

# Evaluation of the $\sigma$ donating and $\pi$ accepting properties of N-heterocyclic boryl anions

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## **ABSTRACT**

The relative  $\sigma$  donor and  $\pi$  accepting capacities of a range of synthetically relevant boryl anions have been evaluated by examining the geometric, thermochemical and electronic properties of their adducts to the  $\text{Li}^+$  cation and Se atom, as compared to the analogous neutral NHCs, by theoretical methods. The results indicate that boryl anions have a weaker  $\pi$  accepting capability than NHCs, but it is still a non-negligible factor in the bonding contributions between boryl and the Se atom. The tuneability of the  $\pi$  accepting capacity of boryl anions is similar to that of NHCs, indicating a potential for modification of the electronic properties of metal complexes incorporating either boryl or NHC ligands. In all cases, the boryl ligands were found to be superior  $\sigma$  donors to NHCs.

## Introduction

Ligands can have a major impact on the electronic properties of metal centers, which can enable bond activations and catalysis, as well as aid in the stabilization of reactive species. A transformative discovery was the isolation of singlet carbenes, which have subsequently become ubiquitous in main group and metal chemistry.<sup>1-7</sup> Since this revelation, researchers have targeted divalent main group congeners of N-heterocyclic carbenes (NHCs) with analogues containing the entire compliment of rows 2-5 for groups 13-16 (except oxygen) being reported.<sup>8-19</sup> Despite the fact that boron is adjacent to carbon in the periodic table, the boryl anion analogue of an NHC was not generated until 2006 by Nozaki and Yamashita (Figure 1a).<sup>20</sup> The compound was isolated with an unsaturated  $\text{BN}_2\text{C}_2$  system akin to an unsaturated NHC, however the boron remains bound to the lithium center from the reducing agent. Nozaki and Yamashita subsequently isolated lithiated boryl anions with saturated C-C and benzannulated C-C backbones (Figure 1b-c), which are analogous to synthetically important NHCs.

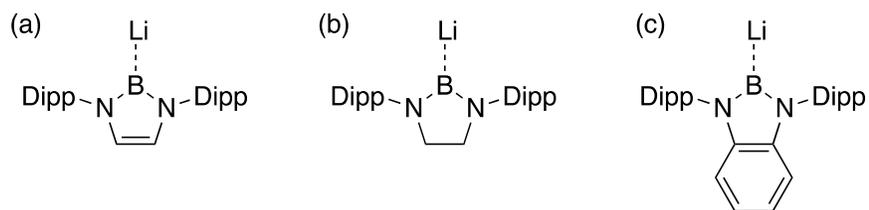


Figure 1. Isolated lithium boryl complexes (Dipp = 2,6-diisopropylphenyl, isolated with two THF or DME solvates coordinated to lithium).<sup>20, 21</sup>

N-heterocyclic carbenes are highly effective ancillary ligands, which has led to a vast library of singlet carbenes with differing properties having been developed that have become invaluable in the synthetic chemist's arsenal. The large collection of accessible carbenes has facilitated the evaluation of their donor properties. There are several experimental means for assessing the donor properties,<sup>22-28</sup> with the simplest and most widely used described here. The Tolman electronic parameter (TEP) quantifies the

overall donating property of the ligand by measuring the CO infrared stretching frequency of late metal carbene-metal carbonyl complexes by taking advantage of the  $\pi$ -backbonding capabilities of CO to correlate the electron density at the metal to the ligand.<sup>29, 30</sup> The  $\pi$ -accepting properties have also been assessed by preparing carbene-phosphinidene or selenourea complexes and subsequently analyzing the corresponding <sup>31</sup>P and <sup>77</sup>Se NMR shifts, using both experimental and theoretical means.<sup>31-34</sup> Very recently, Szostak proposed evaluating  $\sigma$ -donor properties of carbenes by analyzing the <sup>1</sup>H NMR C-H signals of ligand precursors.<sup>35</sup> Steric factors are also important for understanding the activity of NHC ligated compounds and this aspect has been thoroughly investigated. In the present study we have focused only on electronic aspects.<sup>36, 37</sup>

Despite the significant progress in the experimental evaluation of the donor properties of carbenes, the situation is reversed for N-heterocyclic boryl (NHB) analogues with only a limited number of known boryl analogues. The donor-acceptor properties of NHBs have not been investigated using any of the experimental techniques highlighted above. From the aforementioned studies on cyclic carbenes, factors including ring size, backbone saturation vs. unsaturation, substitution on the backbone and adjacent atoms, as well as the type of atoms adjacent to carbon, can all have a significant impact on the donor-acceptor properties of the ligand.

The reported studies on NHB ligands<sup>38, 39</sup> confirm that these species are both highly basic and very nucleophilic, systematically reacting with a diverse range of organic electrophiles.<sup>20, 21, 40</sup> An increasing number of metal and main group complexes of NHB anions are also being reported.<sup>41-52</sup> Jones has also used the boryl fragment as a constituent of bulky amido ligands.<sup>53, 54</sup> NHBs have been demonstrated to act as a substituent that can modulate the properties of electronically active organic compounds.<sup>55-57</sup> Trzaskowski and coworkers carried out theoretical studies comparing the second-generation Grubbs-Hoveyda catalyst, which bears an NHC ligand, to an analogue featuring an anionic NHB ligand in

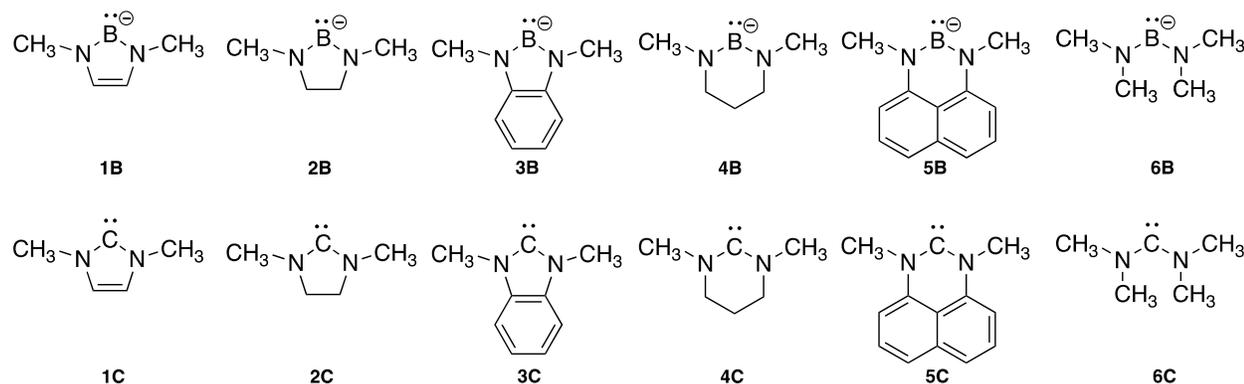
place of the NHC.<sup>58,59</sup> With the NHB analogue there is a substantial increase in the Ru-O bond distance of the *trans* ether ligand, and a decrease in energy for the dissociation of the ether, which is attributed to the increased  $\sigma$ -donation of the NHB in comparison with the NHC. These findings suggest that Ru-NHB complexes could be superior catalysts to Ru-NHC complexes for metathesis reactions. Theoretical studies of NHBs, along with other boryl ligands, suggest that they are strong *trans* donor ligands.<sup>60</sup> For NHCs, variation of the electronic structure of the ring such as changing from an unsaturated to saturated backbone CC bond, results in orders of magnitude differences in catalysis kinetics in olefin metathesis reactions.<sup>61</sup>

The donor-acceptor properties of boron-containing systems have been explored by numerous groups. Marder has reported that boron is a good  $\sigma$  donor, but that the  $\pi$ -accepting or  $\pi$ -donating character is dependent on the chemical environment.<sup>55, 57, 62</sup> For example, in organoboron compounds the boron ligand can act as a  $\pi$ -donor in a 1,2,3-diazaborole and a  $\pi$ -acceptor in a BMe<sub>2</sub> group where the boron in NHB is less  $\pi$ -accepting than in Ar<sub>2</sub>B.<sup>57</sup> Jäkle has noted that boron acts as a  $\pi$ -acceptor in a study of extended oligomers, whereby inclusion of boron provided promising applications in optoelectronics.<sup>63</sup> The  $\pi$ -accepting character of boron has also been highlighted by Braunschweig in an investigation of a thiophene with two tetraphenylborole substituents.<sup>64</sup> Aldridge has investigated several NHBs complexed to AuCl with  $\sigma$ -donor components of the interaction energy being larger than for NHCs (due to anionic nature of boryl anion), while  $\pi$ -accepting character is reduced in comparison with NHCs.<sup>65</sup>

The potential of NHBs prompted us to study the donor properties of a series of boryl anions, with an overall goal of evaluating the electronic tuneability of boryl anions in comparison with NHC ligands. In this study, we selected six ligand frameworks based on currently known boryl species together with

some unknown derivatives analogous to prominent carbene frameworks. As illustrated in Scheme 1, we investigated the five-membered unsaturated NHB (**1B**), five-membered saturated NHB (**2B**), benzofused NHB (**3B**), six-membered saturated NHB (**4B**), six-membered unsaturated NHB with a naphthyl backbone (**5B**), and the simple acyclic diamino boryl (**6B**). The former three have been isolated as the lithium complexes by Nozaki and Yamashita,<sup>21</sup> while the latter three are unknown as the free species. **6B** has been incorporated as a ligand on Pt complexes via oxidative addition of the bromoborane precursor onto Pt(0).<sup>66</sup> Six analogous carbenes were also considered (**1C-6C**), by replacement of the B<sup>-</sup> anion with an isoelectronic C atom (Scheme 1). Model compounds with methyl substituents on the nitrogen atoms were utilised for computational efficiency.

Scheme 1. Boryl anions and analogous NHC ligands investigated in this study.



Compound **1B** has previously been investigated by Tuononen at the PBE1PBE/TZVP DFT level of theory as part of a study of group 13-16 isoelectronic analogues of NHCs.<sup>67</sup> While their results are insightful and reveal **1B** to be a weak  $\pi$ -acceptor, their broad study on the group 13-16 species did not examine the  $\sigma$ -donating and  $\pi$ -accepting properties of boryl anions in detail. Importantly, the N-substituent (-H, -CH<sub>3</sub>, or -Ph) was found to have no significant effect on the donor-acceptor properties, justifying our use of N-methyl substitution. Schoeller has investigated the general electronic structure of analogues of unsaturated **1B**, as well as the other group 13 analogues, concluding that the central B

atom is electron rich containing a lone pair, which has now been experimentally borne out.<sup>68</sup> Fuentealba studied the effect of modifying the N atoms of the boryls on calculated proton affinities, although more synthetically relevant modifications of the organic backbone that are known to have a big impact on NHCs were not explored. Compound **1B** and its lithiated complex were also investigated using DFT methods by Nozaki and Yamashita.<sup>21</sup> They noted that the presence of the Li cation with an ionic B-Li bond serves to highlight electron localization with a prominent lone-pair and subsequent nucleophilicity at the boron center, from which they concluded that B-Li bonds in boryllithium species would have similar character to C-Li bonds in alkyllithium reagents. Changes in the B-N bond distances and angles for **1B-3B** were also considered in this study, with an elongated bond in **3B** (1.50 Å) as compared to **1B** and **2B** (~ 1.45 Å). Schleyer has investigated a lithiated complex of an acyclic diamino boryl anion, Li-B(NH<sub>2</sub>)<sub>2</sub>, that is a simpler version of **6B**, similarly identifying a directional lone-pair on the B atom.<sup>69</sup> A combined experimental and theoretical study of anionic NHC derivatives including **1B**, **2B** and **3B** (with aryl N-substituents) by Aldridge, primarily evaluating  $\sigma$  donating ability lead to the conclusion that the B-centred species were significantly stronger donors than anionic NHCs remotely incorporating the anionic fragment.<sup>65</sup>

The complexation of boryl anions with appropriate partner elements allows an exploration of boryl anion donor properties. Here we have assessed the tuneability of both  $\sigma$ -donor and  $\pi$ -acceptor properties of the series of boryl anions in comparison with NHCs by considering Li<sup>+</sup> and Se complexes of each ligand (Figure 2). Li<sup>+</sup> was chosen as there is no possibility of  $\pi$  backbonding, and Se was chosen, since with NHCs the degree of  $\pi$  backbonding has been demonstrated to be correlated with the easily observable experimental parameter of <sup>77</sup>Se NMR spectroscopy.<sup>32, 33, 70</sup>

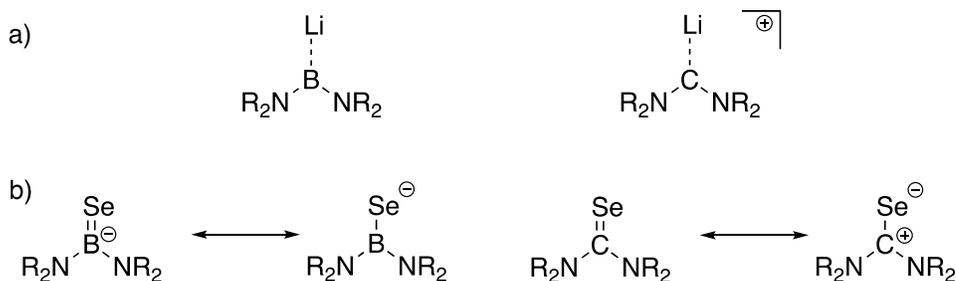


Figure 2. a) Lewis structure of boryl and NHC complexes with Li<sup>+</sup> studied for  $\sigma$ -donating properties for this work. b) Two canonical structures of boryl and NHC selenium complexes examined for  $\pi$ -accepting character in this work.

## Computational Methods

All calculations were performed using Gaussian 16 revision A.03 unless noted.<sup>71</sup> Geometry optimizations were carried out with the M06-2X density functional<sup>72</sup> utilizing the def2-TZVP basis sets<sup>73</sup> inclusive of solvation with Truhlar's SMD model<sup>74</sup> with parameters for acetonitrile solvent. Harmonic vibrational frequencies were computed analytically at the same level of theory in order to characterise the stationary points as minima on the potential energy surface and determine thermochemical properties. B3LYP-D3(BJ) yielded equivalent geometries.<sup>75-78</sup> Molecular orbital and natural bond orbital (NBO) analysis was carried out at the B3LYP-D3(BJ)/def2-TZVP (SMD, acetonitrile) level of theory at the M06-2X/def2-TZVP(SMD, acetonitrile) geometries. NBO analysis was performed using NBO 6.0.<sup>79</sup>

The nature of the chemical bond was investigated by means of an energy decomposition analysis (EDA) developed independently by Morokuma<sup>80</sup> and subsequently by Ziegler and Rauk.<sup>81, 82</sup> The bonding analysis focuses on the instantaneous interaction energy  $\Delta E_{\text{int}}$  of a bond A–B between two fragments A and B in the particular electronic reference state and in the frozen geometry of AB. This interaction energy is divided into three main components [Eq. (1)].

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{Disp}} + \Delta E_{\text{orb}} \quad (1)$$

$\Delta E_{\text{elstat}}$  represents the quasiclassical electrostatic interaction energy between the unperturbed charge distributions of two fragments and is usually attractive.  $\Delta E_{\text{Pauli}}$  comprises the destabilising interactions between electrons of the same spin on either fragment.  $\Delta E_{\text{Disp}}$  represents the contribution from dispersion.  $\Delta E_{\text{orb}}$  represents the energy change due to the overlap of orbitals of the two fragments and is attractive. The orbital interaction  $\Delta E_{\text{orb}}$  accounts for bond pair formation (electron sharing), charge transfer, and polarisation effects. The  $\Delta E_{\text{orb}}$  term can be decomposed into contributions from each irreducible representation of the point group of the interacting system.

The EDA-NOCV<sup>83</sup> method combines charge (NOCV) and energy (EDA) decomposition schemes to decompose the deformation density associated with bond formation,  $\Delta\rho$ , into different components of the chemical bond. The EDA-NOCV calculations provide pairwise energy contributions for each pair of interacting orbitals to the total bond energy. The EDA-NOCV scheme thus provides both qualitative ( $\Delta\rho_{\text{orb}}$ ) and quantitative ( $\Delta E_{\text{orb}}$ ) information about the strength of orbital interactions in chemical bonds. An alternative energy decomposition scheme that has been developed to probe  $\pi$ -accepting character is charge density analysis,<sup>84</sup> although only EDA-NOCV was employed in the current work. The EDA-NOCV calculations were carried out with the program package ADF2016.01<sup>85, 86</sup> at the B3LYP-D3(BJ)/TZ2P level of theory (gas phase) using the M06-2X/def2-TZVP(SMD, acetonitrile) optimised geometries.

## Results and Discussion

### Binding Energies

The relative  $\sigma$ -donor strength of the NHBs **1B-6B** was initially evaluated by calculating the binding free energy of a Li cation, since  $\text{Li}^+$  is the typical cation for boryl and it is a pure  $\sigma$ -acceptor with no ability to participate in  $\pi$ -backbonding. The results are summarized in Table 1. Solvation has a large effect on the binding free energies ( $\Delta G$ ), which range from -20.0 to -22.4 kcal/mol, with results

suggesting that acyclic **6B** is the strongest  $\sigma$ -donor and **5B** the weakest of the cyclic systems. Analogues **2B** and **4B** are also relatively strong  $\sigma$ -donor in the series with  $\text{Li}^+$  binding energies of -22.3 kcal/mol. Calculation of  $\text{Li}^+$  binding to the analogous NHCs **1C-6C** yielded smaller binding energies as expected, mostly due to the effect of modelling a neutral species binding to a cation as opposed to a boryl anion, as well as the reduced nucleophilicity of the NHC. However, an important observation for the present study is that the inclusion of solvation leads to a variation in binding energy between the NHCs of 3.5 kcal/mol (from -9.7 to -13.2 kcal/mol), which is slightly larger than the variation in binding energies with the boryl anions (2.4 kcal/mol). The trend is reversed in gas phase calculations, with variation in binding energy between NHCs being smaller than with the boryl anions. Here **4C** and **5C** are the strongest and weakest  $\sigma$ -donors (as defined as energy of binding  $\text{Li}^+$ ) respectively, with acyclic **6C** and unsaturated **1C** also being relatively strong  $\sigma$ -donors, consistent with results for the boryl analogues.

The  $\text{Li}^+$  binding energy results indicates that in terms of pure  $\sigma$ -donor strength, boryl anions appear marginally less tuneable than NHCs. It is noted that the  $\sigma$ -donor strength towards  $\text{Li}^+$  is nearly identical for the unsaturated five-membered **1** and saturated five-membered **2**, which are the most common classes of boryl and NHC ligands, respectively.

**Table 1.** M06-2X/def2-TZVP(SMD,acetonitrile) calculated binding energy ( $\Delta G$ , kcal/mol) of  $\text{Li}^+$  and Se to boryl anions and NHCs.<sup>a</sup>

	<b>1X</b>	<b>2X</b>	<b>3X</b>	<b>4X</b>	<b>5X</b>	<b>6X</b>
$\text{Li}^+$						
NHB	-22.0	-22.3	-21.0	-22.3	-20.0	-22.4
NHC	-13.1	-12.6	-11.7	-13.2	-9.7	-13.1
Se						
NHB	-117.6	-120.8	-117.2	-121.8	-116.2	-123.3
NHC	-63.4	-64.9	-63.8	-63.6	-56.5	-66.2

<sup>a</sup> For NHB ligands **1B-6B**, X = B, for NHC ligands **1C-6C**, X=C.

To evaluate capacity for  $\pi$ -backbonding, we initially examined the binding of the boryl anions and NHCs to a Se atom, as the perturbation of the electron density (resulting in experimental NMR changes) about the Se atom is a measure of the  $\pi$ -accepting capacity of NHCs. The saturated NHC **2C** is known to be a better  $\pi$ -acceptor than the unsaturated NHC **1C**, which is reflected in the calculated Se binding energies. The binding of Se is 1.5 kcal/mol more favorable for saturated **2C** compared to **1C**. In contrast, the binding of  $\text{Li}^+$  is 0.5 kcal/mol more favorable with unsaturated **1C**. The difference in binding of Se between the corresponding boryl anions (**1B**, **2B**) is slightly greater at 3.2 kcal/mol with **2B** also being stronger. Of the boryl anions considered in this work, **3B** and **5B** appear to be the superior  $\pi$ -acceptors based on the comparison with  $\text{Li}^+$  binding energies; **3B** and **5B** have 1.0-2.0 kcal/mol smaller  $\text{Li}^+$  binding energies (poorer  $\sigma$  donors) compared to **1B** and **2B**, however they are only 0.4-1.3 kcal/mol less favourable in their binding to Se. Overall, from the binding energy of Se, acyclic **6B** forms the strongest bond. Analogous to results with  $\text{Li}^+$ , variation in binding energy with NHCs (9.7 kcal/mol), is slightly larger than the variation in binding energies with the boryl anions (7.1 kcal/mol), which suggests that boryl anions are marginally less tuneable for both  $\sigma$  and  $\pi$  interactions.

## Geometries

Geometric parameters of the ligand-metal complexes (Table 2) are consistent with the binding energy analysis, with **3B** having slightly shorter B-Se bonds and larger Wiberg bond indices (WBI) than the other derivatives. The differences in WBIs for the boryl anions are similar in magnitude to the differences for the NHCs. The WBIs for the boryls are generally higher than the WBIs for the corresponding NHCs, indicating that boryls are possibly similar in capacity to NHCs for  $\pi$ -backbonding.

Table 2. Calculated metal-ligand bond distances (Å) for complexes of **1X-6X** bound to Li<sup>+</sup> or Se. Wiberg bond indices (WBI) in parentheses.<sup>a</sup>

	<b>1X</b>	<b>2X</b>	<b>3X</b>	<b>4X</b>	<b>5X</b>	<b>6X</b>
Li <sup>+</sup>						
NHB; <i>r</i> (B-Li)	2.251 (0.34)	2.268 (0.34)	2.250 (0.32)	2.289 (0.36)	2.263 (0.31)	2.294 (0.37)
NHC; <i>r</i> (C-Li)	2.068 (0.09)	2.086 (0.09)	2.080 (0.09)	2.090 (0.09)	2.103 (0.09)	2.092 (0.09)
Se						
NHB; <i>r</i> (B-Se)	1.956 (1.25)	1.957 (1.27)	1.939 (1.31)	1.992 (1.20)	1.960 (1.30)	1.993 (1.21)
NHC; <i>r</i> (C-Se)	1.863 (1.21)	1.862 (1.26)	1.857 (1.26)	1.891 (1.21)	1.871 (1.29)	1.881 (1.25)

<sup>a</sup>For NHB ligands **1B-6B**, X = B, for NHC ligands **1C-6C**, X=C.

### Frontier Molecular Orbitals

A comparison of the frontier molecular orbital energies of the boryl anions and NHCs (Figure 3-4) yields trends consistent with the above binding energy data. Plots of representative MOs are illustrated in Figure 5. For **1B-6B** the  $\sigma$ -donor orbital is consistently the HOMO, whereas for NHCs it is the HOMO for **1C**, **4C**, and **6C**, but HOMO-1 for **2C** and **5C**, and HOMO-2 for **3C**. The  $\pi$ -acceptor orbital of the carbene ligands **1C-6C** is always the LUMO or LUMO+1. For the boryl anions **1B-6B** the  $\pi$ -acceptor MO is generally the LUMO, but for **3B** and **5B** it is LUMO+2. Of the boryl anions, the HOMO energy levels for **4B** and **6B** are the highest, which is indicative of strong  $\sigma$ -donation and consistent with these ligands exhibiting the strongest bonds to Li<sup>+</sup>. The  $\pi$ -acceptor orbital energy levels are lowest for **4B** (LUMO) and **5B** (LUMO+2), consistent with these ligands being the best  $\pi$  acceptors. Of the most synthetically relevant boryl anions **1B** and **2B**, **2B** is both a better  $\sigma$ -donor and  $\pi$  acceptor, based on a higher energy HOMO and lower energy acceptor (LUMO), consistent with the properties of the analogous NHC ligands.

In terms of differences, there is only a 0.15 eV difference in the HOMO energy level for **1B** and **2B**, whereas the difference for **1C** and **2C** is 0.23 eV, suggesting greater tuneability in  $\sigma$  donation for the NHC ligands. The difference in energy in the  $\pi$ -accepting LUMO for the two boryls is 0.19 eV; the

difference for the corresponding NHCs is 0.11 eV. This suggests that in terms of  $\pi$ -accepting capacity, there is potentially a larger scope for tuneability in the most synthetically relevant boryl anions.

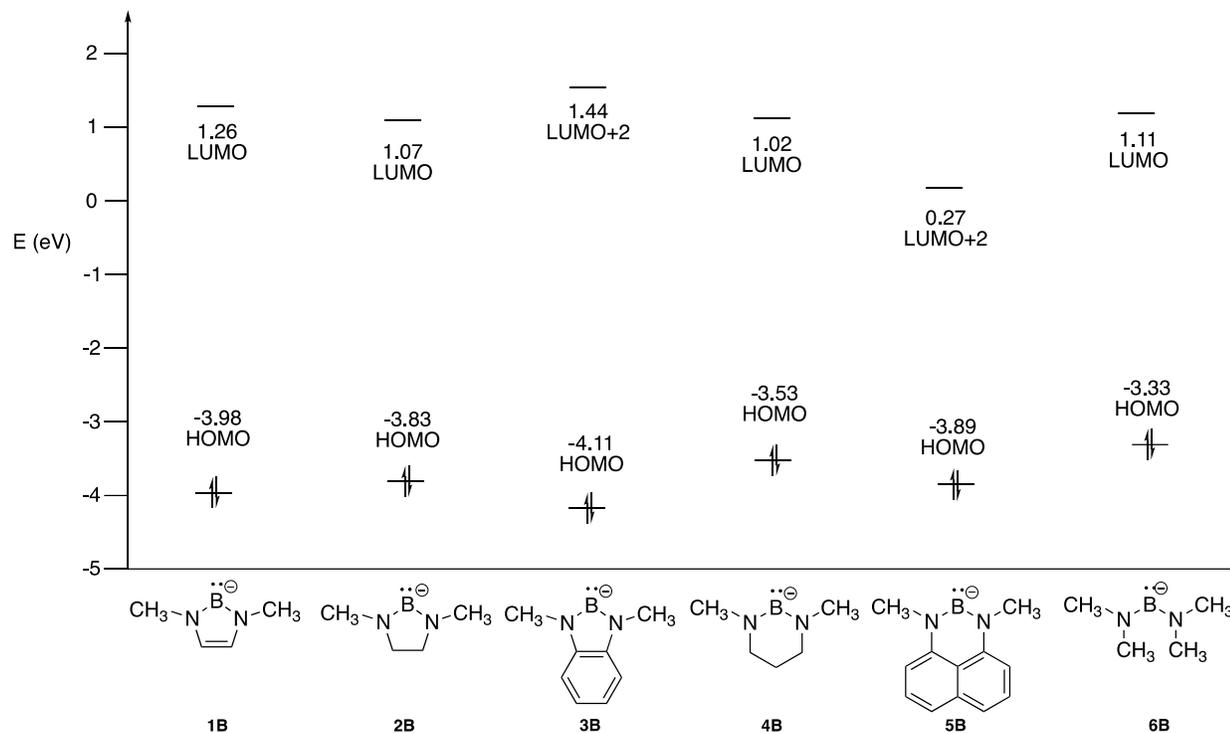


Figure 3: Relative energy diagram of the  $\sigma$ -donor and  $\pi$ -acceptor orbitals for the NHBs **1B-6B**.

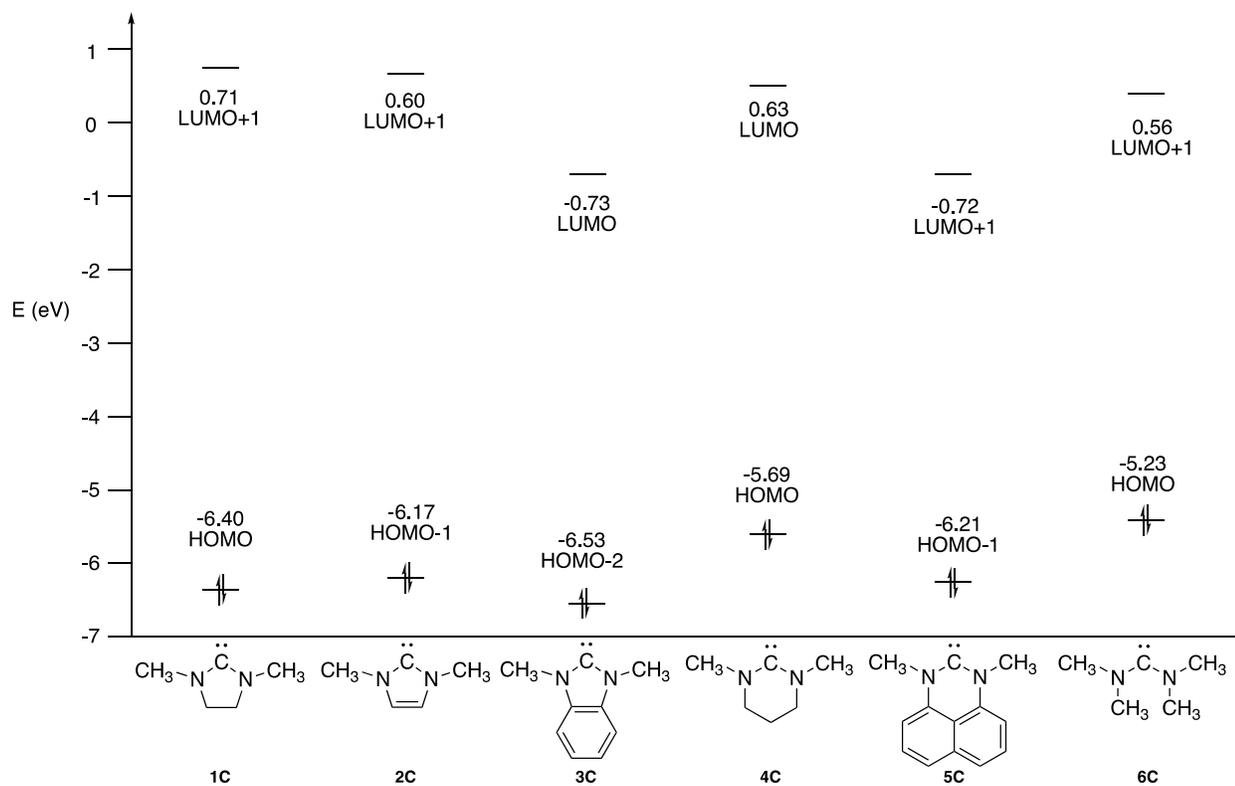


Figure 4: Relative energy diagram of the  $\sigma$ -donor and  $\pi$ -acceptor orbitals for the NHCs **1C-6C**.

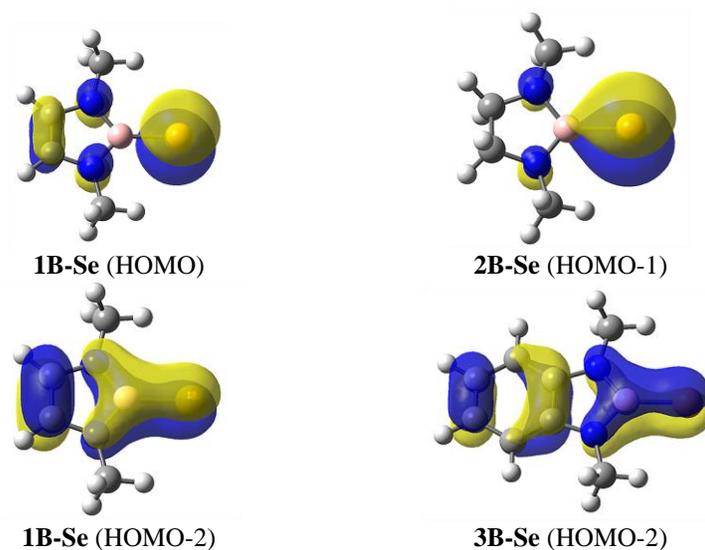


Figure 5. Selected frontier molecular orbitals of B-Se adducts.

In the boryl-Se complexes (**1B-Se** to **6B-Se**) a  $\pi$ -symmetric lone-pair on the Se atom oriented perpendicular to the plane of the boryl cycle is typically found in the HOMO or HOMO-1 orbital, which potentially  $\pi$ -donate electrons (Figure 5). Little delocalization to the B atom is apparent in these MOs. Orbitals associated with B-Se  $\pi$ -bond are found in the HOMO-2 or HOMO-3, while the orbital associated with B-Se  $\sigma$ -bonding is energetically stabilised and typically found in the HOMO-3 or HOMO-4 orbital. A second  $\pi$ -symmetric orbital characterized as a lone-pair on the Se atom (atomic p orbital) is found in the plane of the boryl heterocycle paired with the lone-pair perpendicular to the heterocycle plane. This molecular orbital may be associated with a  $\pi$ -backbonding interaction. There is also a  $\pi$ -type interaction that arises from overlap of the occupied  $\pi$ -system of the boryl ring and the  $p\pi$  orbital of the Se atom that is found lower in energy in either the HOMO-2 or HOMO-3. These are similar to the interactions calculated for the NHC-Se complexes. This type of  $\pi$ -donor interaction is also a non-negligible contributor to the metal-C bonds in NHC complexes.<sup>87</sup>

### Energy Decomposition Analysis

In order to quantify the donor-acceptor properties of the boryl and NHC rings, energy decomposition analysis (EDA) in combination with natural orbital for chemical valence (EDA-NOCV) theory calculations were carried out for the lithium metal complexes. To shed light into the nature of bonding of  $\text{Li}^+$  and Se by these ligands, a donor-acceptor approach was taken with both the donor ligand and the metal atom considered as closed-shell fragments. The Se atom was considered in the  $^1\text{D}$  excited state, with an empty  $p_z$  orbital (B-Se or C-Se bond is along the  $z$ -axis) and with  $p_x$  and  $p_y$  orbitals doubly occupied. In this manner, the  $\sigma$ -donor and  $\pi$ -accepting properties of the ligands can readily be compared. For  $\text{Li}^+$  the metal is trivially a closed shell fragment in a  $^1\text{S}$  state. It is important to note that in EDA the value of  $\Delta E_{\text{int}}$  differs from the dissociation energy ( $D_e$ ) since  $\Delta E_{\text{int}}$  is calculated with the fragments at the frozen geometry of complex and in the appropriate electronic state for the complex

rather than the lowest energy structure and electronic state of the separate fragments. Results are presented in Table 3 (lithium) and Table 4 (selenium).

Table 3. EDA-NOCV results of boryl-lithium complexes with a donor-acceptor bonding description at the B3LYP-D3(BJ)/TZ2P//M06-2X/def2-TZVP(SMD,acetonitrile) level of theory. Fragments of Li<sup>+</sup> (singlet), boryl anion (singlet) and NHC (singlet).<sup>a</sup>

NHB-Li	1B-Li	2B-Li	3B-Li	4B-Li	5B-Li	6B-Li
$\Delta E_{\text{int}}$	-169.9	-169.9	-162.1	-171.7	-156.9	-169.9
$\Delta E_{\text{Pauli}}$	34.4	34.7	33.3	35.9	34.8	36.0
$\Delta E_{\text{elstat}}^{\text{b}}$	-176.7 (86.5)	-177.4 (86.7)	-167.4 (85.7)	-178.4 (85.9)	-162.0 (84.5)	-177.3 (86.1)
$\Delta E_{\text{disp}}^{\text{b}}$	-1.6 (0.8)	-1.5 (0.7)	-1.6 (0.8)	-1.7 (0.8)	-1.8 (0.9)	-1.8 (0.9)
$\Delta E_{\text{orb}}^{\text{b}}$	-26.0 (12.7)	-25.7 (12.6)	-26.4 (13.5)	-27.5 (13.2)	-27.9 (14.5)	-26.8 (13.0)
$\Delta E_{\text{orb}}(\sigma)^{\text{c}}$	-17.4 (66.8)	-18.2 (70.7)	-16.2 (61.2)	-18.6 (67.6)	-15.7 (56.4)	-17.9 (66.8)
NHC-Li <sup>+</sup>	1C-Li	2C-Li	3C-Li	4C-Li	5C-Li	6C-Li
$\Delta E_{\text{int}}$	-61.5	-60.9	-60.1	-62.8	-55.9	-61.7
$\Delta E_{\text{Pauli}}$	21.7	21.0	20.7	22.7	20.6	22.7
$\Delta E_{\text{elstat}}^{\text{b}}$	-58.0 (69.7)	-57.2 (69.8)	-53.8 (66.6)	-58.3 (68.2)	-46.7 (61.0)	-57.5 (68.1)
$\Delta E_{\text{disp}}^{\text{b}}$	-2.5 (3.0)	-2.5 (3.1)	-2.5 (3.1)	-2.8 (3.3)	-2.9 (3.8)	-2.9 (3.4)
$\Delta E_{\text{orb}}^{\text{b}}$	-22.7 (27.3)	-22.7 (27.3)	-24.4 (30.3)	-24.4 (28.5)	-26.9 (35.2)	-24.1 (28.5)
$\Delta E_{\text{orb}}(\sigma)^{\text{c}}$	-11.2 (49.2)	-11.2 (49.2)	-11.0 (45.0)	-12.1 (49.4)	-11.1 (41.4)	-12.2 (50.6)

<sup>a</sup> kcal/mol.

<sup>b</sup> Values in parentheses give the percentage contribution to the attractive interactions,  $\Delta E_{\text{elec}} + \Delta E_{\text{orb}} + \Delta E_{\text{Disp}}$ .

<sup>c</sup> ETS-NOCV. Values in parentheses give the percentage contribution to the orbital interaction,  $\Delta E_{\text{orb}}$ .

Table 4. EDA-NOCV results of boryl-selenium complexes with a donor-acceptor bonding description at the B3LYP-D3(BJ)/TZ2P//M06-2X/def2-TZVP(SMD, acetonitrile) level of theory. Fragments of Se ( $^1D$  state), boryl anion (singlet) and NHC (singlet).<sup>a</sup>

NHB-Se <sup>-</sup>	1B-Se	2B-Se	3B-Se	4B-Se	5B-Se	6B-Se
$\Delta E_{\text{int}}$	-174.5	-176.5	-174.5	-176.9	-173.9	-177.6
$\Delta E_{\text{Pauli}}$	367.7	376.9	375.8	375.1	388.4	369.9
$\Delta E_{\text{elstat}}^b$	-285.9 (52.7)	-293.9 (53.1)	-292.4 (53.1)	-291.5 (52.8)	-302.7 (53.8)	-287.4 (52.5)
$\Delta E_{\text{disp}}^b$	-4.2 (0.8)	-4.2 (0.8)	-4.3 (0.8)	-4.5 (0.8)	-4.8 (0.8)	-4.6 (0.8)
$\Delta E_{\text{orb}}^b$	-252.1 (46.5)	-255.3 (46.1)	-253.7 (46.1)	-256.0 (46.4)	-254.9 (45.3)	-255.5 (46.7)
$\Delta E_{\text{orb}}(\sigma)^c$	-224.9 (89.2)	-228.5 (89.5)	-224.0 (88.3)	-229.9 (89.8)	-224.3 (88.0)	-229.3 (89.7)
$\Delta E_{\text{orb}}(\pi_1)^c$	-11.6 (4.6)	-12.4 (4.9)	-14.0 (5.5)	-11.4 (4.5)	-14.5 (5.7)	-12.9 (5.1)
$\Delta E_{\text{orb}}(\pi_2)^c$	-7.9 (3.1)	-7.4 (2.9)	-8.3 (3.3)	-7.9 (3.1)	-9.1 (3.6)	-6.4 (2.5)
NHC-Se	1C-Se	2C-Se	3C-Se	4C-Se	5C-Se	6C-Se
$\Delta E_{\text{int}}$	-115.1	-116.4	-114.8	-115.8	-112.6	-120.1
$\Delta E_{\text{Pauli}}$	273.8	278.2	279.6	276.2	286.6	282.5
$\Delta E_{\text{elstat}}^b$	-209.3 (53.8)	-211.5 (53.6)	-211.1 (53.5)	-212.2 (54.1)	-214.0 (53.6)	-216.7 (53.8)
$\Delta E_{\text{disp}}^b$	-5.3 (1.4)	-5.4 (1.4)	-5.3 (1.3)	-6.0 (1.5)	-6.1 (1.5)	-5.9 (1.5)
$\Delta E_{\text{orb}}^b$	-174.3 (44.8)	-177.6 (45.0)	-177.9 (45.1)	-173.8 (44.3)	-179.1 (44.9)	-180.0 (44.7)
$\Delta E_{\text{orb}}(\sigma)^c$	-138.1 (79.2)	-140.2 (79.0)	-138.6 (77.9)	-139.0 (80.0)	-137.9 (77.0)	-142.5 (79.2)
$\Delta E_{\text{orb}}(\pi_1)^c$	-19.3 (11.1)	-21.0 (11.8)	-21.1 (11.9)	-19.1 (11.0)	-23.3 (13.0)	-21.9 (12.2)
$\Delta E_{\text{orb}}(\pi_2)^c$	-8.6 (4.9)	-8.4 (4.7)	-10.0 (5.6)	-7.8 (4.5)	-9.4 (5.2)	-7.3 (4.1)

<sup>a</sup> kcal/mol.

<sup>b</sup> Values in parentheses give the percentage contribution to the attractive interactions,  $\Delta E_{\text{elec}} + \Delta E_{\text{orb}} + \Delta E_{\text{Disp}}$ .

<sup>c</sup> ETS-NOCV. Values in parentheses give the percentage contribution to the orbital interaction,  $\Delta E_{\text{orb}}$ .

For the lithium ion complexes ( $n\mathbf{C-Li}$  and  $n\mathbf{B-Li}$ ,  $n=1-6$ ), the data in Table 4 reveals that the interaction ( $\Delta E_{\text{int}}$ ) between  $1\mathbf{B-6B}$  and  $\text{Li}^+$  is rather strong, being -156.9 to -171.7 kcal/mol, which is significantly greater than for  $1\mathbf{C-6C}$  (-55.9 to -61.7 kcal/mol). For both boryl and NHC ligands, the attractive interaction is dominated by Coulombic interactions, which are larger for the boryls in both magnitude (-162.0 to -178.4 kcal/mol) and proportion (~85%) compared to NHCs (-46.7 to -58.3 kcal/mol; 61-70%). The increased Coulombic attraction in boryl-Li complexes is largely responsible for the greater overall  $\Delta E_{\text{int}}$  compared to  $\text{NHC-Li}^+$ . The orbital interaction ( $\Delta E_{\text{orb}}$ ) contributes 13-14% of the attractive interaction. Analysis of pairwise energy contributions for each pair of interacting orbitals indicates that the  $\Delta E_{\text{orb}}$  is dominated by  $\sigma$ -donation ( $\Delta E_{\text{orb}}(\sigma)$ ). There is no evidence of  $\pi$ -back

donation as expected, with the only other non-negligible orbital interaction being of  $\pi$  symmetry, that is associated with donation from the cyclic N atoms to the empty  $p_\pi$  orbital of the B or C atoms. Interestingly,  $\sigma$ -donation is calculated to be greater in the NHB-Li complexes in both magnitude of interaction and proportion of the total covalent interaction. The larger  $\sigma$ -donating ability of **1B-6B** over **1C-6C** is clearly understood from the relative magnitude of  $\Delta E_{\text{orb}}(\sigma)$ . The associated charge flow (red→blue) of  $\sigma$ -donation is readily reflected from the corresponding plots of deformation densities ( $\Delta\rho$ ) associated with each pairwise  $\Delta E_{\text{orb}}$  component in Figure 6. For the purpose of comparing tuneability, it is of interest to note that the variation in  $\sigma$ -donation for the boryls (2.8 kcal/mol) is slightly greater than for NHCs (1.2 kcal/mol).

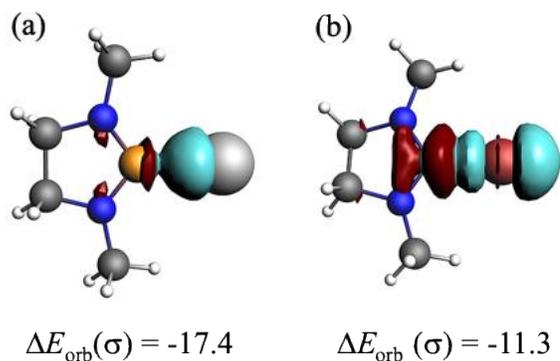


Figure 6. Shape of the deformation density  $\Delta\rho$  associated with the orbital interaction  $\Delta E_{\text{orb}}(\sigma)$  (kcal/mol) in (a) **2B-Li** and (b) **2C-Li**. The isosurface value is 0.003. The color code of the charge flow is red → blue.

For the selenium complexes ( $n\text{C-Se}$  and  $n\text{B-Se}$ ,  $n = 1-6$ ), the data in Table 5 indicates that the interaction ( $\Delta E_{\text{int}}$ ) with Se is stronger than for  $\text{Li}^+$ , with the boryls (-173.9 to -177.6 kcal/mol) again exhibiting a stronger interaction than the NHCs (-112.6 to -120.1 kcal/mol). For both boryl and NHC ligands the Coulombic and covalent interactions are calculated to be approximately equal in

importance. Electrostatic interactions are very slightly more dominating in both cases, ranging from 52.5-53.8% of the interaction in the boryls and 53.5-54.1% in the NHCs. Analysis of the orbital interaction indicates that  $\sigma$ -donation ( $\Delta E_{\text{orb}}(\sigma)$ ) is dominant for boryl and NHC, however they are larger in magnitude (and percentage) for the boryl. The trend matches that for interactions with  $\text{Li}^+$  (Table 4). In boryl-Se complexes, the  $\pi$ -backbonding contribution ( $\Delta E_{\text{orb}}(\pi_1)$ ) is in the range of 4.6-5.7%, but for NHC it is larger at 11.0-13.0%. Interestingly, there is also a noticeable  $\pi$ -donating contribution,  $\Delta E_{\text{orb}}(\pi_2)$ , being -6.4 to -8.3 kcal/mol (2.5-3.3%) for boryl and -7.3 to 10.0 kcal/mol (4.1-5.6%) for NHC. The strength of the  $\pi$ -donating contribution is about half that of the  $\pi$ -backbonding contribution. The larger  $\sigma$ -donating ability of **1B-6B** over **1C-6C**, and weaker  $\pi$ -backbonding, is clearly understood from the relative magnitude of  $\Delta E_{\text{orb}}(\sigma)$ ,  $\Delta E_{\text{orb}}(\pi_1)$ , and  $\Delta E_{\text{orb}}(\pi_2)$ . The associated charge flow (red→blue) of  $\sigma$ -donation,  $\pi$ -backbonding, and  $\pi$ -donation is readily reflected from the corresponding plots of deformation densities ( $\Delta\rho$ ) in Figure 7. These results indicate that NHCs are better  $\pi$ -acceptors from the Se atom than the boryls. In both sets of ligands, the most synthetically relevant saturated (**1X**) and unsaturated (**2X**) analogues have a larger  $\pi$  component in the bonding interaction. The difference in  $\pi$ -backbonding orbital contribution between the least  $\pi$ -accepting boryl **4B** and most  $\pi$ -accepting **5B** is 3.1%. For NHCs the corresponding difference is 4.2%. The NHCs and boryl anions both exhibit similar  $\pi$ -donating characteristics from EDA-NOCV results.

Overall, for the interaction with Se the analysis of the  $\pi$ -accepting orbital contribution indicates that NHCs are better  $\pi$  acceptors than boryls, and also exhibit slightly greater  $\pi$ -accepting tunability. In contrast, boryls are stronger  $\sigma$ -donors than NHCs, but with similar  $\sigma$ -donating tunability.

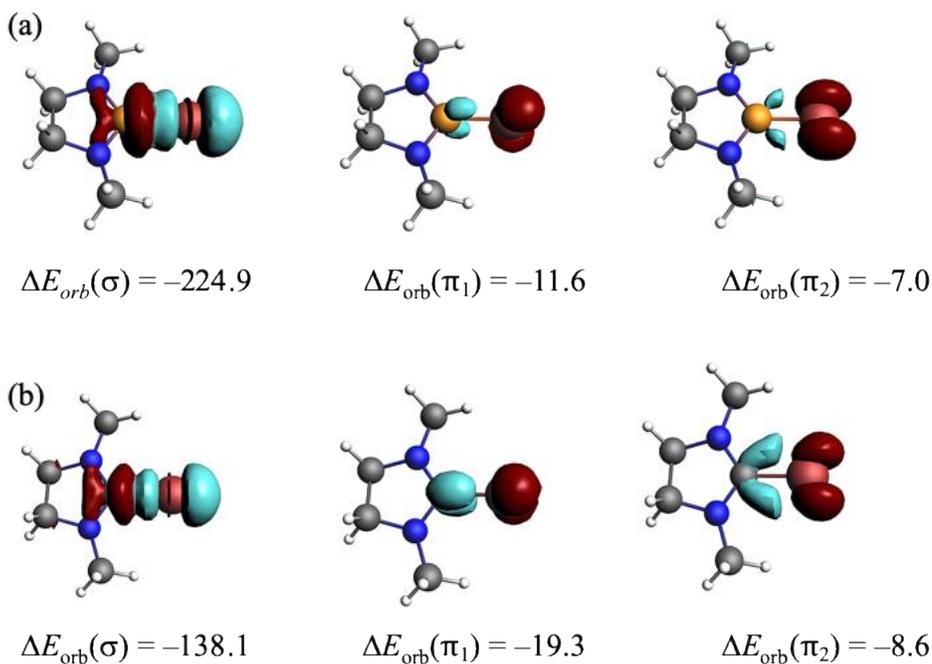


Figure 7. Shape of the deformation densities  $\Delta\rho(\sigma)$ ,  $\Delta\rho(\pi_1)$ , and  $\Delta\rho(\pi_2)$ , which are associated with the orbital interactions  $\Delta E_{orb}(\sigma)$ ,  $\Delta E_{orb}(\pi_1)$ , and  $\Delta E_{orb}(\pi_2)$  (kcal/mol) in (a) **2B-Se** and (b) **2C-Se**. The isosurface value is 0.005. The color code of the charge flow is red  $\rightarrow$  blue.

## Conclusion

Energy decomposition analysis calculations indicate that NHCs are better  $\pi$  acceptors than boryl anions, but that the boryl anions do have some ability to act as a  $\pi$  acceptor. The  $\pi$ -accepting tuneability across the different boryl anions is also reduced in comparison with NHCs. It appears that estimation of the importance of  $\pi$ -backbonding for the boryl anions is likely insufficient from purely a geometrical analysis, indicating the importance of performing more detailed theoretical analysis beyond simple geometry calculations. The boryls are calculated to be significantly better  $\sigma$ -donors than NHCs, which suggests that replacing a ligand from NHC to boryl would give a much more electron-rich metal complex including a more negative formal charge. Using a boryl with better  $\pi$ -accepting capability could potentially reduce the charge at the metal if that was desired for a given application.

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## **Supporting information**

Cartesian coordinates for calculated geometries in xyz format.

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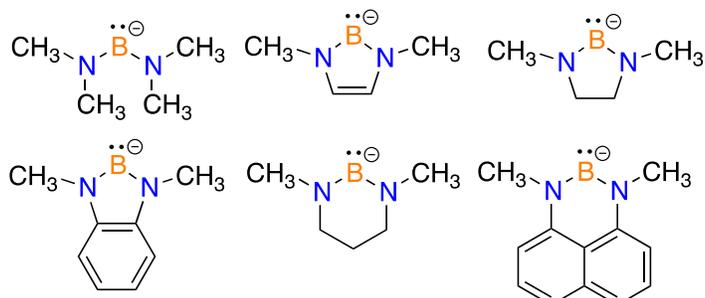
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## TOC Figure and Synopsis

### NHBs: Tuneable Ligands for the Synthetic Chemist



Strong  $\pi$ -donors and  $\sigma$ -donors, Weak  $\pi$ -acceptors

The electron donating and accepting properties of a selection of synthetically relevant N-heterocyclic boryl anions were examined. A similar tuneability in these properties as compared to analogous N-heterocyclic carbenes is predicted, indicating that modification of the boryl ligand in metal complexes can be expected to modulate the properties of complexes in a similar fashion.