A Comparison of Donor-acceptor Interactions in Borane Complexes of Divalent Tetrylenes(II) and Divalent Tetrylones(0) using Energy Decomposition Analysis Method with Natural Orbital for Chemical Valence Theory

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ABSTRACT
A scheme for chemical bond analysis by combining the energy decomposition analysis (EDA) method with natural orbitals for chemical valence (NOCV) theory has been investigated. Quantum chemical calculations at the BP86/TZ2P+ level of theory are performed for a comparison of chemical bond analysis between tetrylones \([\text{BH}_3\{\text{E(PH}_3\}_2}\] \((\text{B}_3\text{-EP}_2)\) and tetrylenes \([\text{BH}_3\{\text{NHEMe}_2}\] \((\text{B}_3\text{-NHE})\) \((\text{E} = \text{C to Pb})\). The EDA-NOCV results suggest that the \(\text{B}–\text{E}\) bond dissociation energies (BDEs) in tetrylones and tetrylenes decrease from the slighter to the heavier homologs. The decrease in the bond strengths from the lighter to the heavier homologs of \(\text{B}_3\text{-EP}_2\) comes mainly from the decrease in the electrostatic attractions \(\Delta E_{\text{elstat}}\) and the orbital interactions \(\Delta E_{\text{orb}}\), while the decrease in the bond strength from carbene \(\text{B}_3\text{-NHC}\) to plumbylene \(\text{B}_3\text{-NHPb}\) strongly correlates with the decrease in electrostatic term \(\Delta E_{\text{elstat}}\).

1. Introduction
The first divalent carbon(0) compound (carbones) \(\text{CL}_2\) synthesized already in 1961 by Ramirez et al. [1] is the carbodiphosphorane \(\text{C(PPh}_3)_2\). The carbon atom in \(\text{CL}_2\) retains two electron lone pairs and is bonded to two \(\sigma\)-donor ligands \(\text{L}\rightarrow\text{C}\leftarrow\text{L}\).[2,3] Carbones \((\text{CL}_2\) ) have two donor–acceptor bonds \(\text{L}\rightarrow\text{C}\) to a bare carbon atom in the \(1D\) exited singlet state. In contrast to carbones \((\text{CL}_2\) ), carbenes \((\text{CR}_2\) ) possess only one electron lone pair at the carbon, have two electron-sharing bonds \((\text{CR})\) to a carbon atom in the \(3P\) ground state.[4,5] Recent theoretical studies suggested that the bonding situation in \(\text{CL}_2\) is not limited to carbon as the central atom, but that is can be extended to the heavier homologs \(\text{EL}_2\) with \(\text{E} = \text{Si to Pb}[2,5–7]\) in which the ligands \(\text{EL}_2\) are strong \(\sigma\)-donors and weak \(\pi\)-donors.[5–10] The reaction of the carbodiphosphorane \(\text{C(PPh}_3)_2\) complex \((\text{PPh}_3)_2\text{C(BH}_3\) ) with the strong Lewis acid \(\text{B(C}_6\text{F}_5)_3\) yielded the first complex of a cation \((\text{PPh}_3)_2\text{C}\rightarrow\text{C(BH}_3\) ) that could be isolated in a condensed phase.[5,11] This is because the \(\text{C(PPh}_3)_2\) always possesses two lone pair donor orbitals which leads the complex to be stabilized through double donation of the \(\sigma\) and \(\pi\) electron lone pairs of the carbene \(\text{C(PPh}_3)_2\) into the vacant \(\sigma\) and \(\pi\) orbitals of the \(\text{BH}_3\) ligand. In contrast, carbenes NHCs possess only one lone pair for donation; this leads to the reaction of the carbene complex \(\text{NHC(BH}_3\) ) with \(\text{B(C}_6\text{F}_5)_3\) that affords the hydrogen-bridged cation \((\text{NHC}ightarrow\text{BH}_3\cdot\text{H-H-H-B}\) ) in NHC. The structures and bonding situation of a complex of borane \((\text{BH}_3\) ) with carbodiphosphorane-\([\text{H}_3\text{B(C(PPh}_3)_2}\) ] and carbodicarbenes-\([\text{H}_3\text{B(NHEMe}_2\) ]\) were analyzed using DFT calculations by Frenking et al. [8,9,12,13]

Further, new types of borane complexes that carry N-heterocyclic carbenes (NHC boranes) have been investigated theoretically as stable molecules.[14] Work focused first on structural determinations,[15,16] then gradually encompassed inorganic,[17–22] organic (in particular astin hydride surrogates),[23–29] and organometallic chemistry.[30] Experimental and theoretical calculations on NHC-boranes have shown recently that coupling of NHC-BH3 changes the electronic properties of the borane considerably,[14,24,25] The energy decomposition analysis (EDA)-natural orbitals for chemical valence (NOCV) [31] method combines charge (NOCV) and energy (EDA)
partitioning schemes to decompose the deformation density that is associated with the bond formation, $\Delta \rho$, into different components of the chemical bonds. The EDA-NOCV calculations also provide pairwise energy contributions for each pair or interacting orbitals to the total bond energy. Moreover, it has been found that the set of orbitals which has been discussed in the recent past, NOCV, is defined as eigenvectors of the overall chemical valence operator and the NOCV set of orbitals can be especially useful for a description of bonding in transition metal complexes as it also allow for separation of the deformation density contributions originating from the ligand to metal donation and metal to ligand back donation.[32]

In view of the above, the main purpose of this study is to investigate donor–acceptor interactions between the two typical ligands carbodiphosphorane-analogs (called tetrylones) $\text{E(PH}_3\text{)}_2$ and N-heterocyclic carbene-analogs (called tetrylenes) $\text{NHEMe}$ in borane complexes. Here, we report a comparative investigation of the bonding situation of the complexes $[(\text{BH}_3\text{E(PH}_3\text{)}_2)]$ (B3-EP2) and $[\text{BH}_3\text{-NHEMe}]$ (B3-NHE) with E = C, Si, Ge, Sn, and Pb shown in Scheme 1. The electronic structures of the borane complexes that carry tetrylone $\{\text{E(PH}_3\text{)}_2\}$ and tetrylene $\{\text{NHEMe}\}$ ligands are analyzed by energy partitioning method.

### 2. Computational methods

We use the EDA [33,34] with the NOCV [35–37] to investigate the nature of chemical bonding in complexes. In the EDA-NOCV method,[31] the bond dissociation energy (BDE) of a molecule is divided into the instantaneous interaction energy $\Delta E_{\text{int}}$ and the preparation energy $\Delta E_{\text{prep}}$:

$$\Delta E = -D_e = \Delta E_{\text{int}} + \Delta E_{\text{prep}} \quad (1)$$

The BDE, $D_e$ (kcal/mol), for a bond carbene/carbene-BH$_3$ is broken through the reaction: carbene/carbene-BH$_3$ $\rightarrow$ carbene/carbene $+$ BH$_3$ of a molecule and forms from the two fragments $E_{\text{carbene/carbene}}^0$ and $E_{\text{borane}}^0$, which is given by:

$$\Delta E = (-D_e) = E_{\text{carbene/carbene}} - E_{\text{borane}} \quad (2)$$

In the Equation (1), the preparation energy $\Delta E_{\text{prep}}$, is the energy that is required to promote the fragments in complexes from their equilibrium geometries in the ground electronic state to the geometries and electronic reference state which they have in the molecule. The interaction energy $\Delta E_{\text{int}}$ can be further divided into three main components:

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}} \quad (3)$$

where $\Delta E_{\text{elstat}}$ is the quasi-classical electrostatic interaction energy between the fragments; $\Delta E_{\text{Pauli}}$ refers to the repulsive interactions between the fragments, which are caused by the fact that two electrons with the same spin cannot occupy the same region in space, and can be calculated by enforcing the Kohn–Sham determinant on the superimposed fragments to obey the Pauli principle by anti-symmetrization and renormalization; and $\Delta E_{\text{orb}}$ is the stabilizing orbital interaction term which is calculated in the final step of the energy partitioning analysis when the Kohn–Sham orbitals relax to their optimal forms.

The EDA-NOCV method combines charge (NOCV) and energy (EDA) partitioning schemes to decompose the deformation density that is associated with the bond formation, $\Delta \rho$, into different components of the chemical bond. Furthermore, the EDA-NOCV calculations also provide pairwise energy contributions for each pair or interacting orbitals to the total bond energy. NOCV [35–37] is defined as the eigenvector of the valence operator, $\mathbf{v}$, given by Equation (4):

$$\mathbf{v}\psi_i = \psi_i \quad (4)$$

In the EDA-NOCV scheme, the orbital interaction term, $\Delta E_{\text{orb}}$, is given by Equation 5:

$$\Delta E_{\text{orb}} = \sum_{k=1}^{N/2} \Delta E_{\text{orb}}^k = \sum_{k=1}^{N/2} \nu_k \left[ -F_{-k,-k}^{TS} + F_{k,k}^{TS} \right] \quad (5)$$

in which $F_{-k,-k}^{TS}$ and $F_{k,k}^{TS}$ are diagonal transition state Kohn–Sham matrix elements corresponding to NOCVs with the eigenvalues $-\nu_k$ and $\nu_k$, respectively. The $\Delta E_{\text{orb}}^k$ term of a particular type of bond is assigned by visual inspection of the shape of the deformation density, $\Delta \rho_k$. The

![Scheme 1](image-url)
EDA-NOCV scheme so provides information about the strength of orbital interactions in terms of both charge ($\Delta \rho_{\text{orb}}$) and energy contributions ($\Delta E_{\text{orb}}$) in chemical bonds, even in molecules without symmetry.

In this work, the parent compounds (B3-EP2 and B3-NHE) and free ligands (EP2 and NHE) were optimized for the EDA with the program package ADF 2013.01 [38] with BP86 in conjunction with a triple-zeta-quality basis set using un-contracted Slater-type orbitals (STOs) augmented by two sets of polarization function with a frozen-core approximation for the core electrons. [39] An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle. [40] Scalar relativistic effects have been incorporated by applying the zeroth-order regular approximation. [41] The chemical bonding of the B–E bonds in B3-EP2 and B3-NHE was investigated at BP86/TZ2P+ level of theory using the EDA-NOCV method [31] under C1 symmetric geometries.

### 3. Results and discussion

In this study, we want to draw a picture that the EDA-NOCV calculations give a thorough insight into the nature of the BH₃-ligands bonding in B3-EP2 and B3-NHE. Firstly, the structures of BH₃-tetrylones and BH₃-tetrylenes are presented. The optimized geometries of complexes B3-EP2 with calculated values for the most important bond lengths and angles are shown in Figure 1. All members of tetrylones in this study are experimentally unknown. Note that the borane complex that carries the more bulky ligand C(PPh₃)₂ was reported in the experimental study. [12] Figure 1 shows that the calculated B–C bond length of B3-CP2 gives the shortest value (1.691 Å) and is similar to the B–C bond length in BH₃-C(PH₃)₂ (1.685 Å) and BH₃-C(PPh₃)₂ (1.689 Å) which was recently calculated at the BP86/SVP level of theory by Frenking. [42] The borane complex with the more bulky ligand C(PPh₃)₂ exhibits the experimental B–C bond length of 1.673 Å. [12] The theoretically predicted B–E bond lengths of tetrylone complexes B3-CP2–B3-PbP₂ in this study increased from 1.691 to 2.409 Å. This could be easily explained by the increasing radii of the group-14 atoms. The calculated equilibrium structures of tetrylone complexes B3-EP2 showed that all ligands EP2 were bonded in a tilted orientation relative to the fragment BH₃. The bending angle, $\alpha$, of B3-CP2 is 134.8° and becomes much more acute when E became heavier.

The structures of tetrylene complexes B3-NHE are shown in Figure 2. The calculated BH₃-NHCH₃ bond length of B3-NHC gives the shortest value (1.587 Å) and is extremely similar with the theoretical B–C bond length of 1.587 Å in BH₃-NHC/H₁ which was recently calculated at the BP86/SVP level of theory by Frenking. [42] The B–E bond length increases from B3-NHC to B3-NHPb (2.564 Å). Note that a related carbene complex BH₃-NHCS has an experimental B–C bond length of 1.603 Å. [43] Unlike the structures of tetrylone complexes, the structures of tetrylene complexes B3-NHE have the NHE ligands (E = C to Ge) bonded in a head-on way to the BH₃ fragment with a bending angle, $\alpha$, 180°. In contrast, the B3-NHSn complex has the NHSnMe ligand bonded in a side-on way to the BH₃ fragment with the bending angle 129.4°. The strongest side-on bonded ligand when E = Pb has a bending angle of 108.0°.

We continuously investigate bonding analysis for borane complexes of tetrylones and tetrylenes. In the EDA-NOCV calculations, the tetrylones B3-EP2 and tetrylenes B3-NHE are divided into the fragments \{E(PH₃)₂ and NHEMe\} as donor fragments and BH₃ as an acceptor fragment and both are in the singlet state. To the best of our knowledge, there are no experimental results available for complexes B3-EP2 and B3-NHE. Note that the EDA results of the borane complexes BH₃ that carry the more bulky carbodiphosphorane ligand as carbene have been recently described by Frenking et al. [8,12] In this study, we wanted to extend the carbene to heavier homologs as tetrylones and compare the bonding situation of tetrylone complexes B3-EP2 with tetrylene complexes B3-NHE (E = C to Pb). EDA-NOCV results at the BP86/TZ2P+ level for complexes B3-CP2–B3-PbP₂ using the moieties (BH₃) and (E(PH₃)₂) as interacting fragments are shown in Table 1. The results demonstrate that the decrease in the borane–ligand bonding comes from the intrinsic interaction $\Delta E_{\text{int}}$ which slightly decreases from the lighter B3-CP2 to the heavier homologs. The trend of the bond dissociation energies (BDEs), $D_e$ (kcal/mol), for the B–E bond in the B3-EP2 system is B3-CP2 > B3-SiP₂ > B3-GeP₂ > B3-SnP₂ > B3-PbP₂. The decrease in BDEs is determined by the intrinsic strength of the borane–ligand bond $\Delta E_{\text{int}}$. The preparation energy of tetrylone-BH₃ complexes decreases from B3-CP2 ($\Delta E_{\text{prep}} = 21.6$ kcal/mol) to the B3-PbP₂ ($\Delta E_{\text{prep}} = 13.8$ kcal/mol). The three main terms, Pauli repulsion $\Delta E_{\text{Pauli}}$, electric interaction $\Delta E_{\text{elstat}}$, and orbital interaction $\Delta E_{\text{orb}}$ are considered to inspect their contribution to the intrinsic energy $\Delta E_{\text{int}}$ of the complexes. The Pauli repulsion $\Delta E_{\text{Pauli}}$ has the largest value of 135.9 kcal/mol for B3-CP2 and gets smaller from E = C to Pb (98.8 kcal/mol). Moreover, the electrostatic term $\Delta E_{\text{elstat}}$ continuously decreases from B3-CP2 (−88.3 kcal/mol) to heavier complexes. Note that the largest contributions to the $\Delta E_{\text{int}}$ values of the system come from the orbital term $\Delta E_{\text{orb}}$. The orbital interaction $\Delta E_{\text{orb}}$ in B3-CP2 is −109.0 kcal/mol and becomes weaker for heavier homologs. The $\pi$-orbital contributions $\Delta E_{\pi}$
are much weaker than $\Delta E_\sigma$ and they also decrease for heavier homologs in B3-EP2. The decrease in the bond strength from B3-CP2 to B3-PbP2 comes mainly from the decrease in the electrostatic attractions $\Delta E_{\text{dista}}$ and the orbital interactions $\Delta E_{\text{orb}}$. This is because the tetrylones have two lone pair orbitals available for donation and they use mainly one lone pair for strong $\sigma$-donation in B3-EP2. Thus, the EDA-NOCV results suggest that the ligand E(PH$_3$)$_2$ in B3-EP2 is a strong $\sigma$-donor and very weak $\pi$-donor.[5,42]

The plots of the pairs of orbitals $\Psi_{-k}/\Psi_k$ that yield the NOCVs providing the most important contributions to the $\sigma$- and $\pi$-orbital terms $\Delta E_{\sigma}$ and $\Delta E_{\pi}$ in B3-CP2 and B3-PbP2, as well as the associated deformation densities $\Delta \rho$ and stabilization energies are shown in Figure 3. Note that the shape of orbital pairs in the B3-EP2 exhibits the side-on mode between E(PH$_3$)$_2$ and BH$_3$. The shapes of B3-SiP2–B3-SnP2 exhibit similar shapes like the adduct B3-PbP2 and are therefore not shown in Figure 3. Note that the white/red colors in the figures for $\Psi_{-k}/\Psi_k$ indicate the sign of the orbitals, and the yellow/blue colors in the deformation densities $\Delta \rho$ indicate the charge flow which occurs in the direction from yellow to blue. Figure 3(a) and (d) gives the NOCV pairs of $\sigma$-orbitals for B3-CP2 and B3-PbP2. The orbital pairs $\Psi_{-1}/\Psi_1$ can be considered as the dominant sources of the $\sigma$-bonding of the ligands in the complexes. The shape of the orbital
the associated energy stabilization comes not only from the weak π-donation BH₃←C(PH₃)₂ but also from the charge relaxation within the BH₃ donor fragment BH₃→C(PH₃)₂. Figure 3(e) clearly shows that deformation density Δρ₂ can be assigned to BH₃→Pb(PH₃)₂ π-backdonation where the Pb-P vacant anti-bonding orbital in the ligand Pb(PH₃)₂ acts as an acceptor (∆E₂ = −3.1 kcal/mol). Figure 3(f) shows that the very weak π-type orbital interaction in B₃-PbP₂ comes from pairs clearly indicates that σ-orbital interactions take place between the donor orbital of CP₂ and PbP₂ ligands and the acceptor orbital of the BH₃ fragment. The contributions of the π-orbital stabilization ΔE π in B₃-EP₂ are quite small. Figure 3(b) and (c) shows the NOCV pairs Ψ₋₂/Ψ₂ and Ψ₋₃/Ψ₃ that dominate the total stabilization ΔE π in B₃-CP₂. The shape of the NOCV pairs and deformation densities Δρ₂ (∆E₂ = −6.1 kcal/mol) and Δρ₃ (∆E₃ = −3.3 kcal/mol) reveals that the associated energy stabilization comes not only from the weak π-donation BH₃←C(PH₃)₂ but also from the charge relaxation within the BH₃ donor fragment BH₃→C(PH₃)₂. Figure 3(e) clearly shows that deformation density Δρ₂ can be assigned to BH₃→Pb(PH₃)₂ π-backdonation where the Pb-P vacant anti-bonding orbital in the ligand Pb(PH₃)₂ acts as an acceptor (∆E₂ = −3.1 kcal/mol). Figure 3(f) shows that the very weak π-type orbital interaction in B₃-PbP₂ comes from

Figure 2. Optimized geometries of B₃-NHE at the BP86/TZ2P+ level. Notes: Bond lengths are given in Å; angles in degrees. The bending angle, α, is the angle B–E–X where X is the midpoint between the N–N distance:

B₃ – NHC
α = 180°

B₃ – NHSi
α = 180°

B₃ – NHGe
α = 180°

B₃ – NHSn
α = 129.4°

B₃ – NHPb
α = 108.0°
We continuously consider the chemical bonding of borane complexes of tetrylenes $B_3$-NHE. The EDA-NOCV results at the BP86/TZ2P+ level for complexes $B_3$-CP2, $B_3$-SiP2, $B_3$-GeP2, $B_3$-SnP2, and $B_3$-PbP2 using the moieties $[BH_3]$ and $[E(PH_3)_2]$ as interacting fragments. The complexes are analyzed with C1 symmetry. Energy values in kcal/mol.

### Table 1.

| Compound   | $B_3$-CP2 | $B_3$-SiP2 | $B_3$-GeP2 | $B_3$-SnP2 | $B_3$-PbP2 |
|------------|-----------|-----------|-----------|-----------|-----------|
| Fragment   | $BH_3$    | $Si(PH_3)_2$ | $Ge(PH_3)_2$ | $Sn(PH_3)_2$ | $Pb(PH_3)_2$ |
| $\Delta E_{el}^{[a]}$ | $-61.4$ | $-53.6$ | $-51.3$ | $-48.2$ | $-45.5$ |
| $\Delta E_{orb}^{[a]}$ | $135.9$ | $121.2$ | $113.5$ | $104.4$ | $98.8$ |
| $\Delta E_{el}^{[b]}$ | $-88.3 (44.7\%)$ | $-67.4 (38.5\%)$ | $-65.4 (39.7\%)$ | $-62.1 (40.7\%)$ | $-59.5 (41.3\%)$ |
| $\Delta E_{orb}^{[b]}$ | $-92.3 (84.7\%)$ | $-95.5 (88.9\%)$ | $-88.9 (91.9\%)$ | $-83.2 (93.0\%)$ | $-78.9 (93.0\%)$ |
| $\Delta E_{im}$ | $21.6$ | $17.7$ | $16.7$ | $15.4$ | $13.8$ |
| $\Delta E_{im}$ | $-39.8$ | $-35.9$ | $-34.6$ | $-32.8$ | $-31.7$ |

$^{[a]}$The values in parentheses are the percentage contributions to the total attractive interaction $\Delta E_{el}^{total} + \Delta E_{orb}^{total}$.

$^{[b]}$The values in parentheses are the percentage contributions to the total orbital interaction $\Delta E_{orb}^{total}$.

![Figure 3.](image)

Figure 3. Most important NOCV pairs of orbitals $\Psi_{\pm k}$, $\Psi_k$ with their eigenvalues $-\upsilon_k, \upsilon_k$ given in parentheses, and the associated deformation densities $\Delta \rho_k$ and orbital stabilization energies $\Delta E$ for the complexes $B_3$-CP2 and $B_3$-PbP2. The charge flow in the deformation densities is from the yellow $\rightarrow$ blue region. (a) $\sigma$-NOCV of $B_3$-CP2; (b), (c) $\pi$-NOCVs of $B_3$-CP2; (d) $\sigma$-NOCV of $B_3$-PbP2; and (e), (f) $\pi$-NOCVs of $B_3$-PbP2. Energy values in kcal/mol.

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The decrease in the bond strength from carbene $\text{B3-NHC}$ to plumbylene $\text{B3-NHPb}$ strongly correlates with the decrease in electrostatic term $\Delta E_{\text{elstat}}$. This can be explained as: the tetrylenes have only one lone pair orbital available for donation and the ligands $\text{NHE Me}$ are $\sigma$-donors and weak $\pi$-acceptors.

Table 2. EDA-NOCV results at the BP86/TZ2P+ level for compounds $\text{B3-NHC–B3-NHPb}$ using the moieties $[\text{BH}_3]$ and $[\text{NHE}_{\text{Me}}]$ as interacting fragments. The complexes are analyzed with C1 symmetry. Energy values in kcal/mol.

| Compound | $\text{B3-NHC}$ | $\text{B3-NHSi}$ | $\text{B3-NHGe}$ | $\text{B3-NHSn}$ | $\text{B3-NHPb}$ |
|----------|------------------|------------------|------------------|------------------|------------------|
| Fragments | $\text{BH}_3$ | $\text{NHSiMe}$ | $\text{NHGeMe}$ | $\text{NHSnMe}$ | $\text{NHPbMe}$ |
| $\Delta E_{\text{elstat}}$ | $-80.7$ | $-44.4$ | $-29.3$ | $-19.3$ | $-16.5$ |
| $\Delta E_{\text{prep}}$ | $165.0$ | $116.4$ | $87.3$ | $56.7$ | $41.6$ |
| $\Delta E_{\text{orb}}$ | $-120.5$ (49.0%) | $-59.4$ (37.0%) | $-41.9$ (35.9%) | $-25.0$ (32.9%) | $-17.8$ (30.7%) |
| $\Delta E_{\text{int}}$ | $-125.3$ (51.0%) | $-101.3$ (63.0%) | $-74.7$ (64.1%) | $-51.0$ (67.1%) | $-40.3$ (69.3%) |
| $\Delta E_{\text{pair}}$ | $-105.6$ (84.3%) | $-86.9$ (82.8%) | $-65.3$ (87.4%) | $-45.7$ (89.6%) | $-37.1$ (92.1%) |
| $\Delta E_{\text{orb}}$ | $-18.9$ (15.1%) | $-14.2$ (14.0%) | $-9.2$ (12.3%) | $-5.1$ (10.0%) | $-2.5$ (6.2%) |
| $\Delta E_{\text{elstat}}$ | $-0.8$ (0.6%) | $-0.2$ (0.2%) | $-0.2$ (0.3%) | $-0.2$ (0.4%) | $-0.7$ (1.7%) |
| $\Delta E_{\text{prep}}$ | $22.0$ | $13.4$ | $9.4$ | $4.5$ | $3.1$ |
| $\Delta E$ | $-58.7$ | $-31.0$ | $-19.9$ | $-14.8$ | $-13.4$ |

$^{[a]}$The values in parentheses are the percentage contributions to the total attractive interaction $\Delta E_{\text{elstat}} + \Delta E_{\text{orb}}$.

$^{[b]}$The values in parentheses are the percentage contributions to the total orbital interaction $\Delta E_{\text{orb}}$.

Figure 4. Most important NOCV pairs of orbitals $Ψ_−$, $Ψ_+$ with their eigenvalues $−\nu_−$, $\nu_+$ given in parentheses, and the associated deformation densities $\Delta \rho_k$ and orbital stabilization energies $\Delta E_k$ for the complexes $\text{B3-NHC}$ and $\text{B3-NHPb}$. The charge flow in the deformation densities is from the yellow → blue region. (a) $\sigma$-NOCV of $\text{B3-NHC}$; (b), (c) $\pi$-NOCVs of $\text{B3-NHC}$; (d) $\sigma$-NOCV of $\text{B3-NHPb}$; and (e), (f) $\pi$-NOCVs of $\text{B3-NHPb}$. Energy values in kcal/mol.

$\text{B3-NHC–B3-NHPb}$ using the moieties $[\text{BH}_3]$ and $[\text{NHE}_{\text{Me}}]$ as interacting fragments are shown in Table 2. The largest preparation energy $\Delta E_{\text{prep}}$ is 22.0 kcal/mol for $\text{B3-NHC}$ and strongly decreases from $\text{B3-NHC}$ to $\text{B3-NHPb}$. The BDEs trend in tetrylene complexes $\text{B3-NHE}$ strongly decreases from the lighter ($−D_e = −58.7$ kcal/mol for $\text{B3-NHC}$) to the heavier homologs ($−D_e = −13.4$ kcal/mol for $\text{B3-NHPb}$). The strong decrease in the BDEs from the lighter to heavier adduct is determined by the intrinsic strength $\Delta E_{\text{int}}$ of the $\text{BH}_3$-tetrylene bonds. The electrostatic term $\Delta E_{\text{elstat}}$ decreases from $\text{B3-NHC}$ ($−120.5$ kcal/mol) to lighter tetrylenes and is rather weak in the $\text{B3-NHPb}$ ($−17.8$ kcal/mol). Table 2 also shows that the orbital interactions $\Delta E_{\text{orb}}$ decrease for heavier homologs. The decrease in the bond strength from carbene $\text{B3-NHC}$ to plumbylene $\text{B3-NHPb}$ to plumbylene $\text{B3-NHPb}$ strongly correlates with the decrease in electrostatic term $\Delta E_{\text{elstat}}$. This can be explained as: the tetrylenes have only one lone pair orbital available for donation and the ligands $\text{NHE}_{\text{Me}}$ in $\text{B3-NHE}$ are $\sigma$-donors and weak $\pi$-acceptors.\[5,42\]

Figure 4 shows the plots of the pairs of orbitals $Ψ_−/Ψ_+$ that yield the NOCVs providing the most important contributions to the $\sigma$- and $\pi$-orbital terms $\Delta E_σ$ and $\Delta E_π$. 
the associated deformation densities $\Delta \rho$, and stabilization energies in $\text{B}_3\text{-NHC}$ and $\text{B}_3\text{-NHPb}$. Note that the shapes of complexes $\text{B}_3\text{-NHSi}$ and $\text{B}_3\text{-NHGe}$ are similar like the adduct $\text{B}_3\text{-NHC}$, whereas $\text{B}_3\text{-NHSn}$ exhibits similar shape with the lead complex $\text{B}_3\text{-NHPb}$ and therefore the shapes of $\text{B}_3\text{-NHSi}$, $\text{B}_3\text{-NHGe}$, and $\text{B}_3\text{-NHSn}$ are not shown in Figure 4. NOCV pairs $\Psi_{-1}/\Psi_1$, $\Psi_{-2}/\Psi_2$, and $\Psi_{-3}/\Psi_3$ as well as the deformation densities of $\sigma$- and $\pi$-orbitals for $\Delta E_{\text{orb}}$ of $\text{B}_3\text{-NHC}$ are shown in Figure 4(a)–(c). The $\sigma$-type interaction in Figure 4(a) is clearly from the donor fragment $\text{NHC}_{\text{Me}}$ to the acceptor fragment $\text{BH}_3$. Figure 4(b) shows that weak $\pi$-type orbital interactions in $\text{B}_3\text{-NHC}$ do not come from a typical $\pi$-backdonation $\text{H}_3\text{B} \rightarrow \text{NHC}_{\text{Me}}$ only but also come from a very weak $\pi$-donor $\text{H}_3\text{B} \leftarrow \text{NHC}_{\text{Me}}$ with the charge flow $\Psi_{-2}/\Psi_2$ indicating stabilization at $-9.8$ kcal/mol. Figure 4(c) shows that a very weak $\pi$-type orbital interaction in $\text{B}_3\text{-NHC}$ comes from typical $\pi$-backdonation $\text{H}_3\text{B} \rightarrow \text{NHC}_{\text{Me}}$ with the charge flow $\Psi_{-2}/\Psi_2$ indicating stabilization at $-5.9$ kcal/mol. Note that the structures and orbital pairs of the lighter homologs $\text{B}_3\text{-NHE}$ with $E = \text{C}$ to $\text{Ge}$ have head-on modes between the ligands and $\text{BH}_3$, whereas the heavier species $\text{B}_3\text{-NHSn}$ and $\text{B}_3\text{-NHPb}$ exhibit side-on bonded ligands to the $\text{BH}_3$ fragment. Figure 4(d)–(f) shows significant different EDA-NOCV results for $\text{B}_3\text{-NHPb}$. Figure 4(d) clearly shows that the $\sigma$-type interaction has the direction from charge donation at the $\text{NHPb}_{\text{Me}}$ (yellow area) to $\text{BH}_3$ fragment $\text{H}_3\text{B} \leftarrow \text{NHPb}_{\text{Me}}$ with stabilization at $-35.7$ kcal/mol. Figure 4(e) shows that the very weak $\pi$-type orbital interactions in $\text{B}_3\text{-NHPb}$ come from typical $\pi$-backdonation $\text{H}_3\text{B} \rightarrow \text{NHPb}_{\text{Me}}$ with the charge flow $\Psi_{-2}/\Psi_2$ indicating stabilization at $-1.5$ kcal/mol. Like the Figure 4(b) of carbene, Figure 4(f) of plumbylene shows weak $\pi$-type orbital interactions in $\text{B}_3\text{-NHPb}$ which also exhibit a typical $\pi$-backdonation $\text{H}_3\text{B} \rightarrow \text{NHPb}_{\text{Me}}$ and a very weak $\pi$-donor $\text{H}_3\text{B} \leftarrow \text{NHPb}_{\text{Me}}$ with the charge flow $\Psi_{-3}/\Psi_3$ indicating stabilization at $-1.1$ kcal/mol. The fact is that the tetrylenes have only one lone pair orbital available for donation and the ligands $\text{NHE}_{\text{Me}}$ in $\text{B}_3\text{-NHE}$ are $\sigma$-donors and weak $\pi$-acceptors. However, a strange thing that was found is that the NOCV pairs also exhibit the $\pi$-interactions in $\text{B}_3\text{-NHE}$ and are due to very weak $\pi$-donors $\text{BH}_3 \leftarrow \text{NHE}_{\text{Me}}$ which are also irrelevant for the bond strength. This means the ligands $\text{NHE}_{\text{Me}}$ in $\text{B}_3\text{-NHE}$ are $\sigma$-donors and weak $\pi$-acceptors, and very weak $\pi$-donors. From this, it can be asserted that the ligand $\text{NHE}_{\text{Me}}$ might be considered to have a resonance tetrylene form $\text{NHE}_{\text{Me}}$ in which the central $E$ atom may have two lone pairs and thus be able to show the characteristics of divalent $E(0)$ compounds (Scheme 3). A comparison of donor–acceptor interactions in borane complexes of tetrylenes and tetrylones using EDA-NOCV method indicates that the $B–E$ BDEs in tetrylones and tetrylenes decrease from slighter to heavier homologs. Furthermore, the tetrylone ligands $E(\text{PH})_2$ in $\text{B}_3\text{-EP2}$ are strong $\sigma$-donors and very weak $\pi$-donors, and weak $\pi$-acceptors $\text{H}_3\text{B} \rightarrow \text{Pb}(\text{PH})_2$, while the ligands $\text{NHE}_{\text{Me}}$ in $\text{B}_3\text{-NHE}$ are $\sigma$-donors and weak $\pi$-acceptors, and very weak $\pi$-donors $\text{BH}_3 \leftarrow \{\text{NHE}_{\text{Me}}\}$. These lead the tetrylone ligands to act as tetrylene ligands in borane complexes and vice versa.

4. Conclusion

The EDA-NOCV results suggest that the $B–E$ BDEs in tetrylones and tetrylenes decrease from the lighter to the heavier homologs. The decrease in the bond strengths from the lighter to the heavier homologs of $\text{B}_3\text{-EP2}$ comes mainly from the decrease in the electrostatic attractions $\Delta E_{\text{elstat}}$ and the orbital interactions $\Delta E_{\text{orb}}$, while the decrease in the bond strength from carbene $\text{B}_3\text{-NHC}$ to plumbylene $\text{B}_3\text{-NHPb}$ strongly correlates with the decrease in electrostatic term $\Delta E_{\text{elstat}}$. The EDA-NOCV results show tetrylone ligands $E(\text{PH})_2$ in $\text{B}_3\text{-EP2}$ are strong $\sigma$-donors and very weak $\pi$-donors, and weak $\pi$-acceptors $\text{H}_3\text{B} \rightarrow \text{Pb}(\text{PH})_2$, while the ligands $\text{NHE}_{\text{Me}}$ in $\text{B}_3\text{-NHE}$ are $\sigma$-donors and weak $\pi$-acceptors, and very weak $\pi$-donors $\text{BH}_3 \leftarrow \{\text{NHE}_{\text{Me}}\}$. These lead the tetrylone ligands to act as tetrylene ligands in borane complexes and vice versa. The theoretical results point toward new directions for experimental research in the field of low-coordinate tetrylone and tetrylene compounds in the future.
Acknowledgment

The jobs of this study were run via Erwin cluster which is an excellent service provided by the Hochschulrechenzentrum of the Philipps-Universität Marburg-Germany. NTAN thanks Prof. Dr Gernot Frenking for allowing continuously to use her own computer accounts at Frenking's group. Further computer time provided by the HLRS Stuttgart, the HHLRZ Darmstadt, and the CSC Frankfurt is also acknowledged.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work is supported by the Vietnam National Foundation for Science and Technology Development (NAFOSTED), Vietnam, under grant no. 104.06-2014.13 (Nguyen Thi Ai Nhung).

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