

Article

Design and Construction of Novel Frustrated Lewis Pairs Based on Modified Lewis Acid $B(C_6F_5)_3$

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Abstract

This study aims to systematically investigate the influence of substituent effects on the strength of Lewis acid–base interactions in frustrated Lewis pairs (FLPs). Specifically, $-C_6F_5$ groups of the classical Lewis acid $B(C_6F_5)_3$ are sequentially replaced with $-C_6Cl_5$, $-C_6Br_5$, and $-C_6I_5$ groups, and the Lewis acids are paired with the Lewis base 1,3-disubstituted imidazol-2-ylidene (*ItBu*) to form FLPs. Further energy decomposition analysis (sobEDA), orbital analysis, and molecular fragment density difference (MFDD) analysis reveal the nature of the substituent effect on the interaction energy (ΔE_{int}) of the FLPs. The research findings indicate that the ΔE_{int} of $B(C_6F_5)_3$ -*ItBu*, $B(C_6F_5)_x(C_6Y_5)_{3-x}$ -*ItBu* ($x = 0, 1, 2$; $Y = Cl, Br, I$) originates mainly from the interaction between the outermost halogen atom of the Lewis acid and the central carbon (C) atom of the Lewis base, rather than from the interaction between the central atoms boron (B) and carbon (C). This mechanism ultimately leads to a ΔE_{int} for $B(C_6F_5)_2(C_6Y_5)$ -*ItBu* ($Y = Cl, Br, I$) that is comparable to that of $B(C_6F_5)_3$ -*ItBu*. This indicates that modified $B(C_6F_5)_2(C_6Y_5)$ ($Y = Cl, Br, I$) exhibits greater potential for the construction of novel FLPs.

Keywords: frustrated lewis pairs; substituent effect; steric hindrance effect; ligand effect; energy decomposition analysis

1. Introduction

Since the Stephan group discovered and defined the concept of frustrated Lewis pairs (FLPs) in 2006, FLPs have attracted widespread interest for their metal-free catalytic potential [1]. After more than a decade of development, FLPs have evolved into a highly versatile tool for the activation of small molecules [2–5]. The “push–pull” hypothesis posits that FLPs activate small molecules through a cooperative electron transfer process: the Lewis acid accepts electron density from the reactant bonding orbital, while the Lewis base donates electron density into its antibonding orbital, thereby achieving activation [6]. Steric hindrance prevents the formation of a stable adduct between the Lewis acid and base, thereby preserving their independent “push–pull” action. Hence, the design of FLPs requires the delicate balancing of both steric and electronic factors in component selection. Notably, Tris(pentafluorophenyl)borane- $B(C_6F_5)_3$ and its derivatives exhibit high acidity and significant steric bulk. The presence of an empty orbital on the boron (B) atom facilitates the acceptance of electron pairs from small molecules, while the steric



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hindrance of substituents can effectively impede interaction with Lewis bases, thus ensuring the sterically frustrated state of the FLPs. Numerous experimental achievements have been made in the activation of small molecules by FLPs, which are derived from the rational substitution of substituents on the B atom of the $B(C_6F_5)_3$ [7–12]. Ashley et al. reported the activation of hydrogen (H_2) by $B(C_6F_5)_3$ and $B(C_6F_5)_x(C_6Cl_5)_{3-x}$ ($x = 0, 1, 2$). Experimentally, $B(C_6F_5)_2(C_6Cl_5)$ exhibits enhanced air stability and H_2 activation activity comparable to $B(C_6F_5)_3$, marking it as a promising alternative [13]. Nevertheless, $B(C_6F_5)_x(C_6Cl_5)_{3-x}$ ($x = 0, 1$) show lower H_2 activation rates. The result challenges the prevailing understanding derived from the work of Ashley et al. Theoretically, the larger atomic radius of the Cl atom compared with the F atom should lead to more pronounced steric effects within the FLP framework. This is favorable for H_2 activation. When F atoms are replaced by Cl atoms, the electrophilicity weakens, leading to a decrease in Lewis acidity. This results in a lower bond energy of the formed FLPs, thereby making them more favorable for H_2 activation. Therefore, $B(C_6F_5)_x(C_6Cl_5)_{3-x}$ ($x = 0, 1$), with a higher Cl content, should be more active towards H_2 activation than $B(C_6F_5)_2(C_6Cl_5)$. But this is inconsistent with the experimental results reported by Ashley et al.

To explain the above issues, we employ halogenated aryl substituents ($-C_6Cl_5$, $-C_6Br_5$, $-C_6I_5$) to systematically replace the $-C_6F_5$ group in $B(C_6F_5)_3$, as shown in Figure 1 [14,15]. Thus, the FLPs are designed by combining Lewis acids $B(C_6F_5)_3$ and $B(C_6F_5)_x(C_6Y_5)_{3-x}$ ($x = 0, 1, 2$; $Y = Cl, Br, I$) with the Lewis base 1,3-disubstituted imidazol-2-ylidene (*ItBu*) [16]. To elucidate the substituent effects, we systematically investigate the formation of the FLPs based on the modified Lewis acids in comparison with the classical $B(C_6F_5)_3$. This investigation is conducted through a combination of structural, energy, orbital and electron density analyses. This study has two main objectives: (i) to examine the chemical properties of the $B(C_6F_5)_x(C_6Y_5)_{3-x}$ ($x = 0, 1, 2$; $Y = Br, I$) in comparison with $B(C_6F_5)_x(C_6Cl_5)_{3-x}$ ($x = 0, 1, 2$) and (ii) to elucidate the mechanism underlying the enhanced interaction in FLPs with halogen atom substitution. On this basis, the fundamental factors governing the interactions of FLPs are identified, thereby enabling the construction of novel FLPs through systematic modification of the classical $B(C_6F_5)_3$.

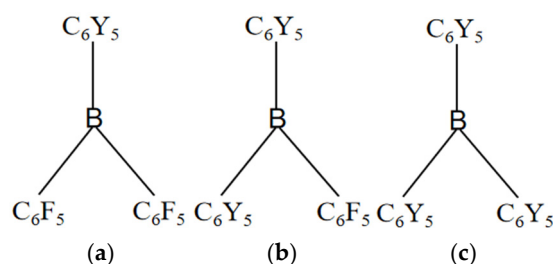


Figure 1. Schematic diagrams of the modified structures of the Lewis acid $B(C_6F_5)_3$. (a) $(-C_6Y_5)$, (b) $(-C_6Y_5)_2$ and (c) $(-C_6Y_5)_3$ groups ($Y = Cl, Br, I$).

2. Methods

All geometry optimizations and vibrational frequency calculations in this work are performed at the B3LYP-D3(BJ)/def2-TZVP level of theory with the Gaussian 09 software package [17,18]. The investigated systems include both the monomers and the corresponding FLPs. To decompose the interaction energy of the FLPs into physically meaningful components, we employ the energy decomposition analysis method (sobEDA) [19–21]. It is a powerful DFT-based approach that incorporates dispersion correction, enabling the quantification of multiple interaction components. This method facilitates the rapid and accurate partitioning of interaction energy into seven terms (ΔE_{int} , ΔE_{els} , ΔE_x , ΔE_{rep} ,

$\Delta E_{\text{orb}}, \Delta E_{\text{DFTc}}, \Delta E_{\text{dc}})$, thereby elucidating the dominant and secondary factors governing the interactions. The individual energy terms are related as follows:

$$\Delta E_{\text{int}} = \Delta E_{\text{els}} + \Delta E_{\text{x}} + \Delta E_{\text{rep}} + \Delta E_{\text{orb}} + \Delta E_{\text{DFTc}} + \Delta E_{\text{dc}}.$$

Here, $\Delta E_{\text{els}}, \Delta E_{\text{x}}, \Delta E_{\text{rep}}$ and ΔE_{orb} represent the classical electrostatic interaction, the exchange interaction, the Pauli repulsion and the orbital interaction energies, respectively. ΔE_{DFTc} and ΔE_{dc} correspond to the DFT and the dispersion correction terms, respectively. Essentially, ΔE_{x} arises from the quantum interference effect induced by the antisymmetrization of the wavefunction due to electrons being identical particles with no corresponding classical effect. In practice, ΔE_{x} is commonly grouped with ΔE_{rep} to define the exchange–repulsion energy $\Delta E_{\text{xrep}} = \Delta E_{\text{x}} + \Delta E_{\text{rep}}$. ΔE_{DFTc} , which is contributed by the DFT correlation functional, accounts for the Coulombic contribution to the intermolecular interaction. However, it performs poorly in describing long-range Coulomb effects, necessitating the inclusion of ΔE_{dc} for correction.

The Multiwfn program is a powerful and practical wavefunction analysis tool, which is widely used in quantum chemical calculations [22–25]. Among these, molecular electrostatic potential (ESP) analysis, orbital analysis, and molecular fragment density difference (MFDD) analysis can all be realized through its powerful functionality. The ESP extreme points near the central atom of the optimized monomer serve as a direct criterion for the construction of FLP structures and the prediction of interaction strength. The orbital analysis module is used to quantify the overlap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), as well as the electron population on the center atoms (B and C) of the FLPs. This constitutes a critical basis for assessing the magnitude of the interaction between the B and C of the FLPs. The MFDD analysis is employed to map electron migration between the fragments. The variation in the FLP interaction energy directly correlates with the redistribution of electron density in the interfacial region between the acid and base. The key factors governing the binding energy of FLPs are determined through a comparative analysis of electron density migration between various atoms within the FLPs [26–35].

3. Results and Discussion

3.1. Comparison of Bond Energy of the FLPs on Modified Lewis Acid $\text{B}(\text{C}_6\text{F}_5)_3$

This study investigates a series of FLPs derived from *ItBu* and various borane Lewis acids. These acids include $\text{B}(\text{C}_6\text{F}_5)_3$ and a systematic set of $\text{B}(\text{C}_6\text{F}_5)_x(\text{C}_6\text{Y}_5)_{3-x}$ ($x = 0, 1, 2$; $\text{Y} = \text{Cl}, \text{Br}, \text{I}$) [34]. Under normal conditions, the B atom of $\text{B}(\text{C}_6\text{F}_5)_3$ and $\text{B}(\text{C}_6\text{F}_5)_x(\text{C}_6\text{Y}_5)_{3-x}$ ($x = 0, 1, 2$; $\text{Y} = \text{Cl}, \text{Br}, \text{I}$) typically possesses an empty orbital, while the C atom of *ItBu* has a lone pair of electrons. A molecular ESP analysis of Lewis acids and Lewis base is performed, and the results are presented in S1. For Lewis acids, a positive region of ESP exists outside the B atom. For *ItBu*, the negative region of ESP exists outside the C atom of the imidazole ring. For the classical $\text{B}(\text{C}_6\text{F}_5)_3$, the positive ESP value outside the B atom is 33.87 kcal/mol. For the modified $\text{B}(\text{C}_6\text{F}_5)_x(\text{C}_6\text{Y}_5)_{3-x}$ ($x = 0, 1, 2$; $\text{Y} = \text{Cl}, \text{Br}, \text{I}$), the positive ESP values are 17.70 kcal/mol, 17.07 kcal/mol, and 14.98 kcal/mol at $x = 2$; 17.36 kcal/mol, 11.66 kcal/mol, and 6.84 kcal/mol at $x = 1$; and 15.35 kcal/mol, 9.85 kcal/mol, and 4.88 kcal/mol at $x = 0$; Therefore, the positive ESP values outside the B atom of $\text{B}(\text{C}_6\text{F}_5)_x(\text{C}_6\text{Y}_5)_{3-x}$ decrease gradually in the order of $x = 2, x = 1, x = 0$ and $\text{Y} = \text{Cl}, \text{Br}, \text{I}$, but all values are lower than that of the classical $\text{B}(\text{C}_6\text{F}_5)_3$.

Based on the analysis of the molecular ESP of S1, the FLPs are constructed and optimized. The optimized structures of the most stable FLPs are shown in Figure 2, and the distance between B and C ($R_{\text{B} \cdots \text{C}}$) and the corresponding bond energies (ΔE) are listed

in Table 1. The other isomers of FLPs and relative zero-point energy are shown in S2. For FLPs, significant steric hindrance forces the Lewis acid and base to adopt a perpendicular orientation, thereby enabling their interaction.

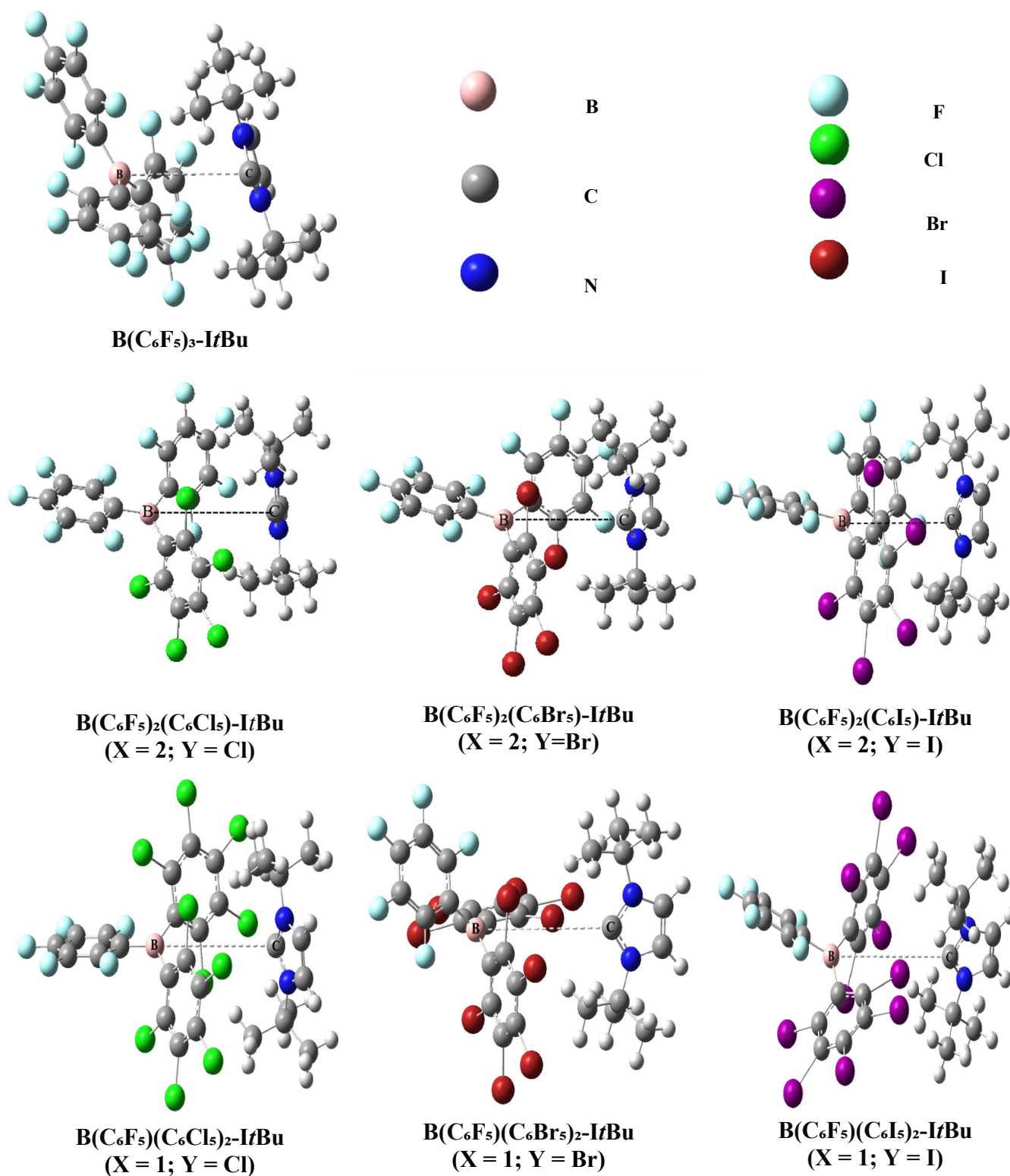


Figure 2. Cont.

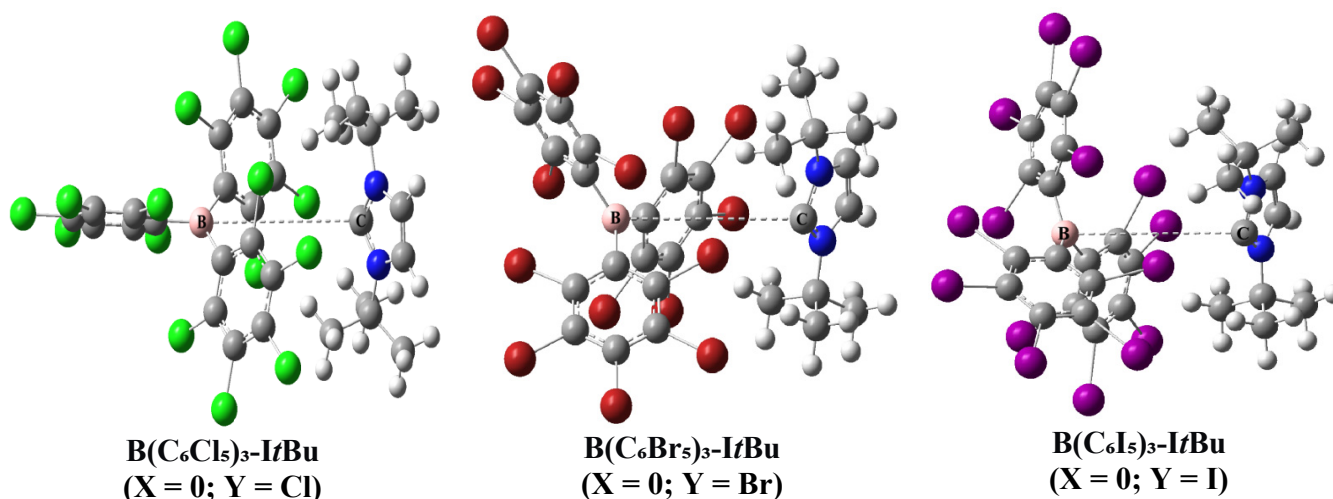


Figure 2. Optimized structural of the FLPs $B(C_6F_5)_3-ItBu$ and $B(C_6F_5)_x(C_6Y_5)_{3-x}-ItBu$ ($x = 0, 1, 2$; $Y = Cl, Br, I$).

Table 1. The distance $R_{B \cdots C}$ between the B and C and the bond energy ΔE of the FLPs.

FLPs	$R_{B \cdots C}$ (Å)	ΔE (kcal/mol)
$B(C_6F_5)_3-ItBu$	4.908	−10.15
$B(C_6F_5)_2(C_6Cl_5)-ItBu$ ($X = 2$; $Y = Cl$)	5.490	−11.68
$B(C_6F_5)(C_6Cl_5)_2-ItBu$ ($X = 1$; $Y = Cl$)	5.364	−13.24
$B(C_6Cl_5)_3-ItBu$ ($X = 0$; $Y = Cl$)	5.485	−12.88
$B(C_6F_5)_2(C_6Br_5)-ItBu$ ($X = 2$; $Y = Br$)	5.284	−12.37
$B(C_6F_5)(C_6Br_5)_2-ItBu$ ($X = 1$; $Y = Br$)	5.655	−13.43
$B(C_6Br_5)_3-ItBu$ ($X = 0$; $Y = Br$)	5.571	−15.49
$B(C_6F_5)_2(C_6I_5)-ItBu$ ($X = 2$; $Y = I$)	5.297	−12.36
$B(C_6F_5)(C_6I_5)_2-ItBu$ ($X = 1$; $Y = I$)	5.967	−20.00
$B(C_6I_5)_3-ItBu$ ($X = 0$; $Y = I$)	5.458	−20.08

As shown in Figure 2, compared with $B(C_6F_5)_3-ItBu$, $B(C_6F_5)_2(C_6Y_5)-ItBu$ ($Y = Cl, Br, I$) exhibits larger intermolecular separations $R_{B \cdots C}$ from 4.908 Å to 5.490 Å, 5.284 Å, and 5.297 Å, with the corresponding ΔE enhanced from −10.15 kcal/mol to −11.68 kcal/mol, −12.37 kcal/mol and −12.36 kcal/mol. For $B(C_6F_5)_3-ItBu$ and $B(C_6F_5)_x(C_6Y_5)_{3-x}-ItBu$ ($x = 0, 1$; $Y = Cl, Br, I$), the Lewis acid and Lewis base fragments are found to remain separated by relatively large distances $R_{B \cdots C}$, increasing from 4.908 Å to 5.364 Å, 5.655 Å and 5.967 Å for $x = 1$, as well as from 4.908 Å to 5.485 Å, 5.571 Å and 5.458 Å for $x = 0$. Nevertheless, the corresponding ΔE are enhanced, changing from −10.15 kcal/mol to −13.24 kcal/mol, −13.43 kcal/mol and −20.00 kcal/mol for $x = 1$ and from −10.15 kcal/mol to −12.88 kcal/mol, −15.49 kcal/mol and −20.08 kcal/mol for $x = 0$.

Therefore, the ΔE between the modified Lewis acid $B(C_6F_5)_x(C_6Y_5)_{3-x}$ ($x = 0, 1, 2$) and the *ItBu* enhances gradually in the order of $Y = Cl, Br, I$. For the same halogen substitution,

when $x = 1$ or 0 , the atom types and distances in the interaction region are highly similar, so their ΔE are also very comparable and larger than that at $x = 2$. Moreover, all these ΔE are larger than that of the classical $B(C_6F_5)_3$.

Normally, for $B(C_6F_5)_3$ and $B(C_6F_5)_x(C_6Y_5)_{3-x}$ ($x = 0, 1, 2$; $Y = Cl, Br, I$), a larger ESP value outside the B atom is expected to lead to a stronger bond energy with the *ItBu*. However, an opposite trend is observed in FLPs. Therefore, besides steric hindrance and electronegativity, other additional effects must be taken into account.

3.2. Energy Decomposition Analysis of the FLPs Based on Modified Lewis Acid $B(c_6f_5)_3$

Only by considering ΔE and the various physical components that influence ΔE can we gain a deeper understanding of the nature of the interaction between Lewis acids and Lewis bases. In general, the ΔE of FLPs comprises two components: the deformation energy (ΔE_s) and the interaction energy (ΔE_{int}). The former is associated with the structural distortion of the Lewis acid and base upon association, while the latter represents the actual energy of interaction between the distorted monomers. The relationship can be expressed as follows:

$$\Delta E = \Delta E_s + \Delta E_{int}.$$

Table S1 summarizes the zero-point energy changes in the Lewis acid and Lewis base in FLPs before and after association, which originate from structural deformation. Its formula is expressed as follows:

$$|\Delta E_s| = |\Delta E_{before} - \Delta E_{after}|$$

where, whether $B(C_6F_5)_3$, $B(C_6F_5)_x(C_6Y_5)_{3-x}$ ($x = 0, 1, 2$; $Y = Cl, Br, I$) or *ItBu*, ΔE_{before} represents the zero-point energy before association and ΔE_{after} represents the zero-point energy after association. For the FLPs formed between $B(C_6F_5)_3$, $B(C_6F_5)_x(C_6Y_5)_{3-x}$ ($x = 0, 1, 2$; $Y = Cl, Br, I$) and *ItBu*, the energy changes associated with structural deformation are very small. Consequently, the ΔE of these FLPs are approximately equal to their corresponding ΔE_{int} .

In this section, the ΔE_{int} of the FLPs arising from variations in the substituents on the B atom is discussed and the main origins of these differences are analyzed using the sobEDA method [36]. The results of the sobEDA are compiled in Table 2. Comparative analysis reveals that for $B(C_6F_5)_3$ -*ItBu*, $B(C_6F_5)_x(C_6Y_5)_{3-x}$ -*ItBu* ($x = 0, 1, 2$; $Y = Cl, Br, I$), ΔE and ΔE_{int} are not only close in value but also follow identical trends. For $B(C_6F_5)_2(C_6Y_5)$ -*ItBu* ($Y = Cl, Br, I$), the ΔE_{int} is slightly larger than that of $B(C_6F_5)_3$ -*ItBu*, from -11.09 kcal/mol to -12.04 kcal/mol, -12.58 kcal/mol and -12.57 kcal/mol. The enhancement of ΔE_{int} arises from the concerted variation in its components: ΔE_{els} , ΔE_{Xrep} and ΔE_{dc} . ΔE_{els} becomes slightly larger, changing from -6.11 kcal/mol to -7.67 kcal/mol, -8.49 kcal/mol and -7.61 kcal/mol. ΔE_{Xrep} becomes larger, changing from 22.31 kcal/mol to 26.37 kcal/mol, 27.31 kcal/mol and 27.14 kcal/mol. ΔE_{dc} becomes significantly larger, changing from -14.28 kcal/mol to -17.64 kcal/mol, -18.91 kcal/mol and -18.45 kcal/mol. Interestingly, ΔE_{orb} is weakened from -3.87 kcal/mol to -2.77 kcal/mol, -2.55 kcal/mol and -2.62 kcal/mol.

For $B(C_6F_5)(C_6Y_5)_2$ -*ItBu* ($Y = Cl, Br, I$), ΔE_{int} (-13.04 kcal/mol, -14.05 kcal/mol and -22.18 kcal/mol) is much larger than that of $B(C_6F_5)_3$ -*ItBu* ($\Delta E_{int} = -11.09$ kcal/mol). This behavior is primarily attributed to the pronounced enhancement of ΔE_{els} , from -6.11 kcal/mol to -7.69 kcal/mol, -17.97 kcal/mol and -39.10 kcal/mol. This is accompanied by an enhancement of ΔE_{dc} , which is augmented from -14.28 kcal/mol to -19.17 kcal/mol, -16.38 kcal/mol, and -19.97 kcal/mol. ΔE_{int} becomes much larger, accompanied by a substantial enhancement in ΔE_{Xrep} that rises from 22.31 kcal/mol to

27.41 kcal/mol, 40.25 kcal/mol and 78.51 kcal/mol. In addition, relative to $B(C_6F_5)_3$ -*ItBu*, the ΔE_{orb} in $B(C_6F_5)(C_6Y_5)_2$ -*ItBu* ($Y = Br, I$) is significantly enhanced, from -3.87 kcal/mol to -9.66 kcal/mol and -27.30 kcal/mol. By contrast, for $B(C_6F_5)(C_6Cl_5)_2$ -*ItBu* and $B(C_6F_5)_3$ -*ItBu*, ΔE_{orb} slightly weakens from -3.87 kcal/mol to -3.07 kcal/mol. For $B(C_6Y_5)_3$ -*ItBu* ($Y = Cl, Br, I$), the variation trend of ΔE_{int} is consistent with that observed for $B(C_6F_5)(C_6Y_5)_2$ -*ItBu* ($Y = Cl, Br, I$). Specifically, the ΔE_{int} of this series is much larger than that of $B(C_6F_5)_3$ -*ItBu* (-11.09 kcal/mol), reaching -12.65 kcal/mol, -16.63 kcal/mol and -22.62 kcal/mol, respectively. The ΔE_{orb} of $B(C_6Cl_5)_3$ -*ItBu* is still slightly weaker compared with that of $B(C_6F_5)_3$ -*ItBu*, from -3.87 kcal/mol to -3.07 kcal/mol.

Table 2. Energy decomposition analysis (sobEDA) of the FLPs based on modified Lewis acid $B(C_6F_5)_3$.

FLPs	ΔE_{int} (kcal/mol)	ΔE_{els} (kcal/mol)	ΔE_{Xrep} (kcal/mol)	ΔE_{orb} (kcal/mol)	ΔE_{DFTc} (kcal/mol)	ΔE_{dc} (kcal/mol)
$B(C_6F_5)_3$ - <i>ItBu</i>	−11.09	−6.11	22.31	−3.87	−9.13	−14.28
$B(C_6F_5)_2(C_6Cl_5)$ - <i>ItBu</i> ($X = 2; Y = Cl$)	−12.04	−7.67	26.37	−2.77	−10.33	−17.64
$B(C_6F_5)(C_6Cl_5)_2$ - <i>ItBu</i> ($X = 1; Y = Cl$)	−13.04	−7.69	27.41	−3.07	−10.54	−19.17
$B(C_6Cl_5)_3$ - <i>ItBu</i> ($X = 0; Y = Cl$)	−12.65	−7.49	27.31	−3.07	−10.48	−18.91
$B(C_6F_5)_2(C_6Br_5)$ - <i>ItBu</i> ($X = 2; Y = Br$)	−12.58	−8.49	27.31	−2.55	−10.54	−18.31
$B(C_6F_5)(C_6Br_5)_2$ - <i>ItBu</i> ($X = 1; Y = Br$)	−14.05	−17.97	40.25	−9.66	−10.30	−16.38
$B(C_6Br_5)_3$ - <i>ItBu</i> ($X = 0; Y = Br$)	−16.63	−17.44	42.36	−10.15	−12.00	−19.39
$B(C_6F_5)_2(C_6I_5)$ - <i>ItBu</i> ($X = 2; Y = I$)	−12.57	−7.61	27.14	−2.62	−11.03	−18.45
$B(C_6F_5)(C_6I_5)_2$ - <i>ItBu</i> ($X = 1; Y = I$)	−22.18	−39.10	78.51	−27.30	−14.12	−19.97
$B(C_6I_5)_3$ - <i>ItBu</i> ($X = 0; Y = I$)	−22.62	−27.09	59.88	−17.61	−14.11	−23.69

The sobEDA analysis reveals that, relative to $B(C_6F_5)_3$ -*ItBu*, $B(C_6F_5)_x(C_6Y_5)_{3-x}$ -*ItBu* ($x = 0, 1, 2; Y = Cl, Br, I$) exhibits larger energy components ΔE_{els} , ΔE_{Xrep} and ΔE_{dc} . However, compared with $B(C_6F_5)_3$ -*ItBu*, ΔE_{orb} is weakened in both $B(C_6F_5)_2(C_6Y_5)$ -*ItBu* ($Y = Cl, Br, I$) and $B(C_6F_5)_x(C_6Cl_5)_{3-x}$ -*ItBu* ($x = 0, 1$). This results in ΔE_{int} being weaker for $B(C_6F_5)_2(C_6Y_5)$ -*ItBu* ($Y = Cl, Br, I$) and $B(C_6F_5)_x(C_6Cl_5)_{3-x}$ -*ItBu* ($x = 0, 1$) than for $B(C_6F_5)_x(C_6Y_5)_{3-x}$ -*ItBu* ($x = 0, 1; Y = Br, I$). The results ultimately show that ΔE_{int} is more comparable between $B(C_6F_5)_3$ -*ItBu* and $B(C_6F_5)_2(C_6Y_5)$ -*ItBu* ($Y = Cl, Br, I$). This is consistent with the experimental results reported by Ashley et al. When using $B(C_6F_5)_3$ and $B(C_6F_5)_x(C_6Cl_5)_{3-x}$ ($x = 0, 1, 2$) to activate H_2 , $B(C_6F_5)_3$ and $B(C_6F_5)_2(C_6Cl_5)$ display comparable activation efficiencies, whereas $B(C_6F_5)_x(C_6Cl_5)_{3-x}$ ($x = 0, 1$) exhibits a relatively lower efficiency. Therefore, $B(C_6F_5)_2(C_6Y_5)$ ($Y = Cl, Br, I$) is more favorable for the construction of novel FLPs. However, for $B(C_6F_5)_2(C_6Y_5)$ -*ItBu* ($Y = Cl, Br, I$) and $B(C_6F_5)_x(C_6Cl_5)_{3-x}$ -*ItBu* ($x = 0, 1$), their ΔE_{orb} are weakened compared with that of $B(C_6F_5)_3$ -*ItBu*. This phenomenon warrants further investigation.

3.3. Homo and Lumo Analysis of the FLPs Based on Modified $B(C_6F_5)_3$

In the analysis of the previous section, the anomalous weaker ΔE_{orb} between $B(C_6F_5)_2(C_6Y_5)$ -*ItBu* ($Y = Cl, Br, I$) and $B(C_6F_5)_x(C_6Cl_5)_{3-x}$ -*ItBu* ($x = 0, 1$), compared with $B(C_6F_5)_3$ -*ItBu*, requires further confirmation. The interaction strength of the FLPs is gov-

erned by the interaction between the vacant lowest unoccupied molecular orbital (LUMO) located on the B atom of $B(C_6F_5)_3$ and $B(C_6F_5)_x(C_6Y_5)_{3-x}$ ($x = 0, 1, 2$; $Y = Cl, Br, I$) and the highest occupied molecular orbital (HOMO) associated with the lone pair on the C atom of *ItBu*. In general, bulky substituents hinder the Lewis acid and Lewis base from adopting an optimal spatial arrangement, thereby significantly reducing the effective overlap between the LUMO and HOMO. As a result, charge transfer is restricted and orbital interaction cannot be fully developed. Consequently, a larger electron population associated with the B-centered LUMO and the C-centered HOMO corresponds to a smaller degree of charge transfer during the interaction process of the FLPs [37–41].

From a more intuitive perspective, S3 depicts the LUMO of $B(C_6F_5)_3$ and $B(C_6F_5)_x(C_6Y_5)_{3-x}$ ($x = 0, 1, 2$; $Y = Cl, Br, I$), together with the HOMO corresponding to the *ItBu*. Such orbital mixing is absent in most halogen substituted FLPs, including $B(C_6F_5)_3$ -*ItBu*, $B(C_6F_5)_2(C_6Y_5)$ -*ItBu* ($Y = Cl, Br, I$) and $B(C_6F_5)_x(C_6Cl_5)_{3-x}$ -*ItBu* ($x = 0, 1$), where these orbitals remain relatively independent. It is worth noting that, for $B(C_6F_5)_x(C_6Y_5)_{3-x}$ -*ItBu* ($x = 0, 1$; $Y = Br, I$), a portion of the electrons in the HOMO is transferred onto the substituents of the corresponding Lewis acid. This indicates that the orbital interaction between the fragments of the $B(C_6F_5)_x(C_6Y_5)_{3-x}$ -*ItBu* ($x = 0, 1$; $Y = Br, I$) is enhanced. This phenomenon is highly similar to the trend in the value of ΔE_{orb} .

To further investigate the relationship between electron transfer and orbital interaction in these FLPs, we employ the Multiwfn program to calculate the electron population of the LUMO localized on the B atom and the HOMO localized on the C atom, as well as the overlap integral of norm between the LUMO and HOMO. These results are summarized in Table 3. In a comparison of $B(C_6F_5)_3$ -*ItBu* and $B(C_6F_5)_2(C_6Y_5)$ -*ItBu* ($Y = Cl, Br, I$), the electron population associated with the B atom in the LUMO changes from 41.16% to 42.94, 41.68% and 38.11%, respectively. The electron population localized on the C atom in the HOMO changes from 86.53% to 87.88%, 87.12% and 87.56%. Concurrently, the overlap integral of norm varies from 0.042 to 0.023, 0.084 and 0.050. It is evident that all these values are distributed within a narrow range around those of the $B(C_6F_5)_3$ -*ItBu*. This suggests that comparable orbital interaction strengths are present between $B(C_6F_5)_3$ -*ItBu* and $B(C_6F_5)_2(C_6Y_5)$ -*ItBu* ($Y = Cl, Br, I$).

When comparing $B(C_6F_5)_3$ -*ItBu* with $B(C_6F_5)(C_6Y_5)_2$ -*ItBu* ($Y = Cl, Br, I$), the electron population associated with the B atom in the LUMO changes from 44.16% to 44.61%, 42.78% and 27.05%. The electron population associated with the C atom in the HOMO varies from 86.53% to 86.60%, 81.58% and 46.40%, and the overlap integral of norm changes from 0.042 to 0.042, 0.111 and 0.415. The orbital analysis reveals very similar values for $B(C_6F_5)(C_6Cl_5)_2$ -*ItBu* and $B(C_6F_5)_3$ -*ItBu*, consistent with comparable orbital interactions in the two systems. In contrast, for $B(C_6F_5)(C_6Y_5)_2$ -*ItBu* ($Y = Br, I$), pronounced decreases are observed in the electron populations on both the HOMO and the LUMO, accompanied by a marked increase in the overlap integral of norm. These features indicate the presence of larger orbital interactions in these systems. When comparing $B(C_6F_5)_3$ -*ItBu* with $B(C_6Y_5)_3$ -*ItBu* ($Y = Cl, Br, I$), for the B atom in the LUMO, the electron population changes from 44.16% to 44.61%, 41.37%, 30.26%, and for the C atom in the HOMO, it changes from 86.53% to 86.74%, 80.37%, 40.45%. The overlap integral of norm changes from 0.042 to 0.041, 0.112 and 0.403. These results show that, relative to $B(C_6F_5)_3$ -*ItBu*, $B(C_6Cl_5)_3$ -*ItBu* exhibits a comparable orbital interaction strength, whereas $B(C_6Y_5)_3$ -*ItBu* ($Y = Br, I$) displays the larger orbital interaction.

Subsequently, the FLPs with comparable performance based on the orbital analysis are further investigated. Compared with $B(C_6F_5)_x(C_6Y_5)_{3-x}$ -*ItBu* ($x = 0, 1$; $Y = Br, I$), the electron density on the B atom in the LUMO, the electron density on the C atom in the HOMO, and the orbital overlap integral of norm between LUMO and HOMO for $B(C_6F_5)_2(C_6Y_5)$ -

ItBu ($Y = \text{Cl, Br, I}$) and $\text{B}(\text{C}_6\text{F}_5)_x(\text{C}_6\text{Cl}_5)_{3-x}\text{-ItBu}$ ($x = 0, 1$) are all weaker. These factors collectively lead to a weaker ΔE_{orb} . Moreover, these values are very comparable to the ΔE_{orb} of $\text{B}(\text{C}_6\text{F}_5)_3\text{-ItBu}$. However, the other influencing factors ΔE_{els} , ΔE_{xrep} and ΔE_{dc} of $\text{B}(\text{C}_6\text{F}_5)_x(\text{C}_6\text{Cl}_5)_{3-x}\text{-ItBu}$ ($x = 0, 1$) are larger than that of $\text{B}(\text{C}_6\text{F}_5)_2(\text{C}_6\text{Y}_5)\text{-ItBu}$ ($Y = \text{Cl, Br, I}$). This ultimately leads to the ΔE_{int} of $\text{B}(\text{C}_6\text{F}_5)_2(\text{C}_6\text{Y}_5)\text{-ItBu}$ ($Y = \text{Cl, Br, I}$) being comparable to that of $\text{B}(\text{C}_6\text{F}_5)_3\text{-ItBu}$. As a result, modified $\text{B}(\text{C}_6\text{F}_5)_2(\text{C}_6\text{Y}_5)$ ($Y = \text{Cl, Br, I}$) is more conducive to the development of the novel FLPs.

Table 3. Analysis of the LUMO and HOMO of central atoms in the FLPs based on modified $\text{B}(\text{C}_6\text{F}_5)_3$.

FLPs	LUMO-LA (%)	HOMO-LB (%)	Overlap Integral of Norm
$\text{B}(\text{C}_6\text{F}_5)_3\text{-ItBu}$	41.16	86.53	0.042
$\text{B}(\text{C}_6\text{F}_5)_2(\text{C}_6\text{Cl}_5)\text{-ItBu}$ ($X = 2; Y = \text{Cl}$)	42.94	87.88	0.023
$\text{B}(\text{C}_6\text{F}_5)(\text{C}_6\text{Cl}_5)_2\text{-ItBu}$ ($X = 1; Y = \text{Cl}$)	44.61	86.60	0.042
$\text{B}(\text{C}_6\text{Cl}_5)_3\text{-ItBu}$ ($X = 0; Y = \text{Cl}$)	44.61	86.74	0.041
$\text{B}(\text{C}_6\text{F}_5)_2(\text{C}_6\text{Br}_5)\text{-ItBu}$ ($X = 2; Y = \text{Br}$)	41.68	87.12	0.084
$\text{B}(\text{C}_6\text{F}_5)(\text{C}_6\text{Br}_5)_2\text{-ItBu}$ ($X = 1; Y = \text{Br}$)	42.78	81.58	0.111
$\text{B}(\text{C}_6\text{Br}_5)_3\text{-ItBu}$ ($X = 0; Y = \text{Br}$)	41.37	80.37	0.112
$\text{B}(\text{C}_6\text{F}_5)_2(\text{C}_6\text{I}_5)\text{-ItBu}$ ($X = 2; Y = \text{I}$)	38.11	87.56	0.050
$\text{B}(\text{C}_6\text{F}_5)(\text{C}_6\text{I}_5)_2\text{-ItBu}$ ($X = 1; Y = \text{I}$)	27.05	46.40	0.415
$\text{B}(\text{C}_6\text{I}_5)_3\text{-ItBu}$ ($X = 0; Y = \text{I}$)	30.26	40.45	0.403

3.4. The MFDD Analysis of the FLPs Based on Modified $\text{B}(\text{C}_6\text{F}_5)_3$

Theoretical calculations reveal that the trend in the strength of ΔE_{int} is contrary to the predictions based on ESP analysis. Moreover, comparative studies on the H_2 activation performance of $\text{B}(\text{C}_6\text{F}_5)_2(\text{C}_6\text{Cl}_5)$ and $\text{B}(\text{C}_6\text{F}_5)_x(\text{C}_6\text{Cl}_5)_{3-x}$ ($x = 0, 1$) reveal that, beyond steric hindrance effects, other types of interactions also exert a significant influence on the ΔE_{int} between FLPs. To delineate the influence of non-steric contributions, MFDD analysis is employed across the series of the FLPs. The concept of MFDD analysis has been introduced by Daudel and Roux in the 1950s [42,43]. The corresponding expression is defined as follows:

$$\rho_{\text{d}} = \rho_{\text{FLPs}} - \rho_{\text{LA}} - \rho_{\text{LB}}.$$

Here, ρ_{FLPs} represents the electron density of the FLPs, ρ_{LA} denotes the electron density of the Lewis acid and ρ_{LB} corresponds to the electron density of the Lewis base. Accordingly, ρ_{d} is defined as the electron density difference between the frustrated Lewis pair complex and the isolated monomeric species. In this work, to observe the maps of electron density difference clearly, we place the central atoms B and C of the FLPs and the outermost halogen ligand atom of the Lewis acid in the same position. Consequently, the MFDD map on the plane defined by these three atoms is generated as shown in Figure 3. The electron density accumulation and depletion are indicated by distinct color variations. As indicated by the color scale, the electron density is continuously redistributed from depletion regions (blue) to accumulation regions (red), thus providing a direct visualization of both the direction and magnitude of electron migration between the FLPs.

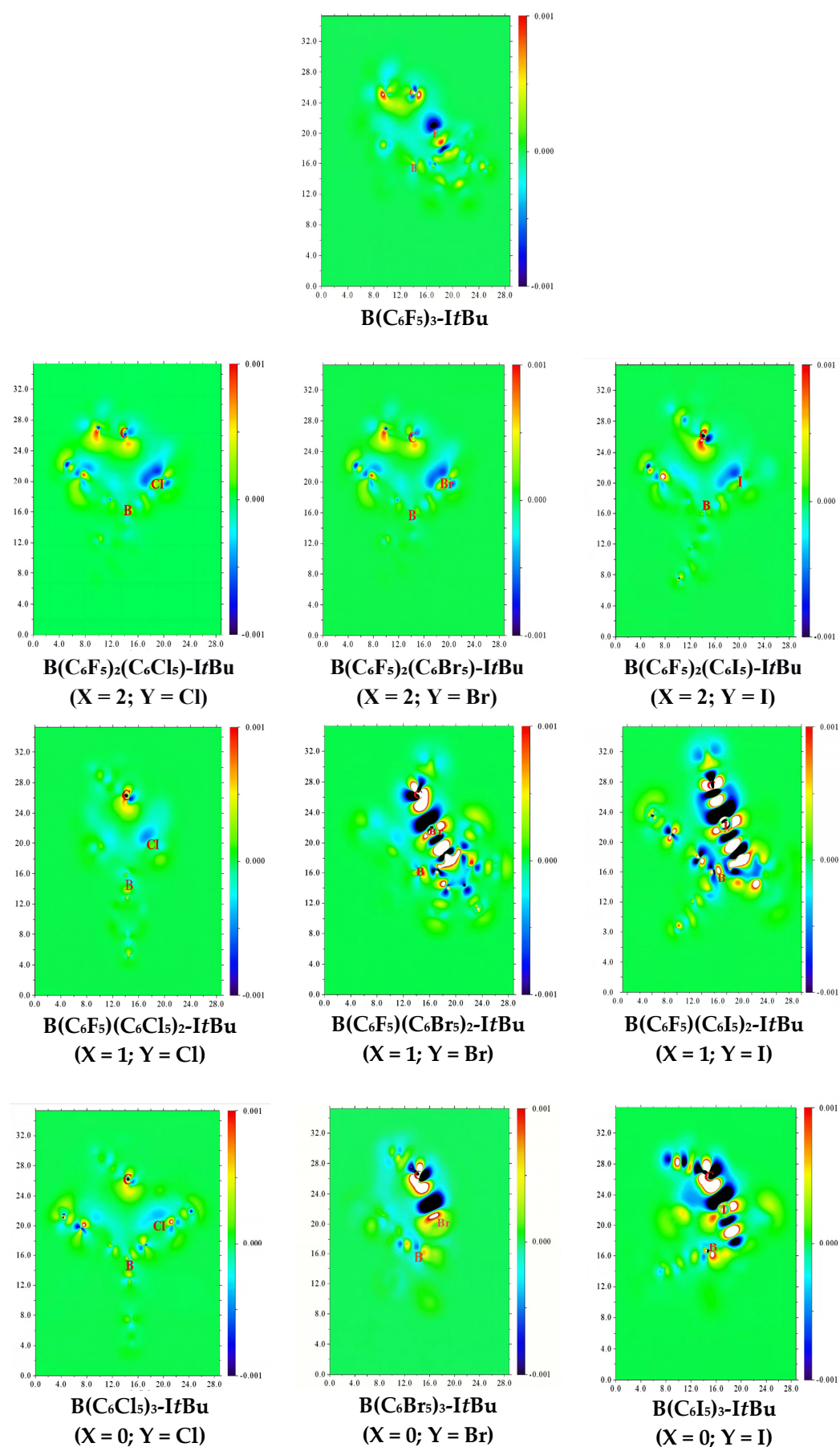


Figure 3. The MFDD analysis of the FLPs B(C₆F₅)₃-ItBu and B(C₆F₅)_x(C₆Y₅)_{3-x}-ItBu (x = 0, 1, 2; Y = Cl, Br, I).

To our surprise, significant electron density changes exist between the outermost halogen ligand atoms of the Lewis acid and the C atom of the Lewis base, as shown in Figure 3. For $B(C_6F_5)_3$ -*ItBu* and $B(C_6F_5)_2(C_6Y_5)$ -*ItBu* ($Y = Cl, Br, I$), the decreases in electron density are observed around the outermost halogen atom F, Cl, Br, I accompanied by a corresponding increase in electron density on the C atom. There is almost no change in the electron density on the B atom of the Lewis acid. Based on the intensity of electron transfer, the ligand effect of $B(C_6F_5)_3$ -*ItBu* and $B(C_6F_5)_2(C_6Cl_5)$ -*ItBu* is more significant than that of $B(C_6F_5)_2(C_6Y_5)$ -*ItBu* ($Y = Br, I$), but the difference is not substantial. This phenomenon indicates that the interaction between the B atom and the C atom is weak, while the ligand effect between the outermost halogen atom of the Lewis acid and the C atom is significant and cannot be ignored.

For $B(C_6F_5)_3$ -*ItBu* and $B(C_6F_5)_x(C_6Y_5)_{3-x}$ -*ItBu* ($x = 0, 1; Y = Cl, Br, I$), when $Y = Br, I$, the pronounced electron density depletion is observed on the outermost halogens atoms Br and I, accompanied by a significant electron density accumulation around the corresponding C atom. This implies that, compared with $B(C_6F_5)_3$ -*ItBu*, the ligand effect between the Lewis acid and base fragments becomes significantly enhanced. However, when $Y = Cl$, the relatively weak electron transfer is observed between the outermost halogen atom Cl and the corresponding C atom. Nevertheless, it remains larger than the electron migration between B and C.

Specifically, the ligand effect between the outermost halogen atom of $B(C_6F_5)_3$, $B(C_6F_5)_x(C_6Y_5)_{3-x}$ ($x = 0, 1, 2; Y = Cl, Br, I$) and the C atom of *ItBu* is considerably larger than the interaction between the central B atom and C atom. As shown in Figure 3, the ligand effects of $B(C_6F_5)_3$ -*ItBu*, $B(C_6F_5)_2(C_6Y_5)$ -*ItBu* ($Y = Cl, Br, I$) and $B(C_6F_5)_x(C_6Cl_5)_{3-x}$ -*ItBu* ($x = 0, 1$) are weaker than that of $B(C_6F_5)_x(C_6Y_5)_{3-x}$ -*ItBu* ($x = 0, 1; Y = Br, I$). According to the sobEDA results, which better reflect the nature of the interaction, the various physical quantities ΔE_{els} , ΔE_{xrep} , ΔE_{orb} and ΔE_{dc} influencing $B(C_6F_5)_x(C_6Cl_5)_{3-x}$ -*ItBu* ($x = 0, 1$) are all larger compared with those of $B(C_6F_5)_2(C_6Y_5)$ -*ItBu* ($Y = Cl, Br, I$). Ultimately, the ΔE_{int} of $B(C_6F_5)_2(C_6Y_5)$ -*ItBu* ($Y = Cl, Br, I$) is comparable to that of $B(C_6F_5)_3$ -*ItBu*. Therefore, modified $B(C_6F_5)_2(C_6Y_5)$ ($Y = Cl, Br, I$) is the most favorable for the construction of novel FLPs.

4. Conclusions

In this study, a theoretical computational approach is employed to systematically examine substituent effects in the prototypical $B(C_6F_5)_3$, achieved through stepwise replacement of the aryl groups with $-C_6Cl_5$, $-C_6Br_5$ and $-C_6I_5$. After association with the *ItBu*, the resulting FLPs are systematically analyzed to evaluate changes in their ΔE_{int} . Further sobEDA analysis, orbital analysis, and MFDD analysis reveal the nature of the substituent effect on the ΔE_{int} of the FLPs. The results indicate that, for $B(C_6F_5)_3$ -*ItBu*, $B(C_6F_5)_x(C_6Y_5)_{3-x}$ -*ItBu* ($x = 0, 1, 2; Y = Cl, Br, I$), the key role is played not by the direct interaction between the central atoms B and C but by the ligand effect between the outermost halogen atom of $B(C_6F_5)_3$ and $B(C_6F_5)_x(C_6Y_5)_{3-x}$ ($x = 0, 1, 2; Y = Cl, Br, I$) and the C atom of *ItBu*. This leads to a gradual enhancement in the ΔE_{int} between the modified $B(C_6F_5)_x(C_6Y_5)_{3-x}$ ($x = 0, 1, 2$) and *ItBu* in the order $Y = Cl, Br, I$. For the same halogen substitution, FLPs with $x = 1$ or 0 exhibit highly similar atomic types and distances in the interaction region, resulting in comparable ΔE_{int} that are both larger than that of the FLPs with $x = 2$. Consequently, $B(C_6F_5)_2(C_6Y_5)$ -*ItBu* ($Y = Cl, Br, I$) exhibits a ΔE_{int} comparable to that of $B(C_6F_5)_3$ -*ItBu*, rendering modified $B(C_6F_5)_2(C_6Y_5)$ ($Y = Cl, Br, I$) more suitable for the development of novel FLPs.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst16040236/s1>, Figure S1: The positive region of ESP (Kcal/mol) outside the B atom of the optimized Lewis acid monomer and the negative region (kcal/mol) of ESP outside the C atom of the optimized Lewis base monomer; Figure S2: The optimized geometries of the FLPs, the relative energies relative to the global minimum structure (kcal/mol) are shown; Figure S3: Schematic representations of the LUMO and HOMO localized on the B and C in the FLPs. Table S1: The absolute change in the zero-point energies of the FLPs monomers before and after association(kcal/mol); Table S2: Structural coordinates of the FLPs.

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