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Carboranes: A New Class of Weakly Coordinating Anions for Strong Electrophiles, Oxidants, and Superacids

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Introduction

Weakly coordinating anions have recently achieved major commercial importance in olefin polymerization[1] and are a likely component of the coming revolution in lithium battery technology.[2] These applications have grown out of two decades of basic research into the special properties of anions containing hydrocarbon and fluorocarbon functionality. Triflate ($OSO_2CF_3^-$), tetrakis(3,5-bis(trifluoromethyl)phenyl)borate ($BAr^F{}_4^-$), and perfluorotetraphenylborate ($F_{20}BPh_4^-$) are prime examples of anions where exceptional characteristics such as low nucleophilicity, chemical inertness, solubility, leaving group lability, and weak coordination have led to applications throughout organic and inorganic chemistry. They are particularly useful for stabilizing highly reactive cations and as counterions for cationic Lewis acid catalysts in a wide variety of electrophilic chemistry.

A new class of weakly coordinating anions has recently been recognized. It is based on the remarkably stable boron cluster framework of monocarborane anions such as the icosahedral $CB_{11}H_{12}^-$, introduced in 1986 as "a new candidate for the least coordinating anion".[3] Carboranes might be perceived as exotic species of only esoteric interest. One of the purposes of this Account is to dispel this notion. Of all the known classes of weakly coordinating anions (oxyanions, fluoroanions, tetraarylborates, carbanions, bis(perfluorosulfonyl)imides, polyoxometalates, and carboranes),[2,4,5] it is the carboranes that perhaps have the greatest potential for further elaboration and application. Paradoxically, carboranes combine a versatile functionalization chemistry with unparalleled inertness. They are something like a 3D analogue of benzene and can be tailored to function at new extremes of electrophilic and oxidative reactivity. They are patented counterions for cationic catalysts.[6] With high symmetry, dipolarity, and a diameter of about 1 nm, they are potential building blocks in nanochemistry and crystal engineering.

History

In the mid-1980s, two visiting boron chemists, Fred Hawthorne and Russell Grimes, gave seminars in our department on neutral and dianionic dicarboranes having impressive stability and functionalization characteristics. Upon inquiry into the existence of monoanionic analogues we learned of the existence of the monocarborane $CB_{11}H_{12}^-$ (see Figure 1). When we found a literature report that alkali metal salts of *closo*-borate anions passed straight through living organisms and had about the toxicity of sodium chloride,[7] we began to appreciate the legendary stability of the icosahedral boron core. They were also species without lone pairs of electrons *and* without π electrons—a very rare property in anions. This suggested that they would have very low nucleophilicity and be very weakly coordinating. An additional attraction was their aesthetic appeal. Prior to C_{60}, the $B_{12}H_{12}^{2-}$ dianion and its dodeca-substituted derivatives were the only discrete molecules to have perfect I_h symmetry.

At the same time, we had been trying to prepare coordinatively unsaturated cations such as $Fe(TPP)^+$ (TPP = tetraphenylporphyrinate) and $Rh(PPh_3)_3^+$ and were beginning to get interested in synthesizing the long-sought silylium ion (R_3Si^+).[8] The so-called noncoordinating anions of that time,[9] such as SbF_6^- and tetraphenylborate, turned out to coordinate or undergo bond cleavage when paired with highly reactive cations such as $Fe(TPP)^+$.[10] Indeed, many weakly coordinating anions are themselves Lewis acid/base conjugates of a superior nucleophile (e.g., $SbF_6^- \rightarrow SbF_5 + F^-$). Their capacity to act as inert counterions is always limited by a competition reaction for that nucleophile (e.g., F^-). The unit integrity of the icosahedral framework of $CB_{11}H_{12}^-$ was therefore a very attractive feature.

First synthesized at Du Pont by Knoth in the 1960s,[11] the preparation of $CB_{11}H_{12}^-$ was later improved by the expert boron group at Rez-near-Prague.[12] Nevertheless, $CB_{11}H_{12}^-$ lay essentially fallow in the literature for a couple of decades. The only significant recognition of the weakly coordinating ability of *closo*-borate anions was in the work of Zakharova,[13] who used the dianions to prepare labile salts of Ni(II) and Pd(II), e.g. $[Ni(MeCN)_6][B_{12}H_{12}]$.

The Special Properties of Carboranes

The icosahedral B_{12} cage of boron chemistry may be the most stable cluster in all of chemistry. Having tangentially delocalized σ bonding (i.e., σ aromaticity), and σ bonds being the strongest in chemistry, the HOMO−LUMO gap in $CB_{11}H_{12}^-$ is enormous—far greater than that of π aromatic systems. It is transparent into the far UV.[14] The cluster electron count is a closed shell for boron chemistry, and this leads to its designation as *closo*-$CB_{11}H_{12}^-$. The

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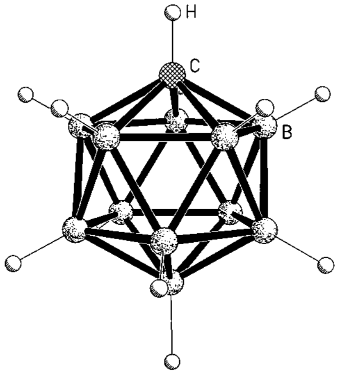

FIGURE 1. Pseudo-icosahedral parent carborane, $CB_{11}H_{12}^-$.

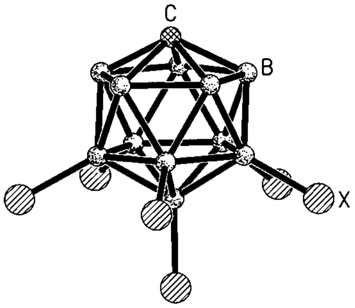

FIGURE 2. The very useful 7,8,9,10,11,12-hexahalocarboranes, $CB_{11}H_6X_6^-$ ($X = Cl, Br, I$). H atoms are not shown.

high energy required for disruption of the cluster framework gives this ion tremendous stability.

Despite this stability, or in fact because of it, the protruding B−H bonds are amenable to electrophilic substitution—in a manner reminiscent of benzene. For example, strong electrophiles such as halogens lead to the very useful hexahalo derivatives $CB_{11}H_6X_6^-$ shown in Figure 2.[15,16] The CB_{11} cage is polarized such that substitution occurs preferentially at the boron end of the cluster. The 12 position (antipodal to carbon) is usually substituted first, followed by the "lower" pentagonal belt (positions 7−11). Full dodeca-substitution has been accomplished with methyl triflate[17] to give $CB_{11}Me_{12}^-$, and undecachlorination can be achieved with excess chlorine, once the C−H bond has been methylated.[18]

While the B−H bonds of $CB_{11}H_{12}^-$ are somewhat hydridic and amenable to electrophilic substitution, the C−H bond is by comparison somewhat acidic. It can be lithiated with butyllithium,[19] and treatment of the lithio species with alkyl halides leads to C-alkylation in 1-R-$CB_{11}H_{11}^-$ derivatives.[15,20] This derivatization at carbon proceeds just as well when the boron cage is hexahalogenated, illustrating how easily C- and B-derivatization can be combined. This is what gives carboranes their versatility. The synthetic potential for varying the constitution and the properties of carborane anions is far from being fully exploited.

In addition to the 12-vertex ions based on $CB_{11}H_{12}^-$, there are related classes of anions based on the 10-vertex $CB_9H_{10}^-$ ion[21−23] as well as the M^{3+} bisdicarbollides e.g., $Co(C_2B_{11}H_9)_2^-$.[21,24] These anions appear to be somewhat less robust than those based on $CB_{11}H_{12}^-$ and have received less attention. Their differing solubility characteristics can, however, prove useful.[22]

Table 1. Average Carbonyl Stretching Frequencies for $FeCp(CO)_2Y$

Y	v_{CO} in toluene, cm^{-1}	Y	v_{CO} in toluene, cm^{-1}
I^-	2016	$Co^{III}(Br_3C_2B_9H_8)_2^-$	2087
$Co^{III}(C_2B_9H_{11})_2^-$	2045	$CB_9H_5Br_5^-$	2096
ClO_4^-	2049	$CB_{11}Me_{12}^-$	2098
$CB_{11}H_{12}^-$	2049	$CB_{11}H_6Br_6^-$	2108
SbF_6^-	2050		

The Least Coordinating Anion

The realization that there can be no such thing as a noncoordinating anion (or solvent)[25] has been slow to take hold.[2,4,5,9] It was greatly accelerated by focusing on the search for the *least* coordinating anion.[3]

Our initial publication used the varying out-of-plane displacement of the Fe atom toward the anion in the tetraphenylporphyrin complex Fe(TPP)(anion) as a criterion of anion coordinating strength.[3] At that time, $CB_{11}H_{12}^-$ (Figure 1) was structurally the least coordinating anion toward the seemingly unattainable "bare" $Fe(TPP)^+$ moiety. Since that time, it has been eclipsed by the less coordinating hexahalogenated carboranes (Figure 2) but coordination of arene solvents then becomes competitive.[26] The current least coordinating anions for various cations have about the same nucleophilicity as toluene. Although limited as a criterion for the least coordinating anion to Fe(TPP)Y species that give single crystals, the $Fe(TPP)^+$ moiety has recently become an important new and very sensitive reporter of the *ligand field* strength of weakly coordinating anions, an electronic property that is not necessarily correlated with coordinating strength. In this novel "magnetochemical series",[27] which complements the familiar Spectrochemical Series, the carboranes rank as the weakest field ligands presently known.

A number of rankings of the relative coordinating ability of anions have been developed. Like all attempts to measure Lewis base strength, they are dependent on the choice of the particular Lewis acid used as a reference. Multiple rankings with somewhat different orderings are therefore inevitable and, in fact, desirable.

A soft, transition-metal-based ranking is the average carbonyl stretching frequency of $FeCp(CO)_2Y$ as a function of anionic ligand Y^-.[21] Increasing νCO correlates with diminished π back-bonding which in turn reflects increasing cationic character in the $FeCp(CO)_2^{\delta+}$ moiety. This is shown in Table 1. Notably, the least coordinating anion to date on this scale is the hexabromo carborane, $CB_{11}H_6Br_6^-$. It is also worth noting that as ligands, the saturated C−H bonds of the permethylated carborane anion $CB_{11}Me_{12}^-$ are slightly more electron releasing than the bromine atoms of $CB_{11}H_6Br_6^-$. A bonding pair in a σ complex can actually be a better electron donor than a traditional lone pair. This is equivalent to finding that the methyl group of bromomethane is a better donor than the bromine atom.

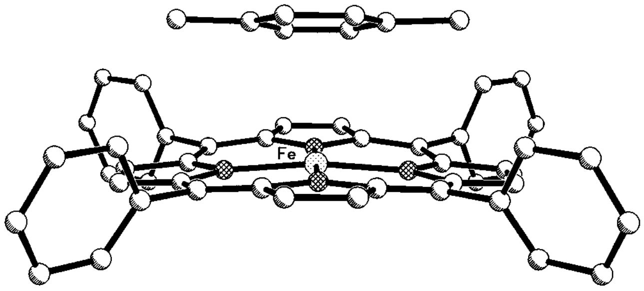

FIGURE 3. Crystal structure of the Fe(TPP)$^+$ cation showing a *p*-xylene molecule functioning as both solvate and ligand.[26]

Table 2. Downfield ^{29}Si Chemical Shifts

compd	$\delta(^{29}Si)$, ppm	compd	$\delta(^{29}Si)$, ppm
$i\text{-}Pr_3SiH$	12	$i\text{-}Pr_3Si(CB_{11}H_6I_6)$	97
$i\text{-}Pr_3Si(OSO_2CF_3)$	40	$i\text{-}Pr_3Si(F_{20}BPh_4)$	107
$i\text{-}Pr_3Si(BrAlBr_3)$	56	$i\text{-}Pr_3Si(CB_{11}H_6Br_6)$	110
$i\text{-}Pr_3Si(toluene)^+$	94	$i\text{-}Pr_3Si(CB_{11}H_6Cl_6)$	115

A ranking to a harder, main group Lewis acid is based on the downfield ^{29}Si chemical shift of a silyl species of the type $i\text{-}Pr_3SiY$ (see Table 2).[16] By this criterion, the hexachlorocarborane is the least coordinating anion, slightly better than the especially inert perfluorinated tetraphenylborate ion, $F_{20}BPh_4^-$. The tetrakis(3,5-bis-(trifluoromethyl)phenyl)borate ($BAr^F{}_4^-$) cannot be ranked on this scale because of a weakness toward fluoride ion abstraction and boron−phenyl bond cleavage.[28,29] We note that some of the data in Table 2 were collected in the solid state to remove any ambiguity about the coordination of the anion. With anions having basicity comparable to that of toluene, possible competition between anion and solvent must always be considered. This is well established for Fe(TPP)$^+$ (see below) and for the case of $R_3Si(toluene)^+$ with perfluorotetraphenylborate as the counterion (eq 1).[30]

$$R_3Si(F_{20}BPh_4) + \text{toluene} \rightleftharpoons R_3Si(\text{toluene})^+F_{20}BPh_4^- \qquad (1)$$

This equilibrium is less pronounced to the right-hand side when the anion is the hexabromo- or hexachlorocarborane[16,31] even though these anions are less coordinating on the $\delta(^{29}Si)$ scale of Table 2. This reminds us that an equilibrium constant is a composite of intrinsic bond strength *and* solvation energy considerations. Apparently, the free $F_{20}BPh_4^-$ ion is better solvated than the hexahalocarboranes in toluene to an extent that the stronger silicon−anion bond is more easily dissociated.

The case of Fe(TPP)$^+$ with carborane anions is similar in some respects but different in others. The first counterion to allow the ionization of Fe(TPP)$^+$ in an arene solvent was neither $F_{20}BPh_4^-$ nor a hexahalocarborane. Rather, it was an even less coordinating anion, a complex ion made up of two hexahalocarborane anions: $[Ag(CB_{11}H_6Br_6)_2]^-$.[26] The silver salt was present in the synthesis, and the complex anion formed spontaneously. By taking the least coordinating anion and halving its overall charge by complexation, electrostatic attraction to cations is diminished. This is conceptually important as a way of lowering the coordinating ability of anions. It is reminiscent of the way SbF_6^- forms Lewis acid/base adducts with SbF_5 in less coordinating, oligomeric anions such as $Sb_2F_{11}^-$ and $Sb_3F_{16}^-$.

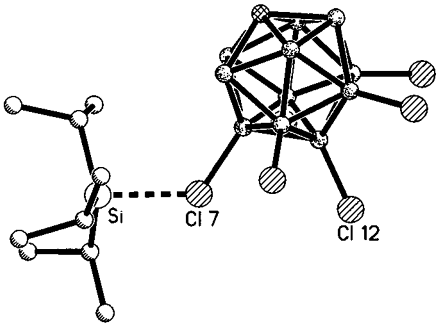

FIGURE 4. Crystal structure of $i\text{-}Pr_3Si^{\delta+}(CB_{11}H_6Cl_6)^{\delta-}$ showing the approach of the silicon atom toward sp^2 planarity and the coordination of the carborane via the chlorine atom in the 7 position.[16]

Structurally, the ionization of Fe(TPP)$^+$ is interesting because of the close approach of arene solvent molecules to the metalloporphyrin moiety. As shown in Figure 3, the association of *p*-xylene with Fe(TPP)$^+$ has some of the characteristics of a solvate, but the less-than-van der Waals separation (Fe···C = 2.94 Å) suggests that the interaction must also be viewed as ligation to iron. This blurring of the distinction between a ligand and a solvate illustrates that there is a continuum between these definitional ideals.

A number of other rankings of the coordinating ability of anions have been developed. Most are based on a spectroscopic probe which reflects bond strength or electron density, but some limited series of anion nucleophilicities have also been derived from kinetic measurements.[32] Electrochemical rankings[33,34] and studies based on thermochemical data[35] are particularly important because they reflect the contribution of solvation enthalpies. Further comprehensive systematic studies of this kind would be very useful. They may lead to a better understanding of the subtleties of ion pairing in low dielectric media. For example, it is well known in olefin polymerization that the nature of the anion affects the polymer characteristics in cationic group 4 metallocene catalysis but the mechanistic role of the anion is only just beginning to be explored.[36] The ready manner in which carboranes can be systematically functionalized to alter their solvation properties makes them attractive candidates for such studies.

$i\text{-}Pr_3Si(CB_{11}H_6Cl_6)$ (see Figure 4) is presently the closest approach to the long sought trialkylsilylium ion.[8] The average C−Si−C angle is 117.3°, about 75% of the way from the 109° of covalent sp^3 to the 120° of ionic sp^2-hybridized silicon. This has led us to view silylium species in terms of a continuum between covalent and ionic ideals. We refer to such species as ion-like and write them as $i\text{-}Pr_3Si^{\delta+}(CB_{11}H_6Cl_6)^{\delta-}$. They react like silylium ions.

One of the other interesting features of the structure of $i\text{-}Pr_3Si^{\delta+}(CB_{11}H_6Cl_6)^{\delta-}$ is the manner in which the carborane is coordinated to silicon. As seen in Figure 4, the chlorine atom at the 7 position rather than that in the 12 position is coordinated. This was unexpected because all evidence points to the 12 position, antipodal to carbon, as the most basic site of the cluster. Access to negative charge at the 12 position is apparently hindered by halogen substituents in the 7–11 positions, and this directs large cations to the pentagonal belt. This is in contrast to the parent $CB_{11}H_{12}^-$ ion which preferentially coordinates through the B–H bond in the 12 position.[3]

Lewis Acid Reagents. Limits to Silver Halide Metathesis

Silver(I) and thallium(I) salts of weakly coordinating anions are useful reagents for halide abstraction reactions. From the earliest days of coordination chemistry, there has been an expectation that labile metal–halide bonds will be subject to facile halide abstraction via silver halide precipitation (eq 2). The exploration of silver salt metathesis with carborane counterions has exposed unanticipated thermodynamic limits to this familiar reaction.[37] For example, the labile chloride in Vaska's compound, $IrCl(CO)(PPh_3)_2$, although readily abstracted with silver perchlorate, is inert to abstraction with silver carborane reagents. Instead, Lewis acid–base adducts are formed. Furthermore, as shown in Figure 5, the silver adduct is not to the chloride ligand but to iridium.[38]

$$\mathrm{AgY} + \mathrm{M{-}X} \xrightarrow{\text{toluene}} \mathrm{M^+Y^-} + \mathrm{AgX(s)} \qquad (2)$$

A second example, with an extractable iodide, is more intuitive. Treatment of $FeCp(CO)_2I$ with silver carborane salts in toluene leads first to a Lewis acid/base adduct of silver to the iodide: $FeCp(CO)_2I{\rightarrow}Ag(carborane)$. Only after several hours does metathesis proceed.[37] In a number of other cases, halide abstraction that normally proceeds with silver perchlorate is completely thwarted by changing the anion to a carborane. This may be kinetic or thermodynamic in origin, although in the exemplary case of silyl halides, it has been shown to be thermodynamic. Equations 3–5 illustrate this. A halide abstraction that proceeds instantly with silver perchlorate (eq 3) does not proceed when the anion is a hexahalocarborane (eq 4). However, the reverse reaction can be shown to proceed in just a few minutes[39] (eq 5) once the metathesis product has been prepared via an alternate route. The *kinetic* solubility of AgI in toluene is excellent.

$$\mathrm{i\text{-}Pr_3SiI} + \mathrm{Ag(ClO_4)} \xrightarrow{\text{toluene}} \mathrm{i\text{-}Pr_3Si(OClO_3)} + \mathrm{AgI(s)} \qquad (3)$$

$$\mathrm{i\text{-}Pr_3SiI} + \mathrm{Ag(carborane)} \xrightarrow{\text{toluene}} \text{no reaction} \qquad (4)$$

$$\mathrm{i\text{-}Pr_3Si(carborane)} + \mathrm{AgI(s)} \xrightarrow{\text{toluene}} \mathrm{i\text{-}Pr_3SiI} + \mathrm{Ag(carborane)} \qquad (5)$$

A third variant of an arrested silver halide metathesis reaction is the partial reaction of $Ag(CB_{11}H_6Br_6)$ with HCl in diethyl ether. The reaction cannot be coerced to proceed more than 25% because of precipitation of a double salt whose formula can be written as $[H(OEt_2)_2][Ag_3(CB_{11}H_6Br_6)_4]$.[39,40] The carborane anions act as bridging ligands to the silver ions, producing a polymeric chain structure of such low solubility that it shuts down the metathesis reaction. A new carborane reagent, the Tl^+ salt,[41] may solve this problem.[40]

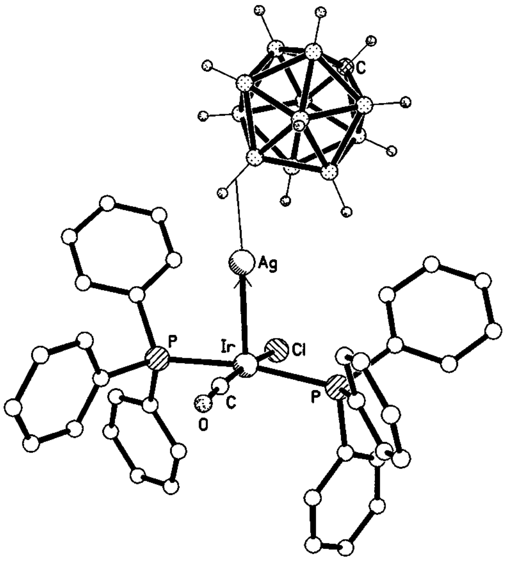

FIGURE 5. Crystal structure of the Lewis acid/base adduct of $Ag(CB_{11}H_{12})$ with $IrCl(CO)(PPh_3)_2$.[38]

The other most useful Lewis acid reagents of weakly coordinating anions are their trityl salts. Hydride abstraction is a familiar and convenient route to labile cations or cation-like species. In many cases there is a greater driving force than with silver salts. For example, while eq 4 was unproductive, eq 6 proceeds smoothly. A kinetic limit to hydride abstraction has been reached with trimesitylsilane, which is apparently unreactive toward trityl ion for steric reasons.[42] There are presumably thermodynamic limits as well. In anticipation of these, we did attempt to prepare a stronger hydride abstraction reagent in Ph_2HC^+ but the carborane salt was not stable to isolation.

$$\mathrm{i\text{-}Pr_3SiH} + \mathrm{Ph_3C^+(CB_{11}H_6Br_6)^-} \xrightarrow{\text{toluene}} \mathrm{i\text{-}Pr_3Si(CB_{11}H_6Br_6)} + \mathrm{Ph_3CH} \qquad (6)$$

Cationic Catalysis

Very weakly coordinating anions such as $F_{20}BPh_4^-$ and $BAr^F{}_4^-$ are counterions for cationic catalysts in an increasingly wide variety of organic and small molecule transformations. These include group 4 metallocenes in homogeneous olefin polymerization,[6,36,43] palladium complexes in olefin/CO copolymerization,[44] boron in enantioselective synthesis,[45] sodium in azo coupling,[46] etc. There is every reason to expect that carboranes will be equal or better in these applications.

The use of carborane counterions for group 4 metallocene cations in olefin polymerization catalysis was first disclosed in a 1988 patent by Exxon.[6] Turner and coworkers subsequently published some of these findings

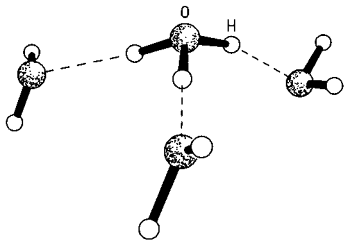

FIGURE 6. Crystal structure of the hydronium ion in $[H_9O_4][CB_{11}H_6Br_6]$.[53]

in the open literature,[47,48] and Jordan has with some success investigated the use of $CB_{11}H_{12}^-$ with zirconium catalysts.[49] The optimization of catalytic performance as a function of carborane anion has not yet been reported. Grieco has found that the cobalt bisdicarbollide anion is a very effective counterion for lithium catalysis of conjugate additions to silyl ketene acetals[50] and the nucleophilic substitution of allylic acetates.[51] The commercial unavailability of carborane anions, even in research quantities, has hampered a more rapid exploration of their possibilities. Given their promise, this should change soon.

New Strong Brønsted Acids

The synthesis of any new anion creates the opportunity to make a new conjugate acid. An unsolvated Brønsted acid of a carborane anion, H(carborane), has yet to be prepared. It is an interesting synthetic target because it may be a very useful, weighable, crystalline superacid. Moreover, it may have a nonreducible anion. Commonly used superacids have reducible anions, and this is why they have limited commercial applications.

The stability of icosahedral boron cages to strong acid was recognized very early on. Knoth et al.[52] made a number of aqueous acids from the all-boron dianions. With the monoanionic monocarboranes we have been able to isolate several interesting Brønsted acids.

One of the more fundamentally important of these is $[H_9O_4][CB_{11}H_6Br_6]$, the first example of an ambiently stable discrete salt of the hydronium ion.[53] As shown in Figure 6, the structure is that of a trihydrated H_3O^+ ion, the same as that believed to be dominant for the proton in liquid water. The dimensions of the cation are very close to those calculated by ab initio methods, suggesting that crystal packing forces and interactions with the anion are of minor importance in this structure. This has been generally true in our structural investigations of carborane salts. The delocalized charge on these large anions tends to make them nearly ideal spectator ions with little opportunity to perturb the structure of the cation.

There is surprisingly little hard information about the structure of the proton in organic solvents despite extensive collections of acidity data in acetonitrile, dimethyl sulfoxide, etc. The crystallization of the solvated proton, $H(\text{solvent})_x^+$, as salts of weakly basic anions should shed light on the structures of these cations and the predominant values of x. The X-ray structure of $[H(OEt_2)_2][Ag_3(CB_{11}H_6Br_6)_4]$[39,40] reveals a $\lesssim 2.4$ Å approach of the two diethyl ether oxygen atoms. This is indicative of very strong, symmetrical, and probably linear H-bonding in the $Et_2O\text{- -H- -}OEt_2^+$ ion. It is no accident therefore, that acids crystallized from diethyl ether, such as the popular $[H(OEt_2)_2][BAr^F_4]$,[54] have two solvent molecules in their formulation.[55] It suggests that this is the predominant structure in solution also. We have also been able to characterize by X-ray crystallography hexahalocarborane salts of the $H_7O_3^+$, $H_5O_2^+$, and $H_2O\text{- -H- -}OEt_2^+$ ions. [39]

The hexahalocarborane anions have greater stability to acid than the tetraarylborates. As counterions to the acids mentioned above, they are indefinitely stable at room temperature whereas the corresponding salts of the fluorinated tetraarylborates, $BAr^F_4{}^-$ and $F_{20}BPh_4^-$, decompose via boron−aryl bond cleavage.[27,54]

An important feature of these strong acids is that they allow access to protonated species that cannot be observed in traditional superacid media because of anion nucleophilicity. A case in point is the isolation of the first example of a protonated silanol in $[t\text{-}Bu_3SiOH_2][CB_{11}H_6Br_6]$.[56] The oxy and fluoro anions of superacid media displace the water and coordinate. An additional example is protonated μ-oxoiron(III) tetraphenylporphyrin dimer, $[(TPP)Fe{-}OH{-}Fe(TPP)]^+$, a rare case of protonation of oxygen without rehybridization.[57]

Of more far-reaching consequence is the recent finding that protonated benzene can be isolated as an ambiently stable, crystalline salt. The counterion is $CB_{11}H_6Cl_6^-$.[58] It takes a superacid to protonate benzene,[59] so $[C_6H_7^+][CB_{11}H_6Cl_6^-]$ is the rare example of a clean, weighable superacid. More importantly, it has a nonoxidizing anion and a nonnucleophilic anion and it is not a mixture of Lewis and Brønsted acids. Traditional superacids, such as HF/SbF_5, are quite limited in this regard. They decompose benzene at room temperature via complex oxidation chemistry because the anion is reducible (e.g., $Sb^V \rightarrow Sb^{III}$). The stability of protonated benzene with a carborane counterion suggests that reagents such as $[H(\text{solvent})_x^+][CB_{11}H_6Cl_6^-]$ can play an important role in the delineation of protonation, electron transfer, and nucleophile-sequestering processes.

New Strong One-Electron Oxidants

The stability of the $CB_{11}H_6X_6^-$ hexahalocarboranes toward acid is matched by an equally impressive stability toward oxidation. Electrochemically, these anions are inert to oxidation throughout the anodic window of dichloromethane (ca. 2.0 V vs ferrocene/ferrocenium at Pt). This has prompted us to prepare new electron abstraction reagents that would function as synthetic equivalents of controlled potential electrochemistry.[60] The challenge of developing a synthetic method for the isolation of a fullerene cation illustrates our approach.[61]

The problem of oxidizing a fullerene to a fullerene cation was to find a clean one-electron oxidant strong enough for the task, but one which did not bring along with it a reacting nucleophile. In addition, the solvent and the reduction product had to be unreactive. This led us to improve the performance of the radical cation of tris(2,4-dibromophenyl)amine, $Ar_3N^{\bullet +}$, as an oxidant. The nearly planar amine is remarkably unreactive as a nucleophile, for steric and electronic reasons. When paired with the hexabromocarborane anion in dichlorobenzene or 1,1′,2,2′-tetrachloroethane as the solvent, the radical cation has a potential of about 1.15 V, quite adequate to oxidize C_{76} to C_{76}^{+} (eq 7). The same reaction with the

$$[Ar_3N^{\bullet +}][CB_{11}H_6Br_6^{-}] + C_{76} \rightarrow [C_{76}^{+}][CB_{11}H_6Br_6^{-}] + Ar_3N \quad (7)$$

$SbCl_6^{-}$ salt of the oxidant also gave C_{76}^{+}, but solutions were stable only for hours, compared to weeks for the carborane. This presumably reflects the greater nucleophilicity of $SbCl_6^{-}$ and the greater ease with which it gives up a halide ion. Current work is aimed at extending these principles to even stronger "electron hole" oxidants. A good method of producing C_{60}^{+} (ca. 1.3 V vs ferrocene)[62] should open up a new route to more controllable functionalization of C_{60}.

A recent novel finding in boron chemistry is the one-electron oxidation of the permethylated carborane anion to a stable radical, $CB_{11}Me_{12}$.[63] With a potential very similar to that of the triarylamine radical discussed above, it too is an excellent oxidant. An added advantage is its solubility in low dielectric media and the absence of a reduction byproduct. Compared to the six halide substituents on the oxidatively inert hexahalocarboranes, the 12 methyl groups must be quite electron releasing. At the same time, they protect the cage from decomposition with a sheath of saturated hydrocarbon. Just as with a series of differently substituted triarylamines, there is considerable opportunity to tune this system to create a series of electron-abstraction reagents with a range of oxidation potentials. The oxidation of metal−metal or element−element bonds as a route to reactive, coordinatively unsaturated cations[60] (eq 8) has yet to be fully exploited.

$$L_nM-ML_n \xrightarrow{-2e^-} 2ML_n^{+} \quad (8)$$

Likewise, these reagents create new possibilities for the synthesis of radical cations and odd-electron complexes for initiating electron chain reactivity and catalysis.[64]

Conclusion

Carborane anions are poised to pass from exotica to specialty chemicals of wide research interest.[65] Inert yet functionalizable, they can be tailored to specific applications, many of which await exploration. Their crystallizability and extremely weak coordination has led to the characterization of a number of unusual cations, particularly those that are inaccessible in traditional superacid media because of anion coordination or anion reactivity. Silver(I), thallium(I), trityl, silyl, $H(solvent)_x^{+}$, and electron-abstraction reagents provide a variety of routes to desirable cations with carboranes as counterions. Electrophilically added substituents at boron allow new extremes of reactivity to be sampled. Substituent chemistry on the carbon atom allows a range of lipophilicity and solvation differences to be manipulated.

Like all boron cluster compounds, commercial uses can only be expected where a specialized application is found and there is no less expensive non-boron counterpart. These are possible in neutron capture therapy, electrolyte function, and radionuclide solvent extraction and waste remediation.[14]

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(65) Strem Chemicals, Inc. is expected to begin marketing carborane salts shortly.

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