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Isolation of Free Phenylide-like Dicoordinate Carbanions with N-Heterocyclic Carbene Frameworks

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A series of 1,3-bis(2,6-diisopropylphenyl)-5-methyl-1,3-diaza-4,6-diborabenzenes with methyl, phenyl and dimethylamino substituents on the ring boron atoms were prepared using the cyclocondensation reaction between N,N'-bis(2,6-diisopropylphenyl)trimethylsilylformamidine and the appropriately substituted 1,1-bis(organochloroboryl)ethane, followed by deprotonation of the cationic ring intermediate. The planar, heterocyclic benzene analogs could be further deprotonated at the other ring carbon using an additional equivalent of potassium hexamethyldisilazide, to yield organometallic derivatives akin to the potassium phenylide. The potassium cations could be efficiently sequestered in both solution and solid state using 18-crown-6 and the crystallographic analysis of the reaction products revealed the absence of carbanion-cation contacts in the solid state. The transformation of a planar, tricoordinate sp^2-carbon to a tricoordinate, contact ion-pair carbanion and further to a solvent-separated, free dicoordinate carbanion was investigated using solution NMR and single-crystal X-ray diffraction. The first isolation and characterization of free dicoordinate carbanions in the solid state is supported by

a charge distribution analysis, and the relationship between phenylide-type carbanions and N-heterocyclic carbenes is discussed through the prism of the results reported herein.

Introduction

Carbanions are essential reactive intermediates in organic and organometallic chemistry.[1] Their intrinsically low stability has rarely allowed for the isolation and characterization of free carbanions in the solid state, although it appears that the first representative was isolated by Schlenk as early as 1916.[2a, d] The few free carbanions that have been structurally characterized are stabilized by employing resonance to decrease the charge density on the carbon center and hence reduce its basicity (Figure 1). Consequently, the vast majority of free carbanions isolated so far are tri-coordinate and planar, with a classical sp^2 hybridization of the carbon atom and the lone pair hosted in the p orbital. The relatively short bonds involving the anionic carbon atom and the overall geometry of the compounds are good indicators for the significant extent of electron delocalization, as observed, for example, in di- and triphenylmethyl carbanions.[2] Stabilization through negative hyperconjugation has enabled the isolation of trisilylmethyl carbanions,[3] while extensive electron delocalization over the ring system or systems allowed for the isolation of free cyclopentadienyl and of free planar polycyclic carbanions.[4] In delocalized carbanionic systems involving heteroatoms, resonance structures that distribute the charge onto the heteroatoms are considered to play a key role in the description of the bonding.[5] This stabilization is considerable in trigonal-planar carbanions featuring small inorganic substituents containing multiple bonds, such as CN^- and NO_2^-, and numerous such derivatives have been structurally characterized. Notable exceptions from the planar geometry are the pyramidal tris(pyrazolyl)methyl anions featuring nitrogen-metal interactions, which were isolated as zwitterionic lithium, silver and copper complexes.[6]

To our knowledge, no free di-coordinate carbanions have been structurally characterized to date. Attempts to isolate such centers integrated in aromatic frameworks (e.g. phenylide) have been unsuccessful due to their considerable basicity, and their consequent reactivity towards solvents.[7]

Although the phenyl ring itself is resonance stabilized, the lone pair of electrons in phenylide is orthogonal to the π system and therefore not involved in the electron delocalization. Efficient stabilization achieved through the incorporation of heteroatoms that are able to host a considerable fraction of the negative charge, akin to the case of N-heterocyclic carbenes, is necessary to isolate free phenylide-like carbanions.

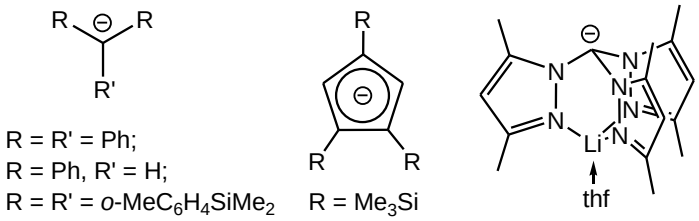


Figure 1. Representative examples of structurally characterized free carbanions

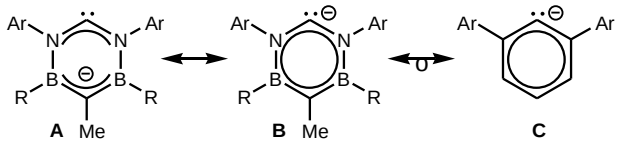
The relationship between anionic carbenes and phenylide-type carbanions was recently the focus of three reports. Yao *et al.* reported an anionic carbene ligand and its complexes,[8] emphasizing the importance of having a neutral carbon donor, and the negative charge localized away from this carbon center, as it is the case in several examples of N-heterocyclic carbenes featuring anionic backbones[9] or anionic, non-coordinating pendant groups.[10] We reported a study showing that, despite obvious similarities, the frontier orbitals of phenylide ligands are higher in energy than those of neutral N-heterocyclic carbenes due to the negative charge.[11a] This is in line with the experimental observation that phenylide ligands are superior σ-donors and poorer π-acceptors as compared to N-heterocyclic carbenes. Accordingly, carbanions tend to be highly nucleophilic as opposed to N-heterocyclic carbenes, which are amphiphilic. The two classes of ligands also have common features including the location of the lone pair of electrons, the hybridization of the carbon atom, the stabilization through π-delocalization, and the shape of the frontier orbitals. César *et al.* published the ingenious synthesis of an anionic N-heterocyclic carbene featuring "a remote anionic functional group within the heterocyclic backbone" derived from malonic acid.[11b] The carbene was isolated as a trimeric lithium salt displaying O-coordination through the oxo substituents on the backbone, and was further used to generate several zwitterionic transition metal complexes displaying classical C-coordination. A series of fascinating zwitterionic, electroneutral

ligands featuring anionic carbene moieties that are formally obtained from pyridine and quinoline through a 1,2 proton shift were recently described, but they have only been isolated as transition metal complexes.[12] Numerous examples of pendant-arm carbenes containing an anionic functionality such as amido and alkoxi have been reported, in these cases the negative charge being usually unmistakably associated to the tethered functionality.[13]

A few methods have been delineated for the separation of carbanions from an ion pair, with the most generally applicable and successful method being the use of crown ethers, pioneered in 1984 by Power. Crown ethers have proven to be ideal due to their ability to strongly and selectively coordinate cations, providing enough stabilization to separate the carbanion from the alkali metal cation.[7] Conveniently, crown ethers also impart favorable crystallization properties, facilitating the isolation and characterization of the free carbanions in the solid state.

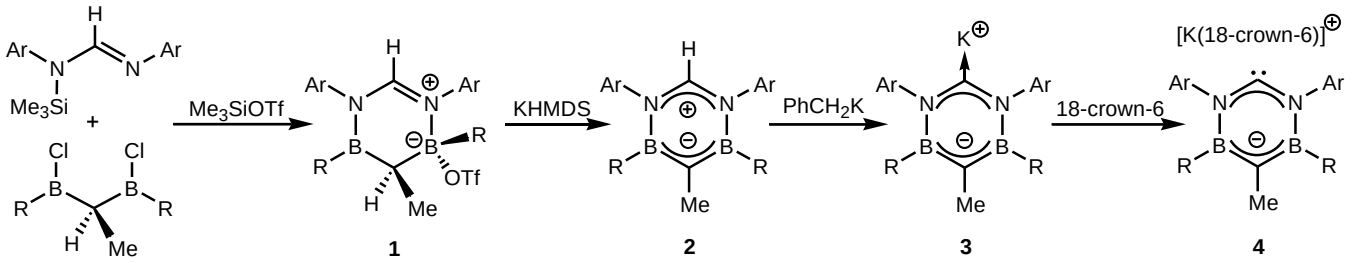
We describe herein the synthesis and characterization of a series of free heterocyclic, terphenyl-like dicoordinate carbanions, as well as their neutral precursors and the corresponding alkali metal salts featuring metal-carbon contacts. The structures and electronic characteristics of the free carbanionic rings, as well as the influence of the substituents on boron onto the ring properties and a detailed comparison between anionic N-heterocyclic carbenes and phenylide carbanions are presented.

Results and Discussion



In an initial communication, we reported the isolation and characterization of the lithium salt [*cyclo*-:C(2,6-*i*Pr$_2$C$_6$H$_3$-N)$_2$(MeB)$_2$CMe]Li(thf)$_2$ (**3'a**) of a heterocyclic, anionic σ-donor **A** featuring a planar 6-π-electron ring framework.[11a] The metric parameters of the cyclic framework suggested that the resonance form **A** proposed by Bertrand for an analogous B_2N_3C ring provided a better description of the structure than the benzene-like form **B**,[14] and computational analyses placed the ligand between N-heterocyclic carbenes and terphenyl anions **C**, although closer to the latter. We expanded this study,

aiming to investigate the influence of the substituents on boron on the electronic properties of the ligand **A** and to better understand the relationship between carbenes and phenylide carbanions.



Scheme 1. Synthesis of derivatives **1** – **4**. Ar = 2,6-*i*Pr$_2$C$_6$H$_3$; R = Me (**a**), Ph (**b**), and Me$_2$N (**c**).

The ionic precursors **1** were prepared cleanly and in high yield via the ring-closing reaction of silylated bis(2,6-diisopropylphenyl)formamadine with 1,1-bis(organochloroboryl)ethane in the presence of Me$_3$SiOTf, as described for imidazolium analogs incorporating inorganic backbones.[11a,15] The phenyl derivative MeCH(PhBCl)$_2$ was synthesized through the metathesis reaction of 1,1-MeCH(BCl$_2$)$_2$ with SnPh$_4$,[16] while MeCH(Me$_2$NBCl)$_2$ was obtained via the reaction of MeCH(BCl$_2$)$_2$ with Me$_3$SiNMe$_2$.[17] The ^{1}H NMR spectrum of **1c** displayed the resonances expected for a solvent-separated ion pair with C_s symmetry of the cation, as observed for **1a**.[11a] However, the ^{1}H NMR spectrum of **1b** in both THF-d$_8$ and C$_6$D$_6$ was more complex, indicative of a lower symmetry. This could be caused by the coordination of the triflate anion to a boron atom with formation of a borate that was long lived on NMR time scale. Such structure was observed in the solid state of **1a**, and is in good agreement with the substituent-induced, increased Lewis acidity of the boron centers in **1b** in comparison to **1a** and **1c**. The chemical shifts for the imidazolium protons, which are found at δ = 8.63, 8.46 and 8.38 ppm for **1b**, **1a** and **1c**, respectively, indicate a slight influence of the B-substituents on the electronic environment of the formamidinic ring proton. The influence of these substituents is obviously more pronounced for the ^{11}B NMR resonances that appear at δ = 40.7 ppm in **1a**, 31.4 ppm in **1b** and 33.0 ppm in **1c** and correspond to tri-coordinate boron, indicating solvent separated ion pairs. This implies that the lifetime of the borate adduct observed in ^{1}H NMR for **1b** is not long enough to allow for its observation by ^{11}B NMR spectroscopy.

Treatment of **1a-c** with potassium bis(trimethylsilyl)amide cleanly yielded the Hückel-stabilized rings **2a-c** (Scheme 1). The longer reaction time required to cleanly deprotonate **1c** suggests a decreased acidity for this species. This is in agreement with the increased electron-donating ability of the dimethylamino substituents, leading to increased electron density at the acidic proton. The ^{1}H NMR data

Table 1. Selected Data and Structure Refinement Details for **2b**, **2c**, **4b**, and **4c**.

	2b	**2c**	**4b**	**4c**
empirical formula	$C_{39}H_{48}B_2N_2$	$C_{31}H_{50}B_2N_4$	$C_{59}H_{89}B_2KN_2O_8$	$C_{58}H_{98}B_2KN_4O_8$
formula weight	566.41	500.37	1015.04	1040.12
crystal system	monoclinic	monoclinic	triclinic	orthorhombic
space group	$P2_1/n$	$P2_1/n$	P-1	Pnma
a (Å)	10.9270 (2)	10.564 (3)	11.411 (2)	26.323 (4)
b (Å)	15.3500 (2)	14.397 (5)	13.544 (2)	15.078 (4)
c (Å)	20.2040 (4)	20.578 (5)	21.362 (4)	15.509 (6)
β (°)	90.8610 (9)	91.090 (15)	78.738 (10)	90
V (Å)	3388.42 (10)	3129.1 (16)	2928.8 (9)	6155 (3)
Z	4	4	2	4
d_{calcd} (g cm^{-3})	1.110	1.062	1.151	1.122
μ (mm^{-1})	0.063	0.061	0.143	0.138
θ range (deg)	2.65 - 27.48	3.42 - 27.46	3.66 - 25.33	3.38 - 25.38
no. of indep. rflns.	7736 (R_{int} = 0.0408)	7116 (R_{int} = 0.0473)	10586 (R_{int} = 0.0288)	5806 (R_{int} = 0.0300)
no. of data / restraints / params	7736 / 0 / 397	7116 / 0 / 347	10586 / 0 / 780	5806 / 0 / 359
GOF on F^2	1.014	1.028	1.020	1.068
R1 ($I > 2\sigma(I)$)	0.0514	0.0530	0.0489	0.0750
wR2 ($I > 2\sigma(I)$)	0.1278	0.1216	0.1213	0.1870

for **2a-c** shows a gradient of δ values corresponding to the ring proton from 8.37 to 8.32 and 7.57 ppm, respectively, deviating from the trend seen for the imidazolium precursors **1a-c**. Derivatives **1c** and **2c** display nevertheless the most upfield shifted resonances, as expected due to the increased electron density. The chemical shifts of the ^{11}B NMR signals are δ = 37.8, 38.4 and 33.5 ppm for **2a, b,** and **c**,

respectively. The signals in the ^{1}H and ^{13}C NMR spectra for **2a-c** are in agreement with a C_{2v} symmetric structure in solution and the purity of derivatives **2b** and **2c** was confirmed by elemental analysis.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2a**, **2b**, **2c**, **3'a**, **4b**, and **4c**.

	2a[11a]	**2b**	**2c**	**3'a**[11a]	**4b**	**4c**
N_{intra}-C_{intra}[a]	1.326(2), 1.327(2)	1.327(2), 1.331(2)	1.323(2), 1.331(2)	1.363(2)	1.362(2), 1.369(2)	1.362(3)
B-N_{intra}	1.498(2), 1.503(2)	1.492(2), 1.502(2)	1.521(2), 1.529(2)	1.495(3)	1.487(2), 1.489(2)	1.503(4)
C_{intra}-B	1.477(2), 1.479(2)	1.481(2), 1.488(2)	1.479(2), 1.485(2)	1.475(3)	1.483(3), 1.494(3)	1.478(4)
N_{intra}-C_{extra}	1.455(2), 1.456(2)	1.462(2), 1.463(2)	1.443(2), 1.449(2)	1.450(2)	1.452(2), 1.454(2)	1.449(4)
B-C_{extra}	1.580(2), 1.583(2)	1.586(2), 1.589(2)	-	1.599(3)	1.602(3), 1.605(3)	-
B-N_{extra}	-	-	1.441(2), 1.451(2)	-	-	1.503(4)
C_{intra}-C_{extra}	1.519(2)	1.528(2)	1.528(2)	1.518(4)	1.528(2)	1.527(5)
N_{intra}-C-N_{intra}	122.83(12)	123.25(12)	124.85(13)	114.0(2)	113.85(15)	114.7(3)
B-C-B	119.57(12)	119.05(12)	120.75(13)	117.2(2)	115.94(16)	117.1(3)
Dipp/Dipp	107.9	116.9	107.0	114.0	115.0	121.6

[a] The subscripts intra and extra indicate atoms that are part of the ring (intraannular) and directly connected to the ring (extraannular), respectively.

Structural determinations using single-crystal X-ray crystallography were carried out for compounds **2b** and **2c** (Table 1). As described for **2a**,[11a] the compounds feature monomeric structures with planar ring skeletons and substituents displaying little deviation from the ring plane (Figure 2). The metric parameters (Table 2) indicate significant delocalization of π electron density over the B–C–B and N–C–N ring moieties. The intraannular N–C bond lengths are equivalent and range from 1.32 to 1.33 Å (*cf.* 1.34 Å in pyridine),[18] while the intraannular B–C bonds measure 1.48 – 1.49 Å (*cf.* 1.46 – 1.49 Å for pyridine adducts of borabenzene).[19] The intraannular B–N bonds show considerable single bond character with lengths of *ca.* 1.50 Å for **2a** and **2b**, and *ca.* 1.52 Å for **2c**, as compared to typical boron-nitrogen bonds, which usually range from 1.36 – 1.40 Å for double bonds and 1.55 – 1.60 Å for single bonds. For comparison, borazine bond lengths measure 1.42 – 1.44 Å.[20] The intraannular B–N bonds are slightly longer in the dimethylamino-substituted derivative **2c,** due to the competitive π donation from the extraannular dimethylamino substituents into the p orbital on boron. Hence, the distribution of the π

electrons on the ring is best described by a zwitterionic structure containing two allyl-like fragments connected by single boron-nitrogen bonds. The coordination environment is essentially planar for all boron and nitrogen atoms in **2b** and **2c**, with sums of the bond angles of at least 359.3°. In order to accommodate the steric demand, the planes of the substituents are substantially twisted with respect to the $B_2N_2C_2$ ring plane (73.6 – 83.0° for 2,6-*i*$Pr_2C_6H_3$, 44.6 and 88.3° for Ph, 33.4 and 40.2° for NMe_2), reducing the π interactions and tempering the electronic impact of the these substituents on the structure and properties of the ring skeleton.

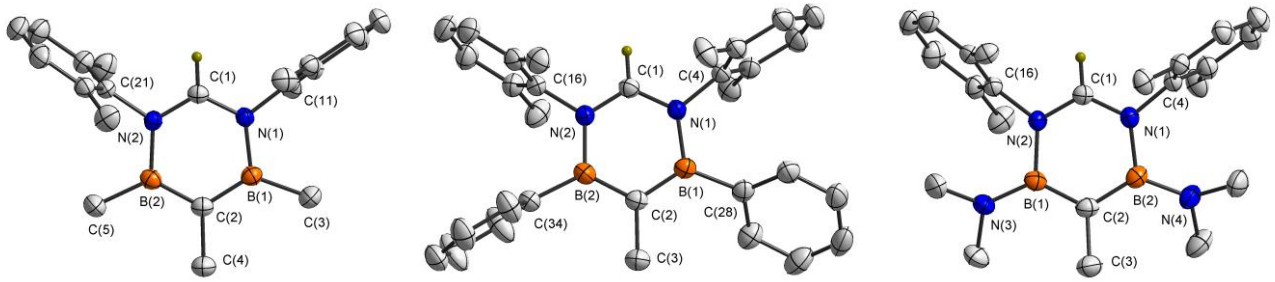


Figure 2. Molecular structures of **2a**, **2b** and **2c** (from left to right) with 50 % probability level thermal ellipsoids. The methyl groups on the isopropyl substituents, as well as the hydrogen atoms on the organic substituents have been omitted for clarity.

Removal of the ring proton of **2a-c** proceeded cleanly using benzyl potassium in THF, to yield the potassium adducts of the carbanionic rings, **3a-c**. The ^{13}C NMR resonances for the anionic carbon atoms displayed considerable downfield shifts with respect to their neutral precursors, reflecting the large local change in electron density: from 157.9 to 239.1 ppm for **3a**, 146.0 to 241.5 for **3b** and 151.4 to 247.5 for **3c**. The signal for the anionic carbon in the previously reported lithium derivative **3'a** could not be observed, likely due to coupling and quadrupolar relaxation caused by the lithium nuclei. A relevant comparison of chemical shifts with organic counterparts is hindered by the lack of ^{13}C NMR data for the highly reactive arylpotassium derivatives. Formation of phenyllithium also results in a considerable low field shift of the signal corresponding to the *ipso* carbon atom from 129 ppm in benzene to 188 and 196 ppm (in THF) for the dimeric and monomeric phenyllithium, respectively.[21a] Comparable shifts were

observed upon formation of (2,4,6-triphenyl)phenyllithium (179 ppm)[21b] from 1,3,5-triphenylbenzene (125 ppm)[21c] and of 2,6-bis(2,4,6-triisopropylphenyl)phenyllithium (177 ppm)[21d] from 1,3-bis(2,4,6-triisopropylphenyl)benzene (132 ppm).[21e] This type of low-field shift has been correlated with a decrease in the occupancy of the p orbital (π-electron density) of the respective carbon atom.[22] No other remarkable changes were observed upon deprotonation in the ^{1}H, ^{13}C and ^{11}B NMR spectra and the symmetry of the compounds appeared to remain unchanged. The high reactivity and poor crystallization properties of **3a-c** prevented their structural characterization.

The free carbanions **4a-c** were obtained easily through the addition of 18-crown-6 to the potassium adducts **3a-c**. The indicative ^{13}C NMR signals for the anionic carbon underwent a clear downfield shift upon the generation of the free carbanion, from 239.1 to 252.2 ppm for **4a**, 241.5 to 254.2 ppm for **4b** and 247.5 to 260.1 ppm for **4c**. The signal corresponding to the other ring carbon, which would have been useful for the evaluation of the extent of charge delocalization on the ring backbone, could not be located at low temperature nor through correlation experiments owing to the efficient quadrupolar broadening by the two neighboring boron centers.

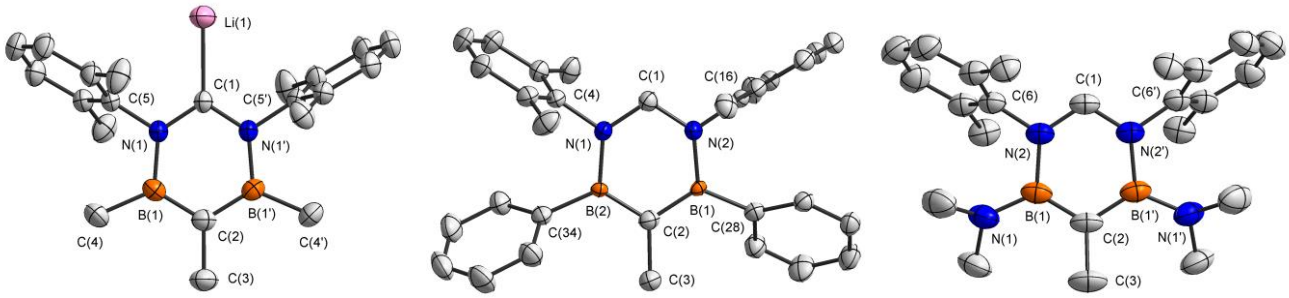


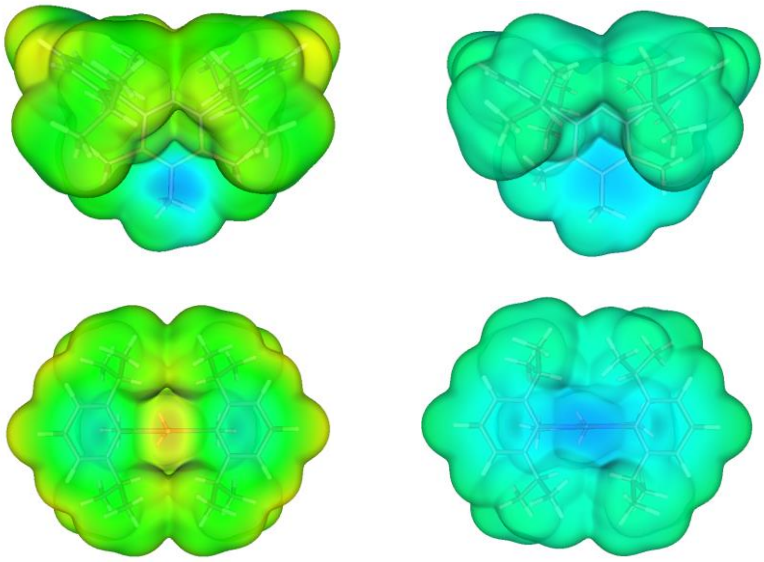
Figure 3. Structures of **3'a**, and of the free anions in **4b** and **4c** (from left to right) with 50 % probability level thermal ellipsoids. For clarity, the two THF molecules coordinated to lithium in **3'a**, as well as the methyl groups on the isopropyl substituents and all hydrogen atoms have been omitted.

X-ray structural determinations on derivatives **4b** and **4c** (Figure 3) revealed a lengthening of the intra-annular nitrogen carbon bonds of approximately 0.03 Å in comparison to the neutral rings **2b** and **2c**. This behavior, which was mirrored by the structure of the lithium salt **3'a** featuring a Li-C contact, is typical of deprotonation reactions at the benzene ring[23] and the imidazolium anions, and can be

correlated with the aforementioned decrease of π-electron density on the carbon atom upon the increase in negative charge and consequent charge redistribution.[22] An indication for the resulting increase in π-electron density on the ring backbone upon deprotonation is the slight increase (0.02 - 0.05 Å) in the bond lengths involving the exocyclic substituent to boron. As expected, this effect is most notable for **4c**, where the competing π-electron donation from the exocyclic substituent to boron is most pronounced. The N–C–N angle decreased by 10° upon deprotonation of **2a-c**, leading to an overall lateral compression of the rings and concomitant increase of the distance between the two ring carbons by *ca.* 0.14 Å. In a simple VSEPR evaluation this is not surprising, given the repulsive effect of the σ-electron pair located on carbon, and computational studies predicted a decrease in the bond angle at the carbanionic center upon deprotonation of benzene by *ca.* 14°.[23] The similar metrical parameters observed in the contact ion par **3'a** show that the removal of the counterion induces minimal structural modifications in alkali metal aryls. Very limited literature data is available in this regard, and in fact the only direct structural comparison between a contact ion pair and its ion-separated carbanion is provided by lithium triphenylmethyl.[24] In this case it was found that, aside from a change in the geometry of the carbanionic carbon from pyramidal to planar, the removal of the cation did not result in major structural changes. A solution ^{13}C NMR study found similar results for other tricoordinate carbanions and their lithium salts.[25]

The electronic structures of the neutral molecules **2** and the free anions in **4** were also examined using theoretical methods. As expected, all anions display a σ-symmetric lone pair-type orbital centered on the C(1) atom, which is high in energy and has suitable morphology for coordination to metal centers. More informative in the context of the present study is however the charge distribution in the anions $\mathbf{4}^-$ as compared to the neutral precursors **2**. This was examined by calculating the molecular electrostatic potentials (ESPs) and plotting the results on the van der Waals surfaces, *i.e.* the surfaces for which the total electron density equals 0.001 a.u. (Figure 4). The molecular electrostatic potential is a very appealing tool in this regard since it is rigorously defined in terms of the electron density and has interesting topological characteristics as it explicitly reflects opposing contributions from the nuclei and

the electrons.[26] Despite the obvious benefits that the analysis of ESP offers, it is not used nearly as often as the various population analyses due to the fact that it is computationally somewhat more demanding and does not directly provide numeric values for atomic charges.



2a **4a⁻**

Figure 4. Molecular electrostatic potentials for **2a** and **4a⁻**. For clarity, the potentials are shown in direction perpendicular to the $C_2B_2N_2$ ring (above) and along the transannular C···C axis of the $C_2B_2N_2$ ring (below). Color code: blue (negative) – turquoise – green (neutral) – yellow – orange (positive).

As evident from Figure 4, the neutral **2a** displays negative charge concentrations only around the backbone ring carbon C(2) and throughout the phenyl rings. The corresponding anion shows a more even charge distribution though local accumulation of negative charge is seen at C(2) and especially C(1). We note that the ESPs for the phenyl and dimethylamino substituted systems are analogous to those in Figure 4, thereby precluding an in-depth discussion. In addition to the direct analysis of the ESP, we calculated numeric values for atomic charges by employing Mulliken[27] and natural population analyses (NPA)[28] as well as via ESP fitting.[29] The calculated atomic charges are given in Table 3. The charges mirror the trend visible in the ESP though the absolute values obtained with different methods differ notably. For example, all analysis methods show that a transition from the neutral precursor to the

corresponding anion leads to concentration of negative charge mostly on the C(1) atom and that the total charge accumulation within the ring skeleton equals roughly one half of an electron charge. However,

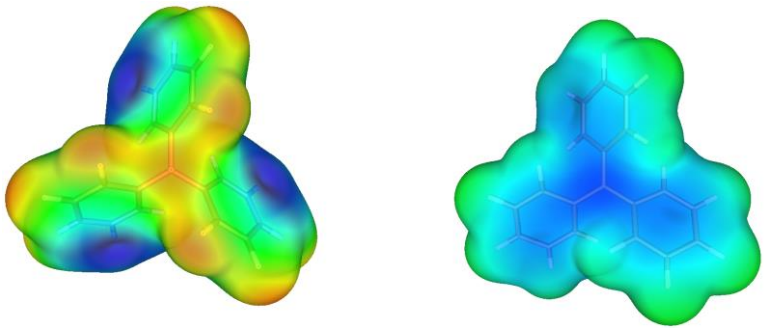
Table 3. Calculated atomic charges for **2** and **4**$^{-}$.

	Method	C(1)	C(2)	B[a]	N[a]
2a	NPA	0.33	-0.73	0.71	-0.55
	ESP	0.16	-0.20	-0.08	0.07
	Mulliken	0.09	-0.26	0.16	-0.15
2b	NPA	0.35	-0.83	0.84	-0.62
	ESP	0.15	-0.26	0.00	0.08
	Mulliken	0.03	-0.41	0.31	-0.09
2c	NPA	0.33	-0.73	0.72	-0.55
	ESP	0.11	-0.26	0.00	0.06
	Mulliken	0.07	-0.23	0.00	-0.10
4a^{-}	NPA	0.13	-0.81	0.71	-0.67
	ESP	-0.59	-0.19	-0.20	0.39
	Mulliken	-0.20	-0.28	0.11	-0.20
4b^{-}	NPA	0.15	-0.89	0.84	-0.68
	ESP	-0.50	-0.22	-0.10	0.34
	Mulliken	-0.15	-0.39	-0.27	-0.18
4c^{-}	NPA	0.16	-0.80	0.71	-0.66
	ESP	-0.45	-0.22	-0.11	0.32
	Mulliken	-0.16	-0.23	-0.10	-0.14

[a] Average values.

the NPA method indicates that C(1) remains positively charged though both Mulliken and ESP charges show a change from positive to negative upon the removal of a proton. These results illustrate the fact that different computational methods give rise to vastly different values for atomic properties since there exists multiple ways to divide the total electron density between atoms in a molecule. The NPA method generally overestimates the ionicity of bonds between elements with a large difference in electronegativity[30] whereas the Mulliken population analysis neglects the effects of electronegativity by construction.[27] On the other hand, ESP charges can be assigned only for atoms close to the surface of the

molecule and they do not necessarily reproduce the dipole moment obtained from the total density.[31] Hence, it is best not to put too much weight on absolute values, but instead look at the predicted trends.

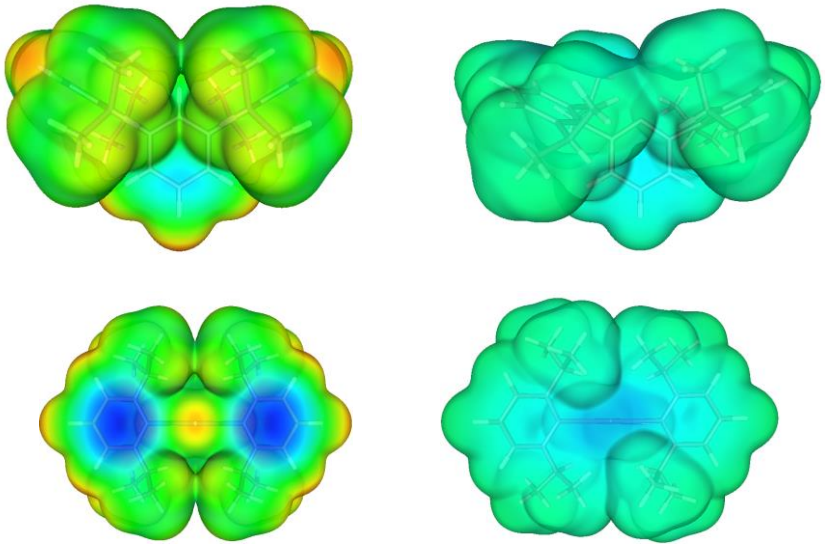


$HCPh_3$ **CPh_3^-**

Figure 5. Molecular electrostatic potentials for $HCPh_3$ and CPh_3^-. Color code: blue (negative) – turquoise – green (neutral) – yellow – orange (positive).

The charge distributions of **2** and **4**$^-$ can be compared to those calculated for classical carbanions such as triphenylmethide (Figure 5) and terphenylide, as well as to those obtained for the recently reported anionic N-heterocyclic carbene **5**$^-$ with *tert*-butylmalonyl backbone.[11b] There exists a considerable charge separation in $HCPh_3$ which, as expected, smoothens out upon the removal of a proton. In fact, the negative charge in triphenylmethylide is uniformly spread over the entire carbon framework. In an analogous fashion, the charge distribution in 1,3-bis(2,6-diisopropylphenyl)benzene, **6**, and in the corresponding phenylide **6**$^-$ (Figure 6) mirrors that found for the **2a**/**4a**$^-$ pair, revealing significant charge delocalization for the latter species. Hence, as far as the charge distribution is concerned, there appears to be no significant differences between the terphenylide **6**$^-$ and the **4**$^-$ anions. We also note that the recently reported anionic N-heterocyclic carbene **5**$^-$ displays delocalization of negative charge akin to **4a**$^-$ (see Supporting Information). While the direct comparison of computed atomic charges for different structures needs to be treated with caution, both the molecular electrostatic potentials and the trends in calculated charges confirm that, akin to classical carbanions such as triphenylmethylide and terphenylide, deprotonation to form anions **4a-c**$^-$ and **5**$^-$ leads to an increase in the negative charge

hosted by the carbanionic center as well as a considerable charge delocalization over the molecular skeleton. This charge delocalization is certainly crucial to the stability of these carbanions and hence to



6 **6⁻**

Figure 6. Molecular electrostatic potentials for **6** and **6⁻**. For clarity, the potentials are shown in direction perpendicular (above) and parallel (below) the C_6 plane. Color code: blue (negative) – turquoise – green (neutral) – yellow – orange (positive).

the feasibility of their isolation in the solid state. As observed in N-heterocyclic carbenes, the heterocyclic skeleton of **4a-c⁻** provides more efficient means for electron redistribution in comparison to classical phenylide-type anions, reducing the charge density on the carbanion center and accounting for the superior stability of the former (calculated Mulliken atomic charge on the carbanionic center, C_q = –0.20 - –0.15 in **4a-c⁻** and –0.14 in **5⁻** *vs.* C_q = –0.14 in CPh_3^- and –0.31 in **6⁻**). Other factors, such as the energies of the frontier orbitals,[11a] have nevertheless a major contribution to the reactivity of these anions, as evinced by the limited experimental observations that are available: Although the computed charge distribution in **4a-c⁻** is similar to that computed for **5⁻**, the former have a pronounced carbanion character, being able to deprotonate solvents such as THF and toluene and so far proving reluctant to form transition metal complexes, while the latter appear to display a carbene-like character and have been incorporated in transition metal complexes.[11b]

Conclusions

We have isolated and structurally characterized the first examples of divalent free carbanions by implementing stabilization through vicinal nitrogen atoms, delocalization of charge over the heterocyclic backbone and steric protection through 2,6-diisopropylphenyl groups. The phenylide-like carbanions showed little structural change upon the removal of the alkali metal cation from the coordination sphere but the corresponding ^{13}C NMR shift was sensitive to the change, reflecting the reduction in electron density in the p orbital of the anionic carbon. The electronic properties of this carbon could be influenced by altering the substituents on boron, albeit not significantly.

The present study highlights the similarity between stable singlet carbenes and penylide-type carbanions and emphasizes the fact that no obvious distinction can be made between such anionic carbenes and carbanions, if the charge of the carbene can be delocalized over the dicoordinate carbon. The presence of a negative charge delocalized over a classical carbene framework imparts considerable carbanionic character to the carbon center, as in the ligands **A** reported herein, while the addition of a positive charge to typical phenylide carbanions results in the formation of zwitterionic, neutral carbene ligands such as the reported pyridine and quinoline derivatives that were isolated as transition metal complexes.[12]

The suitability of the anionic ligands reported here as substituents in main group chemistry, as a direct comparison with the classical terphenyl groups, is currently under investigation.

Experimental Section

General considerations. Except for the synthesis and isolation of the free amidines, all other operations were carried out with careful exclusion of air and moisture using standard Schlenk and glove box techniques. The solvents were dried and deoxygenated prior to use. Derivatives **1a** – **3a**,[10] as well as $MCH(RBCl)_2$ (R = Ph, Me_2N)[12, 13] and (2,6-*i*$Pr_2C_6H_3$)N=CH-N($SiMe_3$)(2,6-*i*$Pr_2C_6H_3$)[32] were prepared according to literature procedures. All NMR spectra were run on a Bruker Avance DRX-400 instrument and chemical shifts are reported in δ units (ppm) using the solvent as an internal reference: C_6D_6H (7.15

ppm, ^{1}H) and C_6D_6 (128.0 ppm, ^{13}C); THF-d_7 (3.58 ppm, ^{1}H) and THF-d_8 (67.57 ppm, ^{13}C). A Micromass VG7070F instrument was used for recording the low resolution mass spectra while the high resolution mass spectra were obtained using a Kratos MS80 RFA instrument.

Synthesis of [cyclo-:C(2,6-*i*Pr$_2$C$_6$H$_3$-N)$_2$(MeB)$_2$CMe]|(18-crown-6)K] (4a). 18-crown-6 (8 mg, 32 μmol) was added to a solution of **3a** (15 mg, 32 μmol) in THF (5 mL) on an NMR scale. ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ 1.02 (d, 3H, $^{3}J_{HH}$ = 6.8 Hz, HCC*H*$_3$), 1.09 (d, 3H, $^{3}J_{HH}$ = 7.3 Hz, HCC*H*$_3$), 1.11 (d, 12H, $^{3}J_{HH}$ = 6.9 Hz, HCC*H*$_3$), 1.88 (s, 3H, CC*H*$_3$), 2.31 (s, 6H, BC*H*$_3$), 3.35 (sep, 2H, $^{3}J_{HH}$ = 6.8 Hz, *H*C(CH$_3$)$_2$), 3.45 (s, 24H, 18-crown-6), 3.76 (sep, 2H, $^{3}J_{HH}$ = 6.8 Hz, *H*C(CH$_3$)$_2$), 6.61 - 7.43 (m, H, *o-, m-*, *p*-C$_6$*H*$_5$). ^{13}C NMR (100 MHz, THF-d_8, 25 °C): δ 18.2 (s, B$_2$C(*C*H$_3$)), 21.7 (s, B*C*H$_3$), 24.4 (s, CH(*C*H$_3$)$_2$), 25.7 (s, CH(*C*H$_3$)$_2$), 27.9 (s, CH(*C*H$_3$)$_2$), 28.2 (s, CH(*C*H$_3$)$_2$), 29.1 (s, *C*H(CH$_3$)$_2$), 71.2 (s, 18-crown-6), 119.6 (s, *C*$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 122.5 (s, *C*$_6$H$_3$(CH(CH$_3$)$_2$)$_2$, 122.7 (s, *C*$_6$H$_3$(CH(CH$_3$)$_2$)$_2$, 142.9 (s, *C*$_6$H$_3$(CH(CH$_3$)$_2$)$_2$, 146.2 (s, *C*$_6$H$_3$(CH(CH$_3$)$_2$)$_2$, 151.5 (s, *C*$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 252.2 (s, N$_2$*C*). ^{11}B NMR (128 MHz, THF-d_8, 25 °C): δ 37.4 (s, br, LW$_{1/2}$= 1753 Hz Hz).

Synthesis of [cyclo-HC(2,6-*i*Pr$_2$C$_6$H$_3$-N)$_2$(PhB)$_2$CHMe](OTf) (1b). 1,1-bis(chlorophenylboryl)ethane (0.315 g, 1.14 mmol) was added to a solution of (2,6-*i*Pr$_2$C$_6$H$_3$)N-CH=N(SiMe$_3$)(2,6-*i*Pr$_2$C$_6$H$_3$) (0.500 g, 1.14 mmol) in CH_2Cl_2 (30 mL). The solution was stirred for one hour, followed by the addition of trimethylsilyltriflate (0.253 g, 1.14 mmol). After another thirty minutes of stirring, the volatiles were removed in vacuo and the remaining white residue was washed with hexane, yielding the desired product as a white solid (0.644 g, 0.899 mmol, 79 %). ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ 0.74 (d, br, 6H), 1.04 (d, 6H, $^{3}J_{HH}$ = 6.3 Hz, HCC*H*$_3$), 1.14 (q, 1H, $^{3}J_{HH}$ = 6.8 Hz, *H*CCH$_3$), 1.26 (d, 6H, $^{3}J_{HH}$ = 5.8 Hz, HCC*H*$_3$), 1.28 (d, 6H, $^{3}J_{HH}$ = 6.8 Hz, HCC*H*$_3$), 1.40 (d, 3H, $^{3}J_{HH}$ = 6.8 Hz, CHC*H*$_3$), 2.93 (sep, br, 2H, *H*CCH$_3$), 3.53 (sep, br, 2H, *H*CCH$_3$), 6.99 – 7.50 (m, 16H, *m-*, *p*-C$_6$*H*$_3$), 8.63 (s, 1H, N$_2$C*H*). ^{13}C NMR (100 MHz, THF-d_8, 25 °C): δ 14.2 (s, B$_2$C(*C*H$_3$)), 23.7 (s, CH(*C*H$_3$)$_2$), 23.9 (s, CH(*C*H$_3$)$_2$), 23.9 (s, *C*H(CH$_3$)$_2$), 26.9 (s, *C*H(CH$_3$)$_2$), 29.3 (s, CH(*C*H$_3$)$_2$), 29.7 (s, CH(*C*H$_3$)$_2$), 125.1 (s, *o*-*C*$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 125.6 (s, *o*-*C*$_6$H$_5$), 127.5 (s, *m*-*C*$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 129.9 (s,

m-C_6H_5), 135.5 (s, *i*-$C_6H_3(CH(CH_3)_2)_2$, 135.5 (s, *i*-C_6H_5), 139.9 (s, *m*-$C_6H_3(CH(CH_3)_2)_2$), 146.2 (s, *m*-C_6H_5), 168.0 (s, N_2CH). ^{11}B NMR (128 MHz, C_6D_6, 25 °C): δ 31.4 (s, br, $LW_{1/2}$= 1112 Hz).

Synthesis of [*cyclo*-HC(2,6-*i*Pr$_2$C$_6$H$_3$-N)$_2$(PhB)$_2$CMe] (2b). A solution of **1b** (1.80 g, 2.50 mmol) and potassium hexamethyldisilazide (0.501 g, 2.50 mmol) in benzene (50 mL) was stirred for one hour. The white precipitate was filtered off, and the volatiles were removed *in vacuo*. The residue was washed with hexane and dried *in vacuo*, yielding the desired compound as a white powder (1.19 g, 2.10 mmol, 84 %). ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ 0.95 (d, 12H, $^3J_{HH}$ = 6.8 Hz, HCCH_3), 1.26 (d, 12H, $^3J_{HH}$ = 6.8 Hz, HCCH_3), 2.04 (s, 3H, CCH_3), 2.95 (sep, 4H, $^3J_{HH}$ = 6.8 Hz, HC(CH$_3$)$_2$), 6.98-7.30 (m, H, C_6H_5), 8.32 (s, 1H, N_2CH). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 20.0 (s, $B_2C(CH_3)$), 23.9 (s, CH(CH_3)$_2$), 26.4 (s, CH(CH_3)$_2$), 29.0 (s, CH(CH$_3$)$_2$), 124.6 (s, *p*-$C_6H_3(CH(CH_3)_2)_2$), 127.2 (s, *i*-C_6H_5), 127.5 (s, *o*-C_6H_3), 128.9 (s, *m*-C_6H_3), 129.3 (s, *p*-C_6H_3), 135.1 (s, *o*-$C_6H_3(CH(CH_3)_2)_2$, 140.5 (s, *i*-$C_6H_3(CH(CH_3)_2)_2$), 145.2 (s, (s, *m*-$C_6H_3(CH(CH_3)_2)_2$, 148.5 (s, N_2C). ^{11}B NMR (128 MHz, THF-d_8, 25 °C): δ 38.4 (s, br, $LW_{1/2}$= 785 Hz). TOF MS EI+ (*m/z* (%)): 566.4038 (80) [M^+]. Elem anal. Calcd. for $C_{31}H_{50}B_2N_4$ (%): C, 82.70; H, 8.54; N, 4.95. Found: C, 82.12; H, 8.73; N, 4.89.

Synthesis of [*cyclo*-:C(2,6-*i*Pr$_2$C$_6$H$_3$-N)$_2$(PhB)$_2$CMe]K (3b). Benzyl potassium (34 mg, 0.26 mmol) was added to a solution of **2b** (120 mg, 0.264 mmol) in tetrahydrofuran (25 mL). Solution was stirred for five minutes, after which the volatiles were removed in vacuo, leaving the desired product as a pale yellow powder (116 mg, 0.193 mmol, 73 %). ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ 0.92 (d, 12H, $^3J_{HH}$ = 6.8 Hz, HCCH_3), 1.06 (d, 12H, $^3J_{HH}$ = 6.8Hz, HCCH_3), 1.81 (s, 3H, CCH_3), 3.39 (sep, 4H, $^3J_{HH}$ = 6.8Hz, HC(CH$_3$)$_2$), 6.78 - 7.19 (m, H, *o-, m-*, *p*-C_6H_5). ^{13}C NMR (100 MHz, THF-d_8, 25 °C): δ 18.1 (s, $B_2C(CH_3)$), 22.6 (s, CH(CH_3)$_2$), 25.1 (s, CH(CH_3)$_2$), 27.5 (s, CH(CH$_3$)$_2$), 122.5 (s, *p*-$C_6H_3(CH(CH_3)_2)_2$), 123.5 (s, *i*-C_6H_5), 124.9 (s, *o*-C_6H_3), 125.2 (s, *m*-C_6H_3), 128.6 (s, *p*-C_6H_3), 134.4 (s, *o*-$C_6H_3(CH(CH_3)_2)_2$, 145.1 (s, *i*-$C_6H_3(CH(CH_3)_2)_2$), 148.7 (s, *m*-$C_6H_3(CH(CH_3)_2)_2$, 241.5 (s, N_2C). ^{11}B NMR (128 MHz, THF-d_8, 25 °C): δ 36.0 (s, br, $LW_{1/2}$= 1095 Hz).

Synthesis of [*cyclo*-:C(2,6-*i*Pr$_2$C$_6$H$_3$-N)$_2$(PhB)$_2$CMe][(18-crown-6)K] (4b). 18-crown-6 (12 mg, 45 μmol) was added to a solution of **3b** (27 mg, 45 μmol) in THF (5 mL). The solution was cooled to –30 °C, resulting in clear, colorless crystals of the desired product (20 mg, 29 μmol, 64%). ^{1}H NMR (400 MHz, THF-d$_8$, 25 °C): δ 0.92 (d, 12H, $^3J_{HH}$ = 6.7 Hz, HCC*H*$_3$), 1.04 (d, 12H, $^3J_{HH}$ = 6.6Hz, HCC*H*$_3$), 1.80 (s, 3H, CC*H*$_3$), 3.37 (s, 24H, 18-crown-6), 3.46 (sep, 4H, $^3J_{HH}$ = 6.7Hz, *H*C(CH$_3$)$_2$), 6.72 - 7.11 (m, H, *o-, m-*, *p*-C6*H*5). ^{13}C NMR (100 MHz, THF-d$_8$, 25 °C): δ 19.1 (s, B$_2$C(*C*H$_3$)), 23.8 (s, CH(*C*H$_3$)$_2$), 26.5 (s, CH(*C*H$_3$)$_2$), 28.6 (s, *C*H(CH$_3$)$_2$), 71.2 (s, 18-crown-6), 122.7 (s, *p*-*C*$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 124.1 (s, *i*-*C*$_6$H$_5$), 124.8 (s, *o*-*C*$_6$H$_3$), 126.0 (s, *m*-*C*$_6$H$_3$), 129.8 (s, *p*-C$_6$H$_3$), 135.7 (s, *o*-*C*$_6$H$_3$(CH(CH$_3$)$_2$)$_2$, 146.2 (s, *i*-*C*$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 150.4 (s, *m*-*C*$_6$H$_3$(CH(CH$_3$)$_2$)$_2$, 254.2 (s, N$_2$*C*). ^{11}B NMR (128 MHz, THF-d$_8$, 25 °C): δ 36.6 (s, br, LW$_{1/2}$= 235 Hz).

Synthesis of [*cyclo*-HC(2,6-*i*Pr$_2$C$_6$H$_3$-N)$_2$(Me$_2$NB)$_2$CHMe](OTf) (1c). 1,1-bis(chlorodimethylaminoboryl)ethane (0.100 g, 0.475 mmol) was added to a solution of *N,N'*-bis(2,6-diisopropylphenyl)trimethylsilylformamidine (0.207 g, 0.475 mmol) in CH_2Cl_2 (30 mL). The solution was stirred for one hour, followed by the addition of trimethylsilyltriflate (0.105 g, 0.475 mmol). After thirty minutes of stirring, the volatiles were removed in vacuo. The remaining white oily solid was washed with hexane yielding the desired product as a white solid (0.264 g, 0.438 mmol, 92 %). ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 1.00 (d, 6H, $^3J_{HH}$ = 6.8 Hz, HCC*H*$_3$), 1.11 (d, 6H, $^3J_{HH}$ = 6.8 Hz, HCC*H*$_3$), 1.22 (d, 6H, $^3J_{HH}$ = 6.8 Hz, HCC*H*$_3$), 1.57 (d, 6H, $^3J_{HH}$ = 6.8 Hz, HCC*H*$_3$), 1.94 (q, 1H, $^3J_{HH}$ = 8.3 Hz, *H*CCH$_3$), 2.02 (s, 6H, N(C*H*$_3$)$_2$), 2.90 (s, 6H, N(C*H*$_3$)$_2$), 2.97 (sep, 2H, $^3J_{HH}$ = 6.8 Hz, *H*CCH$_3$), 3.74 (sep, 2H, $^3J_{HH}$ = 6.8 Hz, *H*CCH$_3$), 7.00 - 7.25 (m, 6H, *m-*, *p-* C$_6$*H*$_3$), 7.29 (s, 1H, *H*CN$_2$). ^{1}H NMR (400 MHz, THF-d$_8$, 25 °C): δ 1.17 (d, 6H, $^3J_{HH}$ = 6.8 Hz, HCC*H*$_3$), 1.21 (d, 6H, $^3J_{HH}$ = 6.8 Hz, HCC*H*$_3$), 1.24 (d, 6H, $^3J_{HH}$ = 6.8 Hz, HCC*H*$_3$), 1.30 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CHC*H*$_3$), 1.94 (q, 1H, $^3J_{HH}$ = 6.8 Hz, *H*CCH$_3$), 1.99 (s, 6H, N(C*H*$_3$)$_2$), 2.92 (s, 6H, N(C*H*$_3$)$_2$), 3.11 (sep, 2H, $^3J_{HH}$ = 6.8 Hz, *H*CCH$_3$), 3.58 (sep, 2H, $^3J_{HH}$ = 6.8 Hz, *H*CCH$_3$), 7.28 - 7.44 (m, 6H, *m-*, *p*-C$_6$*H*$_3$), 8.38 (s, 1H, *H*CN$_2$). ^{13}C NMR (100 MHz, C$_6$D$_6$, 25 °C): δ 19.1 (s, B$_2$C(*C*H$_3$)), 23.6 (s, CH(*C*H$_3$)$_2$), 24.6 (s, CH(*C*H$_3$)$_2$), 24.7 (s, *C*H(CH$_3$)$_2$),

25.7 (s, *C*H(CH$_3$)$_2$), 28.3 (s, CH(*C*H$_3$)$_2$), 29.0 (s, CH(*C*H$_3$)$_2$), 39.3 (s, N(*C*H$_3$)$_2$), 41.4 (s, N(*C*H$_3$)$_2$), 125.0 (s, *o*-*C*$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 126.5 (s, *o*-*C*$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 130.6 (s, *p*-*C*$_6$H$_3$(CH(CH$_3$)$_2$)$_2$, 139.5 (s, *i*-*C*$_6$H$_3$(CH(CH$_3$)$_2$)$_2$, 144.6 (s, *m*-*C*$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 146.6 (s, *m*-*C*$_6$H$_3$(CH(CH$_3$)$_2$)$_2$, 169.0 (s, N$_2$*C*H). ^{11}B NMR (128 MHz, C$_6$D$_6$, 25 °C): δ 33.0 (s, br, LW$_{1/2}$= 898 Hz).

Synthesis of [*cyclo*-HC(2,6-*i*Pr$_2$C$_6$H$_3$-N)$_2$(Me$_2$NB)$_2$CHMe] (2c). A solution of **5** (0.428 g, 0.658 mmol) and potassium hexamethyldisilazide (0.159 g, 0.800 mmol) in benzene (50 mL) was stirred for two hours. The white precipitate was removed via filtration, followed by the removal of the volatiles in vacuo. The desired compound was isolated by recrystallization from hexane, resulting in a yellow crystalline solid (0.227 g, 0.454 mmol, 69 %). ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 1.12 (d, 12H, $^3J_{HH}$ = 6.8 Hz, HCC*H*$_3$), 1.33 (d, 12H, $^3J_{HH}$ = 6.8 Hz, HCC*H*$_3$), 2.70 (s, 3H, CC*H*$_3$), 2.73 (s, 12H, N(C*H*$_3$)$_2$), 3.31 (sep, 4H, $^3J_{HH}$ = 6.8Hz, *H*C(CH$_3$)$_2$), 7.14-7.28 (m, 6H, C$_6$*H*$_3$, *H*CN$_2$). ^{1}H NMR (400 MHz, THF-d$_8$, 25 °C): δ 1.12 (d, 12H, $^3J_{HH}$ = 6.8 Hz, HCC*H*$_3$), 1.24 (d, 12H, $^3J_{HH}$ = 6.8 Hz, HCC*H*$_3$), 1.96 (s, 3H, CC*H*$_3$), 2.33 (s, 12H, N(C*H*$_3$)$_2$), 3.08 (sep, 4H, $^3J_{HH}$ = 6.8 Hz, *H*C(CH$_3$)$_2$), 7.20-7.29 (m, 6H, C$_6$*H*$_3$), 7.57 (s, 1H, *H*CN$_2$). ^{13}C NMR (100 MHz, C$_6$D$_6$, 25 °C): δ 3.0 (s, B$_2$C(*C*H$_3$)), 20.9 (s, CH(*C*H$_3$)$_2$), 24.0 (s, CH(*C*H$_3$)$_2$), 26.0 (s, *C*H(CH$_3$)$_2$), 28.9 (s, *C*H(CH$_3$)$_2$), 42.5 (s, N(*C*H$_3$)$_2$), 124.7 (s, *o*-*C*$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 128.8 (s, *p*-*C*$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 141.5 (s, *i*-*C*$_6$H$_3$(CH(CH$_3$)$_2$)$_2$, 145.4 (s, *m*-*C*$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 151.4 (s, N$_2$*C*H). ^{11}B NMR (128 MHz, C$_6$D$_6$, 25 °C): δ 33.5 (s, br, LW$_{1/2}$= 579 Hz). TOF MS EI+ (*m/z* (%)): 500.4222 (69) [M$^+$]. Elem anal. Calcd. for C$_{39}$H$_{48}$B$_2$N$_2$ (%): C, 74.41; H, 10.07; N, 11.2. Found: C, 73.90; H, 10.25; N, 10.83.

Synthesis of [*cyclo*-:C(2,6-*i*Pr$_2$C$_6$H$_3$-N)$_2$(Me$_2$NB)$_2$CMe]K (3c). Benzyl potassium (6 mg, 44 μmol) was added to a solution of 6 (20 mg, 44 μmol) in tetrahydrofuran (5 mL). Solution was stirred for five minutes, after which the volatiles were removed *in vacuo*, leaving the desired product as a dark orange solid (12 mg, 24 μmol, 55 %). ^{1}H NMR (400 MHz, THF-d$_8$, 25 °C): δ 0.61 (d, 6H, $^3J_{HH}$ = 9.8 Hz, HCC*H*$_3$), 0.76 (d, 6H, $^3J_{HH}$ = 9.8 Hz, HCC*H*$_3$), 1.50 (s, 3H, B$_2$CC*H*$_3$), 1.99 (s, 12H, N(C*H*$_3$)$_2$), 3.30 (sep, 4H, $^3J_{HH}$ = 9.8 Hz, *H*CCH$_3$), 7.13 (s, 6H, C$_6$*H*$_3$), ^{13}C NMR (100 MHz, THF-d$_8$, 25 °C): *δ* 20.6 (s,

$B_2C(CH_3)$), 23.9 (s, $CH(CH_3)_2$), 25.8 (s, $CH(CH_3)_2$), 43.2 (s, $N(CH_3)_2$), 123.9 (s, *o*-$C_6H_3(CH(CH_3)_2)_2$), 125.5 (s, *p*-$C_6H_3(CH(CH_3)_2)_2$), 146.5 (s, *i*-$C_6H_3(CH(CH_3)_2)_2$, 150.9 (s, *m*-$C_6H_3(CH(CH_3)_2)_2$), 247.5 (s, N_2C:). ^{11}B NMR (128 MHz, THF-d_8, 25 °C): δ 32.5 (s, br, $LW_{1/2}$= 404 Hz).

Synthesis of [*cyclo*-:C(2,6-*i*Pr$_2$C$_6$H$_3$-N)$_2$(Me$_2$NB)$_2$CMe][(18-crown-6)K] (4c). 18-crown-6 (12 mg, 45 μmol) was added to a solution of 3 (27 mg, 45 μmol) in THF (5 mL). The solution was cooled to –30 °C, resulting in clear, colorless crystals of the desired product (20 mg, 29 μmol, 64 %). ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ 0.92 (d, 12H, $^3J_{HH}$ = 6.7 Hz, HCCH_3), 1.04 (d, 12H, $^3J_{HH}$ = 6.6 Hz, HCCH_3), 1.80 (s, 3H, CCH_3), 3.37 (s, 24H, 18-crown-6), 3.47 (sep, 4H, $^3J_{HH}$ = 6.7 Hz, $HC(CH_3)_2$), 6.72-7.13 (m, 6H, *m*-, *p*-C_6H_3). ^{13}C NMR (100 MHz, THF-d_8, 25 °C): δ 21.4 (s, $B_2C(CH_3)$), 24.0 (s, $CH(CH_3)_2$), 25.5 (s, $CH(CH_3)_2$), 26.3 (s, $CH(CH_3)_2$), 28.4 (s, $CH(CH_3)_2$), 43.4 (s, $N(CH_3)_2$), 71.2 (s, 18-crown-6), 122.9 (s, *o*-$C_6H_3(CH(CH_3)_2)_2$), 124.2 (s, *p*-$C_6H_3(CH(CH_3)_2)_2$), 146.6 (s, *i*-$C_6H_3(CH(CH_3)_2)_2$, 151.2 (s, *m*-$C_6H_3(CH(CH_3)_2)_2$), 260.1 (s, N_2C). ^{11}B NMR (128 MHz, THF-d_8, 25 °C): δ 32.1 (s, br, $LW_{1/2}$= 1095 Hz).

Computational Details. Molecular geometries of all studied compounds were optimized with DFT using the hybrid PBE1PBE exchange-correlation functional[33] with Ahlrichs' def-TZVP basis sets.[34] All calculations were carried out with the Turbomole 5.10 program package.[35] Visualizations of ESPs were done with the gOpenMol program.[36]

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Supporting Information Available: Complete crystallographic data of complexes **2b**, **2c**, **4b** and **4c** in CIF format, as well as NMR spectra of all new compounds. This material is available free of charge

via the Internet at http:/pubs.acs.org. CIF files are also available on-line from the Cambridge Crystallographic Data Centre (CCDC Nos. 697074 (**2b**), 697075 (**2c**), 697076 (**4b**), and 697077 (**4c**)).

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