Bi is the new B: high Lewis acidity at a planar, trivalent, neutral, electropositive, p-block element

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Dedication

Dedicated to the essential workers who sustained us during the COVID-19 pandemic.

Abstract

Geometric perturbation away from VSEPR-predicted structures can engender unusual frontier MO situations leading to high Lewis acidity. Recently we reported a T-shaped bismuth triamide, which exhibited planar Lewis acidity that was unprecedented for neutral Group 15 compounds. We now report a comprehensive computational assessment of the origins of planar Lewis acidity in such compounds. We subsequently use several metrics such as MO energies, the Global Electrophilicity Index, ligand coordination strengths, and Fluoride Ion Affinity to show that electronic variation can be combined with the unusual geometry at bismuth to achieve fine tuning of Lewis acid strength. Our calculations reveal for the first time a surprisingly high Lewis acidity – comparable to or exceeding that of polyfluorinated triarylboranes – as well as high rigidity at neutral planar bismuth triamides. These results foreshadow the potentially broad applications of a hitherto unexplored class of compounds – planar bismuthanes – in several contexts such as anion sensing, Lewis acid catalysis, weakly-coordinating anion chemistry and materials science that are currently dominated by Lewis acidic triarylboranes.

1.0 Introduction

Main group Lewis acids are an important class of molecules in the context of bond activation, catalysis, and our fundamental understanding of electronic structure and bonding.[1] The classical approach to accessing strong Lewis acids has been the introduction of very electronegative (usually polyhalogenated) substituents or cationic charge at a central element to create low energy acceptor orbitals due to Coulombic, inductive or mesomeric effects.[1c, 2] Using this electronic tuning strategy, even some neutral compounds can surpass the threshold of Lewis "superacidity".[3]
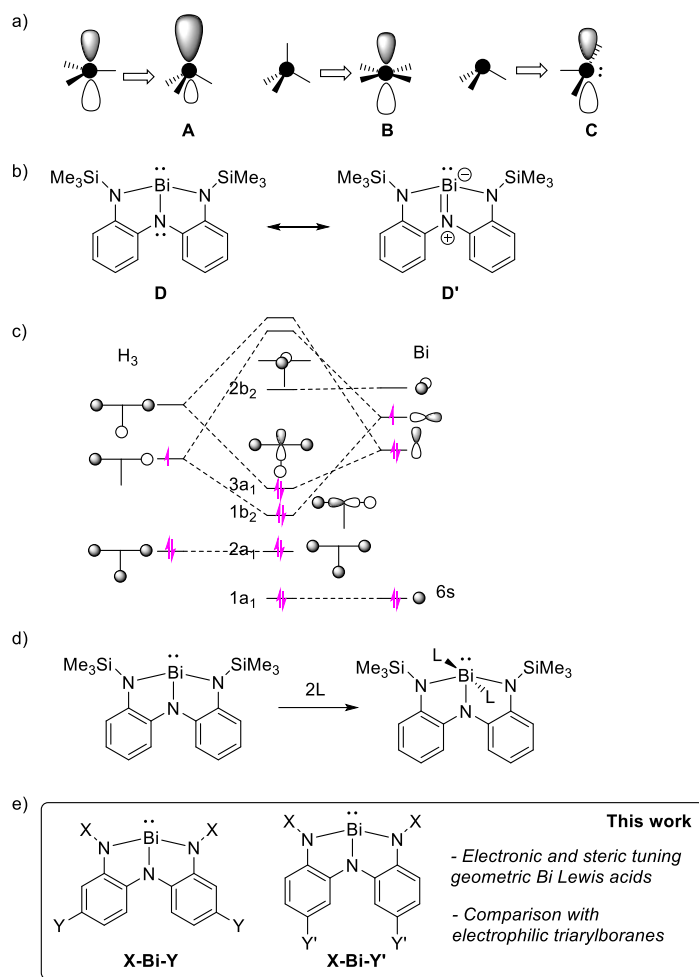

Figure 1. a) Geometric distortion of Group 13, 14, and 15 compounds to create high Lewis acidity. b) Resonance forms for a planar Bi triamide, where charges represent *formal* not actual charges. c) MO diagram for BiH_3 in the C_{2v} point group. d) Coordination chemistry at a planar Bi compound. e) Scope of this work.

In recent years, *geometric* tuning has also emerged as a powerful strategy for engendering high Lewis acidity at p-block centres. For example, planar tricoordinate Group 13 elements can be pyramidalized through ligand constraint to boost their acidity by increasing the accessibility and directionality of the acceptor p-orbital (Figure 1, **A**).[4] Similarly, coercing tetrahedral aluminates or silanes to adopt a non-VSEPR planar geometry results in the availability of a vacant p-orbital perpendicular to the molecular plane (Figure 1, **B**) resulting in surprisingly high hydride affinity in each case.[5] Geometric tuning has also been used as a strategy to achieve Lewis acidity at distorted Group 15 centres (Figure 1, **C**) giving unusual open-shell species and compounds with applications in challenging bond activations and catalysis.[6] In these examples, increased Lewis acidity has an intrinsic, geometric, origin rather than being contingent upon the use of electronegative substituents or molecular charge – a consequence of the intimate relationship between molecular symmetry and frontier orbital arrangement as predicted by group theory.

We recently reported a T-shaped bismuth complex (**D**) with a planar ground state, whose structure can be interpreted as reflecting a hypervalent resonance form (**D'**).[6l, 6m] The existence of a (partially) vacant 6p orbital at Bi in the electron-precise resonance form (i.e. **D**) of the compound can be seen from a first-order MO analysis of a T-shaped (C_{2v}) molecule of BiH_3, which lacks a π-donor group (Figure 1c). This analysis clearly identifies the $2b_2$ MO – an unused 6p valence orbital – as the LUMO. As a result, despite lacking electron-withdrawing groups, we showed that **D/D'** behaves as a geometric Lewis acid and accepts up to two ligands, with retention of the planar BiN_3 core (Figure 1d).[6l, 6m] We emphasize that this mode of Lewis acidity is completely distinct from the vast body of literature reporting "σ-hole" interactions[7] that occur at pyramidal Bi(III) centres via σ*-antibonding orbitals *trans* to a Bi-X bond (X = halide or pseudohalide).[8]

In contrast, given that the bismuth centre in this molecule engages Lewis bases through a vacant p-orbital, and is planar, trivalent, electropositive, and neutral, we considered it to be more analogous to electrophilic triaryl boranes rather than classical pyramidal electron-poor bismuth(III) compounds. Indeed, the possibility of a counterintuitive "diagonal relationship"[9] between the heaviest stable p-block element, bismuth ($\chi_{Pauling}$ = 1.9), and the lightest p-block element (boron, $\chi_{Pauling}$ = 2.0) is further supported by the electronegativity of the two elements being essentially identical.

Since Lewis acidic triarylboranes have manifold applications in catalysis and materials chemistry,[1m, 1n, 10] we envisioned that planar trivalent bismuth compounds may also exhibit such valuable properties if their electrophilicity could be predictably controlled by layering *electronic* tuning atop their existing geometric Lewis acidity. Herein, we computationally investigate the

effects of electronic tuning on the Lewis acidity of such compounds using a variety of theoretical methods. We vary the electronic effect of the substituent, the position of the substituent (two positions on the aryl ring, and on the nitrogen), and the steric bulk of the substituent. We include four prototypical triaryl boranes in all our assessments as a means of comparing our calculations to well-understood real systems.

Our results show that remarkably high electrophilicity (comparable to that of tris(pentalfluorophenyl)borane) can be achieved even by relatively modest electronic tuning when it is overlaid upon a geometrically derived Lewis acidity. These theoretical findings provide a strong motivation for future experimental work in this area by showing the potential utility of bismuth compounds in contexts where boron derivatives are presently dominant.

2.0 Experimental

All geometries were optimized in Gaussian 16[11] using the hybrid PBE[12] functional (implemented within Gaussian via the PBE1PBE keyword) with D3BJ dispersion correction[13] and the def2-TZVP[14] basis set containing a relativistic small-core pseudopotential (ecp-46).[15] Frequency calculations were performed to confirm structures as true minima (zero negative frequencies). MO energies were obtained at the same level and the HOMO and LUMO values were used for calculation of the Global Electrophilicity Index (GEI) using the following equation:

$$\omega = \mu^2/2\eta$$

$$\mu = 0.5(E_{HOMO}-E_{LUMO})$$
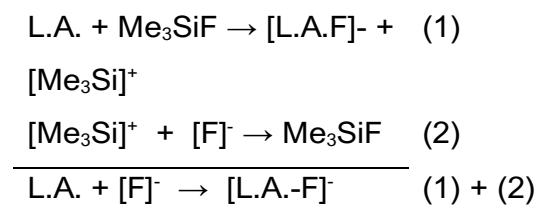
$$\eta = 0.5(E_{LUMO}-E_{HOMO})$$

All reaction energies (except fluoride ion affinities, *vide infra*) correspond to uncorrected single point energies at absolute zero temperature.

Using the def2-TZVP optimized structures, all reaction energy calculations we repeated at the aug-cc-pVDZ[16] basis set for non-metal atoms and the aug-cc-pVDZ-PP[17] basis set with relativistic ECP60MDF[15] pseudopotential for bismuth. The reaction energies were generally within 5-10 kJ mol^{-1} of the values obtained at the def2-TZVP level (see Supporting Information), ruling out significant basis set size effects.

EDA calculations[18] were performed using the Amsterdam Density Functional (ADF 2017)[19] package using the hybrid PBE functional, D3BJ dispersion correction, scalar relativistic correction,[20] and the AUG/ADZP[21] basis set. Closed shell neutral fragments were used in EDA calculations to model heterolytic dissociation.

Fluoride Ion Affinity (FIA) calculations were performed on geometries optimized using the B3LYP functional with D3BJ dispersion correction, in line with the reported suitability of this

combination in an extensive benchmarking study.[22] The following pseudo-isodesmic scheme was employed with the benchmark value of 952.5 kJ mol^{-1} from CCSD(T)/CBS extrapolation used for reaction (2):

$$\text{L.A.} + \text{Me}_3\text{SiF} \rightarrow [\text{L.A.F}]\text{- } + \quad (1)$$
$$[\text{Me}_3\text{Si}]^+$$
$$[\text{Me}_3\text{Si}]^+ + [\text{F}]^- \rightarrow \text{Me}_3\text{SiF} \quad (2)$$
$$\overline{\text{L.A.} + [\text{F}]^- \rightarrow [\text{L.A.-F}]^-} \quad (1) + (2)$$

For the FIA calculations, the cc-pVDZ basis set was used for light atoms. Although large anions like the ones in this study can usually be described reasonably-well without diffuse basis sets due to more efficient charge delocalization, the aug-cc-pVDZ-PP basis set with the ECM60MDF pseudopotential was used at bismuth due to the high polarizability and electron count of this 6th row element. The values provided are enthalpy values for fluoride removal at 298 K for consistency with literature data. Using these parameters, the FIA of B(C$_6$F$_5$)$_3$ was calculated to be 456 kJ mol^{-1}, which reproduces the DLPNO-CCSD(T)/aug-cc-pVQZ level benchmark value of 445 kJ mol^{-1} reasonably well given the size of the system.

3.0 Results and discussion

3.1 Labelling scheme

The bismuth Lewis acids are defined using a **X-Bi-Y** nomenclature (Scheme 1e), where **X** defines the substituent at the external nitrogen atoms and **Y** defines the substituent on the aryl ring, *para* to the central nitrogen atom (Figure 1e). The notation **Y'** is used to denote substitution *para* to the external nitrogen atoms on the aryl ring. No substitution *ortho* to the central atom was considered as this was envisioned to be sterically unfeasible. The methoxy and methyl electron donating groups were considered at the **Y** positions but only the methyl group was considered at the **X** position as N-O bonds are quite reactive, limiting the relevance of such substitution in future experimental work. The trifluoromethyl, pentafluorophenyl, and bromo electron withdrawing groups were considered, but again due to the poor stability of N-Br bonds, bromo substitution at the **X** position was not considered. The bulky trimethylsilyl group was used to model high steric bulk only at the **X** position atoms as it is proximate to the Lewis acidic bismuth centre.

For comparison with triarylboranes, the following derivatives were used: triphenylborane – Ph$_3$B, tris(2,6-difluorophenyl)borane – (2,2-F$_2$C$_6$H$_3$)$_3$B, tris(2,4,6-trifluorophenyl)borane – (2,4,6-F$_3$C$_6$H$_2$)$_3$B , and

tris(pentafluorophenyl)borane – $(C_6F_5)_3B$. The acidity of these species has been established through a combination of experimental and theoretical methods previously.[23]

3.2 Origins of Lewis acidity in X-Bi-Y

While the MO diagram for BiH_3 shown in Figure 1c provides a rough sketch of the frontier molecular orbital situation at a T-shaped bismuthane, it does not illustrate the type of metal-ligand π interactions that might be envisioned in the π-electron rich ligands in **X-Bi-Y**. To understand the mechanism through which ligand tuning can influence metal-centred Lewis acidity via mesomeric effects, we considered the frontier MOs of compounds **X-Bi-Y**, which fall within two cases.
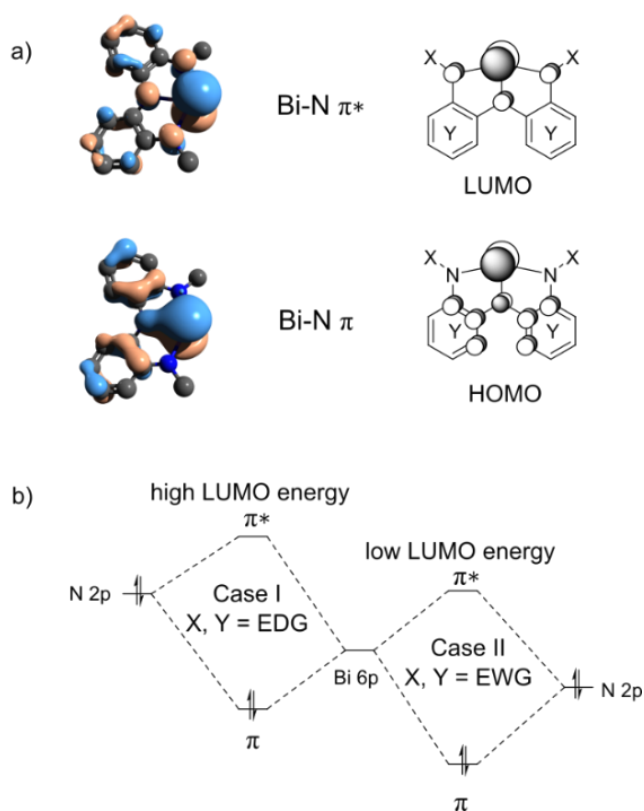

Figure 2. a) Visual representations of the frontier MOs of **Me-Bi-H**. b) Energetic representations of the frontier MOs of X-Bi-Y with electron-donating groups (EDG, Case 1) and electron-withdrawing groups (EWG, Case II).

The LUMO and HOMO of **Me-Bi-H** (Figure 2a) show combinations of Bi 6p and N 2p atomic orbitals, reminiscent of a π-bonding and π*-antibonding set, recapitulating the electronic structure implied by resonance form **D'** in Figure 1b. However, interpretation of this MO as

representing a classical double bond is challenged by the fact that the Bi-N bond length in experimentally known derivative **TMS-Bi-H** [2.181(4) Å][6m] is longer than even the longest Bi-N single bond in the closely related pyramidal derivative Bi[N(SiMe₃)(*p*-tol)]₃ [2.150(3) Å].[24] We therefore propose that the frontier orbital manifold shown in Figure 2a represents a rather weak multiple bonding interaction that may qualify as a "charge-shift bond".[25] Irrespective of its precise classification, the MO visualizations in Figure 2a connect the metal-based LUMO to the π electron-richness of the ligand, as further described below.

When X and Y are electron-donating group, (Figure 2b, Case I), the N 2p lone pair energy is elevated, resulting in the formation of a high energy π-bonding and π*-antibonding MOs. When X and Y represent electron-withdrawing groups (Figure 2b, Case II), the associated lowering of the N 2p lone pair generates a correspondingly low energy set of π/π* MOs. Crucially, a lowering of the π* LUMO should result in higher Lewis acidity for derivatives of **X-Bi-Y** that contain electron-withdrawing groups on the ligand. In this context, it is noteworthy that the prominent localization of the LUMO on the metal is retained even when very electron-poor aromatic groups are present, as in **C₆F₅-Bi-H**, emphasizing the metal-centred Lewis acidity in derivatives of **X-Bi-Y**.

3.3 Electron Affinity: LUMO energies, Global Electrophilicity Index (GEI), and 1-electron reduction energies.

The LUMO energies and GEI for derivatives of **X-Bi-Y** as well as for some commonly employed triarylborane Lewis acids are shown in Figure 3.

The LUMO energies vary smoothly across the full range of studied compounds. In terms of their ability to lower the LUMO energy and boosting the GEI, the substituents at N show the trend CF₃ > TMS ≈ Me (compare **CF₃-Bi-H**, **TMS-Bi-H**, and **Me-Bi-H**) as might be expected from group electronegativity considerations. Similarly, substituents at the aryl ring show the trend CF₃ > Br > H > Me > OMe (compare **Me-Bi-CF₃**, **Me-Bi-Br**, **Me-Bi-H**, **Me-Bi-Me**, and **Me-Bi-OMe**), which is understood in light of their relative σ-inductive effects. Interestingly, the position of the substituent on the ring also has a significant effect with **TMS-Bi-Br** showing a lower LUMO energy and higher GEI than **TMS-Bi-Br'**. In the former case the bromine is positioned *para* with respect to the central N atom whereas in **TMS-Bi-Br'**, it is *para* to the external N atoms (*meta* to the central N atom). This position effect is somewhat unexpected given the LUMO shape, which shows equal contributions from both the external and the central N atoms (Figure 2a). Lastly, a comparison of LUMO energies and GEI in **CF₃-Bi-Me** and **Me-Bi-CF₃** shows that substitution at the N atoms has a larger effect than substitution on the aryl ring. Taking the combined influence

of substituent electronegativity and position into account, the species with the lowest LUMO energy and highest GEI is expected and found to be **CF₃-Bi-CF₃**. Within the limitations of these intrinsic Lewis acidity measures (i.e. ignoring steric factors), the data suggest that some derivatives of **X-Bi-Y** can be even more Lewis acidic than polyfluorinated arylboranes.
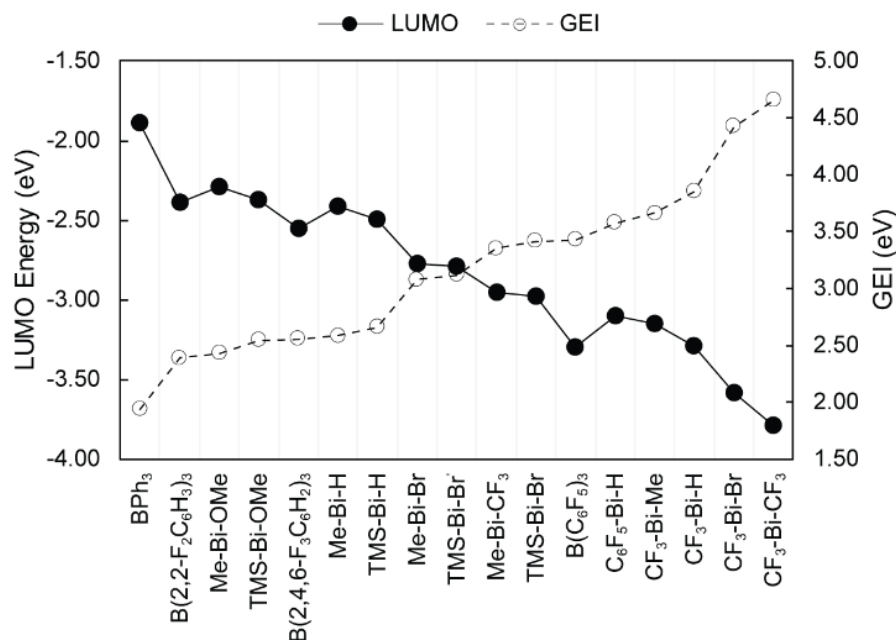

Figure 3. LUMO energies and GEI values for derivatives of selected bismuth and boron Lewis acids.

The electron affinities of all Lewis acids were estimated as the energy change upon addition of one electron to the system with and without allowing geometric relaxation (Figure 4). The primary geometric consequence of reduction is an elongation of the two external Bi-N distances by approximately 0.05 Å and the central Bi-N distance by approximately 0.02 Å. The planar N₃Bi core is retained in the anions, which show no other significant distortions relative to their neutral precursors. In this context, the behaviour of derivatives of **X-Bi-Y** is analogous to that of triarylboranes, which also retain their planarity at boron upon one-electron reduction.[26] The minimal structural deformation required to accommodate the added electron is reflected in the fact that the difference between the adiabatic and non-adiabatic reduction energies is less than 25 kJ mol⁻¹ in all cases.
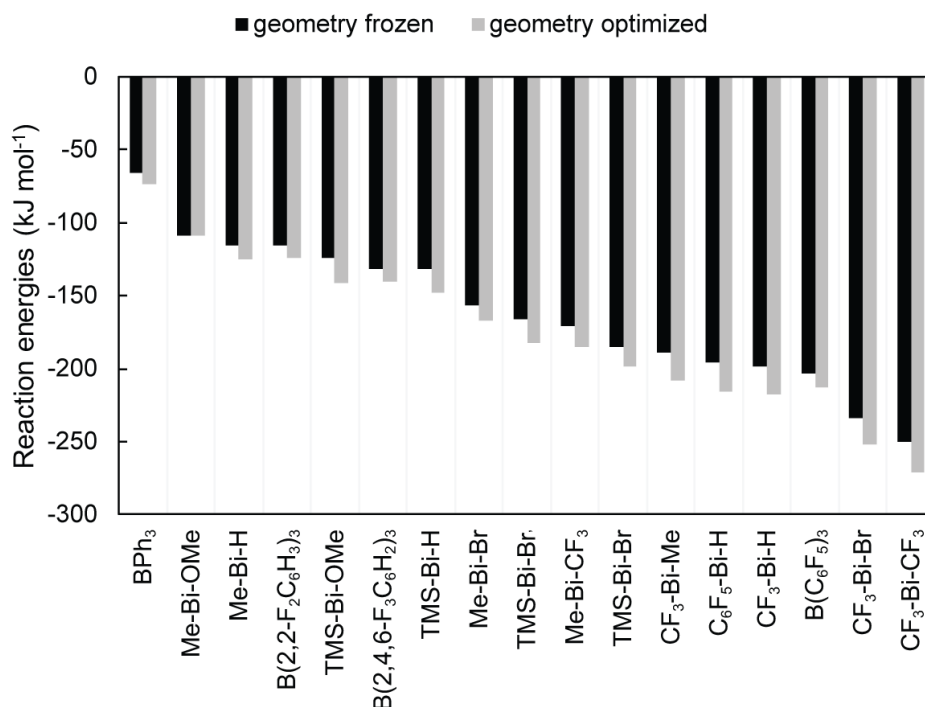
Figure 4. One electron reduction energies with and without geometry optimization for selected bismuth and boron Lewis acids at the PBE1PBE(D3BJ)/def2-TZVP level in the gas phase.

Overall, the reduction energies bear out the trend predicted by LUMO energies and GEI values, supporting the view that i) fine tuning of Lewis acidity in derivatives of **X-Bi-Y** is possible by variation of substituents, and ii) that some derivatives match or exceed the Lewis acidity calculated for polyfluorinated triarylboranes.

3.4 Ligand Affinity: Ligand coordination energies, Fluoride Ion Affinities, and HSAB Considerations.

While the preceding section considered calculated electron affinities, the experimental mode of usage for most Lewis acids, particularly in the context of catalysis, involves their ligand binding affinity. We have previously shown the **TMS-Bi-H** can coordinate one or two ligands via the vacant p-orbitals centred at the metal.[6l, 6m]
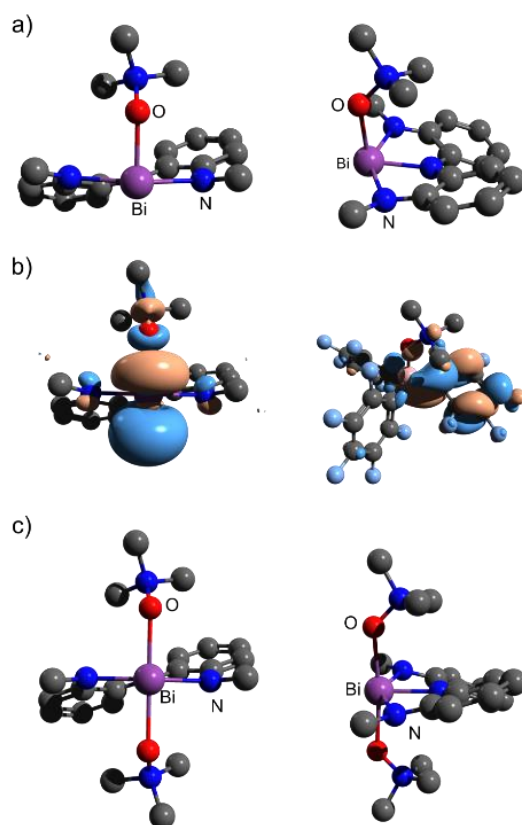
Figure 5. a) Two views of the structure of the 1:1 adduct between **Me-Bi-H** and Me₃NO, b) LUMO of the 1:1 adduct between Me₃NO and **Me-Bi-H** (left) and B(C₆F₅)₃ (right), c) views of the structures of the 2:1 adduct between **Me-Bi-H** and Me₃NO.

In order to estimate ligand affinities, we selected Me₃NO (trimethylamine oxide, TMAO) as the prototypical donor. The choice of a ligand that is monoatomic at the site of coordination (i.e. oxygen atom) was made to ensure minimal contamination of affinity trends by steric factors, which can be particularly important for hindered triarylboranes. Moreover, we have previously reported the crystal structures of adducts between Me₃NO or Et₃PO and **TMS-Bi-H**, confirming the experimental viability of such adducts (CCDC entries 200023, 2002501). The geometries of the 1:1 adducts of all bismuth derivatives and the selected triarylboranes were optimized and the association energies calculated with respect to the free reactants.
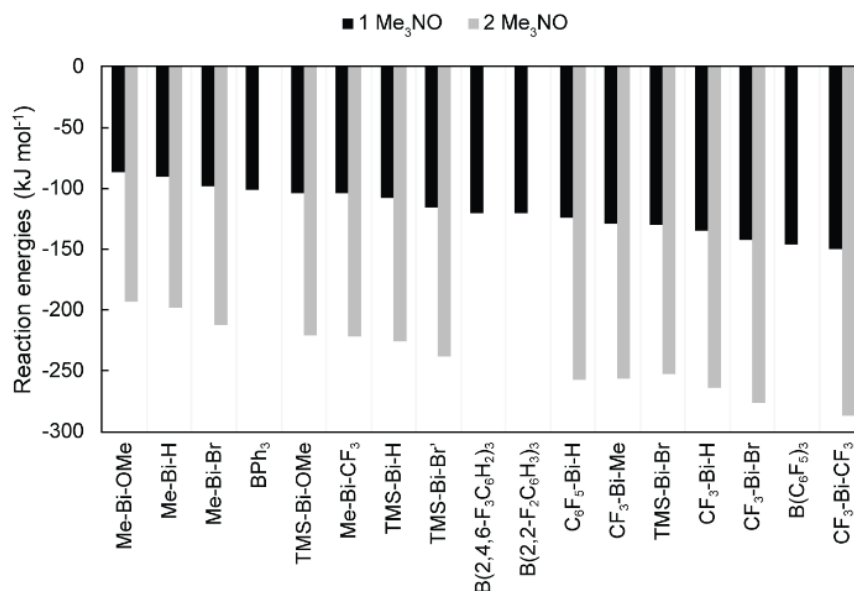
Figure 6. Calculated reaction energies for addition of one or two Me₃NO ligands to bismuth and boron-based Lewis acids.

The calculations show that a planar BiN_3 core is retained upon coordination of one equivalent of TMAO (Figure 5a). The O-Bi-N angle involving the nitrogen atom between the aryl rings is 98-100° in all cases, which is greater than the idealized 90° expected for interaction of a donor with a p-orbital perpendicular to the molecular plane. This deviation arises because the NMe_3 fragment of the ligand is more stable when situated *syn* rather than *anti* to the triamide framework. Indeed, our reported crystal structure of the 2:1 adduct between $ONMe_3$ and **TMS-Bi-H** also shows that the NMe_3 group is situated over the triamide ligand rather than pointing away from it. The resulting steric clash between the methyl groups and the aryl rings imposes a >90° O-Bi-N angle. The Bi-O lengths vary from 2.461 Å (**Me-Bi-H**) to 2.253 Å (**CF₃-Bi-CF₃**) suggesting a wide range of interactions strengths, as reflected by the calculated coordination energies, which vary from -86 kJ mol⁻¹ to -150 kJ mol⁻¹ (Figure 6). The coordination strengths of Me_3NO towards **CF₃-Bi-CF₃** (-150 kJ mol⁻¹) and $B(C_6F_5)_3$ (-146 kJ mol⁻¹) are very similar, indicating a similarly high ligand affinity in these Lewis acids. The interaction of **C₆F₅-Bi-H** towards Me_3NO (-125 kJ mol⁻¹) is surprisingly lower than expected based on predictions made using GEI, LUMO energies or one-electron reduction energies alone. which we ascribe to greater steric bulk of the C_6F_5 group compared to the CF_3 group. On the other hand, the sterically more hindered **TMS-Bi-H** shows significantly higher binding affinity than the less bulky **Me-Bi-H**, which may in part be due to the negative-hyperconjugation boosted electron-withdrawing influence of silyl groups when adjacent to a π system.[27]

The calculated LUMO of the 1:1 adducts containing bismuth Lewis acids is best described as a partially occupied but sterically accessible p-orbital centred at the metal (Figure 5b, left), which implies the potential for addition of a second ligand. In contrast the LUMO of the 1:1 adducts of Me_3NO with triarylboranes lie primarily on the aryl rings which, together with the smaller coordination sphere of boron, precludes addition of a second ligand (Figure 5b, right).

Not only is the addition of a second ligand to the bismuth Lewis acids viable but, to our surprise, it is nearly as exothermic as addition of the first ligand, indicating a substantial, unquenched Lewis acidity even in the 1:1 adducts (Figure 6). The optimized structures of the adducts show a nearly linear O-Bi-O arrangement, as expected from the symmetry of the 6p acceptor orbital (Figure 5c). These findings also imply that the origin of the Lewis acidity in these systems is primarily contingent upon orbital accessibility rather than electrostatic attraction, which would diminish substantially upon addition of one ligand due to attenuation of the Coulomb force.

Table 1 Energy Decomposition Analysis for the 1:1 and 1:2 adducts of Me_3NO and **CF_3-Bi-CF_3** and the 1:1 adduct of Me_3NO and $B(C_6F_5)_3$. The ΔE values are given in kJ mol^{-1}. ΔE_{int} (interaction energy) is the energy change upon E-O bond formation starting from fragments frozen in the geometry found in the bonded compound, assuming closed shell fragments. Values in parentheses denote percentages of overall attractive interactions.

Parameter	**CF_3-Bi-CF_3 +** 1 Me_3NO	**CF_3-Bi-CF_3 +** 2 Me_3NO	$B(C_6F_5)_3$ + 1 Me_3NO
ΔE_{int}	-144.1	-289.8	-277.1
ΔE_{Pauli}	1101.8	1836.3	2601.8
ΔE_{elstat}	-373.3 (29.9%)	-603.8 (28.4%)	-685.5 (23.8%)
ΔE_{orb}	-834.7 (66.9%)	-1452.3 (68.3%)	-2156.7 (74.9%)
ΔE_{disp}	-37.9 (3.0%)	-70.0 (3.3%)	-36.7 (1.3%)

This proposal was explored quantitatively by means of an energy decomposition analysis (EDA) involving the 1:1 and 1:2 adducts between **CF_3-Bi-CF_3** and $ONMe_3$ (Table 1). Indeed, ligand coordination is driven primarily by the ΔE_{orb} term in both cases, which makes a >65% contribution to the total attractive interactions. The analogous EDA results for $B(C_6F_5)_3$ show a larger relative contribution from orbital interactions (ca. 75%), which we attribute to the better 2p-2p overlap in the B-O dative bond compared to the 6p-2p overlap required for the Bi-O dative bond. The dominance of orbital interactions is in contrast with the long-established history of

non-covalent metal-oxygen interactions in hypervalent bismuth complexes[28] and further underscores the fundamentally unique Lewis acidity of **X-Bi-Y** compounds, validating their comparison to triarylboranes.

Fluoride ion affinities (FIAs) have been used widely as a probe of Lewis acidity in main group systems. To assess whether the significantly smaller and negatively charged fluoride ligand reveals different acidity trends compared to the neutral and larger $ONMe_3$, we have calculated the FIA for the full set of Lewis acids studied here. Previous work has revealed that FIA values are a poor indicator of *absolute* Lewis acidity when calculations have been performed in the gas phase (without a solvent model),[29] but *relative* Lewis acidity can be reasonably predicted through gas-phase calculations.[2, 22] For consistency with the rest of the calculations in this study and other studies in this field, the gas-phase FIA values are reported (Figure 7).
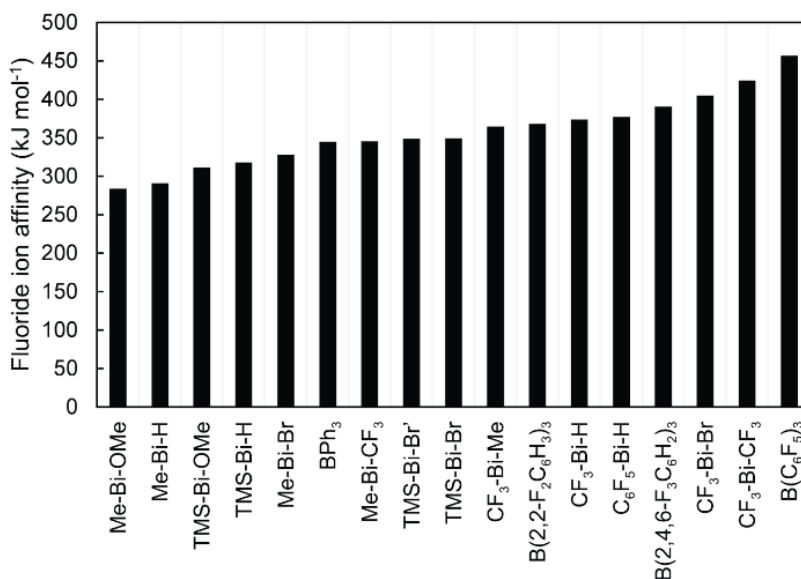

Figure 7. Fluoride Ion Affinities (FIAs) for bismuth and boron-based Lewis acids.

The FIA values and acidity trends of the triarylboranes reproduce benchmark values within ~10 kJ mol^{-1},[22, 23c] validating the calculation methodology. Note that the FIA values are significantly more exothermic than the coordination energies involving the neutral TMAO ligand, which we attribute to the Coulombic effect of bringing an anion to a Lewis acid in the fluoride case. Significantly less steric repulsion is also experienced with the small fluoride anion compared to TMAO. As a result, the FIA value of **CF₃-Bi-H** is essentially the same as the bulky **C₆F₅-Bi-H**, in contrast to the results obtained for the bulkier TMAO ligand. Overall, the FIA data also supports the view that some derivatives of **X-Bi-Y** approach the high fluoride affinity that is characteristic of polyfluorinated triarylboranes.

We have investigated the question of where the bismuth acids considered here fall on the spectrum between classical hard (e.g. BF_3) and soft (e.g. BH_3) Lewis acids. The coordination strengths of **CF₃-Bi-CF₃** towards Me_3PS (-106.1 kJ mol^{-1}) and Me_3PO (-127.4 kJ mol^{-1}) show only a 21 kJ mol^{-1} difference, indicating a small preference for the hard oxygen-based donor. Analogous calculations involving the coordination of $B(C_6F_5)_3$ towards Me_3PS (-69.2 kJ mol^{-1}) and Me_3PO (-123.7 kJ mol^{-1}) showed a more pronounced preference (54 kJ mol^{-1}) for the hard donor. We conclude that the strong **X-Bi-Y** Lewis acids lie on the border between hard and soft, in contrast to strong borane Lewis acids, which show a preference for interaction with hard bases.

4.0 Conclusions

We have comprehensively explored the origins of "geometric" Lewis acidity in an unusual new class of planar bismuth compounds reported recently. The presence of a very polarized, primarily metal-centred, Bi-N π-bonding HOMO involving the central nitrogen atom (hinted by resonance form **D'** in Figure 1), and the associated π* antibonding LUMO, enables exquisite ligand control of metal-based Lewis acidity via inductive and mesomeric effects. Using this understanding, we show that electronic tuning can be laid atop a geometric origin to achieve exceptionally Lewis acidic neutral bismuth compounds, as shown using several acidity indicators. All indicators converge upon the conclusion that the electrophilicity of some derivatives easily approaches and often surpasses the values calculated for widely-employed polyhalogenated triarylboranes. The latter class of compounds is of course ubiquitous in the context of ion sensing, Lewis acid catalysis, weakly-coordinating anion chemistry, and materials science, and the calculations presented here predict for the first time a similar potential for planar bismuth compounds.

In contrast to borane Lewis acids, the bismuth derivatives are extremely rigid and retain their planarity upon coordination – a consequence of the tethered ligand and the large coordination sphere of the metal – enabling equally exothermic sequential binding of two substrates, which, to the best of our knowledge, is unprecedented in main group Lewis acid/base chemistry. The bismuth-based acids are also softer by comparison to borane Lewis acids which show a strong preference for hard bases.

Given that derivatives of **X-Bi-Y** can be made simply by condensing the corresponding ligand with $Bi(NMe_2)_3$,[6m] and that versions of the tethered ligand with electron-withdrawing groups have already been reported separately in the context of transition metal chemistry,[30] we are now pursuing experimental realization of the predictions made here by preparing and studying a broad range of **X-Bi-Y** Lewis acids.

Acknowledgements

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