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The Effect of Carborane Substituents on the Lewis Acidity of Boranes

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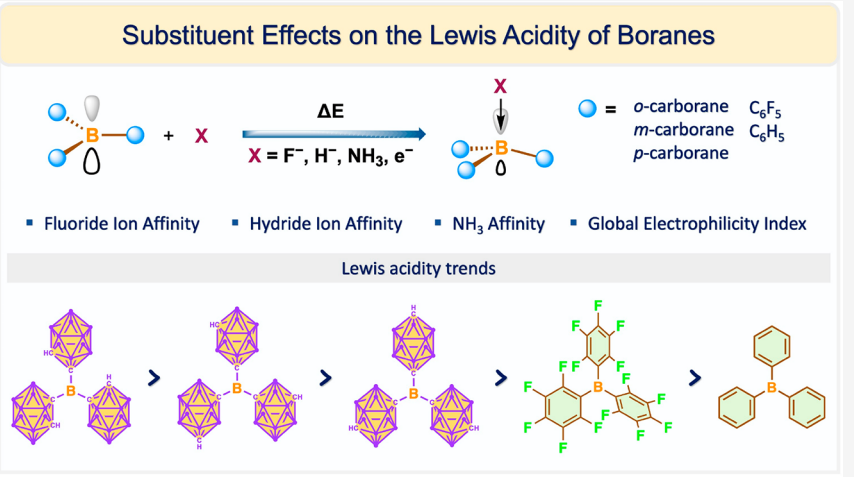

ABSTRACT: The Lewis acidity of primary, secondary, and tertiary boranes with phenyl, pentafluorophenyl, and all three isomers of the C-substituted icosahedral carboranes (*ortho*, *meta*, and *para*) was investigated by computing their fluoride, hydride, and ammonia affinities as well as their global electrophilicity indices and LUMO energies. From these calculations, it was determined that the substituent effects on the Lewis acidity of these boranes follow the trend of *ortho*-carborane > *meta*-carborane > *para*-carborane > C_6F_5 > C_6H_5.

INTRODUCTION

Boranes are classical Lewis acids that are widely used due to their electron deficiency and desire to fill their vacant p orbital in order to satisfy their octet.[1−6] The substituents that are bound to the boron center greatly influence the accessibility and energy of the empty p orbital, thereby providing a way to tune the Lewis acidity and steric profile of boranes.[7] The application of trihalo- and trialkylboranes in catalysis is limited in comparison to triaryl species.[8,9] While trihaloboranes are generally the most Lewis acidic boranes,[7] their B−X bonds are reactive with many functional groups and are difficult to manipulate due to their moisture sensitivity and volatility; thus, they are not useful for many applications (Figure 1). Trialkylboranes are the least Lewis acidic boranes, and modifying the groups on the alkyl chain results in only small permutations in the acid strength, thus making them challenging to tune and only weak Lewis acids. In comparison, triarylboranes have garnered the greatest interest because of their exceptional stability and the possibility of fine-tuning their Lewis acidity by modifying the substituents on the aryl group.[8,9] Electron-withdrawing groups such as −F, −Cl, and $-CF_3$ can be installed to increase the Lewis acidity at the boron center (Figure 1).[10−18] The perfluorinated triarylborane, tris(pentafluorophenyl)borane ($B(C_6F_5)_3$),[18] has found the most extensive applications in Lewis acid mediated chemistry, notably in catalysis, in olefin polymerization, and as the Lewis acid component in frustrated Lewis pairs.[9,19−31] Conversely, fluoroarylboranes with a *para*-fluorine atom can be susceptible to deleterious reactivity via nucleophilic substitution at that position, which limits their use.[32,33] Beyond fluorinated arene-substituted boranes, little research has been directed toward finding new Lewis acids with similar or better catalytic activity. Alternative means have emerged, which involve using cationic substituents,[34−43] functional groups that chelate metals,[44−47] and anti-aromatic BC_4 rings as electron-withdrawing groups (Figure 1).[48−51] The cationic substituents and metals can be

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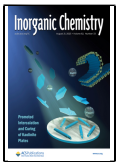

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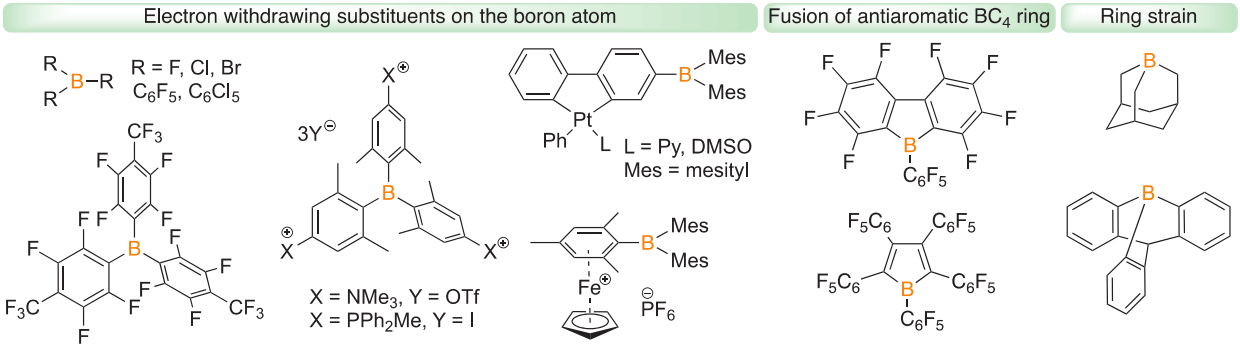

Figure 1. Representative approaches that are used to influence the Lewis acidity on neutral boranes.

reactive themselves, rather than simply behaving as spectator ligands. Recently, Berionni and co-workers have been leveraging the constrained geometry at the boron center in order to generate extremely Lewis acidic boranes in situ (Figure 1).[52−54]

Dicarbadodecaboranes, or carboranes, are $C_2B_{10}H_{12}$ icosahedral clusters composed of boron, carbon, and hydrogen atoms that are bonded nonclassically (Figure 2).[55] The three isomers

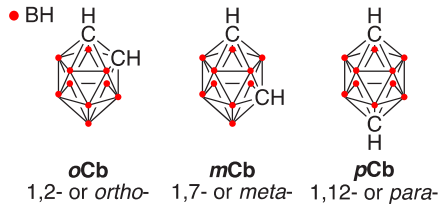

Figure 2. *closo*-$C_2B_{10}H_{12}$ carborane isomers.

of neutral $C_2B_{10}H_{12}$ are named based on the relative positions of the two carbon atoms in the icosahedron: *ortho* (carbon atoms are adjacent, 1- and 2-positions), *meta* (carbon atoms are separated by a boron atom, 1- and 7-positions), and *para* (carbon atoms are separated by two boron atoms on opposite sides of the cage, 1- and 12-positions).[55] The molecular orbital diagrams of the C_2B_{10} cages in all isomers have all of the 13 cluster bonding orbitals fully occupied and all of the antibonding orbitals unoccupied, leading to high kinetic stability. Icosahedral carboranes are often termed as three-dimensional (3D) aromatics due to the high delocalization of the electron density that exists throughout the cluster. Since their disclosure in the 1960s, carboranes have been explored in many fields of chemistry, including medicine, catalysis, polymers, optoelectronic applications, and the metal−ion extraction of nuclear waste.[56−59]

The research groups of Lee and Park have prepared aryl boranes that feature C-bound *ortho*-carboran-1-yl groups on the *para*- and *meta*-positions of the aryl groups.[60−64] When compared to species lacking carboranes, it was determined that fluoride binding was enhanced by 3 orders of magnitude with one carborane-substituted arene on boron and by 4 orders of magnitude when three carborane-substituted arenes were on boron. These *ortho*-carborane-functionalized aryl boranes demonstrate that C-bound *o*-carborane serves as an effective electron-withdrawing group, though it is more effective to directly bind it to boron rather than having an arene spacer.[65−68] Fox and co-workers prepared C-dimesitylboryl-*o*-carboranes (**1** and **2** in Figure 3) and calculated their fluoride ion affinities to be 556 and 533 kJ/mol, respectively, which exceed that of the arene bridged species (518 and 513 kJ/mol, respectively).[69,70] Welch and co-workers prepared a derivative of **1** and **2** with a methyl group on the other carbon (**3**) that exhibited similar Lewis acidity.[71] Marder and co-workers synthesized a bis(*ortho*-carboranyl)-(*para*-tolyl)-borane (**4**) that could be reduced and isolated as the corresponding radical anion due to the low energy of its lowest unoccupied molecular orbital (LUMO).[72]

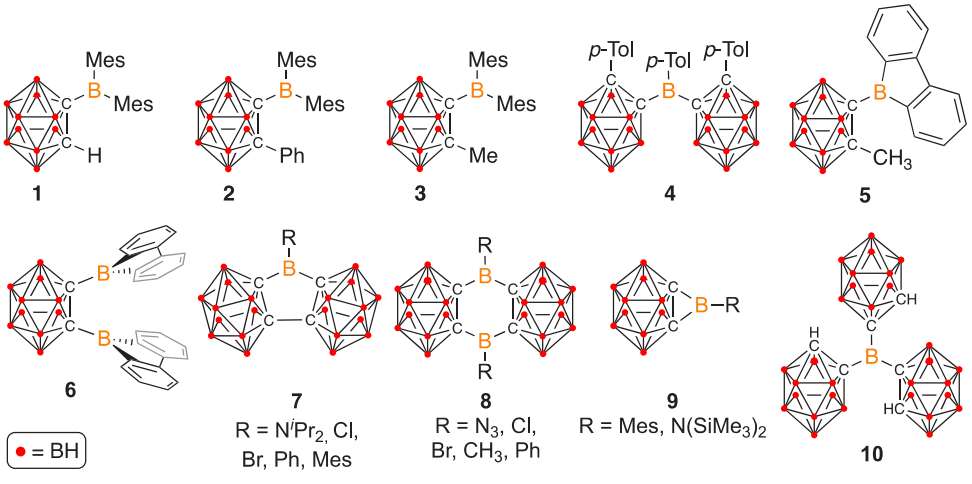

Figure 3. Known C-bound carborane-substituted boranes with measured Lewis acidity.

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Marder, Braunschweig, and co-workers reported the mono- and bis-borafluorene *ortho*-carboranyl species **5** and **6**[73,74] that are both susceptible to endocyclic B−C bond cleavage or insertion to access heterocycles,[75] which are, in many cases, similar to 9-borafluorenes with B-aryl or B-halo substitutions.[50,51,76−87] Carboranes are considered to be 3D analogues of benzene, so accordingly, carborane that contains analogues of fluorene and anthracene have been targeted. The Ye[88] and Dobrovetsky[89] groups, along with our group,[90] have reported bis-*ortho*-carboranyl-borane analogues of a 9-borafluorene with various substitutions on boron (**7**). The diisopropylamino and mesityl species were not classified as Lewis superacids due to π-donation and bulk, respectively, but Br, Cl, and Ph were all classified as Lewis superacids (LSAs). An LSA is a species that has a theoretically calculated fluoride ion affinity exceeding that of SbF_5.[91,92] Ye and co-workers have prepared analogues of anthracene, in which the two phenyl groups are replaced with *ortho*-carboranes (**8**).[93,94] Both the calculated hydride and fluoride ion affinities (HIA and FIA, respectively) follow the Lewis acidity trend of Br > Cl > Ph > N_3 > CH_3, with all five species exceeding the HIA of $B(C_6F_5)_3$ and the FIA of SbF_5. The boracyclic analogues of the cyclopropenium cation were also prepared, featuring the two carbon atoms of *ortho*-carborane (**9**).[95,96] Amino substituents as π-donors or bulky mesityl groups were required to isolate these species due to the reactivity of the strained three-membered ring.

Our team recently prepared tris(*ortho*-carboranyl)borane (**10**), a Lewis superacid that promotes catalytic C−F bond functionalization reactions.[97] The aforementioned studies clearly indicate *ortho*-carboranes have the ability to act as electron-withdrawing moieties. However, the relative Lewis acidic properties are not clearly evaluated, nor do any examples of the other carborane isomers exist. Notably, B-bound carboranes are electron-donating and are not presently discussed.[65−67] In this work, we examine the electron-withdrawing effect of all three carborane isomers on the Lewis acidity of boranes, with all species being C-bound.

RESULTS AND DISCUSSION

To analyze the carborane substituent effects on Lewis acidity, three sets of compounds were investigated: H_2BR, HBR_2, and BR_3 complexes, where R is either an *ortho*-, *para*-, or *meta*-carborane (*o*-$C_2B_{10}H_{11}$, *p*-$C_2B_{10}H_{11}$, or *m*-$C_2B_{10}H_{11}$, respectively; see Figure 4). The only known compounds for these are

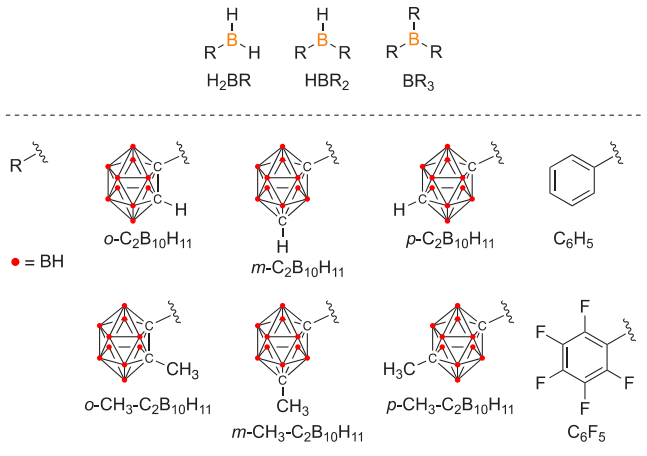

Figure 4. Substituents used in this study.

the homoleptic tris(*ortho*-carboranyl)borane (**10**) and the secondary borane HB(*o*-CH_3−$C_2B_{10}H_{10})_2$, where the *ortho*-carbon bears C−CH_3 rather than C−H for the latter.[97−99] The results are compared to the phenyl- and pentafluorophenyl-substituted variants. The computational methods that were used to assess the Lewis acidity are the hydride, fluoride, and ammonia affinity calculations, the global electrophilicity index (GEI), and LUMO energy levels.[100] Fluoride and hydride ions exhibit high basicity and are small in size; thus, their steric effects are minimized. Stephan and co-workers recently developed the GEI, which calculates the ability of a Lewis acid to accept a single electron; this is advantageous in some aspects, as it reduces the structural reorganization in comparison to the coordination of an atom or ion and it is not influenced by the hardness of the base.[101]

For the H_2BR molecules, it was found that there is a substantial effect on the hydride and fluoride affinities when the relatively electron-withdrawing C−H carborane cage substituent changes from the *ortho*- to the *meta*-position, dropping nearly 30 kJ/mol (Table 1). There is a smaller decrease that occurs in the ammonia affinity as well. The same effect is seen as the C−H is moved to the *para*-position, albeit with less magnitude with a further drop of 10 kJ/mol for the fluoride and hydride affinities and a slight decrease in the ammonia affinity. Substituting the C−H for a C−CH_3 group on the carborane cage has a minimal effect, slightly reducing the Lewis acidity; this result is in line with the inductive effect −CH_3 has on carbon. In all cases, the Lewis acidity is significantly higher than in the corresponding −C_6H_5- and −C_6F_5-substituted systems. The calculated hydride and fluoride affinities are pegged to the fluoride and hydride affinity of $[Me_3Si]^+$ by using the method suggested by Krossing and co-workers (the BP86/SV(P) computational method).[11] This method gives an excellent compromise between accuracy and the computational efficiency that is required for dealing with a large system. Often, direct gas-phase calculated values are also calculated and then PCM solvent-phase corrections are incorporated. To allow for comparisons with the carborane-based system under consideration here, we have done select derivatives using B3LYP/def2-SVP with and without an *ortho*-dichlorobenzene PCM solvent force field. For H_2BR with R = *o*-$C_2B_{10}H_{11}$, the gas-phase fluoride affinity was calculated to be 606 kJ/mol, while in the solvent field, the affinity was calculated to be 421 kJ/mol (a difference of 185 kJ/mol). For R = −C_6F_5, the corresponding fluoride affinities were calculated to be 530 and 368 kJ/mol, respectively, a difference of 162 kJ/mol. The carborane-substituted species is still predicted to have higher affinities, though it experiences slightly more moderation from a solvent force field than the −C_6F_5-substituted compound. For ammonia affinity, examining a more bulky amine in NH_3 versus NMe_3 resulted in a slight drop in the affinity from 119 to 99 kJ/mol. The bulkier *ortho*-Me-substituted carborane saw a further slight drop to 94 kJ/mol, but overall, a bulkier amine is predicted to be accommodated for this monosubstituted system.

The LUMO energies and GEIs follow the same trend, with the LUMO increasing in energy as the C−H becomes more distant from the central boron. The LUMO of the −C_6F_5-substituted H_2BR is lower in energy than the carborane-substituted species; however, it is more delocalized with contribution on the −C_6F_5 ring, whereas the LUMO of the carborane-substituted species is localized on B, as previously determined for the isolated tris(*ortho*-carboranyl)borane (**10**).

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Table 1. Calculated Values of the H_2BR Model Complexes[a]

R	HIA	FIA	NH_3 affinity	NMe_3 affinity	RE	LUMO (eV)	GEI	$\%V_{Bur}$
o-$C_2B_{10}H_{11}$	482	464	119	99	123	−2.81	2.82	41.1
o-$C_2B_{10}H_{11}$[b]	525	606						
o-$C_2B_{10}H_{11}$[c]	315	421						
o-CH_3−$C_2B_{10}H_{10}$	482	465	117	94	119	−2.77	2.77	44.8
m-$C_2B_{10}H_{11}$	451	437	112			−2.53	2.56	41.9
m-CH_3−$C_2B_{10}H_{10}$	448	434	111			−2.48	2.51	41.9
p-$C_2B_{10}H_{11}$	441	427	110			−2.44	2.49	41.7
p-CH_3−$C_2B_{10}H_{10}$	434	421	104			−2.37	2.43	41.7
C_6H_5	354	326	61			−2.24	2.24	34.2
C_6F_5	415	383	90		157	−3.02	3.07	37.5
C_6F_5[b]		530						
C_6F_5[c]		368						

[a]HIA = hydride ion affinity, FIA = fluoride ion affinity, all affinities are in kJ/mol; RE = reorganization energy; GEI = global electrophilicity index; and $\%V_{Bur}$ = Lewis acid % buried volume. In all cases, the carborane is bound to the central boron via a carbon. [b]Calculated in the gas phase. [c]Calculated in a 1,2-dichlorobenzene solvent system.

Table 2. Calculated Values of the HBR_2 Model Complexes[a]

R	HIA	FIA	NH_3 affinity	NMe_3 affinity	RE	LUMO (eV)	GEI	$\%V_{Bur}$
o-$C_2B_{10}H_{11}$	549	542	118	3	155	−3.33	3.24	57.1
o-$C_2B_{10}H_{11}$[b]	595	688						
o-$C_2B_{10}H_{11}$[c]	341	457						
o-CH_3−$C_2B_{10}H_{10}$	540	527	120	−16	134	−3.10	3.10	64.7
o-CH_3−$C_2B_{10}H_{10}$[b]		674						
o-CH_3−$C_2B_{10}H_{10}$[c]		446						
m-$C_2B_{10}H_{11}$	498	489	109			−2.75	2.76	58.0
m-CH_3−$C_2B_{10}H_{10}$	494	485	113			−2.66	2.68	58.0
p-$C_2B_{10}H_{11}$	482	469	106			−2.59	2.61	58.0
p-CH_3−$C_2B_{10}H_{10}$	479	465	101			−2.43	2.47	57.9
C_6H_5	358	351	44			−2.19	2.20	44.3
C_6F_5	457	429	100	72	149	−3.26	3.40	47.0
C_6F_5[b]		582						
C_6F_5[c]		386						

[a]HIA = hydride ion affinity, FIA = fluoride ion affinity, all affinities are in kJ/mol; RE = reorganization energy; GEI = global electrophilicity index; and $\%V_{Bur}$ = Lewis acid % buried volume. In all cases, the carborane is bound to the central boron via a carbon. [b]Calculated in the gas phase. [c]Calculated in a 1,2-dichlorobenzene solvent system.

Reorganization energies were also calculated for the selected derivatives. This was performed by optimizing the geometry for the fluoride adduct, deleting the fluorine atom, obtaining the single-point energy of the resulting pyramidal species, and then comparing to the parent planar borane.[102] The reorganized energies essentially give the energy penalty for accommodating the change in geometry for a given Lewis acid on complexing a Lewis base. For both the parent *ortho*-carborane and the *ortho*-methyl-substituted variants, the reorganization energy is substantially less than when R = $-C_6F_5$ (123, 119, and 157 kJ/mol, respectively). These results potentially explain the greater Lewis acidity of the carborane species despite them having lower GEIs and higher energy LUMOs.

Next, the steric implications of changing −H to $-CH_3$ at the carbon atoms of each isomer were considered by determining the Lewis acid % buried volume via the SambVca 2.1 tool on the respective fluoride adducts, a method developed by Radius and co-workers.[118] It was found that the C−H and C−CH_3 carborane-substituted boranes are more sterically protected at boron than $-C_6F_5$ and $-C_6H_5$ in all cases. Additionally, the steric effect at boron for C−CH_3 rather than C−H only impacts the *ortho*-substituted carborane species; no change was found if the methyl substitution is at the *meta*- or *para*-position.

We recently reported HB(*o*-CH_3−$C_2B_{10}H_{10}$)$_2$,[99] the carborane analogue of Piers' borane HB(C_6F_5)$_2$,[103−105] with C−CH_3 substituents on the *ortho*-carbon positions of the carborane cages. In this work, the other possible isomers and analogues are considered. In all cases, a substantial increase in Lewis acidity toward hydride and fluoride is calculated in the secondary borane over the primary boranes (Table 2). The ammonia affinities are less affected and even decrease slightly. There is also a lowering of the LUMO energies and a corresponding increase in the GEIs when compared to the H_2BR species. With two carboranes, there is stronger effect on the hydride and fluoride affinities when changing from *ortho*- to *meta*- to *para*-positioning of the C−H when compared to that of H_2BR; the hydride and fluoride affinities drop by ∼50 kJ/mol when changing from *ortho*- to *meta*-positioning with two carboranes, compared to a drop of only ∼30 kJ/mol for the same change with H_2BR. As with the H_2BR species, there is a weaker effect when changing from *meta*- to *para*-positioning, albeit still increased with a drop of ∼20 kJ/mol in this case. In line with the H_2BR species, all carborane-substituted analogues have a greater Lewis acidity than the $-C_6H_5$ and $-C_6F_5$

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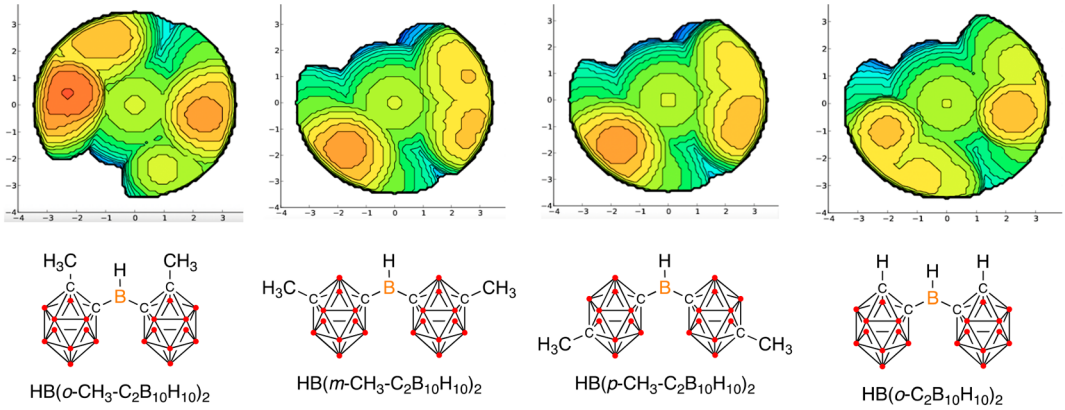

Figure 5. Lewis acid % buried volume plots for HB(*o*-CH_3−$C_2B_{10}H_{10}$)$_2$, HB(*m*-CH_3−$C_2B_{10}H_{10}$)$_2$, HB(*p*-CH_3−$C_2B_{10}H_{10}$)$_2$, and HB(*o*-$C_2B_{10}H_{11}$) (from left to right, respectively).

Table 3. Calculated Values of the BR_3 Complexes[a]

R	HIA	FIA	NH_3 affinity	NMe_3 affinity	RE	LUMO (eV)	GEI	$\%V_{Bur}$
o-$C_2B_{10}H_{11}$	622	605	149	−69	120	−3.99	4.22	71.9
o-$C_2B_{10}H_{11}$[b]	674	756						
o-$C_2B_{10}H_{11}$[c]	401	511						
m-$C_2B_{10}H_{11}$	551	538	102		119	−3.28	3.32	73.4
p-$C_2B_{10}H_{11}$	527	514	96			−3.08	3.09	73.6
C_6H_5	356	356	30			−2.09	2.11	53.1
C_6F_5	484	452	97	5	133	−3.50	3.78	58.9
C_6F_5[b]		612						
C_6F_5[c]		396						

[a]HIA = hydride ion affinity, FIA = fluoride ion affinity, all affinities are in kJ/mol; RE = reorganization energy; GEI = global electrophilicity index; and $\%V_{Bur}$ = Lewis acid % buried volume (%). In all cases, the carborane is bound to the central boron via a carbon. [b]Calculated in the gas phase. [c]Calculated in a 1,2-dichlorobenzene solvent system.

substitutions. In the gas phase versus the solvent phase, the same trends hold with the *ortho*-carborne substitution conferring greater Lewis acidity than the −C_6F_5 substitution. For the parent species, there is a drop of fluoride affinity from 688 to 457 kJ/mol, and for *o*-CH_3, there is a drop from 674 to 446 kJ/mol (a difference of 231 and 228 kJ/mol, respectively). For −C_6F_5, the difference is 196 kJ/mol. A slightly larger effect is apparent here than for the monosubstituted species, and again for carborane versus −C_6F_5, the carborane appears more affected by the incorporation of a solvent force field. There is, however, a large and substantial difference in the predicted behavior for these HBR_2 species when examining a more sterically challenging base. In this case, for the parent *ortho*-substituted derivative, the affinity for NMe_3 is nearly flat while the dissociated species is predicted to be more stable by 16 kJ/mol for *o*-CH_3. The less sterically encumbered HB$(C_6F_5)_2$ only experiences a drop of 28 to 72 kJ/mol for NMe_3 versus NH_3. Reorganization energies are also increased over the mono-carborane-substituted derivatives, in this case in the same regime as for −C_6F_5.

With two carboranes on boron, changing C−H to C−CH_3 at the *ortho*-position has a significant impact on the Lewis acid % buried volume at the central boron, with an increase from 57.1% to 64.7%. If the C−H is at the *meta*- or *para*-position, as with H_2BR changing to C−CH_3, there is no impact on the Lewis acid % buried volume at the central boron, with the Lewis acid % buried volume equal to 58% in all cases (Figure 5). In the secondary boranes, the steric imposition of the carborane notably affects the C−B−C bond angles more than the −C_6F_5 and −C_6H_5 substituents do. For the BR_3 and H_2BR compounds, the bond angles are exactly or nearly 120°. For the secondary boranes, the −C_6F_5- and −C_6H_5-substituted species have C−B−C bond angles of 125−126°, but for the carborane variants, they are more obtuse at 128−129°. Surprisingly, installing methyl groups, regardless of the isomer, has a negligible effect on the bond angle, presumably due to the ability of the icosahedron to rotate with the small H substituent.

For the BR_3 species, only the C−H carboranes were evaluated, as changing C−H to C−CH_3 had only meager effects on the Lewis acidity in the primary and secondary borane systems. The *o*-C−CH_3 derivative is too sterically congested to be synthesized, and C−CH_3 at the *meta*- and *para*-positions has a negligible effect on sterics. Hydride and fluoride ion affinities are higher for BR_3 than for the other HBR_2 and H_2BR sets of compounds that were considered, with a maximum for **10** (Table 3). This is further exemplified in the graphs shown in Figure 6. The hydride and fluoride affinities drop ∼70 kJ/mol upon changing the isomer from the *ortho*- to *meta*-position and decrease by 24 kJ/mol upon changing from the *meta*- to *para*-position in the BR_3 systems. Notably, because the fluoride ion affinity for a Lewis superacid is set at the value for SbF_5 at 493 kJ/mol, all three of the carborane-substituted BR_3 species are considered to be Lewis superacids, while the *ortho*-carboranyl-substituted secondary borane is the only Lewis superacid in that class. These data indicate that there is a general additive effect on the fluoride and hydride affinities when increasing the number of carborane sub-

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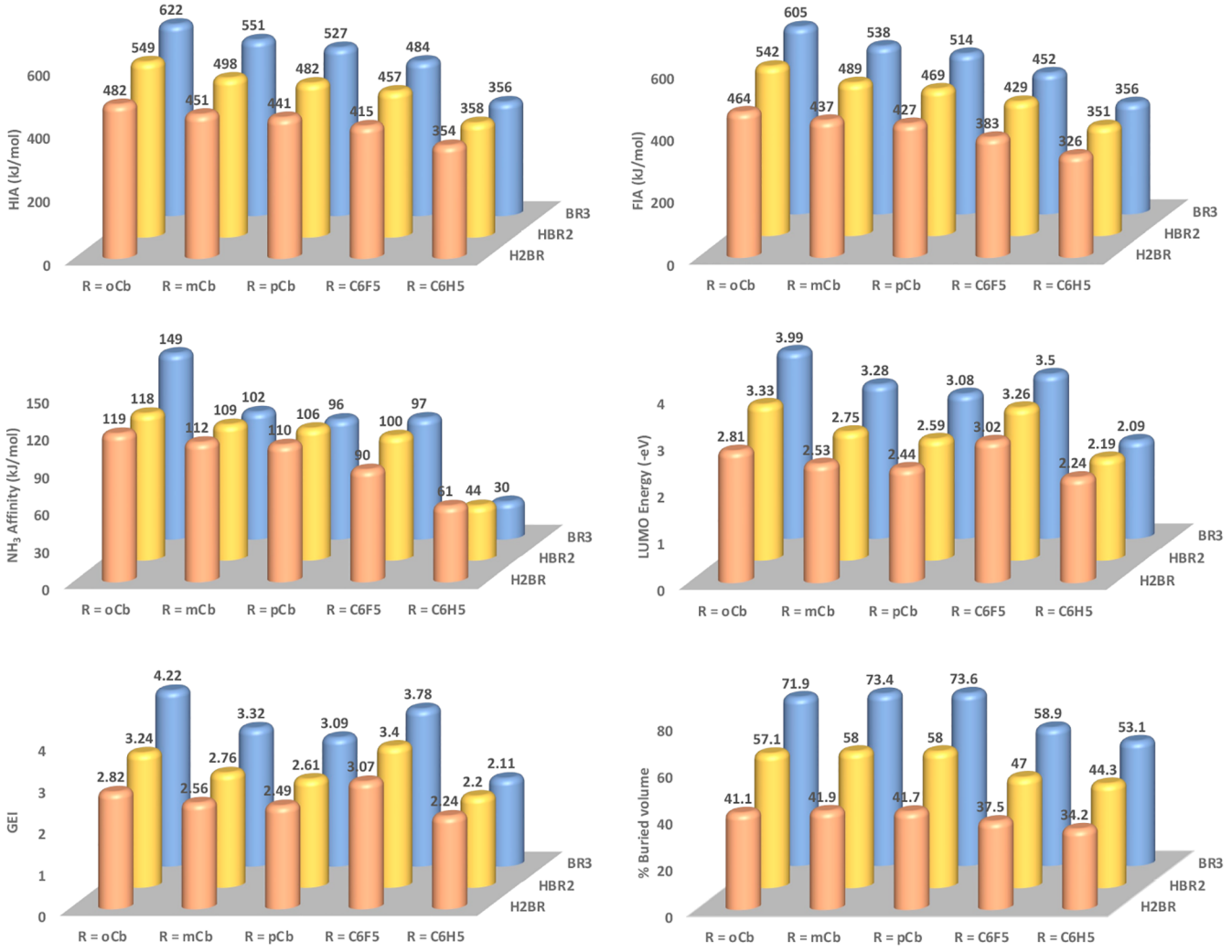

Figure 6. Hydride ion affinity (HIA), fluoride ion affinity (FIA), NH_3 affinity, LUMO energy, GEI, and % buried volume graphs of the compounds examined in this work.

stituents. In this case, looking at the gas phase versus the solvent phase gives a difference of 245 kJ/mol in the fluoride affinity; for $B(C_6F_5)_3$, the difference is 216 kJ/mol, thus holding with the trends obtained for the mono- and bi-substituted derivatives. The general trend for the LUMO energy level also follows this.[106] For the ammonia affinity, there is less of a trend, with it being less variable when adding more substituents. The bulkier NMe_3 is predicted to not make a complex with an affinity, favoring separated species of 69 kJ/mol. This is consistent with recent experimental observations, where $B(o\text{-}C_2B_{10}H_{11})_3$ was shown to be competent in frustrated Lewis pair chemistry.[107] Compound **10** is the bulkiest trisubstituted borane reported to date, and moving the C−H position to the *meta*- or *para*-position increases the Lewis acid percent % buried volume at boron even more, due to the slightly longer B−H that is adjacent to the central boron as compared to C−H. If these derivatives could be synthesized, it would represent a new limit for steric congestion at a boron Lewis acid.

CONCLUSIONS

This study indicates that all three isomers of the C-bound carboranes (*ortho*, *meta*, and *para*) are substituents that are superior to pentafluorphenyl or phenyl groups in increasing the Lewis acidity of boranes. The high fluoride ion affinities comfortably place all three of the homoleptic tris(carborane)-boranes in the Lewis superacid regime. While the tris(*ortho*-carboranyl)borane is known, the *para* and *meta* variants are not yet known and represent interesting targets. This report establishes carborane-substituted boranes as powerful Lewis acids and offers much needed diversification in the field of boron Lewis acids. Although fluorinated arene substituents are effective, their planar steric profile is very different than the 3D profile of the boranes. In addition, the bulk in these carborane Lewis acids should make them effective as components in frustrated Lewis pair chemistry.

COMPUTATIONAL METHODS

Calculations were performed using Gaussian 16.[108] Coordinates and electronic energies are given for the BP86/SV(P) geometry optimizations and single-point vibrational frequency calculations.[109−112] Fluoride and hydride affinities were calculated using Krossing's method, which uses an isodesmic comparison to the fluoride and hydride affinity of $[(CH_3)_3{-}Si]^+$.[11]

Ammonia affinities were calculated using B3LYP-D3/def2-SVP.[108,113−115] Gas-phase versus solvent-phase calculations for select derivatives of the fluoride and hydride affinities were performed using

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B3LYP/def2-SVP with and without an *ortho*-dichlorobenzene PCM force field. The molecular orbitals were calculated using B3LYP/def2-TZVP and global electrophilicity indices that were calculated based on the method from Stephan and co-workers.[116,117] Lewis acid % buried volume calculations were performed using the SambVca method on .xyz files from the fluoride adducts, which used BP86/SV(P) geometry optimizations as per the method from Radius and co-workers.[118,119] First, the F atom was selected as the center of the sphere, Z was defined by B, the *xy* plane was defined by a carbon atom bound to boron, and then the F atom was omitted. Reorganization energies were calculated using B3LYP/def2-SVP in the gas phase by using the optimized geometry of the fluoride adduct, deleting the fluorine atom, and then calculating the single-point energies based on the pyramidal geometry and taking the difference with the parent planar borane.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.3c01872.

Energies of the optimized geometries in hartrees (PDF)

Cartesian coordinates of optimized geometries in .xyz format (ZIP)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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