids are the strongest Brønsted acids present-

ly known – in solid, solution and gas phases. One should never say never, but it is hard to imagine another class of conjugate base anions fulfilling the necessary requirements of lower basicity *and* chemical stability towards  $H^+$  such that an even stronger class of acids could be synthesized. The extraordinary stability of the icosahedral  $CB_{11}$  carborane core, ascribed to  $\sigma$  aromatic bonding, is the underlying reason for the existence of carborane acids. We have explored the conjugate acid of the even more stable all-boron  $B_{12}Cl_{12}^{2-}$  anion but we find that the diprotic acid  $H_2(B_{12}Cl_{12})$  has close to the same acid strength as its isoelectronic monoprotic carborane counterpart  $H(HCB_{11}Cl_{11})$ .<sup>28</sup> The presence of  $\sigma$ -aromatic bonding in the core of the carborane anion also explains the gentleness of carborane acids. Carborane acids separate protic acidity from corrosive anion reactivity in a manner not previously attained. This property, above all others, is what has made carborane acids so useful in stabilizing protonated species. On the other hand, carboranes are expensive and will only find applications where small amounts are needed and no cheaper substitute can be found; these are most likely in catalysis at the extremes of electrophilicity.<sup>29</sup> Ozerov's discovery of catalytic dehydrofluorination of freons with silyl carboranes,<sup>30</sup> and our finding that chloroalkanes can be protonated to eliminate HCl and form carbocations,<sup>31</sup> point the way forward, offering potential solutions for environmental remediation of halocarbon solvent waste. At this point in time, however, carborane acids are having their greatest impact in stabilizing protonated species and illuminating concepts of acidity. Carborane acids have also exposed chemists to some unique chemistry of boron, the fascinating fifth element of the periodic table.

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## NZIC Annual General Meeting

The NZIC AGM will take place during the NZIC Conference in Hamilton at the University of Waikato in the S Lecture Theatre Block, Room S1.04, at 12.30 pm on Thursday 1 December 2011. The S Lecture Theatre Block is that to be used for all NZIC Conference sessions save the plenary lectures.

### Agenda

- Apologies
- Minutes of 2010 AGM held at Victoria University of Wellington, 17 November 2010
- Matters arising
- Financial Report – including auditor's report
- Election of Officers
  - President
  - 1<sup>st</sup> Vice-President
  - 2<sup>nd</sup> Vice-President
  - Treasurer
  - Honorary General Secretary
6. Other Business

*Nominations for the Officers of Council close with NZIC administration on 31 October 2011;*  
email: [NZIC.office@nzic.org.nz](mailto:NZIC.office@nzic.org.nz)