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Unique Reactivity of B in B[Ge9Y3]3(Y = H, CH3, BO, CN): Formation of Lewis Base

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The chemistry of boron compounds usually exhibits Lewis acidity at the boron centers, due to the presence of its vacant p-orbitals. We show that this chemistry can be altered by appropriate choice of ligands, decorating the boron center. To elucidate this effect, we studied the interaction of boron with two classes of ligands, one based on penta-substituted phenyl species (C_6X_5, X = F, BO, CN) and the other on Zintl-ion based groups (Ge_9Y_3., Y = H, CH_3, BO, CN). An in-depth analysis of charge and Fukui function values at the local atomic sites of substituted boron derivatives, [B(C_6X_5)$_3$] and B[Ge_9Y_3]$_3$, shows that the B-center in the former is electrophilic, while it is nucleophilic in the latter. The chemical stability of the B[Ge_9Y_3]$_3$ species is shown to be due to the presence of strong 2c–2e bonds between the B and Ge centers. Thus, the usual notion of the Lewis acid nature of a boron center depends upon the choice of the ligands.

Lewis acid and Lewis base concepts, developed by G. N. Lewis in 1923,[1] constitute a vital domain of acid-base chemistry and is a topic well-researched over the years. Elements having vacant or partially vacant available orbitals act as Lewis acid sites, while those having available electron pairs for donation act as Lewis base. Boron and Aluminum atoms, having available vacant p orbitals, therefore, serve as good candidates for Lewis acid in their compounds. But an interesting revelation about the electronic response of the Boron center has been noticed upon changes in the nature of the substituents. The Boron atom in its substituted analogs is customarily no more an electrophilic site, it rather turns nucleophilic, hence a Lewis base! Such a finding opened up new vistas of seminal research towards deciphering the mechanistic courses of reactivity tendencies of substituted Boron complexes and their applications in organic syntheses. A number of studies[2-14] on the synthesis and characterization of tri-coordinated Boron complexes reveal the experimental existence of a nucleophilic Boron center which shows

Lewis basicity. Some literature studies feature substituted Boron complexes having both electrophilic and nucleophilic B-sites.[15-16] However, the modeling of Zintl-substituted trivalent Boron complexes exhibiting reversal of reactivities upon changing the substituents is probably not found so far in literature.

At first we have taken tris(pentafluorophenyl)borane [B(C_6F_5)$_3$],[17-19] a well-known Lewis acid. Because of the presence of the electronegative F atoms bonded to the carbon centers of the C6 ring, the pentafluoro- benzene has a positive electron affinity (E.A. = 4.42 eV) and an electronegativity of 6.75 eV. This enables the pentafluorophenyl ligand to withdraw electron density from the B-center, leaving B with a charge of 0.884 |e|. As a result, the substituted boron derivative acts as a Lewis acid. The calculated ground state energy, natural bond orbital (NBO)[20] charges on the B and C centers, and the Wiberg bond indices of the [B(C_6F_5)$_3$] molecule are given in supporting information(SI) S1 further confirm the stability and electrophilic nature of the B-center. To further substantiate this finding, we considered other ligands such as $C_6(CN)_5$ (EA= 4.25 eV) and $C_6(BO)_5$ (EA = 3.85 eV) that form [B($C_6(CN)_5$)$_3$] and [B($C_6(BO)_5$)$_3$]. For all these cases, we found that the B center bears a positive charge. The optimized geometries and Cartesian coordinates of C_6F_5, $C_6(CN)_5$, $C_6(BO)_5$ and their B complexes with NBO charges are given in the SI-S2-3.

With the above results as our benchmark, we designed a Zintl-substituted Lewis acid where the Zintl cluster acts as an electron-withdrawing ligand. From our earlier work on Ge_9^{4-} Zintl ion based-superhalogen Ge_9R_3 (R = CN, CF_3, NO_2),[21] we first used the Ge_9H_3 cluster to model a Zintl-substituted Lewis acid complex, B[Ge_9H_3]$_3$. The Ge_9H_3 species, with 39-electrons, will have the tendency to gain an electron to achieve the stable 40-electron configuration, a stability criterion satisfied by the Wade-Mingos rule.[22] This expectation is consistent with the ionization energy (IE = 6.58 eV) and the positive electron affinity (E.A. = 2.87 eV) of the Ge_9H_3 species. The electronegativity of Ge_9H_3 is also 4.72 eV, which is larger than that of Boron (4.31 eV). Such an electronegativity difference between the ligand and the central B atom is at par with our hypothesis that more electronegative Ge_9H_3 would withdraw electron density from the B-center, thereby rendering B[Ge_9H_3]$_3$ as a

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site for nucleophilic attack. From the structural similarity between $B[Ge_9H_3]_3$ and $[B(C_6F_5)_3]$, one would expect $B[Ge_9H_3]_3$ to behave like a Lewis acid. But, an in-depth analysis of the NBO charges on the B and Ge centers of the $B[Ge_9H_3]_3$ cluster, computed at different levels of theory (B3LYP[23,24], wB97XD[25], PBE[26]) told a different story (Figure 1). The B-center bears negative charge and is nucleophilic. To examine if this result could be due to computational limitation, we calculated the NBO and Hirshfeld[27] charges using different basis sets (SDD, def2-TZVPP[28]). The trends in the atomic charges on the B-center of $B[Ge_9H_3]_3$ species remained unaltered. The ground state optimized geometry, NBO and Hirshfeld charge on B center at different levels and basis sets of $B[Ge_9H_3]_3$ complex are shown in figure 1. The optimized geometries and Cartesian coordinates of $B[Ge_9H_3]_3$ and $B[Ge_9H_3]_3^-$ are shown in SI-S4. All the calculations have been performed using Gaussian09[29] suite of programs.

	NBO	Hirshfeld
B3LYP/SDD	-0.696	-0.011
wB97XD/SDD	-0.604	-0.057
PBE/SDD	-0.687	-0.072
B3LYP/Def2-TZVPP	-0.662	-0.088
B3LYP/6-31+G(d,p)//B3LYP/SDD	-0.643	-0.090
PBE/6-31+G(d,p)//B3LYP/SDD	-0.520	-0.087
wB97XD/6-31+G(d,p)//B3LYP/SDD	-0.846	-0.065
AIM(PBE/SDD)	-0.329	
AIM(Wb97xd/SDD)	-0.330	

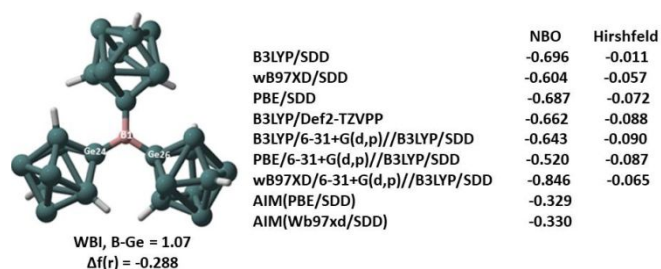WBI, B-Ge = 1.07
$\Delta f(r)$ = -0.288

Fig. 1 Ground state optimized geometry, NBO and Hirshfeld charge on B center, of $B[Ge_9H_3]_3$ complex.

To confirm the dynamical stability $B(Ge_9H_3)_3$, we performed an Atom Centered Density Matrix Propagation (ADMP)[30,31] simulation for 1.5 ps at 300K temperature. The potential energy surface (Figure 2(a)) showed no distortion of the $B[Ge_9H_3]_3$ complex. We performed a full Quantum Theory of Atoms In Molecules (QTAIM)[32,33] analysis on $B(Ge_9H_3)_3$ structure using the AIMAll software[34] to evaluate the bonding pattern. We recall that the critical points are points in real space where density $\rho r(r)=0$, and that they can be classified according to their rank and signature - one bond critical point (BCP) $r(3, -1)$ being located between the two nuclei and ring critical point (RCP) $r(3, +1)$. When $\nabla^2 \rho(r)$ is positive (negative), the electron density is locally depleted (concentrated).
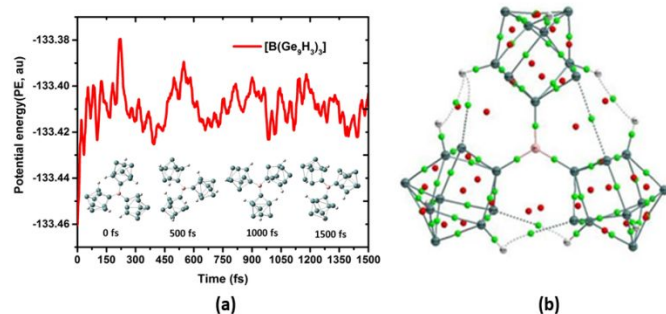

Fig. 2 (a) ADMP molecular dynamics simulation on $[B(Ge_9H_3)_3]$. (b) Atoms in molecules (AIM) (Green dots: BCP; Red dots: RCP).

The electron density Laplacian at the mentioned critical points (CPs) serves as a way of characterizing the nature of the formed bonds. The negative value is consistent with the shared interaction nature (i.e. covalent interaction) and the positive value is associated with mainly electrostatic or ionic interaction. The AIM calculation (Figure 2(b)) shows that the three Ge_9H_3 ligands are covalently bonded with B. For the reactivity at the B center, the Fukui function[35,36] for

nucleophilic attack (f(r)+) is -0.28, while for electrophilic attack it is (f(r)-) = 0.008. Thus, the dual descriptor, which is the difference between f(r)$^+$ and f(r)$^-$, yields a negative value. According to Morell et al,[37] if $\Delta f(r) < 0$, the site can hardly undergo a nucleophilic attack, making an electrophilic attack more favorable. Thus, the B center in $B[Ge_9H_3]_3$ indeed acts as an electron donor and, hence, $B[Ge_9H_3]_3$ complex forms a Lewis base. Similar results emerge from studies of $B[Ge_9Y_3]_3$, Y = CH_3, BO, CN. These results are summarized in supporting information Table S1. From the literature we found that for the superatomic complexes[38] it is also possible to explain the hybridization by using localized molecular orbitals. The resulting natural localized molecular orbitals (NLMOs) of $B[Ge_9H_3]_3$ complex, involving the 2s-B, 2p-B atomic shells are shown in figure 3. The three degenerate NLMOs are oriented at about 120° from each other leading to a trigonal planar arrangement. From the comparision of the three sp^2 hybrid orbitals in the BH_3 molecule, shown in figure 3, it is clear that such NLMOs derived from the 2s- and 2p-Boron shells can be viewed as a set of $B[Ge_9H_3]_3$ complex sp^2 hybrids.
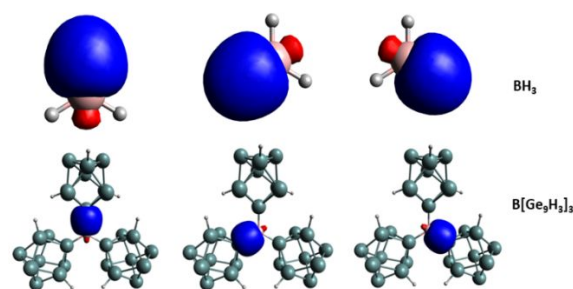

Fig. 3 Differentiation of natural localized molecular orbitals (NLMOs) for proposed $B[Ge_9H_3]_3$ and BH_3 molecule.

To gain an understanding of such an alteration in the reactivity trends, we investigated the nature of the ligand and the role of dual descriptors, which accurately describe the reactivity trends of atomic sites in a molecule. As noted before, the 39-electron Ge_9H_3 cluster is stabilized in the anionic form by becoming a 40-electron system, consistent with the Wade-Mingos rule, where the geometrical configuration of the Ge_9H_3 anion is nido. However, if Ge_9H_3 would donate an electron, it will become a 38-electron system, attaining a closo configuration. Note that a closo configuration is more stable than a nido form. Thus, if the Ge_9H_3 ligand could attain the closo configuration by donating an electron to the B-center, it would enable B to possess an excess negative charge. This would suggest that Ge_9H_3 could be stabilized in cationic form, rather than in the anionic form. We checked the dynamical stability of $[Ge_9H_3]^+$ cation cluster by performing an Atom Centered Density Matrix Propagation (ADMP) molecular dynamics simulation to generate the trajectory. The optimized geometry, cartesian coordinates of Ge_9H_3 cation and its corresponding trajectories are presented in SI-S5. Note that there is no marked deviation in energy, making $[Ge_9H_3]^+$ cation dynamically stable.

To further investigate the origin of the negative charge on the B-center, we calculated the ionization energy (IE) of the Ge_9H_3 ligand. The corresponding value (6.58 eV) is lower than that of the IE of Boron (8.302 eV). This suggests that the Ge_9H_3 ligand is more likely to lose an electron than B, making the latter carry excess negative charge. This trend is opposite to what we observed with $B(C_6F_5)_3$ as a ligand. Note that IE of the C_6F_5 ligand (9.09 eV) is larger than that of

B. Thus, whether B would gain or lose electron will be determined by a competition between the ionization energy and electronegativity of B and the ligands. To substantiate this hypothesis, we studied other Zintl-based groups such as $Ge_9(BO)_3$, $Ge_9(CN)_3$ and $Ge_9(CH_3)_3$. The resulting tri-substituted boron complexes are shown in figure 4. The optimized geometries and cartesian coordinates are shown in SI-S6. The calculated electronegativity's and ionization energies are given in SI-Table S1.

For a detailed understanding of the reactivity of these compounds we also performed dual descriptor analysis as well as Fukui functions of $B(Ge_9H_3)_3$. This reactivity descriptor is calculated from the charge differences of a particular atom inside a molecule in its cation, neutral and anionic form. Details of this calculation are given in SI.
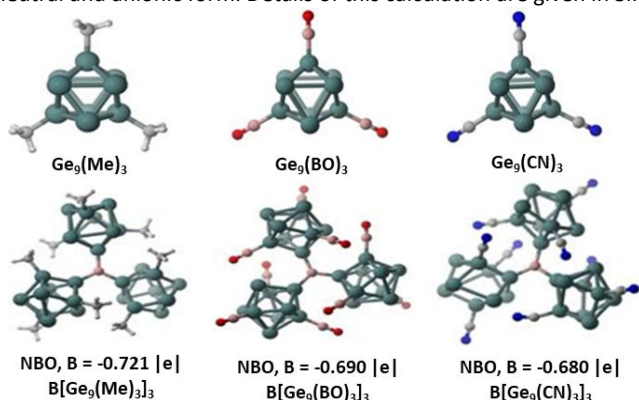

Fig. 4 Optimized geometries of $[Ge_9Me_3]$, $[Ge_9(BO)_3]$, $[Ge_9(CN)_3]$, $B[Ge_9Me_3]_3$, $B[Ge_9(BO)_3]_3$, $B[Ge_9(CN)_3]_3$ clusters with B center NBO charge.

To further confirm the Lewis base nature of B, we built a complex with a well-known Lewis acid BF_3 and compared the charge separation with BF_3-NH_3 complex, which is a known Lewis acid-base pair. The optimized geometry, NBO charges of $BF_3[B(Ge_9H_3)_3]$ are given in Figure 5. An adaptive natural density partitioning (AdNDP)[39] analysis of the $BF_3[B(Ge_9H_3)_3]$, shows that the occupation number (ON) in between B–B bonds is 1.85 |e|. which supports the presence of a strong 2c – 2e sigma bond between the B-atom of $[B(Ge_9H_3)_3]$ and the B-atom of BF_3 molecule, which equally share one-electron(see figure 5). The optimized geometries and cartesian coordinates of BF_3, NH_3, BF_3-NH_3 and $BF_3[B(Ge_9H_3)_3]$ are shown in SI-S7-8.
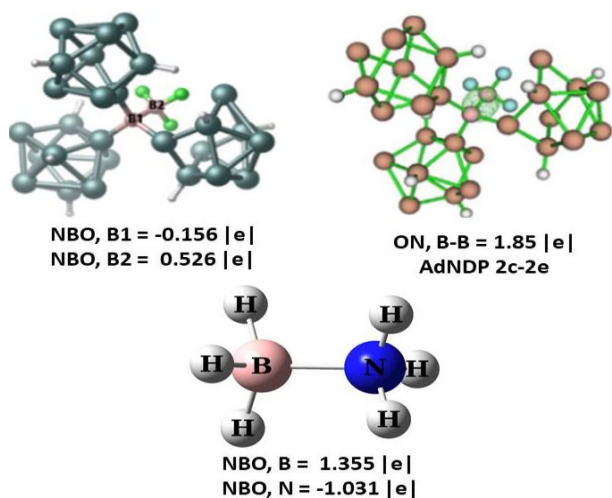
Fig. 5 Optimized geometries of $BF_3[B(Ge_9H_3)_3]$ and BF_3-NH_3 complexes along with their NBO charge separation between Lewis acid-base centers and AdNDP 2c-2e bond results of $BF_3[B(Ge_9H_3)_3]$ complex.

The binding energy of $BF_3[B(Ge_9H_3)_3]$, namely, 17.05 kcal/mol, confirms the formation of Lewis acid-base pair. The NBO charge separation also supports the claim that the $[B(Ge_9H_3)_3]$ complex is indeed a Lewis base as NH_3 is in the BF_3-NH_3 complex.

The calculation of 2c-2e bond also suggests that there exists a sigma bond between the two boron centers. These findings confirm that the boron complex $[B(Ge_9H_3)_3]$ behaves like a Lewis base and the boron center, being electron rich, favors an electrophilic attack.

We also optimized $BF_3[B\{Ge_9(CH_3)_3\}_3]$ and $BF_3[B\{Ge_9(CN)_3\}_3]$ complexes and calculated the NBO charges. From the calculated NBO charges, we found that in $B[Ge_9(CH_3)_3]_3$ and $B[Ge_9(CN)_3]_3$ complexes B center also behaves like Lewis base. The optimized geometries and cartesian coordinates of $BF_3[B\{Ge_9(CH_3)_3\}_3]$ and $BF_3[B\{Ge_9(CN)_3\}_3]$ complexes shown in SI-S8.

In this context, a recent work by Hicks et al[40] is noteworthy. These authors have established the existence of a nucleophilic aluminyl anion. Aluminum compounds, like boron, hitherto considered as electron-deficient molecules, undergo a reversal in their reactivity trends where an anionic Aluminium(I) nucleophile is stabilized by the dimethylxanthene ligand to produce the potassium aluminyl $[K\{Al(NON)\}]_2$ (NON = 4,5-bis(2,6-diisopropylanilido) 2,7-di-tert-butyl-9,9-dimethylxanthene).

Inspired by the above findings, we followed a similar strategy and coupled H^+ and K^+ ions with the anionic $[B(Ge_9H_3)_3]^-$ complex. The calculated $\Delta f(r)$ values at the B-center of the $[B(Ge_9H_3)_3]^-$ complex is found to be negative, which is consistent with our findings. In fact, in $[B(Ge_9H_3)_3]^-$, B center bears more negative charge than $[B(Ge_9H_3)_3]$, as revealed by NBO charge analysis. The optimized geometries, Cartesian coordinates and binding energies (positive values) of the complexes $H[B(Ge_9H_3)_3]$ and $K[B(Ge_9H_3)_3]$ are shown in SI-S9-10, which render stability to these molecules. A frontier molecular orbital analysis of these complexes (showed in supporting information SI-S11) clearly shows that the HOMO is mainly housed on the B-centers, thereby guaranteeing its nucleophilic nature.

In conclusion, our comprehensive study revealed a complete reversal in the reactivity trends of a B-center in Zintl-based cluster Ge_9Y_3, Y = H, CH_3, BO, CN compared to that of $[B(C_6X_5)_3$, X= F, BO, CN]. A detailed charge analysis on the various atomic sites using different basis sets and levels of theory showed that the B-center in $[B(Ge_9Y_3)_3$, Y = CH_3, BO, CN] is nucleophilic, while they are electrophilic in $[B(C_6X_5)_3$, X = F, BO, CN]. This trend is further supported by analyzing the local reactivity indices through the Fukui function values. The existence of strong 2c–2e bonds between the B and Ge centers establishes the chemical stability of $B[Ge_9Y_3]_3$. The sharp departure in the chemistry of B can be understood by comparing the relative strength of ionization energies and electronegativity B with those of its ligands. For pentafluorophenyl-substituted ligands, the ionization energies are larger than that of B, while reverse is the case with Zintl-substituted ligands. In addition, the electronegativity of penta-substituted phenyl-ligands are much larger than those of the Zintl-substituted ligands. These results are summarized in Table S1. Thus, a Zintl-substituted boron compound renders the B-center nucleophilic. An analogous behavior of an Al-center, reported recently, complements the conclusion reached in our study and demonstrates the power of the ligands in manipulating the chemistry
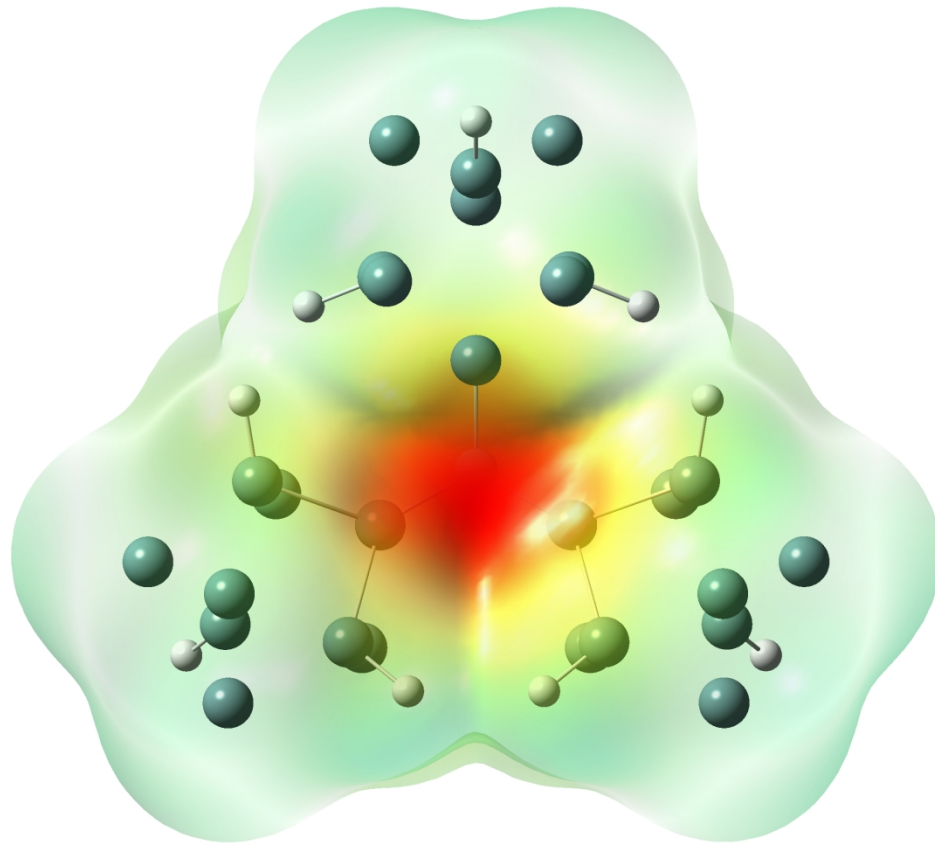
of compounds. We hope that this study will stimulate synthesis of these Zintl-based compounds where B acts as a base.

Acknowledgements

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