Periodic Trends and Index of Boron Lewis Acidity

Joshua A. Plumley and Jeffrey D. Evanseck*

Contribution from the Center for Computational Sciences and the Department of Chemistry and Biochemistry, Duquesne University, 600 Forbes Avenue, Pittsburgh, Pennsylvania 15282-1530

Received: December 18, 2008; Revised Manuscript Received: March 31, 2009

Lewis acidity is customarily gauged by comparing the relative magnitude of coordinate covalent bonding energies, where the Lewis acid moiety is varied and the Lewis base is kept constant. However, the prediction of Lewis acidity from first principles is sometimes contrary to that suggested by experimental bond energies. Specifically, the order of boron trihalide Lewis acidities predicted from substituent electronegativity arguments is opposite to that inferred by experiment. Contemporary explanations for the divergence between theory, computation, and experiment have led to further consternation. Due to the fundamental importance of understanding the origin of Lewis acidity, we report periodic trends for 21 boron Lewis acids, as well as their coordinate covalent bond strengths with NH_3, utilizing ab initio, density functional theory, and natural bond orbital analysis. Coordinate covalent bond dissociation energy has been determined to be an inadequate index of Lewis acid strength. Instead, acidity is measured in the manner originally intended by Lewis, which is defined by the valence of the acid of interest. Boron Lewis acidity is found to depend upon substituent electronegativity and atomic size, differently than for known Brønsted−Lowry periodic trends. Across the second period, stronger substituent electronegativity correlates ($R^2 = 0.94$) with increased Lewis acidity. However, across the third period, an equal contribution from substituent electronegativity and atomic radii is correlated ($R^2 = 0.98$) with Lewis acidity. The data suggest that Lewis acidity depends upon electronegativity solely down group 14, while equal contribution from both substituent electronegativity and atomic size are significant down groups 16 and 17. Originally deduced from Pauling's electronegativities, boron's substituents determine acidity by influencing the population of its valence by withdrawing electron density. However, size effects manifest differently than previously considered, where greater σ bond (not π bond) orbital overlap between boron and larger substituents increase the electron density available to boron's valence, thereby decreasing Lewis acidity. The computed electronegativity and size effects of substituents establish unique periodic trends that provide a novel explanation of boron Lewis acidity, consistent with first principle predictions. The findings resolve ambiguities between theory, computation, and experiment and provide a clearer understanding of Lewis acidity.

Introduction

In 1923, Gilbert N. Lewis published landmark ideas on acid−base theory, where a base and an acid donate and accept a pair of electrons, respectively.[1,2] Lewis originally defined acids and bases merely from chemical behavior in reactions without the need for any theory of molecular structure.[1] Despite the fact that Lewis' revered concept of valency made it easier to understand the essential characteristics of acids and bases, he was hesitant in its use in the definition, because valency could not be measured directly. Without other recourse, indirect measurements of acidity have ensued, principally based upon the assumption that a stronger acid is more willing to accept an electron pair to complete its valence, thus resulting in a stronger coordinate covalent bond. An overview of different procedures that measure relative Lewis acid and base strengths has been given by Anslyn and Dougherty.[5] Examples include Pearson's hard soft acid base (HSAB) principle,[6−9] Gutmann's donor (DN) and acceptor numbers (AN),[10−12] Drago, Marks, and Wayland's *E* & *C* and *D* & *O* equations,[13−15] and Christe and co-worker's fluoride affinities.[16] Regardless of the scale utilized to predict the relative strengths of Lewis acids, it is assumed that a stronger coordinate covalent bond is due to the increased Lewis acidity when the Lewis base is held constant.

From the beginning, Lewis cautioned that other factors could be important in determining the adduct's bond strength, other than its tendency to accept an electron pair.[1] Subsequently, it has been reported that the coordinate covalent bond is influenced by other forces between the Lewis acid and base, such as orbital and steric interactions.[17−19] Lewis observed that relative acidity depends on the choice of Lewis base. For example, BH_3 forms a more stable adduct with thioethers as compared to BF_3; however, the reverse is true when the Lewis acids are bound to ethers.[3] A similar exchange is observed when BF_3 and BH_3 are bound to pyridine *N*-oxide and *p*-methylpyridine oxide, where BF_3 forms a more stable adduct with pyridine *N*-oxide as compared to BH_3; however, BH_3 forms a more stable adduct with *p*-methylpyridine oxide.[4] Lewis summarized "that the relative strength depends not only upon the chosen solvent but also upon the particular base or acid used for reference."[1] Nevertheless, the indirect gauge of Lewis acidity based upon bond strengths remains.

Even today, valency cannot be directly measured by experimental means, but computational methods and resources have now evolved such that valency and perturbations can be evaluated. As a result, a quantitative value indicating the degree

---

* Corresponding author. E-mail: evanseck@duq.edu.

10.1021/jp811202c CCC: $40.75

of Lewis acidity is possible from the computed valency of boron. Thus, relative Lewis acidity is estimated in the manner originally intended by Lewis,[1] based upon the valence deficiency of the acid of interest.

Among the Lewis acids available, boron halides are commonly and widely utilized, due to their simplicity and strong influence over many diverse organic reactions.[20−33] The problem of assessing Lewis acidities based upon coordinate covalent bond strength is illustrated by a long-standing problem in organic chemistry, where opposite to that expected, the Lewis acidity of boron trihalides has been reported to increase as $BF_3 < BCl_3 < BBr_3$.[4,34−42] The observed trend eludes explanations based upon Pauling's electronegativity indices,[43] Bent's Rule of hybridization,[44] steric hindrance,[45] and HSAB.[46] Despite extensive theoretical[47−55] and experimental investigations,[4,34−42,51,56−59] the origin of Lewis acidity differences between boron halides remains controversial, primarily due to the assessment of Lewis acidity as referenced against coordinate covalent bond dissociation energies.

Other ideas have been explored to account for Lewis acidities determined by coordinate covalent bond strengths. Specifically, the importance of halogen lone pairs in Lewis acids has been considered in terms of resonance,[37,56] $p(\pi) \rightarrow p(\pi)$ hyperconjugation,[51,52,58] π-bonding,[57] and energy necessary to reorganize planar Lewis acids during adduct formation.[18,47,48,51−53,59] Despite the terms used, the underlying mechanism involved is the same, where halogen lone pairs interact with boron's formally empty 2p orbital, yielding coordinate covalent π-bonds. The question of which halogen demonstrates a larger resonance or $p(\pi) \rightarrow p(\pi)$ hyperconjugation within boron halides continues to be debated.[43,60−63] Furthermore, the $p(\pi) \rightarrow p(\pi)$ hyperconjugation cannot account for the observed differences in Lewis acidity regarding BH_3 when compared to BF_3[3,4,35,42] or BCl_3.[35,41,42] Thus, the impact of halogen lone pairs upon understanding Lewis acidity is dubious.

Computational studies of boron halides coordinated to nitrogen centered Lewis bases and ammonia borane have been reported.[47−50,53−55,60,61,64−72] However, it has been shown that the electronic description of coordinate covalent bonding is highly sensitive to the level of theory applied, and that post-SCF methods or M06-2X coupled with large basis sets are necessary to predict the binding energies of coordinate covalent systems accurately.[73,74] Commonly employed computational methods can result in binding enthalpy errors as great as 87% (15.2 kcal/mol), as found for methyl substituted ammonia boranes.[66,73,74] Consequently, lower levels of theory have resulted in conflicting ideas on coordinate covalent bonding and gauging Lewis acidity.[47−50,53,54,60,61,64−74]

Due to the importance of understanding Lewis acidity, 21 isolated boron Lewis acids ($BH_{3-n}F_n$, $BH_{3-n}Cl_n$, $BCl_{3-n}F_n$, $BH_{3-n}(OH)_n$, $BH_{3-n}(SH)_n$, $BH_{3-n}(CH_3)_n$, and $BH_{3-n}(SiH_3)_n$; $n = 0-3$) as well as their corresponding adducts with NH_3 have been analyzed. Unique to this study is that second and third period substituents are assessed in a systematic evaluation of boron Lewis acidity to capture periodic trends. Lewis acidity trends down groups 14, 16, and 17 are also reported. The ability of a Lewis acid to accept electron density is investigated in terms of boron's valence, and its stereoelectronic dependence upon substituents. Our observations are rationalized in terms of first principle concepts including the Pauling electronegativity[43,75] and atomic radii[76] of the atom from the substituent that is directly coordinated to boron. The periodic trends are contrasted against well-known Brønsted−Lowry acid−base behavior and extended to explain aluminum halide Lewis acidity.

Computational Methods

A systematic computational investigation is employed, utilizing a level of theory suitable for coordinate covalent bonds within Lewis acid adducts.[73,74] Ab initio, density functional theory, and natural bond orbital (NBO) analysis have been utilized to analyze stereoelectronic effects of substituted boron Lewis acids. All electronic structure calculations were carried out using the computational resources at the Center for Computational Sciences at Duquesne University. Gaussian03[77] has been employed for all electronic structure methods, except M06-2X where NWChem 5.1[78] was used. All adducts and isolated Lewis acids have been fully optimized with M06-2X[79] and the 6-311++G(3df,2p) Pople style basis set.[80−86] In addition, all isolated boron halide Lewis acids and corresponding adducts with NH_3 have been optimized with Møller−Plesset second-order perturbation theory (MP2)[87,88] employing 6-311++G(3df,2p). Subsequently, single point (SP) energy calculations have been employed on MP2 optimized structures utilizing quadratic configuration interaction with single and double substitutions, incorporating a perturbational treatment of the triples contribution (QCISD(T))[89,90] utilizing Dunning's[91−94] aug-cc-pVQZ correlation consistent basis set. As previously reported, B3LYP yields mean absolute deviations of ca. 9.0 kcal/mol regarding the binding enthalpies of coordinate covalent bonds, specifically on the experimental high resolution gas phase work of the methylated series of $(CH_3)_3B-N(CH_3)_{3-n}H_n$ ($n = 0-3$).[95] Furthermore, B3LYP did not model the binding enthalpy trend accurately within the methylated series. However, both M06-2X/6-311++G(3df,2p)[74] and QCISD(T)/6-311++G(3df,2p)//MP2/6-311++G(3df,2p)[73] were found to model the B−N coordinate covalent bond trend for $(CH_3)_3B-N(CH_3)_{3-n}H_n$ ($n = 0-3$) within experimental accuracy, with MADs of 0.3 and 0.4 kcal/mol, respectively. Higher order derivatives of the energy are found to be necessary within the DFT formalism, specifically the spin-dependent electronic kinetic energy within both the exchange and correlation functional to provide an accurate description of short and medium exchange−correlation interactions within sterically hindered adducts. Consequently, M06-2X instead of the B3LYP functional has been employed within this work. Further details concerning the inaccuracies of B3LYP have been summarized by Truhlar[96] and Sousa.[97] 6-311++G(3df,2p) has been exchanged with aug-cc-pVQZ to avoid a convergence correction factor necessary for QCISD(T), discussed elsewhere.[73,74] Basis set superposition error (BSSE) has been corrected with the counterpoise method developed by Boys and Bernardi[98] as implemented and reported previously.[73,74] All minima have been confirmed by the absence of imaginary frequencies utilizing B3LYP/6-31G(d). Enthalpy corrections were predicted utilizing B3LYP/6-31G(d) and scaled by 0.9989[99] to predict binding enthalpies at 298 K for all Lewis acids adducts.

Natural bond orbital (NBO) analysis[100] was performed using the NBO 5.G program,[101] embedded within Gaussian03. NBO is discussed in detail elsewhere.[100,102−105] Goodman reported inadequacies in the triple-split 6-311++G Pople basis set, where diffuse function augmentation lead to misleading conclusions drawn from NBO analysis regarding the stability of common four heavy atom molecules.[106] However, double-split 6-31G Pople and correlation consistent basis sets are less sensitive to error with diffuse augmentation, and allow for accurate assess-

TABLE 1: Binding Enthalpies with NH_3,[a] Boron's Valence Deficiency (BVD),[b] and Atomic Charge (q_B)

	BVD	q_B	QCISD(T)[c] ΔH_{298}	M06-2X[d] ΔH_{298}
BF_3	1.64	1.60	−19.6	−20.2
$B(OH)_3$	1.42	1.38		1.1
$BClF_2$	1.35	1.30	−20.8	−21.9
BHF_2	1.30	1.27	−15.2	−16.1
$BH(OH)_2$	1.11	1.08		−1.3
$B(CH_3)_3$	1.00	0.98		−14.1
BCl_2F	0.97	0.91	−22.2	−23.5
BH_2F	0.92	0.90	−18.8	−19.6
$BH(CH_3)_2$	0.79	0.77		−17.5
$BH_2(OH)$	0.77	0.76		−10.1
$BH_2(CH_3)$	0.61	0.60		−22.0
BCl_3	0.50	0.44	−23.8	−25.1
$BHCl_2$	0.50	0.46	−24.0	−25.4
BH_2Cl	0.47	0.45	−25.2	−26.2
BH_3	0.43	0.43	−27.1	−27.7
$BH_2(SH)$	0.26	0.24		−18.1
$BH_2(SiH_3)$	0.17	0.16		−30.9
$BH(SH)_2$	0.17	0.14		−12.6
$B(SH)_3$	0.11	0.07		−9.3
$BH(SiH_3)_2$	−0.11	−0.14		−33.1
$B(SiH_3)_3$	−0.41	−0.44		−35.1

[a] kcal/mol. [b] electrons. [c] QCISD(T)/aug-cc-pVQZ//MP2/6-311++G-(3df,2p). [d] M06-2X/6-311++G(3df,2p).

ments. Consequently, specific stereoelectronic effects have been investigated utilizing HF/cc-pVQZ//M06-2X/6-311++G(3df,2p) since the requisite density matrix necessary for these types of analyses are not available for MP2 or QCISD(T) computations. NBO analysis has been employed to determine the natural hybrid overlap (NHO) integral, *S*, as well as the atomic charge and boron valence deficiency. Briefly, atomic charge is defined as the nuclear charge minus the sum of electron populations from each natural atomic orbital on the corresponding atom, including core and valence orbitals.[102] In contrast, valence deficiency is the formal valence minus the sum of electron populations from each valence natural atomic orbital.

Results and Discussion

Lewis Acidity. Boron's electrophilicity within the isolated Lewis acid is considered in terms of boron's atomic charge and its valence deficiency, calculated by subtracting the NBO predicted valence (HF/cc-pVQZ//M06-2X//6-311++G-(3df,2p))[106] from the formal valence of three (Table 1). As expected, boron's valence deficiency and atomic charge are highly correlated ($R^2 = 0.999$), indicating that both similarly reflect the degree of boron's electrophilicity and thus Lewis acidity. However, boron's valence deficiency and binding enthalpy are not correlated (Figure 1; $R^2 = 0.28$), which underscores the need for a new paradigm regarding the prediction of Lewis acidity. Confidence in the data is engendered, since the same trend in binding enthalpy is predicted by using both QCISD(T)//MP2 and the M06-2X functional. Furthermore, the M06-2X predicted binding enthalpy for $(CH_3)B-NH_3$ lies within the uncertainty of the experimental value, $\Delta H_{298} = -13.8 \pm 0.3$ kcal/mol.[107] In addition, the M06-2X and QCISD(T)//MP2 predicted binding enthalpies of −25.1 and −23.8 kcal/mol, respectively, are in excellent agreement with the experimental value of −24.0 kcal/mol regarding the Cl_3B-NH_3 adduct.[108] As far as we are aware, there are no other experimental binding enthalpies regarding the NH_3 adducts of interest for further comparison.

The average substituent electronegativity is estimated as one-third the sum of all atomic electronegativities coordinated to boron.

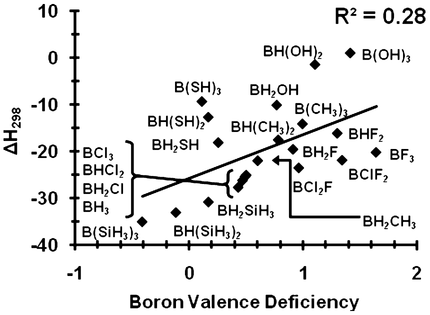

Figure 1. M06-2X/6-311++G(3df,2p) predicted BSSE corrected binding enthalpies with NH_3, ΔH_{298} (kcal/mol) vs boron's valence deficiency (electrons).

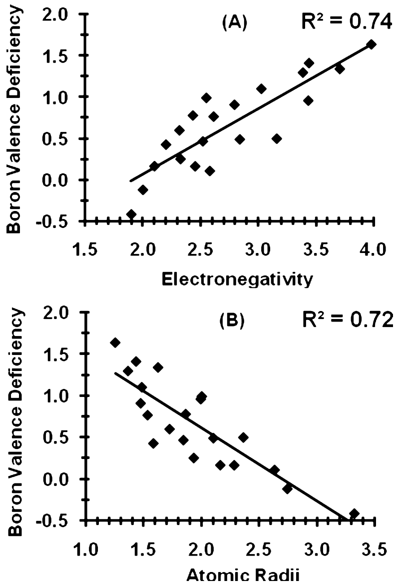

Figure 2. (A) Boron's valence deficiency (electrons) vs the average substituent electronegativity. (B) Boron's valence deficiency vs the sum of atomic radii (Å) coordinated to boron. Second and third period atoms as well as hydrogen are considered.

Considering all 21 Lewis acids, a moderate linear correlation is observed ($R^2 = 0.74$; Figure 2A), indicating that as substituents coordinated to boron become more electronegative, boron's valence becomes more deficient, yielding a stronger Lewis acid. Other electronegativity scales have been considered, yielding comparable results, as shown by Figure S1−S4 within the Supporting Information. Considering Brønsted−Lowry acids,[19] a binary acid increases in strength across a period, because the conjugate base is stabilized with increasing electronegativity without significant atomic size changes. However, within a periodic group, electronegativity effects become negligible compared to atomic size changes and Brønsted−Lowry acids strengthen with increasing size. In contrast to Brønsted−Lowry acid behavior, increasing substituent atomic radii results in weaker Lewis acids for all systems considered ($R^2 = 0.72$, Figure 2B).

Trends Across Periods. When second period substituted boron Lewis acids ($BH_{3-n}(CH_3)_n$, $BH_{3-n}(OH)_n$ and $BH_{3-n}F_n$; $n = 0-3$) are considered, boron's valence deficiency is highly correlated with substituent electronegativity ($R^2 = 0.94$, Figure 3), but not with atomic radii ($R^2 = 0.33$, Figure S5 (Supporting Information)). This suggests that substituent electronegativity accounts for 61% more of the observed differences in Lewis acidity for second period substituted boron Lewis acids than does substituent atomic radii. This is in accordance with Brønsted−Lowry theory, where substituent electronegativity

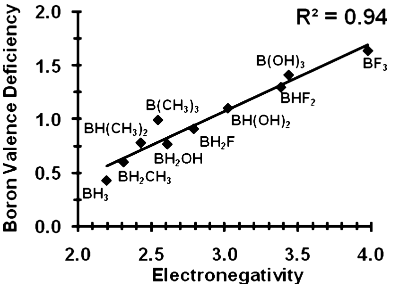

Figure 3. Boron's valence deficiency (electrons) vs the average substituent electronegativity. Only second period atoms and hydrogen are considered.

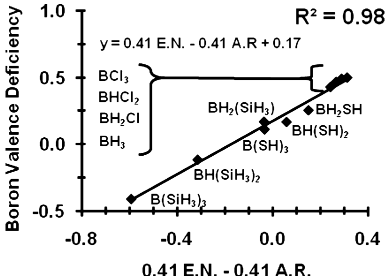

Figure 4. Boron's valence deficiency (electrons) vs a linear combination of average substituent electronegativities (E.N.) and atomic radii sums (A.R.) of atoms coordinated to boron. Only third period atoms and hydrogen are considered.

differences explain the differences in strength of acids within the same period. In contrast, when third period substituted boron Lewis acids ($BH_{3-n}Cl_n-NH_3$, $BH_{3-n}(SH)_n$, and $BH_{3-n}(SiH_3)_n$; $n = 0-3$) are considered, only a moderate correlation is observed with atomic radii ($R^2 = 0.72$; Figure S6) and little correlation is observed with electronegativity ($R^2 = 0.54$; Figure S7 (Supporting Information)). To explain the variance of third period substituted boron Lewis acidity, an equal balance[109] of electronegativity and atomic radii is necessary ($R^2 = 0.98$; Figure 4 (Supporting Information)).

Coordinate covalent π-bonds between halogen lone pairs and boron's formally empty 2p orbital were previously thought to regulate boron halide Lewis acidity and explain periodic trends. It was reported that fluorine lone pairs yield stronger coordinate covalent π-bonds, thus occupying more of boron's 2p orbital and accounting for the weaker acidity of BF_3 compared to BCl_3.[43,48,56] However, heavier halogens with more diffuse polarizable lone pairs were predicted to form stronger coordinate covalent π-bonds.[60−62] Thus, a weaker interaction between fluorine's lone pair and boron's formally empty 2p orbital is expected when compared to chlorine.[60−62] However, the overlap integral, S_π, representing the magnitude of π-overlap between p_B and p_F, is marginally greater than that between p_B and p_{Cl} (Figure 5), in accord with previous reports.[43,48,56] Thus, the importance of substituent effects on Lewis acidity solely through coordinate covalent π-bond interactions is questionable.[18,37,47,48,51−53,56−59]

σ bond orbital overlap, S_σ, reported in this work represents a novel approach to understanding the correlation between atomic size and Lewis acidity. S_σ between sp^n hybrid orbitals on boron and substituents is correlated with atomic radii (Figure 6), where both decrease upon moving across the second and third period from carbon to fluorine ($S_\sigma = 0.82 > 0.78 > 0.72$) and from silicon to chlorine ($S_\sigma = 0.83 > 0.79 > 0.76$), respectively. Differences in S_σ are also correlated with atomic radii, where both increase upon moving down a periodic group. Larger atoms possess larger sp^n orbitals and thus result in a greater S_σ with boron's hybrid sp^n orbital. Increased S_σ provides additional electron density for electron deficient boron, decreasing its valence deficiency, and ultimately decreasing its acidity. The increase in S_σ between the second and third period within the same group underscores the need to consider a balance of both electronegativity and size effects for a complete description of third period substituted boron Lewis acid strength.

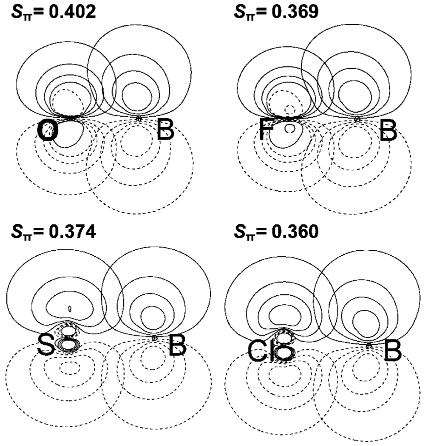

Figure 5. Natural hybrid orbital overlap yielding coordinate covalent π-bonds between boron and X (X = OH, F, SH, and Cl) within BH_2X. S_π is the overlap integral corresponding to the natural hybrid orbitals involved.

Trends Down Groups. Only two elements in groups 14 (carbon and silicon), 16 (oxygen and sulfur), and 17 (fluorine and chlorine) have been considered due to basis set limitations. Interesting differences with Brønsted−Lowry trends are apparent. Group 14 substituent electronegativity is highly correlated with boron's electron deficiency ($R^2 = 0.98$, Figure 7) and atomic radii is only moderately correlated ($R^2 = 0.68$, Figure S8 (Supporting Information)). For example, the difference in S_σ of 0.003, concerning BH_2SiH_3 and BH_2CH_3 can hardly explain the variance in boron's valence deficiency of 0.44 *e*. Consequently, the large differences in electronegativity between carbon and silicon are necessary to account for the differences in boron's valence deficiency. Electronegativity best explains the variance in boron's valence deficiency as compared to substituent size regarding group 14 substituents. An equal balance[109] of electronegativity and atomic radii is required when considering groups 16 and 17, as shown by Figures 8 and 9, respectively. Again, S_σ influences boron's valence in the same manner as described in the previous section. It is suspected that considering atoms further down groups 16 and 17 will reveal that boron's valence deficiency exhibits an even greater dependence on size effects through σ bond orbital overlap.

Comparison to Previous Models. The present work demonstrates that boron's valence deficiency accounts for the electrophilicity of boron and ultimately determines its Lewis acidity. The influence of $p(\pi) \rightarrow p(\pi)$ hyperconjugation on Lewis acid reorganization energy[18,47,48,51,52,59] was previously assumed to be an intrinsic property of the acid, independent from external Lewis bases. However, Drago and co-workers have shown a weakness with this assumption and that reorganization energies are a function of the coordinate covalent bond strength.[51] Furthermore, our results suggest that the $p(\pi) \rightarrow p(\pi)$ hyperconjugation strength is not consistent with boron's valence deficiency. Consequently, our comparison to other models is limited to that described by the lowest unoccupied molecular orbital (LUMO).[48,49,54,64,70]

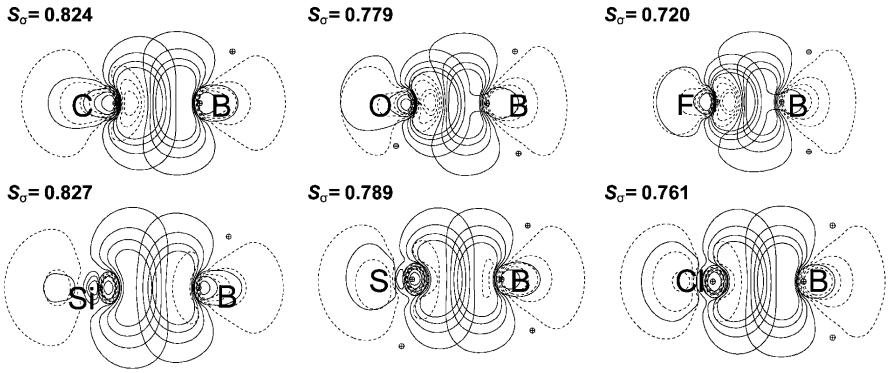

Figure 6. Natural hybrid orbital overlap yielding the σ between boron and X (X = CH_3, OH, F, SiH_3, SH, and Cl) within BH_2X. S_σ is the overlap integral corresponding to the natural hybrid orbitals involved.

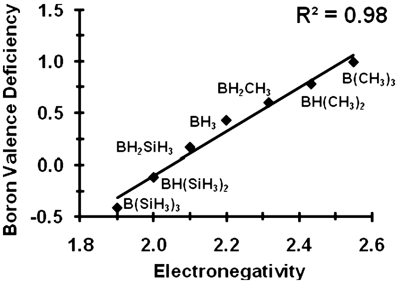

Figure 7. Boron's valence deficiency (electrons) vs average substituent electronegativity. Only group 14 atoms and hydrogen are considered.

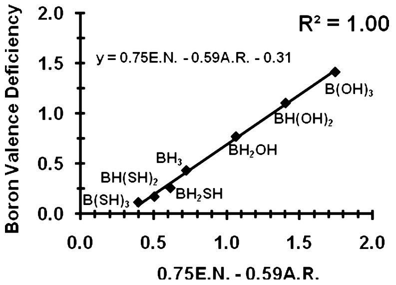

Figure 8. Boron's valence deficiency (electrons) vs a linear combination of average substituent electronegativities (E.N.) and sums of atomic radii (A.R.) coordinated to boron. Only group 16 atoms and hydrogen are considered. Boron's valence deficiency vs electronegativity and vs atomic radii are shown by Figures S9 and S10 (Supporting Information), respectively.

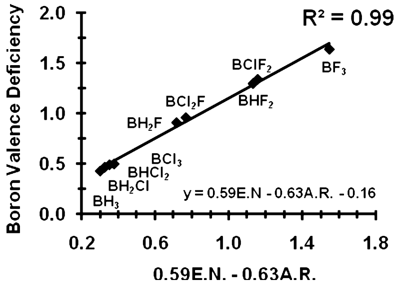

Figure 9. Boron's valence deficiency (electrons) vs a linear combination of average substituent electronegativities (E.N.) and sums of atomic radii (A.R.) coordinated to boron. Only group 17 atoms and hydrogen are considered. Boron's valence deficiency vs electronegativity and vs atomic radii are shown by Figures S11 and S12 (Supporting Information), respectively.

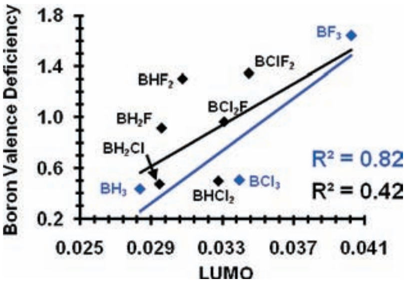

Figure 10. Boron's valence deficiency (electrons) vs the LUMO energy level (hartrees). Energy levels refer to Hartree−Fock orbitals. The black trend line indicates that all boron halide Lewis acids are considered. The blue trend line considers only BX_3 homogeneous Lewis acids (X = H, F, Cl).

It has been reported, utilizing ab initio electronic structure theory, that BCl_3 is a stronger Lewis acid than BF_3 when coordinated to NH_3 due to BCl_3's lower energy LUMO.[48,49,54,64,70] Thus, the relationship between boron halide LUMOs and its acidity in terms of valence deficiency were reinvestigated in this study. First, only BX_3 (X = H, F, Cl) Lewis acids are considered to establish a direct comparison with previous theoretical investigations, where only homogeneous Lewis acids such as BF_3 and BCl_3 were analyzed.[48,49,54,64,70] Indeed, a moderately strong correlation (Figure 10, $R^2 = 0.82$) is found between increasing boron valence deficiency (stronger Lewis acidity) and higher energy LUMOs. The relative LUMOs regarding BF_3 and BCl_3 are in accord with previous studies.[48,49,54,64,70] To further probe the boron Lewis acid LUMO and its consequence upon Lewis acidity, the systematic halogen substituted Lewis acids, $BH_{3-n}F_n$−NH_3, $BH_{3-n}Cl_n$−NH_3, and $BCl_{3-n}F_n$−NH_3 ($n = 0-3$) were analyzed. Upon analyzing all nine boron halide Lewis acids, the correlation decreases from $R^2 = 0.82$ to 0.42 (Figure 10) essentially eliminating the correlation that was demonstrated when only BX_3 Lewis acids were considered. When the mixed halogen substituted Lewis acids are considered, more subtle differences are revealed, indicating that Lewis acidity is not a strict consequence of the LUMO energy level.

It is common to gauge the strength of a Lewis acid from the strength of the coordinate covalent bond formed with a common base, as discussed in the Introduction. The binding enthalpies of X_3B−NH_3 adducts (X = H, F, Cl) vs the corresponding boron valence deficiency supports previous results, where Lewis acidity increases as $BF_3 < BCl_3 < BH_3$ (Figure 11; $R^2 = 0.91$) with $(CH_3)_3P$ and $(CH_3)_3As$ as Lewis bases;[41] however, when the systematically substituted halogen Lewis acids were analyzed the correlation decreases from $R^2 = 0.91$ to 0.63 (Figure 11). More subtle differences are revealed, similarly to that observed for boron's valence deficiency vs LUMO, supporting that adduct stability is not a useful indicator of Lewis acidity, as discussed previously and shown by Figure 1.

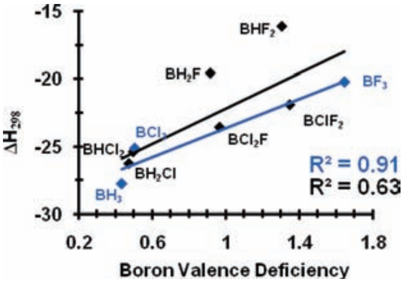

Figure 11. Binding enthalpy (kcal/mol) with NH_3 vs the boron valence defciency (electrons). The black trend line indicates that all boron halide Lewis acids are considered. The blue trend line considers only BX_3 homogeneous Lewis acids (X = H, F, Cl).

Extension to Aluminum Halides. A similar conundrum between predicted and observed Lewis acidities is found for the aluminum halide series, where complications arise from using coordinate covalent bond strengths as an acidity index, insufficient levels of theory, and different Lewis bases.[16,60,110−117] It was initially predicted, utilizing MP2/PDZ, that AlF_3 had a stronger fluoride affinity than $AlCl_3$.[16] However, experimental evaluation in conjunction with additional theoretical work revealed that $AlCl_3$ had a larger affinity for fluoride than AlF_3.[111,114] Furthermore, MP2/II+//MP2/II predicts that $AlCl_3$ forms a stronger coordinate covalent bond with NH_3 than with AlF_3.[110] However, when NH_3 is exchanged with CO or H_2O, reverse trends are predicted by MP2/II+//MP2/II,[110] MP2/VTZ+D+P,[60] and MP2/6-31G(d,p)[115] calculations. Furthermore, inappropriate levels of theory obscure clear conclusions. For example, coordinate covalent bond strengths between AlX_3 (X = F, Cl, Br, and I) and NH_3 predicted by B3LYP in conjunction with effective core potentials were reported to decrease as the halogen size increased.[113] In contrast, $AlBr_3$[116] forms a stronger bond with NH_3 than with $AlCl_3$[117] according to experimental bond dissociation energies, and $AlCl_3$ forms a stronger bond than found for AlF_3, according to MP2/II+//MP2/II predicted results.[110] Interestingly, a quantitative Lewis acid scale regarding AlX_3 (X = F, Cl, Br, and I) was attempted by comparing electron pair affinities.[118] It was reported that AlX_3 Lewis acidities increase as the halogen size increases. Although the external effects of the Lewis base were eliminated, the reorganization energy demonstrated by the Lewis acid remains as a contaminant in describing the innate ability of a Lewis acid to capture electron density.

Extension of our ideas on boron Lewis acidity indicates that both substituent atomic size and electronegativity regulate aluminum halide Lewis acidity through modifications of its valence. For example, fluorine possesses a larger electronegativity compared to other halides, thus creating a more electrophilic aluminum center and a stronger Lewis acid. In addition, fluorine possesses a smaller atomic radius, yielding a smaller S_σ by 0.02, decreasing the electron population available to boron's valence, increasing its deficiency and thus its Lewis acidity. NBO results support this prediction, where the aluminum valence deficiency for AlF_3 is greater than that predicted for $AlCl_3$ by 0.77 electrons. It is also of interest to predict Lewis acidities by exchanging the group 13 atom rather than the substituent. The intrinsic Lewis acidity of YX_3 (Y = group 13 atom) should increase upon moving down group 13 due to electronegativity differences between the group 13 atom and the halide. For example, the electronegativity difference between aluminum and fluorine ($\Delta = 2.37$) is greater than that between boron and fluorine ($\Delta = 1.94$). Therefore, the valence deficiency and ultimately the Lewis acidity of aluminum halides should be greater than that exhibited by boron halides. A NBO analysis of AlF_3 and BF_3 supports this prediction, where the valence deficiency on aluminum and boron is 2.43 and 1.64 electrons, respectively. Preliminary data suggest that size is not important when comparing the acidity of group 13 substituted Lewis acids. For example, S_σ is greater between boron and fluorine than predicted for aluminum and fluorine by only 0.06. This may be an indication that the large electronegativity difference found between aluminum and fluorine dominates over size differences. Electron density is more localized on fluorine when coordinated to aluminum than when coordinated to boron and therefore overlap with aluminum is decreased. Aluminum halide Lewis acids follow the same periodic trends as boron halides, further illustrating that valence deficiency is an apparent index of Lewis acidity that may be rationalized utilizing first principle ideas such as substituent atomic radii and electronegativity.

Conclusion

Two main points are realized in describing Lewis acidity from a systematic analysis of 21 isolated boron Lewis acids. First, coordinate covalent bond strengths are not an adequate measure of Lewis acidity. Rather, Lewis acidity should be gauged by determining boron's valence deficiency, or its ability to accept an electron-pair. Second, Lewis acidity may be rationalized by the same principles that regulate Brønsted−Lowry acidity, but by different contributions. Specifically, substituent electronegativity explains boron Lewis acidity when second period atoms are coordinated to boron, while an equal balance of substituent electronegativity and atomic size are necessary when third period atoms are considered. Furthermore, substituent electronegativity explains group 14 substituted boron Lewis acidity, while an equal balance of substituent electronegativity and atomic size are necessary when group 16 and 17 substituents are considered. Atomic size is found to influence intrinsic boron Lewis acidity, through σ-bond overlap, independent of π-overlap. Specifically, the overlap between the hybrid orbitals present on boron and the substituents that form the σ bond are found to regulate Lewis acidity. A larger overlap increases the electron population available to boron's valence, decreasing its deficiency and thus its Lewis acidity. The present analysis delivers a fundamental report on Lewis acidity, consistent with first principle periodic trends, such as substituent electronegativity and atomic size, which has the potential to realign our understanding and prediction of Lewis acidities.

Acknowledgment. This work was funded in part by the NSF and DoD (CHE-0723109, CHE-0649182, CHE-0321147, CHE-0354052, AAB/PSC CHE-030008P), Department of Education (P116Z080180, P116Z050331, and P116Z040100), the Silicon Graphics Inc., James River Technical, Inc. and Gaussian Corporations. We acknowledge Dr. Doug Fox (Gaussian) and Dr. John C. Kern II (Mathematics) for their expertise, knowledge, and discussions crucial to this study.

Supporting Information Available: All optimized structures, thermodynamic data, Figures S1−S12, and discussion of partial coefficients of determination. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Lewis, G. N. *J. Franklin Inst.* **1938**, *226*, 293–313.

(2) Lewis, G. N. *Valence and the Structure of Atoms and Molecules*, 1st ed.; Chemical Catalog Co.: New York, 1923.

(3) Coyle, T. D.; Kaesz, H. D.; Stone, F. G. A. *J. Am. Chem. Soc.* **1959**, *81*, 2989–2994.

(4) Kulevsky, N.; Sveum, L. *J. Inorg. Nucl. Chem.* **1965**, *27*, 2111–2113.

(5) Anslyn, E. V.; Dougherty, D. A. *Modern Physical Organic Chemistry*, 1st ed.; University Science: Sausalito, CA, 2006.

(6) Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 643–648.

(7) Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 581–587.

(8) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533–3539.

(9) Pearson, R. G. *Benchmark Papers in Inorganic Chemistry: Hard and Soft Acids and bases*, 1st ed.; Dowden: Stroudsburgh, 1973.

(10) Gutmann, V.; Steininger, A.; Wychera, E. *Monatsh. Chem.* **1966**, *97*, 460–467.

(11) Gutmann, V. *Coord. Chem. Rev.* **1975**, *15*, 207–237.

(12) Mayer, U.; Gutmann, V.; Gerger, W. *Monatsh. Chem.* **1975**, *106*, 1235–1257.

(13) Drago, R. S.; Wayland, B. B. *J. Am. Chem. Soc.* **1965**, *87*, 3571–3577.

(14) Drago, R. S. *Struct. Bonding (Berlin)* **1973**, *15*, 73–139.

(15) Marks, A. P.; Drago, R. S. *Inorg. Chem.* **1976**, *15*, 1800–1807, and references therein.

(16) Christe, K. O.; Dixon, D. A.; McLemore, D.; Wilson, W. W.; Sheehy, J. A.; Boatz, J. A. *J. Fluorine Chem.* **2000**, *101*, 151–153.

(17) Jensen, W. B. *Chem. Rev.* **1978**, *78*, 1–22.

(18) Mortimer, C. T. *Reaction Heats and Bond Strengths*; Pergamon Press: New York, 1962.

(19) Luder, W. F.; Zuffanti, S. *The Electronic Theory of Acids and Bases*, 1st ed.; John Wiley & Sons, Inc.: New York, 1946.

(20) Christov, V. C.; Ivanov, I. K. *Synth. Commun.* **2007**, *37*, 3201–3209.

(21) Maruoka, K.; Akakura, M.; Saito, S.; Ooi, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1994**, *116*, 6153–6158.

(22) Corey, E. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 1650–1667.

(23) Jorgensen, K. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3558–3588.

(24) Kabalka, G.; Borella, S.; Yao, M.-L. *Synthesis* **2008**, 325–329.

(25) Li, C.; Wang, J. *J. Org. Chem.* **2007**, *72*, 7431–7434.

(26) Huang, J.-W.; Shi, M. *Tetrahedron Lett.* **2003**, *44*, 9343–9347.

(27) Olah, G. A.; Kuhn, S. J. *J. Org. Chem.* **1964**, *29*, 2317–2320.

(28) D'Aniello, F.; Mann, A.; Mattii, D.; Taddei, M. *J. Org. Chem.* **1994**, *59*, 3762–3768.

(29) Mayr, H.; Gorath, G. *J. Am. Chem. Soc.* **1995**, *117*, 7862–7868.

(30) Malladi, R. R.; Li, N.-S.; Tejedor, D.; Kabalka, G. W. *Synth. Commun.* **2000**, *30*, 3613–3616.

(31) Bellur, E.; Langer, P. *J. Org. Chem.* **2005**, *70*, 3819–3825.

(32) Bhatt, M. V.; Kulkarni, S. U. *Synthesis* **1983**, 249–282.

(33) Pons, J.-M.; Santelli, M. *Lewis Acids and Selectivity in Organic Synthesis*; CRC-Press: New York, 1996.

(34) Miller, J. M.; Onyszchuk, M. *Can. J. Chem.* **1965**, *43*, 1877–1879.

(35) Bax, C. M.; Katritzky, A. R.; Sutton, L. E. *J. Chem. Soc.* **1958**, 1258–1263.

(36) Shriver, D. F.; Swanson, B. *Inorg. Chem.* **1971**, *10*, 1354–1365, and references therein.

(37) Brown, H. C.; Holmes, R. R. *J. Am. Chem. Soc.* **1956**, *78*, 2173–2176.

(38) Miller, J. M.; Onyszchuk, M. *Can. J. Chem.* **1966**, *44*, 899–902, and references therein.

(39) Rothe, E. W.; Mathur, B. P.; Reck, G. P. *Inorg. Chem.* **1980**, *19*, 829–831.

(40) Kuhn, S. J.; McIntyre, J. S. *Can. J. Chem.* **1965**, *43*, 375–380.

(41) Mente, D. C.; Mills, J. L.; Mitchell, R. E. *Inorg. Chem.* **1975**, *14*, 123–126.

(42) Miller, J. M.; Onyszchuk, M. *Can. J. Chem.* **1964**, *42*, 1518–1523.

(43) Pauling, L. C. *The Nature of the Chemical Bond and the Structure of Molecules and Crystals. An Introduction to Modern Structural Chemistry*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(44) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275–311.

(45) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451.

(46) Pearson, R. G. *Inorg. Chem.* **1988**, *27*, 734–740.

(47) Hirao, H.; Omoto, K.; Fujimoto, H. *J. Phys. Chem. A* **1999**, *103*, 5807–5811.

(48) Branchadell, V.; Oliva, A. *THEOCHEM* **1991**, *82*, 75–84.

(49) Branchadell, V.; Oliva, A. *J. Am. Chem. Soc.* **1991**, *113*, 4132–4136.

(50) Branchadell, V.; Sbai, A.; Oliva, A. *J. Phys. Chem.* **1995**, *99*, 6472–6476.

(51) Brown, D. G.; Drago, R. S.; Bolles, T. F. *J. Am. Chem. Soc.* **1968**, *90*, 5706–5712.

(52) Cotton, F. A.; Leto, J. R. *J. Chem. Phys.* **1959**, *30*, 993–998.

(53) Rowsell, B. D.; Gillespie, R. J.; Heard, G. L. *Inorg. Chem.* **1999**, *38*, 4659–4662.

(54) Bessac, F.; Frenking, G. *Inorg. Chem.* **2003**, *42*, 7990–7994.

(55) Bessac, F.; Frenking, G. *Inorg. Chem.* **2006**, *45*, 6956–6964.

(56) Liebman, J. F. *Struct. Chem.* **1990**, *1*, 395–397.

(57) Miller, J. M.; Lanthier, G. F. *J. Chem. Soc. A* **1971**, 346–350, and references therein.

(58) Fenwick, J. T. F.; Wilson, J. W. *Inorg. Chem.* **1975**, *14*, 1602–1604.

(59) Swanson, B.; Shriver, D. F.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 2182–2189.

(60) Frenking, G.; Fau, S.; Marchand, C. M.; Gruetzmacher, H. *J. Am. Chem. Soc.* **1997**, *119*, 6648–6655.

(61) Brinck, T.; Murray, J. S.; Politzer, P. *Inorg. Chem.* **1993**, *32*, 2622–2625.

(62) Kutzelnigg, W. *Angew. Chem.* **1984**, *96*, 262–286.

(63) Lappert, M. F.; Litzow, M. R.; Pedley, J. B.; Riley, P. N. K.; Tweedale, A. *J. Chem. Soc. A* **1968**, 3105–3110.

(64) Cho, H. G.; Cheong, B. S. *THEOCHEM* **2000**, *496*, 185–198.

(65) Allendorf, M. D.; Melius, C. F. *J. Phys. Chem. A* **1997**, *101*, 2670–2680.

(66) Gilbert, T. M. *J. Phys. Chem. A* **2004**, *108*, 2550–2554.

(67) Anane, H.; Boutalib, A.; Nebot-Gil, I.; Tomas, F. *J. Phys. Chem. A* **1998**, *102*, 7070–7073, and references therein.

(68) Jonas, V.; Frenking, G.; Reetz, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 8741–8753.

(69) Hirota, F.; Miyata, K.; Shibata, S. *THEOCHEM* **1989**, *60*, 99–111.

(70) Cai, Z.-T.; Li, C.-R.; Zhang, R.-Q.; Deng, C.-H. *Chin. J. Chem.* **1997**, *15*, 17–20.

(71) Mo, Y.; Lin, M.; Wu, W.; Zhang, Q.; Schleyer, P. v. R. *Sci. China, Ser. B: Chem.* **1999**, *42*, 253–260.

(72) Ghosh, D. C.; Jana, J. *Int. J. Quantum Chem.* **2003**, *92*, 484–505.

(73) Plumley, J. A.; Evanseck, J. D. *J. Phys. Chem. A* **2007**, *111*, 13472–13483.

(74) Plumley, J. A.; Evanseck, J. D. *J. Chem. Theory Comput.* **2008**, *4*, 1249–1253.

(75) Allred, A. L. *J. Inorg. Nucl. Chem.* **1961**, *17*, 215–221.

(76) Clementi, E.; Raimondi, D. L.; Reinhardt, W. P. *J. Chem. Phys.* **1967**, *47*, 1300–1307.

(77) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision E.01; Gaussian, Inc.: Pittsburgh, PA, 2004.

(78) Bylaska, E. J.; Jong, W. A. d.; Govind, N.; Kowalski, K.; Straatsma, T. P.; Valiev, M.; Wang, D.; Apra, E.; Windus, T. L.; Hammond, J.; Nichols, P.; Hirata, S.; Hackler, M. T.; Zhao, Y.; Fan, P. D.; Harrison, R. J.; Dupuis, M.; Smith, D. M. A.; Nieplocha, J.; Tipparaju, V.; Krishnan, M.; Wu, Q.; Voorhis, T. V.; Auer, A. A.; Nooijen, M.; Brown, E.; Cisneros, G.; Fann, G. I.; Fruchtl, H.; Garza, J.; Hirao, K.; Kendall, R.; Nichols, J. A.; Tsemekhman, K.; Wolinski, K.; Anchell, J.; Bernholdt, D.; Borowski, P.; Clark, T.; Clerc, D.; Dachsel, H.; Deegan, M.; Dyall, K.; Elwood, D.; Glendening, E.; Gutowski, M.; Hess, A.; Jaffe, J.; Johnson, B.; Ju, J.; Kobayashi, R.; Kutteh, R.; Lin, Z.; Littlefield, R.; Long, X.; Meng, B.; Nakajima, T.; Niu, S.; Pollack, L.; Rosing, M.; Sandrone, G.; Stave, M.; Taylor, H.; Thomas, G.; Lenthe, J. v.; Wong, A.; Zhang, Z. *NWChem, A Computational Chemistry Package for Parallel Computers*, version 5.1; Pacific Northwest National Laboratory: Richland, WA , 2007.

(79) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215–241.

(80) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257–2261.

(81) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265–3269.

(82) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650–654.

(83) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939–947.

(84) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724–728.

(85) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657–2664.

(86) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213–222.

(87) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(88) Head-Gordon, M.; Head-Gordon, T. *Chem. Phys. Lett.* **1994**, *220*, 122–128.

(89) Gauss, J.; Cremer, D. *Chem. Phys. Lett.* **1988**, *150*, 280–286.

(90) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968–5975.

(91) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358–1371.

(92) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007–1023.

(93) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1994**, *100*, 2975–2988.

(94) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796–6806.

(95) Brown, H. C.; Bartholomay, H., Jr.; Taylor, M. D. *J. Am. Chem. Soc.* **1944**, *66*, 435–442.

(96) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157–167.

(97) Sousa, S. F.; Fernandes, P. A.; Ramos, M. J. *J. Phys. Chem. A* **2007**, *111*, 10439–10452.

(98) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553–556.

(99) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502–16513.

(100) Weinhold, F.; Landis, C. *Valency and Bonding: A Natural Bond Orbital Donor - Acceptor Perspective*, 1st ed.; Cambridge University Press: Cambridge, U.K., 2005.

(101) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. *NBO 5.G*; Theoretical Chemistry Institute, University of Wisconsin: Madison, WI, 2001; http://www.chem.wisc.edu/~nbo5.

(102) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735–746.

(103) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211–7218.

(104) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899–926.

(105) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736–1740.

(106) Goodman, L.; Sauers, R. R. *J. Comput. Chem.* **2007**, *28*, 269–275.

(107) Haaland, A. *Angew. Chem., Int. Ed.* **1989**, *101*, 1017–1032.

(108) Allendorf, M. D.; Melius, C. F.; Osterheld, T. H. *Mater. Res. Soc. Symp. Proc.* **1996**, *410*, 459–464.

(109) The coefficients of partial determination have been utilized to determine the influence of electronegativity and atomic size within the multiple linear regression. This is discussed in detail within the Supporting Information.

(110) Beste, A.; Kramer, O.; Gerhard, A.; Frenking, G. *Eur. J. Inorg. Chem.* **1999**, 2037–2045.

(111) Krahl, T.; Kemnitz, E. *J. Fluorine Chem.* **2006**, *127*, 663–678.

(112) Krossing, I.; Bihlmeier, A.; Raabe, I.; Trapp, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 1531–1534.

(113) Timoshkin, A. Y.; Suvorov, A. V.; Bettinger, H. F.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1999**, *121*, 5687–5699.

(114) Pervova, Y. V.; Korobov, M. V.; Sidorov, L. N. *Zh. Fiz. Khim.* **1992**, *66*, 1199–1204.

(115) Ball, D. W. *J. Phys. Chem.* **1995**, *99*, 12786–12789.

(116) Trusov, V. I.; Suvorov, A. V. *Zh. Neorg. Khim.* **1974**, *19*, 3253–3256.

(117) Timoshkin, A. Y.; Bettinger, H. F.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1997**, *119*, 5668–5678.

(118) Mercier, H. P. A.; Moran, M. D.; Schrobilgen, G. J.; Suontamo, R. J. *J. Fluorine Chem.* **2004**, *125*, 1563–1578.

JP811202C