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Computational Studies of Lewis Acidities of Tris(fluorophenyl)-Substituted Boranes: An Additive Relationship between Lewis Acidity and Fluorine Position

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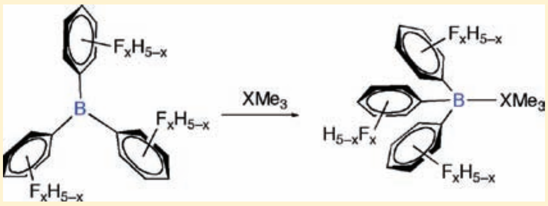

ABSTRACT: Computational studies of the binding energies of all possible tris(fluoroaryl)boranes $B(C_6H_xF_{5-x})_3$ to NMe_3 and PMe_3 show that they (and by extension, the Lewis acidities of the boranes) can be tuned to a sizable range of values through judicious placement of fluorines. This holds despite the fact that the B−X bond distance changes little regardless of substitution, save when the aryl ring is 2,6-disubstituted. Fluorine substitution appears to affect the binding energies additively. Least-squares regression finds substitution at the 2-position to increase the binding energy by ca. 13 $kcal\cdot mol^{-1}$, while substitution at the 3- and 5-positions increases it by ca. 3 $kcal\cdot mol^{-1}$. Substitution at the 4-position has little to no impact, while substitution at the 6-position decreases the binding energy by ca. 3−6 $kcal\cdot mol^{-1}$. The last observation arises from steric congestion because the 6-position can only be substituted in tandem with substitution at the 2-position. Models suggest that the pattern arises from polarization effects that decrease exponentially as the distance between boron and fluorine increases.

The concept of Lewis acidity enhances understanding of reactivity. Its central theme is that a Lewis acidic atom in a species is somehow electron-deficient, and increasing its electron deficiency increases its Lewis acidity. However, efforts to quantify this or to create a consistent relationship with chemical intuition have proven challenging. A primary consideration is the means by which one measures Lewis acidity and/or electron deficiency. The classic example involves comparing energetics of coordination of Lewis bases to the boron trihalides. On the basis of electron-withdrawing capacity, one expects the exothermicity of base coordination, and by extension, the Lewis acidity, to trend $BF_3 > BCl_3 > BBr_3 > BI_3$. In fact, with most bases, the opposite trend holds.[1,2] This has been attributed to several issues, but the main one involves the degree of multiple bonding between the halides and boron in the borane, which is greatest for fluorine and least for iodine.[2] The phenomenon results in different deformation energies (ΔE_{prep}) for the boranes as their structures change from trigonal planar to pseudotetrahedral upon complexation to a base,[3] in the loss of the stabilization associated with multiple bonding,[2] and in the differing electron affinities of the boranes.[4] Other factors considered include the relative energy of the lowest unoccupied molecular orbital (LUMO) in boranes with different halide substituents,[5] and the ability of the halides to support the formally negatively charged boron in the complex.[6] Viewing this range of effects, Bessac and Frenking[7] used energy decomposition analyses for a series of $Y_3M{-}XY_3$ complexes (Y = H, Cl, Me; M = B, Al; X = N, P) to determine that several energy terms contributed to the overall dissociation energy, so they could not order relative Lewis acidities solely on the bases of electrostatic, orbital, or steric issues for these relatively simple borane complexes.

Recently, Lewis acidity scales have appeared that rely on computational assessment of electronic deficiency using theoretical electron distribution models. These have the benefits of minimizing steric effects and being generally consistent with chemical intuition regarding substituent effects. The scales have provided insight into the issues but suffer to varying degrees from model chemistry dependence, methodology dependence, and disagreement with intuition and experiment. A recent example[8] suggests redefining Lewis acidity to reflect the valence deficiency of the acidic atom, as extracted from NBO calculations.[9] By this approach, BF_3, $B(CH_3)_3$, BCl_3, and $B(SiH_3)_3$ show boron valence deficiencies of 1.64, 1.00, 0.50, and −0.41, respectively. This order does not match predicted or experimental exothermicities of base binding, nor is an intuitive relationship between substituent donor/acceptor characteristics and valence deficiency apparent.

Recently, computational studies addressing the energetics-based Lewis acidity of tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, have appeared. This molecule is of interest owing to its ability to form "frustrated Lewis pairs" (FLPs)[10] and its behavior as a cocatalyst in olefin polymerization reactions.[11] Jacobsen et al.[12] found that $B(C_6F_5)_3$ is approximately as Lewis-acidic as BF_3 when the Lewis base is CO. In contrast to the findings of Bessac and Frenking[7] for smaller boranes, bonding in $(F_5C_6)_3B{-}L$

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complexes is dominated by the electrostatic energy term. Timoshkin and Frenking[13] examined the relative Lewis acidities of $M(C_6H_5)_3$, $M(C_6H_4\text{-}4\text{-}F)_3$, and $M(C_6F_5)_3$ (M = B, Al, Ga) toward a variety of small bases, finding that the first two are quite similar in acidity for a particular M and much weaker than the last. Gille and Gilbert[14] compared dissociation energies for a series of $(F_3C)_3M{-}XR_3$ and $(F_5C_6)_3M{-}XR_3$ complexes (M = B, Al; X = N, P; R = Me, Et, *i*-Pr, *t*-Bu, Ph), finding the former are substantially more tightly bound, implying that $B(CF_3)_3$ is considerably more Lewis-acidic than $B(C_6F_5)_3$. It was noted that the intrinsic dissociation energies for the group 13 atom cases were similar until R = *t*-Bu, whereupon the boron system formed an FLP in agreement with experiment, while the aluminum system formed a classical Lewis complex. Pápai and coworkers[15] examined a number of borane/base combinations as part of a study of H_2 splitting by FLPs; they noted a general relationship between the number of fluorines on the borane aryl substituents and the ability of the FLP to split dihydrogen.

We have been interested in relative energetics-based Lewis acidities of other tris(fluoroaryl)boranes as part of our collaboration studying FLPs.[16] In particular, we examined the borane exchange reaction between *t*-$Bu_3PNNOB(C_6H_4\text{-}4\text{-}F)_3$ and $B(C_6F_5)_3$, providing *t*-$Bu_3PNNOB(C_6F_5)_3$ and $B(C_6H_4\text{-}4\text{-}F)_3$, described by Neu et al.[17] We felt that computationally predicting the binding energetics of all possible boranes $B(C_6H_xF_{5-x})_3$ would provide a useful database for further experiments where tuning of the borane in the FLP is essential. We also hoped that comparing a limited range of structurally similar compounds would minimize the effect of steric considerations and allow for sole comparison of electronic effects. In this regard, we were curious to see whether trends, if any, would follow those observed in classical physical organic chemistry for arene carboxylic acids and phenols, on which organic linear free energy relations and σ terms are built.[18] To this end, we examined formation energies of all possible tris(fluorophenyl)borane–trimethylamine and –trimethylphosphine complexes, $(F_{5-x}H_xC_6)_3B{-}XMe_3$ (X = N, P; x = 0–5), with an eye toward describing the results in terms of relative Lewis acidities. The data show that placing fluorine substituents at ortho, meta, and para positions has predictable, apparently additive, effects and that one can tune the energetic Lewis acidities of the boranes to a fine degree by using this knowledge.

COMPUTATIONAL METHODS

The Gaussian suite (G09)[19] was employed for all optimizations and OG2R3calculations. Aryl rings in the starting structures of free and complexed boranes were oriented in pseudo-C_3 symmetry; beyond this, however, structures were optimized by use of the HF/3-21G model without constraints. Frequency calculations were performed at that level to confirm that stationary points were minima (no imaginary frequencies). Structures were then reoptimized by use of the density functional theory (DFT) models MPW1K/6-31+G(d,p), M06/6-311+G(d,p), and M06-2x/6-311+G(d,p). The MPW1K model[20] was employed because it was shown to accurately reproduce borane–amine and borane–phosphine geometries.[21] The M06 and M06-2x models[22] were used as examples of recently published (and so potentially more accurate) DFT models. The MPW1K and M06-2x model chemistries predicted very similar structures, in particular indicating nearly identical B–X distances (Tables S1 and S2, Supporting Information). The M06 model chemistry predicted rather longer B–X bonds, particularly for X = N. In a few cases, the M06 predictions seemed unrealistic, given the associated bond energies. Therefore, the similar MPW1K and M06-2x geometries were taken as most trustworthy, and the latter are the only ones discussed below.

Energies obtained from the DFT optimizations differed dramatically for the same complex, pointing out the difficulty associated with "black box" use of DFT models (Table 3).[23] Because DFT methods generally suffer from insufficient medium-range correlation and inadequate treatment of van der Waals interactions,[24] their ability to predict energetics for datively bonded molecules is often poor and worsens with molecule size.[21] It is thus crucial to calibrate DFT calculations against experimental data, or against high-level calculations when experimental data are unavailable. At the very least, one should examine molecules and reactions using multiple DFT models, to provide "error bars" for the associated energetics.

To address this diversity of energies, the optimized structures were used for ONIOM G2R3 (OG2R3)[25] composite single-point energy determinations. The OG2R3 approach approximates a CCSD(T)/6-311+G(2df,2p) energy calculation for the high ONIOM layer and so provides a more accurate energy prediction at a cost only slightly greater than that for a DFT calculation.[26] A graphic illustrating the separation of layers for the ONIOM approach appears in the Supporting Information. Test calculations for 16 of the 40 molecules examined indicated that OG2R3 energy determinations that used the MPW1K-, M06-, and M06-2x-derived structures were essentially identical (see Table S3 in Supporting Information), so for the balance, only OG2R3 calculations with the MPW1K structures (denoted OG2R3//MPW1K in Table 3) were undertaken. Formation energies in Table 3 were corrected by use of scaled zero-point energies from the frequency analyses.[27]

Table 3 includes the root-mean-square deviations of the DFT energy predictions from those from the OG2R3 approach. One sees that no DFT method performed well overall, although the M06-2x method appeared usable, if not fully trustworthy. As the most trustworthy energy calculations, only OG2R3//MPW1K values are used for discussion of relative Lewis acidities below.

Energy decomposition analyses were performed by the local molecular orbital energy decomposition analyses (LMOEDA) approach[28] within the GAMESS program.[29] Pictorial representations of molecules in Figure 1 were created with Molecule for Macintosh.[30] Statistical *t*-test analyses (two-sample unpooled *t*-test with unequal variances) and least-squares fits (LINEST keyword) were performed with Microsoft Excel 2008 for Macintosh.[31] Equations and cutoff values for the former were obtained from Wikipedia.[32]

RESULTS AND DISCUSSION

Structural Data. Few experimental data exist to compare with those from computations. The crystal structure of $(F_5C_6)_3B{-}PMe_3$ was determined by Chase et al;[33] the M06-2x/6-311+G(d,p)-predicted value of 2.065 Å for the B–P bond distance is in excellent agreement with the experimental one of 2.061(4) Å (Table 1). While no other structures of trimethylamine or trimethylphosphine complexes of this type have been determined, we note that those of $(F_5C_6)_3B{-}PEt_3$ and $(2,3,5,6\text{-}F_4HC_6)_3B{-}PEt_3$ were.[34] The former exhibits a B–P distance of 2.081(4) Å, some 0.02 Å longer than that in the analogous trimethylphosphine complex, presumably reflecting the greater steric demands of PEt_3 versus PMe_3. If it is assumed that this holds for the $(2,3,5,6\text{-}F_4HC_6)_3B{-}PEt_3$ complex as well, then the observed 2.078(2) Å distance for this translates to a B–P distance of 2.058 Å in the uncharacterized PMe_3 analogue. This agrees well with the computationally predicted distance of 2.063 Å, indicating that the model chemistries used for structure determinations are likely adequate for OG2R3 energy determinations.

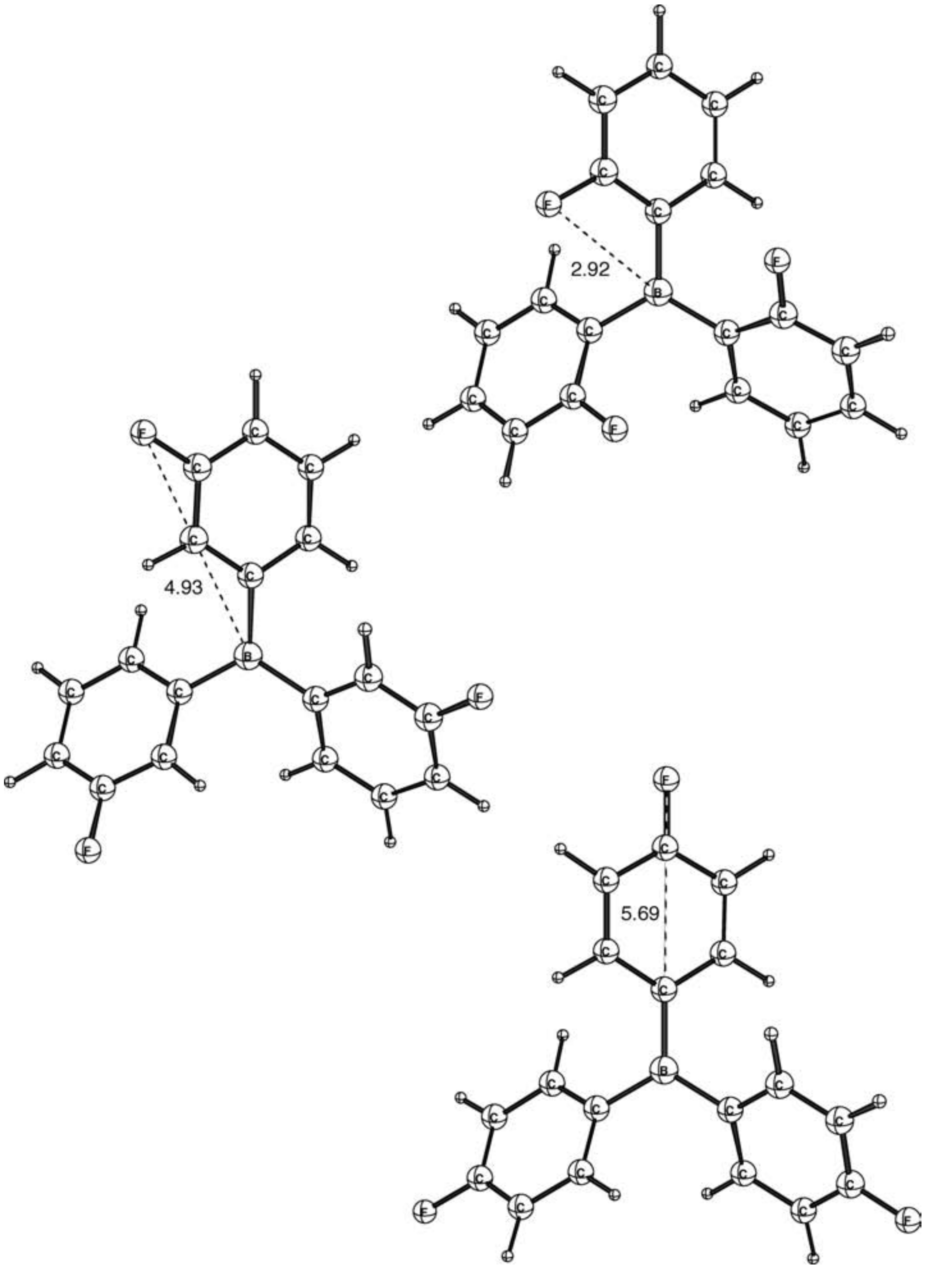

Figure 1. Optimized [M06-2x/6-311+G(d,p)] structures (distances in angstroms) of $B(C_6H_4\text{-}2\text{-}F)_3$, $B(C_6H_4\text{-}3\text{-}F)_3$, and $B(C_6H_4\text{-}4\text{-}F)_3$, showing the nonbonded distances used in the polarization calculation.

As seen in Table 2, the B−N distances of the tris(fluoroaryl)-borane complexes cover a sizable range of values (1.712−1.804 Å), while the B−P distances vary less (2.029−2.068 Å). Inspection of the B−N distances for the tris(monofluoroaryl)borane−amines indicates the trend 3-F < 2-F < 4-F, which is at odds with the trend for the corresponding borane−phosphines: 2-F < 3-F < 4-F. Moreover, the trends are inconsistent as more fluorines are added. As an example, compare the trend of 3-F < 2-F < 4-F noted above with the 2,4-F_2 < 3,4-F_2 trend for the 2,4-F_2 and 3,4-F_2 borane−amines. If placing a fluorine in the 4-position is expected to have minimal steric impact and identical electronic impacts for the tris(difluoroaryl)borane complexes, this reversal is difficult to rationalize. Other examples appear throughout the table.

To probe this, we made statistical comparisons involving all cases of fluorine occupying the various ring positions (Table 2). This method assesses average steric effects of fluorine position, lessening the impact of electronic effects. One sees, for example, that the average B−N bond distance for the 14 complexes containing a fluorine in the 2-position on the ring [1.761(28) Å], differs insignificantly from that for the six complexes where this position is occupied by hydrogen [1.756(33) Å]. This conflicts with the view one would take based solely on the data for the tris(monofluoroaryl)borane−amines.

Statistical Student *t*-tests involving unequal populations and unequal variances of the data (*t* values in Table 2) demonstrate only one statistically significant trend: 2,6-substituted complexes exhibit longer bond lengths than those with any other substitution pattern. This is expected, as the 2,6-substitution pattern engenders the greatest steric congestion around the boron atom.[35] The observation has two facets. From the standpoint of preparing frustrated Lewis pairs, without considering energetics, it limits the options; a borane containing a substitution pattern different from 2,6 will likely form a classical Lewis complex, or at best participate in an equilibrium between classical complex and FLP that lies on the side of the complex. That said, $B(C_6H_2\text{-}2,3,6\text{-}F_3)_3$ and $B(C_6H_2\text{-}2,4,6\text{-}F_3)_3$ should form heretofore unknown FLPs that might show reactivities different from those formed by the more acidic $B(C_6H\text{-}2,3,4,6\text{-}F_4)_3$ and $B(C_6F_5)_3$. On the other hand, the data indicate that relative Lewis acidities of these boranes can be assessed energetically by statistical methods, with only minimal bias resulting from steric effects. Thus differences in binding energies should mostly reflect electronic differences between boranes, allowing assessment of "tuning" of Lewis acidity.

Table 1. Computed [M06-2x/6-311+G(d,p)] and Experimental B−X Distances in $(F_{5-x}H_xC_6)_3B{-}XMe_3$ Complexes

complex	B−N (Å)	B−P (Å)
$(H_5C_6)_3B{-}XMe_3$	1.790	2.053
$(2\text{-}FH_4C_6)_3B{-}XMe_3$	1.747	2.032
$(3\text{-}FH_4C_6)_3B{-}XMe_3$	1.720	2.047
$(4\text{-}FH_4C_6)_3B{-}XMe_3$	1.789	2.055
$(2,3\text{-}F_2H_3C_6)_3B{-}XMe_3$	1.740	2.034
$(2,4\text{-}F_2H_3C_6)_3B{-}XMe_3$	1.747	2.035
$(2,5\text{-}F_2H_3C_6)_3B{-}XMe_3$	1.736	2.029
$(2,6\text{-}F_2H_3C_6)_3B{-}XMe_3$	1.804	2.068
$(3,4\text{-}F_2H_3C_6)_3B{-}XMe_3$	1.765	2.049
$(3,5\text{-}F_2H_3C_6)_3B{-}XMe_3$	1.712	2.041
$(2,3,4\text{-}F_3H_2C_6)_3B{-}XMe_3$	1.742	2.035
$(2,3,5\text{-}F_3H_2C_6)_3B{-}XMe_3$	1.731	2.032
$(2,3,6\text{-}F_3H_2C_6)_3B{-}XMe_3$	1.791	2.066
$(2,4,5\text{-}F_3H_2C_6)_3B{-}XMe_3$	1.738	2.033
$(2,4,6\text{-}F_3H_2C_6)_3B{-}XMe_3$	1.804	2.068
$(3,4,5\text{-}F_3H_2C_6)_3B{-}XMe_3$	1.759	2.041
$(2,3,4,5\text{-}F_4HC_6)_3B{-}XMe_3$	1.733	2.033
$(2,3,4,6\text{-}F_4HC_6)_3B{-}XMe_3$	1.788	2.065
$(2,3,5,6\text{-}F_4HC_6)_3B{-}XMe_3$	1.777	2.063
$(2,3,5,6\text{-}F_4HC_6)_3B{-}PEt_3$		2.078(2)[32]
$(F_5C_6)_3B{-}XMe_3$	1.778	2.065, 2.061(4)[31]
$(F_5C_6)_3B{-}PEt_3$		2.081(4)[32]

Energetic Data. Predicted formation energies for amine− and phosphine−borane complexes appear in Table 3. To begin with general observations, the borane with no fluorines, $B(C_6H_5)_3B$, is predicted to have essentially the lowest base-binding energies, and by inference the lowest Lewis acidity. However, $B(C_6H_4\text{-}4\text{-}F)_3$ and $B(C_6H_3\text{-}3,4\text{-}F_2)_3$ exhibit comparably weak binding, especially to NMe_3. Moreover, $B(C_6H\text{-}2,3,5,6\text{-}F_4)_3$ and $B(C_6F_5)_3$ do not exhibit the strongest binding to bases, with energetics lying approximately in the upper third of all values. These points argue that positioning fluorines at certain sites lowers the binding energies and boron Lewis acidities rather than increasing them.

Comparing the monosubstituted cases presents a simple starting point. One sees that $B(C_6H_4\text{-}2\text{-}F)_3$ is predicted to exhibit base-binding energies distinctly larger than that of $B(C_6H_5)_3$, while those of $B(C_6H_4\text{-}3\text{-}F)_3$ and $B(C_6H_4\text{-}4\text{-}F)_3$ are equal to or only slightly larger than those of the parent, with $B(C_6H_4\text{-}4\text{-}F)_3$ exhibiting the smallest formation energies for each complex. The increasing Lewis acidity trend of $B(C_6H_4\text{-}2\text{-}F)_3 > B(C_6H_4\text{-}3\text{-}F)_3 > B(C_6H_4\text{-}4\text{-}F)_3$ is interesting, as it is opposite the trend in steric congestion at boron. This indicates that electronic effects largely determine Lewis acidities of these boranes; steric effects must only play a role in the most congested, such as 2,6-disubstituted boranes.

Table 2. Statistical Comparisons of Computed [M06-2x/6-311+G(d,p)] B−X Distances in $(F_{5-x}H_xC_6)_3B{-}XMe_3$ Complexes Based on Aryl Ring Fluorine Position[a]

		avg(*s*)[b] of B−N (Å)			avg(*s*) of B−P (Å)		
F position	trials (met, unmet)	met	unmet	*t*	met	unmet	*t*
2	14, 6	1.761(28)	1.756(33)	0.32	2.047(17)	2.048(6)	0.19
3	12, 8	1.753(27)	1.769(30)	1.22	2.048(14)	2.047(16)	0.14
4	10, 10	1.764(25)	1.755(33)	0.69	2.048(14)	2.047(15)	0.15
2,3	8, 12	1.760(26)	1.759(32)	0.08	2.049(17)	2.046(13)	0.42
2,4	7, 13	1.761(28)	1.759(30)	0.15	2.048(17)	2.047(13)	0.14
2,5	6, 14	1.749(22)	1.764(31)	1.23	2.043(17)	2.049(13)	0.77
2,6	**6, 14**	**1.790(12)**	**1.746(23)**	**5.60**	**2.066(2)**	**2.039(9)**	**10.63**
3,4	6, 14	1.761(21)	1.759(32)	0.17	2.048(14)	2.047(15)	0.14
3,5	6, 14	1.748(27)	1.764(29)	1.19	2.046(15)	2.048(15)	0.27
2,3,4	4, 16	1.760(27)	1.759(30)	0.06	2.050(18)	2.047(14)	0.31
2,3,5	4, 16	1.755(26)	1.761(30)	0.40	2.048(18)	2.047(14)	0.10
2,3,6	**4, 16**	**1.784(7)**	**1.754(29)**	**3.73**	**2.065(1)**	**2.043(13)**	**6.69**
2,4,5	3, 17	1.750(25)	1.761(30)	0.68	2.044(18)	2.048(14)	0.37
2,4,6	**3, 17**	**1.790(13)**	**1.754(27)**	**3.61**	**2.066(2)**	**2.044(13)**	**6.55**
3,4,5	3, 17	1.757(23)	1.760(30)	0.20	2.046(17)	2.047(15)	0.10

[a] Differences that are statistically significant at the 98% confidence level are shown in boldface type. [b] Avg is the average of the values meeting the criterion; *s* is the standard deviation of the individual values from the average. *t* is the value of Student's *t*-statistic for a two-sample unpooled *t*-test with unequal variances.

Table 3. Formation Energies Computed for Amine−Borane and Phosphine−Borane Complexes $(F_{5-x}H_xC_6)_3B{-}XMe_3$ at Various Computational Levels

complex	computed formation energy (kcal·mol^{-1}) MPW1K	M06-2x	M06	OG2R3// MPW1K
$(H_5C_6)_3B{-}NMe_3$	−0.2	−11.9	−6.7	−12.0
$(2\text{-}FH_4C_6)_3B{-}NMe_3$	−7.4	−23.2	−13.9	−24.8
$(3\text{-}FH_4C_6)_3B{-}NMe_3$	−2.6	−15.1	−9.4	−14.1
$(4\text{-}FH_4C_6)_3B{-}NMe_3$	0.4	−11.4	−6.0	−11.9
$(2,3\text{-}F_2H_3C_6)_3B{-}NMe_3$	−9.7	−25.3	−15.7	−26.7
$(2,4\text{-}F_2H_3C_6)_3B{-}NMe_3$	−7.3	−22.9	−13.6	−24.9
$(2,5\text{-}F_2H_3C_6)_3B{-}NMe_3$	−10.1	−26.1	−16.5	−27.2
$(2,6\text{-}F_2H_3C_6)_3B{-}NMe_3$	1.5	−16.7	−5.6	−17.6
$(3,4\text{-}F_2H_3C_6)_3B{-}NMe_3$	−2.3	−14.3	−8.6	−14.3
$(3,5\text{-}F_2H_3C_6)_3B{-}NMe_3$	−5.7	−18.0	−12.1	−17.1
$(2,3,4\text{-}F_3H_2C_6)_3B{-}NMe_3$	−9.7	−25.2	−15.6	−26.9
$(2,3,5\text{-}F_3H_2C_6)_3B{-}NMe_3$	−12.4	−28.2	−18.5	−29.0
$(2,3,6\text{-}F_3H_2C_6)_3B{-}NMe_3$	−1.3	−19.3	−7.5	−19.8
$(2,4,5\text{-}F_3H_2C_6)_3B{-}NMe_3$	−9.8	−25.6	−16.1	−27.1
$(2,4,6\text{-}F_3H_2C_6)_3B{-}NMe_3$	1.0	−17.0	−5.6	−17.9
$(3,4,5\text{-}F_3H_2C_6)_3B{-}NMe_3$	−5.0	−17.0	−11.1	−16.5
$(2,3,4,5\text{-}F_4HC_6)_3B{-}NMe_3$	−22.5	−28.4	−18.5	−29.5
$(2,3,4,6\text{-}F_4HC_6)_3B{-}NMe_3$	−11.9	−20.3	−8.6	−21.1
$(2,3,5,6\text{-}F_4HC_6)_3B{-}NMe_3$	−14.3	−22.9	−10.7	−23.0
$(F_5C_6)_3B{-}NMe_3$	−4.8	−22.6	−10.8	−22.9
$(H_5C_6)_3B{-}PMe_3$	−10.8	−18.2	−15.0	−25.2
$(2\text{-}FH_4C_6)_3B{-}PMe_3$	−21.4	−32.2	−25.7	−41.0
$(3\text{-}FH_4C_6)_3B{-}PMe_3$	−18.2	−25.4	−22.0	−31.8
$(4\text{-}FH_4C_6)_3B{-}PMe_3$	−14.5	−21.8	−18.6	−29.4
$(2,3\text{-}F_2H_3C_6)_3B{-}PMe_3$	−24.1	−34.6	−28.0	−43.0
$(2,4\text{-}F_2H_3C_6)_3B{-}PMe_3$	−21.1	−31.7	−25.2	−41.0
$(2,5\text{-}F_2H_3C_6)_3B{-}PMe_3$	−24.3	−35.2	−28.5	−43.4
$(2,6\text{-}F_2H_3C_6)_3B{-}PMe_3$	−16.7	−29.5	−21.9	−37.5
$(3,4\text{-}F_2H_3C_6)_3B{-}PMe_3$	−13.6	−20.8	−17.4	−27.7
$(3,5\text{-}F_2H_3C_6)_3B{-}PMe_3$	−20.7	−27.9	−24.4	−33.8
$(2,3,4\text{-}F_3H_2C_6)_3B{-}PMe_3$	−23.8	−34.2	−27.5	−43.0
$(2,3,5\text{-}F_3H_2C_6)_3B{-}PMe_3$	−27.1	−37.7	−30.9	−45.3
$(2,3,6\text{-}F_3H_2C_6)_3B{-}PMe_3$	−19.8	−32.1	−24.2	−39.8
$(2,4,5\text{-}F_3H_2C_6)_3B{-}PMe_3$	−23.9	−34.5	−27.9	−43.1
$(2,4,6\text{-}F_3H_2C_6)_3B{-}PMe_3$	−16.9	−29.3	−21.7	−37.7
$(3,4,5\text{-}F_3H_2C_6)_3B{-}PMe_3$	−17.2	−24.3	−20.6	−30.7
$(2,3,4,5\text{-}F_4HC_6)_3B{-}PMe_3$	−36.6	−37.4	−30.4	−45.5
$(2,3,4,6\text{-}F_4HC_6)_3B{-}PMe_3$	−29.7	−32.4	−24.7	−40.4
$(2,3,5,6\text{-}F_4HC_6)_3B{-}PMe_3$	−33.0	−35.8	−27.5	−42.8
$(F_5C_6)_3B{-}PMe_3$	−22.9	−34.9	−27.0	−42.3
rmsd[a]	16.1	5.6	12.3	

[a] rmsd = root-mean-square deviation = $\{[\Sigma(E_{\text{expt}} - E_{\text{calc}})^2]/(N-1)\}^{1/2}$.

Closer inspection of the data, however, indicates that this simple trend requires expansion when applied to more substituted boranes. One sees, for example, that $B(C_6H_3\text{-}2,6\text{-}F_2)_3$ binds bases more weakly than other 2,*x*-substituted boranes, despite the fact that the 6-position, like the 2-position, is ortho to the boron. This presumably reflects steric congestion in this borane, as noted above. Placing fluorines at both the 2- and 5-positions seems to provide the strongest binding, regardless of other substitution. Intriguingly, $B(C_6H\text{-}2,3,4,5\text{-}F_4)_3$ binds bases most strongly, 6.6 kcal·mol^{-1} more so than does $B(C_6F_5)_3$ to NMe_3.

To examine this statistically, we calculated the average formation energies and their standard deviations as above (Table 4). The data were scaled by subtracting the energies of the fluorine-free $(H_5C_6)_3B{-}XMe_3$ complexes from those of the fluorinated analogues. The amine− and phosphine−boranes did not give identical results within the limits of the null hypothesis but did show similar general trends. The data confirm that placing fluorines at the aryl 2-positions generally increases the binding energy and Lewis acidity versus the parent borane. Even in cases where the increase is not statistically significant, as for 2,4-substitution, the data suggest greater binding energies than for opposing complexes. This holds particularly for phosphine−boranes and holds whether or not the aryl ring is also substituted at the 3-, 4-, or 5-positions. In contrast, placing fluorines at the 3-, 4-, or 5-positions solely or in combination increases the binding energies only slightly over that for $B(C_6H_5)_3$, and never do these differ to a statistically significant degree from the opposing complexes. As a notable pair of examples, the binding energies of $B(C_6H_2\text{-}3,4,5\text{-}F_3)_3$ toward trimethylamine and trimethylphosphine are only ca. 5 kcal·mol^{-1} larger than those of $B(C_6H_5)_3$, despite the presence of nine electron-withdrawing fluorines in the former borane. It is impossible to determine the effect of substitution at the 6-position, since this can only occur with concomitant substitution at the 2-position. However, Table 4 shows that the 2,3-, 2,4-, and 2,5-patterns all exhibit sizable *t* values, while the 2,6-pattern does not. This suggests that substitution at the 6-position cancels the benefit of substitution at the 2-position to a degree.

An alternative, more revealing way to view the data involves the assumption that substitution has an additive effect on the binding energies. Treating the data as an overdetermined set of linear equations and performing least-squares regression on the scaled energies gave remarkably good fits, as gauged by statistical parameters (see Supporting Information for details) and by the rms errors in energies. The data appear in Table 5. The results for the different bases are notably similar, indicating that the assumption is reasonable. One sees that substitution at the 2-position increases the trimethylamine binding energy by 12.6(2) kcal·mol^{-1} and the trimethylphosphine binding energy by 14.7(8) kcal·mol^{-1}. In contrast, substitution at the 4-position has no discernible impact, and substitution at the 3- and 5-positions has only a modest benefit, increasing the binding energies by 2−3 kcal·mol^{-1}. Substitution at the 6-position lowers the binding energy, quite a bit when trimethylamine is the base and less so when trimethylphosphine is. This surely reflects steric congestion in the former complex versus the latter. Overall, the Lewis acidity substitution trend is 2-position ≫ 3- and 5-positions > 4-position > 6-position.

Explaining the trend presents challenges. The structural similarities [in particular, the fact that the B−X bond distance changes little between $B(C_6H_4\text{-}2\text{-}F)_3$, $B(C_6H_4\text{-}3\text{-}F)_3$, and $B(C_6H_4\text{-}4\text{-}F)_3$] means that structural issues that determine Lewis acidity in other species, like deformation energies,[3b,7] do not apply here. Inspection of the LUMO energies of the boranes, a technique commonly used to assess Lewis acidity[36] and acid hardness,[37] shows the pattern $B(C_6H_4\text{-}3\text{-}F)_3 < B(C_6H_4\text{-}2\text{-}F)_3 < B(C_6H_4\text{-}4\text{-}F)_3$ for all models examined, also inconsistent with the trend.

Table 4. Statistical Comparisons of Computed (OG2R3) Formation Energies in $(F_{5-x}H_xC_6)_3B{-}XMe_3$ Complexes Based on Aryl Ring Fluorine Position[a]

		avg(s)[b] of ΔE(B−N) (kcal·mol^{-1})			avg(s) of ΔE(B−P) (kcal·mol^{-1})		
F position	trials (met, unmet)	met	unmet	$\lvert t\rvert$	met	unmet	$\lvert t\rvert$
2	**14, 5**	**−12.2(3.9)**	**−2.8(2.1)**	**6.70**	**−16.6(2.4)**	**−5.5(2.3)**	**9.16**
3	12, 7	−9.7(5.5)	−9.6(5.9)	0.04	−13.6(6.2)	−13.8(4.8)	0.08
4	10, 9	−9.3(6.0)	−10.1(5.2)	0.31	−12.9(6.4)	−14.6(4.6)	0.67
2,3	**8, 11**	**−12.9(3.7)**	**−7.4(5.6)**	**2.58**	**−17.6(2.0)**	**−10.9(5.7)**	**3.61**
2,4	7, 12	−12.3(4.0)	−7.9(6.0)	1.91	−16.7(2.5)	−11.5(6.2)	2.57
2,5	**6, 13**	**−14.5(2.9)**	**−7.5(5.0)**	**3.84**	**−18.5(1.3)**	**−11.5(5.4)**	**4.41**
2,6	6, 13	−8.4(2.4)	−10.3(6.4)	0.94	−14.9(2.2)	−13.2(6.6)	0.83
3,4	6, 13	−9.9(5.9)	−9.6(5.5)	0.11	−13.1(7.3)	−14.0(4.9)	0.27
3,5	6, 13	−11.0(5.6)	−9.1(5.6)	0.69	−14.9(6.3)	−13.2(5.4)	0.57
2,3,4	4, 15	−13.1(3.8)	−8.8(5.6)	1.80	**−17.6(2.1)**	**−12.7(5.8)**	**2.68**
2,3,5	4, 15	−14.1(3.6)	−8.5(5.4)	2.46	**−18.8(1.7)**	**−12.4(5.5)**	**3.87**
2,3,6	4, 15	−9.7(1.5)	−9.7(6.2)	0.00	−16.1(1.5)	−13.1(6.1)	1.72
2,4,5	3, 16	−14.5(3.3)	−8.8(5.4)	2.44	**−18.4(1.7)**	**−12.8(5.6)**	**3.28**
2,4,6	3, 16	−8.6(2.5)	−9.9(5.9)	0.63	−14.9(2.3)	−13.5(6.0)	0.70
3,4,5	3, 16	−11.0(6.5)	−9.5(5.5)	0.38	−14.3(7.8)	−13.6(5.4)	0.15

[a] Data were scaled by subtracting the energies of the $(F_{5-x}H_xC_6)_3B{-}XMe_3$ complexes. Differences that are statistically significant at the 98% confidence level are shown in boldface type. [b] Avg is the average of the values meeting the criterion; s is the standard deviation of the individual values from the average. $\lvert t\rvert$ is the absolute value of Student's t-statistic for a two-sample unpooled t- test with unequal variances.

Table 5. Substituent Effect Energies and Errors Derived from Least-Squares Fitting, Computed for Amine−Borane and Phosphine−Borane Complexes $(F_{5-x}H_xC_6)_3B{-}XMe_3$ by Use of OG2R3 Energies

	substituent effect energy (kcal·mol^{-1})	
	$(F_{5-x}H_xC_6)_3B{-}NMe_3$	$(F_{5-x}H_xC_6)_3B{-}PMe_3$
2-F	−12.6(2)	−14.7(8)
3-F	−2.2(2)	−3.3(7)
4-F	−0.1(1)	−0.5(7)
5-F	−2.5(2)	−2.7(8)
6-F	6.6(2)	3.2(9)
rms error energies[a]	0.3	1.0

[a] Root-mean-square error energies were determined by use of the least-squares-derived substituent effect energies to calculate the hypothetical binding energies for each isomer, and comparing them to the OG2R3-calculated energies. The rms formula appears in Table 3.

One approach, based on linear free energy relationships in organic chemistry, involves comparing the tris(fluoroaryl)boranes to monofluoro-substituted phenols and benzoic acids, which have been studied in the gas phase by McMahon and Kebarle[38] and Taft and co-workers.[39] However, the acidities of these protic acids increase in the order 4-position < 2-position < 3-position,[38] in stark contrast to the tris(fluoroaryl)borane trend for Lewis acidity. Thus the usual resonance and inductive arguments applied to protic acids[18] do not apply. However, protic acidities are also affected by polarization. Polarization effects are often assessed in protic acids by use of the simplified electrostatic equation $E = -\alpha e^2/2r^4$, where α is the polarizability of the substituent and r is the distance between the substituent and the charge site. In anions, the charge site is generally the most electronegative atom(s), assumed to be where most of the negative charge resides; in the boranes, one can treat the electron-poor boron as the site of positive charge (electron deficiency). Use of the electrostatic equation to compare tris(fluoroaryl)boranes removes most of the terms, allowing simplification of the mathematics and cancellation of errors. Equation 1 gives the comparison between $B(C_6H_4\text{-}2\text{-}F)_3$ and the other two isomers $B(C_6H_4\text{-}3\text{-}F)_3$ and $B(C_6H_4\text{-}4\text{-}F)_3$:

$$E[B(C_6H_4\text{-n-}F)_3] = E[B(C_6H_4\text{-}2\text{-}F)_3]\left(\frac{r_{B\text{-}2F}}{r_{B\text{-}nF}}\right)^4 \qquad (1)$$

By use of distances from the optimized structures (Figure 1), and the average value from Table 5 of $E[B(C_6H_4\text{-}2\text{-}F)_3] = 13.7$ kcal·mol^{-1}, eq 1 predicts $E[B(C_6H_4\text{-}3\text{-}F)_3] = 1.7$ kcal·mol^{-1} and $E[B(C_6H_4\text{-}4\text{-}F)_3] = 1.0$ kcal·mol^{-}. The agreement with the data in Table 5 is only fair, but it is reasonable given the assumptions involved and indicative that polarization contributes to determining Lewis acidities in these tris(fluoroaryl)boranes.

To examine complexation energies from another perspective, we performed local molecular orbital energy decomposition analyses (LMOEDA)[28] on several complexes at the M06-2x/6-311+G(d,p) level (Table 6). The methodology of decomposition analyses is arbitrary, but we hoped that comparing these closely related complexes would provide further insight into issues that dominate the binding energetics.

An energy decomposition analysis treats the total energy as a sum of structural and electronic factors:

$$\Delta E_T = \Delta E_{prep} + \Delta E_{int} \qquad (2)$$

The ΔE_{prep} term represents the energy associated with deforming a free molecule to prepare it to form the complex. In the cases of the complexes here, the major contributor to ΔE_{prep} is the energy difference between trigonal planar $B(C_6H_xF_{5-x})_3$ and its pyramidal form in the complex. As PMe_3 is pyramidal in free and complexed forms, its contribution to

Table 6. Data Extracted from Localized Molecular Orbital Energy Decomposition Analyses

	LMOEDA data (kcal·mol^{-1})						
	ΔE_{ele}[a]	ΔE_{exc}[b]	ΔE_{rep}[c]	ΔE_{st}[d]	ΔE_{pol}[e]	ΔE_{dis}[f]	ΔE
$(H_5C_6)_3B-PMe_3$	−95.3	−114.6	301.4	91.5	−89.7	−40.3	−38.5
$(2\text{-}FH_4C_6)_3B-PMe_3$	−101.1	−113.6	306.2	91.5	−100.2	−47.3	−56.0
$(3\text{-}FH_4C_6)_3B-PMe_3$	−96.3	−113.8	300.7	90.6	−92.7	−40.5	−42.6
$(4\text{-}FH_4C_6)_3B-PMe_3$	−95.2	−114.1	300.6	91.3	−89.7	−40.2	−38.6
$(2,3\text{-}F_2H_3C_6)_3B-PMe_3$	−101.2	−112.2	303.4	90.0	−101.8	−47.5	−59.3
$(2,4\text{-}F_2H_3C_6)_3B-PMe_3$	−101.0	−113.3	305.7	91.4	−100.2	−47.3	−56.1
$(2,5\text{-}F_2H_3C_6)_3B-PMe_3$	−101.9	−113.0	305.4	90.5	−102.7	−47.4	−59.6
$(2,6\text{-}F_2H_3C_6)_3B-PMe_3$	−100.6	−114.4	310.3	95.3	−98.7	−50.2	−53.6

[a] ΔE_{ele} is the electrostatic contribution to bonding. [b] ΔE_{exc} is the exchange contribution to bonding. [c] ΔE_{rep} is the repulsion contribution to bonding. [d] $\Delta E_{st} = \Delta E_{ele} + \Delta E_{exc} + \Delta E_{rep}$. [e] ΔE_{pol} is the polarization contribution to bonding. [f] ΔE_{dis} is the dispersion contribution to bonding.

ΔE_{prep} is small. Since the Lewis acids are all tris(aryl)boranes, one expects that E_{prep} should be nearly identical for all species examined. To test this, we determined E_{prep} for the borane moieties of $(H_5C_6)_3B-PMe_3$, the analogous tris(monofluoroaryl) complexes, and $(F_5C_6)_3B-PMe_3$ at the OG2R3//M06-2x/6-311+G(d,p) level. The average value was 18(1) kcal·mol^{-1}, with $(F_5C_6)_3B-PMe_3$ showing the largest value of 20.0 kcal·mol^{-1}. These data demonstrate that E_{prep} is indeed essentially constant for all complexes examined. Thus this term is not included in the data in Table 6.

In the LMOEDA model, the ΔE_{int} term is decomposed into five parts:

$$\Delta E_{int} = \Delta E_{ele} + \Delta E_{exc} + \Delta E_{rep} + \Delta E_{pol} + \Delta E_{dis} \qquad (3)$$

In order, these terms represent the electrostatic, exchange, repulsion, polarization, and dispersion contributions to the energy. The sum of the first three is often referred to as the steric interaction energy, ΔE_{st},[40] which essentially represents the energy associated with joining the two moieties (borane and phosphine) and allowing their filled orbitals to interact. The last two effectively correspond to incorporating the effects of virtual orbitals into the calculation, allowing for charge transfer, delocalization, and donor−acceptor interactions.[41]

For the complexes in Table 6, one notes first that the ΔE_{st} term, representing the sum of $\Delta E_{ele} + \Delta E_{exc} + \Delta E_{rep}$, is nearly constant for all entries. The only case where it is unusual is for $(2,6\text{-}F_2H_3C_6)_3B-PMe_3$, where the repulsion term ΔE_{rep} is larger, because of the steric congestion at the boron (see above). Supporting this is the observation that complexes containing 2-fluorosubstituted aryls consistently exhibit larger repulsion energies than those that do not. The exchange energy term ΔE_{exc} is reasonably constant, implying that ΔE_{ele} and ΔE_{rep} change to compensate for each other. This is consistent with their natures: ΔE_{ele} approximates the attractions associated with interpenetration of electron density from the two moieties, while ΔE_{rep} approximates the repulsions associated with interpenetration.

Since ΔE_{st} is nearly constant, it is clear that differences in base-binding energies largely stem from differences in ΔE_{pol} and ΔE_{dis}. Comparing first the tris(monofluoroaryl) complexes with $(H_5C_6)_3B-PMe_3$, one sees that $(2\text{-}FH_4C_6)_3B-PMe_3$ exhibits the more negative (more stabilizing) values for both, and that the total stabilization is 17.5 kcal·mol^{-1} over that for $(3\text{-}FH_4C_6)_3B-PMe_3$. This agrees reasonably with the 14.7 kcal·mol^{-1} difference between the two in Table 5. However, the ΔE_{dis} values for $(3\text{-}FH_4C_6)_3B-PMe_3$ and $(4\text{-}FH_4C_6)_3B-PMe_3$ are nearly identical to that for $(H_5C_6)_3B-PMe_3$, meaning that the differences in base-binding energies for these are determined essentially entirely by ΔE_{pol}. The differences in these terms are 3.0 and 0.0 kcal·mol^{-1}, respectively, nearly identical to the additivity values in Table 5.

Data for the tris(monofluoroaryl) complexes alone is similarly self-consistent. $(2\text{-}FH_4C_6)_3B-PMe_3$ exhibits ΔE_{pol} 7.5 kcal·mol^{-1} and ΔE_{dis} 6.8 kcal·mol^{-1} more stabilizing than that for $(3\text{-}FH_4C_6)_3B-PMe_3$, for a total stabilization of 14.3 kcal·mol^{-1}. This agrees reasonably with the 11.4 kcal·mol^{-1} difference between 2- and 3-substitution in Table 5. Similarly, the two parameters summed predict $(3\text{-}FH_4C_6)_3B-PMe_3$ to be 3.3 kcal·mol^{-1} more stable than $(4\text{-}FH_4C_6)_3B-PMe_3$, again agreeing with the predictions of Table 5. Comparing the tris(difluoroaryl)-borane complexes, one sees similar trends consistent with Table 5. For example, $(2,3\text{-}F_2H_3C_6)_3B-PMe_3$ and $(2,5\text{-}F_2H_3C_6)_3B-PMe_3$ exhibit nearly identical values for ΔE_{pol} and ΔE_{dis}, consistent with the prediction that fluorine substitution at the 3- and 5-positions stabilizes base binding to a nearly identical degree. In addition to having a large ΔE_{rep} because of steric congestion, $(2,6\text{-}F_2H_3C_6)_3B-PMe_3$ exhibits the smallest value for ΔE_{pol}, indicating that the long B−P distance in this complex lowers the ability of the base to transfer charge to the acid, thus weakening the B−P bond and lowering the Lewis acidity of the acid.

Thus the computational data support the view that, all other things being equal, the strongest Lewis acids in this class will have electron-withdrawing substituents closest to the boron and that Lewis acidity will decrease regularly as the substituents are placed farther away. Only in the cases where steric congestion becomes important, that is, when the aryl ring is 2,6-disubstituted, will this not hold.

■ CONCLUSIONS

The computational data indicate that the Lewis acidities of tris(fluoro-substituted aryl)boranes can be tuned to a significant degree through selection of which positions are occupied by fluorines. Further tuning via steric congestion can be employed through substitution at the 2,6-positions. The tris(perfluoroaryl)borane $B(C_6F_5)_3$ is not the strongest Lewis acid in the set; experimentalists looking for a stronger acid—but one not as strong as $B(CF_3)_3$[42]—should investigate $B(C_6H\text{-}2,3,4,5\text{-}F_4)_3$ and $B(C_6H_2\text{-}2,3,5\text{-}F_3)_3$. Those seeking a very weak acid should consider $B(C_6H_4\text{-}4\text{-}F)_3$.

Frustrated Lewis pair systems have largely been based on inhibiting coordination between acid and base through steric congestion. The results here suggest that the alternative method employing acids and bases that inherently bind weakly is also viable, even when the Lewis acid is highly fluorinated. The likeliest example involves $B(C_6H_2\text{-}3,4,5\text{-}F_3)_3$, which binds the Lewis bases examined here only slightly better than does $B(C_6H_5)_3$; however, as a constituent of an FLP, it might be significantly more reactive.

That the effect of fluoride substitution on binding energies appears additive is interesting, as it allows predictable tuning. While it remains uncertain why additivity holds, it appears that the influence of fluorine on boron depends on the polarization of the acid induced by the fluorines. This seems to follow an exponential decay law of significant order, quickly diminishing the effect of the fluorines as they are placed farther from the boron.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Twenty-four tables listing B−N and B−P distances in all complexes calculated for different model chemistries, optimized [MPW1K/6-31+G(d)] Cartesian coordinates and absolute energies for all compounds described, and information regarding the least-squares fitting; and one graphic showing ONIOM layering selected for OG2R3 calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(35) A reviewer queried how this congestion was assessed, given that substitution solely at the 2-position did not lead to longer B−N/B−P bonds. This might cause one to conclude that H and F are isosteric when attached to a boron aryl. As the steric effect between boron and the aryl substituents is largely through space, we view the van der Waals radius as a reasonable indicator of steric size. For H and F, the vdW radii are 1.2 and 1.5 Å, respectively (Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; HarperCollins: New York, 1993; p 292). It appears that borane can adjust the aryl rings to accommodate one fluorine at the 2-position but not two at the 2- and 6-positions.

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(41) In the better-known energy decomposition analysis implemented in the ADF program, $\Delta E_{\mathrm{int}} = \Delta E_{\mathrm{elet}} + \Delta E_{\mathrm{Pauli}} + \Delta E_{\mathrm{oi}}$, where these terms represent electrostatic, Pauli, and "orbital interaction" energies. In terms of the mathematics within the LMOEDA approach, $\Delta E_{\mathrm{elet}} \approx \Delta E_{\mathrm{ele}}$, $\Delta E_{\mathrm{Pauli}} \approx \Delta E_{\mathrm{exc}} + \Delta E_{\mathrm{rep}}$, and $\Delta E_{\mathrm{oi}} \approx \Delta E_{\mathrm{pol}} + \Delta E_{\mathrm{dis}}$. See ref 28.

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