

## Article

# $\pi$ -Hole Triel Bonds between $\text{TrPhX}_2$ ( $\text{Tr} = \text{B}, \text{Al}, \text{Ga}$ ; $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{CH}_3, \text{OH}$ ) and $(\text{BH})_2(\text{NHC})_2$ ( $\text{NHC} = \text{Nitrogen-Heterocyclic Carbene}$ )

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**Abstract:** The  $\pi$ -hole triel bond formed by  $(\text{BH})_2(\text{NHC})_2$  (NHC denotes nitrogen-heterocyclic carbene) and  $\text{TrPhX}_2$  ( $\text{Tr} = \text{B}, \text{Al}$ , and  $\text{Ga}$ ;  $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{CH}_3$ , and  $\text{OH}$ ) was investigated computationally, with the  $\text{B}=\text{B}$  bond in  $(\text{BH})_2(\text{NHC})_2$  being the electron donor. A large interaction energy ensures that the complex is quite stable. When the substituent  $\text{X}$  in the electron acceptor is fixed, the magnitude of the interaction energy varies with the identity of the  $\text{Tr}$  atom. When  $\text{Tr}$  is  $\text{Al}$  or  $\text{Ga}$ , the interaction energy is stronger than when it is  $\text{B}$ . With an increase in the electron-withdrawing ability of the substituents, the interaction energy shows distinct changes. When  $\text{Tr}$  is  $\text{B}$  or  $\text{Al}$ , the interaction energy varies as  $\text{TrPhBr}_2 > \text{TrPhCl}_2 > \text{TrPhF}_2$ , which is different from the order of their positive electrostatic potentials. When  $\text{Tr} = \text{Ga}$ , the interaction energy hardly changes with an increase in the electronegativity of the halogen atoms. For  $\text{CH}_3$  and  $\text{OH}$  substitution, larger interaction energies were obtained, with the interaction energy for the  $\text{OH}$  substituent being the largest. The main interactions in these systems are a triel bond and an  $\text{X} \cdots \text{H}$  hydrogen bond. When the substituents are fixed, the interaction energy of the triel bond increases in the order  $\text{AlPhX}_2 < \text{GaPhX}_2 < \text{BPhX}_2$ , which is different from the order of the positive electrostatic potentials on the  $\text{Tr}$  atom in  $\text{TrPhX}_2$ . When  $\text{X}$  is a halogen atom, the interaction energy of the triel bond decreases in the order  $\text{Br} > \text{Cl} > \text{F}$ , which is opposite to the trend for the positive electrostatic potentials on  $\text{Tr}$  in  $\text{TrPhX}_2$ . In most complexes, the interaction energy for the hydrogen bond is less than that for the triel bond; there is no hydrogen bond in the methyl-substituted complex. In general, the interaction energy of the hydrogen bonds increases with an increase in the electronegativity of the halogen atoms.

**Keywords:** triel bonds; hydrogen bonds;  $\pi$ -hole; AIM



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## 1. Introduction

As a basic concept in the field of supramolecular chemistry, non-covalent interactions have usually been a main research focus, with important applications in crystal materials, catalysis, biological systems, molecular recognition, molecular assembly, and other fields [1–4]. Non-covalent interactions may be conveniently divided into several categories depending on the type of Lewis acid involved. The interaction arising from a group 13 element acting as a Lewis acid center and a Lewis base is called a triel bond (TrB). Because of its unique molecular structure and wide variability, TrBs have wide applications in asymmetric catalysis, material construction, dye synthesis, molecular recognition, hydrogen storage, and other fields [5–7]. The electron-deficient p orbitals of group 13 elements give rise to a  $\pi$ -hole, which is a positive electrostatic potential region above the triangular plane containing the group 13 element and the three nearest atoms to which it is bonded. This region has an attraction to electrons and can theoretically interact with the negative potential region of a Lewis base to form a TrB.

As early as the 1960s, TrB complexes were thought to be a theoretical possibility, but there was no concept of a TrB at that time. A 1:1 van der Waals complex was found in the infrared spectrum study of a mixture of ethylene and propylene with  $\text{BF}_3$ , in which an electron-deficient  $\text{BF}_3$  was combined with a  $\text{C}=\text{C}$  double bond [8]. Subsequent studies found similar effects between  $\text{BF}_3$  and other Lewis bases ( $\text{NH}_3$ ,  $\text{HCN}$ ,  $\text{NCPh}$ , and  $\text{N}(\text{CH}_3)_3$ ) [9–11]. In addition, very weak coordination bonds in the gas phase and very short N–B distances in the solid phase were found in the spectral and theoretical studies of  $\text{X}-\text{CH}_3\text{CN}-\text{BF}_3$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ), which suggested the existence of an N–B interaction [12]. Grabowski's computational work on the complexes formed by  $\text{TrF}_3$  ( $\text{Tr} = \text{B}$  and  $\text{Al}$ ) and a Lewis base found that the N of linear  $\text{HCN}$  and  $\text{N}_2$ , acting as Lewis base centers, interacted with B and Al in a direction perpendicular to the  $\text{BF}_3$  and  $\text{AlF}_3$  planes to form a  $\text{C}_{3v}$  symmetric complex [13]. In a subsequent study, Grabowski defined this interaction as a TrB [14]. It was also found that this interaction is often very strong, and its stability mainly depends on the charge transfer caused by the coordination. The properties of Lewis base centers, the ability of substituents to absorb electrons, and the feedback bond effect are also closely related to the strength of the interaction [14]. The situation for other group 13 elements acting as Lewis acid centers has also been studied; the TrB formed by B appears to be the weakest, and different Tr atoms exhibit different properties as Lewis acid centers.

Neutral electron lone pair molecules are a common TrB electron donor, the most typical of which is related to research on the N–Lewis bases. The TrB formed by  $\text{NCH}$ ,  $\text{NH}_3$ , and  $\text{N}_2$  as electron donors has been extensively studied using theoretical calculations [13,14].  $\text{NH}_3$  is the strongest electron donor and  $\text{N}_2$  is the weakest. The N in pyrazine can form stable TrBs, and the substituent effect on the strength of TrBs has also been studied. The change in the relative stabilities of Lewis acids containing Al and Ga is consistent with the electron-withdrawing ability of the substituents, i.e.,  $\text{F} > \text{Cl} > \text{Br} > \text{H}$ , whereas B shows the opposite trend. Covalency also plays an important role in the formation of TrBs, and the orbital effect on B is stronger than on Al and Ga [15]. Transition metals (TMs) contain more lone-pair electrons. The shorter B–TM distance and the pyramidalization of the chemical environment around group 13 atoms in their complexes suggest the existence of strong TrBs [16]. The NPA analysis of the Au–B interaction in  $[\text{PBCy}_2\text{AuCl}]$  and  $[(\text{PBFlu})\text{AuCl}]$  shows that there is charge transfer from Au to B, and that the amount of charge transfer is inversely related to the interaction distance [17,18]. Theoretical studies of  $\text{AuCl}_2-\text{BX}_3$  ( $\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) indicate that orbital interactions dominate the TrBs of most systems [19].

The interactions of  $\text{CN}^-$ ,  $\text{NO}^-$ ,  $\text{OH}^-$  and  $\text{HF}$ ,  $\text{HCl}$ , and  $\text{XF}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) with  $\text{TrF}_3$  ( $\text{Tr} = \text{Al}$  and  $\text{Ga}$ ) have also been studied. When  $\text{TrF}_3$  is surrounded by 2–4 ligand molecules, the structures formed differ according to the number of ligands. With an increase in the number of ligands, when forming triel bonds with  $\text{TrF}_3$ , the ligands tend to form a cage-like structure around the central negative ion, and the triel bonds thus formed tend to be stronger than those formed by hydrogen or halogen bonds [20].

In addition, the  $\pi$ -electron system is also a good electron donor. Although there are few reports on its participation in the formation of TrBs, it is often found to have a strong interaction with Lewis acids, such as the  $\text{A}-\text{H}\cdots\pi$  hydrogen bond formed by  $\pi$ -electrons as a proton acceptor [21]. The theoretical study of the interaction between  $\text{AlX}_3$ ,  $\text{BX}_3$  ( $\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}$ ), and ethylene/acetylene found that strong TrBs are usually formed with a partially covalent character and that the orbital interaction originates from the formation of a 3c-2e orbital [22].

Because B is electron-deficient, it has several different bonding modes, such as those via the double bond formed in transition metal–boron complexes [23]. In the past few decades, the study of homonuclear and heteronuclear polybonding molecules based on the group IIIA–V elements has been widely undertaken and has become a research “hot topic” in academic and industrial laboratories [24–27]. It is difficult to establish multiple bonds between two group IIIA atoms (B, Al, Ga, In, and Tl) because of their electron-deficient properties. However, the synthesis and separation of diboron compounds with B–B multi-bonds have been successfully realized by many chemists. In 2007, carbene stabilization technology [28] was applied to the reduction of haloboranes and the synthesis

of boron polybonds [29]. Through the reduction of nitroheterocyclic carbene-stabilized tribromoboranes, via the catalysis of potassium-containing graphite, the neutral bicarbene dibromodiene containing B-B bonds was prepared and separated. The B-B separation is very short (1.561 Å), indicating double bonds between the two B atoms.

Braunschweig et al. carried out the reaction of diborodivane or diborotellurine [30], respectively. Because carbon is more electronegative, it cannot participate in the reduction of elements with lower electronegativity, but the high reducibility of the B=B double bond can stimulate the reaction of C with Se and Te. The ability to donate electrons to multiple bonds between boron atoms suggests that diborides can be used as nucleophilic reagents. Diboride can attack one of the two Te atoms of diaryl telluride to form a salt composed of diborotelluride cations and aromatic telluride anions.

By studying the complex formed by compounds with M=M (M = B, Al, Ga, In, and Tl) double bonds and two ligands with large spatial volumes ( $L_1L_2M = ML_1L_2$  ( $L_1 = tBu_2MeSi$  and  $L_2 = NHCiPr$ )), it was found that the central element M plays an important role in its geometry. Computations show that with an increase in the central M atomic number, the bond distances (M-M, M-C, and M-Si) increase and the dihedral angles ( $M_b-M_a-Si_a-C_a$  and  $M_a-M_b-Si_b-C_b$ ) decrease [31].

There are few studies on the formation of TrBs by  $\pi$ -electron systems acting as electron donors, and, through an extensive literature search, it was found that the B=B double bond can participate in reactions as an electron donor, which opens up the possibility of a B=B double bond acting as a Lewis base to form TrBs. In the present work, we performed a theoretical study of TrBs with  $(BH)_2(NHC)_2$  (NHC is a nitrogen heterocyclic carbene) as a Lewis base and  $TrPhX_2$  (Tr = B, Al, and Ga; X = F, Cl, Br,  $CH_3$ , and OH) as a Lewis acid. The factors affecting the strength of a TrB were investigated by changing the Lewis acid center and substituents, and this TrB was analyzed by using MEP, NCI, NBO, and AIM computational methods.

## 2. Computational Methodology

All calculations were performed at the M06-2X/aug-cc-pVDZ [32,33] level of theory using Gaussian 09 [34]. The geometries of all species were fully optimized, and the ensuing frequency calculations confirmed the optimized dimers as true minima by the absence of any imaginary frequencies. The interaction energy was computed as the difference between the energy of each complex and the sum of the monomer energies (evaluated at the geometries that they adopted within the optimized complex). This quantity was corrected for the basis set superposition error (BSSE) by the counterpoise correction procedure advocated by Boys and Bernardi [35].

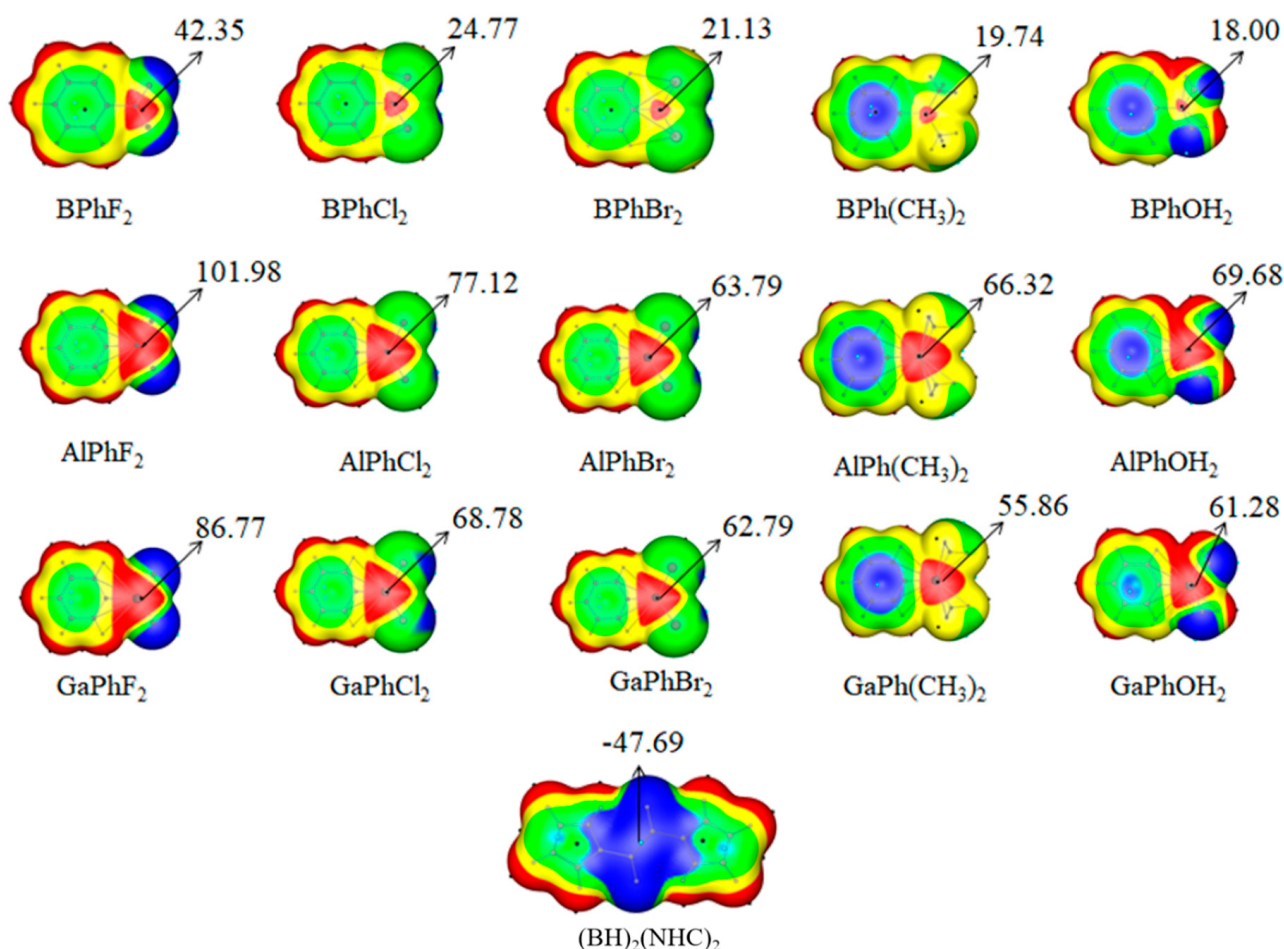
The wave function was calculated by the WFA-SAS program [36] to obtain the molecular electrostatic potential (MEP) diagrams of the monomers on the 0.001 a.u. isosurface in order to predict the interaction site for complex binding. Using the atoms in the molecule (AIM) theory [37], selected properties at the intermolecular bond critical points (BCPs) were computed, including the electron density, Laplacian, and energy density using the AIM2000 program [38] and the Multiwfn program [39]. The non-covalent interaction (NCI) figure was obtained by the Multiwfn and VMD programs [40]. The charge transfer between the interacting monomers was analyzed by the NBO 3.0 program using the natural population analysis (NPA) [41].

## 3. Results

### 3.1. Analysis of Molecular Electrostatic Potential

The first three rows of Figure 1 show the electrostatic potential diagrams for each electron acceptor  $TrPhX_2$  molecule. It can be seen that  $TrPhX_2$  has a red area above and below the Tr atom, with the most positive electrostatic potential value marked on the figure. The positive electrostatic potential values differ for different Tr atoms. When the substituent X is fixed, the electrostatic potential value is largest when Tr is Al, the second largest for Ga,

and the smallest for B, due mainly to the varying electronegativities of the Tr atoms. B has the largest electronegativity (2.0), followed by Ga (1.6) and Al (1.5). The trend for the electrostatic potentials is opposite to that for the varying electronegativity of the Tr atoms [14], which is consistent with previous research on TrBs [13,14]. The greater the electronegativity of Tr, the smaller the  $\pi$ -hole on the atom. Different substituents for X will also affect the maximum positive electrostatic potential on the Tr atom. When Tr is B, the maximum positive electrostatic potential value on Tr decreases in the order  $F > Cl > Br > CH_3 > OH$ . When Tr is Al and Ga, the maximum positive electrostatic potential value also changes in the same way for the halogen substituents (i.e.,  $F > Cl > Br$ ), but increases going from the halogens to the  $CH_3$  substituents to the OH substituents. The effect of halogen substitution on the positive electrostatic potential of Tr can be explained by the electronegativity of the halogen atom. The greater the electronegativity of the halogen atom, the greater the positive electrostatic potential on the Tr atom. However,  $CH_3$  and OH tend to be electron-donating, so the most positive electrostatic potential on Tr for these substituents tends to be smaller than that for the F substituent.

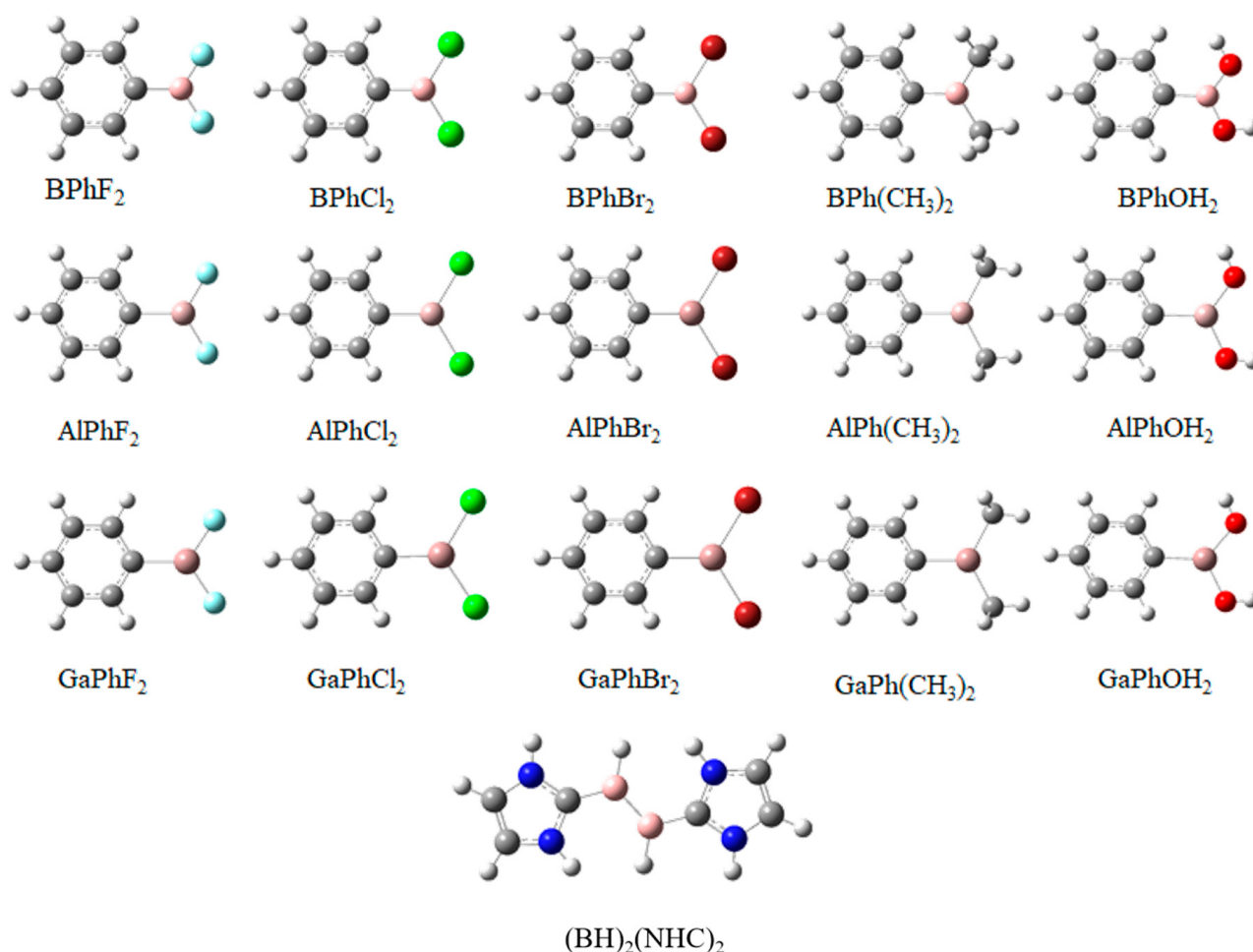


**Figure 1.** MEP maps of  $TrPhX_2$  and  $(BH)_2(NHC)_2$ . The red regions represent the most positive MEPS, the yellow regions the less positive MEPS, the green regions represent negative MEPS, and the blue regions represent the most negative MEPS. All MEP values in kcal/mol.

The electrostatic potential diagram of the  $(BH)_2(NHC)_2$  molecule is also shown in Figure 1. It can be seen that the B=B double bond is surrounded by a blue area, indicating that it has a negative electrostatic potential, with a value of  $-47.69$  kcal/mol. When the blue electrostatic potential region on the  $(BH)_2(NHC)_2$  molecule is close to the red electrostatic potential region on the  $TrPhX_2$  molecule, a TrB interaction forms.

### 3.2. Structures

The first three rows in Figure 2 show the optimized geometry for each electron acceptor  $\text{TrPhX}_2$ . The  $\text{TrPhX}_2$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ) molecules have  $\text{C}_{2v}$  symmetry, with the two  $\text{X}$  substituents in the same plane as the benzene molecule. The last row in the figure shows the optimized structure of the electron donor  $(\text{BH})_2(\text{NHC})_2$ , which is planar.



**Figure 2.** Structures of  $\text{TrPhX}_2$  and the  $(\text{BH})_2(\text{NHC})_2$  monomer. For the color scheme: light blue = F, green = Cl, dark red = Br, grey = C, white = H, blue = N, O = light red, Tr = pink.

The optimized structures of these neutral closed-shell dimers are shown in Figure 3. It can be observed from the figure that the  $\text{Tr}$  atom in  $\text{TrPhX}_2$  is located above the bond joining the two  $\text{B}$  atoms, and the two monomers have different degrees of deformation due to the interaction, especially the  $\text{TrPhX}_2$ , which changes from its original planar structure to an umbrella-like structure. When the  $\text{X}-\text{Tr}-\text{C}$  angle ( $\alpha$ ) is  $120^\circ$ ,  $\text{TrPhX}_2$  is planar. The difference between  $\alpha$  and  $120^\circ$  can therefore indicate the degree of the geometric deformation of  $\text{TrPhX}_2$ . Table 1 lists the  $\alpha$  values, which range between  $107.78$  and  $114.97^\circ$ . The degree of deformation can be represented by the deviation from  $120^\circ$  ( $\Delta\alpha$ ). The greater the absolute value of  $\Delta\alpha$ , the greater the deformation. When  $\text{X}$  is a halogen,  $\Delta\alpha$  varies in the order  $\text{F} < \text{Cl} < \text{Br}$ . For  $\text{CH}_3$  and  $\text{OH}$  substituents,  $\Delta\alpha$  is larger for the latter. When  $\text{X}$  is fixed, the  $\text{BPhX}_2$  complexes have the largest  $\alpha$ , indicating that they are easier to deform than the  $\text{Al}$  and  $\text{Ga}$  analogs.  $(\text{BH})_2(\text{NHC})_2$  also changes from a planar to a non-planar structure. The degree of deformation can also be measured by the deformation energy, which is also listed in Table 1. The larger the deformation energy value, the more significant the deformation on complexation, with values ranging between 10 and 48 kcal/mol, indicating

that the corresponding molecules suffer large distortions. The deformation energy of  $(\text{BH})_2(\text{NHC})_2 \cdots \text{BPh}(\text{OH})_2$  is the largest, attaining a value of 47.92 kcal/mol.

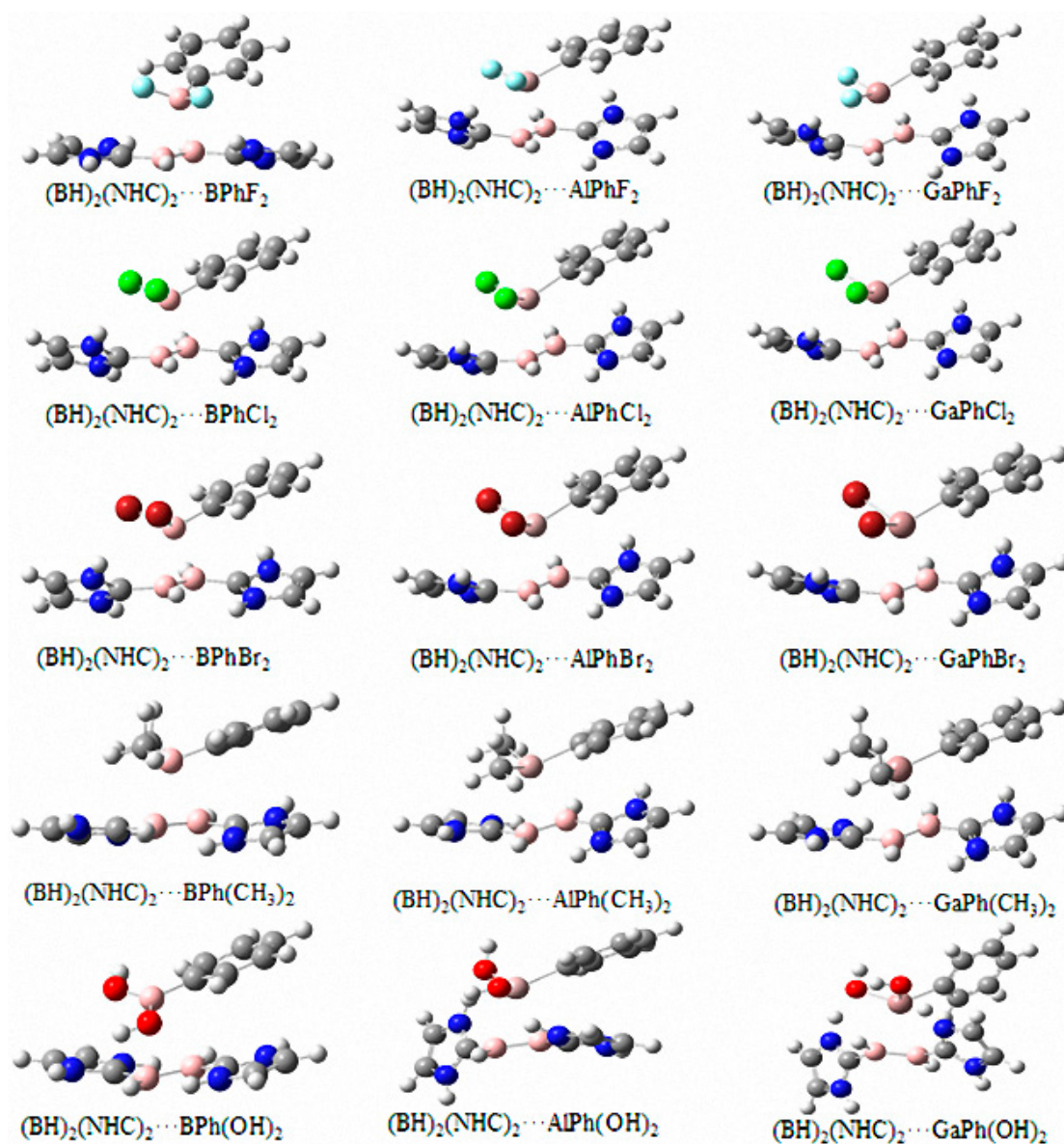


Figure 3. Optimized structures of  $(\text{BH})_2(\text{NHC})_2 \cdots \text{TrPhX}_2$ .

Table 2 lists the intermolecular distances in the complexes, where  $R_1$  and  $R_2$  represent the binding distance between the Tr atom and the two B atoms,  $R(\text{X}-\text{H})$  represents the distance between the F, Cl, Br (of  $\text{TrPhX}_2$ ), and the H (in NHC), or the binding distance between C in  $\text{CH}_3$  or O in OH and the H (in NHC),  $R(\text{H}-\text{N})$  represents the binding distance between the H on the benzene ring and N (in NHC),  $R(\text{C}-\text{H})$  represents the binding distance between the C on the benzene ring and H (in NHC), and  $R(\text{C}-\text{N})$  represents the binding distance between the C on the benzene ring and N (in NHC). The distance between the Tr atom and the two B atoms is almost the same, ranging between 2.1 and 2.6 Å. This distance is much smaller than the sum of the van der Waals radii of the Tr and the B atoms. For the substituent  $\text{X} = \text{F}, \text{Cl}, \text{or Br}$ , the  $\text{Tr} \cdots \text{B}$  distance increases in the order  $\text{B} < \text{Ga} < \text{Al}$ , which is not consistent with the electronegativity trend for Tr atoms; the electronegativity of Tr varies as  $\text{B} > \text{Ga} > \text{Al}$ , which is the same trend for their maximum positive electrostatic potentials. When X is methyl or hydroxyl, the binding distance increases in the order of  $\text{B} < \text{Al} < \text{Ga}$ , which reverses the electronegativity trend for Tr

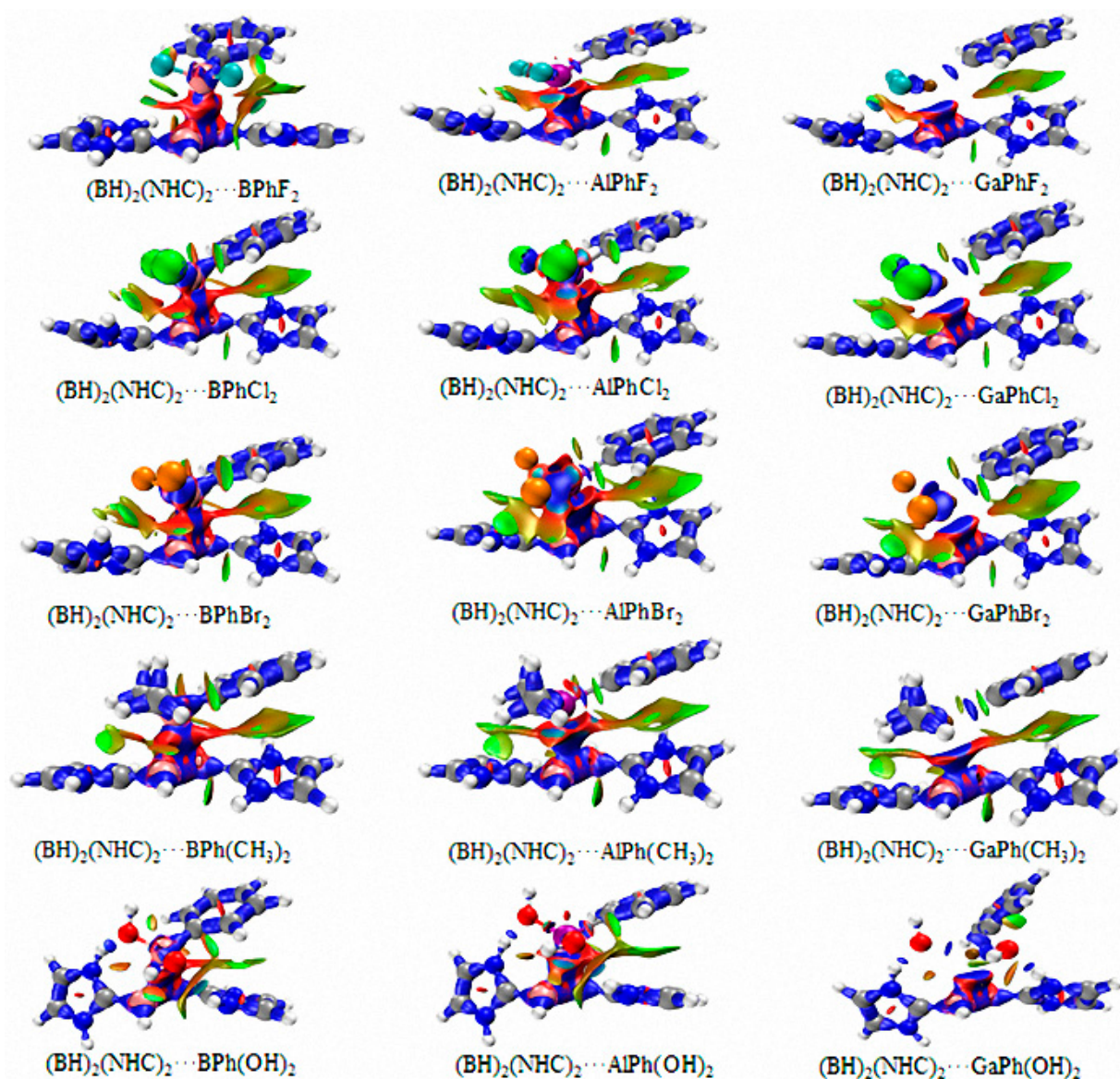
atoms. For R(X–H), except for the methyl substituent, this distance is smaller than the sum of the van der Waals radii of the corresponding atoms, indicating that there is an interaction between the two, namely a weak hydrogen bond. The R(H–N) value is larger than the sum of the van der Waals radii of the corresponding atoms, indicating that there is no attraction between the two atoms, but there are yellow and green overlapping areas between the two atoms in the NCI diagram (Figure 4). In addition to the hydroxyl group, the R(C–H) value is less than the sum of the van der Waals radii of the corresponding atoms, suggesting an attraction between the C and H atoms. In (BH)<sub>2</sub>(NHC)<sub>2</sub>⋯AlPhF<sub>2</sub>, (BH)<sub>2</sub>(NHC)<sub>2</sub>⋯AlPh(CH<sub>3</sub>)<sub>2</sub>, (BH)<sub>2</sub>(NHC)<sub>2</sub>⋯AlPh(OH)<sub>2</sub>, and (BH)<sub>2</sub>(NCH)<sub>2</sub>⋯GaPhBr<sub>2</sub>, the R(C–N) value is also less than the sum of the van der Waals radii of the corresponding atoms, indicating the existence of attractive interactions.

**Table 1.** Deformation energy (DE, kcal/mol), X–Tr–C angle ( $\alpha$ , deg), its difference relative to 120° ( $\Delta\alpha$ , deg), and dipole moment ( $\mu$ , D) for the (BH)<sub>2</sub>(NHC)<sub>2</sub>⋯TrPhX<sub>2</sub> dimers.

| Complexes                                                                 | DE    | $\alpha$ | $\Delta\alpha$ | $\mu$ |
|---------------------------------------------------------------------------|-------|----------|----------------|-------|
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯BPhF <sub>2</sub>                   | 29.46 | 112.11   | −7.89          | 5.08  |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯BPhCl <sub>2</sub>                  | 41.52 | 109.94   | −10.06         | 6.45  |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯BPhBr <sub>2</sub>                  | 41.89 | 109.50   | −10.50         | 7.36  |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯BPh(CH <sub>3</sub> ) <sub>2</sub>  | 23.84 | 110.50   | −9.50          | 5.12  |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯BPh(OH) <sub>2</sub>                | 47.92 | 109.90   | −10.10         | 1.48  |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯AlPhF <sub>2</sub>                  | 20.76 | 113.49   | −6.51          | 5.10  |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯AlPhCl <sub>2</sub>                 | 21.88 | 110.96   | −9.04          | 6.79  |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯AlPhBr <sub>2</sub>                 | 21.62 | 110.30   | −9.70          | 7.28  |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯AlPh(CH <sub>3</sub> ) <sub>2</sub> | 11.23 | 113.68   | −6.32          | 4.97  |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯AlPh(OH) <sub>2</sub>               | 31.19 | 108.39   | −11.61         | 4.97  |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯GaPhF <sub>2</sub>                  | 25.25 | 114.97   | −5.03          | 6.00  |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯GaPhCl <sub>2</sub>                 | 23.82 | 111.05   | −8.95          | 7.35  |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯GaPhBr <sub>2</sub>                 | 23.22 | 110.12   | −9.88          | 7.79  |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯GaPh(CH <sub>3</sub> ) <sub>2</sub> | 10.68 | 111.37   | −8.63          | 4.88  |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯GaPh(OH) <sub>2</sub>               | 47.27 | 107.78   | −12.22         | 5.81  |

**Table 2.** Binding distances (R, Å) of different types of interactions in (BH)<sub>2</sub>(NCH)<sub>2</sub>⋯TrPhX<sub>2</sub>.

| Complexes                                                                 | R <sub>1</sub> | R <sub>2</sub> | R(X–H) | R(H–N) | R(C–H) | R(C–N) |
|---------------------------------------------------------------------------|----------------|----------------|--------|--------|--------|--------|
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯BPhF <sub>2</sub>                   | 2.211          | 2.184          | 2.065  | 2.792  | 2.802  | 3.501  |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯BPhCl <sub>2</sub>                  | 2.136          | 2.108          | 2.637  | 3.291  | 2.715  | 3.404  |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯BPhBr <sub>2</sub>                  | 2.110          | 2.091          | 2.701  | 3.270  | 2.719  | 3.385  |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯BPh(CH <sub>3</sub> ) <sub>2</sub>  | 2.166          | 2.149          | 3.072  | 3.256  | 2.725  | 3.382  |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯BPh(OH) <sub>2</sub>                | 2.120          | 2.291          | 2.470  | 3.341  | 3.834  | 3.399  |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯AlPhF <sub>2</sub>                  | 2.407          | 2.416          | 2.149  | 3.901  | 2.541  | 3.152  |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯AlPhCl <sub>2</sub>                 | 2.393          | 2.426          | 2.648  | 3.647  | 2.795  | 3.745  |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯AlPhBr <sub>2</sub>                 | 2.388          | 2.426          | 2.801  | 3.650  | 2.670  | 3.501  |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯AlPh(CH <sub>3</sub> ) <sub>2</sub> | 2.513          | 2.491          | 3.275  | 3.003  | 2.650  | 3.252  |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯AlPh(OH) <sub>2</sub>               | 2.343          | 2.510          | 1.648  | 3.075  | 3.423  | 3.353  |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯GaPhF <sub>2</sub>                  | 2.385          | 2.399          | 1.899  | 3.730  | 2.663  | 3.579  |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯GaPhCl <sub>2</sub>                 | 2.390          | 2.415          | 2.577  | 3.658  | 2.679  | 3.763  |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯GaPhBr <sub>2</sub>                 | 2.389          | 2.415          | 2.756  | 3.609  | 2.707  | 3.278  |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯GaPh(CH <sub>3</sub> ) <sub>2</sub> | 2.538          | 2.515          | 3.274  | 3.269  | 2.707  | 3.694  |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ⋯GaPh(OH) <sub>2</sub>               | 2.416          | 2.359          | 1.564  | 3.912  | 3.559  | 4.161  |



**Figure 4.** NCI diagram of  $(\text{BH})_2(\text{NHC})_2 \cdots \text{TrPhX}_2$ . Blue, red, and green regions denote strong attractive, strong repulsion, and weak attractive interactions, respectively.

From the optimized structures in Figure 3, it can be seen that the two B atoms in  $(\text{BH})_2(\text{NHC})_2$  tend to combine with the Tr atom connected to the benzene ring. The two NHC ligands in  $(\text{BH})_2(\text{NHC})_2$  are arranged on opposite sides of the B=B double bond in a trans configuration. These two NHC ligands can provide charge density for the B=B double bond, thus increasing its  $\pi$ -electron density and thereby enabling the formation of a strong TrB. The binding distances of most  $\text{Tr} \cdots \text{B}$  suggest partial covalency of the TrB.

Table 3 lists the bond length changes for the B=B and Tr-X bonds and the frequency shift of the stretching vibration of the corresponding bonds. For all complexes, the B=B bond length change is quite small, some lengthen and some shorten, which is characteristic of B=B double bonds. Except for  $(\text{BH})_2(\text{NHC})_2 \cdots \text{BPhF}_2$ ,  $(\text{BH})_2(\text{NHC})_2 \cdots \text{BPhCl}_2$ ,  $(\text{BH})_2(\text{NHC})_2 \cdots \text{BPh(OH)}_2$ ,  $(\text{BH})_2(\text{NHC})_2 \cdots \text{AlPhF}_2$ ,  $(\text{BH})_2(\text{NHC})_2 \cdots \text{AlPh(CH}_3)_2$ , and  $(\text{BH})_2(\text{NHC})_2 \cdots \text{AlPh(OH)}_2$ , the length of the B=B bond in the other complexes is extended, but this elongation is not large. Generally, the elongation causes a red shift of the vibrational stretching frequency of the corresponding bond. However, the B=B vibrational frequency is blue-shifted in most structures, though the blue shift is quite small.

**Table 3.** Change of B=B and Tr–X bond lengths ( $\Delta r$ , Å) and frequency shifts of B=B and Tr–X stretching vibrations ( $\Delta \nu$ ,  $\text{cm}^{-1}$ ) in the complexes.

| Complexes                                                                   | $\Delta r$ (B=B) | $\Delta r$ (Tr–X) | $\Delta \nu$ (B=B) | $\Delta \nu$ (Tr–X) |
|-----------------------------------------------------------------------------|------------------|-------------------|--------------------|---------------------|
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ···BPhF <sub>2</sub>                   | −0.006           | 0.078             | −6                 | −222                |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ···BPhCl <sub>2</sub>                  | −0.001           | 0.139             | 7                  | −355                |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ···BPhBr <sub>2</sub>                  | 0.002            | 0.160             | 5                  | −288                |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ···BPh(CH <sub>3</sub> ) <sub>2</sub>  | 0.000            | 0.056             | −1                 | −151                |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ···BPh(OH) <sub>2</sub>                | −0.002           | 0.099             | −11                | −205                |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ···AlPhF <sub>2</sub>                  | −0.002           | 0.054             | 10                 | −163                |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ···AlPhCl <sub>2</sub>                 | 0.001            | 0.096             | 7                  | −270                |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ···AlPhBr <sub>2</sub>                 | 0.002            | 0.109             | 6                  | −287                |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ···AlPh(CH <sub>3</sub> ) <sub>2</sub> | −0.001           | 0.040             | 1                  | −159                |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ···AlPh(OH) <sub>2</sub>               | −0.001           | 0.079             | −16                | −39                 |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ···GaPhF <sub>2</sub>                  | 0.004            | 0.074             | 10                 | −61                 |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ···GaPhCl <sub>2</sub>                 | 0.006            | 0.113             | 8                  | −409                |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ···GaPhBr <sub>2</sub>                 | 0.007            | 0.126             | 6                  | −104                |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ···GaPh(CH <sub>3</sub> ) <sub>2</sub> | 0.002            | 0.040             | 1                  | −30                 |
| (BH) <sub>2</sub> (NHC) <sub>2</sub> ···GaPh(OH) <sub>2</sub>               | 0.004            | 0.115             | −13                | −141                |

The Tr–X bond length is elongated in the dimer relative to the monomer, which is larger than the elongation of the B=B bond, and this elongation ranges between 0.005 Å and 0.160 Å. When X = F, Cl, or Br, the Tr–X elongation increases in the order Al < Ga < B, consistent with the electronegativity of Tr but contrary to the trend for the maximum positive electrostatic potentials. For X = CH<sub>3</sub>, the Tr–X bond elongation is the same for Al and Ga and less than for B, whereas, for X = OH, the bond elongation increases in the order Al < B < Ga. With the elongation of the bond, the Tr–X stretching vibration frequency is red-shifted, and the red shift is large in most complexes; for example, in (BH)<sub>2</sub>(NHC)<sub>2</sub>···GaPhCl<sub>2</sub>, as high as 409  $\text{cm}^{-1}$ . This red shift is so large that it should be readily detected in the infrared spectrum and thus may be considered as a spectral feature for the formation of the TrB.

In order to characterize the existence of a TrB, we have drawn NCI diagrams of all structures, as shown in Figure 4. It can be observed that two B atoms and the Tr atoms form blue and red overlapping ring regions, which indicates that they form a strong TrB. In most of the complexes, there are green and yellow overlapping areas between the benzene ring and NHC ring, indicating an attractive interaction, similar to  $\pi$ – $\pi$  stacking. There is also a green and yellow overlapping area between a halogen atom and the N–H bond on the NHC ring, indicating an attraction between the two, namely a hydrogen bond. In addition, there is a similar region between the other halogen atom and the NHC ring. The NCI area between the hydrogen atom on the methyl group and the NHC ring is lighter, indicating that the effect is weak. When the substituent is OH, there is a blue region between the O atom in OH and the N–H atom in NHC, indicating that the corresponding hydrogen bond is strong. In addition to the intermolecular interaction, there is also an intramolecular attraction. There is a green region between the H atom connected with the B atom in the (BH)<sub>2</sub>(NHC)<sub>2</sub> molecule and the H atom in the NHC, which indicates that there is a weak interaction, namely a weak hydrogen bond. To sum up, the stability of this system depends on a number of different interactions, so does the TrB play the leading role? Consequently, we analyzed the total interaction energy and the constituent interaction energy components of the system for a possible answer to this question.

### 3.3. Interaction Energy

Table 4 shows the total interaction energy of all complexes, which ranges between 49 and ~100 kcal/mol. The binary structures are quite stable, with (BH)<sub>2</sub>(NHC)<sub>2</sub>···GaPh(OH)<sub>2</sub> having the largest total interaction energy (−100.16 kcal/mol). This indicates the possibility of covalent bonds between the two monomers. When the substituents are the same, the total interaction energies of complexes with Tr = Al and Ga are larger than those with Tr = B,

increasing in the order  $\text{BPhX}_2 < \text{AlPhX}_2 < \text{GaPhX}_2$ , which is different from the order for the maximum positive electrostatic potential on Tr atoms in  $\text{TrPhX}_2$ . With an increase in the electron-withdrawing ability of the substituents, the total interaction energy trend changes. When  $\text{Tr} = \text{B}$  or  $\text{Al}$ , with an increase in the electronegativity of the halogens, the order of the total interaction energy is  $\text{TrPhBr}_2 > \text{TrPhCl}_2 > \text{TrPhF}_2$ , which is different from the order of their maximum positive electrostatic potential. When  $\text{Tr} = \text{Ga}$ , the total interaction energy changes only slightly with an increase in the electronegativity of the halogen atoms. Comparing  $\text{CH}_3$  and  $\text{OH}$ , the total interaction energy for the  $\text{OH}$  substituent is larger than for the  $\text{CH}_3$  substituent, regardless of the Tr atom.

**Table 4.** Total interaction energy ( $E_{\text{total}}$ ) and interaction energies ( $E_{\text{int}}$ ) of the triel bond (TrB) and the  $\text{X}\cdots\text{H}$  hydrogen bond (HB), all in kcal/mol.

| Complexes                                                     | $E_{\text{total}}$ | $E_{\text{int}} (\text{TrB})$ | $E_{\text{int}} (\text{HB})$ |
|---------------------------------------------------------------|--------------------|-------------------------------|------------------------------|
| $(\text{BH})_2(\text{NHC})_2\cdots\text{BPhF}_2$              | −50.54             | −14.78                        | −3.65                        |
| $(\text{BH})_2(\text{NHC})_2\cdots\text{BPhCl}_2$             | −76.81             | −16.93                        | −1.91                        |
| $(\text{BH})_2(\text{NHC})_2\cdots\text{BPhBr}_2$             | −82.95             | −17.53                        | −2.09                        |
| $(\text{BH})_2(\text{NHC})_2\cdots\text{BPh}(\text{CH}_3)_2$  | −49.36             | −14.36                        | −                            |
| $(\text{BH})_2(\text{NHC})_2\cdots\text{BPh}(\text{OH})_2$    | −57.92             | −14.94                        | −4.73                        |
| $(\text{BH})_2(\text{NHC})_2\cdots\text{AlPhF}_2$             | −74.51             | −9.00                         | −3.01                        |
| $(\text{BH})_2(\text{NHC})_2\cdots\text{AlPhCl}_2$            | −79.27             | −9.52                         | −1.78                        |
| $(\text{BH})_2(\text{NHC})_2\cdots\text{AlPhBr}_2$            | −80.88             | −9.65                         | −1.59                        |
| $(\text{BH})_2(\text{NHC})_2\cdots\text{AlPh}(\text{CH}_3)_2$ | −53.21             | −7.42                         | −                            |
| $(\text{BH})_2(\text{NHC})_2\cdots\text{AlPh}(\text{OH})_2$   | −80.24             | −9.39                         | −5.46                        |
| $(\text{BH})_2(\text{NHC})_2\cdots\text{GaPhF}_2$             | −82.61             | −12.46                        | −5.21                        |
| $(\text{BH})_2(\text{NHC})_2\cdots\text{GaPhCl}_2$            | −81.43             | −12.46                        | −2.10                        |
| $(\text{BH})_2(\text{NHC})_2\cdots\text{GaPhBr}_2$            | −81.96             | −12.51                        | −1.77                        |
| $(\text{BH})_2(\text{NHC})_2\cdots\text{GaPh}(\text{CH}_3)_2$ | −49.37             | −9.32                         | −                            |
| $(\text{BH})_2(\text{NHC})_2\cdots\text{GaPh}(\text{OH})_2$   | −100.16            | −13.09                        | −13.48                       |

Using the formula  $E = -223.08 \times \rho + 0.7423$  [42], the interaction energy of the TrB and the  $\text{X}\cdots\text{H}$  hydrogen bond can be estimated, where  $\rho$  is the electron density at the bond critical point. When the substituents are the same, the interaction energy of the TrB increases in the order  $\text{AlPhX}_2 < \text{GaPhX}_2 < \text{BPhX}_2$ , which is different from the order for the maximum positive electrostatic potential on the Tr atom in  $\text{TrPhX}_2$ . When X is a halogen atom, the interaction energy of TrB decreases in the order  $\text{Br} > \text{Cl} > \text{F}$ , which is the opposite trend for the maximum positive electrostatic potential on Tr in  $\text{TrPhX}_2$ . OH substitution yields a greater TrB interaction energy than  $\text{CH}_3$  substitution, and this difference increases in the order  $\text{BPhX}_2 < \text{AlPhX}_2 < \text{GaPhX}_2$ .

The increase in the TrB interaction energy as X becomes larger (for fixed Tr) follows the same trend as that for the extent of deformation, as measured by the deformation of the  $\text{X}-\text{Tr}-\text{C}$  angle ( $\Delta\alpha$ ), and the dipole moment ( $\mu$ ). As is evident from the values in Table 1, both parameters,  $\Delta\alpha$  and  $\mu$ , increase in the order  $\text{F} < \text{Cl} < \text{Br}$ , as do the  $E_{\text{int}} (\text{TrB})$  values shown in Table 4. These trends due to the deformation of both  $\text{TrPhX}_2$  and  $(\text{BH})_2(\text{NHC})_2$  are rationalized later in the Discussion section.

In most complexes, the interaction energy of the hydrogen bond is less than that of the TrB, but in  $(\text{BH})_2(\text{NHC})_2\cdots\text{GaPh}(\text{OH})_2$ , the interaction energy associated with the hydrogen bond is slightly larger. This hydrogen bond does not exist in the methyl-substituted complex. In general, the interaction energy of the hydrogen bond increases with an increase in the electronegativity of the halogen atom. The hydrogen bonding energy in the OH-substituted complex is greater than in the halogen-substituted complex, with this difference increasing in the order  $\text{BPhX}_2 < \text{AlPhX}_2 < \text{GaPhX}_2$ . The interaction energy of the hydrogen bond is the largest in  $(\text{BH})_2(\text{NHC})_2\cdots\text{GaPh}(\text{OH})_2$ , at −13.48 kcal/mol, which indicates that it is a strong interaction.

### 3.4. Topological Analysis

In order to characterize the intermolecular interaction, a topological analysis of the dimer was carried out. Values for the electron density  $\rho$ , Laplace function  $\nabla^2\rho$ , and energy density  $H$  at the intermolecular bond critical point are listed in Table 5. It can be seen from Table 5 that the value of  $\rho$  ranges between 0.0087 a.u. and 0.0819 a.u. When  $\text{Tr} = \text{B}$  or  $\text{Al}$ ,  $\rho$  increases in the order  $\text{X} = \text{CH}_3 < \text{F} < \text{OH} < \text{Cl} < \text{Br}$ ; when  $\text{Tr} = \text{Ga}$ ,  $\rho$  increases in the order  $\text{X} = \text{CH}_3 < \text{F} \approx \text{Cl} < \text{Br} < \text{OH}$ . Regardless of how the electron density changes, the interaction energy variation with the  $\text{TrB}$  remains the same. When  $\text{Tr}$  is  $\text{B}$ , the values of  $\nabla^2\rho$  are all negative, whereas some  $H$  values are positive, which is counterintuitive. When  $\text{Tr}$  is  $\text{Al}$ , the values of  $\nabla^2\rho$  are positive, while  $H$  is negative in the complexes of  $\text{AlPh}(\text{CH}_3)_2$ , inconsistent with this complex having the smallest  $\text{TrB}$  interaction energy. When  $\text{Tr}$  is  $\text{Ga}$ , the signs of  $\nabla^2\rho$  and  $H$  are both positive, which is inconsistent with these complexes having the largest interaction energies. Therefore, care should be exercised in using the signs of  $\nabla^2\rho$  and  $H$  to assess the type of interaction. Generally, the intermolecular distance is strongly correlated with  $\rho$ , but there is no good exponential relationship for these systems.

**Table 5.** Electron density ( $\rho$ ), Laplacian ( $\nabla^2\rho$ ), and energy density ( $H$ ) at the intermolecular bond critical point (BCP) in the complexes, all values in a.u.

| Complexes                                                       | $\rho$ | $\nabla^2\rho$ | $H$     |
|-----------------------------------------------------------------|--------|----------------|---------|
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{BPhF}_2$              | 0.0696 | −0.0490        | 0.0254  |
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{BPhCl}_2$             | 0.0792 | −0.0528        | −0.0291 |
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{BPhBr}_2$             | 0.0819 | −0.0536        | 0.0303  |
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{BPh}(\text{CH}_3)_2$  | 0.0677 | −0.0316        | 0.0245  |
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{BPh}(\text{OH})_2$    | 0.0703 | −0.4858        | −0.0259 |
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{AlPhF}_2$             | 0.0437 | 0.0721         | 0.0115  |
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{AlPhCl}_2$            | 0.0460 | 0.0637         | 0.0134  |
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{AlPhBr}_2$            | 0.0466 | 0.0609         | −0.0138 |
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{AlPh}(\text{CH}_3)_2$ | 0.0366 | 0.0596         | −0.0087 |
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{AlPh}(\text{OH})_2$   | 0.0454 | 0.0753         | 0.0124  |
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{GaPhF}_2$             | 0.0592 | 0.0229         | 0.0211  |
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{GaPhCl}_2$            | 0.0592 | 0.0175         | 0.0207  |
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{GaPhBr}_2$            | 0.0594 | 0.0160         | 0.0207  |
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{GaPh}(\text{CH}_3)_2$ | 0.0451 | 0.0394         | 0.0123  |
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{GaPh}(\text{OH})_2$   | 0.0620 | 0.0143         | 0.0227  |

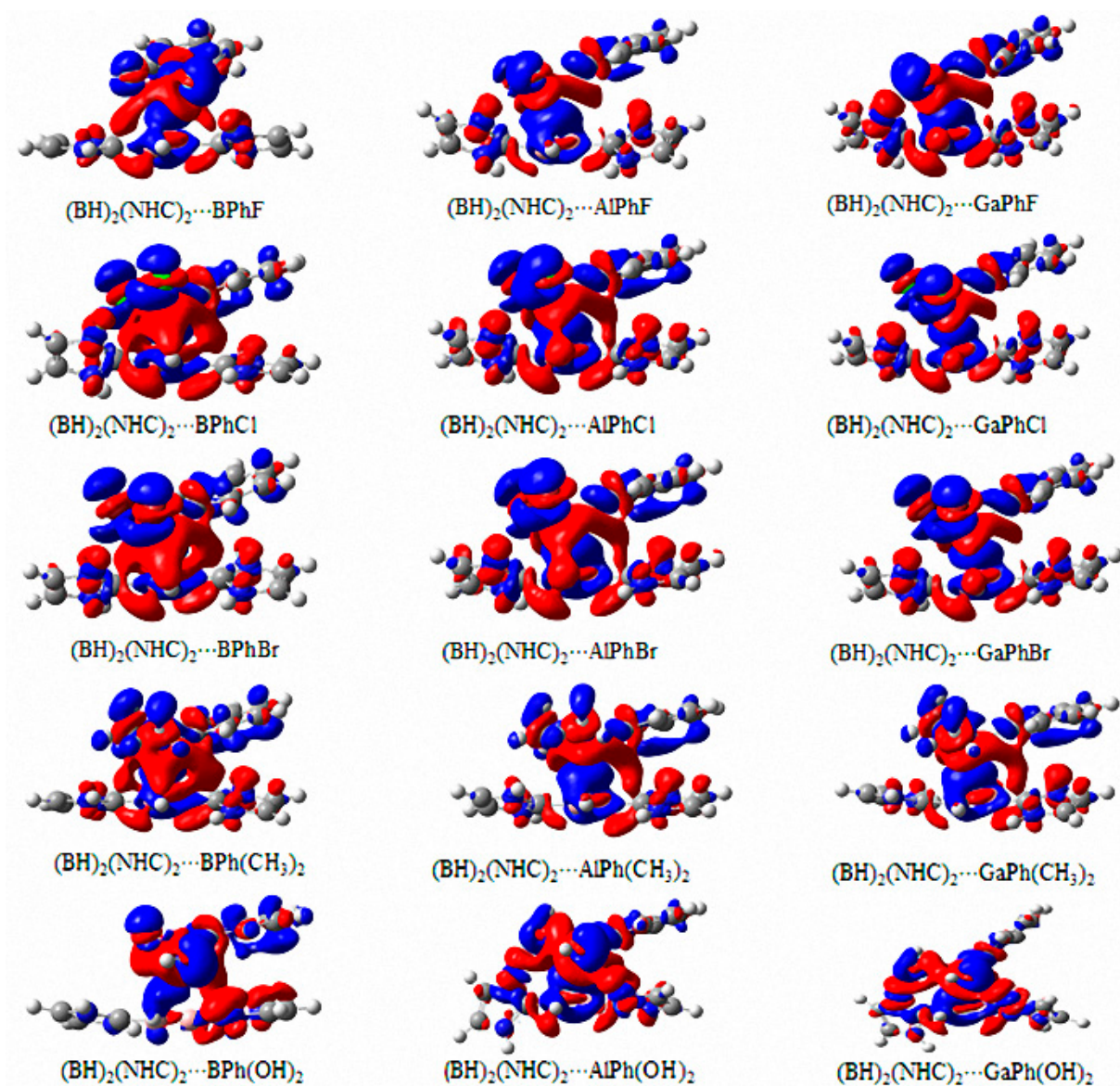
### 3.5. Charge Transfer

The interaction strength can also be gauged from the magnitude of charge transfer. Table 6 shows the charge transfer values from electron donor to electron acceptor. The charge transfer values of the complexes are quite large, even reaching 0.684  $e$  when  $\text{Tr} = \text{B}$ . Therefore, the  $\text{TrB}$  exhibits some covalent characteristics. For the same substituent  $\text{X}$ , when the electron acceptor is  $\text{BPhX}_2$ , its charge transfer value is almost twice that of  $\text{AlPhX}_2$  and  $\text{GaPhX}_2$ . There are several different types of interactions operative in the complex, which makes it difficult to identify obvious or straightforward correlations between the charge transfer value and the total interaction energy. For example, the  $\text{BPh}(\text{CH}_3)_2$  complex has a higher charge transfer value than the  $\text{BPhF}_2$  complex, but the total interaction energy of the former is smaller than that of the latter.

As mentioned earlier, the electronic density difference diagram can be obtained by subtracting the electronic density of the two monomers from the electronic density of the binary complex, which can illuminate important features of the interactions in the binary complex. The red areas in Figure 5 show the increase in electron density due to the interaction of the two monomers, while the blue areas show the decrease in electron density. One thing they have in common is that there is a red region near the  $\text{Tr}$  atom in  $\text{TrPhX}_2$  ( $\text{Tr} = \text{B}$ ,  $\text{Al}$ , and  $\text{Ga}$ ), and there is a blue region near the two  $\text{B}$  atoms in  $(\text{BH})_2(\text{NHC})_2$ , so the electrons transfer from the blue region to the red region, thereby stabilizing the interaction.

**Table 6.** NBO charge transfer (CT, e) in the complexes from  $(\text{BH})_2(\text{NHC})_2$  to  $\text{TrPhX}_2$ .

| Complexes                                                       | CT    |
|-----------------------------------------------------------------|-------|
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{BPhF}_2$              | 0.482 |
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{BPhCl}_2$             | 0.663 |
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{BPhBr}_2$             | 0.684 |
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{BPh}(\text{CH}_3)_2$  | 0.577 |
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{BPh}(\text{OH})_2$    | 0.471 |
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{AlPhF}_2$             | 0.211 |
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{AlPhCl}_2$            | 0.274 |
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{AlPhBr}_2$            | 0.290 |
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{AlPh}(\text{CH}_3)_2$ | 0.225 |
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{AlPh}(\text{OH})_2$   | 0.189 |
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{GaPhF}_2$             | 0.263 |
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{GaPhCl}_2$            | 0.325 |
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{GaPhBr}_2$            | 0.341 |
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{GaPh}(\text{CH}_3)_2$ | 0.242 |
| $(\text{BH})_2(\text{NHC})_2 \cdots \text{GaPh}(\text{OH})_2$   | 0.188 |

**Figure 5.** Electron density shift maps of triel-bonded complexes.

#### 4. Discussion

$(\text{BH})_2(\text{NHC})_2$  can combine with  $\text{TrPhX}_2$  to form several interactions at different sites in the resulting complexes and the interaction energy for these complexes lies between 49.37 kcal/mol and 100.16 kcal/mol in magnitude. The strength of the intermolecular interaction is related to the size or depth of the  $\pi$ -hole or  $\sigma$ -hole. Generally, the deeper the hole, the stronger the resulting composite. However, this is not evident in the present study. For example,  $\text{AlPhF}_2$  has the deepest  $\pi$ -hole, but the  $\text{TrB}$  interaction energy of the complex formed with  $(\text{BH})_2(\text{NHC})_2$  is not the most strongly bound because the interaction strength is not solely determined by the electrostatic interaction. After the formation of the complex between  $(\text{BH})_2(\text{NHC})_2$  and  $\text{TrPhX}_2$ , the geometries of the individual monomers experience varying degrees of deformation, relative to the monomers. The degree of deformation is assessed by the angle between the substituent X and the Tr atom ( $\alpha$ ). The greater the deviation from  $120^\circ$ , the greater the deformation. The data in Table 1 shows that the deformation is most severe when  $\text{Tr} = \text{B}$ .

The larger deformation in the  $\text{BPhX}_2$  complexes, vis-à-vis the Al and Ga analogs, is probably due to the relatively small size of B, which allows the  $\text{TrPhX}_2$  moiety to get closer to the  $\text{B}=\text{B}$  electron cloud of the  $(\text{BH})_2(\text{NHC})_2$  moiety, more so than the other Tr atoms (see the shorter binding distances in Table 1 for the B species). Furthermore, the closer distance facilitates a greater charge transfer between the individual monomers (Table 6) and, consequently, stronger triel bonds in the  $\text{BPhX}_2$  complexes (Table 4).

The deformation of the individual monomers on complexation is likely due to intermolecular repulsion which causes the previously mentioned pyramidalization of the  $\text{TrX}_2$  groups (adjacent to the benzene ring) of the  $\text{TrPhX}_2$  subunit, as well as distortion of the  $(\text{BH})_2(\text{NHC})_2$  subunit, from their original planar geometries when isolated. This deformation increases with the size of the halogen atom substituents (i.e., in the order  $\text{F} < \text{Cl} < \text{Br}$ ) and a consequence of this geometric change is the appearance of a dipole moment due to the  $\text{TrX}_2$  group and perpendicular to the  $\text{B}=\text{B}$  bond which, along with the charge transfer, reinforces the  $\text{TrB}$  interaction. The data for the increased deformation angles ( $\alpha$  and  $\Delta\alpha$  in Table 1), increased dipole moments ( $\mu$  in Table 1), shorter binding distances ( $R_1$  in Table 2), increased  $\text{TrB}$  interaction energy (Table 4), increased AIM electron densities (Table 5), and increased charge transfer (Table 6) for the corresponding dimers in going from F to Cl to Br supports the preceding analysis. We also noticed this important role of deformation in our previous study of triel bonds involving Au atoms acting as electron donors [19].

There are various different interactions between the atoms constituting  $(\text{BH})_2(\text{NHC})_2$  and  $\text{TrPhX}_2$ . For the total interaction energy, the heavier Tr atoms give rise to larger total interaction energies, inconsistent with the trend for positive electrostatic potentials for Tr in  $\text{TrPhX}_2$ . On the other hand, substituents modify the total interaction energy. When the substituent is a halogen, the trend is roughly the same when the Tr atom is B or Al. When  $\text{Tr} = \text{Ga}$ , it is different from the former two, possibly because Ga is heavier.  $\text{CH}_3$  substitution weakens the total attraction, and the weakening effect of  $\text{CH}_3$  also differs for different Tr atoms. When Tr is Ga, the weakening effect is the largest, about 30 kcal/mol, greater than that for B and Al. This shows that  $\text{CH}_3$ -substituted compounds can play a role in regulating intermolecular interactions when used as electron acceptors.

For the same substituents, the interaction energy of the  $\text{TrB}$  in the dimer increases in the order  $\text{AlPhX}_2 < \text{GaPhX}_2 < \text{BPhX}_2$ , similar to the trend for the positive electrostatic potentials of Tr atoms in  $\text{TrPhX}_2$ . For varying halogen atoms, the interaction energy of the  $\text{TrB}$  for different Tr systems increases as the halogen atom becomes larger, which is opposite to the trend for the positive electrostatic potentials of the Tr atom in the  $\text{TrPhX}_2$  molecule.

In addition to the  $\text{TrBs}$ , most of the complexes have hydrogen bonds, and the interaction energy of most hydrogen bonds is less than that of the  $\text{TrBs}$ , consistent with the work of Matondo [43]. However, there are also exceptions. For example, in  $(\text{BH})_2(\text{NHC})_2 \cdots \text{GaPh}(\text{OH})_2$ , the two types of interactions are similar in magnitude, but the hydrogen bond is slightly stronger than the  $\text{TrB}$ . In general, the interaction energy of hydrogen bonds increases with

an increase in the electronegativity of the halogen atoms. When OH is the substituent, the hydrogen bond energy in the complex is greater than in the halogen-atom substitution complex.

$(\text{BH})_2(\text{NHC})_2$  contains two nitroheterocyclic carbenes (NHCs). The synthesis and structure of NHC have been previously reviewed [23–31]. It is often used directly or indirectly (in the present study) as an electron donor. There is also a negative electrostatic potential region above the N atom in  $(\text{BH})_2(\text{NHC})_2$  so there is a weak interaction between the atoms in the benzene ring and NHC, as seen in Figure 4.

## 5. Conclusions

$(\text{BH})_2(\text{NHC})_2$  contains a B=B moiety that can be used as an electron donor in interactions with the aromatic compound  $\text{TrPhX}_2$  (Tr = B, Al, and Ga; Ph =  $\text{C}_6\text{H}_5$ ; X = F, Cl, Br,  $\text{CH}_3$ , and OH), and the resulting complexes can be very strongly bound. Most TrBs have partially covalent properties. There are various interactions between different sites in the dimer. In most of the complexes, the interaction energy associated with the hydrogen bond is less than that associated with the triel bond. The heavier Tr atoms give rise to larger interaction energies, which is inconsistent with the trends for the positive electrostatic potentials on their surfaces. The strength of the interactions in these complexes is dependent on the substituents and the trends for the interaction energy (for varying Tr atoms) are sometimes not consistent for the halogen-substituted complexes.

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