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Main group chemistry: from molecules to materials

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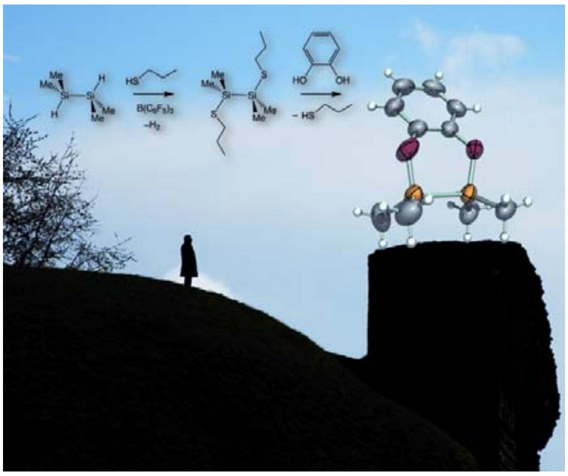
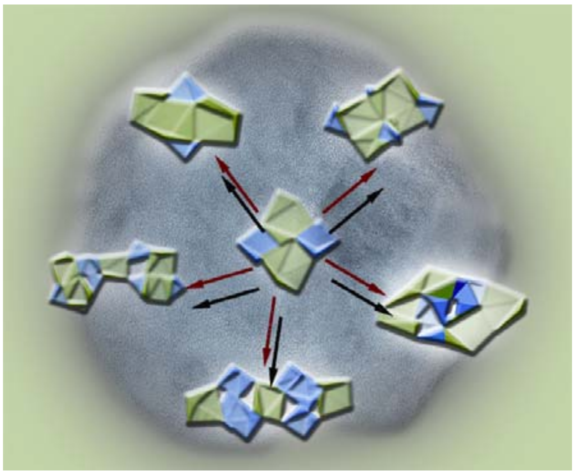
Published in issue 26, 2008 of *Dalton Transactions*





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Tuning the electronic properties of cyclopentadienyl analogs with CB_2N_2 frameworks: 1,2-diphenyl-1,2-diaza-3,5-diborolyl ligands and their alkali metal salts†

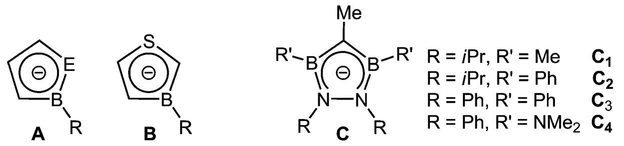
Hanh V. Ly, Jari Konu, Masood Parvez and Roland Roesler*

Received 22nd February 2008, Accepted 22nd April 2008
First published as an Advance Article on the web 20th May 2008
DOI: 10.1039/b802930j

Two heterocyclic cyclopentadienyl analogs with a CB_2N_2 skeleton, 4-methyl-1,2,3,5-tetraphenyl-1,2-diaza-3,5-diborolidine and 4-methyl-3,5-dimethylamino-1,2-diphenyl-1,2-diaza-3,5-diborolidine were prepared through cyclocondensation of the corresponding 1,1-bis(organochloroboryl)ethane with 1,2-diphenylhydrazine. The former diazadiborolidine featured a cyclopentadiene-like structure with short B–N bonds and a planar ring framework, while in the latter the B–N bonds were noticeably longer and the ring framework was considerably folded as a result of the interaction between boron and the electron donating NMe_2 groups. The dimethylamino substituted diazadiborolidine could not be deprotonated due to the reduced acidity of the ring proton, however, the B-phenylated analog was easily deprotonated and the lithium, sodium and potassium 1,2-diaza-3,5-diborolyls were isolated and structurally characterized. The solid state structures of the lithium and sodium salts were similar, with an η^1-coordinated π ligand and three THF molecules completing the coordination sphere of the metal. The potassium salt featured a highly unusual mono-dimensional polymeric structure with the metal π-coordinated by the CB_2N_2 ligand and two of the phenyl groups on boron and nitrogen, and σ-coordinated by one THF molecule.

Introduction

The tremendous importance of cyclopentadienyl as a ligand in coordination chemistry and catalysis[1] has driven the quest for the development of heterocyclic analogs displaying similar coordination behavior and different electronic properties. Anionic heterocycles featuring, aside from carbon, boron alone or in combination with nitrogen or chalcogens and displaying excellent π-coordinating properties have been extensively investigated in this regard. Pioneered by Schmid and co-workers, the 1,2-azaborolidines **A** (E = N)[2a–c] have been further investigated by Ashe[2f,j] and subsequently extended to 1,2-oxa[2k] and thiaborolidines **A**[2g] (E = O, S) and 1,3-thiaborolidines **B**.[2d,e] The synthesis and properties of 1,2-azaborolidines **A** (E = N) have also been investigated by Fu,[2h,i,l] and the suitability of some of these five-membered heterocycles as ancillary ligands in catalytic systems has been examined.[2e,l]



Aiming to explore the π-coordinating properties of cyclopentadienyl analogs with low carbon content in the ring framework, we characterized ligands of type **C**, and reported on sandwich complexes of these ligands with metals from Groups 1 and 12 of the periodic table.[3a–c] These studies showed that the metal complexes of the electron rich, pentaalkyl substituted ligands $\mathbf{C_1}$ were difficult to purify and crystallize because of their extreme solubility in organic solvents. The less electron rich trialkyl diphenyl ligands $\mathbf{C_2}$ proved to be easier to prepare through deprotonation because of the increased acidity of the ring proton in the neutral precursor, and had superior crystallization properties. Bicyclic ligands derived from $\mathbf{C_2}$ demonstrated excellent π-bridging properties in dinuclear ruthenium complexes, and the potential to generate multidecker sandwich compounds.[3d]

We report herein on further studies concerning the tuning of the coordination properties of ligands of type **C**. The synthesis and characterization of the ligands $\mathbf{C_3}$ and $\mathbf{C_4}$, which were expected to have good crystallization properties and differ considerably in their electron donating abilities, was enticing because of the stability and commercial availability of 1,2-diphenylhydrazine.

Results and discussion

The ligand precursors **1** and **2** were prepared through the condensation of previously reported geminal bis(organochloroboryl)ethanes[4] with symmetric diphenylhydrazine in the presence of triethylamine (Scheme 1). The products were isolated as colorless crystalline solids showing good solubility in ethers and aromatic hydrocarbons and poor solubility in hexane and pentane.

The ^1H and ^{13}C NMR spectra of **1** and **2** featured the expected signals. The distinctive doublet-quartet pattern of the Me–CHB_2 moiety was observed in the ^1H NMR spectra of both substances, and only one signal was observed for the methyl protons of the

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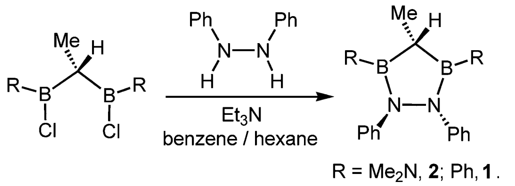
Department of Chemistry, University of Calgary, 2500 University Drive, Calgary, Alberta, T2N 1N4, Canada

† Electronic supplementary information (ESI) available: NMR spectra of all new compounds. CCDC reference numbers 678560–678564. For ESI or crystallographic data in CIF or other electronic format see DOI: 10.1039/b802930j



Scheme 1 Synthesis of ligand precursors **1** and **2**.

dimethylamino groups in **2**, indicative of a low rotational barrier around the exocyclic B–N bond. The ^{13}C NMR spectrum of **2** featured two independent, yet very close, broad signals for the dimethylamino group, suggesting that the spectrum was collected in the proximity of the coalescence temperature. The signals corresponding to the ring carbon and proton in **2** are considerably high field shifted with respect to **1** (0.65 *vs.* 1.65 ppm for ^{1}H and 8.9 *vs.* 23.0 ppm for ^{13}C), as a consequence of the increased electron density ascribed to the electron donating ability of the dimethylamino groups on boron. The EI mass spectra of **1** and **2** displayed intense signals for the molecular ions and products of their fragmentation.

The structural determinations for **1** and **2** (Table 1) confirmed the identity of the compounds and, since the structures of the neutral precursors to ligands **C**$_1$ and **C**$_2$ had not been determined, offered a first insight into the molecular structures of such derivatives. To our knowledge, no crystal structure for either of the protonated precursors to the much investigated ligands **A** (E = N) have been reported. The ring framework of **1** showed excellent planarity (Fig. 1), with a sum of the pentagon angles of 539.8° (Table 2), a folding along the B···B axis of only 2.8° and a propeller-like arrangement of the phenyl substituents that is typical for tetra- and penta-phenylcyclopentadienyl. The ring skeleton in **2** however, featured an envelope conformation with a considerable folding angle along the B(1)···N(2) axis (28.7°), likely in order to alleviate the steric strain between the ring substituents (Fig. 2). The strong π-interaction between the extraannular nitrogen centers and the boron atoms imposes very small dihedral angles between the planes defined by the substituents on boron and the exocyclic nitrogen (5.8 and 14.8°).

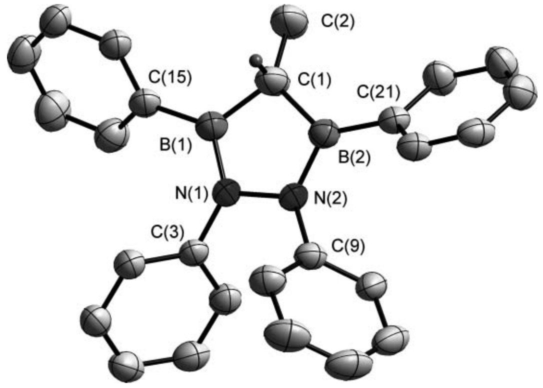


Fig. 1 Molecular structure of **1**, with thermal ellipsoids drawn at 50% probability. For clarity, all hydrogen atoms except for the one on the ring carbon have been omitted.

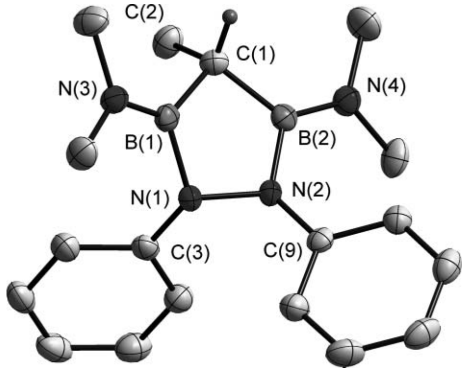


Fig. 2 Molecular structure of **2**, with thermal ellipsoids drawn at 50% probability. For clarity, all hydrogen atoms except for the one on the ring carbon have been omitted.

By comparison, in **1** the phenyl substituents on boron form dihedral angles of 43.8 and 46.8° with the planes defined by the substituents on boron. The phenyl groups in **2** need to accommodate the nearly planar arrangement of the (Me$_2$N–B)$_2$CHMe unit and especially the steric bulk of the dimethylamino

Table 1 Selected data and structure refinement details for **1**, **2**, **3a**(thf)$_3$, **3b**(thf)$_3$, and **3c**(thf)

	1	**2**	**3a**(thf)$_3$	**3b**(thf)$_3$	**3c**(thf)
Empirical formula	$C_{26}H_{24}B_2N_2$	$C_{18}H_{26}B_2N_4$	$C_{38}H_{47}B_2LiN_2O_3$	$C_{38}H_{47}B_2N_2NaO_3$	$C_{30}H_{31}B_2KN_2O$
Formula weight	386.09	320.05	608.34	624.39	496.29
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P2_1$	$P2_1/n$
a/Å	9.274(5)	9.751(3)	22.732(7)	9.154(5)	11.393(2)
b/Å	10.117(7)	10.426(3)	8.931(2)	14.153(5)	9.782(2)
c/Å	12.837(8)	10.457(3)	35.3500(11)	13.912(7)	24.168(5)
α/°	106.43(3)	117.055(15)	90	90	90
β/°	91.33(3)	90.450(18)	104.183(11)	100.47(2)	99.73(3)
γ/°	110.43(3)	101.589(17)	90	90	90
V/Å^3	1072.6(12)	921.4(5)	6958(3)	1772.4(15)	2654.8(9)
Z	2	2	8	2	4
d_{calc}/g cm^{-3}	1.195	1.154	1.161	1.170	1.242
$2\theta_{max}$/°	50.5	50.6	54.9	54.9	50.0
μ(Mo Kα)/mm^{-1}	0.068	0.068	0.0712	0.083	0.226
Independent reflections	3854 (R_{int} = 0.027)	3333 (R_{int} = 0.023)	7828 (R_{int} = 0.037)	4189 (R_{int} = 0.047)	4623 (R_{int} = 0.036)
Data/restraints/parameters	2854/0/272	3333/0/217	7828/0/415	4189/1/416	4623/0/325
GOF on F^2	1.021	1.05	1.006	1.020	1.028
$R_1(F)$ [$I > 2\sigma(I)$]	0.0605	0.0436	0.0557	0.0555	0.0479
$wR_2(F^2)$ [all data]	0.1801	0.1148	0.1540	0.1440	0.1323

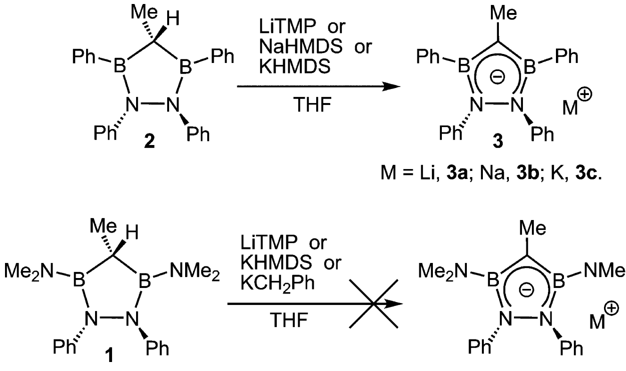
Table 2 Selected bond lengths (Å) and angles (°) for **1**, **2**, **3a**(thf)$_3$, **3b**(thf)$_3$, and **3c**(thf)

	1	**2**[a]	**3a**(thf)$_3$ (M = Li)	**3b**(thf)$_3$ (M = Na)	**3c**(thf) (M = K)
C_{intra}–B[b]	1.572(4), 1.581(4)	1.578(2), 1.592(2)	1.490(3), 1.501(3)	1.482(6), 1.499(6)	1.479(3), 1.499(3)
C_{extra}–B	1.565(4), 1.568(4)	1.389(2), 1.399(2)	1.579(3), 1.586(3)	1.583(5), 1.584(5)	1.583(3), 1.585(3)
B–N	1.412(3), 1.416(3)	1.467(2), 1.497(2)	1.464(2), 1.481(3)	1.466(5), 1.486(5)	1.458(3), 1.494(3)
N–N	1.452(3)	1.4572(17)	1.4374(19)	1.438(4)	1.443(2)
C_{intra}–C_{extra}	1.462(4)	1.550(2)	1.527(3)	1.522(5)	1.524(3)
N–C_{extra}	1.429(3), 1.438(3)	1.4087(19), 1.4146(19)	1.407(2), 1.431(2)	1.415(4), 1.418(5)	1.404(3), 1.427(3)
M–C_{intra}	—	—	2.351(4)	2.680(4)	3.021(2)
M · · · B	—	—	2.908(4), 2.983(4)	2.939(5), 3.189(5)	3.249(3), 3.466(3)
M–O	—	—	1.947(4)–2.009(3)	2.325(3)–2.360(4)	2.6443(19)
B–C_{intra}–B	102.3(2)	98.87(12)	104.62(16)	105.7(3)	105.01(19)
C_{extra}–C_{intra}–B	121.0(2), 125.3(2)	111.18(13), 111.33(13)	126.50(17), 128.55(16)	125.6(3), 128.2(3)	126.8(2), 128.2(2)
C_{intra}–B–N	107.6(2), 108.4(2)	108.95(13), 109.52(13)	108.63(15), 109.73(15)	108.3(3), 108.7(3)	108.92(19), 109.51(19)
C_{intra}–B–C_{extra}	126.8(2), 127.9(2)	126.75(14), 128.92(14)	129.51(17), 131.02(17)	128.1(4), 129.4(3)	127.4(2), 129.7(2)
C_{extra}–B–N	124.2(2), 124.7(2)	122.07(14), 123.51(14)	119.23(16), 121.54(17)	121.8(3), 123.3(3)	120.68(19), 123.2(2)
B–N–N	110.44(18), 111.11(18)	104.46(11), 109.05(11)	107.11(13), 109.52(14)	107.6(3), 109.2(3)	106.72(16), 109.33(17)
B–N–C_{extra}	128.48(19), 129.66(19)	122.49(12), 129.60(12)	120.51(14), 131.56(14)	125.0(3), 128.5(3)	119.92(17), 131.20(18)
N–N–C_{extra}	117.56(17), 118.05(17)	114.43(12), 114.45(11)	113.54(13), 115.25(14)	115.5(3), 116.0(3)	114.15(17), 118.25(16)
C_{extra}–N–N–C_{extra}	30.1	97.2	58.1	52.8	49.0
$\sum$pentagon angles	539.8	530.8	539.6	539.5	539.5

[a] For **2**, (B)C_{extra} is (B)N_{extra}. [b] C_{intra} and C_{extra} indicate carbon atoms that are part of the ring (intraannular) and directly connected to the ring (extraannular), respectively.

groups, and are pushed considerably out of planarity, forming a CNNC torsion angle of 97.2° (*vs.* 30.1 in **1**). This deviation from planarity would be expected to have a negative impact on the electron delocalization along the ring framework of $\mathbf{C_4}$ and consequently on its ligand properties.

The N–N bond lengths in **1** and **2** (1.452(3) and 1.4572(17) Å, respectively) are practically identical with the value measured in hydrazine[4] and in the alkali metal salts of ligands $\mathbf{C_1}$ and $\mathbf{C_2}$.[2a,b] In **1**, the B–N bonds measure 1.412(3) and 1.416(3) Å and are situated in the range observed for acyclic $R_2B{=}NR'_2$ compounds (R = fluorenyl, R′ = *i*Pr, 1.390(14) Å;[5a] R = R′ = Me, 1.403(1) Å;[5b] R = fluorenyl, R′ = Me, 1.400(12) Å[5c]). Very similar B–N bond lengths, ranging between 1.380(6) and 1.430(6) Å have been measured in other neutral five-membered rings featuring a BNC_3 skeleton and tricoordinated boron and nitrogen centers.[6] The intraannular B–N bonds in **2** are, with 1.467(2) and 1.497(2) Å, considerably longer than those in **1**, as a result of the competitive electron donation to boron from the endo and exocyclic nitrogen atoms. The electron donation from the more electron rich exocyclic nitrogen is facilitated by the coplanar arrangement of the substituents (*vide supra*) and results in shorter extraannular B–N bonds (1.4087(19) and 1.4146(19)). The intra and extraannular B–C bonds in **1** are similar in length (1.565(4)–1.592(2) Å), and comparable to the intraannular B–C bonds observed in **2** (1.578(2), 1.592(2) Å), as well as in simple, unassociated organoboranes, R_3B (R = Mes, 1.579(2), 1.580(3) Å;[7a,c] R = Ph, 1.571(3), 1.589(5) Å;[7b] R = *t*Bu, 1.618(3) Å;[7d] R = Me_3SiCH_2, 1.563(3)–1.573(3) Å[7e]). It can be concluded that the structure of **1** resembles strongly the structure of cyclopentadienes.[8] The steric and electronic effects of the dimethylamino substituents have a considerable impact on the structure of **2**, which by comparison to **1** appears substantially distorted.



Scheme 2 Deprotonation of ligand precursors **1** and **2**.

The deprotonation of **1** was accomplished using a variety of reagents (Scheme 2) and the alkali metal salts **3a–c** were isolated as white crystalline solids. The disappearance of the ring proton and the resulting collapse of the doublet signal corresponding to the methyl group were easily noticeable in the ^{1}H NMR spectra, which displayed all the expected resonances. The most remarkable change in the ^{13}C NMR spectra upon deprotonation was the shift of the broad signal corresponding to the ring carbon from 23.0 ppm in the neutral precursor to 93.6–98.1 ppm in the alkali metal salts, indicative of the change in hybridization and electron density of this atom. Such a dramatic shift is typical for cyclopentadienyl derivatives with highly ionic character and has been observed for $\mathbf{C_1}$ and $\mathbf{C_2}$.[3b] All other signals in the ^{13}C NMR spectra of **3a–c** could be assigned. The ^{11}B NMR spectrum of **1** underwent little change upon deprotonation, the broad singlet shifting from 44 ppm in **1** to 41–42 ppm in **3a–c**. Deprotonation of **2** was unsuccessfully attempted using several strong bases (Scheme 2). While the nitrogen bases showed no reaction with **2** in THF, *n*BuLi resulted in decomposition to a complex mixture of products. This is likely a consequence of the excellent π donating ability of the dimethylamino groups, resulting in increased electron density on the CB_2 moiety and ultimately a decreased acidity of the ring proton. The lack of reactivity is in good agreement with the results of the NMR studies of **2** (*vide supra*).

The structures of the alkali metal salts **3a**(thf)$_3$, **3b**(thf)$_3$ and **3c**(thf) feature the ligand **C$_3$** and one or three additional THF molecules coordinated to the metal (Table 1). These structures offer the first opportunity to directly assess the transformations suffered by a cyclopentadienyl analog with a CB_2N_2 framework upon deprotonation and coordination to a metal (Table 2). The metric parameters of the ligand **C$_3$** in its alkali metal salts, **3a**(thf)$_3$, **3b**(thf)$_3$ and **3c**(thf), are very similar if not identical to the metric parameters of the related ligands **C$_1$** and **C$_2$** in their alkali metal salts. A detailed comparison of the bond lengths and angles of the cyclopentadienyl analogs with CB_2N_2 skeletons in these latter salts to the metric parameters of other boron compounds was already presented,[3b] and hence the current discussion will focus on the changes suffered by the ligands upon deprotonation, and on the changes in the structure of the ligands as a result of the change of organic substituents on boron and nitrogen.

The N–N bonds in the alkali metal salts described herein are practically equal in length with the N–N bonds observed in the neutral precursors **1** and **2**. The B–N bonds in **1**, however, are lengthened by *ca.* 0.05 Å upon deprotonation. Consequently, the B–N bonds in the alkali metal salts of ligand **C$_3$** (1.458(3)–1.494(3) Å) are slightly longer than the typical bonds in borazines (1.42–1.44 Å)[9] and similar to the intraannular B–N bonds in **2**. The deprotonation of **1** has its most dramatic effect on the intraannular B–C bonds, which are shortened by 0.07–0.10 Å in the alkali metal salts **3a–c** and lie within the range observed for other boron heterocycles featuring a delocalized π system, such as 1,2-azaborolinyl (1.46–1.50 Å).[2a–c,i] The immediate conclusion of the comparison between the structures of **1** and **3a–c** supports previous observations on the electron distribution in anionic cyclopentadienyl analogs with CB_2N_2 framework: The deprotonation of the neutral precursor results in the shortening of the B–C bonds and lengthening of the B–N bonds, very similar to the effect of the deprotonation of cyclopentadienes to cyclopentadienyls. However, the resulting electron delocalization appears to be limited to the N–B–C–B–N system and does not extend over the N–N bond, which retains a single-bond character.

The CB_2N_2 ring skeletons in the salts **3a–c** are slightly folded along the B(1)···N(2) axis, with dihedral angles of 6.0–7.8°. The CNNC torsion angles are wider than in **1** by 20 to 30° and this appears counterintuitive at first, as deprotonation results in the formation of extended π systems. The difference is however, in good agreement with the reduction in the bond order of the B–N bonds, which is not complemented by an increase in the bond order of the N–N bond. The addition of the M(thf)$_n$ ($M = Li$, Na, K; $n = 1, 3$) moiety to the coordination sphere of the ligand also results in an increased steric strain, which could contribute to the widening of the CNNC torsion angles.

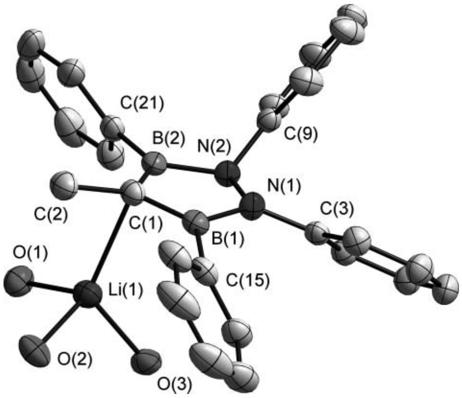


Fig. 3 Molecular structure of **3a**(thf)$_3$, with thermal ellipsoids drawn at 50% probability. For clarity, all hydrogen atoms as well as the methylene groups in THF have been omitted.

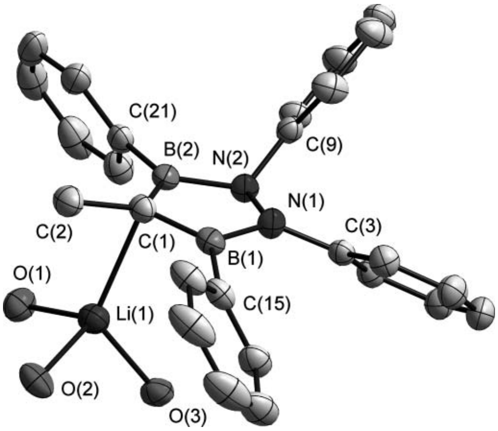


Fig. 4 Molecular structure of **3b**(thf)$_3$, with thermal ellipsoids drawn at 50% probability. For clarity, all hydrogen atoms as well as the methylene groups in THF have been omitted.

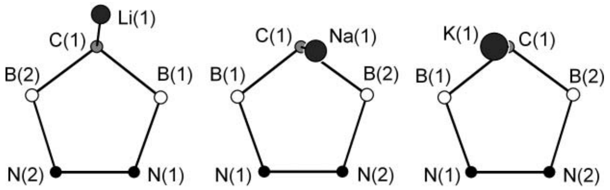


Fig. 5 Perpendicular projection onto the CB_2N_2 plane, revealing the η^1 hapticity of the ligand in **3a**(thf)$_3$ (left), **3b**(thf)$_3$ (center) and **3c**(thf) (right).

The salts **3a**(thf)$_3$ (Fig. 3) and **3b**(thf)$_3$ (Fig. 4) feature piano stool structures with distorted tetrahedral coordination geometries of the metals and $\eta^1{}_{\mathrm{C}}$ coordination modes of the ligand (Fig. 5). A very similar structure was determined for the sodium salt of the ligand **C$_2$**, with a very short C–Na distance of 2.616(2) Å.[3b] With 2.680(4) Å, the slightly longer C–Na distance in **3b**(thf)$_3$ is in agreement with the expected lower donor ability of the ligand **C$_3$** as compared to **C$_2$**. Somewhat more common in mixed cyclopentadienyl salts of alkali metals and lanthanoids, three-legged piano stool geometries are surprisingly rare in the coordination chemistry of ether containing alkali metal cyclopentadienyls, and the η^1 coordination mode is highly uncommon in these salts.[10] In the structures available for comparison, the distance between the metal ion and the plane of the η^5 coordinated cyclopentadienyl ligand measures 2.04 Å for Li,[11b] 2.44–2.48 Å for Na[11c,d] and 2.74–2.78 Å for K.[11a,e] Although the bonding between the alkali metals and the cyclopentadienyl ligands is mainly ionic in nature,[10a] the considerably larger distances between the lithium and sodium ions and the plane of the CB_2N_2 ligands in **3a**(thf)$_3$ (2.25 Å) and **3b**(thf)$_3$ (2.68 Å) are good indicators for the reduced coordinating ability of the ligand **C$_3$**. Because the π ligand clearly coordinates in an η^1 fashion through the carbon atom (Fig. 5) the larger covalent radius of boron (0.822 Å *vs.* 0.772 Å for carbon)[12] is not likely to be a considerable contributing factor to the increased distance.

In the solid state, **3c**(thf) features a highly unusual monodimensional polymeric structure (Fig. 6). The potassium ion is $\eta^1{}_C$ coordinated by the CB_2N_2 ligand, as observed in the lithium and sodium analogs, and η^6 (NPh) and η^3 (BPh) coordinated by two phenyl groups of another ligand. The coordination sphere of the metal ion is completed by a THF molecule, leading to a distorted tetrahedral geometry. Polydecker sandwich architectures are common solid state arrangements in alkali metal cyclopentadienyls, especially in the absence of coordinating solvents. However, structures where the metal coordinates to one or more phenyl ligands, despite the availability of one face of the cyclopentadienyl ligand, have to our knowledge not been reported. Such preference has only been observed for a cyclopentadienyl analog featuring a carbon-free B_2N_3 framework.[13] Two solid state structures of potassium fluorenyls are known, where the potassium ion coordinates to the phenyl instead of the cyclopentadienyl ring of the ligand.[14] This type of solid state π-interaction between phenyl groups and potassium ions are nevertheless common in potassium tetraphenylborates,[15] and enable the selective precipitation of potassium ions from aqueous solutions using tetraphenylborate as a counterion.[16] The distances between potassium and the planes of the phenyl ligands in **3c**(thf) measure 2.99 Å, and are very similar to the values observed in tetraphenylborates (2.92–3.02 Å).[14,15] The distance between the potassium ion and the plane of the CB_2N_2 ligand in **3c**(thf) measures 3.01 Å, but this value is difficult to use for comparison because of the lack of similar substitution patterns for the metal in the chemistry of cyclopentadienyls. The preference of the potassium ion for π-coordination by the phenyl groups instead of the CB_2N_2 ring is another indication of the poor coordinating ability of ligand $\mathbf{C_3}$.

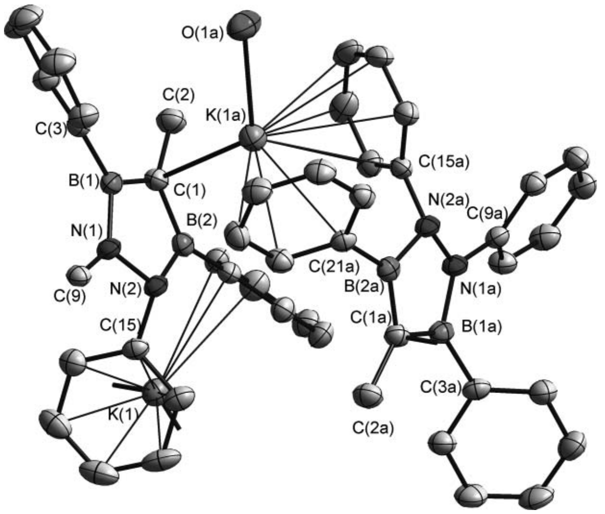


Fig. 6 Fragment from the polymeric chain of **3c**(thf) in the solid state, with thermal ellipsoids drawn at 50% probability. For clarity, only the *ipso* carbon atom in the phenyl substituent on N(1) is represented and all hydrogen atoms, as well as the methylene groups in THF, have been omitted.

Conclusion

In an attempt to assess the limits in the tuning of the coordinating ability of cyclopentadienyl analogs with a CB_2N_2 skeleton, the ligand precursors **1** and **2** have been synthesized and structurally characterized. Diazadiborolidine **1** featured a cyclopentadiene-like structure with short B–N bonds and could be easily deprotonated, yielding the lithium, sodium and potassium salts **3**. A comparison between the metric parameters of the protonated ligand **1** and the salts **3a–c** confirmed that the π electron delocalization over the N–B–C–B–N skeleton in the anionic CB_2N_2 ligand does not extend over the N–N bond, which displays a single bond character. The combined effects of the four electron-withdrawing phenyl groups imparted poor electron donating properties to the ring skeleton of the ligand, which proved to have inferior coordinating ability in comparison to ligands $\mathbf{C_1}$ and $\mathbf{C_2}$. This was reflected by the long metal to ligand distances in the lithium and sodium salts, and by the π coordination of the potassium ion by the phenyl groups of the ligand instead of the CB_2N_2 ring. Diazadiborolidine **2** represented the other extreme, with the excellent π donating ability of the dimethylamino substituents increasing the electron density at the ring carbon to an extent sufficient to prevent its deprotonation and preclude the synthesis of its alkali metal salts.

As expected, the two or four phenyl substituents imparted excellent crystallization properties to the neutral ligands and their salts, an important asset for the purification and structural characterization of these derivatives. It was concluded however, that for electronic reasons attributed to the substitution pattern, **1** and **2** are not optimal precursors for the design and synthesis of transition metal sandwich compounds featuring "inorganic" ligands.

Experimental section

General considerations

All operations were performed under an argon atmosphere using standard Schlenk and glove box techniques. Solvents were dried and deoxygenated prior to use. Starting materials were prepared according to reported procedures or purchased from commercial suppliers. The 1,2-diphenylhydrazine was purchased from Sigma Aldrich and the small amount of diazobenzene it contained was removed prior to use by washing with hexane. NMR spectra were collected on a Bruker Advance DRX-400 spectrometer and calibrated with respect to C_6D_5H (^1H, 7.15 ppm), THF-d_7 (^1H, 3.58 ppm), toluene-d_7 (^1H, 2.09 ppm), C_6D_6 (^{13}C, 128.39 ppm), THF-d_8 (^{13}C, 67.57 ppm), toluene-d_8 (^{13}C, 20.4 ppm), $BF_3{\cdot}Et_2O$ (^{11}B, 0 ppm), and LiCl (^7Li, 0 ppm). Mass spectra were performed by the Analytical Instrumentation Laboratory, Department of Chemistry, University of Calgary.

Synthesis of 4-methyl-1,2,3,5-tetraphenyl-1,2-diaza-3,5-diborolidine, 1

A mixture of 1,2-diphenylhydrazine (737 mg, 4.00 mmol) and triethylamine (810 mg, 8.00 mmol) in benzene (50 mL) was slowly added to a stirring solution of 1,1-bis(chlorophenylboryl)ethane (1.10 g, 4.00 mmol) in hexane (20 mL), producing a pale yellow suspension. The mixture was stirred at ambient temperature for 12 h and the white precipitate was subsequently filtered off. Volatiles were removed under full vacuum, leaving behind a pale yellow solid that was washed twice with hexane. Yield: 63% (0.98 g) colorless solid. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$, 298 K): δ 1.45 (3H, d, $^3J_{\mathrm{HH}} = 8.2$ Hz, $\mathrm{HCC}H_3$), 1.65 (1H, q, $^3J_{\mathrm{HH}} = 8.2$ Hz, $H\mathrm{CCH_3}$), 6.65 (2H, t, $^3J_{\mathrm{HH}} = 7.3$ Hz, p-$\mathrm{NC_6}H_5$), 6.75 (4H, t, $^3J_{\mathrm{HH}} = 7.5$ Hz, m-$\mathrm{NC_6}H_5$), 6.87 (4H, d, $^3J_{\mathrm{HH}} = 7.5$ Hz, o-$\mathrm{NC_6}H_5$), 7.11 (6H, m, m- and p-$\mathrm{BC_6}H_5$), 7.44 (4H, d, o-$\mathrm{BC_6}H_5$). ^{1}H NMR (400 MHz, THF-$\mathrm{d_8}$, 289 K): δ 1.28 (3H, d, $^3J_{\mathrm{HH}} = 8.2$ Hz, $\mathrm{HCC}H_3$), 1.67 (1H, q, $^3J_{\mathrm{HH}} = 8.2$ Hz, $H\mathrm{CCH_3}$), 6.97 (2H, m, p-$\mathrm{NC_6}H_5$), 7.04 (8H, m, o- and m-$\mathrm{NC_6}H_5$), 7.15 (6H, m, m- and p-$\mathrm{BC_6}H_5$), 7.29 (4H, d, o-$\mathrm{BC_6}H_5$). ^{13}C{^{1}H} NMR (100 MHz, THF-$\mathrm{d_8}$, 298 K): δ 11.0 (s, $\mathrm{HC}C\mathrm{H_3}$), 23.0 (s, br, $\mathrm{H}C\mathrm{CH_3}$), 127.1 (s, p-$\mathrm{N}C_6\mathrm{H_5}$), 128.2 (s, m-$\mathrm{N}C_6\mathrm{H_5}$), 129.1 (s, o-$\mathrm{N}C_6\mathrm{H_5}$), 129.3 (s, p-$\mathrm{B}C_6\mathrm{H_5}$), 130.2 (s, m-$\mathrm{B}C_6\mathrm{H_5}$), 134.9 (s, o-$\mathrm{B}C_6\mathrm{H_5}$), 137.5 (s, br, i-$\mathrm{B}C_6\mathrm{H_5}$), 142.1 (s, i-$\mathrm{N}C_6\mathrm{H_5}$). ^{11}B{^{1}H} NMR (128 MHz, THF-$\mathrm{d_8}$, 298 K): δ 44.0 (s, br). EI-MS (70 eV): m/z (%): 386 (76) [M]$^+$, 371 (21) [M − Me]$^+$. Colorless thin plate-like crystals of **1** were obtained by cooling a concentrated solution of **1** in a mixture of $\mathrm{C_6H_6}$ and hexane to −35 °C.

Synthesis of 4-methyl-1,2-diphenyl-3,5-dimethylamino-1,2-diaza-3,5-diborolidine, 2

A mixture of 1,2-diphenylhydrazine (175 mg, 0.950 mmol) and triethylamine (192 mg, 1.90 mmol) in benzene (20 mL) was slowly added to a stirring solution of 1,1-bis(dimethylamino-chloroboryl)ethane (200 g, 0.950 mmol) in hexane (20 mL). The resulting orange-yellow suspension was stirred at ambient temperature for 3 h and the white precipitate was filtered off. Volatiles were removed under full vacuum, leaving behind the product as a colorless solid. Yield: 51% (154 mg). ^{1}H NMR (400 MHz, toluene-$\mathrm{d_8}$, 298 K): $\delta = 0.65$ (q, 1H, $^3J_{\mathrm{HH}} = 8.1$ Hz, $H\mathrm{CCH_3}$), 1.01 (d, 3H, $^3J_{\mathrm{HH}} = 8.1$ Hz, $\mathrm{HCC}H_3$), 2.57 (s, 12H, $\mathrm{N(C}H_3)_2$), 6.82 (t, 2H, p-$\mathrm{C_6}H_5$), 6.96 (m, 4H, m-$\mathrm{C_6}H_5$), 7.19 (m, 4H, o-$\mathrm{C_6}H_5$); ^{13}C NMR (100 MHz, toluene-$\mathrm{d_8}$, 298 K): $\delta = 8.9$ (s, br, $\mathrm{H}C\mathrm{CH_3}$), 10.2 (s, $\mathrm{HC}C\mathrm{H_3}$), 39.3 (s, br, $\mathrm{N(}C\mathrm{H_3)_3}$), 40.3 (s, br, $\mathrm{N(}C\mathrm{H_3)_3}$), 116.6 (s, m-$C_6\mathrm{H_5}$), 119.8 (s, p-$C_6\mathrm{H_5}$), 129.0 (s, o-$C_6\mathrm{H_5}$), 149.5 (s, i-$C_6\mathrm{H_5}$); ^{11}B NMR (128 MHz, toluene-$\mathrm{d_8}$, 298 K): $\delta = 37.4$ (s, br); EI-MS (70 eV): m/z (%): 320 (26) [M]$^+$; HRMS for $\mathrm{H_{26}C_{18}N_4{}^{11}B_2}$ calcd 320.2344, found 320.2356. Colorless thin plate crystals of **2** were obtained by cooling a concentrated solution of **2** in a toluene–hexane mixture to −35 °C.

Synthesis of 4-methyl-1,2,3,5-tetraphenyl-1,2-diaza-3,5-diborolyl lithium, 3a

A yellow solution of lithium 2,2,6,6-tetramethylpiperidide, LiTMP, was prepared from N-butyllithium in hexane (1.6 M, 0.33 mL, 0.53 mmol) and tetramethylpiperidine, TMP (75 mg, 0.53 mmol) in THF (3 mL). A solution of **1** (0.20 g, 0.53 mmol) in THF (10 mL) was pre-cooled to −35 °C and mixed with the pre-cooled solution of LiTMP and the reaction was allowed to take place for 2 h at −35 °C. The solvent was removed under vacuum leaving behind a pale yellow solid that was washed twice with hexane (30 mL) and dried under vacuum. The product was obtained as an off-white powder. Yield: 90% (0.26 g). ^{1}H NMR (400 MHz, THF-$\mathrm{d_8}$, 298 K): δ 1.73 (3H, s, $\mathrm{CC}H_3$), 1.77 (7H, m, $\mathrm{O(CH_2C}H_2)_2$), 3.62 (7H, m, $\mathrm{O(C}H_2\mathrm{CH_2)_2}$), 6.35 (2H, t, $^3J_{\mathrm{HH}} = 7.2$ Hz, p-$\mathrm{NC_6}H_5$), 6.70 (4H, t, $^3J_{\mathrm{HH}} = 7.3$ Hz, m-$\mathrm{NC_6}H_5$), 6.84 (4H, d, $^3J_{\mathrm{HH}} = 7.5$ Hz, o-$\mathrm{NC_6}H_5$), 6.94 (2H, t, $^3J_{\mathrm{HH}} = 6.1$ Hz, p-$\mathrm{BC_6}H_5$), 7.06 (4H, t, $^3J_{\mathrm{HH}} = 7.2$ Hz, m-$\mathrm{BC_6}H_5$), 7.34 (4H, d, $^3J_{\mathrm{HH}} = 7.2$ Hz, o-$\mathrm{BC_6}H_5$). ^{13}C{^{1}H} NMR (100 MHz, THF-$\mathrm{d_8}$, 298 K): δ 14.8 (s, $\mathrm{C}C\mathrm{H_3}$), 26.5 (s, $\mathrm{O(CH_2}C\mathrm{H_2)_2}$), 68.4 (s, $\mathrm{O(}C\mathrm{H_2CH_2)_2}$), 98.1 (s, br, $\mathrm{B_2}C\mathrm{CH_3}$), 118.1 (s, p-$\mathrm{N}C_6\mathrm{H_5}$), 122.5 (s, m-$\mathrm{N}C_6\mathrm{H_5}$), 124.5 (s, p-$\mathrm{B}C_6\mathrm{H_5}$), 126.7 (s, o-$\mathrm{N}C_6\mathrm{H_5}$), 127.5 (s, m-$\mathrm{B}C_6\mathrm{H_5}$), 135.1 (s, o-$\mathrm{B}C_6\mathrm{H_5}$), 148.8 (s, br, i-$\mathrm{B}C_6\mathrm{H_5}$), 149.6 (s, i-$\mathrm{N}C_6\mathrm{H_5}$). ^{11}B{^{1}H} NMR (128 MHz, THF-$\mathrm{d_8}$, 298 K): δ 40.5 (s, br). ^{7}Li{^{1}H} NMR (155 MHz, THF-$\mathrm{d_8}$, 298 K): δ −0.82 (s). Colorless block crystals of **3a**(thf)$_3$ were obtained by slow diffusion of liquid hexane into a THF solution of **3a**.

Synthesis of 4-methyl-1,2,3,5-tetraphenyl-1,2-diaza-3,5-diborolyl sodium, 3b

A solution of **1** (0.358 g, 0.927 mmol) in THF (10 mL) was added to a stirring solution of sodium bis(trimethylsilyl)amide, NaHMDS (0.170 g, 0.927 mmol) in THF (15 mL) and the yellow mixture was subsequently stirred at ambient temperature for 3 h. The volatiles were removed under vacuum leaving behind a colorless solid that was washed twice with hexane (30 mL) and dried under vacuum. The product was obtained as a colorless powder. Yield: 97% (0.40 g). ^{1}H NMR (400 MHz, THF-$\mathrm{d_8}$, 298 K): δ 1.77 (2H, m, $\mathrm{O(CH_2C}H_2)_2$), 1.82 (3H, s, $\mathrm{CC}H_3$), 3.62 (2H, m, $\mathrm{O(C}H_2\mathrm{CH_2)_2}$), 6.45 (2H, t, $^3J_{\mathrm{HH}} = 7.1$ Hz, p-$\mathrm{NC_6}H_5$), 6.76 (4H, t, $^3J_{\mathrm{HH}} = 7.5$ Hz, m-$\mathrm{NC_6}H_5$), 6.87 (4H, d, $^3J_{\mathrm{HH}} = 8.4$ Hz, o-$\mathrm{NC_6}H_5$), 7.02 (2H, t, $^3J_{\mathrm{HH}} = 7.4$ Hz, p-$\mathrm{BC_6}H_5$), 7.12 (4H, t, $^3J_{\mathrm{HH}} = 7.8$ Hz, m-$\mathrm{BC_6}H_5$), 7.27 (4H, d, $^3J_{\mathrm{HH}} = 7.8$ Hz, o-$\mathrm{BC_6}H_5$). ^{13}C{^{1}H} NMR (100 MHz, THF-$\mathrm{d_8}$, 298 K): δ 13.8 (s, $\mathrm{C}C\mathrm{H_3}$), 26.5 (s, $\mathrm{O(CH_2}C\mathrm{H_2)_2}$), 68.4 (s, $\mathrm{O(}C\mathrm{H_2CH_2)_2}$), 93.6 (s, br, $\mathrm{B_2}C\mathrm{CH_3}$), 119.5 (s, p-$\mathrm{N}C_6\mathrm{H_5}$), 123.0 (s, m-$\mathrm{N}C_6\mathrm{H_5}$), 125.4 (s, p-$\mathrm{B}C_6\mathrm{H_5}$), 127.1 (s, o-$\mathrm{N}C_6\mathrm{H_5}$), 127.8 (s, m-$\mathrm{B}C_6\mathrm{H_5}$), 134.9 (s, o-$\mathrm{B}C_6\mathrm{H_5}$), 146.7 (s, br, i-$\mathrm{B}C_6\mathrm{H_5}$), 148.5 (s, i-$\mathrm{N}C_6\mathrm{H_5}$). ^{11}B{^{1}H} NMR (128 MHz, THF-$\mathrm{d_8}$, 298 K): $\delta = 40.1$ (s, br). Colorless block crystals of **3b**(thf)$_3$ were obtained after several days by cooling a concentrated solution of **3b** in a mixture of THF and pentane to −35 °C.

Synthesis of 4-methyl-1,2,3,5-tetraphenyl-1,2-diaza-3,5-diborolyl potassium, 3c

A solution of **1** (0.200 g, 0.518 mmol) in THF (10 mL) was added to a stirring solution of potassium bis(trimethylsilyl)amide, KHMDS (0.116 g, 0.518 mmol) in THF (15 mL) and the yellow mixture was subsequently stirred at ambient temperature for 2 h. The volatiles were removed under vacuum leaving behind a pale yellow solid, which was washed twice with hexane (30 mL) and dried under vacuum. The product was obtained as a light brown powder. Yield: 89% (0.20 g). ^{1}H NMR (400 MHz, THF-$\mathrm{d_8}$, 298 K): $\delta = 1.12$ (3 H, t, $^3J_{\mathrm{HH}} = 7.0$ Hz, $\mathrm{O(CH_2C}H_3)_2$), 1.78 (3H, s, $\mathrm{CC}H_3$), 3.39 (2 H, q, $^3J_{\mathrm{HH}} = 7.0$ Hz, $\mathrm{O(C}H_2\mathrm{CH_3)_2}$), 6.46 (2H, t, $^3J_{\mathrm{HH}} = 7.2$ Hz, p-$\mathrm{NC_6}H_5$), 6.77 (4H, t, $^3J_{\mathrm{HH}} = 7.4$ Hz, m-$\mathrm{NC_6}H_5$), 6.84 (4H, d, $^3J_{\mathrm{HH}} = 8.0$ Hz, o-$\mathrm{NC_6}H_5$), 7.01 (2H, t, $^3J_{\mathrm{HH}} = 7.4$ Hz, p-$\mathrm{BC_6}H_5$), 7.12 (4H, t, $^3J_{\mathrm{HH}} = 7.3$ Hz, m-$\mathrm{BC_6}H_5$), 7.34 (4H, d, $^3J_{\mathrm{HH}} = 6.9$ Hz, o-$\mathrm{BC_6}H_5$). ^{13}C{^{1}H} NMR (100 MHz, THF-$\mathrm{d_8}$, 298 K): δ 14.4 (s, $\mathrm{C}C\mathrm{H_3}$), 15.9 (s, $\mathrm{O(CH_2}C\mathrm{H_3)_2}$), 66.5 (s, $\mathrm{O(}C\mathrm{H_2CH_3)_2}$), 97.7 (s, br, $\mathrm{B_2}C\mathrm{CH_3}$), 119.4 (s, p-$\mathrm{N}C_6\mathrm{H_5}$), 122.8 (s, m-$\mathrm{N}C_6\mathrm{H_5}$), 125.3 (s, p-$\mathrm{B}C_6\mathrm{H_5}$), 127.2 (s, o-$\mathrm{N}C_6\mathrm{H_5}$), 128.0 (s, m-$\mathrm{B}C_6\mathrm{H_5}$), 134.8 (s, o-$\mathrm{B}C_6\mathrm{H_5}$), 147.2 (s, br, i-$\mathrm{B}C_6\mathrm{H_5}$), 148.5 (s, i-$\mathrm{N}C_6\mathrm{H_5}$). ^{11}B{^{1}H} NMR (128 MHz, THF-$\mathrm{d_8}$, 298 K): δ 40.1 (s, br). Colorless block crystals of **3c**(thf) were obtained by slow diffusion of liquid hexane into a THF solution of **3c**.

Crystal structure determinations

Data were collected at a temperature of 173(2) K using the ω and φ scans on a Nonius Kappa CCD diffractometer with graphite monochromated Mo-K_α radiation with $\lambda = 0.71073$ Å (Table 1), and corrected for Lorentz and polarization effects and for absorption using the multi-scan method.[17] The structures were solved by the direct methods[18] and expanded using Fourier techniques.[19] Non-hydrogen atoms were refined anisotropically using SHELXL97.[20] Hydrogen atoms were included at geometrically calculated positions during the refinement using the riding model. For **3b**, in the absence of significant anomalous scattering effects, the Flack parameter did not give a refinable value and an absolute structure could not be established and therefore, Friedel pairs were merged[21] (CCDC reference numbers 678560 (**1**), 678561 (**2**), 678562 (**3a**$(\text{thf})_3$), 678563 (**3b**$(\text{thf})_3$), and 678564 (**3c**(thf))).

Acknowledgements

This work was supported by the Natural Sciences and Engineering Research Council of Canada, the Canada Foundation for Innovation, and the Alberta Science and Research Investments Program.

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