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

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ABSTRACT

The relative σ donor and π 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 Li^+ cation and Se atom, as compared to the analogous neutral NHCs, by theoretical methods. The results indicate that boryl anions have a weaker π 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 π accepting capacity of boryl anions is similar to that of NHCs, indicating a similar 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 σ 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.[1-7] 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.[8-19] 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).[20] The compound was isolated with an unsaturated BN_2C_2 system akin to an 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.

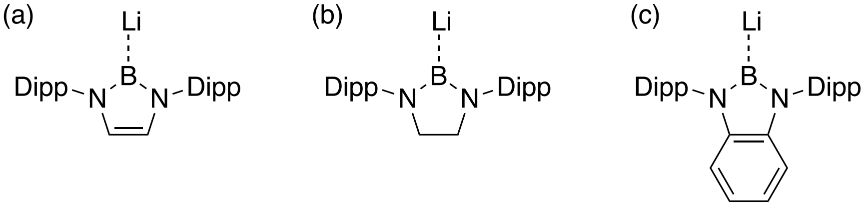


Figure 1. Isolated lithium boryl complexes (Dipp = 2,6-diisopropylphenyl, isolated with two THF or DME solvates coordinated to lithium).[20, 21]

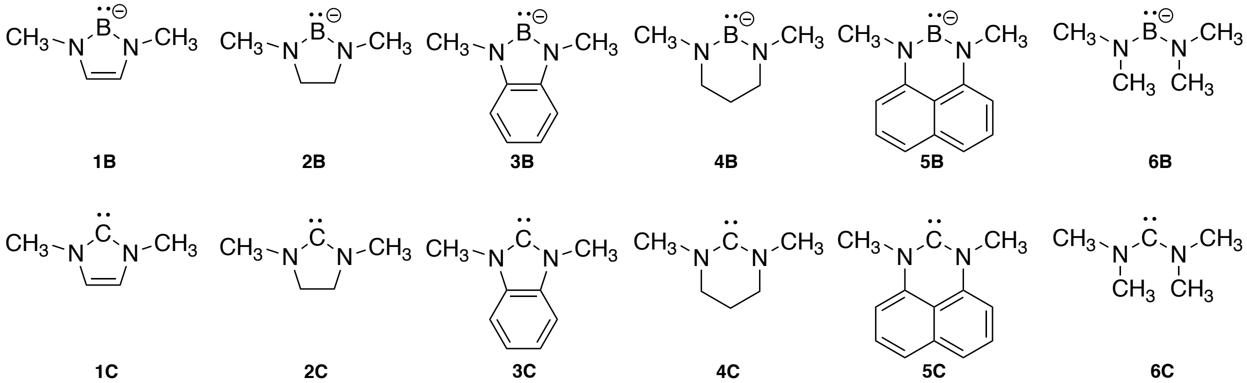
N-heterocyclic carbenes are highly effective ancillary ligands, which has lead to a vast library of singlet carbenes with differing properties having been developed that have become invaluable in the synthetic chemist's arsenal. The large collection of accessible carbenes has facilitated the evaluation of their donor properties. There are several experimental means for assessing the donor properties,[22-28] 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 π-backbonding capabilities of CO to correlate the electron density at the metal to the ligand.[29, 30] The π-accepting properties have also been assessed by preparing carbene-phosphinidene and selenourea complexes and subsequently analyzing the corresponding ^{31}P and ^{77}Se NMR shifts.[31, 32] Very recently, Szostak proposed evaluating σ-donor properties of carbenes by analyzing the ^{1}H NMR C-H signals of ligand precursors.[33]

Despite the significant progress in the experimental evaluation of the donor properties of carbenes, the situation is reversed for boryl analogues with only a limited number of known boryl analogues, and their donor-acceptor properties 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 properties of the ligand.

The reported studies on boryl ligands[34, 35] confirm that these species are both highly basic and very nucleophilic, systematically reacting with a diverse range of organic electrophiles.[20, 21, 36] An increasing number of metal and main group complexes of boryl anions are also being reported.[37-45] Jones has also used the boryl fragment as a constituent of bulky amido ligands.[46, 47] 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 N-heterocyclic boryl (NHB) ligand in place of the NHC.[48, 49] 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 σ-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.

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,[21] while the latter three are unknown. Six analogous carbene complexes were also considered (**1C**-**6C**), by replacement of the B^- 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.[50] While their results are insightful and reveal **1B** to be a weak π-acceptor, their broad study on the group 13-16 species did not examine the σ-donating and π-accepting properties of boryl anions in detail. Importantly, the N-substituent (-H, $-CH_3$, or -Ph) was found to have no significant effect on the donor-acceptor properties, justifying our use of N-methyl substitution. The general electronic structure of analogues of unsaturated **1B**, as well as the other group 13 analogues, were described by Schoeller, reaching the conclusion that the central atom is electron rich containing a lone pair, which has now been experimentally borne out.[51] Fuentealba studied the effect of modifying the N atoms of the boryls on calculated proton affinities, but not modifying the organic backbone, which is more synthetically relevant and known to have a big impact on NHCs.[52] Compound **1B** and its lithiated complex were also investigated using DFT methods by Nozaki and Yamashita.[21] 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 would have similar character to C-Li bonds in alkyllithium. Schleyer has similarly investigated a lithiated complex of an acyclic diamino boryl anion, Li-B(NH_2)$_2$, that is a simpler version of **6B**, identifying a directional lone-pair on the B atom.[53]

The complexation of boryl anions with appropriate partner elements allows an exploration of boryl anion donor properties. Here we have assessed the tuneability of the series of boryl anions in comparison with NHCs by considering Li$^+$ and Se complexes of each ligand (Figure 2), including binding energies, electronic structure and a detailed analysis of bonding, which enables an investigation of both σ-donor and π-acceptor properties.

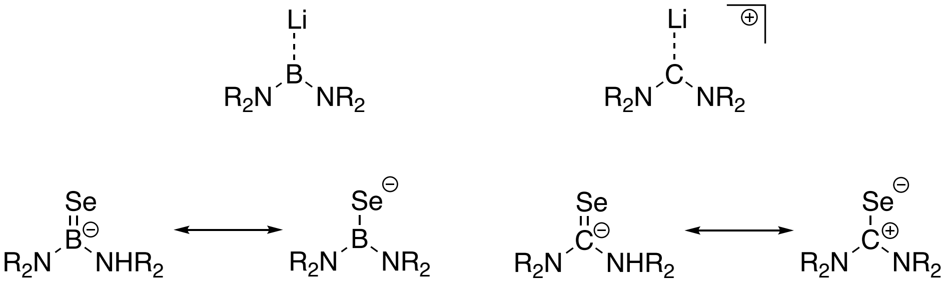


Figure 2. Complexes of boryl anions and NHCs with Li$^+$ and Se, illustrating the potential for σ-donating and π-accepting character explored in this work.

Computational Methods

All calculations were performed using Gaussian 16 revision A.03 unless noted.[54] Geometry optimizations were performed in the gas phase using the M06-2X density functional utilizing the def2-TZVP basis sets.[55-57] B3LYP-D3(BJ)[58] yielded equivalent geometries. 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. NBO analysis was performed using NBO 6.0.[59]

The nature of the chemical bond was investigated by means of an energy decomposition analysis (EDA) developed independently by Morokuma[60] and subsequently by Ziegler and Rauk.[61, 62] The bonding analysis focuses on the instantaneous interaction energy ΔE_{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)].

$$\Delta E_{\mathrm{int}} = \Delta E_{\mathrm{elstat}} + \Delta E_{\mathrm{Pauli}} + \Delta E_{\mathrm{orb}} \qquad (1)$$

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

The EDA-NOCV[63] 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 ($\Delta\rho_{orb}$) and quantitative (ΔE_{orb}) information about the strength of orbital interactions in chemical bonds. The EDA-NOCV calculations were carried out with the program package ADF2016.01[64, 65] at the BP86/TZ2P level of theory using the M06-2X/def2-TZVP optimised geometries.

Results and Discussion

Binding Energies

The relative σ-donor strength of the NHBs **1B-6B** was initially evaluated by calculating the binding free energy of a Li cation, since Li^+ is the typical cation for boryl and it is a pure σ-acceptor with no ability to participate in π-backbonding. The results are summarized in Table 1. Binding free energies (ΔG) range from -146.2 to -162.7 kcal/mol, with results suggesting that **4B** is the strongest σ-donor and **5B** the weakest of the cyclic systems. Acyclic analogue **6B** is a relatively strong σ-donor in the series with a Li^+ binding energy of -162.1 kcal/mol. Calculation of 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 an anion, as well as the reduced nucleophilicity of the NHC. However, an important observation for the present study is that the variation in binding energy between the NHCs of 6.3 kcal/mol (from -44.9 to -51.2 kcal/mol), is smaller than the variation in binding energies with the boryl anions (16.5 kcal/mol). Here **4C** and **5C** are the strongest and weakest σ-donors (as defined as energy binding Li^+) respectively, with acyclic **6C** also being a relatively strong σ-donor, consistent with results for the boryl analogues. The Li^+ binding energy results indicates that in terms of pure σ-donor strength, boryl anions appear more tuneable than NHCs. It is noted that the σ-donor strength towards 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. Calculated binding energy (kcal/mol) of Li^+ and Se to boryl anions and NHCs.[a]

	1X	**2X**	**3X**	**4X**	**5X**	**6X**
Li^+						
NHB	-160.6	-160.8	-151.5	-162.7	-146.2	-162.1
NHC	-51.2	-50.2	-49.4	-51.1	-44.9	-50.8
Se						
NHB	-126.0	-127.9	-124.7	-128.8	-123.5	-129.6
NHC	-63.7	-65.7	-64.9	-62.7	-59.6	-67.2

[a] For NHB ligands **1B**-**6B**, X = B, for NHC ligands **1C**-**6C**, X=C.

To evaluate capacity for π-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 π-accepting capacity of NHCs. The saturated NHC **2C** is known to be a better π-acceptor than the unsaturated NHC **1C**, which is reflected in the calculated Se binding energies. The binding of Se is 2.0 kcal/mol more favourable for saturated **2C** compared to **1C**. In contrast, the binding of Li^+ is 1.0 kcal/mol more favourable with unsaturated **1C**. The difference in binding of Se between the corresponding boryl anions (**1B**, **2B**) is slightly smaller at 1.9 kcal/mol with **2B** also being stronger. Of the boryl anions considered in this work, **3B** and **5B** appear to be the superior π-acceptors based on the comparison with Li^+ binding energies; **3B** and **5B** have 9.1-14.7 kcal/mol smaller Li^+ binding energies (poorer σ donors) compared to **1B** and **2B**, however they are only 1.3-4.4 kcal/mol less favourable in their binding to Se. Overall, from the binding energy of Se, acyclic **6B** forms the strongest bond.

Geometry

Geometric parameters (Table 2) are consistent with the binding energy analysis, with **3B** and **5B** having slightly shorter B-Se bonds and larger Wiberg Bond Indices (WBI) than the other derivatives. The differences in WBIs for the boryls are similar in magnitude to the differences for the NHCs. The WBIs for the boryls are in all cases higher than the WBIs for the corresponding NHCs, indicating that boryls are possibly similar in capacity to NHCs for π-backbonding.

Table 2. Calculated metal-ligand bond distances (Å) for complexes of **1X-6X** bound to Li^+ or Se. Wiberg bond indices in parentheses.[a]

	1X	**2X**	**3X**	**4X**	**5X**	**6X**
Li^+						
NHB; *r*(B-Li)	2.165 (0.56)	2.184 (0.56)	2.172 (0.53)	2.209 (0.60)	2.201 (0.52)	2.225 (0.61)
NHC; *r*(C-Li)	2.026 (0.12)	2.046 (0.12)	2.032 (0.12)	2.048 (0.12)	2.051 (0.12)	2.054 (0.12)
Se						
NHB; *r*(B-Se)	1.919 (1.43)	1.913 (1.48)	1.899 (1.51)	1.942 (1.41)	1.918 (1.50)	1.935 (1.45)
NHC; *r*(C-Se)	1.833 (1.35)	1.826 (1.42)	1.826 (1.40)	1.850 (1.36)	1.847 (1.40)	1.836 (1.43)

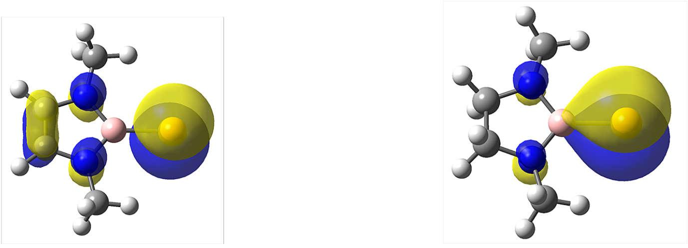
[a] For NHB ligands **1B-6B**, X = B, for NHC ligands **1C-6C**, X=C.

Frontier Molecular Orbitals

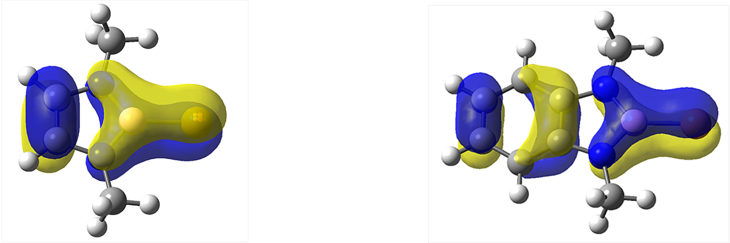
A comparison of the frontier molecular orbital energies of the boryl anions and NHCs (Table 3) yields trends consistent with the above binding energy data. Plots of representative MOs are illustrated in Figure 3. For **1X-6X** the σ-donor orbital is consistently the HOMO (except **5C** with it being HOMO-1). The π-acceptor orbital of the carbene ligands **1C**-**6C** is always the LUMO or LUMO+1, however for the boryl anions **1B-6B** the π-acceptor varies from LUMO (**3B**) to LUMO+4 (**1B**). Of the boryl anions, the HOMO energy levels for **2B** and **4B** are the highest, which is indicative of strong σ-donation and consistent with these ligands exhibiting the strongest bonds to Li^+. The π-acceptor orbital energy levels are lowest for **3B** (LUMO) and **5B** (LUMO+2), consistent with these ligands being the best π acceptors. Of the most synthetically relevant boryl anions **1B** and **2B**, **2B** is both a better σ-donor and π acceptor, based on a higher energy HOMO and lower energy acceptor (LUMO+2), consistent with the properties of the analogous NHC ligands. In terms of differences, there is only a 0.08 eV difference in the HOMO energy level for **1B** and **2B**, whereas the difference for **1C** and **2C** is 0.17 eV, suggesting greater tuneability in σ donation for the NHC ligands. The difference in energy in the π-accepting orbital for the two boryls is 0.43 eV; the difference for the corresponding NHCs is 0.25 eV. This suggests that in terms of π-accepting capacity, there is potentially a larger scope for tuneability in the most synthetically relevant boryl anions. The greater variation in energy for boryl anions matches the variation in unoccupied orbitals (up to LUMO+4) for the boryls.

Table 3. Molecular orbital energies (eV) of boryl anion (**1B**-**6B**) and NHC (**1C**-**6C**) ligands.

Boryl anions	**1B**	**2B**	**3B**	**4B**	**5B**	**6B**
σ donor MO	1.41 (HOMO)	1.49 (HOMO)	0.80 (HOMO)	1.72 (HOMO)	0.68 (HOMO)	1.75 (HOMO)
π acceptor MO	5.78 (LUMO+4)	5.35 (LUMO+2)	3.72 (LUMO)	5.06 (LUMO+2)	3.87 (LUMO+2)	5.33 (LUMO+2)
NHC	**1C**	**2C**	**3C**	**4C**	**5C**	**6C**
σ donor MO	-5.82 (HOMO)	-5.65 (HOMO)	-6.05 (HOMO)	-5.17 (HOMO)	-5.88 (HOMO-1)	-4.89 (HOMO)
π acceptor MO	1.03 (LUMO+1)	0.78 (LUMO+1)	-0.73 (LUMO)	0.51 (LUMO)	-0.72 (LUMO+1)	0.73 (LUMO+1)



1B-Se (HOMO) **2B-Se** (HOMO-1)



1B-Se (HOMO-2) **3B-Se** (HOMO-3)

Figure 3. Selected frontier molecular orbitals of B-Se adducts.

In the boryl-Se complexes (**1B-Se** to **6B-Se**) the potentially π-donating electrons on the Se atom (identified as a π-symmetry lone-pair oriented perpendicular to the plane of the boryl cycle) are found in the HOMO or HOMO-1 orbitals, with appropriate symmetry to interact with the π system of the boryl anion (Figure 3). The σ-donor orbital associated with B-Se bonding is energetically stabilised and typically found in the HOMO-3 or HOMO-4 orbital. In the π-symmetry HOMO of **1B-Se**, little delocalization to the B atom is apparent, but for **2B-Se** (HOMO-1 is the p_π orbital) there is a non-negligible coefficient for the orbital at the B atom. The HOMO for **2B-Se** is the orthogonal p-orbital on the Se atom in the plane of the boryl heterocycle. The π-backbonding interaction is found in the HOMO for **3B-Se** and the HOMO-1 for **4B-Se** through **6B-Se**. There is also a π-type interaction that arises from overlap of the occupied π-system of the boryl ring and the pπ 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.

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 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 ^1D 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 σ-donor and π-accepting properties of the ligands can readily be compared. For Li^+ the metal is trivially a closed shell fragment in a ^1S state. It is important to note that in EDA the value of ΔE_{int} differs from the dissociation energy (D_e) since ΔE_{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 4 (lithium) and Table 5 (selenium).

Table 4. EDA-NOCV results of boryl-lithium complexes with a donor-acceptor bonding description at the BP86/TZ2P//M06-2X/def2-TZVP level. Fragments of Li^+ (singlet), boryl anion (singlet) and NHC (singlet). [a]

NHB-Li	**1B-Li**	**2B-Li**	**3B-Li**	**4B-Li**	**5B-Li**	**6B-Li**
ΔE_{int}	-168.4	-168.1	-160.5	-170.0	-155.6	-169.3
ΔE_{Pauli}	41.3	41.1	39.8	42.2	40.2	41.2
ΔE_{elstat} [b]	-181.1 (86.4)	-180.7 (86.4)	-171.5 (85.6)	-182.0 (85.8)	-165.5 (84.5)	-179.4 (85.3)
ΔE_{orb} [b]	-28.5 (13.6)	-28.5 (13.6)	-28.8 (14.4)	-30.2 (14.2)	-30.3 (15.5)	-31.0 (14.7)
ΔE_1 (σ) [c]	-19.0 (66.8)	-20.2 (70.9)	-17.8 (61.8)	-20.4 (67.5)	-17.3 (57.1)	-21.1 (67.9)
NHC-Li^+	**1C-Li**	**2C-Li**	**3C-Li**	**4C-Li**	**5C-Li**	**6C-Li**
ΔE_{int}	-59.3	-58.9	-58.0	-60.5	-53.9	-59.7
ΔE_{Pauli}	24.7	23.9	24.2	26.0	24.7	25.7
ΔE_{elstat} [b]	-59.8 (71.2)	-58.9 (71.0)	-56.0 (68.2)	-60.3 (69.7)	-49.4 (62.8)	-59.3 (69.5)
ΔE_{orb} [b]	-24.2 (28.8)	-24.0 (29.0)	-26.2 (31.8)	-26.2 (30.3)	-29.2 (37.2)	-26.0 (30.5)
ΔE_1 (σ) [c]	-12.2 (50.3)	-13.4 (55.8)	-12.0 (45.9)	-13.2 (50.5)	-12.4 (42.5)	-13.5 (51.9)

[a] kcal/mol.

[b] Values in parentheses give the percentage contribution to the attractive interactions, $\Delta E_{elec} + \Delta E_{orb}$.

[c] ETS-NOCV. Values in parentheses give the percentage contribution to the orbital interaction, ΔE_{orb}.

Table 5. EDA-NOCV results of boryl-lithium complexes with a donor-acceptor bonding description at the BP86/TZ2P//M06-2X/def2-TZVP level. Fragments of Se (^1D state), boryl anion (singlet) and NHC (singlet). [a]

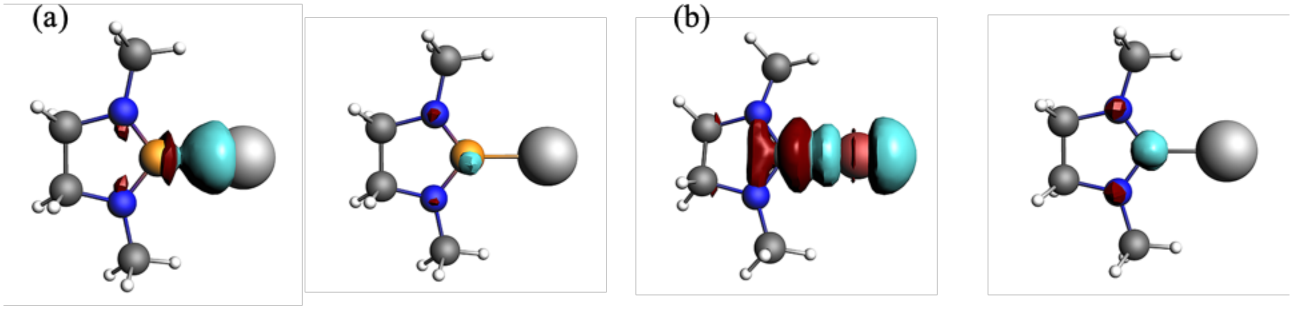
NHB-Se^-	**1B-Se**	**2B-Se**	**3B-Se**	**4B-Se**	**5B-Se**	**6B-Se**
ΔE_{int}	-175.2	-176.9	-175.6	-177.2	-175.2	-177.5
ΔE_{Pauli}	350.1	355.2	358.0	354.8	370.5	347.7
ΔE_{elstat} [b]	-272.2 (51.8)	-276.8 (52.0)	-278.7 (52.2)	-275.9 (51.9)	-288.1 (52.8)	-269.4 (51.3)
ΔE_{orb} [b]	-253.1 (48.2)	-255.3 (48.0)	-254.9 (47.8)	-256.1 (48.1)	-257.6 (47.2)	-255.8 (48.7)
ΔE_1 (σ) [c]	-224.5 (88.7)	-227.1 (89.0)	-223.7 (87.8)	-228.5 (89.2)	-224.9 (87.3)	-228.0 (89.2)
ΔE_2 (π) [c]	-12.4 (4.9)	-13.2 (5.1)	-15.0 (5.9)	-12.1 (4.7)	-15.6 (6.1)	-13.8 (5.4)
ΔE_{rest} [c]	-16.2 (6.4)	-15.0 (5.9)	-16.1 (6.3)	-15.5 (6.1)	-17.1 (6.6)	-13.9 (5.4)
NHC-Se	**1C-Se**	**2C-Se**	**3C-Se**	**4C-Se**	**5C-Se**	**6C-Se**
ΔE_{int}	-118.3	-119.4	-118.6	-118.6	-115.8	-124.1
ΔE_{Pauli}	262.4	265.4	269.9	263.0	275.6	270.0
ΔE_{elstat} [b]	-201.0 (52.8)	-202.3 (52.6)	-204.2 (52.5)	-202.8 (53.1)	-206.3 (52.7)	-208.0 (52.8)
ΔE_{orb} [b]	-179.7 (47.2)	-182.5 (47.4)	-184.4 (47.5)	-178.8 (46.9)	-185.1 (47.3)	-186.1 (47.2)
ΔE_1 (σ) [c]	-141.4 (78.7)	-143.4 (78.6)	-142.3 (77.2)	-142.4 (79.6)	-141.3 (76.3)	-146.5 (78.8)
ΔE_2 (π) [c]	-20.6 (11.5)	-21.7 (11.9)	-22.6 (12.3)	-19.9 (11.1)	-24.1 (13.0)	-23.3 (12.5)
ΔE_{rest} [c]	-17.7 (9.9)	-17.4 (9.5)	-19.5 (10.6)	-16.5 (9.2)	-19.7 (10.6)	-16.2 (8.7)

[a] kcal/mol.

[b] Values in parentheses give the percentage contribution to the attractive interactions, $\Delta E_{elec} + \Delta E_{orb}$.

[c] ETS-NOCV. Values in parentheses give the percentage contribution to the orbital interaction, ΔE_{orb}.

For the lithium ion complexes (***n*C-Li** and ***n*B-Li**, *n*=1-6), the data in Table 4 reveals that the interaction (ΔE_{int}) between **1B**-**6B** and Li^+ is rather strong, being -155.6 to -170.0 kcal/mol, which is significantly greater than for **1C**-**6C** (-53.9 to -60.5 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 (-165.5 to -182.0 kcal/mol) and proportion (~85%) compared to NHCs (-49.4 to -60.3 kcal/mol; ~70%). The increased Coulombic attraction in boryl-Li complexes is largely responsible for the greater overall ΔE_{int} compared to NHC-Li^+. As expected, the covalent interaction (ΔE_{orb}) is dominated by σ-donation ($\Delta \mathrm{E}_{orb(1)}$). There is no evidence of π-back donation, with the only other non-negligible orbital interaction ($\Delta \mathrm{E}_{orb(2)}$) being of π symmetry, but is associated with donation from the cyclic N atoms to the empty p_π orbital of the B or C atoms. Interestingly, σ-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 σ-donating ability of **1B**-**6B** over **1C**-**6C** is clearly understood from the relative magnitude of $\Delta \mathrm{E}_{orb(1)}$. The associated charge flow (red→blue) of σ-donation is readily reflected from the corresponding plots of deformation densities (Δρ) in Figure 4. For the purpose of comparing tuneability, it is of interest to note that the variation in σ-donation for the boryls (3.8 kcal/mol) is greater than for NHCs (1.5 kcal/mol).

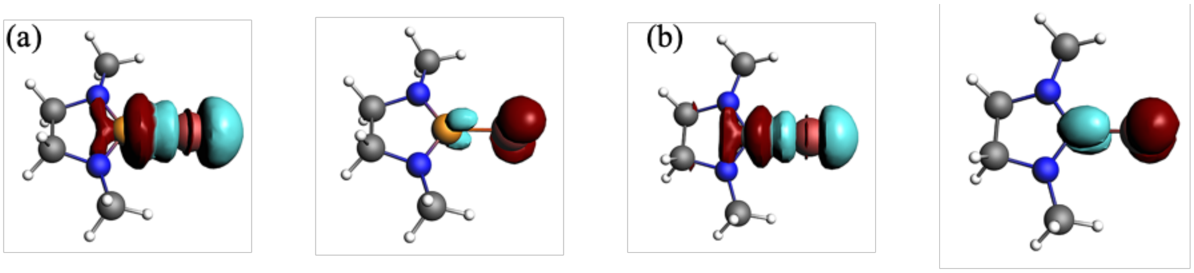


$\Delta E_{\mathrm{orb}(1)} = -20.18$ $\Delta E_{\mathrm{orb}(2)} = -2.76$ $\Delta E_{\mathrm{orb}(1)} = -13.39$ $\Delta E_{\mathrm{orb}(2)} = -3.75$

Figure 4. Shape of the deformation densities $\Delta\rho_{(1)}$ and $\Delta\rho_{(2)}$, which are associated with the orbital interactions $\Delta E_{\mathrm{orb}(1)}$ and $\Delta E_{\mathrm{orb}(2)}$ (kcal/mol) in (a) **2B-Li** and (b) **2C-Li** of the charge flow. The isosurface value is 0.003. The color code of the charge flow is red → blue.

For the selenium complexes (***n*C-Se** and ***n*B-Se**, *n* = 1-6), the data in Table 5 indicates that the interaction (ΔE_{int}) with Se is stronger than for Li^+, with the boryls (-175.2 to -177.5 kcal/mol) again exhibiting a stronger interaction than the NHCs (-115.8 to -124.1 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 51.3-52.8% of the interaction in the boryls and 52.5-53.1% in the NHCs. Within the orbital interaction, σ-donation is dominant for boryl and NHC, however they are larger in magnitude (and percentage) for the boryl. The trend matches that for interactions with Li^+ (Table 4). In boryl, the π-backbonding contribution is in the range of 4.7-6.0%, but for NHC it is larger at 11.1-13.0%. The larger σ-donating ability of **1B-6B** over **1C-6C**, and weaker π-backbonding, is clearly understood from the relative magnitude of $\Delta E_{orb(1)}$ and $\Delta E_{orb(2)}$. The associated charge flow (red→blue) of σ-donation and π-backbonding is readily reflected from the corresponding plots of deformation densities ($\Delta\rho$) in Figure 5. These results indicate that NHCs are better π-acceptors from the Se atom than the boryls. In both sets of ligands, the most synthetically relevant saturated **1X** and **2X** analogues have a larger π component in the bonding interaction. The difference in π-bonding orbital contribution between the least π-accepting boryl **4B** and most π-accepting **5B** is 1.3%. For NHCs the corresponding difference is 1.9%.

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



$\Delta E_{\mathrm{orb}(1)} = -227.1$ $\Delta E_{\mathrm{orb}(2)} = -13.2$ $\Delta E_{\mathrm{orb}(1)} = -143.4$ $\Delta E_{\mathrm{orb}(2)} = -21.7$

Figure 5. Shape of the deformation densities $\Delta\rho_{(1)}$ and $\Delta\rho_{(2)}$, which are associated with the orbital interactions $\Delta E_{\mathrm{orb}(1)}$ and $\Delta E_{\mathrm{orb}(2)}$ (kcal/mol) in (a) **2B-Se** and (b) **2C-Se** of the charge flow. The isosurface value is 0.005. The color code of the charge flow is red → blue.

Finally, to assess the utility of the EDA analysis with closed-shell fragments, we considered an alternative choice with electron-sharing ligand-metal bonds. For lithium complexes this equates to doublet Li and doublet $[\mathrm{NHC}]^+$ or [NHB] interacting fragments, while for Se (with a ligand-Se double bond) this equates to a triplet state Se (p_z^1 p_y^1 with a principal axis of *z* and the heterocycle in the *xz* plane), with a triplet NHC or triplet NHB^- fragment with matching unpaired electrons. Results for unsaturated **1B** and **1C** ligands illustrate that the donor-acceptor scheme is better suited to describe the bonding in these compounds since it gives a lower orbital value, ΔE_{orb}, than the electron-sharing scheme. It is nevertheless instructive to analyse the results. Here the interaction with Li^+ is almost exclusively σ-donation as expected, while the interaction with Se contains a larger π-bonding contribution than arises from a donor-acceptor scheme. These results are consistent with the predictions based on the WBI values for bonds to Se (larger WBI and hence π-bonding for boryls).

Table 6. EDA-NOCV results of **1B** and **1C** complexes with an electron-sharing bonding description at the BP86/TZ2P//M06-2X/def2-TZVP level. Selenium complexes use triplet state fragments, and lithium complexes use doublet state fragments. Energy values are given in kcal/mol.

	1B-Li	**1C-Li**	**1B-Se**	**1C-Se**
ΔE_{int}	-48.9	-115.8	-188.7	-174.3
ΔE_{Pauli}	33.4	45.6	206.3	181.5
ΔE_{elstat} [b]	-38.2 (46.4)	-29.4 (18.2)	-168.3 (42.6)	-132.3 (37.2)
ΔE_{orb} [b]	-44.2 (53.6)	-132.1 (81.8)	-226.7 (57.4)	-223.5 (62.8)
ΔE_1 (σ) [c]	-42.6 (96.4)	-131.3 (99.4)	-124.4 (54.9)	-149.7 (67.0)
ΔE_2 (π) [c]	-0.5 (1.2)	-0.5 (0.4)	-91.5 (40.4)	-58.5 (26.2)

[a] kcal/mol.

[b] Values in parentheses give the percentage contribution to the attractive interactions, $\Delta E_{elec} + \Delta E_{orb}$.

[c] ETS-NOCV. Values in parentheses give the percentage contribution to the orbital interaction, ΔE_{orb}.

Conclusion

Energy decomposition analysis calculations indicate that NHCs are better π acceptors than boryl anions, but that the boryl anions do have some ability to act as a π acceptor. The π-accepting tuneability across the different boryl anions is also reduced in comparison with NHCs. It appears that π-backbonding for the boryl anions is overestimated from purely a geometrical analysis, with calculated WBI values indicating much greater contribution from π-backbonding than predicted by energy decomposition analysis, indicating the importance of performing more detailed theoretical analysis beyond simple geometry calculations. The boryls are calculated to be significantly better σ-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 π-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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